EPA 402-R-10-001c
www.epa.gov/narel
October 2011
Revision 0.1

Rapid Radiochemical Method for Radium-226 in Water for Environmental Remediation Following Homeland Security Events

U.S. Environmental Protection Agency

Office of Air and Radiation
Office of Radiation and Indoor Air
National Air and Radiation Environmental Laboratory
Montgomery, AL 36115

Office of Research and Development
National Homeland Security Research Center
Cincinnati, OH 45268

Revision History

Revision 0	Original release.	02/23/2010
Revision 0.1	• Corrected typographical and punctuation errors. • Improve wording consistency with other methods. • Added pH paper to list of equipment and supplies (6.9). • Added ^{225}Ra decay diagram to Section 17.4. • Added Section 12.2.1 header (no change to process). • Updated equations in sections 12.2.1 (A_t), 12.3 (A_{Ca}), and 12.3.2 (S_c), to consistently apply factor for I_t (no impact on calculations). • Updated equation objects in section 12.2.1 (equation for A_t) since MSWord Equation Editor ensure that minus signs would be displayed). • Updated footnote 9 to further clarify origin of critical value and minimum detectable concentration formulations. • Updated values in Table 17.2 to reflect ^{217}At concentration (no impact on calculations in 12.2.1). • Updated rounding example in 12.4.2.2 for clarity. • Deleted Appendix A (composition of Atlanta tap water) as irrelevant. Redesignated Appendix B ("Preparation and Standardization of ^{225}Ra Tracer Following Separation from ^{229Th}") as Appendix A.	10/28/2011

This report was prepared for the National Air and Radiation Environmental Laboratory of the Office of Radiation and Indoor Air and the National Homeland Security Research Center of the Office of Research and Development, United States Environmental Protection Agency. It was prepared by Environmental Management Support, Inc., of Silver Spring, Maryland, under contracts 68-W-03-038, work assignment 43, and EP-W-07-037, work assignments B-41 and I-41, all managed by David Garman. Mention of trade names or specific applications does not imply endorsement or acceptance by EPA.

RADIUM-226 IN WATER:
RAPID METHOD TECHNIQUE FOR HIGH-ACTIVITY SAMPLES

1. Scope and Application
   1.1. The method will be applicable to samples where contamination is either from known or unknown origins. If any filtration of the sample is performed prior to starting the analysis, filterable 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. This method uses rapid radiochemical separations techniques for the isotopic determination of ^{226}Ra in water samples following a nuclear or radiological incident. Although the method can detect ^{226}Ra concentrations 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 ^{226}Ra.
   1.3. The method is specific for ^{226}Ra and uses MnO_2 fixed on a resin bed (MnO_2 resin) to separate radium from interfering radionuclides and matrix constituents with additional separation using Diphonix® resin[1] to improve selectivity by removing radioactive impurities.
   1.4. The method is capable of satisfying a required method uncertainty for ^{226}Ra of 0.65 pCi/L at an analytical action level of 5 pCi/L. To attain the stated measurement quality objectives (MQOs) (see Sections 9.3, 9.4, and 9.5), a sample volume of approximately 200 mL and count time of 4 hours are recommended. Application of the method must be validated by the laboratory using the protocols provided in *Method Validation Guide for Qualifying Methods Used by Radiological Laboratories Participating in Incident Response Activities* (EPA 2009, reference 16.3). 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.
   1.5. This method is intended to be used for water samples that are similar in composition to drinking water. The rapid ^{226}Ra 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 16.3) and Chapter 6 of *Multi-Agency Radiological Laboratory Analytical Protocols Manual* (MARLAP 2004, reference 16.4). Multi-radionuclide analysis using sequential separation techniques may be possible.

2. Summary of Method
   2.1. A known quantity of ^{225}Ra is used as the yield determinant in this analysis. Since the source of the suspected contamination may not be known, the sample is initially digested using concentrated nitric acid, followed by volume reduction and conversion to the chloride salt using concentrated hydrochloric acid. The solution is adjusted to a neutral pH and batch equilibrated with MnO_2 resin to separate radium from some radioactive and non-radioactive matrix constituents. Further selectivity is achieved

[1] A polyfunctional cation exchange resin containing diphosphonic and sulfonic acid functional groups bonded to a polystyrene/divinylbenzene spherical bead. (Available commercially from Eichrom Technologies, LLC, Lisle, IL, 60561).

using a column which contains Diphonix® resin. The radium (including ^{226}Ra) eluted from the column is prepared for counting by microprecipitation with $BaSO_4$.

2.2. Low-level measurements are performed by alpha spectrometry. The activity measured in the ^{226}Ra region of interest is corrected for chemical yield based on the observed activity of the alpha peak at 7.07 MeV (^{217}At, the third progeny of ^{225}Ra). See Table 17.1 for a list of alpha particle energies of the radionuclides that potentially may be seen in the alpha spectra.

3. Definitions, Abbreviations and Acronyms

3.1. Analytical Protocol Specifications (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 (micron range).

3.5. *Multi-Agency Radiological Analytical Laboratory Protocols Manual* (MARLAP) (see Reference 16.4).

3.6. Measurement Quality Objective (MQO). The analytical data requirements of the data quality objectives that 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 as an absolute value is applicable at or below an AAL.

3.9. Relative Required Method Uncertainty (φ_{MR}). The relative required method uncertainty is the u_{MR} divided by the AAL and is typically expressed as a percentage. It is applicable above the action level.

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 in the method, such as a solid deposited on a filter for alpha spectrometry analysis.

4. Interferences
   4.1. Radiological:
      4.1.1. All radium isotopes in addition to ^{226}Ra are retained on MnO_2, as are thorium isotopes. Unless other radium isotopes are present in concentrations greater than approximately three times the ^{226}Ra activity concentration, interference from other radium alphas will be resolved when using alpha spectrometry. Method performance may be compromised if samples contain high levels of radium isotopes due to ingrowth of interfering decay progeny. Samples should be pre-screened prior to aliquanting and appropriate limits established to control the amount of activity potentially present in the aliquant.[2]
      4.1.2. Decay progeny from the ^{225}Ra tracer will continue to ingrow as more time elapses between the separation of radium and the count of the sample. Delaying the count significantly longer than a day may introduce a possible positive bias in results near the detection threshold. When MQOs require measurements close to detection levels, and coordinating sample processing and counting schedules is not conducive to counting the sample within ~36 hours of the separation of radium, the impact of tracer progeny tailing into the ^{226}Ra may be minimized by reducing the activity of the ^{225}Ra tracer that is added to the sample. This will aid in improving the signal-to-noise ratio for the ^{226}Ra peak by minimizing the amount of tailing from higher energy alphas of the ^{225}Ra progeny.
         4.1.2.1. The amount of ^{225}Ra added to the samples may be decreased, and the time for ingrowth between separation and counting increased, to ensure that sufficient ^{225}Ac, ^{221}Fr, and ^{217}At are present for yield corrections at the point of the count. Although this detracts from the rapidity of the method, it does not detract from the potential for high throughput.
         4.1.2.2. The size of the sample aliquant can be increased without changing the amount of tracer added.
      4.1.3. Optimally, a purified ^{225}Ra tracer solution[3] should be used when performing this method.
         4.1.3.1. When using a purified source of ^{225}Ra, the beginning of decay for ^{225}Ra is the activity reference date established during standardization of the ^{225}Ra solution.
         4.1.3.2. When a purified ^{225}Ra tracer solution is not available, a solution containing ^{225}Ra in equilibrium with ^{229}Th may be used as a tracer. In this case, the ^{225}Ra activity is supported only until thorium is removed using Diphonix® resin during processing of the sample. When using this variation of the method, the beginning of ^{225}Ra decay is the point when the sample has passed through the Diphonix® column.

[2] For very elevated levels of radium isotopes, it is recommended that laboratories use "The Determination of Radium-226 and Radium-228 in Drinking Water by Gamma-ray Spectrometry Using HPGE or Ge(Li) Detectors," Revision 1.2, December 2004. Available from the Environmental Resources Center, Georgia Institute of Technology, 620 Cherry Street, Atlanta, GA 30332–0335, USA, Telephone: 404–894–3776.
[3] Using a purified ^{225}Ra tracer is the approach recommended for this method. See Appendix B for a method for purification and standardization of ^{225}Ra tracer from ^{229}Th solution.

NOTE: Recording the point in time of the beginning of ^{225}Ra decay to within ½ hour will introduce a maximum bias of 0.1% for this measurement.

4.1.4. Every effort should be made to use the purified ^{225}Ra as a tracer. It is also possible to use ^{225}Ra in equilibrium with ^{229}Th, which may be added to each sample as a tracer.[4] This approach requires complete decontamination of a relatively high activity of ^{229}Th by the Diphonix® column later in the method, however, since the spectral region of interest (ROI) for ^{229}Th slightly overlaps that of ^{226}Ra. Inadequate decontamination of ^{229}Th will lead to high bias in the ^{226}Ra result especially when the levels of ^{226}Ra in the sample are below 1 pCi/L. The spectral region above ^{226}Ra corresponding to ^{229}Th should be monitored as a routine measure to identify samples where ^{229}Th interference may impact compliance with project MQOs. If problematic levels of ^{229}Th are identified in spectra, measures must be taken to address the interference. These might include:

4.1.4.1. Separating ^{225}Ra from ^{229}Th prior to its use as a tracer. Using purified ^{225}Ra tracer is the default approach recommended for running this method since it will completely address any potential for interference by removing the source of the problem.

