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Radiochemical Procedures for Selected Radionuclides in Environmental Samples

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Abstract

Methods are presented for the radiochemical analysis of precipitation, air-filter, and impactor-filter samples for (1) fission products (Sr^{89}, Sr^{90}, Zr^{95}, Ba^{140}, Ce^{141}, and Ce^{144}), (2) induced radioactivities (Mn^{54}, Ag^{110}, W^{181}, and W^{185}), (3) high-altitude tracers (Rh^{102} and Cd^{109}), (4) cosmic-ray spallation products (Be^7, Na^{22}, P^{32}, P^{33}, and S^{35}), and (5) natural radioactivity (Pb^{210}).

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1. INTRODUCTION

During the past several years, the Nuclear Studies Section of the Meteorology Laboratory at the Air Force Cambridge Research Laboratories (AFCRL) has performed radiochemical analyses on a variety of environmental samples. The low radioactivity levels of radionuclides sought in most samples, particularly in impactor-filter collections, have required radiochemical procedures which ensure a high degree of purification and subsequent counting with sensitive low-level β^-, γ, and X-ray measurement techniques. It was felt that a worthwhile contribution would be made to other investigators concerned with the determination of environmental radioactivity by compiling the radiochemical procedures employed at AFCRL. For the most part, the procedures have been gleaned from the bulk of the scientific literature (see references), the references to which are by no means intended to be complete, and have been modified to suit our needs and purposes.

2. PRETREATMENT OF SAMPLES

2.1 Procedure for Precipitation Samples (volume $\leq$ 1000 ml)

(1) Measure volume of appropriately collected precipitation sample and transfer to a beaker.

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(2) Rinse the collection vessel three times with a minimum amount of 2M HCl followed by three distilled water and three 2M NH_4OH rinses. Pour the rinses into the beaker used in 2.1 step (1) and add appropriate carriers.

(3) Filter through Whatman No. 42 filter paper using suction and wash any solids with three 10-ml portions each of 6M HCl, distilled water, and 2M NH_4OH.

(4) Dry solids in an oven at 110°C.

NOTE: Solids are reserved for separate analysis, if necessary.

(5) Concentrate the sample by evaporation in a 2000-ml beaker and complete the evaporation in a 150-ml beaker to a volume of about 25 ml. Subsequent radiochemical procedures are carried out on this solution.

2.2 Procedures for Polystyrene Filter * Samples (Thuman, 1959)

2.2.1 EXTRACTION PROCEDURE

(1) Put filter sections into a beaker containing enough aqua regia to allow the sample to be completely submerged.

NOTE: Aqua regia may be prepared from 18 ml of concentrated HNO_3 and 82 ml of concentrated HCl and should be orange-red in color when used.

(2) Add appropriate carriers and digest on a hot plate with stirring and prodding of the organic filter mass until brown fumes cease to evolve.

NOTE: Extraction and equilibration with carriers.

(3) Carefully add more aqua regia to the organic filter mass and continue digestion with stirring and prodding.

NOTE: Use about the same amount of aqua regia as in 2.2.1 step (1).

(4) Continue digestion until brown fumes cease to evolve, then dilute the resulting mixture with distilled water and continue digestion for another 10 minutes with stirring and prodding.

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*Available as Microsorban 99/97 from Delbag-Luftfilter, GMBH, Schweidnitzenstrasse 11-15, Berlin-Halensee, Germany.

NOTE: Dilute with enough distilled water so the volume will be double that in 2.2.1 step (3).

(5) Cool the resulting mixture and filter through Whatman No. 42 filter paper using suction. Wash the residue with several portions of $4\underline{M}$ HCl followed by several distilled water rinses.

(6) Transfer the clear filtrate to a beaker and evaporate to a minimum volume. Subsequent radiochemical procedures are performed on this solution.

NOTE: Residue is reserved for separate analysis and confirmation of complete extraction, if necessary.

2.2.2 DESTRUCTIVE DISTILLATION PROCEDURE

(1) Cut the filter sample into fractions of convenient size (about 1 sq ft) and pelletize at 20,000 psi using a Carver Laboratory press.*

NOTE: Reduction of sample size to pellets of about 1-inch diameter and 0.5-inch height.

(2) Place the pellets in a 500-ml distilling flask and add appropriate carriers.

(3) Stopper the flask and admit the side arm into a 125-ml Erlenmeyer flask immersed in an ice bath.

(4) Heat the distilling flask using a heating mantle and variable rheostat, gradually increasing the temperature until dense vapors begin to evolve.

NOTE: Polystyrene liquifies at about 150°C and the distillation temperature range of pyrolysis products is 150° to 200°C.

(5) When the vapors have distilled over into the Erlenmeyer flask, continue increasing the temperature in increments until the sample nears dryness as indicated by little or no evolution of vapors.

(6) Carefully complete the ignition over the open flame of a Meker burner.

(7) Cool and treat the residue with about 10 ml of concentrated H_2SO_4 and about 25 ml of concentrated HNO_3. Heat gently over a Meker burner until dense fumes of SO_3 are evolved. Add 1 to 2 ml more of concentrated HNO_3 and again heat to dense fumes of SO_3. Repeat the addition of 1- to 2-ml increments of concentrated HNO_3 with heating to fumes of SO_3 until all organic matter has been destroyed.

