

Rapid Determination of ^{226}Ra in Emergency Urine and Water

Summary of Method ^{226}Ra is isolated from 100mL urine samples or up to 1 liter water samples and measured by alpha spectrometry as described by Maxwell, et al.¹ Radium is precipitated from samples with calcium phosphate. The calcium phosphate precipitate is dissolved in hydrochloric acid, and cation exchange chromatography is used to purify radium and barium from matrix ions. Eichrom DGA Resin is used to remove other alpha emitting nuclides from radium. Samples are prepared for radium measurement by alpha spectrometry via barium sulfate microprecipitation onto Eichrom Resolve® Filters. Sample preparation, including alpha spectrometry source preparation, for batches of 12 samples can be completed by a single operator in as little as 3-4 hours, with >90% yield of Radium. Yields can be traced with ^{133}Ba by gamma spectrometry or ^{225}Ra (^{229}Th) by alpha spectrometry. If tracing with ^{225}Ra , at least 8 hours of ingrowth time are required for the alpha emitting ^{217}At daughter of ^{225}Ra prior to alpha spectrometry measurements.

Reagents

Cation Exchange Resin (Eichrom C8-B500-F-H)
 DGA Resin, Normal 2mL Cartridges (Eichrom DN-R50-S)
 Ammonium Hydroxide (Listed as 28% NH_3 or 56% NH_4OH)
 Nitric Acid (70%) Hydrochloric Acid (37%)
 Deionized Water Hydrogen Peroxide (30%)
 ^{133}Ba or ^{225}Ra (^{229}Th) Tracer*
 1.25M $\text{Ca}(\text{NO}_3)_2$
 3.2M $(\text{NH}_4)_2\text{HPO}_4$
 Barium Carrier (1mg/mL)
 Isopropyl Alcohol
 Ammonium Sulfate
 Denatured Ethanol

* ^{133}Ba allows immediate counting.
 ^{225}Ra (^{229}Th) requires >8hrs ingrowth before alpha meas.
 Ba/Ra recoveries can differ by up to 10% in difficult matrices.

Equipment

Plastic Chromatography Column (Eichrom AC-50E-5M)
 Column Extension Funnel (Eichrom AC-20X-20M)
 Vacuum Box (Eichrom AR-24-BOX or AR-12-BOX)
 Cartridge Reservoir, 20mL (Eichrom AR-200-RV20)
 Inner Support Tubes-PE (Eichrom AR-1000-TUBE-PE)
 Yellow Outer Tips (Eichrom AR-1000-OT)
 Resolve Filter in Disposable Funnel (Eichrom RF-DF-25-25PP01)
 50mL and 250mL Centrifuge Tubes
 Centrifuge
 Hotplate
 150mL Glass beakers
 Vacuum Pump
 Heat Lamp
 Stainless Steel Planchets with adhesive tape
 Alpha Spectrometry System
 Gamma Spectrometry System (if ^{133}Ba tracer used)

Figure 1. Sample Preparation

100 mL urine or 1L water.
 Adjust to pH2 with HNO_3 .
 Add tracer ^{133}Ba or ^{225}Ra (^{229}Th)
 +1 mL 1.25M $\text{Ca}(\text{NO}_3)_3$
 +3mL 3.2 M $(\text{NH}_4)_2\text{HPO}_4$ **

**A calcium phosphate ppt. was chosen to minimize reagent background. A CaCO_3 ppt. (AN1413) can help minimize ^{229}Th in the final Ra fraction, when spiking directly with ^{229}Th for ^{225}Ra tracing.