4.1.4.2. Increasing the sample aliquant size without changing the amount of tracer added will increase analyte signal and reduce the relative impact of the interference to levels that may be amenable with project MQOs.

4.1.4.3. The absolute amount of ^{229}Th added to the samples may be decreased, as long as the time for ingrowth between separation and counting is increased to ensure that sufficient ^{217}At is present for yield corrections at the point of the count. Although this detracts from the rapidity of the method, it allows more flexibility in the timing of the count and does not detract from the potential for high throughput.

4.1.4.4. Developing spill-down factors (peak overlap corrections) to correct for the interference and account for additional uncertainty in the analytical results. This is not a trivial determination and should be validated prior to use.

4.1.5. When a solution containing ^{225}Ra in equilibrium with ^{229}Th is used as a tracer, thorium is removed later in the processing of the sample. The equilibrium between the ^{225}Ra and ^{229}Th is maintained only until the sample is loaded onto the Diphonix® column. At this point, thorium and actinium are retained on the column and the ^{225}Ra activity in the eluate is unsupported and begins to decay.

4.2. Non-radiological:

4.2.1. Low conductivity water (<100 μS cm^{-1}) may cause low-yield issues with some samples. This may be partially corrected for by increasing the conductivity with calcium standard solution.

[4] The single-laboratory validation for this method was performed successfully by adding ^{225}Ra in secular equilibrium with ^{229}Th tracer. Using purified ^{225}Ra will provide better method performance since it will eliminate any concern about breakthrough of the high levels of ^{229}Th added to each sample. See Appendix B of this method for a method for separating (and standardizing) ^{225}Ra tracer from ^{229}Th solution.

4.2.2. Concentrations of non-radioactive barium present significantly in excess of the amount of barium carrier added for microprecipitation may severely degrade the resolution of alpha spectra. The quality of spectra should be monitored for evidence of decreased resolution. A decreased sample size (i.e., smaller) may need to be selected or the barium carrier decreased or omitted if the presence of these interferences leads to unacceptably degraded method performance.

4.2.3. High concentrations of non-radioactive calcium, magnesium or strontium in the sample may not only overwhelm the ability of the MnO_2 resin to effectively exchange radium isotopes but also may degrade the alpha spectrometry peaks and increase analytical uncertainty. A decreased sample size (i.e., smaller) may need to be selected when the presence of these interferences leads to degraded method performance. If it is anticipated that these elements or barium (see Step 4.2.2) are present in quantities exceeding a small fraction of the mass of calcium or barium added in Steps 11.2.3 and 11.1.3, respectively, an analytical determination may need to be performed separately so that the interference can be accommodated.

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 for general chemical safety rules.
   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 <u>not</u> 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 the potential for cross contamination.
   5.3. Procedure-Specific Non-Radiological Hazards:
      5.3.1. Solutions of 30% H_2O_2 can rapidly oxidize organic materials and generate significant heat. Do not mix large quantities of peroxide solution with solutions of organic solvents as the potential for conflagration exists.

6. Equipment and supplies
   6.1. Alpha spectrometer calibrated for use over the range of ~3.5-10 MeV.
   6.2. Centrifuge tubes, polypropylene, 50 mL, disposable; or equivalent.
   6.3. Chromatography columns, polypropylene, disposable:

6.3.1. 1.5 cm I.D. × 15 cm, with funnel reservoir; or equivalent.
6.3.2. 0.8 cm I.D. × 4 cm; or equivalent.
6.4. Filter stand and filter funnels.
6.5. Filter, 0.1 micron, ~25-mm diameter (suitable for microprecipitation).
6.6. Membrane filter, 0.45 micron, ~47-mm diameter.
6.7. Vacuum filtration apparatus.
6.8. Heat lamp, 250-300 watt, with reflectors mounted ~25 cm above the base.
6.9. pH paper.
6.10. Petri dish or other suitable container for storing sample test sources.
6.11. Stainless steel planchets or suitable holders/backing for sample test sources – able to accommodate a 25-mm diameter filter.
6.12. Glass beaker, 600-mL capacity.
6.13. Stirring hot plate.
6.14. Magnetic stir bar (optional).
6.15. Centrifuge bottle, polypropylene, 250 mL, disposable; or equivalent (optional).

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 (ASTM D1193). For microprecipitation, all solutions used in microprecipitation should be prepared with water filtered through a 0.45 µm (or smaller) filter.

7.1. Ammonium sulfate, solid $(NH_4)_2SO_4$, available commercially.
7.2. Barium carrier (nominally 0.5 mg/mL as Ba^{2+}). May be purchased as an atomic absorption standard and diluted, or prepared by dissolving 0.45 g reagent grade barium chloride, dihydrate ($BaCl_2 \cdot 2H_2O$) in water and diluting to 500 mL with water.
7.3. Bromthymol blue indicator solution: Dissolve 0.1 g of bromthymol blue in 16 mL of 0.01 M NaOH. Dilute to 250 mL with water.
7.4. Calcium nitrate solution (1000 ppm as calcium). May be purchased as an atomic absorption standard and diluted or prepared by dissolving 2.5 g of calcium carbonate ($CaCO_3$) in 70 mL of concentrated nitric acid and diluting to 1 L with water.
7.5. Diphonix® resin, 100–200-µm mesh size [available from Eichrom Technologies, Lisle, IL].
7.6. Ethanol, reagent 95 % (C_2H_5OH), available commercially.
7.7. Hydrochloric acid (12 M): Concentrated HCl, available commercially.
7.7.1. Hydrochloric acid (2M): Add 170 mL of concentrated HCl to 800 mL of water and dilute to 1.0 L with water.
7.7.2. Hydrochloric acid (1M): Add 83 mL of concentrated HCl to 800 mL of water and dilute to 1.0 L with water.
7.8. Hydrogen peroxide, H_2O_2 (30 % w/w), available commercially.
7.9. Isopropanol, 2-propanol, (C_3H_7OH), available commercially.
7.9.1. Isopropanol (2-propanol), 20 % (v/v) in water: Mix 20 mL of isopropanol with 80 mL of water.
7.10. Methanol (CH_3OH), available commercially.

7.11. MnO_2 resin, 75-150 μm MnO_2 particle size on non-functionalized polystyrene resin beads of 100-200 mesh [available commercially from Eichrom Technologies, Lisle, IL].
7.12. MnO_2 stripping reagent: Add 2 mL of 30 % H_2O_2 per 100 mL of 2 M HCl. Prepare fresh for each use.
7.13. Nitric acid (16 M): Concentrated HNO_3, available commercially.
7.14. Sodium hydroxide (1 M): Dissolve 4 g of sodium hydroxide (NaOH) in 50 mL of water and dilute the solution to 100 mL.
7.15. Ra-225 tracer in 1-M HCl solution in a concentration amenable to accurate addition of about 180 dpm per sample (generally about 150–600 dpm/mL).
7.15.1. Ra-225 may be purified and standardized using a ^{229}Th / ^{225}Ra generator as described in Appendix A of this method.
7.15.2. Th-229 containing an equilibrium concentration of ^{225}Ra has been successfully used without prior separation of the ^{225}Ra. However, this approach may be problematic due to the risk of high result bias (see discussion in Steps 4.1.4 – 4.1.5).

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 radium 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 a 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 demineralized 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, such as the presence of elemental barium in the sample, may compromise chemical yield measurements, or overall data quality.
9.2.Sample-specific quality control measures

9.2.1. Limits and evaluation criteria shall be established to monitor each alpha spectrum to ensure that spectral resolution and peak separation is adequate to provide quantitative results. When ^{229}Th / ^{225}Ra solution is added directly to the sample, the presence of detectable counts between ~5.0 MeV and the upper boundary established for the ^{226}Ra ROI generally indicates the presence of ^{229}Th in the sample, and in the ^{226}Ra ROI. If the presence of ^{229}Th is noted and the concentration of ^{226}Ra is determined to be an order of magnitude below the action limit or the detection threshold of the method, take corrective actions to ensure that MQOs have not been compromised (e.g., clean-up ^{225}Ra tracer before adding, or re-process affected samples and associated QC samples. See interferences sections Steps 4.1.4 – 4.1.5. for discussion).

9.3. This method is capable of achieving a u_{MR} of 0.65 pCi/L at or below an action level of 5.0 pCi/L. This may be adjusted in the event specific MQOs are different.

9.4. This method is capable of achieving a φ_{MR} 13% above 5 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 1.0 pCi/L.

10. Calibration and Standardization

10.1. Set up, operate, calibrate and perform quality control for alpha spectrometry units in accordance with the laboratory's quality manual and standard operating procedures and consistent with ASTM Standard Practice D7282, Sections 7-13, 18, and 24 (see reference 16.5).

