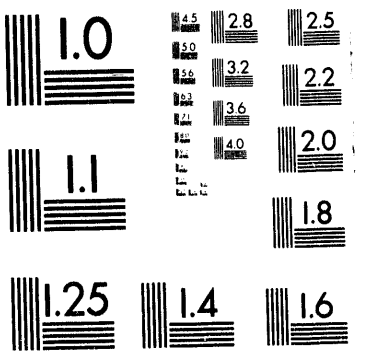
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1 of 1

RADIOCHEMICAL PROCEDURES FOR ANALYSIS OF Pu, Am, Cs, AND Sr IN WATER, SOIL, SEDIMENTS AND BIOTA SAMPLES

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PREFACE

The Environmental Radioactivity Analysis Laboratory (ERAL) was established as an analytical facility for the Marshall Island Program and other environmental radiological studies in the Health and Ecological Assessment Division (formally the Environmental Sciences Division of the Biomedical and Environmental Sciences Directorate) of the Physical Sciences Directorate at Lawrence Livermore National Laboratory. The primary function of ERAL is to provide fast and accurate radiological data of environmental samples. Over the years, many radiochemical procedures have been developed by the staffs of ERAL, and some have been modified, as dictated by the needs and changes in the programmatic studies. The details of these procedures have not always been included in the published reports because of constraints in reporting format and space.

As result, we have found that our procedures exist in many different formats and in many different notebooks, documents and files. Therefore, in order to provide for more complete and orderly documentation of the radiochemical procedures that are being used by ERAL, we have decided to standardize the format and compile them into a series of reports. This first report covers procedures we have developed and are using for the radiochemical analysis of Pu, Am, Cs, and Sr in various matrices. Additional analytical procedures and/or revisions for other elements will be reported as they become available through continuation of these compilation efforts.

CONTENTS

The numbering system in the procedure is a combination of chemical symbols, letters and numbers. Each procedure is identified by the chemical symbol of the element, the major section in each procedure is designated by a letter, and the steps of each procedure are given by a two digit number after the section designation. Thus, Pu-E-3 is Step 3 of Section E in the plutonium procedure.

PLUTONIUM ANALYSIS

A. INTRODUCTION

The preconcentration procedure used in our laboratory for the separation of transuranic elements from water samples is based on the coprecipitation of MnO_2 produced from the *in situ* reaction of $KMnO_4$ and $MnCl_2$ at pH~8[1]. The MnO_2 procedure has been used successfully in the field and laboratory for samples up to 600 liters. The procedure is fast, the precipitates settle rapidly and, unlike $Fe(OH)_2$ or $Fe(OH)_3$, MnO_2 can be collected easily on filter cartridges.

The radiochemical procedure for the analysis of Pu in soil, sediment, and ashed biota samples is an acid leaching method based on the procedure developed by Chu[2] which uses concentrated nitric and concentrated hydrochloric acids for digestion. Chu's original procedure has been modified by Wong et al.[3] to accommodate samples up to 1000 g of calcareous or 300 g of siliceous soil using only concentrated nitric acid for digestion. We have compared the results from our procedure against those using Chu's method for leaching, and those employing total dissolution, such as the use of hydrofluoric and perchloric acid. We find no significant difference in the analytical accuracy among these sample digestion methods for the analysis of Pu (from atmospheric fallout) in shallow or deep marine sediments or in soil and sediment samples collected from the Pacific Test Sites at Bikini and Enewetak Atolls (Close-in fallout). Our method has also been used in the analysis of Pu in NBS Radioactivity Standard Reference Materials (Rocky Flats Soil and Columbia River Sediment) and in certain IAEA interlaboratory comparison samples. Our results have been shown to be in good agreement with those obtained using other digestion and analytical methods.

The following detailed procedure emphasizes the technique of manipulating large samples; the acid leaching method itself is extremely simple. Some of the techniques developed in this laboratory may be unique and not easily adopted by others, but once the principle is understood, a good analyst can easily develop a "best" technique that is most suitable for the resources in their particular laboratory.

This method may also be used, with few modifications, for the sequential separation of other radionuclides of interest, provided the appropriate carriers and tracers are added for the correction of chemical recovery (see Appendix-A).

B. REAGENTS AND EQUIPMENT

The chemicals, supplies, and equipment are listed in Appendix-B.

C. SAMPLE PREPARATION AND PRECONCENTRATION

Each sample is assigned an I.D. number for reference and all pertinent information (e.g. sampling date, location, type, method, collectors, etc.) are recorded in a sample log book. When estimates of sample activity are available, samples are segregated and analyzed by groups to minimize cross-contamination.

D. WATER SAMPLES

1. Water samples (from 10 to 60-liters) are collected and acidified immediately after collection (5 ml of 5N HCl per liter of sample) and the required tracers and carriers are added. The samples, in 60-l shipping containers, are shipped to the laboratory for processing.

2. The sample is transferred from the shipping container to the proper size polyethylene processing container. The following amount of reagents is generally added to a typical 55 liter sea water sample:

3. Add 12 ml of saturated $KMnO_4$, stir to mix, adjust the sample to pH–8 with 10M NaOH, then slowly increase the pH to 9 with 1N NaOH (monitor with a pH meter). Dilute 10 ml of 1M $MnCl_2$ to about 100 ml with water. With stirring, gradually add the diluted $MnCl_2$ solution, a few ml at a time, until the violet color of the $KMnO_4$ changes to brown and fine particles of MnO_2 begin to form. Continuously monitor and adjust the pH to 9 ± 1 with 1N NaOH.

4. Filter the MnO_2 onto a 1 micron filter cartridge or let the precipitate settle overnight and decant the clear liquid (The liquid is saved, if Cs or Sr analysis is required). If the sample was filtered (usually done in the field analysis), remove the plastic cartridge core, ash the filter at 450° C, and proceed to Section PU-E to complete the analysis.

5. If the precipitate was allowed to settle (preferred method), the MnO_2 is collected by a combination of sedimentation and centrifugation. The MnO_2 is finally collected in a 250 ml polybottle.

6. If other radionuclides that are not precipitated by the MnO_2, (such as Cs, Sr), are also to be analyzed in the same sample (see SCHEMATIC OUTLINE OF SEQUENTIAL SEPARATION PROCEDURE in Appendix-A), the MnO_2 preconcentration step is generally performed first to remove the transuranics (to improve Pu and Am recoveries) followed by Cs extraction with AMP (Section CS-C) and, then, the Sr fraction is removed last as the oxalate (Section SR-C).

7. Dissolve the MnO_2 in the 250 ml polybottle with 5 ml of conc. HNO_3 and dropwise addition of about 1–2 ml of 30% hydrogen peroxide. Estimate the volume of the solution, and add an equal amount of conc. HNO_3. Dilute the sample to a final volume of about 150 ml with 8N HNO_3. Cool the sample to room temperature and add about 2–3 g of granular $NaNO_2$ (see NOTE below) or until the color of the sample is slightly green. Cap the 250 ml polybottle loosely for venting and leave the bottle inside a fume hood overnight before proceeding to Pu separation in Section PU-H.

NOTE: Add the $NaNO_2$ in small increments. A vigorous reaction generally occurs when $NaNO_2$ is added to 8M HNO_3.

E. SOLID SAMPLES (SOIL, SEDIMENTS, AND ASHED BIOTA)

1. The sample weight as collected, is first recorded. Soil, sediment, and biota are normally dried at 110° C to constant weight and the dry weight is recorded. If

necessary, the dried sample is heated at 475° C to decompose any organic material. It is not recommended to heat the sample above 500° C because of the possibility of forming refractory materials which may not solubilize by this acid leaching procedure.

2. The samples are normally homogenized using a mortar and pestle or ball mill and sieved through a 0.5 mm stainless steel screen (to remove rocks or other large objects). Aliquots of the fine fraction are taken for processing.

3. The aliquot size may vary and depend on several factors: (1) the actual size of the original sample, (2) the required sensitivity,(3) the estimated activity of the sample, and (4) the time and man power available for processing and counting. Small samples are easier to process, but processing too small of an aliquot may occasionally introduce significant error. Often some compromise has to be made between the quality of the expected results and the available time and effort given to processing a sample. Ideally, the size of the sample selected should be such as to result in an activity (in this case, $^{239+240}$Pu) equal to or greater than the added tracer so that the counting time and the counting error can be minimized. In practice, such a choice is not always possible. Therefore, best judgment should be used in selecting an aliquot size that will give a sample activity within a factor of 50 times that of the added ^{242}Pu tracer.

