Experiment 13

Determination of Radio-strontium Isotopes in Environmental Samples

Objective

To determine radio-strontium isotopes in ash or water samples by conventional radiochemical separation method and counting beta particles.

Introduction

The two fission-produced radio-strontium isotopes of interest in environmental samples are ⁹⁰Sr and ⁸⁹Sr. Sr-90 has a fission yield of ~5.8 %, a half-life is 28.78 a, and the radioactive daughter ⁹⁰Y with a half life of 2.67 d, to which it decays by beta-particle emission. Sr-89 has a fission yield of ~4.7%, a half life of 50.52 d, and decays to the stable daughter ⁸⁹Y. The decay schemes given in Figure 13.1 show that these two radio-strontium isotopes for practical purposes can only be measured by beta-particle counting.

The beta particles from ⁸⁹Sr are readily detectable in relatively recentlyformed fission products. In fission-produced material that is two or more years old, beta particles from radio-strontium consist only of those emitted by ⁹⁰Sr. During the first day after fission, ⁹¹Sr (half life, 9.63 h) and ⁹²Sr (half life, 2.71 h) can be measured by gamma-ray spectral analysis. Radioactive ⁸⁵Sr (half life, 64.84 d) is produced by ⁸⁴Sr (n, γ) or ⁸⁵Rb(p,n) reactions and is used as tracer for radio-strontium analysis by measuring its gamma ray.

In this procedure, strontium is concentrated from the sample with a cation exchange resin. Further steps for radio-strontium purification include precipitation of strontium nitrate in fuming nitric acid and scavenge steps with ferric hydroxide to remove insoluble hydroxides and with barium chromate to remove insoluble barium and radium. Strontium is then precipitated as SrC_2O_4 . The ⁹⁰Y is allowed to grow into radioactive equilibrium and is then "milked" from the strontium by precipitating the hydroxide. The yttrium precipitate is dissolved and $Y_2(C_2O_4)_3$ is then precipitated, weighed, mounted and counted. The amount of ⁹⁰Sr is determined by measuring the beta particles of 2.67-d ⁹⁰Y.

If 89 Sr is present, the 89 Sr and 90 Sr + 90 Y beta-particle counts will have to be resolved. This is done by counting the strontium oxalate precipitate at least

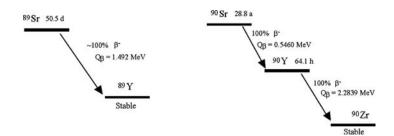


Figure 13.1 Decay schemes of ⁸⁹Sr and ⁹⁰Sr

twice. An interval of 3 weeks allows the ingrowth of ⁹⁰Y to equilibrium with ⁹⁰Sr and an observable decay of ⁸⁹Sr.

The counting efficiencies of ⁸⁹Sr, ⁹⁰Sr, and ⁹⁰Y are determined by adding standard solutions of ⁸⁹Sr and ⁹⁰Sr to different Sr(NO₃)₂ solutions and precipitating SrC₂O₄. The precipitate with ⁹⁰Sr is counted twice – immediately after precipitation and then after about 18 days to recount ⁹⁰Sr also to count the ingrown ⁹⁰Y. The two efficiency values are calculated by solving simultaneous equations. The precipitate with ⁸⁹Sr must be counted only once to determine its counting efficiency, but can be counted a second time to confirm its half life.

Safety Reminders

- Follow the usual safety procedures when working in a radiological laboratory.
- Caution should be exercised when preparing and working with corrosive mineral acids.
- All liquids and solids are to be properly disposed of according to laboratory rules and protocol.
- This experiment uses corrosive glacial acetic acid and fuming nitric acid. Take special precautions and wear protective gloves when using these acids. A face shield is recommended when working with fuming nitric acid.