Note: The calibrated energy range for the alpha spectrometer for this method should be from ~3.5 to 10 MeV

10.2. If ^{225}Ra is separated and purified from ^{229}Th for use as a tracer, the activity reference date established during standardization of the tracer is used as the ^{225}Ra activity reference date (see Appendix A of this method).

10.3. When using ^{229}Th containing an equilibrium concentration of ^{225}Ra, the time of most recent separation / purification of the ^{229}Th standard solution must be known in order to determine the extent of secular equilibrium between ^{229}Th and its ^{225}Ra progeny. Verify the date of purification by examining the Certificate of Analysis, or other applicable documentation, for the standard.

10.4. When using ^{229}Th containing an equilibrium concentration of ^{225}Ra, ^{225}Ra is separated from its ^{229}Th parent as the solution passes through the Diphonix® column. This is the beginning of ^{225}Ra decay and the date and time used for decay correction of the tracer.

10.4.1. If the purification date of the ^{229}Th is not documented, at least 100 days must have elapsed between separation and use to ensure that ^{229}Th, and its progeny ^{225}Ra are in full secular equilibrium (i.e., >99%. See Table 17.3).

11. Procedure

11.1. Initial Sample Treatment

11.1.1. For each sample in the batch, aliquant 0.2 L of raw or filtered water into a beaker.

Note: Smaller or larger aliquants may be used if elevated sample activity is present or as needed to meet detection requirements or MQOs. Method validation must be conducted using approximately the same volume as that to be used in sample analysis.

11.1.2. To each aliquant, add 10 mL of concentrated nitric acid per 100 mL of sample.

11.1.3. To each sample aliquant, add 100 µL of 0.5 mg/mL (nominal) barium carrier solution and approximately 180 dpm of ^{225}Ra tracer solution. The initial amount of ^{225}Ra added as a tracer should be high enough so that the resultant counting uncertainty of the ^{217}At activity ingrown from the tracer is five percent (5 %) or less during the allotted sample count time.

Note: The activity of ^{217}At present at the midpoint of the count is used to calculate the chemical yield for radium by back-calculating the activity of ^{225}Ra recovered. The initial amount of ^{225}Ra added as tracer may need to be varied to accommodate planned differences in the time that has elapsed between chemical separation and the count, but the activity should be sufficient, and the count time long enough, to ensure that the resultant counting uncertainty for the ^{217}At peak is five (5 %) percent or less. See the calculation for A_t, in Step 12.2 for calculation of ingrowth factor for ^{217}At and Table 17.2 for typical ingrowth factors for a series of ingrowth times.

11.1.4. Reduce the sample volume to ~20% of the original volume by bringing the solution to a gentle boil and evaporating.

11.1.5. Following this digestion, add 10 mL of concentrated hydrochloric acid, and carefully evaporate the solution to incipient dryness.

11.1.6. Reconstitute the sample by adding 100 mL of 1-M HCl. The sample may be gently heated if necessary to facilitate dissolution of residual salts.

11.2. Water Sample Preparation and Pre-concentration of Radium on MnO_2 resin:

11.2.1. Add 100 mL of 1-M NaOH to each sample.

11.2.2. If particulate material is visible at this time, filter the sample through a 0.45-µm filter. (Do not rinse the filter). The filter should be saved for possible analysis for DRPs.

11.2.3. Add enough 1000 ppm calcium solution to the filtrate from Step 11.2.2 to ensure that the final calcium concentration is about 10 ppm. For waters that naturally have calcium in them above 10 ppm this step will be unnecessary.

11.2.4. Add a few drops of bromthymol blue indicator solution and adjust each sample to neutral pH by carefully adding 1-M NaOH until the color changes from yellow to blue-green.

Note: Adding too much base will overshoot the blue-green endpoint (indicated by blue color). The amount of NaOH added in Step 11.2.4 may be adjusted by carefully adding a small quantity of 1-M HCl and 1-M NaOH as needed to reach a blue-green endpoint.

11.2.5. The sample is equilibrated with ~1.0 g MnO_2 resin for 0.5–1.5 hours. Two options are provided:

11.2.5.1. Option 1: Add ~1.0 g MnO_2 resin to a beaker containing the neutralized sample. Cover with a watch glass and gently stir on a magnetic stirrer for at least 30 minutes.

11.2.5.2. Option 2: Transfer the neutralized sample to a 250 mL centrifuge bottle which contains ~1.0 g MnO_2 resin. Agitate the bottle gently on a shaker or in a tumbler for at least 30 minutes.

Note: Two options are provided for contacting the sample with MnO_2 resin. The contact time noted above (30 minutes) is to be understood as a minimum. Higher radium yields may be obtained with somewhat longer contact times (up to 90 minutes).

Note: Excessive agitation of the resin may lead to abrasion and loss of some MnO_2 from the resin and result in degraded chemical yields. Although sample quantitation is not significantly impacted since a ^{225}Ra yield tracer is used, uptake on the resin during this step should be reasonably optimized by evaluating the process and time used and choosing a default optimal conditions corresponding to a minimum of 80-85% uptake from a clean water matrix.

11.2.6. Pour the suspension into a 1.5-cm I.D. × 15-cm column fitted with a reservoir funnel. Allow sample to pass through column. Rinse the walls of the funnel reservoir and column with demineralized water. The combined column effluent from this step may be discarded.

11.2.7. Place a clean 50 mL centrifuge tube under each MnO_2 column. Add 10 mL of freshly made MnO_2 Stripping Reagent to the MnO_2 column to elute radium and other elements. Catch the column eluate containing radium and retain for subsequent processing.

Note: Effervescence will be noted upon addition of the MnO_2 Stripping Reagent. Gently tapping the column to dislodge any bubbles that form will help minimize channeling and may improve radium recovery. The resin bed will become light pink in color as MnO_2 dissolves.

11.3. Actinium and Thorium Removal Using Diphonix® resin:

11.3.1. Prepare a Diphonix® resin column for each sample to be processed as follows:[5]

11.3.1.1. Slurry ~1.0-g Diphonix® resin per column in water.

11.3.1.2. Transfer the resin to the 0.8-cm I.D. × 4-cm columns to obtain a uniform resin bed of ~1.4–1.6 mL (bed height ~26–30 mm). A top column barrier (e.g., frit, glass wool, beads) may be used to minimize turbulence that may disrupt the resin bed when adding solution to the column.

11.3.2. Precondition the column by passing 20 mL of 2-M HCl through the column discarding the column effluent.

11.3.3. Place a clean 50-mL centrifuge tube under each Diphonix® column.

[5] Commercially supplied pre-packed columns may be used here. When packing columns using bulk resin, excessive resin fines should be removed by rinsing the resin one or more times with an excess of water and decanting the water containing the fines prior to transferring the material to the column.

11.3.4. Swirl the solution retained in Step 11.2.7 to remove bubbles and carefully load onto the column taking care to minimize disturbing the resin bed. Collect column effluents in the 50-mL centrifuge tube. Allow the solution to flow by gravity.

11.3.5. When the load solution has stopped flowing (or is below the top of the resin bed), rinse the column with two 5-mL volumes of 2-M HCl. Collect the rinse solutions in the same 50-mL centrifuge tube (the total volume will be approximately 20 mL).

11.3.6. Record the date and time of the last rinse (Step 11.3.5) as the date and time of separation of radium from parent and progeny. This is also the beginning of ingrowth of ^{225}Ac (and ^{221}Fr and ^{217}At).

Note: If purified ^{225}Ra tracer is added to the sample (see Step 10.2 and Appendix A), the ^{225}Ra activity was unsupported before the tracer solution was added to the sample. The activity reference date and time established during standardization of the ^{225}Ra tracer is used as the reference date for the ^{225}Ra solution.

Note: If ^{225}Ra at some degree of secular equilibrium with ^{229}Th is added as tracer in the initial step, the activity of ^{225}Ra is dependent upon the total amount of time between the last ^{229}Th purification and Step11.3.6. The decay of ^{225}Ra starts at Step 11.3.6.

Note: The Diphonix® resin contains thorium, actinium and possibly other radionuclides present in the sample and should be disposed of according to applicable laboratory procedures.

11.4. Barium sulfate micro-precipitation of ^{226}Ra

11.4.1. Add ~3.0 g of $(NH_4)_2SO_4$ to the 20 mL of 2M HCl solution collected from the Diphonix® column in Steps 11.3.3 – 11.3.5. Mix gently to completely dissolve the salt (dissolves readily).

11.4.2. Add 5.0 mL of isopropanol and mix gently (to avoid generating bubbles).

11.4.3. Place in an ultrasonic bath filled with cold tap water (ice may be added) for at least 20 minutes.

11.4.4. Pre-wet a 0.1-micron filter using methanol or ethanol. Filter the suspension through the filter using vacuum. The precipitate *will not be* visually apparent.

11.4.5. Rinse the sample container and filter apparatus with three 2-mL portions of 20% isopropanol solution to dissolve residual $(NH_4)_2SO_4$. Allow each rinse to completely pass through filter before adding the subsequent rinse.

