RiO5 METHOD (3)

Provided by: Ken Buesseler
Center for Marine and Environmental Radioactivity
Woods Hole Oceanographic Institution
k.buesseler@whoi.edu

Method by:
Lyn Brady Clarke
William R. Clarke

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

The following is a historical internal technical manual from Dr. Vaughan T. Bowen Laboratory at the Woods Hole Oceanographic Institution, 1982. Further information and descriptions for this method may be found in the following publication:

Bowen, V.T. et al., 1980, Fallout radionuclides in the Pacific Ocean: Vertical and horizontal distributions, largely from GEOSECS stations. *Earth and Planetary Science Letters*, V49, 411-434.

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

Lyn Brady Clarke

and

William R. Clarke

Woods Hole Oceanographic Institution

Woods Hole, MA 02543

Internal Technical Manual

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Sample Preparation

1. Record sample identification in seawater notebook and assign a WHOI number to each sample. Mark sample deldrum with WHOI number and recheck sample identification on barrel and in notebook.

2. Clean thoroughly sample deldrum -- top, sides, handles, caps, etc. -- of dust, dirt, and removable materials.

3. Check to see that deldrum is not full to the brim. Siphon off and discard ~ 1 liter if necessary.

4. Weigh sample in original deldrum. Record weight in notebook.

5. Add approximately 500 ml of 3 N HCl to sample.

6. Add the following carriers and tracers:
   standardized solutions
   20 ml Sr (100 mg Sr/ml)
   5 ml Fe (50 mg/ml)
   2 ml Nd (25 mg/ml)
   2 ml Cs (10 mg Cs/ml)
   1 ml Pu-242 tracer (2-3 dpm/ml)
   1 ml Am-243 tracer (1-2 dpm/ml)

7. Record the carrier number in notebook.

8. Place the clean heater units into each sample deldrum and allow to mix at least 3-4 days.

9. Transfer sample to a clean, 100 liter polyethylene barrel (cleaned between samples with 500 ml 8N HNO_3 followed by one tap water and two distilled water rinses).

10. Add 500 ml of 3N HCl to empty deldrum, recap and agitate barrel to rinse all inner surfaces - let stand one hour.

11. Add the 3N rinse to sample, rinse empty deldrum twice with about 1 liter of deionized water. Combine rinses with sample.

12. Weigh empty deldrum, record weight of barrel in notebook.

13. Stir sample for about 15 minutes. Proceed to Pu-1 of Pu-Am Separation.

Pu and Am Separation

Pu-1 Add 100 mg of Fe to each sample while stirring (2 ml, 50 mg Fe/ml).

Pu-2 Precipitate the Fe $(OH)_3$ with conc. NaOH; pH 9--10. Allow to settle overnight.

Pu-3 Pump the supernate into a clean barrel and save for Cs separation (step Cs-1).

Pu-4 Remove the stir bar and transfer the $Fe(OH)_3$ to 3 L beakers, with water, and allow to settle overnight.

Pu-5 Decant the supernate from each sample into the respective barrel (from Pu-3).

Pu-6 Dissolve the Fe $(OH)_3$, while stirring, with conc. HNO_3. Dilute to 2.5 L with D.I. H_2O.

Pu-7 Re-precipitate the Fe $(OH)_3$ with 10 N NaOH (pH 9-10), remove the stir bar and allow to settle overnight.

Pu-8 Repeat steps Pu-5 and Pu-6.

Pu-9 Re-precipitate the iron hydroxide with conc. NH_4OH. Remove stirrer and allow to settle overnight.

Pu-10 Aspirate and discard supernate. Transfer $Fe(OH)_3$ ppt to a 400 ml beaker with pH 8 deionized water and allow to settle (at least 2 hours).

Pu-11 Aspirate and discard supernate. Transfer $Fe(OH)_3$ ppt to a 50 ml centrifuge tube and spin down. Discard supernate.