Equipment

- Low-level beta-particle counting system, such as an anti-coincidence proportional counter
- Analytical balance to measure within 0.1 mg
- o Pipettes, 1 mL and 2 mL
- Beakers, 1 L, 150 mL
- Ion exchange column, for 10 mL resin (0.8-cm dia. x >20 cm long), with stopcock and glass-fiber plug at bottom (for similar system, see Fig. 15.4)
- Hot plate
- Ice bath
- o Graduated cylinder, 10-mL and 500-mL

- Stirring rods
- Centrifuge tubes, 50-mL
- Filter and filtration apparatus

Reagents

- \bullet Strontium carrier, 10 mg Sr^2+/mL, see preparation and standardization in Experiment 5.
- \bullet Yttrium carrier, 10 mg Y^3+/mL, see preparation and standardization in Experiment 5
- \bullet Barium carrier: 10 mg Ba $^{2+}/mL,$ dissolve 19.0 g Ba(NO_3)_2 in water and dilute to 1 L
- 90 Sr 90 Y standard solution, diluted in 0.01 N nitric acid to a concentration of about 5 Bq per mL
- ⁸⁹Sr standard solution, diluted in 0.01 nitric acid to a concentration of about 5 Bq per mL
- Cation exchange resin, strong base, 8% cross linked, 100-200 mesh, analytical grade
- Fuming (yellow) nitric acid, reagent grade
- 8 M HNO₃: Add 500 mL reagent grade concentrated nitric acid to 400 mL deionized water, mix, and dilute to 1.0 L
- \bullet 0.1 M HNO_3: Add 6.25 mL of concentrated nitric acid to 400 mL deionized water, mix, and dilute to 1 L
- HCl: concentrated, reagent grade.
- 1 M HCl: Add 83 mL of concentrated HCl to 800 mL deionized water, mix, and dilute to 1 L.
- Iron carrier: 10 mg Fe³⁺/mL, dissolve 48 g of FeCl₃. $6H_2O$ in 100 mL of 1 M HCl and dilute with water to 1 L.
- NH₄OH, concentrated ammonium hydroxide
- HC₂H₃O₂, glacial acetic acid
- Na₂CrO₄: 10%, dissolve 10 g Na₂CrO₄ in 100 mL of water
- $(NH_4)_2C_2O_4$: saturated aqueous solution of ammonium oxalate
- Ethanol, 95%
- Deionized water

Procedure

Step 1. Measure the dissolved sample ash with added strontium carrier from Experiment 12 with a graduated cylinder and pour into a 1-L beaker, OR pour 1 L (or less, as specified by the instructor) of a water sample into the 1-L beaker, pipette 2 mL strontium carrier into the water sample, and stir. Add 1 mL of 8 M HNO₃ per 100 mL of sample and mix. Bring to a boil and then cool.

Step 2. Prepare a cation-exchange column that contains 10 mL of the cation exchange resin, has no bubbles or channels, and is covered with water. Condition the resin by passing \sim 50 mL of 0.1 M HNO₃ through the column. Discard the effluent.

Step 3. Pass the sample through the column. The flow rate should not exceed 5 mL/min. Discard the eluent. Wash the column with \sim 30 mL of 0.1 M HNO₃. Discard the eluent.

Step 4. Elute the strontium fraction at a flow rate not to exceed 5 mL/min with 50 mL of 8 M HNO₃. Collect the eluent in a clean 150 mL beaker.

Step 5. Evaporate the sample on a hot plate at low setting until only a small volume (~ 2 mL) remains. Transfer to a clean 50-ml centrifuge tube. Rinse beaker with two 3-mL portions of concentrated nitric acid and transfer each to the centrifuge tube.

Step 6. Add 30 mL of cold fuming nitric acid and stir. (*Cooling the fuming nitric acid reduces the time required for cooling in an ice bath.*) Place the centrifuge tube in an ice bath for approximately 10 minutes. Stir to precipitate white $Sr(NO_3)_2$. Centrifuge and discard the supernate. (*Note: if excess calcium salts were in the sample, it may be necessary to dissolve the precipitate in 5 mL water and reprecipitate it with 30 mL fuming nitric acid.*)

Step 7. Dissolve the Sr(NO₃)₂ precipitate in 20 mL of water and add 5 drops of iron carrier. Make the solution alkaline by adding concentrated NH₄OH dropwise to precipitate reddish-brown Fe(OH₃ scavenger. (*Note: a new bottle of NH₄OH should be used or fresh NH₄OH prepared by bubbling NH₃ in water to insure that no carbonates are in the NH₄OH.) Add 10 drops more of NH₄OH solution. Stir and centrifuge. Decant the supernate into a clean centrifuge tube. Discard the Fe(OH)₃ precipitate, which includes any ⁹⁰Y in the sample.*