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*Fred S. Carver, Inc., Summit, New Jersey.

(8) Subsequent radiochemical procedures are performed on this solution.

NOTE: Some insoluble salts may be present, depending upon carriers added.

2.3 Procedures for IPC Filter * Samples

2.3.1 EXTRACTION PROCEDURE

(1) In a 1000-ml beaker, put 500 ml of distilled water, 50 ml of concentrated HNO_3, appropriate carriers, then add the IPC filter. Add bromine water, with stirring, until a yellow-orange color persists.

NOTE: Filter diameter is about 16 in. If sulfur analysis is not performed, omit the bromine water.

(2) Digest on a hot plate at low temperature with occasional stirring. Add bromine water as needed to maintain the yellow-orange color. Digest cold overnight, then resume digestion on a hot plate at low heat so that total hot digestion time is about eight hours.

NOTE: Extraction and equilibration with carriers.

(3) Filter while hot through Whatman No. 50 filter paper using suction. Wash residue with 50 to 75 ml of 1$\underline{M}$ HNO_3. Press down pulp remaining in the funnel with a clean beaker. Reserve filtrate.

(4) Transfer the pulp and filter paper to the original beaker. Add 100 ml of 1$\underline{M}$ HNO_3 and digest on a hot plate for thirty minutes.

(5) Filter through Whatman No. 50 filter paper using suction. Wash with 50 to 75 ml of 1$\underline{M}$ HNO_3 followed by three 50-ml portions of distilled water. Press down the pulp remaining in the funnel with a clean beaker and suck dry for thirty minutes.

(6) Combine the filtrate from 2.3.1 step (5) with that from 2.3.1 step (3) and evaporate to about one-half the original volume. Subsequent radiochemical procedures are performed on this solution.

(7) Dry the filter paper and pulp in an oven at 110°C.

NOTE: Pulp is reserved for separate analysis and confirmation of complete extraction, if necessary.

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*The Institute of Paper Chemistry, Appleton, Wisconsin. (See Defense Atomic Support Agency (1960) A Study of the Filtration and Permeability Characteristics of IPC 1478 Filter Paper. Publication No. DASA 1168, Washington, D.C.)

2.3.2 EXTRACTION PROCEDURE, ALTERNATIVE METHOD

(1) Carry out 2.3.1 steps (1) and (2).

NOTE: Alternative method destroys organic matter.

(2) Filter while hot through Whatman No. 50 filter paper using suction. Wash residue with 50 to 75 ml of 1M HNO_3 in small portions followed by 50 to 75 ml of warm distilled water in small portions. Continue suction until dry.

(3) Dry filter paper and pulp in an oven.

NOTE: Reserve for separate analysis and confirmation of complete extraction, if necessary.

(4) Evaporate filtrate from 2.3.2 step (2) to dryness and add about 25 ml of concentrated HNO_3 and again evaporate to dryness.

NOTE: Concentration of sample and partial destruction of organic matter.

(5) Add about 25 ml of concentrated HNO_3 and heat to boiling. Cautiously add about 5 ml of $HClO_4$ dropwise. Evaporate to fumes of $HClO_4$, add concentrated HNO_3, and again evaporate to dryness.

(6) Repeat 2.3.2 step (5) until organic matter is destroyed.

NOTE: Complete destruction of organic matter.

(7) Dissolve residue in 50 to 100 ml of 2M HNO_3. Subsequent radiochemical procedures are performed on this solution.

2.3.3 ASHING PROCEDURE

(1) Carefully ash the sample in a platinum crucible over a Meker burner.

(2) Add about 5 ml of 6M HCl to the ash and heat gently. Transfer the resulting mixture to a 150-ml beaker using distilled water in the transfer.

(3) Repeat 2.3.3 step (2) twice.

(4) At this point, add appropriate carriers.

(5) Evaporate the combined mixture to about 5 ml and add about 10 ml of aqua regia.

(6) Boil for about ten minutes and carefully evaporate to incipient dryness. Subsequent radiochemical procedures are performed on this sample.

NOTE: Do not allow salts to bake.

2.4 Procedure for Impactor Samples

2.4.1 TRANSPARENT PRESSURE-SENSITIVE CELLOPHANE TAPE COLLECTION SURFACES COATED THINLY WITH DOW-CORNING HIGH VACUUM SILICONE GREASE*

(1) Place collection surface in a beaker, add appropriate carriers, and cover with aqua regia. Digest carefully on a hot plate with stirring until brown fumes cease to evolve.

NOTE: Collection surface has been stripped from glass slides with dimensions 11.8 by 4.0 by 0.3 cm.

(2) Reduce volume of liquid by evaporation to about one-half of the initial volume and add an equal volume of aqua regia. Continue digestion until brown fumes cease to evolve.

(3) Dilute mixture with distilled water and filter through Whatman No. 42 filter paper using suction.

