# Title: Radium-226 and Radium-228 Separation in Radiochemical Matrices-Adapted from EPA 903.1 and 904.0

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RL-RA-001

REVISION 3

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## 1 SCOPE AND APPLICATION

1.1 This procedure is used to separate Ra-226 and Ra-228, individually or sequentially, in a variety of matrices. Matrices for which this method has been validated include water, soil, bottom sediment, suspended sediment, urine, and feces. However, radium isotopes are usually determined by gamma spectroscopy for soil and bottom sediment.

1.2 Radium is coprecipitated, as a sulfate, with barium and lead carriers. Ra-226 is determined by counting the activity of Rn-222 gas ingrown from the Ra-226 present. This is achieved with a special alpha scintillation system. Ra-228 is allowed to come to secular equilibrium with its daughter, Ac-228, which is then separated from the radium by a yttrium coprecipitation using ammonium oxalate. The resulting oxalate is counted with a beta proportional detector. This procedure uses Ba-133 tracer as a chemical yield during the preparation section.

1.3 Refer to Policy P-R-01 for method detection limit information.

## 2 SUMMARY OF METHOD

2.1 The radium in a sample is coprecipitated, as a sulfate, with barium and lead (including calibrated Ba-133 tracer), and the precipitate is dissolved in an alkaline EDTA solution. If Ra-228 is required, Sr-90 is partially removed by repetitive precipitations and dissolutions which manipulate the relative solubilities of Sr, Ba, and Ra sulfates in a buffered EDTA solution. This also serves to remove Ac-228 and start a measured period of Ac-228 ingrowth.

2.2 The radium fraction is gamma counted to determine the Ba-133 tracer yield and then transferred to a radon bubbler for Ra-226. Helium is bubbled through the sample to remove any Rn-222 present, and the bubbler is sealed to begin a measured period of Rn-222 ingrowth. When the Rn-222 has ingrown sufficiently, helium is again bubbled through the sample and, along with the ingrown Rn-222, collected in an alpha scintillation cell. The Rn-222 is allowed to come to secular equilibrium with its first two alpha emitting progeny, and then the activity in the cell is measured in a specially designed counter.

2.3 After sufficient Ac-228 ingrowth, a calibrated yttrium carrier and a lead carrier are then added to the sample. The lead is separated as the sulfide to remove any radioactive lead which may have ingrown from Ra-226 or Ra-228 since the beginning of the ingrowth interval. The Ac-228 is then separated from the Ra-228 by co-precipitation with yttrium as the hydroxide. The precipitate is dissolved, converted to yttrium and actinium oxalates and counted by a beta proportional counter.

2.4 Appropriately prepared fecal salts are suspended/dissolved in small quantities of concentrated nitric acid. Cold fuming nitric acid is used to ensure precipitation of Sr, Ba, and Ra nitrates. Most other ions remain in solution and are discarded. Water dissolves the nitrate precipitates and the radium separation is continued identically to water matrices.

2.5 Soils and sediments are solubilized by microwave bomb digestion or acid digestion. At the end of these procedures the dried sample is dissolved in a small volume of weak nitric acid. This is diluted further and the resulting solution is analyzed as a water sample.

## 3 DEFINITIONS

3.1 Carrier – Carriers are stable counterparts of the radioactive isotope(s) to be measured. Carriers are added to all samples in an analytical batch such that each sample has a specific measurable QC parameter (yield). From the time of addition, carriers undergo all chemical processing similar to that of the sample. Carriers (non-radioactive) are not counted; a known form of the carrier is weighed to provide radiochemical yield gravimetrically or is measured by an alternative technique

(such as inductively coupled plasma atomic emission spectrometry) to determine radiochemical yield.

3.2 Milking – The separation of the progeny from the parent isotope.

## 4 INTERFERENCES

4.1 There are no known interferences to the Ra-226 analysis; the other naturally occurring radon isotopes are too short-lived.

4.2 Large quantities of Sr-90 and Pb-210 can interfere with the Ra-228 analysis. This procedure is designed to remove ambient levels of Sr-90 and Pb-210. However, higher levels of these nuclides can give a high bias to the Ra-228 result.

4.3 The presence of carbonate in the NaOH solutions lowers the spike yields on Ac-228 in the Ra-228 analysis. Precautions to minimize $CO_2$ adsorption in these and the solid reagent are discussed under reagents.

## 5 SAFETY

Employees must abide by the policies and procedures in the Corporate Safety Manual, Radiation Safety Manual and this document.

5.1 Specific Safety Concerns or Requirements

- All work must be stopped in the event of a known or potential compromise to the health and safety of an associate. The situation must be reported immediately to a laboratory supervisor.
- Eye protection that satisfies ANSI Z87.1, laboratory coat, and appropriate gloves must be worn while samples, standards, solvents and reagents are being handled. Disposable gloves that have become contaminated will be removed and discarded; other gloves will be cleaned immediately.
- Exposure to chemicals must be maintained as low as reasonably achievable; therefore, unless they are known to be non-hazardous, all samples should be opened, transferred and prepared in a fume hood, or under other means of mechanical ventilation.
- Do not use hand to stop centrifuge from spinning.
- WARNING: Fuming nitric acid is a severe health hazard if not handled properly. Contact with skin and breathing of vapors must be avoided, and gloves and eye protection must be worn when handling. If fuming nitric acid contacts skin, immediately hold the exposed area under cool running water for fifteen minutes and call for help. Promptly report burns to supervision.