4. If the activity of $^{239+240}$Pu in the sample is low compared to the tracer, longer counting time will be required to produce good counting statistics. In addition, for low activity samples, other factors such as detector background, reagent blanks, and general contamination become more critical. On the other hand, if the plutonium activity is too high compared to the added ^{242}Pu tracer, it would be difficult to resolve the individual peaks of the ^{242}Pu and $^{239+240}$Pu in the alpha spectrum and larger errors would be introduced in the final calculation.

5. For most environmental samples, we usually add about 5–10 dpm of standardized ^{242}Pu tracer, which gives sufficient counting statistics for an overnight (1000 minute) count with reasonable sample recovery. Therefore, the size of the aliquot for environmental samples should be estimated to give a $^{239+240}$Pu activity within the range of 0.1 to 250 dpm. As mentioned above, the optimal sample activity is one which is equal to the added tracer. For samples with estimated activity much higher than 1 dpm/g, more than 5 dpm of tracer should be used to avoid taking an aliquot of less than one gram in order to minimize sampling errors due to inhomogeneity, weighing, transfer loss, etc.

F. NOTES ON DIGESTION PROCEDURE

Select a group of samples for analysis with comparable levels of activity, and assemble the necessary chemical reagents and equipment. The number of samples that can be processed at a single time depends on the available work space, the equipment and facilities of the laboratory, and the experience of the analyst. Four to 12 samples can usually be processed conveniently as a set in a 1 × 2 m fume hood.

Clear a work space in a fume hood approved for acid digestion. Care should be taken when handling finely powdered samples to avoid loss and contamination of

the work space or other samples. Open containers with concentrated acid should be stored inside the fume hood. Proper safety equipment should be used (e.g. gloves, face shields or approved safety glasses, etc.). Adequate space for the hot plates must be provided so that any hot boiling sample may be removed at any given time quickly and safely. It is suggested that no more than two 1000 ml beakers, or more than 4 beakers of any size, be heated on a 30 cm × 28 cm hot plate at the same time in the initial stages of sample digestion.

G. SOIL PROCEDURE

1. Weigh out an amount of sample to at least 3 significant figures and transfer it to a glass beaker. The volume of the beaker should be 8 to 10 times the volume of the sample. For example, use a 1000 ml beaker for 150 g of dried soil sample (density 2.0). A sample should never require a container larger than 2000 ml. If a large sample is required for analysis, it should be divided into smaller equal weight aliquots (and equal tracer), which are then recombined after the digestion procedure (be sure to a keep good records of the added tracer and sample weights).

2. Add the proper amount of standardized tracer (see note below), 2-3 drops of n-octanol, and slowly add concentrated nitric acid while swirling the beaker, until all the sample is "wet" with acid. If vigorous foaming occurs, add a few more drops of n-octanol. Eventually add a volume of concentrated nitric acid equal to 5–10 times the volume of the dry solid sample. For example, use about 25–50 ml of conc. HNO_3 for a 10 g sample (density 2.0). Mark the top of the liquid level on the outside beaker wall for later reference.

NOTE: Pipetting of tracer is a fairly simple laboratory manipulation, but it is a critical and irretrievable step. Care should be taken since when working with a group of samples, it is possible to miss a sample or add the tracer twice to the same sample, especially if **distracted**. Therefore, take steps to minimize interruptions during pipetting.

3. Rinse down the wall of the beaker with conc. HNO_3 using a polyethylene wash bottle. (Color code and identify this bottle as conc. HNO_3 so it will not be mistaken for water or another reagent!). Cover the beaker with a watch glass and heat the sample slowly on a hot plate to boiling. Set the hot plate control at a moderate setting so that samples will not bump.

4. Continue boiling until brown fumes are no longer visible. Samples may require about 1 to 3 hours of boiling depending on sample size, the concentration of chloride ion, and other oxidizable substances in the sample.

5. Periodically rinse down the beaker wall with conc. HNO_3 during the digestion. Using the level mark made in Step 2 as a guide, maintain approximately the initial liquid volume during the digestion period.

6. After the digestion is complete, once again add conc. HNO_3 to the mark on the beaker made in Step 2.

NOTE: The $Sr(NO_3)_2$ and $Ca(NO_3)_2$ in the sample will generally precipitate at this step. They should be separated if Sr-90 analysis is required.

7. Estimate the volume of conc. HNO_3 (including the volume of the precipitate).

8. Add a volume of water equal to the liquid volume in Step 7 and mix thoroughly with a stirring rod.

9. If necessary, heat the sample to near boiling to dissolve any soluble salts formed during the digestion period.

10. Cool the sample to room temperature, transfer the mixture, or a fraction of the mixture, to a 250 ml polybottle, centrifuge and decant the clear liquid (8M HNO_3) into another polybottle. Use 8M HNO_3 for transfer and rinses (color code and clearly mark the 8M HNO_3 wash bottle).

11. Wash the solid material by shaking it with 8M nitric acid. Use a volume approximately twice the volume of the residual solid. Centrifuge and combine the rinse with the sample in Step 10.

12. Repeat Step 11 two times. The final volume of the liquid should occupy less than 75% of the container; if not, transfer the sample to a larger container before proceeding to the next step.

13. Carefully add 0.5 g increments of $NaNO_2$ crystals to the sample from Step 12; swirl the bottle to mix. Add sufficient $NaNO_2$ to see a visible change in the color of the solution to greenish yellow. Samples will usually require about 1-2 grams of $NaNO_2$ per 100 ml of solution.

14. Loosely cap the sample bottle (for venting) and allow any excess $NaNO_2$ to react overnight (inside the fume hood). The delay is necessary to allow all the $NaNO_2$ to react and to avoid the formation of gaseous products that would interfere during the separation of Pu in the anion-exchange step described in Section H.

H. PLUTONIUM SEPARATION BY ANION EXCHANGE

Plutonium, as well as several other heavy elements (e.g. U, Th, Np, Am, Cm), may be separated and purified by anion-exchange chromatography. If only $^{239+240}Pu$ activity is to be determined, a single anion-exchange column separation, done carefully, is usually sufficient. However, if the ^{238}Pu activity is also required, then a second small column separation will be necessary to eliminate any trace of interfering activities from the naturally occurring elements, Ra and Th, present in all soil and sediment samples as described in Pu-I, PLUTONIUM PURIFICATION

1. Prepare anion-exchange columns as shown in Figure 1, APPENDIX–C. Use the medium size column for sample volumes less than 500 ml or the large size column for samples with final volumes greater than 500 ml.

2. Precondition the columns by passing about 20 ml of 8M HNO_3 through each column.

3. Check the sample solution (from PU-G-14) for particulate material. If insoluble silicates (white, gelatinous materials) or other particles are noted, centrifuge or filter the solution through a glass fiber filter before loading the

sample onto the preconditioned column. This step is important in order to maintain a continuous flow of the sample solution through the column.

4. Load the sample solution onto the column as fast as the column will allow. The plutonium is retained on the ion-exchange column. If insoluble material has been removed from the sample and there is no out gassing in the column, the average flow rate in the medium size column is about 3 to 6 ml per minute, depending on the viscosity of the sample solution.

NOTE: Collect the eluant from Step 4 in a 1-l beaker. If only Pu analysis is required, the combined eluant, rinse and wash from Steps Pu-H-4 through Pu-H-8 may be discarded; otherwise, the liquid from **Steps PU-H-4 and 5** need to be saved if other analysis (Am, Cs, Sr, etc.) are required.

5. After the sample has drained to the top glass wool plug in the column, rinse the wall of the column reservoir thoroughly with 8M HNO_3. This can be done conveniently with a polyethylene wash bottle. Do this at least 3 times with about 5 to 10 ml of 8M HNO_3 and allow each rinse to drain to the top glass wool plug.

6. After the last rinse, wash the column with 8 column-volumes of 8M HNO_3 and discard the rinse (about 150 ml for the medium column or 350 ml for the large column).

7. After the 8M HNO_3 rinse, wash the wall of the column reservoir with about 5–10 ml of conc. HCl. Repeat the conc. HCl wash three times, each time draining the liquid to the top of the glass wool plug.

8. Now wash the column with 8 column-volumes of conc. HCl (about 150 ml for med. column or 350 ml for the large column). Discard HCl rinse.

9. Elute the Pu with 5 column-volumes of NH_4I-HCl solution. Use 100 ml of NH_4I-HCl for the medium size column. Collect the Pu eluant in a 150 ml beaker.

NOTE: Prepare the NH_4I-HCl solution just prior to the elution by mixing 1.5 g of NH_4I per 100 ml of conc. HCl. Dissolve the NH_4I in a minimum volume of water before adding the conc. HCl.