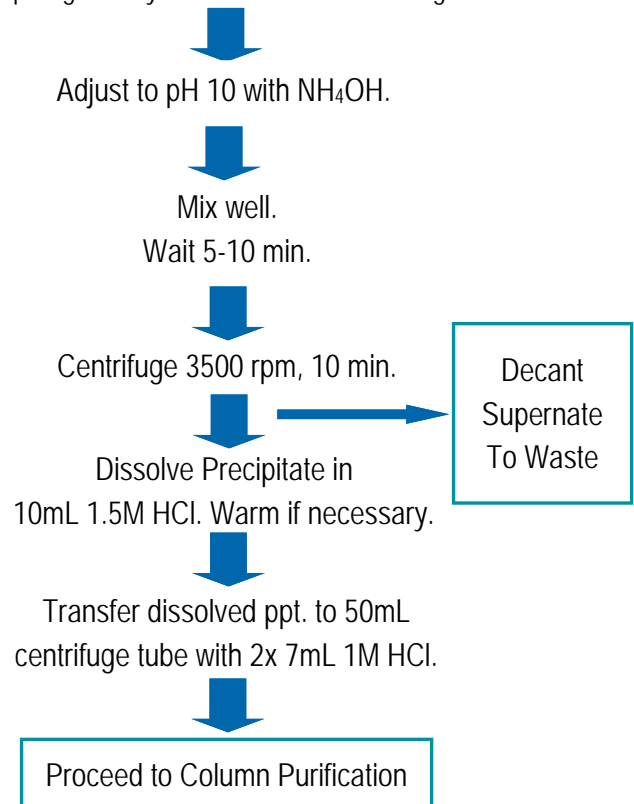

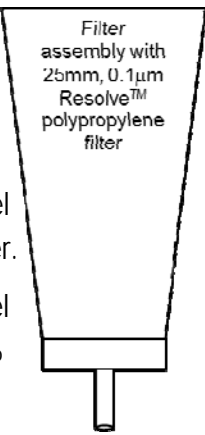
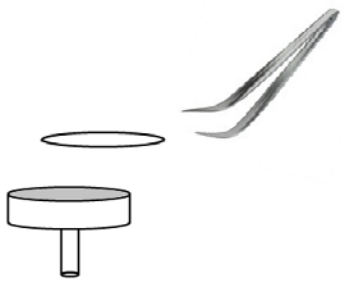

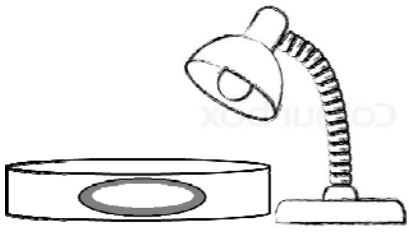


Figure 2. Column Purification and Alpha Source Preparation

<p>(1) Prewash 5.0g 50Wx8 200-400 mesh, cation exchange resin column¹: -10mL deionized water -20mL 6M HCl -10mL 0.5M HCl</p> <p>(2) Load Sample²</p> <p>(3) Rinse 30mL 3M HCl</p> <p>(4) Add 2mL DGA cartridge below cation exchange column.</p>		<p>(8) Add 50ug Ba carrier. Mix well.</p> <p>(9) Add 3g (NH₄)₂SO₄ and 5mL iso-propanol. Mix well.</p> <p>(10) Place in ice bath for 30 minutes.</p> <p>(11) Set up Resolve® Filter Funnel on vacuum box.</p> <p>(12) Wet filter with 3mL 80% ethanol followed by 3mL DI water.</p> <p>(13) Filter sample.</p> <p>(14) Rinse sample tube with 5mL DI water and add to filter.</p> <p>(15) Rinse filter funnel with 3mL DI water.</p> <p>(16) Rinse filter funnel with 1-2mL 100% ethanol.</p> <p>(17) Draw vacuum until filter is dry.</p>		<p>(18) Remove filter from funnel assembly and mount filter on stainless steel planchet with adhesive tape.</p>	
<p>(5) Strip Ra/Ba with 25mL 5M HNO₃.</p> <p>(6) Add 2mL 30% H₂O₂. Evaporate to dryness.</p> <p>(7) Dissolve residue in 10mL 1.5M HCl.</p>		<p>(19) Dry filter under heat lamp for 3-5 minutes.</p> <p>(20) Measure ²²⁶Ra and ²²⁵Ra(²¹⁷At) by alpha spectrometry after >8 hours ²¹⁷At ingrowth. (¹³³Ba by gamma, if necessary.)</p>			

¹If using ¹³³Ba tracer, 3.0g of cation exchange resin and proportionally smaller rinse volumes may be used.

²If tracing with ²²⁹Th, a 20mL 1M HCl-1M H₃PO₄ rinse following the sample load can improve purity of final ²²⁶Ra fraction.

Table 1. ²²⁶Ra Analysis Results from 100mL Spiked Urine Samples

Replicates	Tracer			²²⁶ Ra Reference Value (mBq/sample)	²²⁶ Ra Measured Value (mBq/sample)			% Bias
	¹³³ Ba % Recovery	SD	Average		Average	SD		
6	93	± 3	73.7	76.5	± 4.7	3.9		
6	98	± 3	18.4	17.9	± 0.8	-2.7		
6	92	± 5	Blank*	0.15	± 0.12			

*Calculated MDA 15 mBq/L (4 hr count, 100 mL sample)

*Calculated MDA 5 mBq/L (16 hr count, 100 mL sample)

References

- 1) Sherrod L. Maxwell, Brian K. Culligan, Jay B. Hutchinson, Robin C. Utsey and Daniel R. McAlister, "Rapid Determination of ²²⁶Ra in Emergency Urine Samples," *J. Radioanal. Nucl. Chem.*, 300(3), 1159-1166 (2014).