5.2 Primary Materials Used

The following is a list of the materials used in this method, which have a serious or significant hazard rating. **NOTE: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the MSDS for each of the materials listed in the table.** A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.

| Material (1) | Hazards | Exposure Limit (2) | Signs and symptoms of exposure |
|---|---|---|---|
| Ammonium Hydroxide | Corrosive Poison | 50 ppm-TWA | Vapors and mists cause irritation to the respiratory tract. Causes irritation and burns to the skin and eyes. |

| Material (1) | Hazards | Exposure Limit (2) | Signs and symptoms of exposure |
|---|---|---|---|
| Acetic Acid | Corrosive<br>Poison<br>Flammable | 10 ppm-TWA | Contact with concentrated solution may cause serious damage to the skin and eyes. Inhalation of concentrated vapors may cause serious damage to the lining of the nose, throat, and lungs. Breathing difficulties may occur. |
| Nitric Acid | Corrosive<br>Oxidizer<br>Poison | 2 ppm-TWA<br>4 ppm-STEL | Nitric acid is extremely hazardous; it is corrosive, reactive, an oxidizer, and a poison. Inhalation of vapors can cause breathing difficulties and lead to pneumonia and pulmonary edema, which may be fatal. Other symptoms may include coughing, choking, and irritation of the nose, throat, and respiratory tract. Can cause redness, pain, and severe skin burns. Concentrated solutions cause deep ulcers and stain skin a yellow or yellow-brown color. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage. |
| Nitric Acid, Fuming | Corrosive<br>Reactive<br>Oxidizer<br>Poison | ACGIH TLV 2ppm TWA<br>4ppm STEL | Inhalation of vapors can cause breathing difficulties and lead to pneumonia and pulmonary edema, which may be fatal. Other symptoms may include coughing, choking, and irritation of the nose, throat and respiratory track. Symptoms may disappear only to return in a few hours and more severely. Onset of symptoms may be delayed for 4-30 hours. |
| Sodium Hydroxide | Corrosive | 2 $mg/m^3$-Ceiling | Severe irritant. Effects from inhalation of dust or mist vary from mild irritation to serious damage of the upper respiratory tract, depending on severity of exposure. Symptoms may include sneezing, sore throat or runny nose. Contact with skin can cause irritation or severe burns and scarring with greater exposures. Causes irritation of eyes, and with greater exposures it can cause burns that may result in permanent impairment of vision, even blindness. |
| Sulfuric Acid | Corrosive<br>Oxidizer<br>Dehydrator<br>Poison<br>Carcinogen | 1 $mg/m^3$-TWA | Inhalation produces damaging effects on the mucous membranes and upper respiratory tract. Symptoms may include irritation of the nose and throat, and labored breathing. Symptoms of redness, pain, and severe burn can occur. Contact can cause blurred vision, redness, pain and severe tissue burns. Can cause blindness. |
| 1 – Always add acid to water to prevent violent reactions. | | | |
| 2 – Exposure limit refers to the OSHA regulatory exposure limit. | | | |

## 6 EQUIPMENT AND SUPPLIES

6.1 Alpha scintillation cell counter - calibrated for this procedure only.

6.2 Alpha scintillation cell.

6.3 Analytical balance - capable of reading 0.0001 g.

6.4 Aspirator hose.

6.5 Beakers - glass, various sizes.

6.6 Centrifuge.

6.7 Centrifuge tubes - plastic, 50 mL conical bottom and 90 mL with caps.

6.8 Emanation apparatus for radon (figure 1).

6.9 Drying lamp.

6.10 Filter – 0.45 µm Gelman Membrane, Acrodisc #4497 or equivalent.

6.11 Filter Holder – with Swin-Lok fitting or equivalent.

6.12 Hot plate.

6.13 Filter - nitrocellulose membrane, 47 mm, 0.45m pore size, BA 85.

6.14 pH paper - variable ranges, 1-12 or other suitable range to perform indicated tasks.

6.15 Pipet - transfer, glass or plastic.

6.16 Pipettors - various ranges, 0.1 to 5 mL.

6.17 Plastic wrap.

6.18 Planchets - stainless steel, 2.5 cm (1.0") or 3.8 cm (1.5") diameter, approximately 3 mm (1/8") deep, which have been flamed or muffled overnight at approximately 470°C-500°C.

6.19 Radon bubbler.

6.20 Stir rods - long, glass or plastic.

6.21 Syringe - 20 cc, with Leur-lock fitting, or equivalent.

6.22 Tape - plastic, to seal 50-mL plastic centrifuge tubes.

6.23 Vacuum pump.

6.24 Vortex mixer.

6.25 Ascarite II™ - Carbon dioxide adsorbent, 8-20 mesh. **CAUTION**: Corrosive.

6.26 Magnesium perchlorate drying reagent. **CAUTION**: Oxidizer

6.27 Helium gas - High Purity Grade or equivalent.

## 7 REAGENTS AND STANDARDS

7.1 Reagents are prepared from analytical reagent grade chemicals unless otherwise specified below. Reagent water, which must have an electrical resistivity of 1 megohm-cm or greater when obtained, is used throughout. Reagent water is obtained from the Nanopure system. Label all reagents as outlined in procedure RL-RPL-001.

**NOTE**: Consult the Material Safety Data Sheets for the properties of these reagents and how to work with them.

**NOTE**: Any reagent may be prepared at different volumes so long as the proportions of ingredients remain the same.

7.2 Acetic acid (17.4M $HC_2H_3O_2$) - Concentrated (glacial). **CAUTION**: Corrosive.

7.3 Ammonium hydroxide (15M $NH_4OH$) - Concentrated. **CAUTION**: Corrosive.

7.4 Ammonium oxalate ($(NH_4)_2C_2O_4$) 4.4% - Dissolve 2.5 g of ammonium oxalate monohydrate ($(NH_4)_2C_2O_4 \bullet H_2O$) in at least 25 mL of reagent water. Heat to dissolve. Dilute to 50 mL. Prepare fresh on each day of use. **CAUTION**: Corrosive.

7.5 Ammonium sulfate ($(NH_4)_2SO_4$) 200 mg/mL - Dissolve 20 g of ammonium sulfate in reagent water and dilute to 100 mL.

7.6 Ammonium sulfide ($(NH_4)_2S$) 2% - Dilute 2 mL of ammonium sulfide, 20%, to 10 mL with reagent water. Prepare fresh on each day of use. This solution slowly decomposes with age. If it is not "straw yellow", discard. **CAUTION**: Flammable and Corrosive.

7.7 Barium carrier and tracer - Prepared by the Standards Laboratory, and issued in individual vials.

7.8 1M Citric acid (1M $COH(CH_2CO_2H)_2CO_2H$) -Dissolve 19.2 g of citric acid monohydrate in reagent water and dilute to 100 mL.