11.4.6. Rinse the filter apparatus with about 2 mL of methanol or ethanol to facilitate drying. Turn off vacuum.

11.4.7. Carefully remove the filter and place it face-side up in a Petri dish. Carefully dry under a heating lamp for few minutes. Avoid excessive heat which may cause the filter to curl or shrink.

11.4.8. Mount the dried filter on a support appropriate for the counting system to be used.

11.4.9. Store the filter for at least 24 hours to allow sufficient ^{217}At (third progeny of ^{225}Ra) to ingrow into the sample test source allowing a measurement uncertainty for the ^{217}At of < ~5 %.

11.4.10. Count by alpha spectrometry. The count times should be adjusted to meet the uncertainties and detection capabilities identified in Steps 9.3, 9.4, and 9.5.

12. Data Analysis and Calculations

12.1. The final sample test source (filter mounted on a planchet) will need to have at least a 24-hour ingrowth for ^{225}Ac (and ^{221}Fr and ^{217}At) to meet Analytical Protocol Specifications for chemical yield with a counting time of 4 hours. At-217 (third progeny of ^{225}Ra) has a single, distinct alpha peak with a centroid at 7.067 MeV and is used for determining the yield.

Note: Actinium 225 and other decay progeny from the ^{225}Ra (e.g., ^{217}At) tracer will continue to ingrow as time elapses between separation and the count of the sample. Delaying the count significantly longer than a day may introduce a possible positive bias in results near the detection threshold. When sample counting will be delayed longer than 36 hours, and MQOs foresee decisions being made close to detection levels, the impact of tracer progeny tailing should be minimized. Possible approaches for accomplishing this may include improving the signal to noise ratio by: 1) Processing a larger sample aliquant; 2) Decreasing the tracer activity added to a level that will still provide adequate statistics ~400–1500 net counts at the time of the analysis but will minimize spilldown into the ^{226}Ra ROI.

12.2. While the radiochemical yield is not directly used to determine the ^{226}Ra activity of the sample, the following equation can be used to calculate the radiochemical yield (see Reference 16.6), if required:

$$RY = \frac{R_t - R_b}{\varepsilon \times A_t \times I_t}$$

Where:

RY	=	Fractional radiochemical yield based on ^{225}Ra (from ingrown ^{217}At at 7.07 MeV)
R_t	=	Total count rate beneath the ^{217}At peak at 7.07 MeV, cpm
R_b	=	Background count rate for the same region, cpm
ε	=	Efficiency for the alpha spectrometer
I_t	=	Fractional abundance for the 7.07 MeV alpha peak counted (= 0.9999)
A_t	=	Activity (dpm) of ^{217}At at midpoint of the count (see step 12.2.1)

Note: If ^{225}Ra is separated from ^{229}Th for use as a purified tracer, the ^{225}Ra activity is unsupported and begins to decay at the point of separation from ^{229}Th, and not in Step 11.3.6. Instead, the reference date and time established when the tracer is standardized is used for decay correction of the ^{225}Ra activity. If ^{229}Th solution (with ^{225}Ra in full secular equilibrium) is added to the sample, the ^{225}Ra activity is equal to the ^{229}Th activity added and only begins to decay at the point of separation of ^{225}Ra from ^{229}Th in Step 11.3.6.

12.2.1. Activity of ^{217}Ac at the midpoint of the count interval.

A_t = The activity of ^{217}At at midpoint of the count (the target value that should be achieved for 100% yield), in dpm.
$= 3.0408 \left(A_{^{225}\mathrm{Ra}}\right) \left[e^{-\lambda_1 d} - e^{-\lambda_2 d}\right]$

$A_{^{225}\mathrm{Ra}}$ = Activity in dpm of ^{225}Ra tracer[6] added to the sample in Step 11.1.3 decay corrected to the date and time of radium separation in Step 11.3.6.

d = Elapsed ingrowth time for ^{225}Ac [and the progeny ^{217}At], in days from the date and time of Ra separation to the midpoint of the sample count

λ_1 = 0.04652 d^{-1} (decay constant for ^{225}Ra – half-life = 14.9 days)

λ_2 = 0.06931 d^{-1} (decay constant for ^{225}Ac) – half-life = 10.0 days)

3.0408 = $\lambda_2/(\lambda_2 - \lambda_1)$ [a good approximation as the half lives of ^{221}Fr and ^{217}At are short enough so that secular equilibrium with ^{225}Ac is ensured]

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

$$AC_a = \frac{R_{na} \times A_t \times I_t}{V_a \times R_{nt} \times D_a \times I_a \times 2.22}$$

and

$$u_c(AC_a) = \sqrt{u^2(R_{na}) \times \frac{A_t^2 \times I_t^2}{V_a^2 \times R_{nt}^2 \times D_a^2 \times I_a^2 \times 2.22^2} + AC_a^2 \times \left(\frac{u^2(A_t)}{A_t^2} + \frac{u^2(V_a)}{V_a^2} + \frac{u^2(R_{nt})}{R_{nt}^2}\right)}$$

where:

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

R_{na} = net count rate of the analyte in the defined region of interest (ROI), in counts per minute *(Note that the peaks at 4.784 and 4.602 MeV are generally included in the ROI for ^{226}Ra)*

[6] When separated ^{225}Ra tracer is added to the sample, its initial activity, $A_{225\mathrm{Ra\text{-}initial}}$, must be corrected for decay from the reference date established during standardization of the tracer to the point of separation of ^{225}Ra and ^{225}Ac as follows:

$$A_{^{225}Ra} = \left(A_{^{225}Ra-initial}\right)\left(e^{-\lambda_1 d_t}\right)$$

where: λ_1 = decay constant for ^{225}Ra (0.04652 d^{-1}); and d_t = time elapsed between the activity reference date for the ^{225}Ra tracer solution added to the sample and the separation of ^{225}Ra and ^{225}Ac in Step 11.3.6 (days).

When ^{229}Th containing ingrown ^{225}Ra is added directly to the sample, the amount of ^{225}Ra ingrown since purification of the ^{229}Th solution is calculated as:

$$A_{^{225}Ra} = \left(A_{^{229}Th}\right)\left(1 - e^{-\lambda_1 d_i}\right)$$

where: $A_{229\mathrm{Th}}$ = Activity of the ^{229}Th standard on the date of the separation of Th and Ra (Step 11.3.6); λ_1 = decay constant for ^{225}Ra (0.04652 d^{-1}); and d_i = time elapsed between the purification of ^{229}Th solution added to the sample and the separation of ^{225}Ra and ^{229}Th/^{225}Ac in Step 11.3.6 (days).

A_t = the activity of ^{217}At at midpoint of the count that should be achieved for 100% yield, in dpm (see Step 12.2 for detailed calculation)
I_t = Fractional abundance for the 7.07 MeV alpha peak counted (= 0.9999)
R_{nt} = net count rate of the tracer in the defined ROI, in counts per minute
V_a = volume of the sample aliquant (L)
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_a = probability of α emission for ^{226}Ra (*The combined peaks at 4.78 and 4.602 MeV are generally included in the ROI with an abundance of 1.00.*)[7]
$u_c(AC_a)$ = 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 (dpm)
$u(V_a)$ = standard uncertainty of the volume of sample aliquant (L)
$u(R_{na})$ = standard uncertainty of the net count rate of the analyte in counts per minute
$u(R_{nt})$ = standard uncertainty of the net count rate of the tracer in counts per minute

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.**

12.3.1 The net count rate of an analyte or tracer and its standard uncertainty can be calculated using the following equations:

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

and

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

where:

R_{nx} = net count rate of analyte or tracer, in counts per minute[8]

[7] If only the individual peak at 4.78 MeV is used, *and completely resolved from the 4.602 MeV peak*, the abundance would be 0.9445.

C_x	=	sample counts in the analyte or the tracer ROI
t_s	=	sample count time (min)
C_{bx}	=	background counts in the same ROI as for x (x refers to the respective analyte or tracer count)
t_b	=	background count time (min)
$u(R_{nx})$	=	standard uncertainty of the net count rate of tracer or analyte, in counts per minute

12.3.2 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.[9]

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

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

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

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

[8] 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 a total of zero counts are observed for the sample and background.

[9] 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.3.2, 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 when background variance may exceed that predicted by the Poisson model or when other decision error rates may apply.

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:

$$\mathrm{MDC} = \frac{\left[2.71 \times \left(1 + \frac{t_s}{t_b}\right) + 3.29 \times \sqrt{R_{ba}\, t_s \times \left(1 + \frac{t_s}{t_b}\right)}\right] \times A_t \times I_t}{t_s \times V_a \times R_{nt} \times D_a \times I_a \times 2.22}$$

where:

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

$z_{1-\alpha}$ = the 1-α quantile of the normal standard distribution

$z_{1-\beta}$ = the 1-β quantile of the normal standard distribution

12.4 Results Reporting

12.4.1 The following data should be reported for each result: volume of sample used; yield of tracer and its uncertainty; and full width at half maximum (FWHM) of each peak used in the analysis.