(4) Wash the resulting organic residue several times with 4M HCl followed by several distilled water washes. Subsequent radiochemical procedures are performed on this solution.

NOTE: Residue is reserved for separate analysis and confirmation of complete extraction, if necessary.

2.4.2 ALUMINUM DISCS COATED WITH THIN FILM OF DOW-CORNING HIGH VACUUM SILICONE GREASE

(1) Place the disc in a beaker containing about 20 ml of acetone and boil for about five minutes on a water bath.

NOTE: Discs used as impaction surfaces had 1.5-in. diameter and 0.003-in. thickness.

(2) Remove the disc from the acetone and wash surface with 4M HCl, adding the washings to the beaker.

(3) Return the disc to the beaker and boil for two minutes.

(4) Remove disc and wash with distilled water adding the washings to the beaker.

NOTE: Disc is reserved for confirmation of complete particle removal, if necessary.

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*Dow-Corning Corp., Midland, Michigan.

(5) Evaporate the mixture from 2.4.2 step (4) to dryness and add appropriate carriers.

(6) Add 25 ml of 4<u>M</u> HCl and digest for twenty minutes.

(7) Repeat 2.4.2 step (6).

(8) Add about 25 ml of aqua regia and digest for thirty minutes.

(9) Filter the digestate through Whatman No. 42 filter paper using suction and reserve filtrate for subsequent radiochemical procedures.

NOTE: Reserve filter paper for separate analysis, if necessary.

3. SEQUENTIAL RADIOCHEMICAL PROCEDURES

3.1 Mn^{54}, Sr^{89}, Sr^{90}, Zr^{95}, Ce^{141}, and Ce^{144} in Polystyrene Filters and Impactor Samples

3.1.1 STRONTIUM SEPARATION AND PURIFICATION

(1) To the solutions from 2.2.1 step (6), 2.4.1 step (4), or 2.4.2 step (9), containing the following carriers in accurately known amounts: cerium equivalent to about 65 mg $Ce(IO_3)_4$, strontium equivalent to about 265 mg $SrCO_3$, manganese equivalent to about 15 mg MnO_2, and zirconium equivalent to about 70 mg ZrO_2, add 31 parts of fuming HNO_3 (90 percent) per 8 parts of solution.

NOTE: Aqua regia treatment of samples containing manganese carrier exhibit a brown discoloration during the initial stages of extraction.

(2) Harvest the precipitate in a 40-ml centrifuge tube.

NOTE: Collection of strontium nitrate.

(3) Collect the supernate in a beaker, dilute with distilled water, and reserve for manganese, zirconium, and cerium separation and purification.

(4) Dissolve the precipitate from 3.1.1 step (2) in 5 ml of distilled water.

(5) Add slowly, with stirring, 19 ml of fuming HNO_3 (90 percent) to reprecipitate strontium nitrate.

(6) Set in an ice bath for twenty minutes and stir occasionally. Centrifuge at high speed for ten minutes. Discard supernate.

(7) Dissolve the precipitate in about 15 ml of distilled water and add about 20 mg of barium carrier and 5 mg of ferric carrier.

(8) Precipitate ferric hydroxide with 6<u>M</u> NH_4OH. Centrifuge and save supernate in another centrifuge tube.

(9) Dissolve the ferric hydroxide in a minimum of 6M HNO_3.

(10) Reprecipitate the ferric hydroxide with 6M NH_4OH. Centrifuge, discard precipitate, and add supernate to that of 3. 1. 1 step (8).

(11) To the pooled supernates, add 0. 3 ml of 0. 1 percent methyl red solution.

(12) Neutralize with 6M HNO_3. Add 1 ml of 6M acetic acid and 2 ml of 6M ammonium acetate. Heat nearly to boiling in a steam bath.

(13) Add 1 ml of 1. 5 M sodium chromate dropwise, with stirring. Digest in a steam bath for ten minutes.

NOTE: Volume should be $\geqq$ 30 ml to minimize loss of strontium chromate.

(14) Centrifuge and discard the barium chromate precipitate.

(15) To the supernate, add 5 mg of ferric carrier.

(16) Make basic with ammonia gas, centrifuge, and discard the ferric hydroxide precipitate. Transfer supernate to a small beaker.

(17) Heat to boiling and add 10 ml of 10 percent sodium carbonate solution.

NOTE: Add the 10 percent sodium carbonate solution slowly, stirring to avoid supersaturation.

(18) Digest until precipitation of strontium carbonate is complete.

NOTE: About thirty minutes is sufficient.

(19) Cool and harvest the precipitate in a 40-ml centrifuge tube. Discard supernate.

(20) Dissolve the strontium carbonate in a minimum of 6M HNO_3. Dilute with distilled water to about 10 ml, and boil for about ten minutes to expel carbon dioxide.

(21) Add about 5 mg of ferric carrier, make basic with ammonia gas, centrifuge, and discard the ferric hydroxide precipitate.

NOTE: Record time t_s since this is the separation of Sr^{90} from Y^{90}.

(22) Transfer supernate to a centrifuge tube and repeat 3. 1. 1 steps (17) and (18).

(23). Cool and centrifuge. Discard supernate.