7.9 0.25M Disodium ethylenedinitriloacetate dihydrate, EDTA ($C_{10}H_{14}N_2Na_2O_8 \bullet 2H_2O$) - Dissolve 20 g of NaOH in 750 mL of reagent water, heat and slowly add 93 g of EDTA while stirring. After the EDTA is in solution dilute to 1 L with reagent water.

7.10 30% Hydrogen peroxide (30% $H_2O_2$). **WARNING**: Corrosive and Oxidizer.

7.11 Lead carrier (15 mg/mL) - Dissolve 2.397 g of lead nitrate in reagent water, add 0.5 mL of nitric acid and dilute to 100 mL with reagent water. **WARNING**: Chronic, acute and reproductive toxin. **CAUTION**: Oxidizer.

7.12 Methyl orange indicator (0.1%) - Dissolve 0.1 g of solid methyl orange in 100 mL of reagent water.

7.13 90% Nitric acid (90% $HNO_3$) - Fuming. **WARNING**: Corrosive and Oxidizer.

7.14 Nitric acid (Concentrated $HNO_3$) – **WARNING**: Corrosive and Oxidizer.

7.15 6M Nitric acid (6M $HNO_3$) - Add 375 mL of concentrated $HNO_3$ to 625 mL of reagent water and mix well. **WARNING**: Corrosive and Oxidizer.

7.16 1M Nitric acid (1M $HNO_3$) - Add 63 mL of concentrated $HNO_3$ to 500 mL of reagent water then dilute to 1 L final volume. Mix well.

7.17 Sodium hydroxide (NaOH) - Store in a desiccator containing Drierite and soda lime. **WARNING**: Corrosive.

7.18 18M Sodium hydroxide (18M NaOH) - Dissolve 36 g of NaOH to 20 mL of reagent water. Mix the solution in a capped centrifuge tube. Dilute to a final volume of 50 mL. Prepare fresh daily. **WARNING**: Corrosive.

7.19 10M Sodium hydroxide (10M NaOH) - Dissolve 40 g of NaOH in reagent water and dilute to 100 mL. Prepare fresh daily.

7.20 Sodium carbonate ($Na_2CO_3$) - Saturated aqueous. Add 225 g $Na_2CO_3$ to 700 mL of reagent water.

7.21 Strontium carrier (10 mg/mL, uncalibrated) - Dissolve 24.16 g of strontium nitrate in reagent water and dilute to 1 L.

7.22 Strontium-yttrium mixed carrier A (20 mg/mL Sr, 18 mg/mL Y, uncalibrated) - Add 22.85 g of yttrium oxide ($Y_2O_3$) to 20 mL of reagent water. Heat to boiling and slowly add 30 mL of nitric acid while stirring until the yttrium oxide dissolves. Add 400 mL of reagent water to the flask and dissolve 48.32 g of strontium nitrate into the solution. Add 70 mL of concentrated $HNO_3$ and dilute to 1 L with reagent water. Mix well.

7.23 Strontium-yttrium mixed carrier B - Mix 10 mL of 10 mg/mL strontium carrier and 5 mL of 18 mg/mL yttrium carrier, dilute to 100 mL with reagent water.

7.24 Sulfuric acid (18M $H_2SO_4$) - Concentrated. **WARNING**: Corrosive.

7.25 Yttrium carrier (18 mg/mL, uncalibrated) - Add 22.85 g of yttrium oxide ($Y_2O_3$) to 20 mL of reagent water. Heat to boiling and slowly add 30 mL of nitric acid while stirring until the yttrium oxide dissolves. Add 70 mL of concentrated $HNO_3$ and dilute to 1 L with reagent water.

7.26 Yttrium carrier - Prepared by the Standards Laboratory.

## 8 SAMPLE COLLECTION, PRESERVATION, SHIPMENT AND STORAGE

8.1 The sample may be collected in glass or plastic containers. Storage of the sample prior to analysis should not exceed six months.

8.2 It is recommended that water samples be preserved at the time of collection by adding enough 1M $HNO_3$ to the sample to adjust it to pH 2.

## 9 QUALITY CONTROL

9.1 All quality control data shall be maintained and available for easy reference.

9.2 Yield monitors (carriers and tracers) and QC spikes are prepared with a pre-set mass and/or activity and distributed appropriately in coded vials for use during sample analysis. Consult the latest version of the client specific Quality Assurance Summary (QAS) for the appropriate yield monitors, spikes, carriers, and/or tracers to use.

9.3 Consult the Quality Assurance Summary for client specific information regarding QC frequency.

9.4 Refer to SOP RL-DR-001 for QC acceptance criteria and corrective action.

## 10 CALIBRATION

10.1 Each alpha scintillation cell is assigned to a particular counter and must be used only with that counter, because the counting efficiency (cell constant) depends on both the cell and the counter. Each cell is assigned its own unique code.

10.2 Each detector must be source checked every day or prior to use, whichever is less frequent. The process for checking a detector with a source cell is as follows.

10.2.1 Place the source cell assigned to the detector on the detector, and close the lid.

10.2.2 Enter Excursion, type scstart, detector name, and when prompted for the ID, type "chk." After the source check is done, collect the print-out and review it. If the sigma test shows any flags such as; above, below, or action, the detector can be checked once more. If the detector does not pass the second time, label it with a tag that it is out for the day and cannot be used.

10.3 Once a cell has had its identification code assigned, its background must be determined. The general protocol for establishing a cell background and constant is as follows:

10.3.1 All cells must be backfilled before their backgrounds are counted. Cells are backfilled as follows:

10.3.1.1 Attach the cell to the helium purge apparatus. Open the stopcock of the cell.

10.3.1.2 Open the vacuum valve. Allow the cell to "pump down" for a minimum of 6 hours.

10.3.1.3 Close the vacuum valve. Fill the cell to atmospheric pressure with helium, and then close the helium supply valve. DO NOT allow the pressure in the cell to exceed atmospheric pressure.

10.3.1.4 Repeat step 10.3.1.2 (without the 6 hour requirement) and 10.3.1.3 twice for a total of four times. Close the stopcock of the cell and remove the cell from the apparatus.