Date and time of ⁹⁰Y separation with Fe(OH)₃ precipitate:

Step 8. Add 2 mL of glacial $HC_2H_3O_2$ to the supernate to bring the solution to pH 3.5 to 4.0 (check with pH paper). Add 2 mL of barium carrier and stir. Add, while stirring, 2 mL of 10% Na_2CrO_4 solution and digest for 10 to 15 minutes in a hot water bath with occasional stirring to precipitate yellow to orange colored BaCrO₄. Centrifuge, then decant the supernate into a clean centrifuge tube and discard the precipitate (or save for analysis of radio-barium and radium).

Step 9. Add 5 mL of saturated $(NH_4)_2C_2O_4$ to the supernate, neutralize with ammonium hydroxide dropwise, and digest on a hot water bath for 5 to 10 minutes. A white precipitate of strontium oxalate forms. Centrifuge, and discard the supernate. Wash the precipitate by adding 2 mL of saturated $(NH_4)_2C_2O_4$ in 20 mL of water and stir. Centrifuge and discard the supernate

Note: If the sample is being measured for both 89 Sr and 90 Sr, mount the sample for counting as described in Step 10. If the sample is being measured only for 90 Sr, go to Step 10a.

Step 10. Slurry the precipitate from Step 9 with 10 mL of water and filter onto a tared filter circle held in a filtration apparatus. Wash the centrifuge tube twice with 5 mL of water and pour into filtration apparatus onto the precipitate. Wash and dry precipitate with two 5 mL portions of 95% ethanol.

Place on tared planchet and dry in an oven at 110° C for 30 minutes. Remove from oven, cool, and weigh the hydrate, SrC₂O₄.xH₂O. Mount the sample and count it twice for 3,000 s; also count the background twice. Record weighing and counting results in Data Table 13.1.

Dates and times of first and second counts: ____; _____;

The count is repeated 3–9 weeks later (the longer the interval, the more precise the ⁸⁹Sr calculation). When counting for ⁸⁹Sr is completed, the sample may be processed for ⁹⁰Y to determine the amount of ⁹⁰Sr in the sample by transferring the filter to a centrifuge tube and following Step 11.

Date and time of count for ⁸⁹Sr calculation:

Step 10a. Store the $Sr_2C_2O_4$ precipitate in the centrifuge tube to permit the ⁹⁰Y to grow into radioactive equilibrium with the 90Sr. This process requires ~18 days. This time period may be shortened if an ingrowth correction is made for the time interval between the iron scavenge of Step 7 and the Y(OH)₃ precipitation that is described below.

Step 11. After the required time has lapsed, wash down the sides of the tube with 15 mL of 1 M HCl to dissolve the SrC_2O_4 . (If reprocessing the mounted $Sr_2C_2O_4$ precipitate, carefully transfer the filter circle into a centrifuge tube that contains 15 mL of 1 M HCl. To achieve quantitative transfer, remove the filter after the precipitate is dissolved, wash filter with 5 mL water and add the wash to the solution.)

Step 12. Pipette 2 mL of standardized yttrium carrier into the solution and stir, Add concentrated NH_4OH drop-wise until white $Y(OH)_3$ precipitates and then add 5 mL in excess. Centrifuge, decant into a centrifuge tube, and save the supernate until the results of the analysis for yttrium have been checked. Record the time.

Date and time of yttrium separation:

Step 13. Dissolve the $Y(OH)_3$ in a minimal amount of concentrated HCl added dropwise. Add 15 mL of water. Add 3–5 drops of strontium nitrate solution as holdback carrier, stir, and again precipitate $Y(OH)_3$ with 5 mL of concentrated NH₄OH. Centrifuge and discard the supernate. Wash the precipitate with 20 mL water. Centrifuge and discard the wash water.

Step 14. Dissolve the precipitate in the minimum amount of concentrated HCl added dropwise and add 15 mL of water. Adjust to pH 2–3 with ammonium hydroxide, if needed. Add 5 mL of saturated $(NH4)_2C_2O_4$ solution and stir to precipitate $Y_2(C_2O_4)_3$. Digest in a hot water bath for 5 to 10 minutes.

