RiO5 METHOD (36)

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Radiochemical procedures for analyses of strontium, plutonium, cesium, americium and iron radionuclides in biological samples

The following is a historical internal technical manual from Dr. Vaughan T. Bowen Laboratory at the Woods Hole Oceanographic Institution, 1982.

Disclaimer

It is the responsibility of the analyst to follow established safety and health practices. Although each laboratory identified as the source has tested the methods, each user should perform an individual validation procedure.

KEN BOESSEGER

RADIOCHEMICAL PROCEDURES FOR ANALYSES OF STRONTIUM, PLUTONIUM, CESIUM, AMERICIUM AND IRON RADIONUCLIDES IN BIOLOGICAL SAMPLES

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Table of Contents

RADIOCHEMICAL PROCEDURES FOR ANALYSES OF Sr, Cs, Pu, Am AND Fe RADIONUCLIDES IN BIOLOGICAL SAMPLES

I. Introduction

The following radiochemical protocol is used by the Vaughan T. Bowen group at the Woods Hole Oceanographic Institution for biological samples. Due to the varying nature of biological samples and the variations in sampling regimes, scrutiny is given to each sample to determine which if not all isotopic analyses will be performed. The sample is treated so that the isotopes of interest for that particular sample are separated and subsequently prepared for radioactivity measurement. The following procedure, however, is given for a sample from which data are desired for each of the nuclides noted.

II. Summary of Sample Analysis

A. Ashing Methods - Dry and Wet

Biological samples, except seaweeds, are prepared for analysis by dry ashing. The samples are first dried in an oven at 110°C for several days and then ashed in a muffle furnace at 500°C for 2-3 days. Dry ashing reduces the biomass and the amount of organic material and enhances later digestion by acids. Dry ashing works well for most biological samples.

When seaweeds are dry ashed, radiochemistry becomes much more difficult. Organic complexes form which interfere with isotopic separations when using ion-exchange chromatography by either preventing the flow of the sample through the column or by producing colorations which mask colorimetric separations. In dry ashed seaweeds salt formation is a nuisance problem, complete digestion is difficult, and recoveries are often low. Wet ashing

(acid digestion) of seaweeds in the dried, frozen or fresh state solves many of the dry ashing problems and allows an easy merger with the individual isotopic separation procedures.

For a detailed description of the dry ashing sample preparation method, proceed to step A-1 in section III. For a description of the wet ashing sample preparation method, proceed to step B-1 in section III.

B. Isotopic Separations

Radiochemical separation of the isotopes of interest requires that carriers and yield monitors be added to the sample at an early stage of sample analysis. In both ashing methods outlined above, the carriers and yield monitors are added during the acid digestion step. The Sr, Cs, and Fe carriers must be standardized solutions of the stable elements as the recoveries of the respective radioisotopes of these elements are determined gravimetrically or by atomic absorption spectrophotometry. Since the primary function of Nd is as a holdback carrier for Am, the Nd carrier need not be standardized. The ^{242}Pu and ^{243}Am tracers must be added in precisely known amounts since the recoveries of $^{238,239,240}Pu$ and ^{241}Am, respectively are based on the recovery of the isotopic tracers added.

The general elemental separation scheme predominantly uses gravimetric or ion exchange methods. Initially, Sr is precipitated as the nitrate from the acid digested sample. The ^{90}Sr is determined by beta counting ^{90}Y, the 64-hour half life daughter of ^{90}Sr, after a further gravimetric separation. The ^{90}Sr fraction is stored for repetitive milkings of the ^{90}Y.

The supernate from the Sr nitrate precipitation contains Pu, Cs, Am, and Fe. The Pu is separated from the supernate on an anion exchange column

pretreated with HNO_3. It is retained on the column in oxidized form and is reduced with NH_4I for elution. The Pu is electrodeposited on a highly polished stainless steel disc for alpha spectrometry using the ^{242}Pu added with the carriers for recovery determination.

The eluate from the Pu separation (containing Cs, Am, and Fe) is diluted, pH adjusted and ammonium molybdophosphate is added to collect the Cs (via adsorption) from the sample. The AMP is collected, destroyed, and the sample passed through a cation exchange column to separate the Cs from other alkaline metals. The cesium is precipitated as Cs_2PtCl_6 and the recovery is determined gravimetrically. This precipitate is then mounted for beta counting.

The supernate from the AMP separation contains Am and Fe, both of which are next precipitated as hydroxides. The Am is selectively separated from the Fe as an oxalate at low pH (<1.5) and then further separated from the Nd carrier (and any other lanthanides present) by ion exchange as the thiocyanate complex. The Am is separated from residual Pu and Th by a final nitrate anion exchange column and from residual Pb, Bi and Po by piggy-back chloride anion exchange columns. The Am is electrodeposited for alpha spectrometry in the same manner as Pu. The recovery is determined by measuring ^{243}Am alpha spectrometrically and calculating its losses.

The Fe fraction (the supernate from the oxalate precipitation above) is retained for future Fe analysis, should that be determined to be necessary.

The procedures for the individual isotope separations for Sr, Pu, Cs, Am, and Fe are given in section IV.

III. Sample Preparation

A. Dry Ashing Method

A-1 Assign each sample an M number and record the following information in the M logbook: scientific name of the organism, common name, part, date of collection, sample location, and any other pertinent data. If different parts of the same organisms are to be analyzed separately, assign each organ a different M number.