10. Add approximately 5 ml of conc. HNO_3 to the Pu eluant, mix, and evaporate to dryness on a hot plate. A small residue may be visible on the bottom of the beaker after the evaporation, which appears to have no significant effect on the analysis. This material is normally seen and probably results from the decomposition products of strong acids with the resin.

I. PLUTONIUM PURIFICATION BY ANION-EXCHANGE SEPARATION

1. Cool the sample from Step PU-H-10 to room temperature. Rinse the wall of the beaker with 8-10 ml of conc. HCl. Add 2–3 drops of 30% H_2O_2 , 3–5 drops of 1M $NaNO_2$, and heat on a hot plate for about 5 minutes. Again cool the sample to room temperature.

2. Prepare a small column with Dowex 1 × 8, 50–100 mesh (see Fig.1, Appendix-C) and precondition it with 1 ml of conc. HCl. Collect the eluant in a 50 ml C-tube.

3. Load the sample from the beaker onto the column.

4. Rinse the beaker 2 times with 2–3 ml of conc. HCl and load the rinse onto the column.

5. When the liquid has drained to the top glass wool plug of the column, rinse the wall of the reservoir with 2–3 ml of conc. HCl.

6. Rinse the column 2 more times with 2–3 ml of conc. HCl.

7. Wash the column with 10 ml of conc. HCl.

8. Discard the rinse from Step 2 through Step 7.

9. Elute the Pu with 20 ml of NH_4I-HCl solution. Collect the Pu in a 50 ml glass beaker. (Prepare the NH_4I-HCl as described in Step PU-H-9).

13. Add 2–3 ml of conc. HNO_3 and evaporate the solution to dryness on a hot plate.

J. ELECTRODEPOSITION OF PLUTONIUM

1. Assemble the plating cell as shown in Figure 2a or 2b, APPENDIX-C.

2. Fill the cell with water to test for leakage.

3. Add 1 ml of conc. sulfuric acid to the sample from Step PU-I-13.

4. Heat the sample on a hot plate until copious white fumes evolve.

5. Cool the sample to room temperature, carefully rinse the wall of the beaker with 2 ml of 1N H_2SO_4. Add 2 drops of 0.1% methyl red indicator.

6. Transfer the sample to the electroplating cell.

7. Rinse the beaker with 2 ml of lN H_2SO_4. Add the rinse to the plating cell.

8. Repeat Step 7 three times.

9. Add conc. NH_4OH dropwise until the color of the sample changes from red (pH 4.4) to yellow (pH 6.2). Mix the solution by swirling the plating cell.

10. Add 1N H_2SO_4 dropwise to the red end point (pH 4.4) and then add 2 drops excess.

11. Complete the assembly of the electroplating cell by attaching the platinum anode with plastic insulation tape as shown in Fig.2, APPENDIX-C. Position the platinum wire anode about 0.5 cm from the stainless steel disc (cathode).

12. Connect the anode and cathode of the electroplating cell to a constant current power supply.

13. Electroplate at 1.0 amp for 60–70 minutes.

14. Before turning off the power supply when electrodeposition is completed, add 1 ml of conc. NH_4OH to the cell and continue plating for about one minute, then turn off the power supply and as quickly as possible:

    a. Disconnect the cell from the power supply.

    b. Discard the solution from the cell.

    c. Rinse the cell with diluted NH_4OH from a wash bottle. (Make the diluted NH_4OH solution by adding 0.5 ml conc. NH_4OH to 500 ml of water)

    d. Disassemble the plating cell.

    e. Rinse the plated disc with diluted NH_4OH.

    f. Rinse the plated disc with acetone and let the disc air dry on a clean paper tissue.

16. Count the plated disc and determine the activity of the plutonium isotopes by alpha spectrometry.

AMERICIUM ANALYSIS

A. INTRODUCTION

The procedure described for the preconcentration of plutonium from sea water and the dissolution of solids is also used to separate americium. The major difference between the plutonium and americium radiochemical procedures is in the purification step for americium.

Rare earth elements in varying concentrations are present in all environmental samples. Due to their similar chemical properties, quantities of rare earths are preconcentrated with americium from environmental samples. If not separated, rare earths will interfere with the americium measurement by alpha spectrometry.

Older separation schemes for americium from rare earths were often lengthy and complicated. A recent procedure, using a chelating ion exchange resin column of octyl(phenyl)-N,N-diisobutylcarbamoylmethyl-phosphine oxide (TRU-Spec)[4] has simplified and shortened the separation time of americium from days to a few hours. We have adopted this procedure, with some modifications, for americium analysis in our laboratory.

B. SPECIAL REAGENTS

In addition to some of the general reagents and equipment listed in Appendix-B, the following specific supplies are required for the americium radiochemical procedure:

1. TRU-Spec, chelating resin. Available from:
   EIChroM Industries, Inc.
   8205 S. Cass Ave., Suite 107
   Darien, ILL 60559

2. Aluminum nitrate solution, 2M $Al(NO_3)_3$.

3. Nitric acid, 0.075N and 2.0N HNO_3.

4. Feed solution, 0.5M $Al(NO_3)_3$ in 2N HNO_3

5. Standardized ^{243}Am tracer, 5–10 dpm/ml in 3N HNO_3

C. SAMPLE PREPARATION – WATER SAMPLE

Proceed as described in the PLUTONIUM ANALYSIS (Section PU-D).

D. SAMPLE PREPARATION – SOIL, SEDIMENTS, and ASHED BIOTA

Proceed as described in the PLUTONIUM ANALYSIS (Section PU-E).

After completion of Pu separation in Step PU-H-5, dilute the 8N HNO_3 eluant and rinse (which contains the americium fraction) to twice its volume with water. Make the solution basic with conc. NH_4OH to precipitate the hydroxides, then separate the hydroxides by centrifugation and discard the supernate.

Dissolve the hydroxides with a minimum amount of conc. HNO_3, transfer the sample solution to a 50 ml C-tube, and dilute the volume to 15 ml with water. Add 2.5 ml of conc. HNO_3 and 5 ml of 2M $Al(NO_3)_3$. The $Al(NO_3)_3$ is added as a salting agent to improve the column efficiency in the Am purification steps.

E. PURIFICATION OF AMERICIUM

1. Load a small column (see Fig.1, Appendix-C) with TRU-Spec resin and precondition it with feed solution (0.5M $Al(NO_3)_3$ in 2N HNO_3).

2. Transfer the sample solution from Section AM-D to the preconditioned column.

3. After all the solution has passed through the top of the resin, rinse the column wall with several 5 ml portions of 2N HNO_3. Let each rinse drain to the top of the resin column and repeat the 2N HNO_3 rinse until a total of about 40 ml is collected. To facilitate measurement of the rinse volume, collect the rinse solution in a graduated 50 ml C-tube.

   The feed solution can be removed from the column by using a small polyethylene wash bottle to deliver the rinses. To do this step effectively: Hold the wash bottle with one hand, place the tip of the wash bottle at the top of the inside wall of the column reservoir, keep the tip stationary, rotate the column with the other hand while delivering the 2N HNO_3 to the column reservoir.

4. Elute the americium with 30 ml of 0.075N HNO_3 and collect the eluant in a 50 ml beaker. Evaporate the eluant on a hot plate to dryness and electroplate the americium as described in Section PU-J.

CESIUM ANALYSIS

A. INTRODUCTION

For many samples we collect, the concentration of ^{137}Cs is determined directly by gamma spectrometry. Only water samples and a small percentage of the soil, sediment, and biota samples require preconcentration of ^{137}Cs and measurement by beta counting and/or in some cases in low background well-type GeLi detectors.

The radiochemical procedure for the determination of ^{137}Cs in aqueous samples is based on the batch extraction of cesium onto a microcrystalline cation exchanger, ammonium molybdophosphate (AMP), and subsequent purification from potassium and rubidium activities by ion-exchange separation using a strongly acidic cation exchange resin (BIO-REX-40). Natural K and Rb have radioactive isotopes that interfere with the beta counting of ^{137}Cs. The purification of cesium is also necessary to determine the chemical recovery.

Gamma spectrometry is used when samples contain both ^{134}Cs and ^{137}Cs activities. By theory, using the proper absorbers, ^{134}Cs can also be resolved from ^{137}Cs activity because of the difference in beta energy. However, the absorbers greatly reduce the counting efficiency, thereby eliminating any gain in the beta measurements of samples containing both ^{134}Cs and ^{137}Cs.