Note: Step 15a describes the preparation of yttrium as the oxide for chemical yield determination and counting. As an alternative, Step 15b is the description for weighing and mounting yttrium as the oxalate.

Step 15a. Slurry the hydrated $Y_2(C_2O_4)_3$ onto an ash-less filter circle. Wash the centrifuge tube with 10 mL of water and pour through filter. Place the filter with precipitate in a clean porcelain crucible. In a muffle furnace, ignite

⁸⁹ Sr Yield		
⁹⁰ Sr Yield		
⁹⁰ Y Yield		
1^{st} Count Rate (Sr + Y)	Gross, cps	Net, cps
2^{nd} Count Rate (Sr + Y)		
Count Rate (Y)		
Background		
⁹⁰ Y Ingrowth Time		
⁹⁰ Y Ingrowth Fraction		

Data Table 13.1 Data ⁸⁹Sr, ⁹⁰Sr, and ⁹⁰Y count rates

at 900°C for 1 hour. Remove from the furnace and cool. With a blunted or flattened tipped thick glass stirring rod, grind the Y_2O_3 into a powder. If necessary, add a few drops of ethanol and continue grinding to produce a fine precipitate. Take up in a few mL water and slurry the Y_2O_3 through a tared filter circle. Wash the precipitate with ethanol, dry in an over at 110°C, cool, weigh, and mount for counting. Count twice for 3,000 s and record data in Data Table 13.1.

OR

Step 15b. Slurry the hydrated $Y_2(C_2O_4)_3$ onto a tared filter circle in a filtering apparatus. Wash the centrifuge tube with 10 mL of water and pour through filter. Wash and dry the $Y_2(C_2O_4)_3$.xH₂O, precipitate with two 5-mL portions of ethanol. Transfer to oven and dry at 110°C for 15 minutes. Cool, weigh, and mount for counting. Count twice for 3,000 s and record data in Data Table 13.1.

Date and time of counting:_____

Counting

Count the ⁹⁰Y sample with a low-background beta-particle detector. Repeat count-rate measurement for two to three 2.67-d half lives. Plot the net count rate as function of time on a semilog graph, draw straight line of best fit through measured points, and calculate slope of line, which equals $-\lambda$ or $-\ln 2/t_{1/2}$. A suggested counting frequency is twice daily for 8 d. When ⁸⁹Sr is present, count the strontium sample immediately after separation and then every 3 weeks for as much as 2 half lives of ⁸⁹Sr, if time is available.

Calculation of the ⁹⁰Sr concentration from yttrium precipitation and ⁹⁰Y counting data

Calculation of the amount of ⁹⁰*Sr in the sample when no* ⁸⁹*Sr is present is by the following equation:*

$$A_{Sr} = \frac{R_Y}{\left[V_a \varepsilon_y Y_Y Y_{Sr} \left(e^{-\lambda(t_3 - t_2)}\right) \left(1 - e^{-\lambda(t_2 - t_1)}\right)\right]}$$
(13.1)

 $A_{Sr} = {}^{90}$ Sr concentration in Bq/L, R_Y = net count rate in cps of 90 Y

Table 13.1 Calcula	tion for ⁸⁹ Sr in	a mixture	of ⁸⁹ Sr	and ⁹⁰ Sr
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Description	Formula
Initial measurement Second measurement	$R_1 = Y(A_{90}{}_{Sr}\varepsilon_{90}{}_{Sr} + A_{90}{}_{Sr}\varepsilon_{90}{}_{Y}D_{1}{}_{90}{}_{Y} + A_{89}{}_{Sr}\varepsilon_{89}{}_{Sr})$ $R_2 = Y(A_{90}{}_{Sr}\varepsilon_{90}{}_{Sr} + A_{90}{}_{Sr}\varepsilon_{90}{}_{Y}D_{2}{}_{90}{}_{Y} + A_{89}{}_{Sr}\varepsilon_{89}{}_{Sr}D_{2}{}_{89}{}_{Sr})$
Solution for $A_{90}{}_{Sr}$ at the initial count	$A_{90}{}_{Sr} = \frac{(R_1 D_{2^{89} Sr} - R_2)}{\gamma [\epsilon_{90}{}_{Sr} (D_{2^{89} Sr} - 1) + \epsilon_{90}{}_{Y} (D_{2^{89} Sr} D_{1^{90} Y} - D_{2^{90} Y})]}$
Solution for $A_{89}{}_{Sr}$ at the initial count	$A_{89}{}_{Sr} = \frac{\left[\frac{R_1}{Y} - A_{90}{}_{Sr} \left(\varepsilon_{90}{}_{Sr} + \varepsilon_{90}{}_{Y}D_{1}{}_{90}{}_{Y}\right)\right]}{\varepsilon_{89}{}_{Sr}}$