A-2 a) Record fresh weight; place in a Pyrex beaker.

b) Depending on the sample size, the sample beaker should range from 500-2,000 ml and the drying time should range from 3-7 days. Dry the sample at 110°C.

c) Ash the sample according to the following schedule and record the ashed weight:

Temperature-°C	Hours Duration
200	2
250	2
300	2
350	2
400	2
500	48

A-3 Wet the sample with distilled water and mix well. Slowly add 400 ml 8N HNO_3. Control any foaming which may occur by adding a few drops of octyl alcohol.

A-4 Allow the mixture to react at room temperature for one hour.

A-5 Add the appropriate carriers and yield monitors:

10 ml Sr (100 mg Sr/ml)

2 ml Nd (25 mg Nd/ml)

2 ml Cs (10 mg Cs/ml)

1 ml Pu (2 dpm/ml ^{242}Pu tracer)

1 ml Am (1 dpm/ml ^{243}Am tracer)

300 mg Fe

A-6 Digest the sample on a hot plate at 80°C. (Digestion takes from a few hours to several days.)

A-7 If there is any undissolved material in the sample, filter through a 934 AH glass fiber filter.

A-8 Add 200 ml 8N HCl to undissolved material. Digest for 2 hrs on hot plate at 80°C. Cool.

A-9 Filter undissolved material through 934 AH glass fiber filter and save it until counting is completed and the results considered satisfactory.

A-10 Combine fractions from steps A-7 and A-9. Evaporate to 100 ml or until salts appear. Add 200 ml 8N HNO_3. If sample is to be analyzed for Sr and/or Fe, see Note 1 below.

A-11 Evaporate the sample to 100 ml or until salts appear. Remove the sample from the hot plate and allow to cool.

Proceed to individual isotope separation procedures in Section IV.

Note 1:

Sr and/or Fe aliquot. If the sample is to be analyzed for Sr and/or Fe, an aliquot for each must be taken at this time in the following way:

a) Transfer the solution from A-7 to a tared beaker.

b) Record the weight of the beaker and the solution.

c) Transfer 2 drops/100 g of solution to a tared 40 ml vial.

d) Record the weight of the drops and vial.

e) To the Fe aliquot, add 20 ml of distilled water and record the weight. To the Sr aliquot, add 40 ml of 0.1% HCl + 0.01% NaOH as outlined in Note Sr-B below.

f) Store for atomic absorption determination. The amount of stable Sr or Fe present in the sample initially is represented by the difference between the analyte measured by AA and the amount added as standardized carrier.

B. Wet Ashing Method

B-1 After proper sample identification (see step A-1), weigh sample in 2-l beaker (sample should weigh 300-500 gm wet).

B-2 If the samples have been dried, add deionized water to cover and let sit overnight (if samples fresh or frozen proceed to step B-3).

B-3 Add 8N HNO_3 to sample slowly to control fizzing and foaming (if foaming is a problem add few drops octyl alcohol); final volume sample and acid should be approx. 1200-1400 ml.

B-4 Let sample sit for several hours or overnight - "cold" digestion.

B-5 Add appropriate carriers and yield monitors (see step A-5), stir well.

B-6 Heat at 60-80°C until volume is slightly reduced then increase heat to slow boil, if possible, without "bumping".

B-7 Reflux and evaporate for several hours or days depending on the digestion fate of the sample.

B-8 Reduce volume of sample to approx. 300-400 ml, add more 8N HNO_3 to equal approx. 1000 ml and repeat steps 7 and 8 until digestion is complete (some residue might remain).

B-9 Evaporate sample to as low as possible without salting (usually 200-300 ml).

B-10 Filter sample through glass fiber filter in a Buchner funnel using suction (filtering times vary due to the amount of residue left undigested; on occasion additional filters may be necessary); transfer filtrate to 1-l beaker and begin to evaporate.

B-11 Wash filter and solid material back into the 2-l beaker using 8N HCl; add more 8N HCl to equal 300 ml; heat and evaporate to 150 ml (approx.).

B-12 Refilter the HCl fraction from B-11 and add filtrate to HNO_3 fraction (B-10). Save filter and filtered material until analysis is complete and results are satisfactory.

B-13 Evaporate the combined fractions to 200 ml and add deionized water to equal 1200-1400 ml.

B-14 Adjust the solution to pH 8.0 (approx.) with 50% NaOH to precipitate Fe, Am, Pu, etc.

B-15 Let precipitate settle for several hours or overnight.

B-16 Decant supernate into 2-l beaker and save for Cs separation.

B-17 Collect the $Fe(OH)_3$ precipitate in B-15 by centrifugation using 250 ml bottles; add the supernate to the Cs fraction in B-16.

B-18 Adjust the supernate (Cs fraction) in B-16 to pH 1-2 with 8N HCl with stirring; add 1 gm AMP in a slurry, stir for 10 min; let Cs-AMP settle several hours or overnight; collect Cs-AMP by centrifugation in 50 ml tubes; wash with 0.02N HCl - continue with Cs separation procedure at step Cs-9.

B-19 Dissolve the precipitate in B-17 with conc. HNO_3 and transfer to a tared 1-l beaker; rinse centrifuge bottle with 8N HNO_3 and add to beaker.

B-20 Bring volume to 300 ml with 8N HNO_3 and heat.

B-21 Evaporate to 100-150 ml and add equal volume 0.5N HNO_3 (if salts form try to dissolve by stirring and heating; if salts persist and are a large portion of the sample, filter sample before proceeding).

B-22 Weigh sample (cool if necessary), take aliquot for Fe analysis by placing 2 drops/100 ml of solution into a tared vial, weigh, dilute with 20 ml deionized water, weigh; set aside for atomic adsorption measurement of stable Fe.