B. SPECIAL REAGENTS AND EQUIPMENT

In addition to some of the general reagents and equipment listed in Appendix-B, the following supplies are necessary for the cesium radiochemical procedure:

1. BIO-REX-40, 20–50 mesh, hydrogen form cation exchange resin.

2. AMP-1 Resin, Ammonium molybdophosphate (AMP) microcrystalline cation exchange crystals.

   Both resins available from: Bio-Rad Laboratories
   3300 Regatta Boulevard
   Richmond, CA 94804

3. 2% EDTA-0.75M NaOH. Dissolve 60 g tetrasodium ethylenediamine tetracetate dihydrate in water, add 250 ml 10M NaOH, and adjust total volume to 3000 ml with water.

4. Chloroplatinic acid, 0.12M H_2PtCl_6.

5. 5% Sodium chloride, NaCl, solution.

6. 0.75N and 3.0N Hydrochloric acid, HCl, solutions.

7. Standardized stable Cs carrier, 20 mg Cs/ml in 0.1N HNO_3.

8. Nylon ring and discs for mounting of sample for beta counting available from Control Molding Corp., 84 Granite Ave., Staten Island, NY 10303.

C. SAMPLE PREPARATION and PRECONCENTRATION – AQUEOUS SAMPLE

If other radionuclides (Pu, Am, and Sr), are also analyzed in the same sample, the MnO_2 preconcentration steps are generally performed first to remove the transuranics, followed by Cs extraction with AMP; and then, the Sr fraction is removed last as the oxalate.

After the completion of MnO_2 separation in Section PU-D, the water sample is transferred to the proper size polyethylene processing container, adjust to pH 1–4 with nitric acid, add AMP as a slurry in water to extract the cesium (use 0.2 g AMP/liter of sample), stir the sample thoroughly and let the AMP settle, filter or decant the supernate (discard the supernate or save for Sr analysis, if required), separate the AMP by centrifugation and purify the Cs for beta or gamma counting as described in Section CS-E below.

D. SAMPLE PREPARATION – SOIL, SEDIMENT, OR ASHED BIOTA

Dissolve or leach the sample with conc. HNO_3 and separate the residual materials as described in the Step PU-H-5.

The acid sample is diluted with water and adjusted to pH 2–4 with NaOH. Add 1–2 g of AMP to extract the Cs from solution. Use a minimum of 1 g AMP/liter of sample. Larger amounts of AMP are required for soil, sediment, or biota samples than sea water samples, because of the higher ionic strength in the acid leached sample solution, which reduces the extraction efficiency of AMP for Cs.

Separate the AMP as described above for water sample and purified as described below.

E. ^{137}CS PURIFICATION

The amount of AMP collected from the preconcentration step, especially from large water samples, is invariably greater than 1 g. The following steps reduce the amount of AMP to about 1 g in order to perform the ion exchange procedure for the separation of Cs from K and Rb.

1. Dissolve the AMP separated from Section CS-C or CS-D above, with a minimum amount of 10M NaOH. Add an 0.5 ml excess of 10M NaOH for each gram of AMP dissolved. Transfer the sample solution to a 400 ml beaker with a few ml of water, and heat the solution on a hot plate at a medium setting, without a cover glass, to decompose the AMP and to evaporate the ammonia.

2. Periodically check the vapor phase (just above the hot beaker) with a wet pH paper or ammonium specific test paper to check for the presence of ammonia fumes. The sample solution must be kept strongly basic with NaOH for the AMP decomposition to be effective. When the vapor no longer shows the present of ammonia, and the solution is strongly basic (pH greater than 13+), stop the heating, cool the sample to room temperature, and add water to dissolve any salts that may be formed during cooling.

3. Dilute the sample to about 200 ml with water, add 1–2 drops of methyl red indicator, adjust the pH to 1–4 with 8N HNO_3, add 1.0 g of AMP, let the AMP

settle, decant the clear liquid, transfer the AMP slurry to a clean 50 ml C-tube with water, centrifuge, and discard the supernate.

4. Dissolve the AMP with a minimum amount of 10M NaOH and add 10 ml of 2% EDTA-0.75M NaOH solution. The sample solution should be clear. If any precipitates form, centrifuge and decant the clear solution into another clean 50 ml C-tube. Discard the precipitate.

5. Load a medium size ion exchange column with a goose-neck adapter (see Figure 1, Appendix-C) with 20 ml of BIO-REX-40, 20–50 mesh cation exchange resin. Precondition the column with 100 ml of 3N HCl followed by 150 ml of 5% NaCl solution and 50 ml of water.

6. Using a Teflon coated stirring rod, carefully pour the sample solution from Step 4 directly onto the top of the resin column. Try not to splatter any solution on the upper part of the reservoir.

7. After the sample has drained to the top of the glass wool plug, rinse the column walls and the reservoir three times with about 5–10 ml aliquots of water.

8. Rinse the column with another 40 ml of water (necessary to remove any dissolved AMP from the resin and preventing the possibility of AMP reforming in the column when the acid rinse is added in the next step). Total water rinses in Steps 7 and 8 are not critical but should not exceed about 60–70 ml. Discard the rinses.

9. Wash the column with 160 ml of 0.75N HCl (to remove K and Rb). Discard the wash.

10. Elute the Cs with 125 ml of 3N HCl and collect the sample in a 150 ml beaker.

11. Evaporate the cesium eluate to dryness and prepare the Cs for beta counting as describe in the next section.

F. PREPARATION OF Cs SAMPLES FOR BETA COUNTING

1. Dissolve the cesium salts from Step 11 above with 1–2 drops of 8N HNO_3 and 2–3 ml of water. Transfer the solution to a 50 ml C-tube. Rinse the beaker twice with 2–3 ml of water.

2. Add 1 ml of 10N NaOH, dilute the sample to about 10 ml with water, and add 2 ml of 0.12M chloroplatinic acid (H_2PtCl_6) to precipitate Cs_2PtCl_6.

3. Cool sample in a refrigerator or ice bath for 30–40 minutes.

4. Prepare a tared glass-fiber filter paper:

   a. Assemble a filtering apparatus with a 2.54 cm base.

   b. Cut a 2.54 cm diameter glass-fiber filter paper disc.

c. With the vacuum off, center a filter disc on the base of the filter holder, wet the filter with water, apply vacuum, wash the filter with 2–3 ml of water, and 2–3 ml of acetone.

d. Dry the filter under a heat lamp.

e. Weigh the filter to ± 0.01 mg.

5. Filter the sample through the tared filter from Step 4.

6. With the vacuum on, remove the filter chimney, wash the filter and the Cs_2PtCl_6 thoroughly with a few ml of cold acetone. Turn off vacuum, transfer the filter and precipitate to a petri dish.

7. Dry the filter under a heat lamp and cool the filter to room temperature.

8. Weigh the sample to constant weight (± 0.01 mg).

9. Mount the filter containing the Cs_2PtCl_6 on the ring and disc holder as shown in Figure 3, Appendix-C. Count the sample using a low background beta detector or by gamma spectrometry.

STRONTIUM-90 ANALYSIS FOR MARINE SAMPLES

A. INTRODUCTION

This procedure is designed to separate ^{90}Y from a partially purified Sr fraction isolated from various marine samples. It has been used successfully in soil, sediment and ashed biological samples up to 300 g in weight; and, in fresh water and sea water samples, up to 600 liters in volume. ^{90}Sr levels as low as 1 dpm have been measured in these samples.

Several important facts should be kept in mind when planning ^{90}Sr analysis on marine samples. Average sea water contains 8 ppm of stable Sr, or about 8 mg/kg, while average carbonate soil is about 1% (10,000 mg/kg) Sr. Thus even modest size samples require some thought in sample handling and about chemical yield measurements, especially if stable Sr is to be used for a yield monitor. This procedure has been developed to accommodate a Sr carrier from 20 mg to 4 g. For most routine analysis, however, ^{85}Sr, a gamma emitter readily measured by gamma spectrometry and free from ^{90}Sr contamination, is the preferred yield monitor. If stable strontium is used for chemical recovery, the strontium content of the original sample has to be determined.

In average sea water the ^{226}Ra content is about 0.2 dpm/l and ^{238}U (or ^{234}U) is about 2 dpm/l. The uranium usually presents no problem, but a good separation of the final ^{90}Y from Ra and its daughters is important, especially for deep ocean water. During the separation steps, this procedure effectively removes all radionuclides that are chemically similar to yttrium or rare earths from the Sr fraction; and, after the establishment of $^{90}Sr/^{90}Y$ radioactive equilibrium, the final purification steps further remove any interfering radionuclides in the ingrowth ^{90}Y fraction before measurement by beta counting.

B. SPECIAL REAGENTS AND EQUIPMENT

In addition to the general reagents and equipment listed in Appendix-B, the following supplies are also necessary for the ^{90}Sr procedure.

1. Alpha-HIBA, 0.5M alpha-hydroxy-isobutyric acid (also known as 2-Methyllactic acid), adjusted to pH-5.0 with ammonium hydroxide. Available from: Eastman Kodak Co., Rochester, NY 14650.