10.3.2 The counting time for a cell background should equal or exceed the sample count times.

10.3.3 If a cell gives a background count greater than 1 cpm, it must be backfilled and counted again. When the cell gives less than 1 cpm it may be used

10.3.4 Once the background of a cell has been determined, its cell constant must be determined before the cell may be used to process samples. Cell constants are determined by following steps 11.5.6 and 11.5.7 of this procedure using special standard bubblers whose Ra-226 concentrations are traceable to NIST.

**NOTE**: The standard bubblers need to undergo a full 7 day ingrow between uses.

10.3.5 Count the standard twice, for fifty minutes each time. Immediately after the second count, the cell should be removed from the counter and steps 10.3.1.1 and 10.3.1.2 of the backfilling procedure above should be performed.

**NOTE:** The repeat backfill will minimize the buildup of radon daughters in the cell, which would increase the background of the cell. This calibration process is repeated four times for each cell, each time using a different standard bubbler (to minimize any biases due to dilution error in the preparation of the standard bubblers, if necessary one result may be eliminated ). The cell constant to be used with the cell is the average of the eight results so obtained for the four determinations. Additional calibrations may be needed, causing more than four determinations to be used. It should be noted that properly measured cell constants are typically between 1.5 and 2.5 cpm per dpm of Ra-226. This is because the cell counts include not only the alpha particles produced by the decay of Rn-222, but also those produced by decay of Po-218 and Po-214. The half-lives of these two nuclides, and also Pb-214 and Bi-214, are sufficiently short so that all of them can be considered to be in secular equilibrium with the Rn-222 in the cell by the time the first count begins. The true efficiency of most cells is approximately 0.8 counts per disintegration, but it is customary to relate this to the activity of the Ra-226 which produced the Rn-222 because the cells are used to determine (in most cases) not Rn-222 but Ra-226.

10.4 Ra-228

10.4.1 In this procedure, it is not Ra-228 that is directly determined, but Ac-228, the first daughter of Ra-228. It is not practical to calibrate the beta proportional counters with Ac-228 because it has a 6.13 hour half-life. Instead, Sr-89 is used. The $E_{max}$ for Sr-89 is 589 Kev, while the $E_{max}$ of Ac-228 is 404 Kev.

## 11 PROCEDURE

**NOTE**: If any parameter is found to be out of limits, consult supervision. Also, a nonconformance will be issued to the Quality Assurance Group.

**NOTE**: One time procedural variations are allowed if deemed necessary by the professional judgment of supervision to accommodate variation in sample matrix, radioactivity, chemistry, sample size or other parameters. Any variation in procedure shall require approval by supervision and immediate notification of the Quality Assurance Group. If contractually required, the client shall be notified prior to any procedure changes. A nonconformance shall be completed and forwarded to the Quality Assurance Group within one day of the supervisor's approval. The nonconformance will be filed in the project file.

**NOTE**: To resolve problems with instrumentation or support equipment when the solution is not contained in this SOP, refer to SOP RL-QA-005 Troubleshooting Guide.

11.1 Sample Preparation

11.1.1 Soil and Sediments.

11.1.1.1 Samples are prepared by microwave digestion or acid digestion. If necessary, dissolve the sample residue in 2M $HNO_3$ if the samples are not received in solution.

11.1.1.2 Transfer the 2M $HNO_3$ solution to an appropriate size beaker, usually 1-L. Dilute to a working volume (typically 300-500 mL) with reagent water.

11.1.1.3 Continue with the Radium Analysis, step 11.2.

11.1.2 Air Filters

11.1.2.1 Samples are prepared according to RL-PRP-004 in an appropriate sized beaker. Add approximately 500 mL of reagent water to the sample digestate or salts.

11.1.2.2 Continue with the Radium Analysis, step 11.2.

11.1.3 Urine.

11.1.3.1 The sample is acidified with concentrated $HNO_3$.

11.1.3.2 Measure an appropriate volume of urine as stated in the client specific QAS. Quantitatively transfer the contents of the appropriate QC vial.

11.1.3.3 Continue with the Radium Analysis, step 11.2

11.1.4 Water.

11.1.4.1 Mix the sample and measure an appropriate volume of water as stated in the QAS. Quantitatively transfer the contents of the appropriate QC vial.

11.1.4.2 Continue with the Radium Analysis, step 11.2.

11.2 Radium Analysis.

11.2.1 For each aliquot of water or sample solution, add approximately 5 mL of 1M citric acid. Add a small amount of methyl orange indicator. The solution should be red.

**NOTE**: Some samples, contain some chemical species that destroy methyl orange upon heating.

11.2.2 Add approximately 10 mL of 15 mg/mL lead carrier to the sample and if Ra-228 is required, approximately 1 mL of Strontium-Yttrium mixed carrier A. Stir the sample well with a long stir rod, heat for approximately 30 minutes.

11.2.3 Remove the samples from the hot plate; while stirring, slowly add 15M ammonium hydroxide until the pH is greater than 5.0, as verified by the methyl orange indicator changing from orange-red to yellow. Allow the samples to cool.

11.2.3.1 For samples in which the methyl orange indicator is destroyed, or the color change is vague, add ammonium hydroxide until the pH of the solution is greater than 5.0, as verified with pH paper.

11.2.4 While stirring, slowly add 18M $H_2SO_4$ to the sample until the pH is less than 3. The color should change back to red and a precipitate should form.

11.2.5 Add approximately 5 mLof 200 mg/mL ammonium sulfate solution. Return the sample to the hot plate. Stir frequently and keep near boiling for about 15 minutes.

11.2.5.1 For routine sample analysis, proceed as follows:

11.2.5.1.1 Remove the sample from the hot plate and allow it to cool slightly. Tightly cover the beaker with plastic wrap. Allow the sample to cool and the precipitate to settle for at least 6 hours.

11.2.5.1.2 Carefully remove as much of the supernate as possible without losing any of the precipitate. Draw off the supernate through a pipet/pipet tip attached to a vacuum hose or decant to an appropriate waste container. After drawing off each supernate, rinse the end of the apparatus with reagent water.