(24) Wash the precipitate twice with about 10 to 20 ml of 0. 5 percent sodium carbonate solution with stirring. Centrifuge and discard washes.

(25) After final centrifuging, add 10 to 20 ml of 0.5 percent sodium carbonate solution and filter through a Whatman No. 542 filter paper disc using a Millipore* filter chimney and suction.

(26) Wash precipitate with 0.5 percent sodium carbonate solution, followed by distilled water, 95 percent ethyl alcohol, and finally anhydrous ether.

(27) Dry in an oven at 110°C for about one hour and weigh as $SrCO_3$. Record chemical yield and β^- count the Sr^{89} and Sr^{90} (Y^{90}) for Sr^{89} determination.

NOTE: Make first count as soon as possible after t_s.

(28) Allow the strontium carbonate to stand for at least two weeks for Y^{90} growth, then milk for Y^{90}.

3.1.2 YTTRIUM MILKING

(1) Dissolve the strontium carbonate from 3.1.1 step (28) into a 250-ml beaker using 5 to 10 ml of 6M HNO_3.

(2) Boil for about ten minutes to expel carbon dioxide.

(3) Add 5.0 ml of yttrium carrier and dilute to 150 ml with distilled water.

NOTE: Yttrium carrier is accurately standardized and should be equivalent to about 275 mg Y_2O_3 per 5 ml.

(4) Precipitate yttrium hydroxide with ammonia gas and digest for five minutes on a hot plate.

(5) Filter through Whatman No. 42 filter paper using suction. Wash precipitate with distilled water.

NOTE: Save filtrate for redetermination of Sr^{89} and Sr^{90} if necessary, using several distilled water rinses to ensure complete removal.

(6) To the filter funnel, add sufficient 2M HCl to completely dissolve the precipitate, then apply suction.

(7) Wash the filter paper with 2M HCl.

(8) Transfer the filtrate to a 250-ml beaker and dilute to 150 ml with distilled water.

(9) Repeat 3.1.2 steps (4) and (5). Record time of milk t_m as second precipitation of yttrium hydroxide and combine filtrate of second yttrium hydroxide precipitation with filtrate from 3.1.2 step (5).

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*Millipore Filter Corp., Bedford, Mass.

NOTE: If necessary, Y^{90} milking can be repeated on combined filtrates. (Sec. 3. 1. 3.)

(10) Repeat 3. 1. 2 steps (6) and (7).

(11) Transfer filtrate to a 250-ml beaker and add 100 ml of 10 percent oxalic acid solution.

(12) Digest on hot plate for fifteen minutes.

(13) Filter through Whatman No. 42 filter paper using suction. Wash precipitate with distilled water.

(14) Transfer filter paper and precipitate to a porcelain crucible and ignite to yttrium oxide with a Meker burner. Cool in a desiccator.

NOTE: Ignite for at least thirty minutes.

(15) Weigh as Y_2O_3, record chemical yield, and β^- count for Y^{90} determination.

NOTE: Count on several successive days to confirm 62.4 h half life for Y^{90}.

3. 1. 3 REDETERMINATION OF Sr^{89} AND Sr^{90}

(1) Slightly acidify the combined filtrates of both yttrium hydroxide precipitations from 3. 1. 2 step (9) with 4M HCl and add 20 mg of ferric carrier.

(2) Make the solution basic with ammonia gas and heat to boiling.

(3) Filter off the ferric hydroxide precipitate using Whatman No. 42 filter paper and suction.

NOTE: Record time t_s since this is the separation of Sr^{90} from Y^{90}.

(4) To the clear filtrate, add 1 g of solid sodium carbonate.

(5) Digest for about thirty minutes to ensure complete precipitation of strontium carbonate.

(6) Filter through a Whatman No. 542 filter paper disc using a Millipore filter chimney and suction.

(7) Dry in an oven at 110°C for about one hour and weigh as $SrCO_3$. Record chemical yield and β^- count the Sr^{89} and Sr^{90} (Y^{90}) for Sr^{89} redetermination.

NOTE: Make first count as soon as possible after t_s.

(8) Allow strontium carbonate to stand for at least two weeks then proceed with 3. 1. 2.

3. 1. 4 MANGANESE SEPARATION AND PURIFICATION

(1) Evaporate the supernate from 3. 1. 1 step (3) to near dryness.

(2) Add about 10 ml of concentrated HNO_3 to the residue and wash the sides of the beaker with 2 to 3 ml of concentrated HNO_3. Again evaporate to near dryness.

NOTE: Removal of chloride ion allows for better manganese dioxide yield.

(3) Repeat 3. 1. 4 step (2) once.

(4) To the residue, add about 40 ml of concentrated HNO_3 and boil until oxides of nitrogen have been removed.

NOTE: About 0. 3 ml of 30 percent hydrogen peroxide may be necessary to effect complete solution. Boil off excess peroxide, if used.

(5) Cover the beaker with a watch glass and cautiously add 1 to 2 g of potassium chlorate in small increments, replacing the watch glass after each addition.

NOTE: This precipitation of manganese dioxide is best carried out while the mixture is at a brisk boil.