2. Plastic rings and discs for mounting of samples for beta counting. Available from: Control Molding Corporation, 84 Granite Ave., Staten Island, NY 10303.

3. In this laboratory a low background proportional beta counter is used to measure ^{90}Y. The current beta detector system in use is a Model G5000 from Gamma Products, Inc. (7730 W. 115th St. Palos Hill, Ill. 60465) with the following specifications: 1.5 inch detector window and anticoincidence shield, background=0.50 ± 0.15 cpm, ^{90}Y efficiency =0.45 ± 0.05 cpm/dpm. Any counting system with low background beta counting capabilities will suffice.

4. Oxalic acid, dissolve 450 g hydrated oxalic acid in 3000 ml of hot water, dilute to 4500 ml with water, and filter before use.

5. Dowex-50 × 8, 100–200 mesh, H^+ form, cation exchange resin.

6. Bromcreosol green indicator. 0.1 g in 14 ml of 0.01N NaOH diluted to 250 ml with water.

7. ^{85}Sr tracer (^{90}Sr free), 10,000 dpm/ml, in 0.1N HNO_3.

C. SAMPLE PREPARATION - AQUEOUS SAMPLE

See Steps in Pu-D, SAMPLE PREPARATION, PLUTONIUM ANALYSIS for details.

If transuranic elements and/or radiocesium are also to be analyzed from the same sample, they should be separated prior to the preconcentration of the ^{90}Sr fraction in the water sample as outlined in the SEQUENTIAL SEPARATION PROCEDURE, Appendix-A.

1. Strontium-90 (^{90}Sr) is preconcentrated from sea water samples with the alkaline earths as ammonium oxalate by the addition of 40 ml of saturated oxalic acid solution (100 g/liter) per liter of sea water after adjusting the pH to 4–5 with concentrated ammonium hydroxide.

2. The oxalates are separated by filtration, or decantation and centrifugation, and then decomposed by boiling in conc. HNO_3.

3. Strontium-90 is separated from $Ca(NO_3)_2$ by precipitation of $Sr(NO_3)_2$ in conc. HNO_3.

4. Decant the liquid and dissolve the $Sr(NO_3)_2$ with water.

5. Add about 1 ml of Fe^{+3} carrier (10 mg/ml), make the solution basic with ammonium hydroxide.

6. Centrifuge and discard the hydroxide precipitates.

7. Reprecipitate the Sr as $SrCO_3$ from the alkaline solution with Na_2CO_3 solution.

8. The $SrCO_3$ is washed with water, centrifuge, & discard the supernate.

9. Dissolve the $SrCO_3$ in a minimum amount of conc. HCl and transferred to a 50 ml centrifuge tube (or larger container if a larger sample was processed) containing a known amount of Y-carrier (30–40 mg as yttrium oxalate).

10. Dilute the sample with water to 20–30 ml.

11. Fill the 50 ml C-tube to a maximum volume of 30 ml to allow room for subsequent precipitation of $Y(OH)_3$.

12. Mix the solution thoroughly and allow to stand 18 days or longer for the $^{90}Sr/^{90}Y$ equilibrium to be established (99+%).

Meanwhile the sample may be counted for ^{85}Sr (or a small aliquant taken for determination of stable Sr by atomic absorption spectrometry) for chemical recovery.

D. SAMPLE PREPARATION - SOIL, SEDIMENT AND BIOTA SAMPLES.

See Steps Pu-E through Pu-G-6, in PLUTONIUM ANALYSIS for details.

When the digestion is complete as described in Pu-G-6, cool the sample to room temperature and precipitate $Sr(NO_3)_2$. Usually $Sr(NO_3)_2$ crystals appear upon cooling overnight. If no crystals or precipitate appears after cooling, precipitation may be initiated by placing the beaker with the clear sample solution in an ultrasonic water bath or stir the sample solution with a Teflon coated magnetic stirring bar. After separation of $Sr(NO_3)_2$, the Sr fraction is purified as described in Section SR-C for sea water.

E. SEPARATION AND PURIFICATION OF ^{90}Y

When ^{90}Y, in the 50 ml centrifuge tubes from Sr-C, has reached equilibrium;

1. Add 1–2 drops of phenolphthalein and precipitate $Y(OH)_3$ with a few drops of conc. NH_4OH, centrifuge and decant the supernate to another C-tube. Note the time of the start of the centrifugation, and record it as TIME-1.

2. Dissolve the $Y(OH)_3$ in minimum volume of conc. HCl, dilute to 10 ml with water and reprecipitate the Y with a minimum amount of conc. NH_4OH.

3. Centrifuge and combine the supernate from Step 1. Again note the start of the centrifugation time and record it as TIME-2. Add about 10% of the interval between the two centrifugation's to TIME-1 and record this as the SEPARATION TIME in the lab notebook.

NOTE: The interval between Time-1 and Time-2 should be kept as short as possible.

4. Wash the $Y(OH)_3$ with 20 ml of water containing a drop of NH_4OH, centrifuge and discard the wash.

5. Dissolve the $Y(OH)_3$ in 4–5 drops of conc. HNO_3, dilute to 2 ml with water, and transfer the sample solution, with a disposable polyethylene pipet, to a 7 mm i.d. × 6-cm column of Dowex 50 × 8, 100–200 mesh, H^+ form, cation exchange resin. Rinse the tube with 2 ml of water and add to the column. After the solution has passed through the column, wash the column with 3 ml of water.

6. Add about 5 ml of 0.5M alpha-HIBA (pH 5.0) to the top of the column. A light grayish band (actually iron contamination which also mimics the yttrium elution) can usually be seen moving down the column and 5–6 ml should bring the band within a cm or so of the bottom. If no band is seen, there is no iron in the sample and the Y may elute a little early. Discard this effluent.

7. Elute the Y into a clean 50 ml C-tube with a second 5 ml portion of 0.5M alpha-HIBA. This step is the main separation from Ra and its daughters. All the Ra daughters (including Ac) elute long before the Y, while the Ra itself remains at the top of the column during the elution of the Y. Therefore, once

the elution is started, it should be completed without delay to optimize the separation from new Ra daughter products.

8. Dilute the Y solution to twice its volume with water, add 2 ml of sat. oxalic acid, heat in a hot water bath for about 10 min, and cool to room temperature. Centrifuge, discard the supernate, and wash the precipitate with 10 ml water.

9. Filter the Y oxalates onto a tared 1.5 cm glass fiber filter. Wash the precipitate thoroughly with water, then acetone. Dry the yttrium oxalate under a heat lamp, weigh for Y recovery, and mount on a ring and disk holder for beta counting.

(for more details in the filtration and mounting of samples for beta counting, see Section CS-F-4).

E. COUNTING ^{90}Y AND DATA REDUCTION

The ^{90}Y is counted continuously in a low background beta counter for 300–600 minutes over a period of 2 weeks and again 2 weeks later. The counting data is then checked for any short lived components (<64 hrs) and long lived components (>64 hrs), including the detector background. Any short or long lived components are resolved and subtracted from the gross counting data. The net counting data are decay corrected to the ^{90}Y / ^{90}Sr separation time (see Sr-E-3) and the ^{90}Sr concentration is calculated by the following equation:

$$^{90}\text{Sr (dpm / kg)} = \frac{\text{Ncpm} \times \text{Q}}{\text{Eff} \times \text{Rec(Y)} \times \text{Rec(Sr)} \times \text{W}}$$

Where:

Ncpm = Net counting rate of ^{90}Y at separation time, cpm.

Q = ^{90}Y fractional ingrowth from ^{90}Sr.
In 18 days, Q is equal to 1.01

Eff = Detector efficiency, cpm/dpm.

Rec(Y) = Chemical recovery of yttrium oxalate.

Rec(Sr) = Chemical recovery of strontium fraction.

W = Sample weight or volume, kg.

NOTE: The above equation calculates the ^{90}Sr concentration to the separation time of the ^{90}Sr/^{90}Y. An additional decay corrections is necessary to correct the ^{90}Sr results to sample collection time.

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2. Chu, N.(1971), "Plutonium determination in soil by leaching and ion exchange separation." *Analytical Chemistry,* **43** , 449–452.

