

**Title: Determination of Total Radium**

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RL-RA-002



REVISION 2

Facility Distribution No. \_\_\_\_\_

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## 1. SCOPE AND APPLICATION

- 1.1. The purpose of this procedure is to describe the analysis of Total Alpha Radium in water, soil and urine.
- 1.2. This method covers the separation of dissolved radium from water for the purpose of measuring its radioactivity.
- 1.3. Although all radium isotopes are separated, this method is limited to alpha-particle-emitting isotopes by choice of radiation detector. The most important of these radioisotopes are radium-223, radium-224 and radium-226.
- 1.4. The lower limit of concentration for water is 1 pCi/L

## 2. SUMMARY OF METHOD

- 2.1. Radium is coprecipitated in water samples with mixed barium and lead sulfates. The carriers are added to an alkaline solution containing citrate, which prevents precipitation during carrier exchange with the radium isotopes in the sample. Ammonium sulfate is then used to precipitate the sulfates, which are purified by nitric acid washes. The precipitate is dissolved in an alkaline solution containing EDTA, and the barium and radium sulfates are precipitated by addition of acetic acid, thus separating radium from lead and other radionuclides. The precipitate is dried on a plate, weighed to determine chemical yield, and alpha-counted to determine the activity concentration of the radium isotopes.
- 2.2. The radium, barium, and strontium are precipitated from the urine salts and the soil digestate from samples greater than 2 grams by the addition of cold fuming nitric acid. The precipitate is then dissolved in water and the solution is analyzed as a water sample.

## 3. DEFINITIONS

- 3.1. Coprecipitation – Simultaneous precipitation of more than one substance.

## 4. INTERFERENCES

- 4.1. A barium content in the sample exceeding 0.2 mg will cause a falsely high chemical yield.

## 5. SAFETY

Employees must abide by the policies and procedures in the Corporate Environmental Health and Safety Manual (CW-E-M-001), Radiation Safety Manual and this document. This procedure may involve hazardous material, operations and equipment. This SOP does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of the method to follow appropriate safety, waste disposal and health practices under the assumption that all samples and reagents are potentially hazardous. Minimum Personal Protective Equipment (PPE) for this SOP consists of safety glasses, gloves, lab coats and closed-toe, nonabsorbent shoes.

### 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.
- Lead carrier is known to be a chronic, acute reproductive toxin.
- **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.
- Do not use hand to stop centrifuge from spinning.

#### 5.1.1 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
Acetic Acid	Corrosive Poison 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.
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.
Nitric Acid	Corrosive Oxidizer Poison	2 ppm-TWA 4 ppm-STEEL	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 Reactive Oxidizer Poison	ACGIH TLV 2ppm TWA 4ppm STEEL	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 severally. Onset of symptoms may be delayed for 4-30 hours.
Sulfuric Acid	Corrosive Oxidizer Dehydrator Poison Carcinogen	1 mg/m <sup>3</sup> -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. Balance – analytical, capable of weighing to the nearest 0.001g.
- 6.2. Beakers – various sizes.
- 6.3. Centrifuge.
- 6.4. Centrifuge tubes – 90 mL plastic with lids.
- 6.5. Heat lamp.
- 6.6. Hot plate.
- 6.7. Ice bath.
- 6.8. pH paper – wide range, 0 – 14.
- 6.9. Planchet – muffled, 1 ½” stainless steel with cardboard holder.
- 6.10. Transfer pipet – plastic.
- 6.11. Vortex mixer.