B-23 At B-21 the sample is at approx. 8N HNO_3 and is ready for the Pu separation procedure starting at Pu-2.

IV. Individual Isotope Separation

Sr-Separation

Sr-1 Add 150 ml of conc. HNO_3 to the soln. from step A-11 and re-evaporate to 100 ml or until all $Sr(NO_3)_2$ salts have formed. Allow to cool.

Sr-2 Chill the sample, and a wash bottle of conc. HNO_3, on ice. Add 50 ml of fuming (90%) HNO_3 using a glass measuring device.

Sr-3 After chilling for 1/2 hour, filter the sample, with a Buchner funnel, through a 934 AH glass fiber filter. With cold conc. HNO_3, wash the $Sr(NO_3)_2$ precipitate from beaker and wash the filter paper. In a 400 ml beaker, dissolve the $Sr(NO_3)_2$ with as little cold H_2O as possible. Evaporate the solution to 50 ml and cool.

Sr-4 Add 1 ml of Fe carrier ($\sim$ 2 mg Fe/ml), stir with a glass rod and rinse down the beaker walls with H_2O.

Sr-5 Add conc. NH_4OH to the solution until the pH is 9. An iron hydroxide precipitate will form.

Sr-6 Warm the sample to 60-80°C for 10 minutes; then cool to room temp.

Sr-7 Filter through a 15 cm #541 Whatman paper in a glass funnel into a clean, labelled beaker. Wash original beaker and filter with 10 ml of pH 8 H_2O. Discard filter and precipitate.

Sr-8 Adjust the pH of the filtrate to between 4 and 6 with 3N HCl. Repeat steps Sr-4 through Sr-7.

Sr-9 Record the date of the second iron scavenge.

Sr-10 Readjust the pH to 4 to 6 with 3N HCl.

Sr-11 Add 4 ml barium acetate buffer and heat to near boiling. See Note Sr-A.

Sr-12 Add 1 ml 1M Na_2CrO_4 and continue heating with occasional stirring for 30 minutes.

Sr-13 Cool the solution and filter the precipitate on 15 cm Whatman #42 filter paper. Rinse the beaker with H_2O and add the rinsings to the filter paper to ensure washing of the precipitate. Discard the precipitate.

Sr-14 Repeat steps Sr-10 to Sr-12.

Sr-15 Add 50 ml saturated $(NH_4)_2CO_3$ solution and stir with a Teflon-coated magnetic stir bar for 2 minutes; remove stirrer and allow precipitate to settle.

Sr-16 Aspirate off supernate and discard.

Sr-17 Wash precipitate with 100 ml 5% $(NH_4)_2CO_3$; allow to settle and aspirate off the supernate.

Sr-18 Repeat the $(NH_4)_2CO_3$ wash.

Sr-19 Dissolve the precipitate in 3N HCl and transfer to a tared 125/ml polyethylene bottle. Write tare weight on bottle as well as the date of second iron scavenge (see Sr-9). Remove Sr AA aliquot (see Note Sr-B) prior to weighing the sample. Record the sample weight.

Sr-20 Add 1 ml of Fe carrier ($\sim$ 2 mg Fe/ml) at this time to the polyethylene bottle. Since ^{90}Sr is determined by measuring its 64 hour half life daughter, ^{90}Y, the Y separation

procedure is included below. The sample, however, must be stored for at least weeks between the Fe scavenge date and the ^{90}Y milking to permit the ^{90}Y and the ^{90}Sr to come to equilibrium.

Note Sr-A:

The barium acetate buffer is prepared by combining 9 g of $BaCl_2$, 40 ml of conc. acetic acid and 230 g of ammonium acetate and diluting to 1 liter with distilled water.

Note Sr-B:

Since the Sr recovery is determined by the AA determination of the stable Sr added as carrier, an aliquot for AA must be taken at this time. This is done by pipetting one drop of well-mixed sample into two separate, tared, 40 ml vials. The vials are capped, weighed, and the drop diluted with about 40 ml of 0.1% HCl + 0.01% NaOH. (This solution is prepared by mixing 4 ml of conc. HCl and 0.4 ml of 10N NaOH with 4 liters of distilled-deionized water). The full vial is then weighed and all weights recorded.

The chemical recovery of Sr is determined by the difference in AA measurements between this aliquot and the aliquot taken at step A-10 of the Sample Preparation portion of this protocol.

^{90}Y Separation

Sr-21 Precipitate the $Fe(OH)_3$ with conc. NH_4OH in the polyethylene bottle from step Sr-20.

Sr-22 Heat the sample in a water bath (approx. 50°C) for 30 min. Cool to room temperature.

Sr-23 Centrifuge the hydroxide in a 50 ml plastic centrifuge tube. Decant the supernate into a 250 ml beaker and save for step Sr-29.

Sr-24 Record the time and date of $Fe(OH)_3$ separation (midway between the beginning of centrifuging and the end of decanting).

Sr-25 Rinse the polyethylene bottle with 1 ml of 6N HCl. Shake the bottle thoroughly and add the acid rinse to the centrifuge tube from step Sr-23.

Sr-26 Rinse the bottle twice with 5 ml H_2O and add the rinses to the centrifuge tube. Save the polyethylene bottle for step Sr-33.

Sr-27 Swirl the centrifuge tube if necessary to complete the dissolution of the $Fe(OH)_3$ and reprecipitate with conc. NH_4OH.

Sr-28 Heat the centrifuge tube in a water bath (50°C) for 15 min.; then cool to room temperature.