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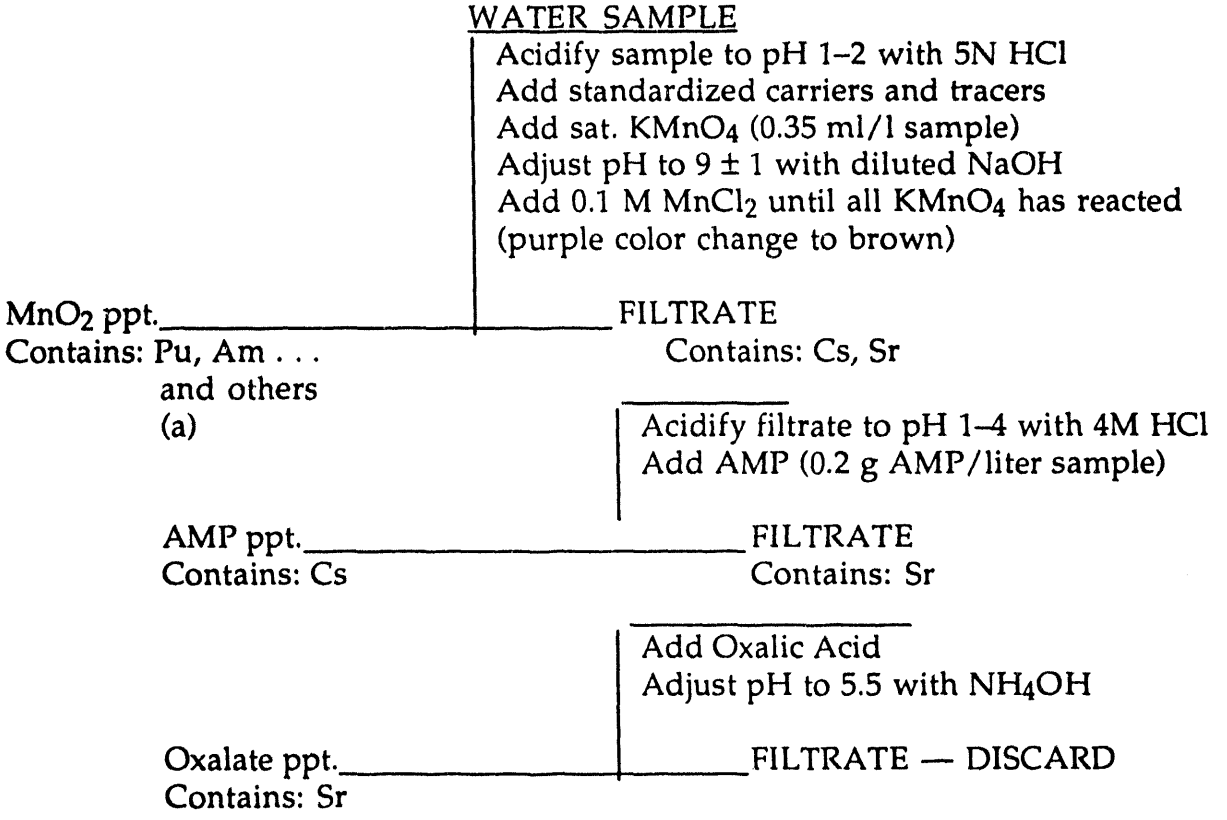
4. Horwitz, E.P, M.L. Dietz, D.M. Nelson, J.J. LaRosa, and W.D. Fairman (1990), "Concentration and separation of actinides from urine using a support bifunctional organophosphorus extractant." *Analytica Chemica Acta,* **238**, 263–271

APPENDIX-A

SCHEMATIC OUTLINE OF SEQUENTIAL SEPARATION PROCEDURES FOR Pu, Am, Cs, Sr IN WATER SAMPLES

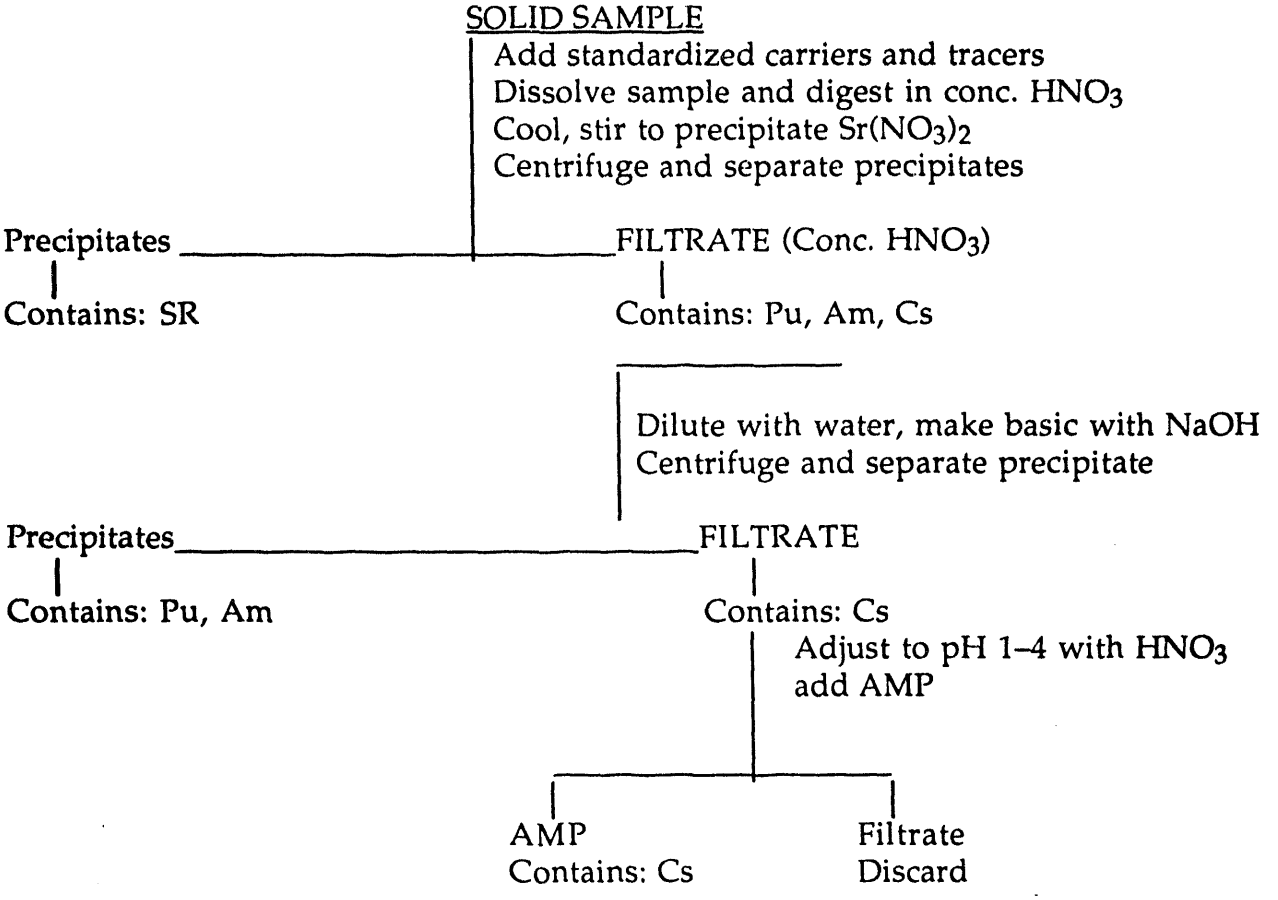


(a) Isotopes of the following elements have been shown to coprecipitate quantitatively with *in situ* produced MnO_2 in fresh and sea water samples:

Sc, V, Cr, Mn, Fe, Co, Ni, Y Zr, Nb, Ru, Ag, Cd, Sb, La, Ce, Eu, Pb, Bi, Po, Ra, Th, U, Np, Pu, Am, Cm

APPENDIX-A

SCHEMATIC OUTLINE OF SEQUENTIAL SEPARATION OF Pu, Am, Cs, & Sr IN SOIL, SEDIMENT AND ASHED BIOTA SAMPLES



APPENDIX-B

REAGENTS AND EQUIPMENT

All chemical reagents should be analytical or reagent grade. Any water used for the preparation of chemical reagents, or in the dilution of samples, should be purified by both ion exchange and distillation.

Specific reagents and equipment used only for the analysis of a particular radionuclide are listed in the individual procedure. The partial list below includes common supplies for plutonium and other procedures is tabulated for convenience and not intended to be complete.