(6) Remove the beaker from the heat source and wash the watch glass with cold distilled water, collecting the washings in the beaker.

(7) Cool the mixture in an ice bath for about ten minutes.

(8) Centrifuge and reserve the supernate in a 250-ml beaker for zirconium and cerium separation.

(9) Wash the precipitate with 10 to 15 ml of distilled water, centrifuging, and adding the washings to the supernate of 3. 1. 4 step (8).

(10) Add 15 ml of 3M HCl and about 0. 3 ml of 30 percent hydrogen peroxide to the manganese dioxide.

(11) Heat until solution is effected, adding 30 percent hydrogen peroxide as necessary.

(12) Add about 10 mg of zirconium carrier and 1 ml of 85 percent phosphoric acid and heat to boiling. Continue boiling for fifteen minutes.

(13) Centrifuge and transfer the supernate to a 40-ml centrifuge tube. Discard the precipitate.

(14) To the supernate, add about 5 mg of zirconium carrier and boil for fifteen minutes.

(15) Repeat 3. 1. 4 step (13).

(16) Adjust the pH to 4 or 5 using 10 percent sodium hydroxide solution.

(17) Heat to about 70°C and pour the mixture into a 150-ml beaker containing 35 ml of boiling 10 percent sodium hydroxide solution and 0.4 ml of 30 percent hydrogen peroxide.

NOTE: Removal of phosphate ion and precipitation of manganese dioxide.

(18) Continue boiling for five minutes, remove the beaker from heat source, and allow the mixture to stand for ten minutes.

(19) Gravity filter the mixture into a 150-ml beaker using Whatman No. 40 filter paper. Discard filtrate.

(20) Wash the precipitate twice with small portions of 5 percent sodium hydroxide solution followed by a distilled water wash. Discard washings.

(21) Dissolve the precipitate on the filter paper using a minimum amount of hot 3M HCl along with the dropwise addition of 15 percent hydrogen peroxide.

(22) Wash the filter paper with distilled water and evaporate the filtrate to incipient dryness.

(23) Wash down the sides of the beaker with several ml of concentrated HNO_3 and again evaporate to incipient dryness.

(24) Repeat 3.1.4 step (23) twice.

NOTE: Complete removal of chloride ion.

(25) Add 40 ml of concentrated HNO_3 and boil for about three minutes.

(26) While gently heating, cautiously add about 2 g of solid potassium chlorate in small increments, covering the beaker with a watch glass after each addition.

NOTE: Allow the reaction to subside before each addition of potassium chlorate.

(27) Remove the beaker from the heat source and wash down the sides of the beaker and watch glass with cold distilled water.

NOTE: Add the washings from the watch glass to the beaker.

(28) Replace the watch glass and cool the beaker in an ice bath. Transfer the mixture to a 40-ml centrifuge tube using cold distilled water in the transfer. Centrifuge and discard the supernate.

(29) Thoroughly wash the precipitate of manganese dioxide with several portions of cold distilled water. Discard washings.

(30) Dissolve the manganese dioxide, using about 2 ml of 6M HCl and the dropwise addition of 30 percent hydrogen peroxide.

NOTE: Gentle heat may be required to effect complete solution.

(31) Adjust volume to about 15 ml with distilled water and add about 2 mg of ferric carrier.

(32) Boil the solution and add enough 10M NH_4OH to precipitate ferric hydroxide.

NOTE: Avoid an excess of 10M NH_4OH.

(33) Continue heating for one or two minutes and centrifuge. Discard precipitate.

(34) Add 2 mg of ferric carrier to the supernate of 3. 1. 4 step (33) and repeat 3. 1. 4 step (32), if required, to precipitate ferric hydroxide.

(35) Heat for one minute and gravity filter through Whatman No. 42 collecting the filtrate in a 150-ml beaker. Discard filter paper and precipitate.

(36) Adjust the volume of the filtrate to about 75 ml with distilled water.

(37) Add 1 g of solid ammonium chloride and 1 ml of 1. 5M dibasic ammonium phosphate.

NOTE: If a precipitate forms here, add 1M HCl dropwise until it dissolves.

(38) Heat the solution to boiling and add 10M NH_4OH dropwise with stirring until complete precipitation is effected.

(39) Continue stirring and boiling until the precipitate loses its flocculent appearance and appears crystalline.

(40) Discontinue heating, add about 0. 5 ml of 10M NH_4OH, cover beaker with a watch glass, and cool in an ice bath for two hours with occasional stirring.

NOTE: A slight excess of NH_4OH should be present.

(41) Filter through a pretreated, tared Whatman No. 542 filter paper disc, using a Millipore filter chimney and suction.

(42) Wash precipitate with three portions of 0. 1M NH_4OH and three portions of 95 percent ethanol.

NOTE: Check filtrate for complete removal of chloride ion using silver nitrate solution.

(43) Dry in an oven at 110°C for thirty minutes to constant weight.

(44) Cool, weigh as $MnNH_4PO_4 \cdot H_2O$, record chemical yield, and γ count for Mn^{54}.