Sr-29 Centrifuge the hydroxide and decant the supernate into the beaker from step Sr-23. Save the supernate for step Sr-32.

Sr-30 Break up the hydroxide with a plastic stirring rod and filter through a 25 mm dia. 0.45 μ type HA Millipore filter. Use a plastic filter chimney and rinse with 5-10 ml of pH 8 H_2O.

Sr-31 Mount the filter for beta counting. See Note Sr-C.

Sr-32 Evaporate the solution from step Sr-29 slowly to about 50 ml.

Sr-33 Transfer the solution to the polyethylene bottle left from step Sr-26; rinse the beaker with a few ml of 6N HCl followed by a water rinse, and add rinsings to bottle. Note the time and date of last extraction on the bottle (step Sr-24).

Sr-34 Add 1 ml of 2 mg/ml Fe carrier and mix thoroughly. Acidify with HCl if necessary.

Sr-35 Should a second ^{90}Y extraction be necessary, repeat the Sr aliquot (see Note Sr-B) and the 14-day waiting period before the second extraction. The extraction may be repeated as many times as necessary.

Note Sr-C:

The hydroxide precipitate which has been collected on the filter contains ^{90}Y, the daughter of ^{90}Sr. This precipitate must be mounted for beta counting in some way, depending on individual laboratory beta counting capabilities. The beta detectors used by the V. T. Bowen group for both ^{90}Sr and ^{137}Cs determinations are described by Noshkin and DeAgazio (Nuclear Instruments and Methods 39 (1966) 265-270). This twin detector configuration permits counting two ^{90}Sr or two ^{137}Cs samples at the same time. The sample filters are mounted 2.6 cm apart on an 0.8 mm thick card of clear lucite which measures 10.2 x 5.6 cm. A filter placement pattern is aligned under the lucite for exact positioning of the sample filters.

Doublesided 3M tape (#136) is affixed to the lucite in accordance with the pattern and the filter is transferred to the taped surface. The sample is then covered with mylar (0.00025 inches thick, about 0.9 mg/cm^2) which is taped down around the edges with single-sided tape to protect the sample during storage and counting. For samples with ^{90}Sr concentrations approaching the detection limit, counting is made through an aluminum sheet of thickness about 60 mg/cm^2. This serves to absorb any ^{212}Pb beta activity without serious, though known, loss of ^{90}Y activity.

Pu Separation

Pu-1 Add an equal volume of 0.5N HNO_3 to either the digested solution from 1-11, 2-23 or the filtrate from Sr-3.

Pu-2 Add 1-g $NaNO_2$ for each 100 ml of solution and mix until dissolved (warm slightly).

Pu-3 Pass the solution through an ion exchange column (see Note Pu-A) at a flow rate of 1 ml/min., collecting the eluate (containing Am, Nd, Cs and Fe) in a 2-liter beaker. Follow with three 5 ml beaker rinses of 8N HNO_3.

Pu-4 Wash with 150-ml 8N HNO_3 collecting the eluate in the same 2-liter beaker. Evaporate this solution to 50 ml and save for Fe and Am analyses.

Pu-5 Pass 150-ml conc. HCl through the column at 4 ml/min. Discard the HCl eluates (Th).

Pu-6 Elute the Pu at a flow rate of 2ml/min with a fresh solution of 5-ml 1 M NH_4I in 100-ml conc. HCl, collecting the eluate in a 250 ml beaker.

Pu-7 Rinse the column with 50 ml of conc. HCl combining this with the eluate from Pu-6.

Pu-8 Evaporate slowly on a hot plate the combined eluates from Pu-6, and Pu-7.

Pu-9 When the solution has evaporated, add five 2 ml portions of aqua regia, evaporating after each addition.

Pu-10 Add 50-mg $NaNO_2$ plus 5-ml 8N HNO_3 to the beaker and swirl to dissolve. Warm gently for a few seconds.

Pu-11 Pass the solution through an ion exchange column (see Note Pu-B) at a flow rate of 2 ml/min. Follow with three 2 ml beaker rinses with 8N HNO_3.

Pu-12 Rinse the column with 20-ml 8N HNO_3 and discard (Trace Am, Fe, and U).

Pu-13 Pass 20-ml conc. HCl through the column at the same flow rate. Discard these HCl eluates containing trace amounts of Th.

Pu-14 Elute Pu with a solution of 1-ml 1M NH_4I in 20-ml conc. HCl, collecting the eluate in a 100-ml beaker. Wash with 10 ml of conc. HCl collecting in the same 100 ml beaker.

Pu-15 Evaporate the eluate slowly on a hot plate.

Pu-16 When the solution has evaporated, add five 2-ml portions of aqua regia, evaporating to dryness after each addition.

Pu-17 Add three 1-ml rinses of conc. HCl and evaporate to dryness after each rinse.

Pu-18 Add 5-ml conc. HCl and 1 drop of 30% H_2O_2.

Pu-19 Pass the solution through an ion exchange column (see Note Pu-C) at a flow rate of 2 ml/min. Follow with three 2 ml beaker rinses of conc. HCl.

Pu-20 Rinse the column with 20-ml conc. HCl and discard traces of Th.

Pu-21 Elute the Pu with a solution of 1-ml 1M NH_4I in 20-ml conc. HCl collecting the eluate in a 100-ml beaker.

Pu-22 Rinse the column with 10-ml of conc. HCl, combining with the eluate from Pu-21.

Pu-23 Evaporate eluate slowly on a hot plate.

Pu-24 Add three 2-ml portions of aqua regia, evaporating to near dryness after each addition.