1. Standardized ^{242}Pu tracer(+4), 5–10 dpm/ml, in 3N HNO
2. Nitric acid, 8M and concentrated.
3. Hydrochloric acid, 5N and concentrated.
4. Sulfuric acid, 1N and concentrated.
5. Ammonium iodide, granular crystal.
6. Sodium nitrite, granular crystal and 1M solution .
7. Hydrogen peroxide, 30% solution.
8. Concentrated ammonium hydroxide.
9. Sodium hydroxide, 50% solution.
10. Methyl red indicator, 0.1%.
11. Potassium permanganate, saturated solution (60g/l).
12. Manganese chloride, 1M solution.
13. N-octanol.
14. Acetone.
15. pH paper, expanded range.
16. pH meter and combination electrode.
17. Glass fiber filter, Whatman GF/A or equivalent.
18. Balance, various capacities, from microgram to 100 kg.
19. Plating cell (See Fig.2).
20. Constant current power supply with 0 to 2 amp control.
21. Centrifuge, with 50 and 250 ml holders.
22. Beaker tongs for 150 to 2000 ml beakers.
23. Polyethylene bottles: 250,500,1000ml.
24. Pipets, disposable tip, adjustable 0- 1ml, 0-5 ml.
25. Pipets, disposable polyethylene, 2 ml, 5 ml.
26. Teflon coated stirring rods.
27. Drying ovens, 0-150° C.
28. Muffle furnace, 0-500° C, 25 × 40 × 60 cm .
29. Standard sieves, 32 um to 2 mm.
30. Heat lamp and stand.
31. Fume hoods, 100 cfm, 2 × 1 × 1.5m (wxlxh).
32. Polyethylene container with cover, capacity: 5, 20, 100, 200 l.
33. Lucite stirring rod for large water sample, 3 cm dia. × 120 cm.

34. Hot plate, 30 cm × 28 cm Pyroceram top.
35. Glass beakers, 50, 150, 400, 1000,2000 ml.
36. Glass beaker covers.
37. Ring and disc sample holders for beta counting.
    Available from:
    Control Molding Corporation
    84 Granite Ave.
    Staten Is., NY 10303

38. Filter cartridge, 6 cm O.D. × 25 cm with a 2.5 polyethylene inner-core support. The filter material is cotton reinforced with acrylic fiber and a rated porosity of 1μm.
39. Glass ion exchange columns:(See Fig. 1)

Column Size	Resin bed Dimension, I.D. × length	Resin bed Volume	Reservoir Capacity
Small	0.7 cm × 6 cm	2.5 ml	25 ml
Medium	1.0 cm × 24 cm	20 ml	250 ml
Large	1.5 cm × 24 cm	40 ml	1000 ml

40. Anion exchange resin, Dowex 1x8 (or equivalent), 20-50 mesh; 50–100 mesh; 100-200 mesh; chloride form.
41. Type 316 stainless steel discs, one side mirror finish, 2.54 cm diameter × 0.0457 cm thick.

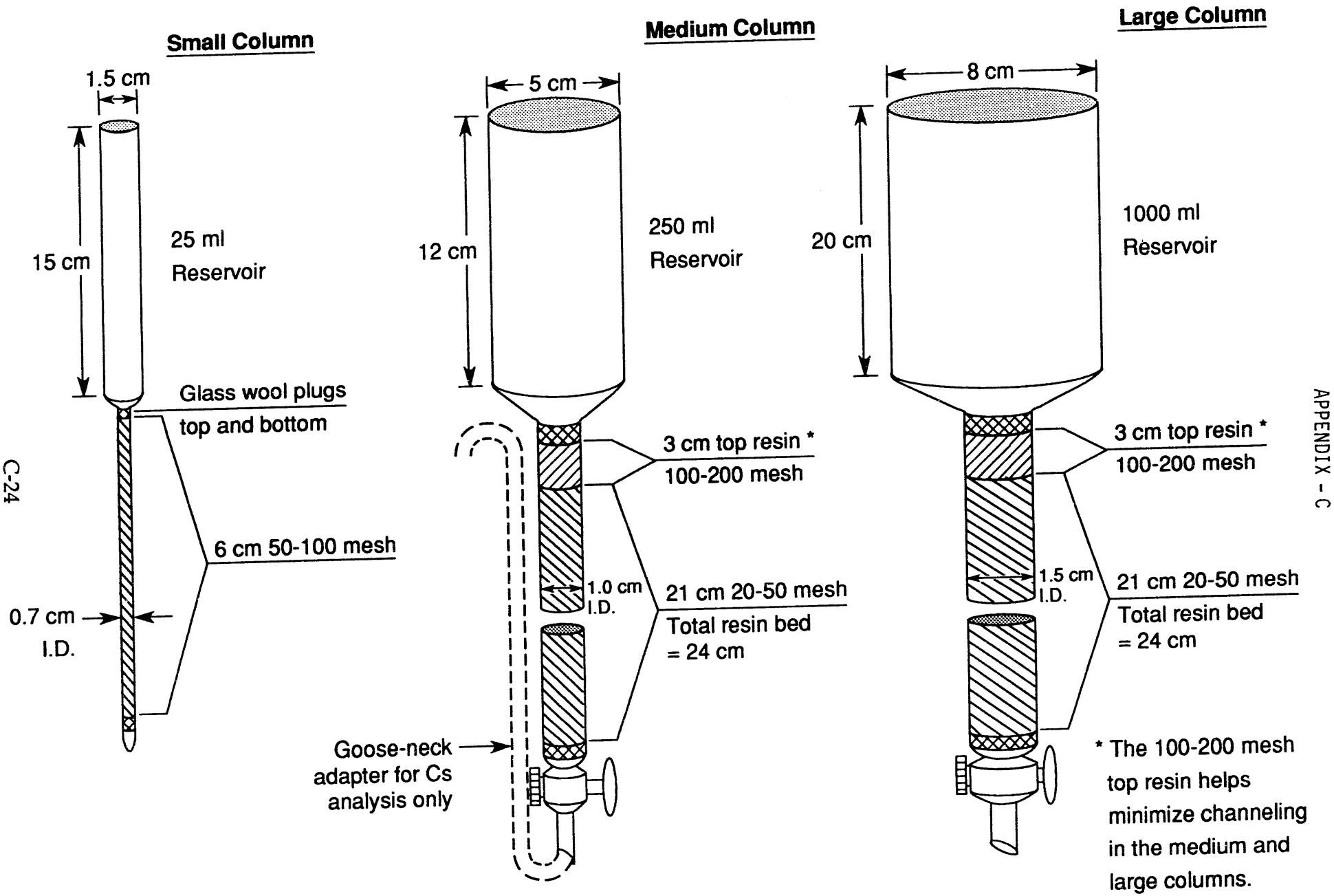


Figure 1. Glass columns for anion exchange separation (Dowex 1 x 8 or equivalent).