3.1.5 ZIRCONIUM AND CERIUM SEPARATION

(1) To the supernate from 3.1.4 step (8), add 100 ml of 0.35<u>M</u> iodic acid and stir vigorously.

(2) Cool in an ice bath for ten minutes.

NOTE: Precipitation of zirconium and cerium iodates.

(3) Centrifuge and harvest the precipitate in a 40-ml centrifuge tube. Discard supernate.

3.1.5.1 Zirconium Separation and Purification

(1) Dissolve the precipitate from 3.1.5 step (3) carefully with stirring, using 10 ml of concentrated HNO_3, 1 ml of concentrated HCl, and 1 ml of 30 percent hydrogen peroxide.

(2) Boil off the peroxide in a water bath and continue boiling, if necessary, until the precipitate has been dissolved.

NOTE: Additional 30 percent hydrogen peroxide and concentrated HCl may be required.

(3) Cool in an ice bath and adjust the pH of the solution extremely cautiously to 10 by the dropwise addition of concentrated NH_4OH with stirring.

NOTE: If volume does not permit the addition of sufficient concentrated NH_4OH to attain pH of 10, continue pH adjustment with ammonia gas.

(4) Digest on a water bath for about 10 minutes. Cool and centrifuge. Discard supernate.

NOTE: Collection of zirconium and cerium hydroxides.

(5) Dissolve the precipitate in a minimum amount of concentrated HCl, with gentle heat, if necessary.

(6) Centrifuge and discard any insoluble residue. Dilute the supernate with distilled water.

(7) Repeat 3.1.5.1 steps (3), (4), (5), and (6).

(8) Repeat 3.1.5.1 steps (3) and (4).

(9) Dissolve the precipitate in 10 ml of concentrated HCl using gentle heat, if necessary, and pass the solution through a prepared Dowex 1-X2 anion exchange column*. (See Figure 1.)

NOTE: For preparation of column, see 7.1 Zirconium Column.

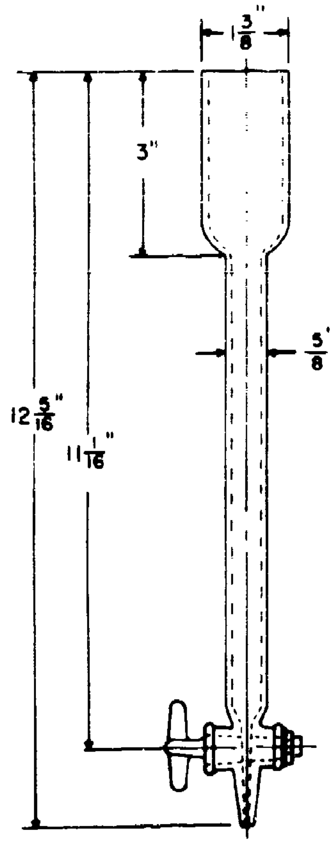

Figure 1. Ion Exchange Column 1 (Harley, 1963)

(10) Wash the column with 100 ml of concentrated HCl, collecting the effluent and wash solution in a 250-ml beaker. Reserve for cerium separation and purification.

(11) Elute the zirconium using 100 ml of 6.5M HCl at a flow rate not exceeding 3 ml per minute.

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*Scientific Glass Apparatus Co., Inc., Bloomfield, New Jersey.

NOTE: Record time t_s since this is separation of zirconium from niobium.

(12) Evaporate the eluate to about 15 ml and transfer to a 40-ml centrifuge tube.

(13) Adjust the pH to 10 with concentrated NH_4OH. Cool, centrifuge, and discard the supernate.

NOTE: Precipitation of zirconium hydroxide.

(14) Dissolve the precipitate in about 3 ml of concentrated HCl using a little heat, if necessary.

(15) Add about 25 ml of distilled water and 4 ml of 16 percent mandelic acid solution with stirring.

(16) Digest the mixture at 95°C for forty-five minutes.

NOTE: Precipitation of zirconium mandelate.

(17) Cool the mixture and gravity filter through Whatman No. 42 filter paper.

(18) Wash the precipitate several times with a 5 percent solution of mandelic acid in 2 percent HCl.

(19) Ignite the filter paper and precipitate in a platinum crucible over a Meker burner. Complete the ignition at 1200°C for at least twenty minutes in a muffle furnace.

NOTE: Ignition to zirconium oxide.

(20) Cool, weigh as ZrO_2, record chemical yield, and β^- count for Zr^{95}.

NOTE: Count soon enough to avoid appreciable Nb^{95} growth.

3.1.5.2 Cerium Separation and Purification

(1) Evaporate the effluent and wash solution from 3.1.5.1 step (10) to about 20 ml and transfer to a 40-ml centrifuge tube using distilled water.

(2) Add about 10 mg of zirconium carrier and carefully adjust the pH to 10 using concentrated NH_4OH.

(3) Digest, cool, and centrifuge. Discard supernate.

(4) Dissolve the precipitate with 10 ml of concentrated HNO_3, add 0.3 ml of 30 percent hydrogen peroxide, and allow five minutes for reaction time.

NOTE: Reduction of Ce(IV) to Ce(III).