## 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.

- 7.2. 17.4M Acetic acid (17.4M HC<sub>2</sub>H<sub>3</sub>O<sub>2</sub>) - Concentrated (glacial). **CAUTION:** Corrosive.
- 7.3. 14.7M Ammonium hydroxide (14.7M NH<sub>4</sub>OH) - Concentrated. **CAUTION:** Corrosive.
- 7.4. Ammonium sulfate ((NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>) 200 mg/mL - Add 20 g of ammonium sulfate to approximately 90 mL of reagent water. Dilute to 100 mL with reagent water and mix well.
- 7.5. 1M Citric acid (1M COH(CH<sub>2</sub>CO<sub>2</sub>H)<sub>2</sub>CO<sub>2</sub>H) - Add 192 g of citric acid monohydrate to approximately 900 mL of reagent water. Dilute to 1 L with reagent water and mix well.
- 7.6. 0.25M Disodium ethylenedinitrioloacetate dihydrate, EDTA (C<sub>10</sub>H<sub>14</sub>N<sub>2</sub>Na<sub>2</sub>O<sub>8</sub> • 2H<sub>2</sub>O) - Add 20 g of NaOH in approximately 750 mL of reagent water, dissolve with heat and slowly add 93 g of EDTA while stirring. Dilute to 1 L with reagent water and mix well.
- 7.7. Lead carrier (15 mg/mL) - Dissolve 2.397 g of lead nitrate in approximately 50 mL of reagent water and add 0.5 mL of nitric acid. Dilute to 100 mL with reagent water and mix well. **WARNING:** Chronic, acute and reproductive toxin. **CAUTION:** Oxidizer.
- 7.8. Methyl orange indicator (0.1%) - Dissolve 0.1 g of solid methyl orange in 100 mL of reagent water.
- 7.9. 16M Nitric acid (16M HNO<sub>3</sub>) - Concentrated. **WARNING:** Corrosive and Oxidizer.
- 7.10. 90% Nitric acid (90% HNO<sub>3</sub>) - Fuming. **WARNING:** Corrosive and Oxidizer.
- 7.11. 18M Sulfuric acid (18M H<sub>2</sub>SO<sub>4</sub>) - Concentrated. **WARNING:** Corrosive.
- 7.12. 2M Sulfuric acid (2M H<sub>2</sub>SO<sub>4</sub>) - Add 100 mL of 18M H<sub>2</sub>SO<sub>4</sub> to 700 mL of reagent water. Dilute to 1 L with reagent water and mix well.. **WARNING:** Corrosive.

## 8. SAMPLE COLLECTION, PRESERVATIVES, 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<sub>3</sub> to the sample to bring 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 sample and QC data acceptance criteria and corrective action.

## 10. CALIBRATION

- 10.1. Refer to appropriate detector SOP for calibration information.

## 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 Memo shall be completed and forwarded to the Quality Assurance Group within one day of the supervisor's approval. The Nonconformance Memo 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 Preparation and Urine Preparation

- 11.1.1.1. Soil Samples are prepared according to the client requested SOP. Urine sample are prepared according to RL-PRP-001. Soil sample greater than 2 grams and urine samples with excessive salts, proceed with step 11.1.1.2. All other samples proceed with step 11.1.1.3.

- 11.1.1.2. **CAUTION:** Fuming nitric acid is used in this procedure. It can cause an explosion and fire in contact with organics. **CAUTION:** If fuming nitric comes in contact with the skin, immediately flush with large amounts of water.

**NOTE:** All waste fractions are generally saved to the end of the procedure. After acceptable recoveries are received they may be surrendered for disposal.

Dissolve the sample residue in a minimum amount of fuming  $\text{HNO}_3$ , mix on a vortex mixer. Add 50-70 mL of fuming nitric acid and cool in an ice bath for 20-30 minutes. Centrifuge and save the supernate for sequential analysis if requested. Proceed to step 11.1.1.3.

**NOTE:** The fuming nitric acid addition may be done in a beaker first, then transferred back to the centrifuge tubes.

11.1.1.3. Dissolve the sample residue in reagent water. Bring the total volume to approximately 500 mL with reagent water.

11.1.1.4. To the sample add 5 mL of 1M citric acid and methyl orange. Adjust the pH to about 9 or 10 using pH paper and concentrated  $\text{NH}_4\text{OH}$ . Add 2 mL of lead carrier. Proceed to step 11.2 .

#### 11.1.2. Water Preparation:

11.1.2.1. Mix the sample prior to measuring out an aliquot of water (specified in the client specific QAS, typically 500mL) to an appropriately sized and labeled beaker. Add appropriate yield monitors (barium carrier) to the sample beakers. Rinse the vials three times with approximately 5 mL of reagent water, transferring the rinses quantitatively to the appropriate beaker.