**NOTE**: Urine samples are wet ashed with $HNO_3$ and $H_2O_2$ until the precipitate is white.

**NOTE**: All $H_20_2$ must be removed prior to continuing with the procedure.

Transfer the precipitate to a clean labeled 50-mL conical centrifuge tube with concentrated $HNO_3$ for urine samples and with reagent water for water samples. Centrifuge for approximately 5 minutes and discard the supernate to the appropriate waste container. Proceed to step 11.2.6.

**NOTE**: If the sample contains large amounts of calcium, as indicated by large amounts of precipitate, perform the "Radium Clean Up" as found in section 16.4.

11.2.5.2 For priority sample analysis, proceed as follows:

11.2.5.2.1 Remove the sample from the hot plate and allow it to cool slightly. Quantitatively transfer the precipitate into a vacuum filter apparatus containing a 47-mm nitrocellulose membrane filter (BA85, 0.45µ pore size). Vacuum filter the precipitate. Discard the supernate to the appropriate waste container.

11.2.5.2.2 Carefully place the filter containing the precipitate in the bottom of a beaker, preferably 250-mL. Add approximately 10 mL of concentrated $HNO_3$ and heat gently until the filter completely dissolves. Transfer the sample with concentrated $HNO_3$ into a 50-mL conical bottom centrifuge tube. Centrifuge and discard supernate to the appropriate waste container. Proceed to step 11.2.6.

11.2.6 Add approximately 10 mL of concentrated $HNO_3$ to the centrifuge tube. Cap the tube and mix on a Vortex mixer. Centrifuge and discard the supernate to the appropriate waste container. The acid wash can be repeated when there is an excessive amount of precipitate present. Usually no more than 2 or 3 acid washes are required.

11.2.7 Add 25 mL of alkaline EDTA reagent. Cap the tube and mix well using a Vortex mixer. Allow the precipitate to dissolve for 5 to 10 minutes by placing the tube in a hot water bath; remove, and mix well again. Examine the tube for undissolved precipitate. If undissolved precipitate is present, check the pH of the sample. If the pH < 10, add a few drops of 10M NaOH, mix vigorously, and heat. Recheck the pH and repeat until the pH ≥ 10.

**NOTE**: Some samples may contain substances that are insoluble in alkaline EDTA reagent. If the pH of the solution is greater than 10, it can be assumed that all barium sulfate is in solution. If this is the case, the sample should be centrifuged and the supernate poured into a clean tube. After confirmation of acceptable Ba-133 tracer yield the precipitate may be discarded to the appropriate waste container. If the yield is less than 70% or above 115%, contact supervision.

**NOTE:** For Ra-226 only, add 15-20 mL EDTA initially instead of 25 mL alkaline EDTA reagent. Ensure the pH ≥ 10. Then bring the solution to 25 mL using the alkaline EDTA reagent.

**NOTE:** In some cases, further attempts to dissolve white precipitate with later portions of EDTA solution will successfully dissolve the residual precipitate. Contact supervision for direction.

11.2.8 If Ra-228 is requested, proceed to step 11.3.

11.2.9 Allow the sample to cool to room temperature. Seal the centrifuge tube with plastic tape.

11.2.10 Submit the sample for a gamma count to determine the Ba-133 tracer yield. Calculate the Ba-133 tracer yield.

**NOTE**: The calculated Ba-133 tracer yield is used as a multiplier value. If the value of the multiplier is less than one (yield is greater than 100%), default to 1.0000 (marked as the default value). If the yield value is greater than 115%, recount the sample.

11.2.10.1 If yields are less than 70% or below the client required yield, and if insoluble material (large amounts of white precipitate) remained in the supernate from step 11.2.7, proceed to the "Radium Clean Up" steps found in section 16.4.

11.2.11 If only Ra-226 is required proceed to step 11.5.

11.3 Ra-228 Analysis

**NOTE**: Thorough mixing of the samples in the following steps is essential. Use of a Vortex mixer is recommended.

**NOTE**: In the following steps, pH adjustment should not have to take place. If it is suspected that the pH may need to be altered, contact supervision.

11.3.1 Add 1 mL of strontium-yttrium mixed carrier B to the sample. Add a few drops of 10M sodium hydroxide if any precipitate forms.

11.3.2 Add 1 mL of 200 mg/mL ammonium sulfate to the sample. Add 17.4M acetic acid to the sample until barium sulfate precipitates, and then add 2 mL in excess. Cap and mix. Digest in a hot water bath until the precipitate settles. Centrifuge and discard supernate to the waste container.

11.3.3 Repeat step 11.2.7, using 20 mL of alkaline EDTA reagent. Add 1 mL of 10M sodium hydroxide if the precipitate does not dissolve. Add additional 10M sodium hydroxide as needed. Repeat steps 11.3.1 and 11.3.2, then go to step 11.3.4.

11.3.4 Add 10 mL of reagent water and 1 mL of 200 mg/mL ammonium sulfate to the sample. Cap and mix. Centrifuge and discard the supernate into the appropriate waste container. Record on the worksheet the date and time that the supernate was decanted; this is the first Ac-228 separation date and time.

11.3.5 Add 15 mL of alkaline EDTA reagent to the sample. Cap and mix. Heat for 5 to 10 minutes in a hot water bath if needed to assist in dissolving. If the precipitate has not dissolved, mix again. Examine the tube for undissolved precipitate. Add a few drops 10M sodium hydroxide if there is undissolved precipitate. Cap the tube, and then mix until the precipitate dissolves.

11.3.6 If directed by supervision to perform the Ra-226 analysis first, proceed to step 11.5. Otherwise, allow the Ac-228 to ingrow at this time for at least 36 hours. While it is ingrowing seal the tube with plastic tape and submit the sample for a gamma count to determine the Ba-133 tracer yield.

**NOTE**: If the value of the yield is greater than 100%, default to 1.0000 (marked as the default value).

11.4 Ac-228 Separation

11.4.1 Transfer the contents of the tube to another tube containing yttrium carrier. Add 0.1 mL of lead carrier (15 mg/mL).