12.4.2 The following conventions should be used for each result:

12.4.2.1 Result in scientific notation ± combined standard uncertainty.

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

^{226}Ra 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 Results of method validation performance are to be archived and available for reporting purposes.

13.2 Expected turnaround time for an individual sample is ~35 hours and per batch is ~38 hours.

14 Pollution Prevention

14.1 The use of MnO_2 and Diphonix® resin reduces the amount of solvents that would otherwise be needed to co-precipitate and purify the final sample test source.

15 Waste Management

15.1 Nitric acid and hydrochloric acid wastes should be neutralized before disposal and then disposed of in accordance with local ordinances.

15.2 All final precipitated materials contain tracer and should be dealt with as radioactive waste and disposed of in accordance with the restrictions provided in the facility's NRC license.

16 References

16.1 RAW04-10, "Radium-226/228 in Water (MnO_2 Resin and DGA Resin Method)," Eichrom Technologies, Lisle Illinois (June 2006).

16.2 A Rapid Method For Alpha-Spectrometric Analysis of Radium Isotopes in Natural Waters Using Ion-Selective Membrane Technology; S. Purkl and A. Eisenhauer. Applied Radiation and Isotopes 59(4):245-54 (Oct 2003).

16.3 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.

16.4 *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.

16.5 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.

16.6 S. Purkl and A. Eisenhauer (2003). "A Rapid Method for Alpha-Spectrometric Analysis of Radium Isotopes in Natural Waters Using Ion-Selective Membrane Technology." *Applied Radiation and Isotopes* 59(4):245-54.

17 Tables, Diagrams, and Flow Charts

17.1 Tables [including major radiation emissions from all radionuclides separated]

Table 17.1 Alpha Particle Energies and Abundances of Importance

Energy (MeV)	Abundance (%)	Nuclide
4.601	5.6	Ra -226
4.784	94.5	Ra -226
4.798	1.5	Th -229
4.815	9.3	Th -229
4.838	5.0	Th -229
4.845	56.2	Th -229
4.901	10.2	Th -229
4.968	6.0	Th -229
4.979	3.2	Th -229
5.053	6.6	Th -229
5.434	2.2	Ra -223
5.449	5.1	Ra -224
5.489	99.9	Rn -222
5.540	9.0	Ra -223
5.580	1.2	Ac -225
5.607	25.2	Ra -223
5.609	1.1	Ac -225
5.637	4.4	Ac -225
5.682	1.3	Ac -225
5.685	94.9	Ra -224
5.716	51.6	Ra -223
5.724	3.1	Ac -225
5.732	8.0	Ac -225
5.732	1.3	Ac -225
5.747	9.0	Ra -223
5.791	8.6	Ac -225
5.793	18.1	Ac -225
5.830	50.7	Ac -225
5.869	1.9	Bi -213
6.002	100.0	Po -218
6.051	25.1	Bi -212
6.090	9.8	Bi -212
6.126	15.1	Fr -221
6.243	1.3	Fr -221
6.278	16.2	Bi -211
6.288	99.9	Rn -220
6.341	83.4	Fr -221
6.425	7.5	Rn -219
6.553	12.9	Rn -219
6.623	83.5	Bi -211
6.778	100.0	Po -216
6.819	79.4	Rn -219
7.067	99.99	At -217
7.386	100.0	Po -215
7.450	98.9	Po -211
7.687	100.0	Po -214
8.376	100.0	Po -213
8.525	2.1	Po -212
11.660	96.8	Po -212

- Analyte

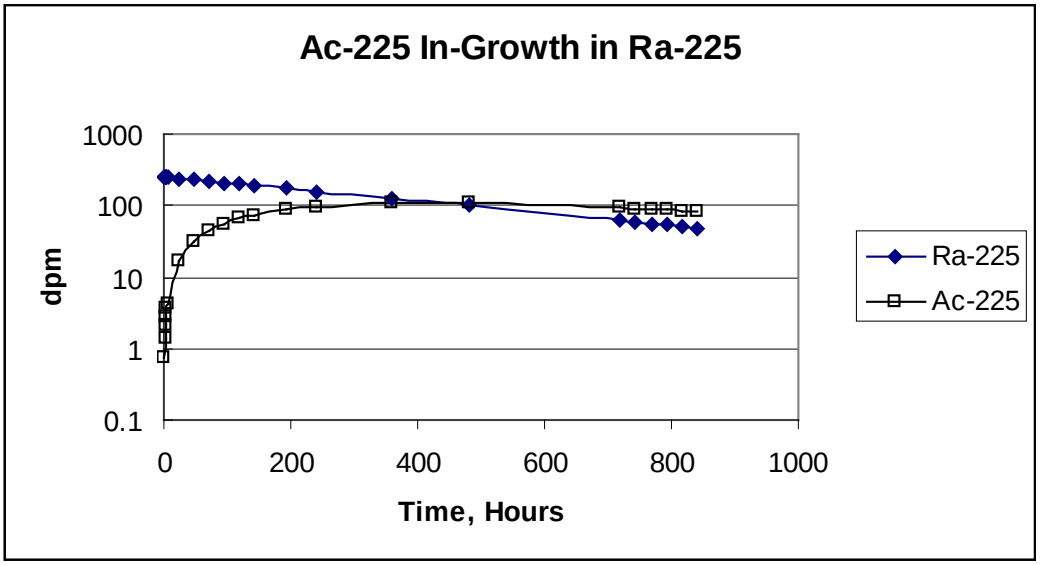
- ^{217}At (3rd progeny of ^{225}Ra tracer)

- ^{229}Th (Check ROI for indications of inadequate clean-up)

Includes only alpha particles with abundance > 1%.

Reference: NUDAT 2.4, Radiation Decay National Nuclear Data Center, Brookhaven National Laboratory; Available at: www.nndc.bnl.gov/nudat2/indx_dec.jsp; Queried: November 11, 2007.

17.2 Ingrowth curves and Ingrowth factors



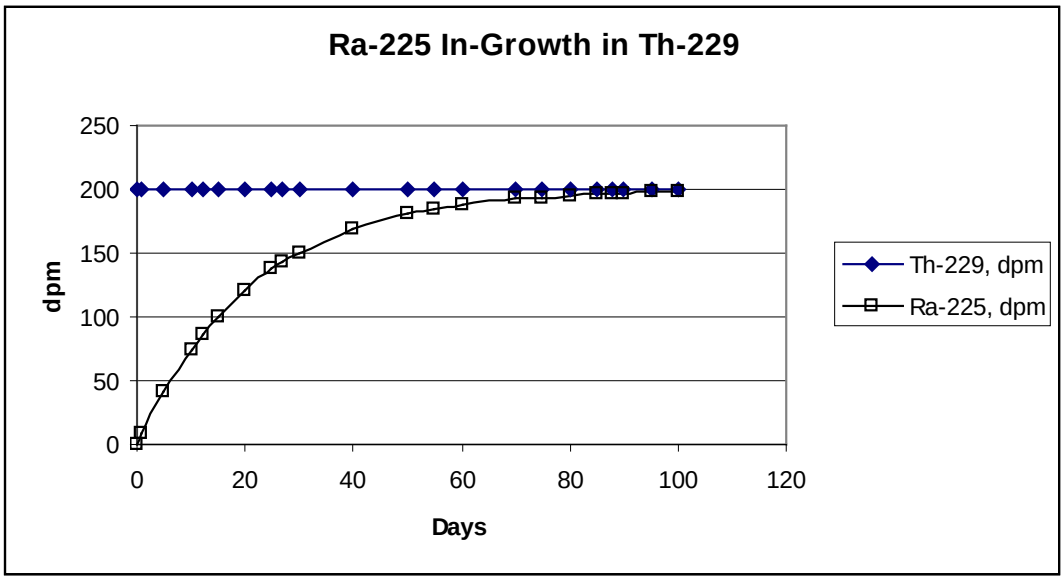


Table 17.2. Ingrowth Factors for ^{217}At in ^{225}Ra

Time elapsed between separation of Ra and midpoint of count in hours	**1**	**2**	**3**	**4**	**5**	**6**	**24**	**48**
Ingrowth Factor*	0.002867	0.005734	0.008588	0.01143	0.01425	0.01707	0.06540	0.1235
Time elapsed between separation of Ra and midpoint of count in hours	**72**	**96**	**120**	**144**	**192**	**240**	**360**	**480**
Ingrowth Factor*	0.1748	0.2200	0.2596	0.2940	0.3494	0.3893	0.4383	0.4391

**Ingrowth Factor represents the fraction of ^{217}Ac activity at the midpoint of the sample count relative to the ^{225}Ra activity present at the date/time of Ra separation. These ingrowth factors may be closely approximated (within a fraction of a percent) using the expression for A_t in Step 12.2.1.*

Table 17.3 Ingrowth Factors for ^{225}Ra in ^{229}Th

Time elapsed between purification of the ^{229}Th standard and date of Ra separation in days	**1**	**5**	**10**	**12**	**15**	**20**	**25**	**27**	**30**	**40**
Ingrowth Factor*	0.04545	0.2075	0.3720	0.4278	0.5023	0.6056	0.6875	0.7152	0.7523	0.8445
Time elapsed between purification of the ^{229}Th standard and date of Ra separation in days	**50**	**55**	**60**	**70**	**80**	**90**	**100**	**130**	**160**	**200**
Ingrowth Factor*	0.9023	0.9226	0.9387	0.9615	0.9758	0.9848	0.9905	0.9976	0.9994	0.9999