Pu-25 Add 1-ml conc. HCl plus 1-ml conc. H_2SO_4 and evaporate to strong H_2SO_4 fumes.

Pu-26 Cool, cover with parafilm and save for electroplating. (See section on electrodeposition).

Note Pu-A:

The first Pu column dimensions are 12 mm ID, 150 mm length, containing 25 ml of wet, settled, anion exchange resin, Bio-Rad AG21 K (50-100 mesh) in chloride form. The column is preconditioned with 80 ml of conc. HNO_3 followed by 100 ml of 8N HNO_3 to which 1 g of $NaNO_2$ has been added.

Owing to the design of the columns used for Pu separation (see Figure 1), additional washings are unnecessary since the reservior modification permits the dripping of a sufficient volume of eluant onto the resin. The gooseneck modification eliminates the possibility of the column channeling due to the resin going dry.

Note Pu-B:

The second Pu column dimensions are 10 mm ID, 50 mm length, containing 2 ml of wet, settled resin as in Note Pu-A above. Precondition column with 20 ml of 8N HNO_3 to which 0.2 g of $NaNO_2$ has been added.

Note Pu-C:

Prepare the third Pu column in the same manner as the second Pu column with the exception that the preconditioning of the resin is made with 20 ml of conc. HCl mixed with 2 drops of 30% H_2O_2.

Cs Separation

Cs-1 Bring the volume of the solution from Pu-4 to 1 liter with deionized water and stir on a stir plate, with a magnetic stir bar.

Cs-2 While stirring, adjust the pH of the solution to 1.5 with 10% NaOH.

Cs-3 Weigh 1 g ammonium molybdophosphate (AMP) in a 20 ml beaker and moisten with deionized water.

Cs-4 Add the AMP slurry to the stirring sample. Stir for 10 min., remove the stir bar, and allow the Cs-AMP to settle for at least 12 but no longer than 24 hours.

Cs-5 Decant the supernate and save for Am and Fe analysis.

Cs-6 Transfer the Cs-AMP to a centrifuge tube with 0.02M HCl.

Cs-7 Centrifuge and add the supernate to the Fe-Am fraction, (Cs-5).

Cs-8 Wash the Cs-AMP with 10 ml 0.02M HCl. Centrifuge and add the supernate to the Fe-Am fraction.

Cs-9 Dissolve the Cs-AMP in 20 ml 0.75M NaOH.

Cs-10 Centrifuge and transfer the supernate to a clean centrifuge tube containing 2 ml 20% EDTA in 0.75N NaOH. Add any precipitate which may have formed to the Fe-Am fraction, (Cs-5).

Cs-11 Pass the solution through an ion exchange column (see note Cs-A) at a flow rate of 1 ml/min.

Cs-12 Elute the Na, K, Rb from the column with 375 ml 0.3M HCl. Discard this fraction.

Cs-13 Elute the Cs with 65 ml 3M HCl, collecting the eluate in a 150 ml beaker.

Cs-14 Slowly evaporate the solution to dryness.

Cs-15 Add 1 ml ~~1~~ 7M NaOH to the dry salt and transfer to a centrifuge tube with 10 ml deionized water.

Cs-16 Heat in a water bath at 60-80°C for 10 min.

Cs-17 Centrifuge the warm solution for 10 min. at a moderate speed.

Cs-18 Transfer the supernate to a clean centrifuge tube and discard any remaining Fe precipitate.

Cs-19 Heat again in the water bath at 60-80°C for 10 min.

Cs-20 Add 2 ml 10% H_2PtCl_6 and continue heating for 10 min.

Cs-21 Cool in the refrigerator for 30 min.

Cs-22 Heat in the water bath at 60-80°C for 10 min.

Cs-23 Cool in the refrigerator overnight.

Cs-24 Surface wash a 25 mm millipore HAWP 0.45 μ filter paper with 3N HCl followed by deionized water.

Cs-25 Dry the filter paper to a constant weight at 60°C (approximately 30-60 min.) and record final weight.

Cs-26 Filter the cesium precipitate onto the tared filter paper while cold, and wash with ~~10 ml~~ cold deionized water.

Cs-27 Dry to constant weight at 60°C, weigh, record final weight, and mount for beta counting (Note Cs-B).

Note Cs-A:

The column dimensions are 10 mm ID by 200 mm long. This column contains 17 ml of wet, settled Bio-Rex 40 resin (50-100 mesh) in the H^+ form. The column is generated and regenerated by passing 100 ml of H_2O through the column followed by 200 ml of 5% NaCl. This is followed by an additional 100 ml of H_2O.

Note Cs-B:

The sample filters are mounted 2.6 cm apart on an 0.8 mm thick card of clear lucite which measures 10.2 x 5.6 cm. A filter placement pattern is aligned under the lucite for exact positioning of the sample filters. Double-sided 3M tape (#136) is affixed to the lucite in accordance with the pattern and the filter is transferred to the taped surface. The sample is then covered with mylar (0.00025 inches thick, about 0.9 mg/cm^2) which is taped down around the edges with single-sided tape to protect the sample during storage and counting.

Am-Purification

Omit steps 1-10 for cartridges.

Am-1 Warm the solution from Cs-5 on a hot plate to approximately 80 c.

Am-2 Place the warm solution on a stir plate and add 50 ml conc. NH_4OH while stirring with a magnetic stir bar to precipitate the Fe hydroxides. Stir for 10 min.

Am-3 Remove the stir bar and allow to cool and settle for at least 4 hours.