Pu-12 If Pu, Am/Fe analyses are not done immediately, store centrifuge tube with $Fe(OH)_3$ ppt. If Pu analysis is to continue, dissolve Fe $(OH)_3$ ppt with conc HNO_3.

Pu-13 Transfer to 150 ml beaker and bring up to 100 ml with conc. HNO_3.

Pu-14 Cover with flat watchsglass and digest for 4 to 5 hours on low heat. Let cool.

Pu-15 There will be a small amount of flocculent material in sample solutions; filter sample, by vacuum, through a 7.0 cm glass fiber filter in a Buchner funnel, into a 250 ml filter flask. Wash beaker and filter with conc. HNO_3.

Pu-16 Transfer to a 250 ml beaker, rinse filter flask with conc. HNO_3, and evaporate down to 25 ml at medium heat.

Pu-17 Transfer to 50 ml beaker, rinsing with conc. HNO_3, and evaporate to 10 ml at low to medium heat.

Pu-18 Bring up to 20 ml with 0.5 N HNO_3 - this makes the sample 8 N HNO_3.

Pu-19 Prepare column (see note Pu-A).

Pu-20 Add 0.25 g $NaNO_2$ to each sample.

Pu-21 Warm sample at low heat 1 to 2 minutes and let cool before adding to column.

Pu-22 Condition column with 50 ml 8 N HNO_3 to which 0.5 g $NaNO_2$ has been added.

Pu-23 At end of conditioning push glass wool down to top of resin bed.

Pu-24 Add sample to column in 2 ml portions, using a transfer pipette. Let column drip at a rate of 1 drop/5 seconds. See step Pu-28.

Pu-25 Rinse beaker 3 x 2 ml 8 N HNO_3 and add to column.

Pu-26 Rinse column wall 2 x 2 ml 8 N HNO_3.

Pu-27 Install 100 ml reservoirs and add 50 ml of 8 N HNO_3. Let column drip at a rate of 1 drop/5 seconds.

Pu-28 Collect sample, all rinses, and 50 ml 8 N HNO_3 in a 400 ml beaker. This is Fe, Am fraction. See step Am-1.

Pu-29 Change to 400 ml waste beaker and add 100 ml 8 N HNO_3. Let column drip at a rate of 1 drop/5 seconds. This fraction contains U - discard.

Pu-30 Elute Th with 150 ml conc. HCl. Stopcock should be fully open. There must be an HCl head of 2-3 cm height on the resin bed.

Pu-31 If Th fraction is to be analyzed, collect the conc. HCl in a 250 ml plastic bottle. If Th fraction is not to be analyzed, the HCl may be collected in the same 400 ml wastebeaker as the 100 ml 8 N HNO_3 and discarded.

Pu-32 Change to 100 ml beaker to collect Pu fraction.

Pu-33 Elute Pu with 50 ml conc. HCl to which 4 ml of 1 N NH_4I has been added. Let column drip at a rate of 1 drop/5 seconds.

Pu-34 Add 10 ml conc. HCl and collect with Pu fraction.

Pu-35 Evaporate Pu fraction to dryness on low to medium heat.

Pu-36 Treat with 2 x 2 ml aqua regia, evaporating to dryness after each addition.

Pu-37 Add 5 drops conc. H_2SO_4 and treat with 2 x 2 ml aqua regia, evaporating to near dryness after each addition.

Pu-38 Add 2 ml conc. HCl and evaporate until only H_2SO_4 fumes remain. It may be necessary to raise the temperature of the hot plate.

Pu-39 Cool, cover with parafilm, and save for electroplating. Use low level electrodes. See section on electrodeposition.

Note: Seawater Pu-A
Column measures 1 cm ID by 10 cm length containing 10 ml of wet settled anion exchanger Bio-Rad AG 21-K (50-100 mesh) in chloride form.

