AN-1417-10

Rapid Determination of $^{226/228}$Ra in Water Samples

Summary of Method Ra isotopes are separated and measured from 1.0-1.5 liter samples of terrestrial waters. Radium is concentrated from samples on MnO_2 Resin. After a >36 hour ingrowth period for ^{228}Ac from ^{228}Ra, radium and ^{228}Ac are separated from matrix ions and potentially interfering radionuclides using stacked 2mL cartridges of Eichrom LN and DGA Resins. ^{228}Ac is prepared for gas flow proportional counting using a cerium fluoride microprecipitation onto Eichrom Resolve® Filters. ^{226}Ra is prepared for alpha spectrometry using a barium sulfate microprecipitation onto Eichrom Resolve® Filters. Chemical yield of radium is determined by adding either a ^{133}Ba or ^{225}Ra(^{229}Th) tracer. A single operator can process batches of 12-24 samples in 4-5 hours. Results for ^{226}Ra and ^{228}Ra can be obtained in 48 hours, including >36 hour ingrowth time for ^{228}Ac. Results for ^{226}Ra and ^{228}Ra in spiked river and ground water samples typically agreed to within 5% of reference values. If tracing ^{226}Ra with ^{225}Ra(^{229}Th) a minimum 8 hour ingrowth time for the ^{217}At daughter of ^{225}Ra is required.

Reagents

MnO_2 Resin (Eichrom MN-B100-A)
LN Resin (Eichrom LN-R50-S)
DGA Resin, Normal 2mL Cartridges (Eichrom DN-R50-S)
Ammonium Hydroxide (listed as 28% NH_3 or 56% NH_4OH)
^{133}Ba or ^{225}Ra(^{229}Th) Tracer
Barium and Cerium Carriers (1mg/mL)
Nitric Acid (70%)
Hydrochloric Acid (37%)
1.25M $Ca(NO_3)_2$
Denatured Ethanol
Deionized Water
Hydrofluoric Acid (50%)
Hydrogen Peroxide (30%)
Ammonium Sulfate
Isopropyl Alcohol

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 Centrifuge Tubes
Stainless Steel Planchets with Adhesive Tape
Alpha Spectroscopy System
Gamma Spectroscopy System (if ^{133}Ba tracer used)
Low Background Gas Flow Proportional Counter
150mL Glass beakers
Vacuum Pump
Hot Plate
Heat Lamp

Figure 1. Sample Preparation

1.0-1.5 Liter Water Samples
Adjust to pH2 with HNO_3
+Tracer ^{133}Ba or ^{225}Ra(^{229}Th)
+1 mL 1.25M $Ca(NO_3)_3$

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Adjust to pH 6-7 with NH_4OH

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1.5g column of MnO_2 Resin, slurry packed from water in 5mL column. (Precondition column with 25mL DI water.) Load sample at up to 15mL/min.

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Rinse column with 50mL DI water.

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Strip MnO_2 with 12mL of 4M HCl-1.5% H_2O_2. Bubbling will occur. Resin will turn from dark brown to white as MnO_2 is dissolved.

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If measuring ^{228}Ra, allow >36 hours for ^{228}Ac ingrowth.

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Proceed to LN/DGA Separation

Figure 2. LN-DGA Separation and Alpha Source Preparation

(1) Precondition LN + DGA Resin with 5mL 4M HCl.
(2) Load samples at 1mL/min.
(3) Rinse sample tube with 5mL 4M HCl.
(4) Add tube rinse to LN + DGA Resin.
(5) Rinse LN + DGA with 5mL 4M HCl.

(6) Separate LN and DGA cartridges.

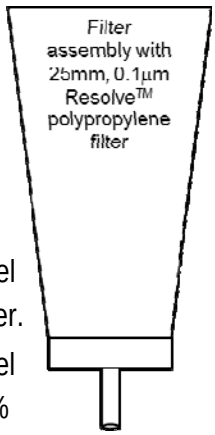
(7) Evaporate radium fraction from steps (2) to (5) to dryness.
(8) Dissolve residue in 10mL of 0.1M HCl + 50uL 30% H_2O_2.
(9) Pass Ra solution through same LN resin cartridge (Ra not retained). Rinse beaker with 5mL 0.1M HCl. Add beaker rinse to LN resin. Collect load/rinse for step (12).

(10) Rinse DGA Resin cartridge with 15mL 4M HCl.
(11) Strip ^{228}Ac from DGA with 10mL of 0.5mL HCl.

(12) ^{226}Ra samples: Add 50ug Ba carrier. Mix well. Add 3g $(NH_4)_2SO_4$. Mix well. Add 5mL isopropanol. Place in ice bath for 30 minutes.

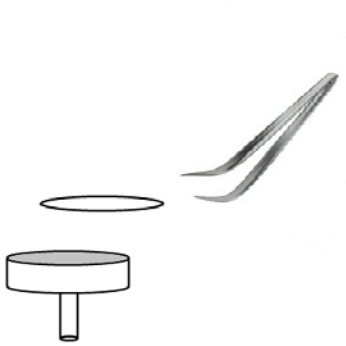
^{228}Ra(Ac) samples: Add 50ug Ce carrier. Mix well. Add 1mL 49% HF. Mix well. Wait 30 minutes.

(13) Set up Resolve® Filter Funnel on vacuum box.
(14) Wet filter with 3mL 80% ethanol followed by 3mL DI water.
(15) Filter sample.
(16) Rinse sample tube with 5mL DI water and add to filter.
(17) Rinse filter funnel with 3mL DI water.
(18) Rinse filter funnel with 1-2mL 100% ethanol.



(19) Draw vacuum until filter is dry.

(20) Remove filter from funnel assembly and mount filter on stainless steel planchet with adhesive tape.



(21) Dry filter under heat lamp for 3-5 minutes.

(22) Measure ^{228}Ra(^{228}Ac) by gas flow proportional counting. Measure ^{226}Ra and ^{225}Ra(^{217}At) by alpha spectrometry after >8 hour ^{217}At ingrowth. (^{133}Ba in ^{226}Ra fraction by gamma if necessary.)

Method Performance $^{226/228}$Ra in Water

Sample	Volume Liters	Replicates	^{133}Ba Tracer % Recovery	% Recovery ^{226}Ra	% Recovery ^{228}Ra
River Water	1.5	3	101 ± 5	103 ± 1	103 ± 7
Ground Water	1.0	5	95 ± 4	104 ± 1	102 ± 8

1040pCi ^{133}Ba, 5.0pCi ^{226}Ra, 20pCi ^{228}Ra

References

1) Sherrod L. Maxwell, "Rapid Method for ^{226}Ra and ^{228}Ra in Water Samples," *J. Radioanal. Nucl. Chem.,* 270(3), 651-655 (2006).