Am-4 Aspirate the supernate and discard. Centrifuge the precipitate in a 250 ml plastic bottle and store to await Am, Fe analyses or continue with procedure.

Am-5 Dissolve the hydroxides precipitate with 12M HCl and transfer into a 2000 ml beaker.

Am-6 Evaporate the solution on a hot plate to 100 ml then dilute to 1500 ml with deionized water. Heat the solution on a hot plate until warm.

Am-7 While stirring on a hot plate, with a Teflon covered magnetic stir bar, add conc. NH_4OH to pH 9, reprecipitating the hydroxides. Settle four hrs.

Am-8 Aspirate and discard the supernate. Centrifuge the PPT. in a 250 ml centrifuge bottle.

Am-9 Wash the PPT. with dilute NH_4OH, centrifuge and discard the supernate.

Am-10 Redissolve the hydroxides with 12M HCl and rinse into a 1000 ml beaker. Evaporate the solution on a hot plate to 50 ml. (Evaporating the solution as low as possible reduces the need for pH adjustment later.)

Am-11 Bring the volume of the eluate solution to 450 ml with deionized water.

Am-12 Add an equal volume of saturated oxalic acid to make a 5% solution, and stir for 30 minutes with a magnetic stir bar.

Am-13 If no neodymium oxalate precipitate forms after 30 min., check the pH. If the pH is < 1.0, adjust with conc. NH_4OH and stir for 30 min. longer.

Am-14 Remove the stir bar and allow to settle overnight.

Am-15 Decant the supernate and save for possible Fe analysis.

Am-16 Rinse the beaker and precipitate with 0.5% oxalic acid. Centrifuge and add the supernate to the Fe fraction.

Am-17 Dissolve the oxalates in 8 ml of 8N HNO_3, warming if necessary.

Am-18 Transfer the solution with deionized water into a 250-ml beaker and dilute to 100 ml.

Am-19 Reprecipitate the oxalates by adding 100 ml of saturated oxalic acid to make a 5% solution. Stir for 15 min. with a magnetic stirrer.

Am-20 If no precipitate forms, add 14M NH_4OH dropwise while stirring until the precipitate starts to form. Do not exceed pH 1.

Am-21 Stir the sample for a total of 30 min. Remove the stir bar and allow to settle.

Am-22 Decant and discard the supernate. Centrifuge the oxalates in a 50 ml plastic centrifuge tube, rinsing with 0.5% oxalic acid.

Am-23 Redissolve the oxalates with 16M HNO_3 while transferring to a 150-ml beaker.

Am-24 Bring the solution to 100 ml with more 16M HNO_3 and boil until almost dry, destroying the oxalate.

Am-25 Dilute the sample to 100 ml with deionized water and warm on hot plate to about 60°C.

Am-26 Precipitate the neodymium hydroxide with 14M NH_4OH at ∿ pH 9 while stirring, let settle. Centrifuge the precipitate in a 50-ml plastic centrifuge tube, discarding the supernate and the dilute NH_4OH washes.

Am-27 Dissolve the hydroxides with 8-ml 8M HNO_3; add 0.1-g $NaNO_2$ and let stand for 5-10 min.

Am-28 Transfer the solution to a previously conditioned anion exchange column. (Note Am-A).

Am-29 Allow the solution to pass through the column at a flow rate of 1-2 ml per min., collecting the eluate plus washings (50 ml 8M HNO_3) in a 100-ml beaker.

Am-30 Evaporate the solution to dryness.

Am-31 Dissolve residue in 2-ml 12M HCl and evaporate to dryness. Repeat this step.

Am-32 Add 4-ml 6M NH_4SCN, then neutralize excess acid carefully by dropwise addition of 1M NH_4OH until the pink color (due to traces of iron) just disappears. Restore the color by dropwise addition of 0.2M HCl. At this stage the solution should be slightly acidic (pH 1-2), should not contain flakes of hydroxide, and should be slightly pink (FE^{III} thiocyanate). The total volume should not exceed 5 ml.

Am-33 Transfer the solution to the top of an anion exchange column (Note Am-B). (Take care not to spread the sample over the walls of the column. Apply the solution using a transfer pipet in small portions, letting each portion soak into the resin bed before applying the next

one). Rinse the beaker with three 2-ml portions of 2M NH_4SCN solution and transfer each rinse to the column in the same manner as the sample.

Am-34 Elute the lanthanons at a flow-rate of 0.7-1.2 ml/min. with 130 ml of 2M NH_4SCN. Discard this fraction.

Am-35 Elute the Am with 70-ml 4M HCl at the same flow-rate.

Am-36 Collect the Am fraction in a 100-ml beaker containing 10-ml 16M HNO_3 which is continuously stirred (magnetic stirrer).

Am-37 Evaporate this fraction until only H_2SO_4 (resulting from the thiocyanate destruction) remains and then heat strongly until the H_2SO_4 is volatilized. Cool.

Am-38 Repeat Steps Am-32 to Am-37.

Am-39 Dissolve the residue in 8-ml 8M HNO_3.

Am-40 Transfer the solution, 1 ml at a time, to a previously conditioned anion exchange column but without adding 0.1-gm $NaNO_2$/ml to the 50-ml conditioning rinse (Note Am-A).

Am-41 Repeat Steps Am-29 to Am-31.

Am-42 Rinse the beaker with 1-ml deionized water and evaporate to dryness. Repeat this step.

Am-43 Dissolve the residue in 2-ml 1.5M HCl.