Cs Separation

Cs-1 Adjust pH on barrel (from step Pu-3) to pH 1.5-2.0 with conc. HCl ($\sim$150 ml).

Cs-2 Weigh out 10 g of AMP (Ammonium Molybdophosphate) in a 50 ml beaker, wet AMP with water and break up lumps with a glass stirring rod.

Cs-3 Add AMP slurry to sample and stir for 10 min. Allow to settle overnight (or at least 4 hours).

Cs-4 Pump the supernate into another clean 100 L barrel and save for Sr analysis (step Sr-1).

Cs-5 Remove stirrer and transfer AMP to a 3 L beaker with water. Let settle (2-3 hours).

Cs-6 Dissolve the remaining AMP on the walls of the 100 L container with 15-20 ml of 10 N NaOH. Transfer the dissolved AMP, with water rinse, to a 600 ml beaker.

Cs-7 Decant the supernate of step Cs-5 into the sample of step Cs-4. Allow AMP in beaker to resettle (2-3 hours).

Cs-8 Aspirate any remaining supernate from the 3 L beaker, then add the dissolved AMP from Step Cs-6 to the AMP in the 3 L beaker. (If insufficient to dissolve all the AMP, add 10 N NaOH dropwise until dissolution is complete.)

Cs-9 Add mixture back to 600 ml beaker from step Cs-6 with water rinse.

Cs-10 Evaporate the solution on a hot plate until NH_3 fumes are no longer detected with wet pH paper. Check the pH of the solution periodically while evaporating and add more NaOH if necessary to maintain the solution basic (pH 12).

Cs-11 When ammonia evaporation is complete, centrifuge hydroxide ppt, if present, and decant supernate to a clean 400 ml beaker. If sample volume is less than 100 ml dilute with water to 100 ml.

Cs-12 Adjust the pH, with conc. HCl, to pH 1-2. Dilute the sample to 250 ml with water.

Cs-13 Add 1.0 g AMP, stir for 10 min., remove stir bar, let AMP settle (about 4 hours), aspirate and discard supernate.

Cs-14 Transfer AMP to a centrifuge tube with 0.02 N HCl. Centrifuge and discard supernate.

Cs-15 Dissolve the Cs-AMP in 20 ml 0.75M NaOH.

Cs-16 Centrifuge and transfer the supernate to a clean centrifuge tube. Add 2 ml 20% EDTA in 0.75N NaOH. Discard any ppt.

Cs-17 Pass sample through an ion exchange column (see note Cs-A) at a flow rate of 1 ml/min.

Cs-18 Elute the Na, K, Rb from the column with 375 ml 0.3N HCl. Discard eluate from Cs-17 and Cs-18.

Cs-19 Elute the Cs with 65 ml 3N HCl, collecting eluate in a 150 ml beaker.

Cs-20 Slowly evaporate the solution to dryness.

Cs-21 Add 1 ml 10N NaOH to the dry salts and transfer to a centrifuge tube with 10 ml deionized water.

Cs-22 Heat in a water bath at 60-80 deg C for 10 min.

Cs-23 Centrifuge the warm solution for 10 min at moderate speed.

Cs-24 Transfer the supernate to a clean centrifuge tube and discard any precipitate.

Cs-25 Heat again in the water bath at 60-80 deg C for 10 min.

Cs-26 Add 2 ml 10% H_2PtCl_6 and continue heating for 10 min.

Cs-27 Cool in the refrigerator for 30 min.

Cs-28 Heat in the water bath at 60-80 deg C for 10 min.

Cs-29 Cool in the refrigerator overnight.

Cs-30 Surface wash a 25 mm Millipore HAWP 0.45 filter paper with 3N HCl followed by deionized water.

Cs-31 Dry the filter paper to a constant weight at 60 deg C (approx 30-60 min.) and record weight.

Cs-32 Filter the Cs ppt onto the tared filter paper while cold, and wash with 10 ml cold deionized water.