 V_a = volume of the sample in L,

- ε_Y = counting efficiency for ⁹⁰Y (see above),
- Y_{Y} = chemical yield for the recovery of the yttrium carrier (mg Y recovered/mg Y added),
- Y_{Sr} = chemical yield for the recovery of the strontium carrier (mg Sr recovered/ mg Sr added),
- λ = the decay constant of ⁹⁰Y (0.260 d⁻¹)
- $t_3 = time when {}^{90}Y is counted in Step 15.$
- t_2 = time when yttrium is separated from strontium when radioactive equilibrium is being approached in Step 12
- $t_1 = time when {}^{90}Sr is scavenged with ferric hydroxide that removes {}^{90}Y, in Step 7$

 $(1 - e^{-\lambda(t_2-t_1)})$ = saturation term for determining the degree of radioactive equilibrium the ⁹⁰Y has obtained from the time of separation for the strontium to the counting time (this term approaches the value of 0.99+ when $t_2 - t_1$ is equal to or greater than 18 days).

Calculation of ⁸⁹Sr and ⁹⁰Sr concentrations by counting the strontium precipitate immediately after preparation and then several weeks later

Table 13.1 describes the calculation for ⁸⁹Sr in a mixture of ⁸⁹Sr and ⁹⁰Sr.

The letter D represents the decay of 89 Sr or the ingrowth or 90 Y at the initial second measurement.

Measurement of Counting Efficiency

Step 1. *Prepare duplicate* ⁹⁰*Sr and* ⁸⁹*Sr solutions*. Into each of four centrifuge tubes with 20 mL of deionized water, add 1 mL of 0.1 M HNO₃. Pipette 2 mL Sr carrier into each tube. Pipette 2 mL of yttrium carrier into each of the first 2 tubes. Into each of the first two tubes, pipette 1 mL of ⁹⁰Sr diluted standard solution; into each of the other two tubes, pipette 1 mL of ⁸⁹Sr diluted standard solution. Stir well.

Step 2. Add 1 ml iron carrier into each of the first 2 tubes and stir. Add fresh ammonium hydroxide drop-wise with stirring until a brown iron hydroxide precipitate forms. Centrifuge and thoroughly transfer both supernatant solutions to clean centrifuge tubes. Add 5 ml of water to each precipitate, stir, and centrifuge. Decant each wash solution into the corresponding supernatant solution. Discard precipitate.

	⁹⁰ Sr Sample #1	⁹⁰ Sr Sample #2	⁸⁹ Sr Sample #1	⁸⁹ Sr Sample #2
Date/Time of				
precipitation				
Gross, weight, mg	3			
Tare weight, mg				
Net weight, mg				
Yield				

Data Table 13.2 Yields of counting efficiency precipitates

Data Table 13.3 Data Prompt count rates of each precipitate

	⁹⁰ Sr Sample #1	⁹⁰ Sr Sample #2	⁸⁹ Sr Sample #1	⁸⁹ Sr Sample #2
Date/Time of count.				
Ingrowth/decay				
interval, hr				
Gross count rate, cps				
Net count rate, cps				
Activity, dps				
Counting efficiency, 89 Sr				
Counting efficiency, 90 Sr				
Counting efficiency, 90 Y				

Step 3. Neutralize each of first 2 solutions with a few drops 0.1 M HNO₃.

Step 4. To each of the 4 centrifuge tubes, promptly add 5 mL of saturated $(NH_4)_2C_2O_4$ and stir well. Record time of precipitation in Data Table 13.2.