Am-44 Transfer the solution to the top one of two previously conditioned anion columns arranged in a piggy-back fashion so that the top column drips directly onto the bottom column. (Note Am-C). Collect the eluate from the bottom column in a 100-ml beaker.

Am-45 Pass two 1-ml beaker rinses and a 4-ml wash of 1.5M HCl through the top column.

Am-46 Remove the top column and discard.

Am-47 Pass a 3-ml rinse of 1.5M HCl through the bottom column, then discard column.

Am-48 Add five drops of conc. H_2SO_4 to the eluate and evaporate to dryness until the H_2SO_4 is volatilized.

Am-49 If a dark residue remains, add 1-ml 30% H_2O_2 and evaporate to dryness. Cool.

Am-50 Sample is now ready for electrodeposition.

Note Am-A

The column dimension is 1 cm ID by 10 cm length containing 10 ml of wet, settled anion exchanger Bio-Rad AG21-K (50-100 mesh) in chloride form. The column is preconditioned with 30 ml of 16M HNO_3, then 50 ml of 8M HNO_3 containing 0.1-g $NaNO_2$/10 ml at a flow rate of 2-3 ml/min. This column is used to purify the Nd/Am fraction from residual traces of Pu or Th.

Note Am-B

This column separates Am from the neodymium carrier, other rare earths, and any traces of Fe.

The thiocynate column measures 1 cm ID by 20 cm length and contains 17 ml of wet settled Bio-Rad AG 1x8 (100-200 mesh) in chloride form. The column is conditioned by passing 200-ml 4M HCl, 100-ml 0.01M HCl, then 50-ml 2M NH_4SCN at a flow-rate of 0.5-1.0 ml/min. The resin can be reconditioned for reuse by rinsing in series with 200-ml 0.01M HCl, resuspending, then another 200-ml rinse of 0.01M HCl, followed by 50-ml 2M NH_4SCN.

Note Am-C

This column measures 0.25 cm x 7 cm (a disposalbe 2-ml transfer pipet can be used) and contains 2 ml of wet, settled Bio-Rad AG 1x8 (mesh 100-200). The column is conditioned by passing 5 ml of 1.5M HCl at a flow rate of 0.5 ml/min.

This column absorbs Pb, Bi, and Po isotopes.

Fe

If the samples contain Fe-Am (see Am-4) skip to Fe-7.

Fe-1 Evaporate the solution from Am-15 to near dryness. If the oxalate has not been destroyed, do Fe-2 and Fe-3; otherwise, skip to Fe-4.

Fe-2 Add 100-ml conc. HNO_3 and evaporate to near dryness.

Fe-3 Repeat Fe-2.

Fe-4 Cool and add 500-ml deionized water. Heat, if necessary, to dissolve the salts.

Fe-5 Precipitate the $Fe(OH)_3$ with conc. NH_4OH and allow to settle.

Fe-6 Centrifuge and discard the supernate.

Fe-7 Add enough conc. HCl to dissolve the $Fe(OH)_3$.

Fe-8 Transfer the solution to a tared 1000(400)-ml beaker (see Note Fe-A); rinse the centrifuge bottle with 1N HCl and add rinse to sample. If necessary, heat sample to completely dissolve $Fe(OH)_3$.

Fe-9 Take an aliquot for AA determination of Fe (see Note Fe-B).

Fe-10 Add equal the sample volume of conc. HCl. Evaporate sample to 100(50)-ml; bring volume up to 200(100)-ml with 6N HCl.

Fe-11 Add 1 drop 30% H_2O_2/10-ml sample and warm slowly for 1 hr. Allow to cool.

Fe-12 Add half the sample volume of conc. HCl (now 8N). Pass this solution through a preconditioned ion exchange column (see Note Fe-C) at a flow rate of 1 drop/2 sec. If the sample contains Am, collect it in a 1000(600)-ml beaker. Samples with Am may contain salts, which should be rinsed with 8N HCl. Add this rinse to the reservoir with the

sample. Wash the salts into the Am fraction with deionized water. Allow entire sample to pass through the column.

Fe-13 Wash column with 120(40)-ml 8N HCl. Collect in Am fraction. For samples without Am, discard the eluate from Fe-12 and Fe-13.

Fe-14 For samples with Co, elute the Co at this time with small amounts of 5N HCl (continue adding HCl until Fe just begins to come off column). Store Co for future analysis. Elute Fe with 120(65)-ml 0.5N HCl into a 250-ml beaker.

Fe-15 Split the sample, using AA measurement, so that the fraction to be analyzed contains 500-600 mg Fe. Store the remainder of the Fe fraction in a 125-ml plastic bottle.

Fe-16 If necessary, bring the volume up to 50-ml with deionized water. While magnetically stirring, add conc. NH_4OH until $Fe(OH)_3$ is near precipitation. Then, complete precipitation using saturated $(NH_4)_2CO_3$ solution.

Fe-17 Centrifuge. Wash the hydroxide with dilute (2:100) $(NH_4)_2CO_3$ and centrifuge again. Discard the supernate.

Fe-18 Add enough conc. HCl (5 ml) to dissolve the $Fe(OH)_3$ and transfer the sample to a 250-ml beaker; rinse the centrifuge tube with 1N HCl. Add rinse to sample.

Fe-19 Add equal the sample volume of conc. HCl. Evaporate sample to 50 ml. Add half the sample volume of conc. HCl (now 8N). Let cool.

Fe-20 Pass this solution through a preconditioned 15-ml ion exchange column (see Note Fe-C). Rinse the sample beaker with 8N HCl and add to sample in reservoir. Allow entire sample to pass through the column.