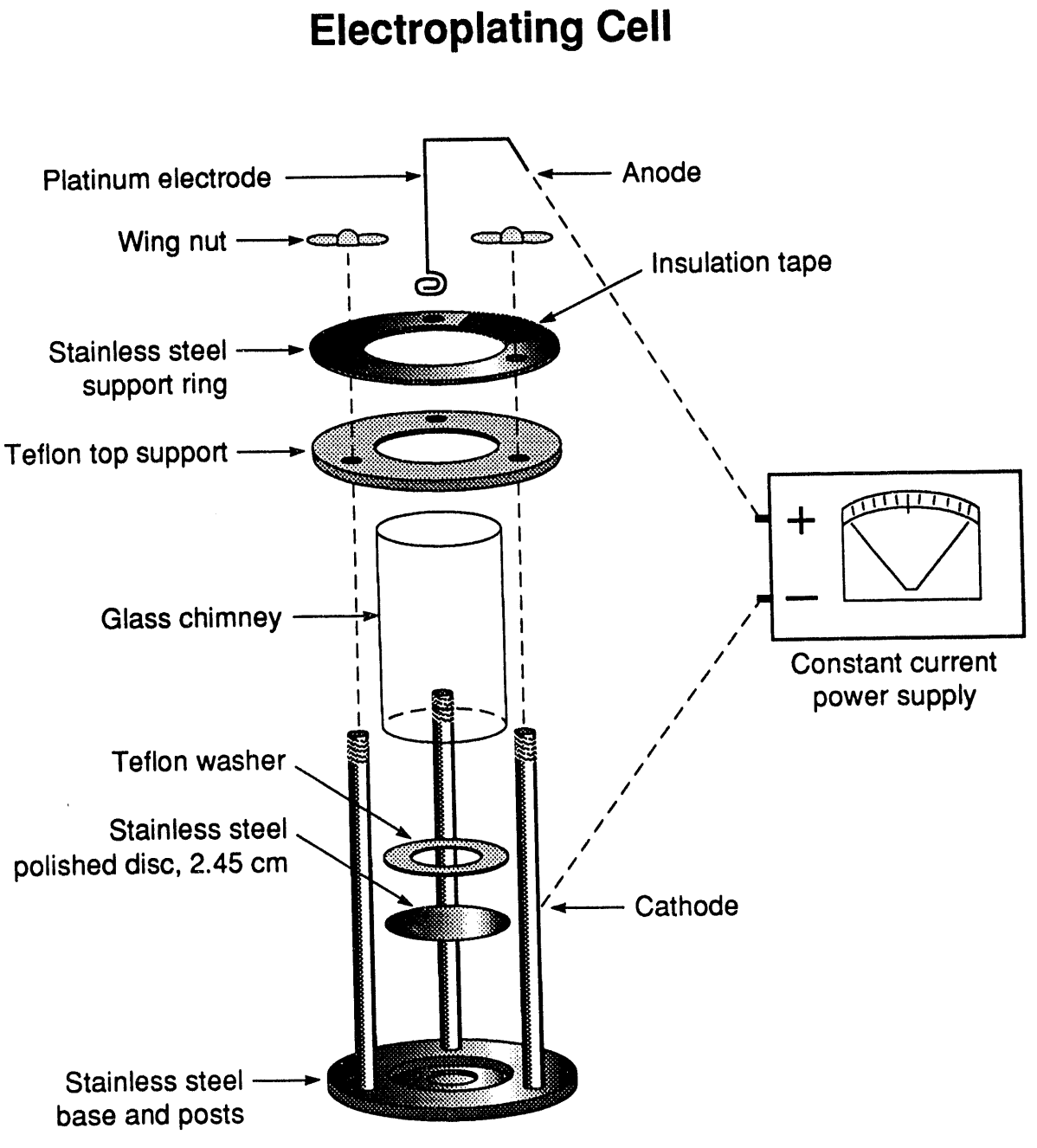


Figure 2a. Electroplating cell.

Alternative Disposable Plating Cell

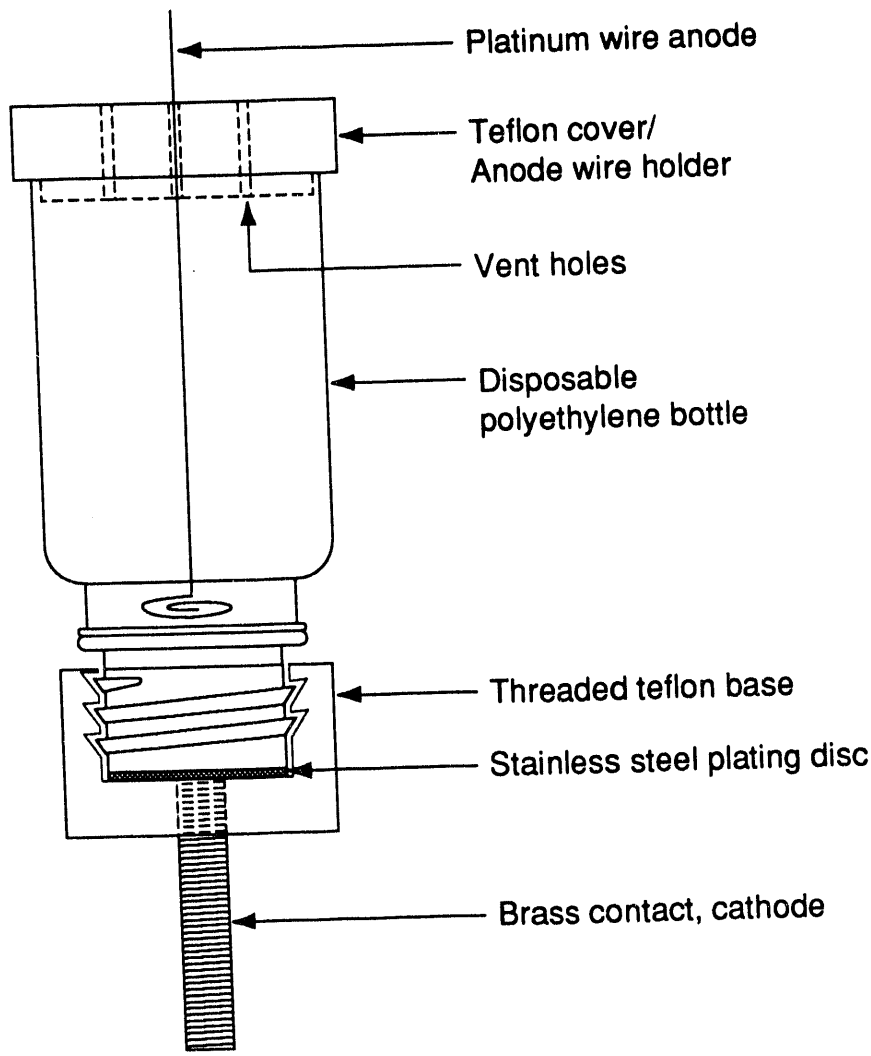


Figure 2b. Alternative disposable plating cell.

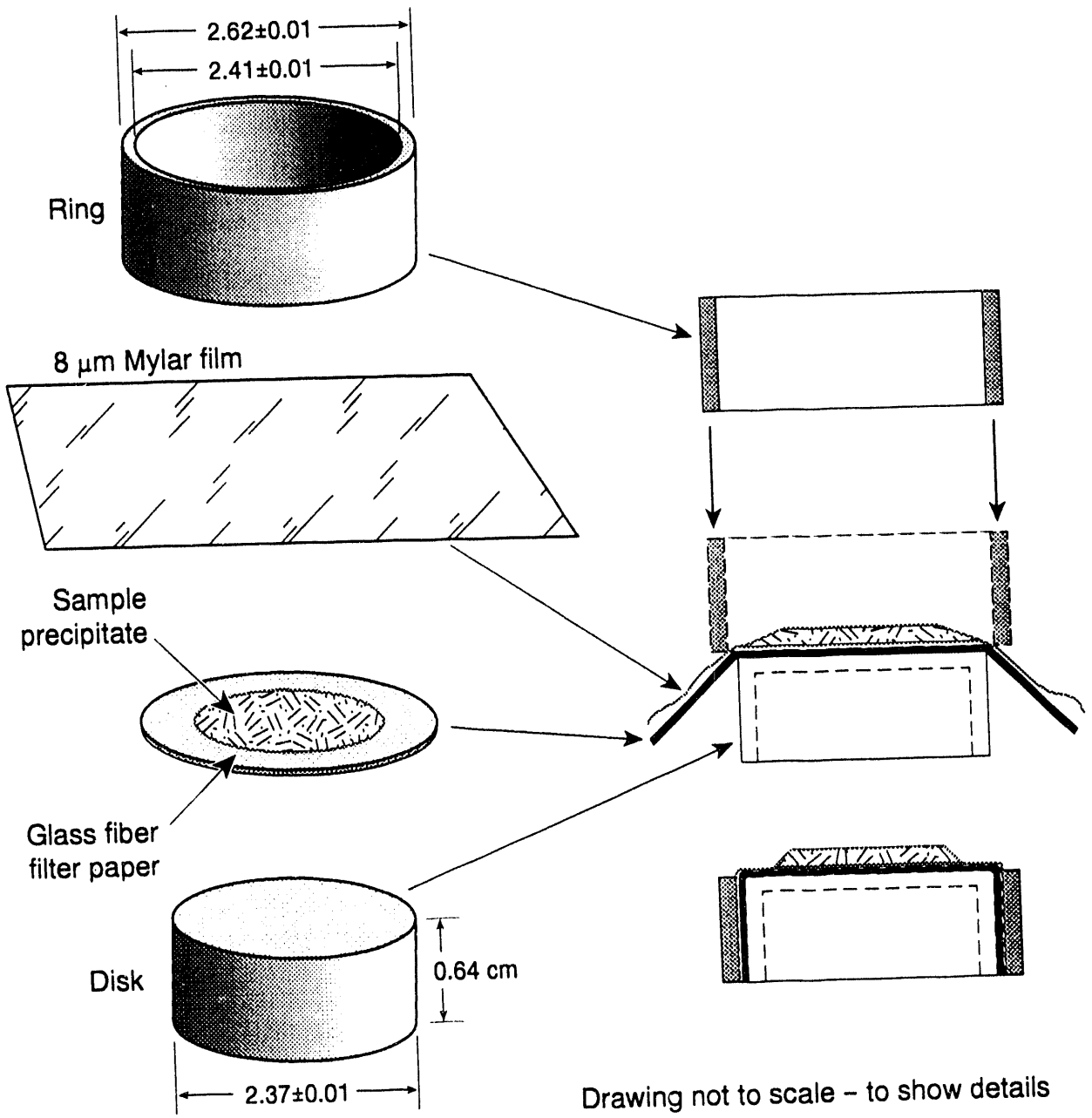


Figure 3. Nylon Ring & Disk Sample Mount for Beta Counting

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