Cs-33 Dry to constant weight at 60 deg C, weigh and record 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.

100L - 2000 mg Sr

Sr Separation

Sr-1 Add 3 liters of 1 M oxalic solution to the supernate from step Cs-4. Prepare the oxalic solution by dissolving 400 g of $H_2C_2O_4\ 2H_2O$ in 2.5 L of hot water.

Sr-2 Adjust solution to pH 5-6 with conc. NH_4OH while stirring.

Sr-3 Stir solution for 10-15 minutes.

Sr-4 Allow precipitate to settle overnight.

Sr-5 Discard supernate and transfer the oxalate ppt, with water, to a 3 L beaker.

Sr-6 Let the oxalate resettle, aspirate and discard as much of the supernate as possible.

Sr-7 Add 1000 ml conc. HNO_3 to the oxalate and stir for 2-3 minutes. In most cases the oxalate will dissolve and, in the case of fresh water samples, the nitrate will precipitate.

Sr-8 Add sufficient 90% HNO_3 (200-400 ml) to dissolve any remaining oxalate and precipitate the nitrate.

Sr-9 Stir sample for 10 min., remove stirrer and allow ppt to settle.

Sr-10 Aspirate and discard supernate. Transfer the ppt to a 400 ml beaker with conc. HNO_3 and allow to settle.

Sr-11 Aspirate and discard supernate. Add 100 ml conc. HNO_3; heat for 30 min.; stir for 10 min. and allow to settle and cool.

Sr-12 Repeat step Sr-11.

Sr-13 Aspirate and discard the supernate.

Sr-14 Dissolve the $Sr(NO_3)_2$ in $\sim$ 50 ml of water.

Sr-15 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-16 Add conc. NH_4OH to the solution until the pH is 9. An iron hydroxide precipitate will form.

Sr-17 Warm the sample to 60-80°C for 10 minutes; then cool to room temp.

Sr-18 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-19 Adjust the pH of the filtrate to between 4 and 6 with 3N HCl. Repeat steps Sr-4 through Sr-7.

Sr-20 Record the date of the second iron scavenge.

Sr-21 Readjust the pH to 4 to 6 with 3N HCl.

Sr-22 Add 4 ml barium acetate buffer and heat to near boiling. See Note Sr-A.

Sr-23 Add 1 ml 1M Na_2CrO_4 and continue heating with occasional stirring for 30 minutes.

Sr-24 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-25 Repeat steps Sr-10 to Sr-12.

Sr-26 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-27 Aspirate off supernate and discard.

Sr-28 Wash precipitate with 100 ml 5% $(NH_4)_2CO_3$; allow to settle and aspirate off the supernate.

Sr-29 Repeat the $(NH_4)_2CO_3$ wash.

Sr-30 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-31 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 two 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.

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.

Am/Fe Separation

Am-1 The solution from step Pu-28 is evaporated to 25 ml.

Am-2 Bring volume up to 150 ml with deionized water and then add 150 ml saturated oxalic acid to make a 5% solution.

Am-3 Stir for 30 minutes on a magnetic stirrer.

Am-4 If neodymium oxalate has not precipitated after 30 minutes, check the pH. If pH is less than 1.0 adjust to pH 1.5 with conc. NH_4OH (back titrate with conc. HNO_3) and stir for 30 minutes longer.

Am-5 Remove the stir bar and allow to settle overnight.

Am-6 Decant supernate into a clean 400 ml beaker if Fe analysis is to be done. See Fe procedure. If Fe will not be done discard supernate.

Am-7 If Am analysis will not be done immediately, transfer Nd ox precipitate to 60 ml plastic bottle and rinse beaker with deionized water. Add rinse to plastic bottle and store.

Am-8 If Am is to be analyzed, proceed.

Am-9 Rinse the beaker and precipitate with 0.5% oxalic acid into a centrifuge tube. Centrifuge and add the supernate to the Fe fraction.