11.4.2 Add 0.3 mL of 2% $(NH_4)_2S$ to the sample. Add 10M NaOH until black lead sulfide precipitates. Cap, vortex, then sit for 10 minutes. Centrifuge and decant the supernate to the original 50-mL centrifuge tube.

**NOTE**: If more than 10 drops of 10M NaOH is needed, consult supervision.

**NOTE:** If precipitate appears gelatinous, contact supervision.

**CAUTION:** Normal precipitate appears black and finely divided. If otherwise, contact supervision.

11.4.3 Add 0.1 mL of lead carrier (15 mg/mL), 0.1 mL of 2% $(NH_4)_2S$ and three drops of 10M NaOH. Cap and vortex, then sit for 10 minutes. Centrifuge and filter the supernate using the syringe filter assembly (a 25 mL syringe with a 0.45 um filter attached). The filtrate may be collected in a clean tube.

**NOTE**: Lead sulfide may precipitate upon the addition of the lead carrier. This is normal, but the $(NH_4)_2S$ and 3 drops of 10M NaOH should be added to insure complete precipitation.

**CAUTION**: It is very important that no lead sulfide particles remain in the filtrate. If any lead sulfide particles are visible in the filtrate, the sample must be re-filtered.

**NOTE:** If precipitate appears gelatinous, contact supervision.

11.4.4 **CAUTION**: Ac-228 has a half-life of 6.13 hours. Once the yttrium hydroxide has been precipitated, it is important to finish the procedure and submit the samples for counting as quickly as possible. As it takes 3 hours to count the samples, there is approximately 3 hours to finish the procedure.

Add 5 mL of 18M NaOH to the sample in the centrifuge tube. Cap and vortex well. Record the time of the yttrium hydroxide precipitation on the worksheet. Digest in a hot water bath until yttrium hydroxide coagulates (approximately 5-7 minutes). Centrifuge and decant the supernate into the original 50-mL centrifuge tube. You may thoroughly rinse the PbS waste from the previous tube with reagent water and reuse that tube. This is the end of the Ac-228 ingrowth time and the start of the Ac-228 decay time. Save the supernate.

11.4.5 Dissolve the precipitate in 2 mL of 6M $HNO_3$. Cap and vortex well. If the precipitate has not dissolved, mix again. Make sure the precipitate is completely dissolved. Add 5 mL of reagent water and 3 mL of 10M NaOH. Cap and vortex. Digest in a hot water bath until yttrium hydroxide coagulates (approximately 5-7 minutes). Centrifuge and discard supernate to the appropriate waste container. Take care not to decant the precipitate.

11.4.6 Dissolve the precipitate with 3 mL of 1M $HNO_3$. Cap and vortex. Make sure the precipitate is completely dissolved. Dilute to 5 mL with reagent water and add 2 mL of 4.4% ammonium oxalate. Mix the sample well on a vortex mixer for approximately 10 seconds. Centrifuge and discard supernate to the appropriate waste container.

**NOTE:** If the precipitate is not dissolving, heat in a hot water bath for approximately 30 seconds.

**NOTE**: More 1M $HNO_3$ may be required to dissolve the precipitate.

11.4.7 Add 10 mL of reagent water, 0.3 mL of 1M $HNO_3$ and 0.3 mL of 4.4% ammonium oxalate. Cap and vortex. Centrifuge and discard the supernate to the appropriate waste container.

11.4.8 Repeat step 11.4.7,once then move on to step 11.4.9.

11.4.9 **NOTE**: The size of the planchet is determined by which beta counters will be used to count the samples.

To determine the yttrium yield, quantitatively transfer the precipitate to a pre-weighed 2.5 cm (1") or 3.8 cm (1.5") stainless steel planchet with a minimum of reagent water. Dry on a hot plate at a temperature of approximately 250ºF for approximately one hour. Weigh the planchet.

11.4.10 Record the final mass, initial mass and precipitate mass on the bench sheets. Fill in the appropriate information on the worksheet. Submit the planchet and worksheet to the counting room for low beta counting as soon as possible. The sample is counted at least three times to verify the decay of Ac-228.

11.5 Ra-226 Analysis

**NOTE:** To build a radon bubbler
-Attach stopcock to bubbler using a small amount grease and clip to secure
-Attach a second stopcock to the T-junction piece using grease and clip to secure.

-After sample is loaded into bubbler, place O ring between bubbler and T-junction, use clip to secure.

11.5.1 If Ra-228 analysis was performed first continue with step 11.5.2. Otherwise, proceed to step 11.5.50.

11.5.2 Add 4 mL of concentrated $HNO_3$ to the Ra-226 supernate from step 11.4.4. Mix well and then add 2 mL of the 200 mg/mL ammonium sulfate solution. Add 17.4M acetic acid to the sample until barium sulfate precipitates, then add 2 mL in excess. Digest in a hot water bath until the precipitate settles. Centrifuge and discard the supernate to an appropriate waste container.

11.5.3 Add 10 mL of reagent water with 1 mL ammonium sulfate to the precipitate. Mix, centrifuge and discard the supernate to an appropriate waste container.

11.5.4 Dissolve the precipitate in 15 mL of alkaline EDTA reagent. Cap, mix, and heat the sample in a hot water bath. Add a few drops of 10M NaOH if the precipitate does not completely dissolve. Allow the tubes to cool to room temperature. Seal the tube with plastic tape and submit the sample for a gamma count to determine the Ba-133 tracer yield.

**NOTE**: The calculated Ba-133 tracer yield is used as a multiplier value. If the value of the multiplier is less than one (yield is greater than 100%), default to 1.0000 (marked as the default value).

11.5.5 **NOTE:** Observe radon bubbler prior to transferring the solution for any defects or grease clogs.

Transfer the solution to a radon bubbler. Open both stopcocks and purge the solution by slowly passing helium gas through the bubbler for at least 15 minutes.

**NOTE:** For samples bubbling excessively causing a foam to form 1-2 drops of octanol can be added.

Shut the two stopcocks, and record the date and time on the worksheet. Store the bubbler for at least 3 days. The storage time may vary according to the RDL. Consult supervision or the QAS for possible shorter length of storage.