(5) Add 20 ml of 0.35M iodic acid. Cool and centrifuge. Decant the supernate into a 40-ml Lusteroid centrifuge tube and discard the precipitate.

NOTE: Precipitation of zirconium iodate.

(6) To the supernate, add 5 ml of concentrated HF while stirring with a polyethylene stirring rod. Centrifuge and discard the supernate.

(7) Slurry the precipitate with 1 ml of a saturated solution of boric acid, add 5 ml of concentrated HNO_3, and transfer to a 40-ml glass centrifuge tube.

(8) Dissolve the precipitate by heating, cool, and adjust the pH carefully to 9 with concentrated NH_4OH. Cool and centrifuge. Discard supernate.

(9) Dissolve the precipitate in 10 ml of concentrated HNO_3. Add 20 ml of 0.35M iodic acid and immerse in an ice bath. Add 1 ml of a saturated solution of sodium bromate. Digest for ten minutes, cool, centrifuge, and discard supernate.

NOTE: Oxidation of Ce (III) to Ce (IV) and precipitation of ceric iodate.

(10) Dissolve the precipitate with 10 ml of concentrated HNO_3, 10 drops of concentrated HCl, and 10 drops of 30 percent hydrogen peroxide. Boil off the peroxide in a water bath and cool in an ice bath.

(11) Add 20 ml of 0.35M iodic acid and about 1 ml of a saturated solution of sodium bromate to reprecipitate ceric iodate.

(12) Digest for ten minutes, cool, centrifuge, and discard supernate.

(13) Collect the precipitate on a Whatman No. 542 filter paper disc using a Millipore filter chimney and suction. Use iodate wash solution (0.175M iodic acid in 10 percent HNO_3) for transfer. Wash the precipitate with a minimum of distilled water.

(14) Dry at 110°C to constant weight. Cool, weigh as Ce $(IO_3)_4$, record chemical yield, and β^- count with and without a 250 mg/cm^2 aluminum absorber for Ce^{141} and Ce^{144} determination.

NOTE: Allow at least two hours to elapse before counting in order to ensure Ce^{144} to Pr^{144} radioactive equilibrium.

3.2 Be^7, P^{32}, P^{33}, S^{35}, Sr^{89}, and Sr^{90} in IPC Filter Samples and Precipitation Samples

3.2.1 STRONTIUM SEPARATION AND PURIFICATION; YTTRIUM MILKING

(1) To the filtrates from 2.1 step (5), 2.3.1 step (6), or 2.3.2 step (7), add concentrated NH_4OH until the pH of the solution is about 8. (At this step, carriers

are present in the following accurately known amounts: 73 mg as S, 85 mg as $SrCO_3$, 35 mg as $Mg_2P_2O_7$, and 359 mg as the beryllium chelate of 8-hydroxyquinaldine. About 30 mg of ferric carrier are also present.)

(2) Digest on a hot plate for about thirty minutes and gravity filter the hydroxide fraction through Whatman No. 42 filter paper, washing three times with 10-ml portions of 2 percent ammonium nitrate solution. Reserve filtrate for 3.2.1 step (6).

(3) Transfer the hydroxide fraction from 3.2.1 step (2) to a beaker using a minimum amount of hot $1\underline{M}$ HNO_3 followed by distilled water rinses.

NOTE: The hydroxide fraction contains some strontium.

(4) Evaporate to about 1 ml and add 40 ml of fuming HNO_3 (90 percent).

(5) Cool in an ice bath for about one hour and harvest the strontium nitrate precipitate in a 40-ml centrifuge tube. Reserve supernate for phosphorus and beryllium separation.

(6) Dissolve the strontium nitrate in 5 to 10 ml of distilled water, combine it with the filtrate from 3.2.1 step (2) and evaporate to a minimum volume.

(7) Adjust the pH to 4 using $6\underline{M}$ HCl and pass the solution through a prepared Dowex 50W-X8 cation-exchange column (see Figure 1), collecting the effluent in a beaker.

NOTE: For preparation of column, see 7.2 Strontium Column.

(8) Wash the column three times with 25-ml portions of distilled water, combining the washes with the effluent from 3.2.1 step (7). Reserve effluent and washes for sulfur separation and determination.

(9) Elute the strontium from the resin bed by passing each of six 25-ml portions of $4\underline{M}$ HCl through the column.

(10) Evaporate the eluate almost to dryness and dissolve in a minimum amount of distilled water.

(11) Add 50 ml of fuming HNO_3 (90 percent), with stirring, in an ice bath and harvest the precipitate of strontium nitrate in a centrifuge tube. Discard supernate.

(12) Dissolve the strontium nitrate in a minimum amount of distilled water and reprecipitate strontium nitrate by adding 40 ml of fuming HNO_3 (90 percent) with stirring in an ice bath.

(13) Harvest the strontium nitrate precipitate in a 40-ml centrifuge tube and discard the supernate.

(14) Proceed as in 3.1.1 steps (7) to (28) and 3.1.2 steps (1) to (15).

3.2.2 PHOSPHORUS SEPARATION AND PURIFICATION

(1) Evaporate the fuming HNO_3 supernate from 3.2.1 step (5) to dryness and dissolve residue in a minimum amount of distilled water.