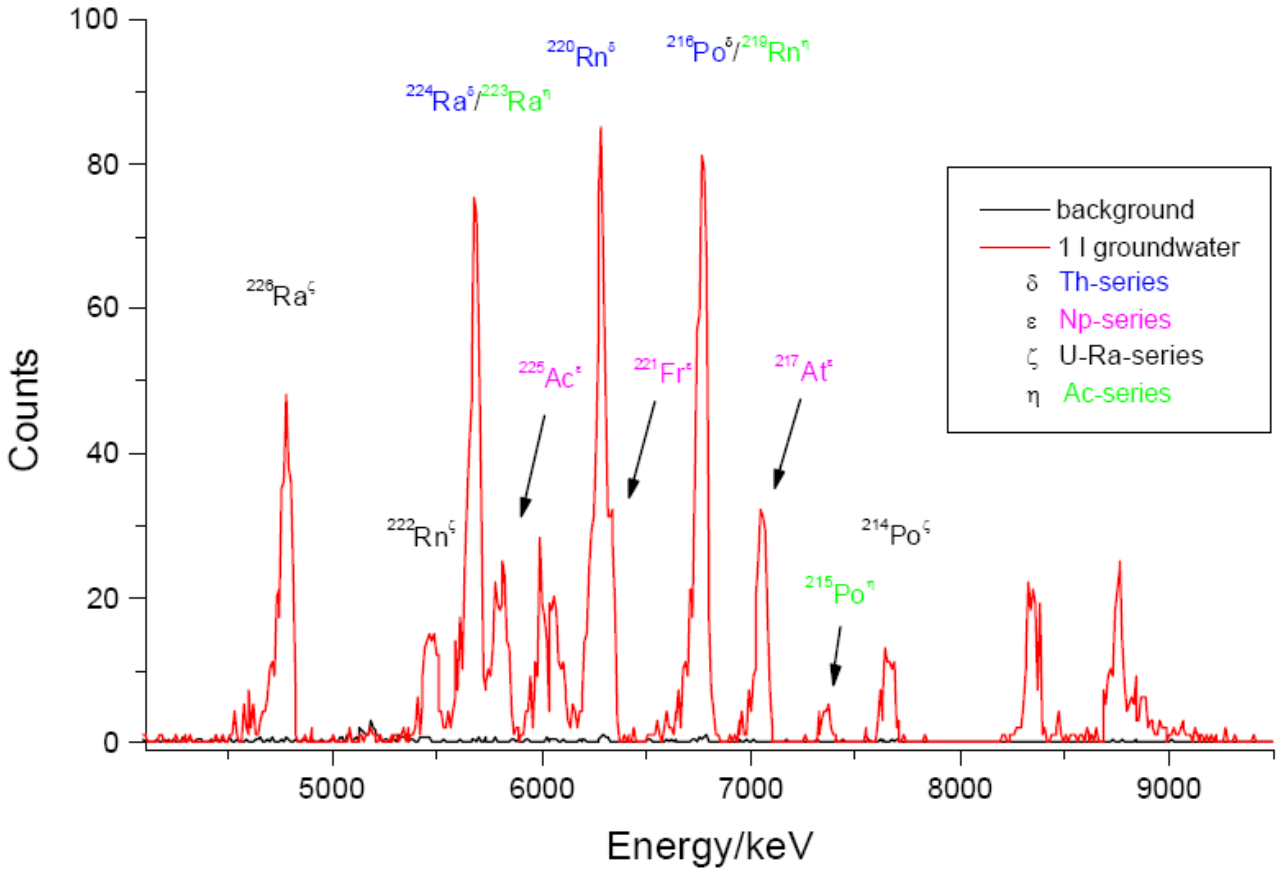
**Ingrowth Factor represents the fraction ^{225}Ra activity/^{229}Th activity at the time of Ra separation.*

Table 17.4 Decay Factors for Unsupported ^{225}Ra

Time elapsed between separation of ^{229}Th and ^{225}Ra in days	**1**	**5**	**10**	**12**	**15**	**20**	**25**	**27**	**30**	**40**
Decay Factor*	0.9545	0.7925	0.6280	0.5722	0.4977	0.3944	0.3125	0.2848	0.2477	0.1555
Time elapsed between separation of ^{229}Th and ^{225}Ra in days	**50**	**55**	**60**	**70**	**80**	**90**	**100**	**130**	**160**	**200**
Decay Factor*	0.09769	0.07741	0.06135	0.03853	0.02420	0.01519	0.00954	0.00236	0.00059	0.00009

**Decay Factor represents the fraction ^{225}Ra activity remaining as calculated using the equation in Footnote 6.*

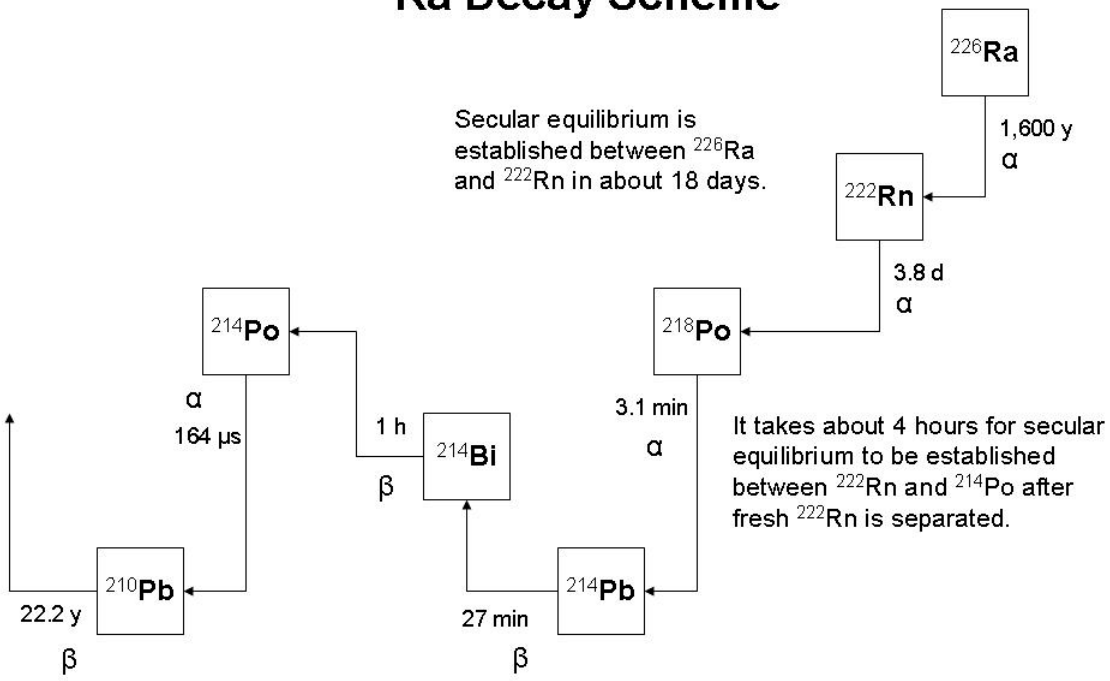
17.3 Example Alpha Spectrum from a Processed Sample