Am-10 Dissolve the oxalates in 8 ml of 8N HNO_3, warming if necessary.

Am-11 Transfer the solution with deionized water into a 250-ml beaker and dilute to 100 ml.

Am-12 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-13 If no precipitate forms, add 14M NH_4OH dropwise while stirring until the precipitate starts to form. Do not exceed pH 1.

Am-14 Stir the sample for a total of 30 min. Remove the stir bar and allow to settle.

Am-15 Decant and discard the supernate. Centrifuge the oxalates in a 50 ml plastic centrifuge tube, rinsing with 0.5% oxalic acid.

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

Am-17 Bring the solution to 100 ml with more 16M HNO_3 and boil until almost dry, destroying the oxalate.

Am-18 Dilute the sample to 100 ml with deionized water and warm on hot plate to about 60°C.

Am-19 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-20 Dissolve the hydroxides with 8-ml 8M HNO_3; add 0.1-g $NaNO_2$ and let stand for 5-10 min.

Am-21 Transfer the solution to a previously conditioned anion exchange column. (Note Am-A).

Am-22 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-23 Evaporate the solution to dryness.

Am-24 Dissolve residue in 2-ml 12M HCl and evaporate to dryness. Repeat this step.

Am-25 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-26 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-27 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-28 Elute the Am with 70-ml 4M HCl at the same flow-rate.

Am-29 Collect the Am fraction in a 100-ml beaker containing 10-ml 16M HNO_3 which is continuously stirred (magnetic stirrer).

Am-30 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-31 Repeat Steps Am-32 to Am-37.

Am-32 Dissolve the residue in 8-ml 8M HNO_3.

Am-33 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-34 Repeat Steps Am-29 to Am-31.

Am-35 Rinse the beaker with 1-ml deionized water and evaporate to dryness. Repeat this step.

Am-36 Dissolve the residue in 2-ml 1.5M HCl.

Am-37 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-38 Pass two 1-ml beaker rinses and a 4-ml wash of 1.5M HCl through the top column.

Am-39 Remove the top column and discard.

Am-40 Pass a 3-ml rinse of 1.5M HCl through the bottom column, then discard column.

Am-41 Add five drops of conc. H_2SO_4 to the eluate and evaporate to dryness until the H_2SO_4 is volatilized.

Am-42 If a dark residue remains, add 1-ml 30% H_2O_2 and evaporate to dryness. Cool.

Am-43 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.

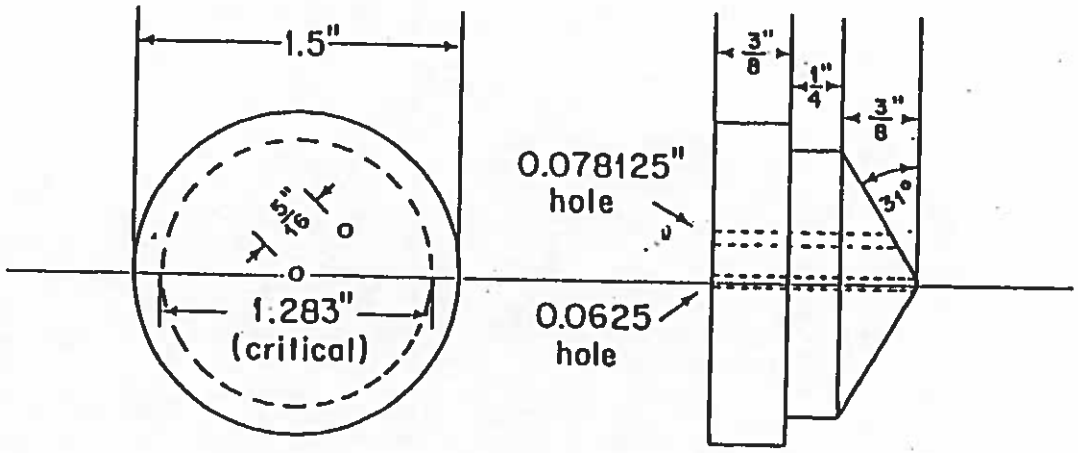
This column absorbs Pb, Bi, and Po isotopes.