11.1.2.2. Scan the vial labels into RadCalc.

11.1.2.3. Add appropriate spikes, yield monitors and carriers to the QC sample beakers containing a volume of reagent water equal to the sample volume. Rinse the vials three times with approximately 5 mL of reagent water, transferring the rinses quantitatively to the appropriate beaker. Remove Scan the vial labels into RadCalc. From this step on, the QC samples are treated the same as the samples.

11.1.2.4. To the sample add 5 mL of 1M citric acid and methyl orange. Add 2 mL of lead carrier. Adjust the pH to about 9 or 10 with concentrated  $\text{NH}_4\text{OH}$  (the solution color will be yellow-orange).

#### 11.2. Separation:

11.2.1. Heat to boiling and add approximately 2 mL of ammonium sulfate solution. Remove sample from hot plate, cool slightly; add 18M  $\text{H}_2\text{SO}_4$  until the solution becomes pink and cloudy.

**NOTE:** If a precipitate does not form here, check to see if the barium carrier was added, otherwise consult supervision.

- 11.2.2. Place the sample back on the hot plate and digest for 10 minutes. Remove the sample from the hot plate and allow to cool slightly. Cover and allow the sample to sit at least 6 hours.
- 11.2.3. Decant or aspirate (urine samples are always aspirated) the supernate to an appropriate waste container.

**NOTE:** If the sample is urine, the precipitate is wet ashed until white using small amounts of concentrated  $\text{HNO}_3$  and 30%  $\text{H}_2\text{O}_2$ .

Transfer the precipitate to a clean labeled centrifuge tube with 10%  $\text{H}_2\text{SO}_4$ . Centrifuge for at least 5 minutes. Decant the supernate to an appropriate waste container.

**NOTE:** Rapid samples may be suction filtered through a 0.45 micron Nitrocellulose filter instead. The filter will dissolve in concentrated  $\text{HNO}_3$ .

- 11.2.4. Wash the sulfate precipitate with approximately 10 mL of concentrated  $\text{HNO}_3$ . Centrifuge for at least 5 minutes and decant the supernate to an appropriate waste container. Repeat once.
- 11.2.5. Dissolve the precipitate by adding approximately 10 mL of reagent water, approximately 15 mL of 0.25M EDTA and 2-3 mL of concentrated  $\text{NH}_4\text{OH}$  to the centrifuge tube. Vortex the sample and place samples in a boiling water bath until samples are totally dissolved.

**NOTE:** If the sample does not dissolve, check the pH of the solution. If the pH is greater than 10, it can be assumed that all the barium sulfate is in solution. Any undissolved material can be separated from the EDTA solution by centrifuging the sample and decanting the supernate to a clean labeled centrifuge tube.

**NOTE:** When satisfactory  $\text{BaSO}_4$  weights have been obtained, the residual material can be discarded to an appropriate waste container.

- 11.2.6. If the sample matrix was soil or urine, seal the centrifuge tube with plastic tape and submit for gamma counting to determine the Ba-133 tracer yield. After gamma counting, proceed with the next step.
- 11.2.7. Add 1 mL of ammonium sulfate solution to the centrifuge tube, then add 3-5 mL of acetic acid until the  $\text{BaSO}_4$  precipitate forms. Record the separation date and time.

**NOTE:** If a  $\text{BaSO}_4$  precipitate does not form, consult supervision.

- 11.2.8. Allow the sample to sit for approximately 20 minutes. Centrifuge for at least 5 minutes and decant the supernate to an appropriate waste container. Wash the precipitate with approximately 10 mL of reagent water. Mix well and centrifuge for at least 5 minutes. Decant the supernate to an appropriate waste container.
- 11.2.9. **NOTE:** Take extreme care when decanting the supernate following centrifuging to avoid sample loss. A few grains of white precipitate could represent a substantial loss as 19 mg  $\text{BaSO}_4$  represents a quantitative recovery.