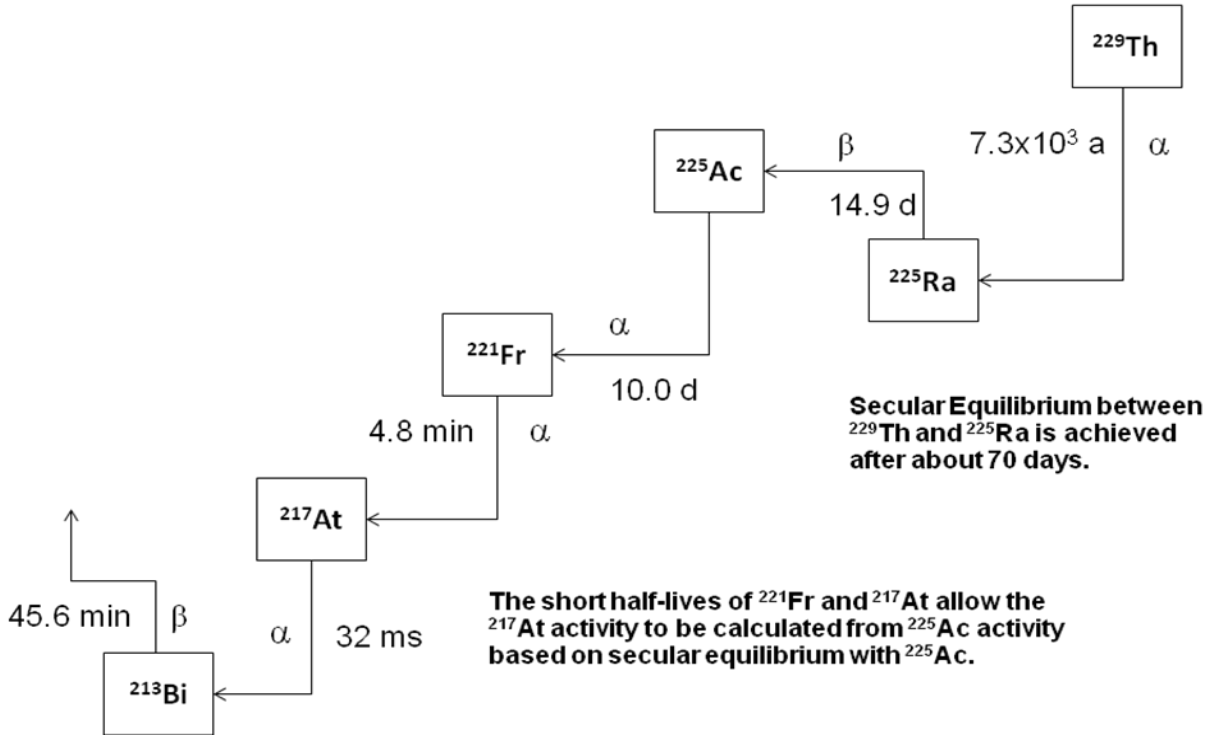
Reference: Purkl, Stefan, Dissertation: Entwicklung und Anwendung neuer analytischer Methoden zur schnellen Bestimmung von kurzlebigen Radiumisotopen und Radon im Grundwasserbeeinflussten Milieu der Ostsee; Chapter 2, Figure 3; Christian-Albrechts Universitaet, Kiel, Germany, 2003.

17.4 Decay Schemes for Analyte and Tracer

^{226}Ra Decay Scheme

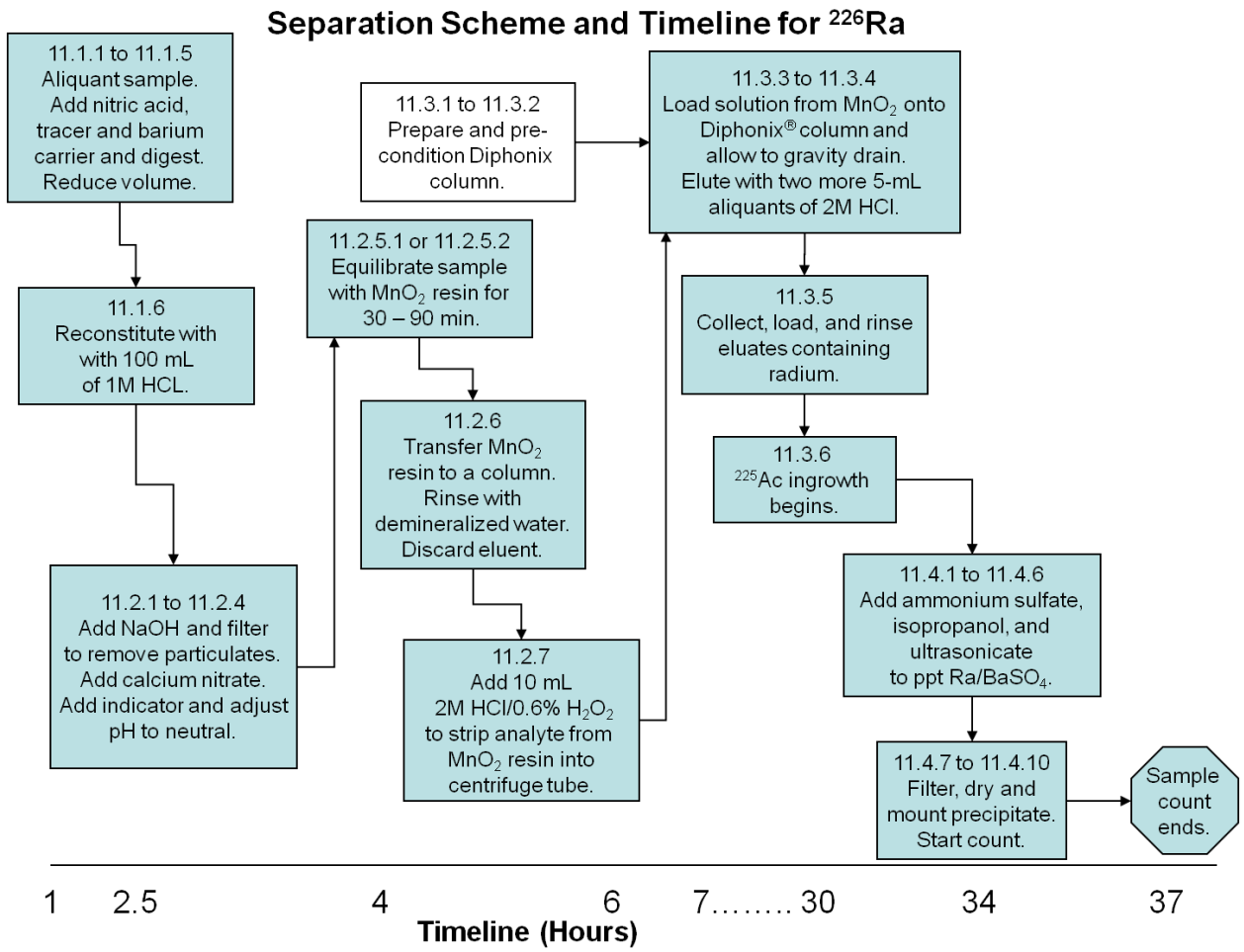


^{225}Ra (Including Parent) Decay Scheme



17.5 Flow chart

Note: Shaded figures are associated with the timeline.



Appendix A:
Preparation and Standardization of ^{225}Ra Tracer Following Separation from ^{229}Th

A1. Summary Description of Procedure

This procedure describes a ^{225}Ra generator to make tracer amounts of ^{225}Ra using a ^{229}Th solution. Th-229 is separated from ^{225}Ra using $Y(OH)_3$ co-precipitation. Th-229 is carried in the precipitate and most of the ^{225}Ra remains in solution. Centrifugation to remove ^{229}Th in the precipitate and filtration of the supernate produces the ^{225}Ra tracer solution. The ^{225}Ra activity of the tracer solution is standardized by counting sample test sources prepared from at least five replicate aliquants of the ^{225}Ra solution, each spiked with a known quantity of a ^{226}Ra standard. This standardized activity concentration, referenced to the date and time of the ^{225}Ra separation described in Step 4.11.7 below, is then decay-corrected to the date and time of subsequent sample analyses.

The $Y[Th](OH)_3$ precipitate may be stored and re-used later to generate more ^{225}Ra tracer solution. ^{225}Ra ingrows in the ^{229}Th fraction ($Y(OH)_3$ precipitate) and after 50 days will be about 90% ingrown. After sufficient ingrowth time ^{225}Ra may be harvested to make a fresh ^{225}Ra tracer solution by dissolving the precipitate and re-precipitating $Y(OH)_3$ to separate ^{229}Th from ^{225}Ra. Multiple ^{225}Ra generators may be prepared to ensure that ^{225}Ra tracer will be continuously available. The ^{225}Ra tracer solution produced is usable for 2–3 half-lives (~30–45 days). To minimize effort involved with standardization of the ^{225}Ra solution, it is recommended that the laboratory staff prepare an amount of ^{229}Th sufficient to support the laboratory's expected workload for 3-5 weeks. Since the ^{229}Th solution is reused, and the half-life of ^{229}Th is long (7,342 years), the need to purchase a new certified ^{229}Th solution is kept to a minimum.

A2. Equipment and Supplies

A2.1. Refer to Section 6 of the main procedure.

A3. Reagents and Standards

A3.1. Refer to Section 7 of the main procedure.

A4. Procedure

A4.1. Add a sufficient amount of ^{229}Th solution (that which will yield at least 150–600 dpm/mL of the ^{225}Ra solution) to a 50-mL centrifuge tube.[10]

A4.2. Add 20 mg Y (2 mL of 10 mg/mL Y metals standard stock solution).

A4.3. Add 1 mg Ba (0.1 mL of 10 mg/mL Ba metals standard stock solution).

A4.4. Add 4 mL of concentrated ammonium hydroxide to form $Y(OH)_3$ precipitate.

A4.5. Centrifuge and decant the supernatant into the open barrel of a 50-mL syringe, fitted with a 0.45-µm syringe filter. Hold the syringe barrel over a new 50-mL centrifuge tube while decanting. Insert the syringe plunger and filter the supernatant into the new centrifuge tube. Discard the filter as potentially contaminated rad waste.

[10] For example, if 40 mL of a ^{229}Th solution of 600 dpm/mL is used, the maximum final activity of ^{225}Ra will be ~510 dpm/mL at Step A4.8. This solution would require about 1.4 mL for the standardization process and about 8 mL for a batch of 20 samples.

A4.6. Cap the centrifuge tube with the precipitate, label clearly with the standard ID, precipitation date, and the technician's initials and store for future use.