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.

ELECTRODEPOSITION ELECTRODE HOLDER



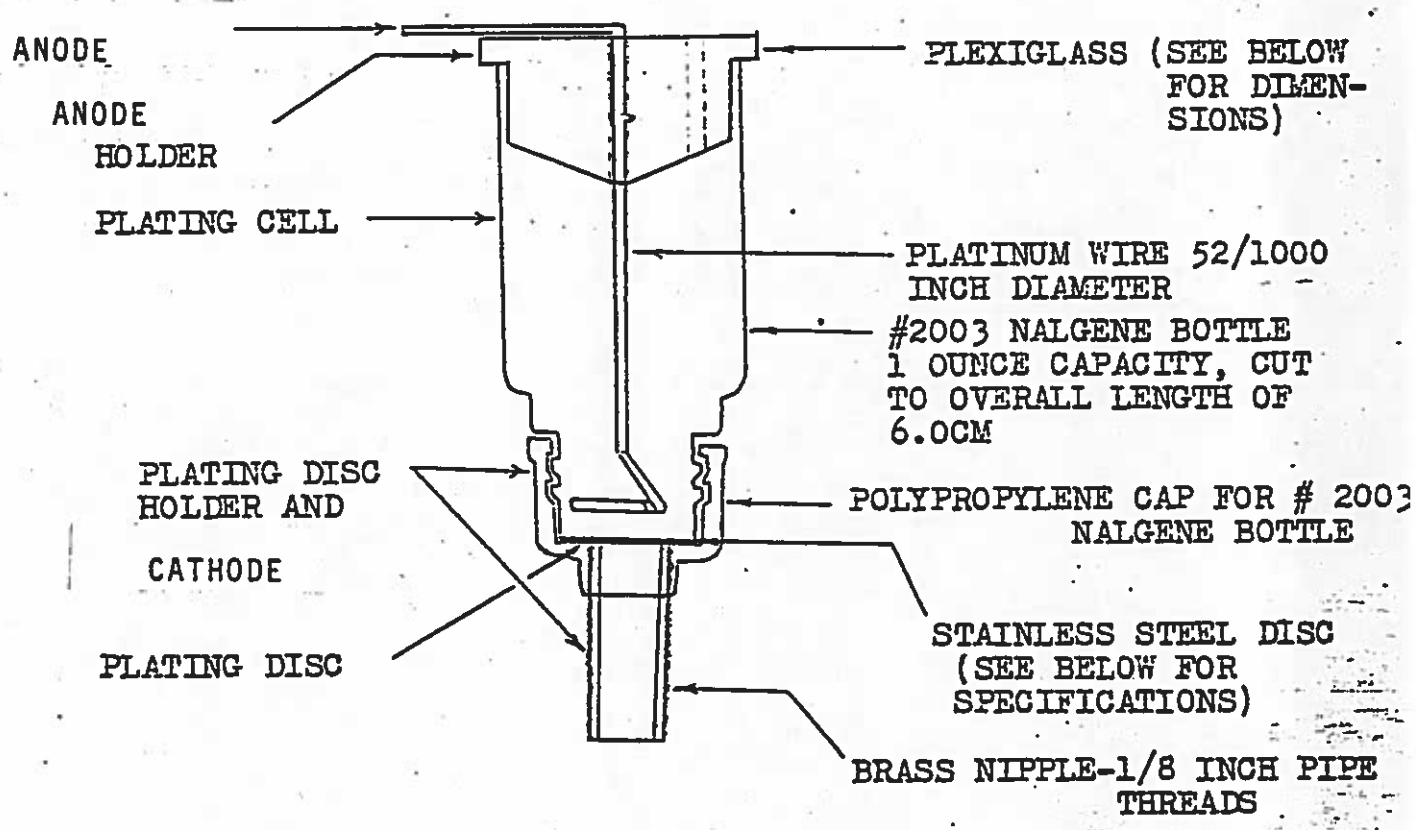
WOODS HOLE OCEANOGRAPHIC INSTITUTION
WOODS HOLE, MASSACHUSETTS 02543

Phone (617) 548-1400

20 JANUARY 1982

The below diagramed apparatus is our present electro-deposition equipment.