**NOTE:** Prior to purging, solution can be left in a bubbler overnight in a cool, dry place.

11.5.6 At the end of the storage period, fill the upper half of an drying tube with magnesium perchlorate and the lower half with Ascarite. To achieve this system, plug one end of the tube with a small amount of glass wool, add the drying agents and cap with another small piece of glass wool.

**NOTE**: For minimizing corrections that would be required in subsequent calculations, the voids above the bubbler must be kept very small. Capillary tubing is recommended whenever possible, and the drying tube volume with the Ascarite and magnesium perchlorate must be kept to a minimum. A typical system consists of a drying tube 10 cm x

1.0 cm (I.D.), with each of the drying agents occupying approximately 4 cm and being contained by small glass wool plugs. The column can be reused several times before the chemicals need to be replaced.

11.5.7 **CAUTION**: Do not expose the scintillation cell to fluorescent lighting without blackout cloth covering the window end of the cell.

Attach the drying tube to the bottom portion of the bubbler station, and then attach the radon bubbler to the drying tube. Attach an evacuated scintillation cell to the top portion of the bubbler station. Open the stopcock on the cell and check the assembly for leaks. Place the cell and the portion of the apparatus above the stopcock under a vacuum and close off the active vacuum to check for leaks. The outlet stopcock may be opened. Once significant bubbling ceases, the outermost stopcock may be slowly opened, making sure no sample bubbles up into the drying tube. After both stopcocks are opened, helium can then be applied to the sample. The helium rate is then adjusted such that it should take about 15-20 minutes for the vacuum to reach a point of slightly above room pressure, when the stopcock can be fully opened without a significant amount of bubbling and there is a reading of between 0-0.5 inches/Hg on the apparatus, the bubbler is essentially at atmospheric pressure again. Once the purge is complete, all stopcocks and toggles are closed and the time is to be recorded. This is the beginning of Rn-222 decay and ingrowth of Rn-222 daughters.

11.5.8 Store the scintillation cell for at least 4 hours to ensure equilibrium between radon and radon daughters. Count the alpha scintillations from the cell in a radon counter with a light-tight enclosure that protects the photomultiplier tube. See the QAS for appropriate counting protocol.

**NOTE**: After each analysis, vacuum the cell and allow the cell to pump down for a minimum of 6 hours. Flush the cell three times by evacuation and filling with helium, and store filled with helium at atmospheric pressure. This procedure removes radon from the cell and prevents the build-up of radon daughter products. Before each analysis, the scintillation cell is evacuated, filled with helium and counted to ascertain the cell background.

11.5.9 After the data have been reviewed, return the sample back to a centrifuge tube, rinsing the bubbler with a small portion of EDTA and store until directed otherwise. If proceeding to a Ra-228 analysis, go to step 11.4.

## 12 DATA ANALYSIS AND CALCULATIONS

12.1 For computer calculation of the Ra-226 concentration, consult the RadCalc Users Guide. If the units selected are dpm per sample, the result given divided by the expected value of the standard bubbler is the cell constant.

12.2 For Ra-226 Lucas cell efficiencies, consult the RadCalc Users Guide. Use the cell ID and enter 1 as the efficiency. The calculated activity divided by the expected activity is the true efficiency for that Lucas cell.

12.3 For computer calculation of the Ra-228 concentration, consult the RadCalc Users Guide.

12.4 Calculation of Ba-133 tracer yield:

$$\text{Ba-133 yields for Ra-226} = \frac{1}{\left(\frac{observed}{\text{expected}}\right)} \qquad \text{Ba-133 yields for Ra-228} = \frac{\text{expected}}{observed}$$

## 13 METHOD PERFORMANCE

13.1 The supervisor has the responsibility to ensure that this procedure is performed by analysts who have been properly trained in its use.

13.2 Method Demonstration of Capability documentation is maintained in the quality files.

## 14 WASTE MANAGEMENT AND POLLUTION PREVENTION

All waste will be disposed of in accordance with Federal, State and Local regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment.

14.1 Waste Streams Produced by the Method

- Aqueous acidic waste pH< 2. Waste is collected in an appropriate container. Transferred into an Acid Waste container color coded with Yellow tape and a Yellow cap.
- Aqueous Basic waste with a pH >2. Waste is collected in an appropriate container and transferred into a Neutral waste container color coded with Green tape and a Green Cap

## 15 REFERENCES

15.1 Beals, D.M., 1989, "Should the Ra-228 or the Ra-226 Analysis be Performed First?", Internal Technical Memorandum 1989-Ra-02, United States Testing Company, Richland Division.

15.2 Beals, D.M., 1989, "Validation Studies for the Addition of Soil and Sediment Matrices to UST-RD Procedure 20-Ra-01", Internal Technical Report 1989-Ra-03, United States Testing Company, Richland Division.

15.3 Noyce, J.R., February 1981, "Evaluation of Methods for the Assay of Ra-228 in Water". NBS Technical Note 1137, Washington, D.C., U.S. Government Printing Office.

15.4 U.S. Environmental Protection Agency, August 1980, "Prescribed Procedures for Measurement of Radioactivity in Drinking Water", Methods 903.1 and 904.0, EPA-600/40-80-032, National Technical Information Services, Springfield, VA.

15.5 American Society for Testing and Materials, "Standard test method for Ra-226 in Water", Annual Book of ASTM Standards, ASTM D3454-05, Philadelphia, PA .

15.6 RadCalc DB, Users Guide, Richland.

15.7 RL-QAM-001 Quality Assurance Manual, latest revision.

15.8 Richland Quality Assurance Summary (QAS), latest revision.

15.9 Associated SOPs

15.9.1 RL-RPL-001 – Reagent and Non-Radioactive Standard Labeling.

15.9.2 RL-PRP-004 - Preparation of Environmental Matrices.

15.9.3 RL-DR-001 – Review of Environmental and Bioassay Data.

15.9.4 RL-QA-005 – Troubleshooting Guide, latest revision.

## 16 MISCELLANEOUS

16.1 Method Differences

16.1.1 The principal difference between the EPA procedures and this procedure is the use of a Ba-133 tracer for yield determination for both Ra-226 and Ra-228. The EPA procedure uses a gravimetric barium yield determination for the Ra-228 analysis, and cannot determine the yield as accurately, or at the correct step, in the analysis. The EPA Ra-226 procedure contains no yield determination, i.e. assumes 100% yield, but in performing these analyses sequentially it is very important to determine a tracer yield prior to the Ra-226 analysis. Even when only Ra-226 is to be analyzed, the Richland procedure includes a yield determination in case the recovery is not 100%.