Step 5. Slurry each solution with precipitate onto a tared filter disk in a filtering apparatus. Rinse each centrifuge tube with two portions of 5 mL water and pour through each filter. Wash and dry filter each with two portions of 5 mL ethanol. Dry in oven at 110°C for 2 hours. Let each filter cool and weigh it on tared planchet. Calculate weight of each precipitate and yield, and record in Data Table 13.2.

Step 6. Place each filter in a filter holder, identical to that used in the procedure. Count as soon as possible (within several hours) after the precipitation. Record gross count rates and background count rate in Data Table 13.3.

Step 7. Count four filters again after about 18 days. Count each filter twice for 3,000 s and also count the background. The two filters with 90 Sr standard solution are counted to calculate the counting efficiency of 90 Y and

Data Table 13.4 Count rates of each precipitate after time interval

	⁹⁰ Sr Sample	⁹⁰ Sr Sample	⁸⁹ Sr Sample	⁸⁹ Sr Sample
	#1	#2	#1	#2
Date/Time of count. Ingrowth/decay interval, d Gross count rate, cps Net count rate, cps Counting efficiency				

⁹⁰Sr on the basis of the ⁹⁰Y ingrowth. Count the two filters with ⁸⁹Sr to calculate the counting efficiency and observe the radioactive decay of the radionuclide. Record the gross count rates and background count rate in Data Table 13.4.

Calculation of Counting Efficiencies

The following equations calculate the counting efficiencies for 90 Y, 90 Sr and 89 Sr. The ingrowth for 90 Y is included in Eq. 13.1 and Table 13.1. The decay of 90 Sr is taken to be negligible between measurements. The activity of 89 Sr and 90 Sr is at the time of the first count.

$$\varepsilon_{90_Y} = \frac{R_2 - R_1}{A_{90_{Sr}}Y(D_2 - D_1)_{90_Y}}$$
(13.2)

$$\varepsilon_{90_{Sr}} = \frac{R_1}{A_{90_{Sr}}Y} - D_{1\,Y^{90}}\varepsilon_{90_Y} \tag{13.3}$$

$$\varepsilon_{^{89}Sr} = \frac{R_1}{A_{^{89}Sr}YD_{^{89}Sr}}$$
(13.4)

- R_2 = net count rate in c/s after lengthy interval (typically, about, 18 days)
- R_1 = net count rate in c/s promptly after strontium separation
- A = activity of radio-strontium in Bq at time of measurement
- D_2 = ingrowth fraction of ⁹⁰Y after lengthy interval (0.996 after 21 days); decay fraction of ⁸⁹Sr (0.750 after 21 days)
- D_1 = ingrowth fraction of ⁹⁰Y promptly after strontium separation (about 0.05 after 5 hours)

 D_{89Sr} = Decay fraction of ⁸⁹Sr

Y = chemical yield of strontium

 $\varepsilon_{\rm Sr-90}$ = counting efficiency of ⁹⁰Sr

- ε_{Y-90} = counting efficiency of ^{90}Y
- $\varepsilon_{\rm Sr-89}$ = counting efficiency of ⁸⁹Sr

Questions

- 1. You are told that a sample contains "1-week-old" fission products in addition to the suspected radio-strontium isotopes. How would you modify the above procedure to respond to the presence of an excess amount of ¹⁴⁰Ba and rare earth fission products? Also, what other radiostrontium isotopes will be present, how does this presence affect the measurements, and what modifications are needed in the counting protocol? Be specific.
- 2. Calculate what the ratio of activity would be for ⁸⁹Sr/⁹⁰Sr if you are told the source of the fission products are from brief thermal neutron fission of ²³⁵U and that the sample was 15.7 days old.

- 3. Why is it necessary to use "scavenge" techniques for the removal of barium (by barium chromate) and plutonium (by ferric hydroxide precipitation)?
- 4. Use calculations as shown in the beta-particle self-absorption experiment (#4) or a comparison of the two sets of efficiency values with and without added mass in Experiment #2 to suggest that the self-absorption of ⁹⁰Y beta particles is small for this experiment.
- 5. Construct a flow diagram for the strontium procedure.

Source

This procedure was developed in part from the procedure STRONTIUM-90 by B. P. Bayhurst in Collected Radiochemical and Geochemical Procedures, Compiled and Edited by Jacob Kleinberg, LA-1721 5th Edition, Los Alamos National Laboratory (May 1990).