Fe-21 Add 40-ml 8N HCl to the reservoir and allow to pass through the column. Discard all the 8N HCl eluate.

Fe-22 Elute the Fe with 65-ml 8N HNO_3 into a 150-ml beaker.

Fe-23 Evaporate to near dryness; allow to cool.

Fe-24 Add 10-ml conc. H_2SO_4; evaporate to dryness (begin by warming slowly and gradually increase the heat until the sample is dry); allow to cool.

Fe-25 Add 120-ml saturated $(NH_4)_2C_2O_4$ and cover the sample with plastic wrap; sample is ready for electroplating the next day.

Fe-26 When ready to electroplate, add 9 drops conc. H_2SO_4 to sample; stir.

Fe-27 Add conc. NH_4OH until a pH of 4-5 is reached; if this pH is exceeded, bring pH back with oxalic acid; pH must be 4-5.

Fe-28 Tare clean Cu tube (see Note Fe-D).

Fe-29 Transfer sample to Cu tube assembly; rinse beaker several times with deionized water and add this rinse to the sample in the Cu tube; bring the volume up in the Cu tube with deionized water until just above the end cap.

Fe-30 Electroplate at 1.5 amps/sample.

Fe-31 Check pH after the first 1/2 hr of plating and every 15 min. thereafter. As the Fe plates out of the solution onto the Cu tube, the pH of the solution increases. A pH of 4-5 must be maintained; if the pH gets too high $Fe(OH)_3$ will form; pH adjustment is made by adding 3.5N H_2SO_4 during plating through an opening in the end cap of the plating cell. This opening permits a pipet to withdraw some sample for pH determination and make acid additions when necessary.

Fe-32 Plate until the solution is clear. The color of the solution is seen by withdrawing some sample with a pipet. It will take approximately 2 hrs to electroplate 300-mg Fe; 2 1/2 to 3 hrs for 600-mg.

Fe-33 Pour off the solution in the plating cell and disassemble the cell; rinse the Cu tube with deionized water followed by acetone; allow to dry.

Fe-34 Weigh plated Cu tube; sample is ready for counting.

Note Fe-A

Throughout the procedure: Samples which contain less than 500 mg of Fe (include small sediment samples and those samples which have had Fe carrier added) should use the volumes indicated in parentheses.

Note Fe-B

a. Weigh the beaker and the sample

Samples with Fe carrier added:

b. Transfer (.1 g) 3-4 drops/100 ml of solution to a tared 40 ml vial and weigh.

c. Dilute the aliquot with 30-ml 0.02N HCl and weigh.

Sediments containing > 1000 mg Fe:

b. Transfer 1 drop/100 ml of sample to a tared 40 ml vial and weigh.

c. Dilute the aliquot with 40 ml 0.02N HCl and weigh.

Note Fe-C

The Fe columns are 16(10) mm ID by 240(200)-mm long. They are designed in the same manner as the Pu ion exchange columns (see Note Pu-A and Fig. 1). These columns contain 40(15)-ml of wet, settled ion exchange resin, Bio-Rad AG 21K (50-100 mesh) in chloride form. The column is preconditioned with 120(100)-ml 0.02N HCl, followed by 50(30)-ml conc. HCl, 80(50)-ml 0.5N HCl, and 120(50)-ml 8N HCl with 1 drop 30% H_2O_2. Note: Samples which have had Fe carrier added may use the smaller (15-ml) columns throughout. Simply decrease the volumes of the sample and HCl used to the amounts appropriate for that size column (indicated in parentheses above and in steps Fe-8, 10, 13 and 14 in the procedure). Typical sediment samples (50 g dry wt.) require the larger (40 ml) columns for the initial Fe separation.

Note Fe-D

Procedure is described in:

Labeyrie, L. D., H. D. Livingston, A. G. Gordon, 1975. Measurement of Iron 55 from Nuclear Fallout in Marine Sediments and Seawater. Nuclear Instruments and Methods 128: (1975) 575-580.

ELECTRODEPOSITION PROCEDURE

1. Prepare plating cells as in Fig. 2 allowing time for each to sit with 5 ml of deionized water to check for leakage.
2. To the Pu eluate from Pu-26 or the Am eluate from Am-50, add exactly 5 ml of deionized water making certain to wash down the walls of the beaker.
3. Add 4 drops of 0.02% thymol blue indicator and 10 drops of 14M NH_4OH. The indicator should turn blue or at least yellow, indicating a basic pH. If the solution is still pink or red, add enough NH_4OH dropwise to make the solution basic. It is important if several samples are being plated in parallel, that the same amount of NH_4OH is added to each cell, since the resulting $(NH_4)_2\ SO_4$ concentration establishes the electrical resistance of the solution and consequently affects the current in each cell.
4. Neutralize the solution with 18M H_2SO_4 and add one drop in excess of the neutral point. The solution should be slightly pink.
5. Transfer the solution to the plating cell rinsing the beaker twice with 2 ml of approximately 0.02M H_2SO_4 (3 drops of 36M H_2SO_4/100-ml H_2O).
6. For plating Pu and Am, adjust the pH to 2-3, using 2M NH_4OH. The end point color of the indicator is salmon pink. The total plating volume should be 10 ± 1 ml and equal in all samples plated in parallel.
7. The samples are then plated for 2 hr at 1 amp per cell. At the end of the plating period, add 1 ml 14M NH_4OH to each sample, mix, wait one min. and switch off.

8. Disassemble the cell as quickly as possible after plating. The plating disc is washed with distilled water and acetone and then dried and stored for counting.