A4.7. Properly label the new centrifuge tube with the supernate. This is the ^{225}Ra tracer solution.

A4.8. Add 3 mL of concentrated HCl to ^{225}Ra tracer solution. Cap centrifuge tube and mix well.

A4.9. Prepare the following solutions in 10 mL of 2-M HCl for standardization of ^{225}Ra tracer.

Solution	**Spike(s)**
Standardization Replicates (5 replicates)	~80 dpm of the ^{225}Ra tracer solution, and ~8 dpm of a ^{226}Ra standard traceable to NIST or equivalent
Blank	~80 dpm of the ^{225}Ra tracer solution *(the blank should be evaluated to confirm that ^{226}Ra is not detected in the ^{225}Ra tracer solution at levels that may compromise sample results when used in the method)*
Standardization Control Sample	~80 dpm of the ^{225}Ra tracer solution, and ~8 dpm of a second source independent traceable ^{226}Ra standard (the Standardization Control Sample should be evaluated to confirm that the standardization process does not introduce significant bias into the standardized value for the ^{225}Ra tracer)

A4.10. Add 75 µg Ba (0.075 mL of 1000 µg/mL Ba) to all solutions.

A4.11. Process the solutions to prepare sources for alpha spectrometry as follows:

- A4.11.1. Slurry ~1.0 g of Diphonix® resin per column in water.
- A4.11.2. Transfer the resin to 0.8 cm (I.D.) × 4 cm columns to obtain a uniform resin bed.
- A4.11.3. Precondition the columns by passing 20 mL 2 M HCl through the columns. Discard the effluent.
- A4.11.4. Place clean 50-mL centrifuge tubes under the columns.
- A4.11.5. Load the solutions from Step A4.10 onto the columns. Collect the effluents in the 50-mL centrifuge tubes. Allow the solutions to flow by gravity.
- A4.11.6. When the load solutions have stopped flowing, rinse columns with two 5-mL volumes of 2-M HCl. Collect the rinse solutions in the same 50-mL centrifuge tubes (the total volume will be about 20 mL).
- A4.11.7. Record the date and time of the last rinse as the date and time of separation of radium (beginning of ^{225}Ac ingrowth).
- A4.11.8. Add ~3.0 grams of $(NH_4)_2SO_4$ to the solutions from Step A4.11.6. Mix gently to dissolve.
- A4.11.9. Add 5.0 mL of isopropanol and mix gently.

A4.11.10. Place in an ultrasonic bath filled with cold tap water for at least 20 minutes.

A4.11.11. Filter the suspensions through pre-wetted (using methanol or ethanol) 0.1-µm filters.

A4.11.12. Rinse the filters with three 2-mL portions of 20% isopropanol. Allow each rinse to completely pass through filter before adding the next rinse.

A4.11.13. Rinse each filter with about 2 mL of methanol or ethanol.

A4.11.14. Carefully place each filter face-side up on a labeled stainless steel planchet, or other suitable source mount, which has previously been prepared with an appropriate adhesive (e.g., double stick tape).

A4.11.15. Dry under a heat lamp for a few minutes.

A4.11.16. After allowing about 24-hours ingrowth, count the standardization sources by alpha spectrometry.

A4.12. Calculate the activity of ^{225}Ra, in units of dpm/mL, in the standardization replicates, at the ^{225}Ra time of separation as follows:

$$A_{225Ra} = \frac{\left(\frac{N_{217At}}{t_{217At}} - \frac{N_b}{t_b}\right) \times \left(A_{226Ra}\right) \times \left(V_{226Ra}\right)}{\left(\frac{N_{226Ra}}{t_a} - \frac{N_b}{t_b}\right) \times \left[(3.0408)(I_t)\left(e^{-\lambda_1 d} - e^{-\lambda_2 d}\right)\right] \times V_{225Ra}}$$

where:

A_{225Ra}	=	Activity concentration of ^{225}Ra, in dpm/mL [at the time of separation from ^{229}Th, Step A4.11.7]
N_{217At}	=	Total counts beneath the ^{217}At peak at 7.07 MeV
N_{226Ra}	=	Total counts beneath the ^{226}Ra peak at 4.78 MeV
N_b	=	Background count rate for the corresponding region of interest,
t_a	=	Duration of the count for the sample test source, minutes
t_b	=	Duration of the background count, minutes
A_{226Ra}	=	Activity of ^{226}Ra added to each aliquant, in dpm/mL
V_{226Ra}	=	volume of ^{226}Ra solution taken for the analysis (mL)
V_{225Ra}	=	volume of ^{225}Ra solution taken for the analysis (mL)
d	=	Elapsed ingrowth time for ^{225}Ac [and the progeny ^{217}At], from separation to the midpoint of the sample count, days
λ_1	=	0.04652 d^{-1} (decay constant for ^{225}Ra – half-life = 14.9 days)
λ_2	=	0.06931 d^{-1} (decay constant for ^{225}Ac) – half-life = 10.0 days)
I_t	=	Fractional abundance for the 7.07 MeV alpha peak counted (= 0.9999)
3.0408	=	$\lambda_2 d / (\lambda_2 d - \lambda_1 d)$ [a good approximation as the half lives of ^{221}Fr and ^{217}At are short enough so secular equilibrium with ^{225}Ac is ensured]

Note: The activity of the separated A_{225Ra} will need to be decay corrected to the point of separation in the main procedure (Step 11.3.6) so that the results can be accurately determined.

A4.13. Calculate the uncertainty of the activity concentration of the ^{225}Ra tracer at the reference date/time:

$$u_c(AC_{225Ra}) = \sqrt{\frac{\left(\frac{N_{217At}}{t_a^2}+\frac{N_b}{t_b^2}\right)\times AC_{226Ra}^2\times I_{226Ra}^2\times V_{226Ra}^2}{\left(\frac{N_{226Ra}}{t_a}-\frac{N_b}{t_b}\right)^2\times\left[3.0408\times I_{217At}\times\left(e^{-\lambda_1 d}-e^{-\lambda_2 d}\right)\right]^2\times V_{225Ra}^2} + AC_{225Ra}^2\times\left(\frac{u^2(AC_{226Ra})}{AC_{226Ra}^2}+\frac{u^2(V_{225Ra})}{V_{225Ra}^2}+\frac{u^2(V_{226Ra})}{V_{226Ra}^2}+\frac{u^2(R_{226Ra})}{R_{226Ra}^2}\right)}$$

where:

$u(AC_{225Ra})$	=	Standard uncertainty of the activity concentration of ^{225}Ra, in dpm/mL
N_{217At}	=	Total counts beneath the ^{217}At peak at 7.07 MeV,
N_{226Ra}	=	Total counts beneath the ^{226}Ra tracer peak at 4.78 MeV
N_b	=	Background count rate for the corresponding region of interest,
t_a	=	Duration of the count for the sample test source, minutes
t_b	=	Duration of the background count, minutes
AC_{226Ra}	=	Activity of ^{226}Ra added to each aliquant, in dpm/mL
$u(AC_{226Ra})$	=	Activity of ^{225}Ra, in dpm/mL
V_{226Ra}	=	Volume of ^{226}Ra solution taken for the analysis (mL)
$u(V_{226Ra})$	=	Volume of ^{226}Ra solution taken for the analysis (mL)
I_{226Ra}	=	Fractional abundance for the ^{226}Ra peak at 4.78 MeV (= 1.000)
V_{225Ra}	=	Volume of ^{225}Ra solution taken for the analysis (mL)
$u(V_{225Ra})$	=	Volume of ^{225}Ra solution taken for the analysis (mL)
d	=	Elapsed ingrowth time for ^{225}Ac [and the progeny ^{217}At], from separation to the midpoint of the sample count, days
λ_1	=	0.04652 d^{-1} (decay constant for ^{225}Ra – half-life = 14.9 days)
λ_2	=	0.06931 d^{-1} (decay constant for ^{225}Ac) – half-life = 10.0 days)
I_{225Ra}	=	Fractional abundance for the 7.07 MeV alpha peak counted (= 0.9999)
3.0408	=	$\lambda_2 d/(\lambda_2 d-\lambda_1 d)$ *[a good approximation as the half lives of ^{221}Fr and ^{217}At are short enough so secular equilibrium with ^{225}Ac is ensured]*
$u(R_{226Ra})$	=	Standard uncertainty of net count rate for ^{226}Ra, in cpm
R_{226Ra}	=	Net count rate for ^{226}Ra, in (cpm)

Note: The uncertainty of half-lives and abundance values are a negligible contributor to the combined uncertainty and are considered during the evaluation of combined uncertainty.

A4.14. Calculate the mean and standard deviation of the mean (standard error) for the replicate determinations, to determine the acceptability of the tracer solution for use. The calculated standard deviation of the mean should be equal to or less than 5% of the calculated mean value.

A4.15. Store the centrifuge tube containing the $Y(OH)_3/Th(OH)_4$ precipitate. After sufficient time has elapsed a fresh ^{225}Ra tracer solution may be generated by dissolving the precipitate with 40 mL of 0.5-M HNO_3 and repeating Steps B4.3 through B4.9 of this Appendix.