16.2 Responsibilities

Analyst: Implements SOP as written.

Counting Room: Performs review on raw instrument data.

Technical Data Reviewer: Performs final data review.

Project Manager: Confirms final review and prepares data for reporting to client.

QA Manager: Performs product quality assessments as defined in the Quality Assurance procedures.

16.3 Records Management/Documentation

16.3.1 All records generated by this analysis will be filed and kept in accordance with TestAmerica SOPs for records management and maintenance.

16.4 Radium Clean Up

16.4.1 Rinse precipitate (insoluble material from11.2.7) into a beaker (typically 600-mL).

16.4.2 Add approximately 100 mL of saturated sodium carbonate to the beaker. Boil the sample for at least 30 minutes using a watch glass or equivalent to prevent splattering. This step metathetizes the sulfate to carbonate.

16.4.3 Transfer the mixture to a 90 mL centrifuge tube and centrifuge. Pour the supernate into a container and save until Ba-133 yield is confirmed or until directed by supervision.

16.4.4 Dissolve the remaining precipitate with a minimum of concentrated nitric acid. Fill the tube with a 1:1 (v:v) mixture of fuming nitric acid and concentrated nitric acid. Chill the sample for about 30 minutes in an ice bath to ensure complete precipitation.

16.4.5 Centrifuge the mixture and discard the supernate to the appropriate waste container.

16.4.6 Add 25 mL of concentrated nitric acid to the precipitate. Mix and centrifuge. Discard the supernate to the appropriate waste.

16.4.7 Dissolve the precipitate with reagent water and bring up to a total of 500 mL.

16.4.8 Restart the analysis at step 11.2.1, except do not add a new barium carrier and tracer QC vial. Perform the analysis as normal until Step 11.2.7. At this step use the original 25 mL alkaline EDTA solution containing the previously counted portion of the sample. Doing this recombines the sample that was counted with the portion originally trapped in the precipitate. Upon completion of 11.2.7 continue to 11.2.11.

16.5 Radium Re-Milk

16.5.1 Add approximately 4 mL of concentrated $HNO_3$ to the reserved supernate from the yttrium hydroxide precipitation from the initial Ac-228 "milking" (step 11.4.4) and mix well.

16.5.2 Add approximately 2 mL of 200 mg/mL ammonium sulfate. Add concentrated glacial acetic acid to the sample until barium sulfate precipitates, then add 2 mL in excess. Cap and mix well. Digest in a hot water bath until the precipitate settles. Centrifuge for approximately 5 minutes and decant the supernate to an appropriate waste container.

16.5.3 Add approximately 10 mL of reagent water and about 1 mL of 200 mg/mL of ammonium sulfate to the sample. Cap and mix well. Centrifuge and decant the supernate to an appropriate waste container. Record the date and time the supernate was decanted on the analytical worksheet. This is the first Ac-228 separation date and time.

16.5.4 Go to step 11.3.5 and continue as normal with the subsequent steps.

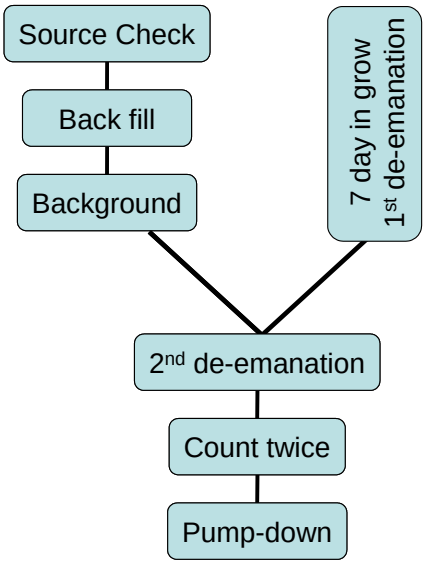
## 17 REVISION HISTORY

- Revision 1, 4/1/2010
  - Reformatted body of text.
  - Updated SOP references.
- Revision 2, 8/12/11
  - Referenced RL-QA-005.
  - Added section 10.2 for source checks, subsequent numbers change by one.

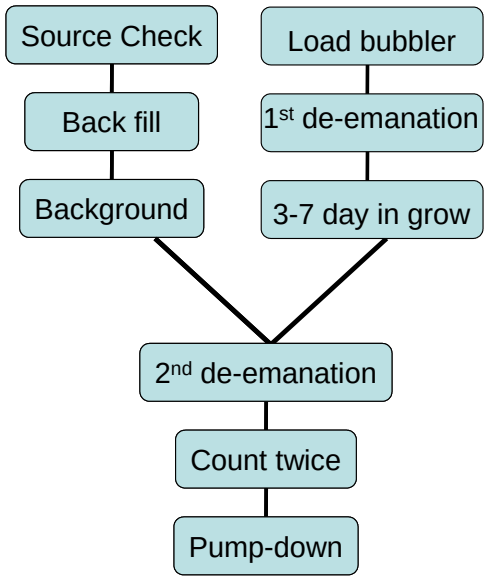
  - Added several notes added for clarity.
  - Reworded for clarity.
  - Update flow charts.
- Revision 3, 8/22/2012
  - Updated Section 10 to include clarifications.
  - Updated Section 11 to include clarifications as well as current practices as per technician requests.
  - Note added to step 11.5.5.
  - Updated step 11.5.9.

## 18 PROCEDURAL FLOWCHARTS

### Calibration




### Samples




### Cell Background

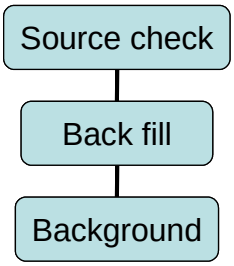


**Figure 1. Example De-emanation Apparatus with Scintillation Cell**