DESCRIPTION MATERIALS



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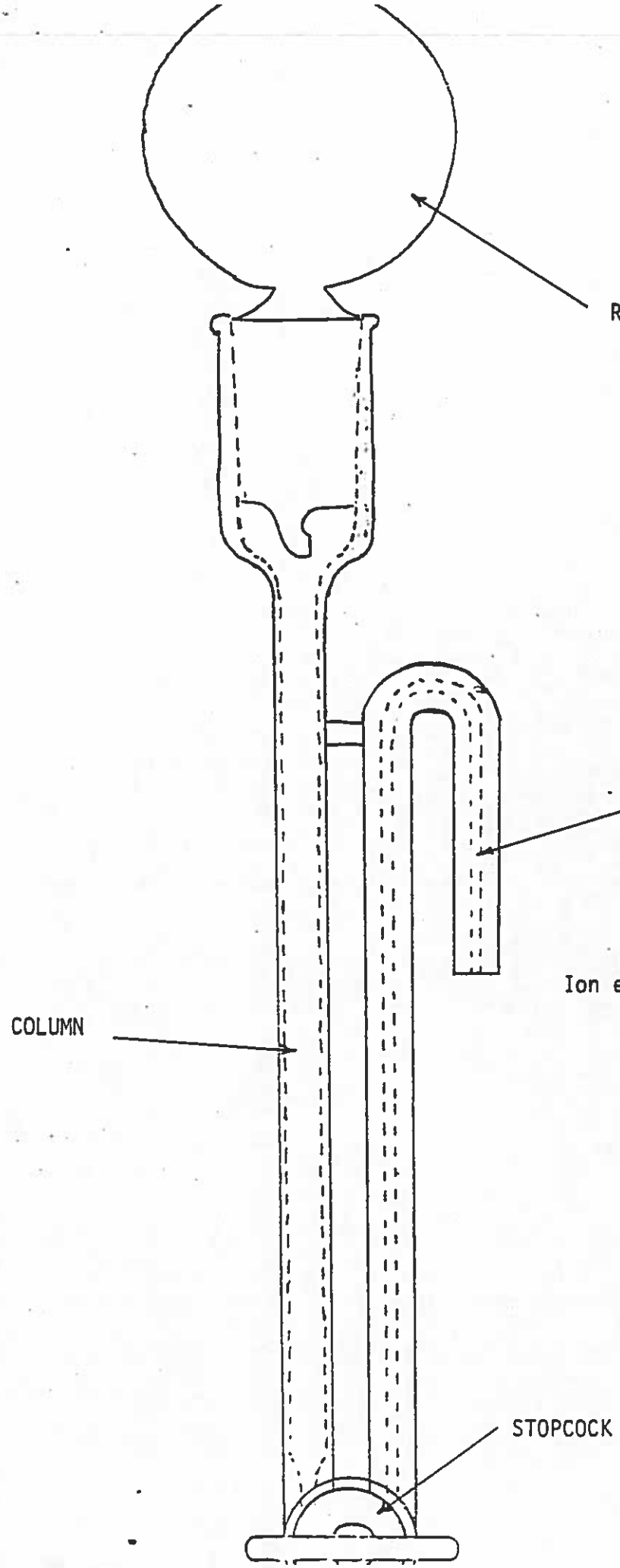

Figure 1
Ion exchange columns for separation of Pu