Wash the precipitate with 10 mL of reagent water and mix well. Centrifuge for at least 5 minutes and decant the supernate to an appropriate waste container.

- 11.2.10. Weigh a clean labeled, previously muffled, planchet. Record the date and sample ID on the planchet holder. Quantitatively transfer the precipitate to the appropriate planchet using reagent water and a plastic transfer pipet.
- 11.2.11. Dry the planchet under a heat lamp or on a hot plate. Allow the planchet to cool and weigh. Record the weight on the planchet holder and analytical worksheet. The precipitate weight is used to determine the chemical yield.
- 11.2.12. Record initial mass, final mass and precipitate mass on bench sheet. Submit samples for counting.

## **12. DATA ANALYSIS AND CALCULATIONS**

- 12.1. For computer calculation of the sample activity and total propagated uncertainty (TPU), consult the RadCalc Users Guide.

## **13. METHOD PERFORMANCE**

- 13.1. The supervisor has the responsibility to ensure that this procedure is performed by an analyst who has 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  $\text{pH} < 2$ . Waste is collected in an appropriate container and transferred into an Acid Waste container color coded with Yellow tape and a Yellow cap.
- Aqueous Basic waste with a  $\text{pH} > 2$ . Waste is collected in an appropriate container and transferred into a Neutral waste container color coded with Green tape and a Green Cap
- Flammable waste. Waste is collected in an appropriate container and placed in a Flammable waste container. Container is red with a self closing metal lid

### **Radioactive Waste**

Dry Radioactive waste shall be placed in a RAD Trash container. This waste stream can be distinguished by its yellow trash bags, and radioactive material stickers on the trash container.

All mixed waste shall be placed in the appropriate radioactive waste stream. The RAD waste stream color codes are the same as the non-radioactive waste streams but there are radioactive material stickers on the SAP container and spill tray.



Broken glassware shall be deposited in the appropriate broken glassware container. All Category I broken glassware is deposited in a White Broken Glass container. All Category II and/or III broken glassware is deposited in Magenta with White Radioactive Material box.

## 15. REFERENCES

- 15.1. ASTM D2460-07; Standard Test Method for Radionuclides of Radium in Water.
- 15.2. Prescribed Procedures for Measurement of Radioactivity in Drinking Water. EPA-6004-80-032, Edited by Herman L. Krieger and Earl L. Whittaker, 1980. Environmental Monitoring and Support Laboratory, Cincinnati, OH 45268.
- 15.3. U.S. Environmental Protection Agency, August 1980, "Alpha-Emitting Radium Isotopes In Drinking Water", Method 903.0, EPA-600/40-80-032, National Technical Information Services, Springfield, VA.
- 15.4. Method 9315 in Test Methods for Evaluating Solid Wastes, USEPA, SW-846, Third Edition (1986).
- 15.5. RadCalc DB, Users Guide, Richland.
- 15.6. RL-QAM-001 Quality Assurance Manual, latest revision.
- 15.7. Richland Quality Assurance Summary, latest revision.
- 15.8. Associated SOPs
  - 15.8.1. RL-RPL-001 – Reagent and Non-Radioactive Standard Labeling.
  - 15.8.2. RL-PRP-001 – Preparation of Urine and Blood Samples.
  - 15.8.3. RL-QA-005 – Troubleshooting Guide, latest revision.

## 16. MISCELLANEOUS

- 16.1. 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.
- 16.2. Records Management/Documentation
  - 16.2.1. All records generated by this analysis will be filed and kept in accordance with TestAmerica QA policies for records management and maintenance.
- 16.3. Drinking Water/ASTM Method Variations
  - 16.3.1 This procedure is compliant with EPA Method 903.0 and ASTM Method D2460.

## 17. REVISION HISTORY

- Revision 1, 4/1/2010
  - Reformatted body of text

- Updated SOP references
- Revision 2, 8/03/2011
  - Referenced RL-QA-005
  - Updated ASTM method reference to latest revision
  - Clarified wording

18. Procedural Flow Chart