(2) Add 3 ml each of concentrated H_2SO_4 and concentrated perchloric acid and evaporate to dryness.

(3) Add 5 ml each of concentrated H_2SO_4 and concentrated perchloric acid and again evaporate to dryness. Dissolve the residue in 20 ml of distilled water.

(4) Neutralize the solution with concentrated NH_4OH and add about 0.4 ml of concentrated H_2SO_4.

(5) Add about 10 mg of copper carrier and heat to boiling.

(6) Continue heating on a hot plate at low heat while gassing with H_2S for about thirty minutes.

(7) Filter through Whatman No. 42 filter paper using suction and wash the beaker and precipitate with 5 to 10 ml of distilled water saturated with H_2S. Discard precipitate.

(8) Evaporate the filtrate to one-half its original volume on a hot plate.

(9) Add about 5 ml of concentrated HNO_3 and approximately 50 ml of ammonium molybdate reagent.

(10) Heat on a steam bath for about five minutes, centrifuge, and reserve the supernate for beryllium separation and purification.

(11) Wash the precipitate with 2 percent ammonium nitrate solution, containing a few drops of 1 percent Aerosol OT solution, and discard the washings.

(12) Dissolve the precipitate in about 1 ml of concentrated NH_4OH and add enough solid citric acid to neutralize the solution.

(13) Dilute with distilled water to about 15 ml and add 10 ml of magnesia mixture I and enough concentrated NH_4OH dropwise until the solution is just alkaline, then add about 0.5 ml in excess.

(14) Swirl the solution for about one minute and, if a precipitate does not begin to form, add an additional 0.5 ml of concentrated NH_4OH.

(15) Swirl the mixture for one minute after precipitation begins, and then add 4 ml of concentrated NH_4OH.

NOTE: Precipitation of magnesium ammonium phosphate.

(16) Allow the mixture to stand in an ice bath for several hours, then centrifuge and discard the supernate.

(17) Wash the precipitate with 0.7$\underline{M}$ NH_4OH, centrifuging and discarding the washings.

(18) Dissolve the precipitate in 5 ml of 70 percent perchloric acid and evaporate to fumes of perchloric acid.

(19) Wash down the sides of the beaker with distilled water and again evaporate to fumes of perchloric acid.

(20) Dilute to 15 ml with distilled water.

(21) Add about 0.5 ml of 0.5M potassium permanganate and heat until the permanganate color is discharged and manganese dioxide precipitates.

NOTE: Manganese dioxide scavenge is necessary to remove niobium contamination.

(22) Centrifuge, cool, and transfer the supernate to a 500-ml separatory funnel. Discard the precipitate.

(23) Add 60 ml of 10 percent butanol-chloroform mixture, 30 ml of concentrated HCl, and 70 ml of 20 percent sodium molybdate solution. Shake for two minutes, allow the layers to separate, and draw off the lower organic phase into a second 500-ml separatory funnel. Discard the upper aqueous phase.

NOTE: Phosphomolybdic acid is extracted into the 10 percent butanol-chloroform mixture.

(24) Add 75 ml of a 3M NH_4OH - 1M ammonium chloride (1:1) buffer solution to the second 500-ml separatory funnel.

(25) Shake for two minutes and allow the layers to separate. Discard the lower organic phase and transfer the aqueous layer to a 250-ml beaker.

(26) Heat the solution to boiling, add 30 ml of magnesia mixture II, and allow to cool.

NOTE: Precipitation of magnesium ammonium phosphate.

(27) Collect the precipitate on a Whatman No. 542 filter paper disc, using Millipore filter chimney and suction.

(28) Wash the precipitate with three small portions of 1:20 NH_4OH followed by three small portions of 95 percent ethanol.

(29) Transfer the precipitate and filter disc to a porcelain crucible and ignite to $Mg_2P_2O_7$ with a Meker burner.

(30) Continue ignition in a muffle furnace at 1000°C for one hour.

(31) Cool in a desiccator, weigh as $Mg_2P_2O_7$, record chemical yield, and β^- count for P^{32} and P^{33}.

3.2.3 BERYLLIUM SEPARATION AND PURIFICATION

(1) To the supernate from 3.2.2 step (10), add about 1.5 ml of bromine water dropwise and adjust the pH to about 8 with concentrated NH_4OH.

NOTE: Oxidation of Fe (II) to Fe (III).

(2) Digest on a hot plate at low heat for about thirty minutes and gravity filter the hydroxides through Whatman No. 42 filter paper. Discard filtrate.

(3) Dissolve the precipitate on the filter paper using a minimum volume of hot 3M HNO_3 and collect the solution in a 150-ml beaker.

(4) Bring the solution to a boil and add about 5 mg of zirconium carrier.

NOTE: Zirconium hydroxide scavengings serve to remove radio-zirconium contamination.

(5) Cautiously pour the hot solution into about 30 ml of 10 percent sodium hydroxide solution and heat with stirring.

NOTE: Resulting pH should be about 10. Beryllium being amphoteric, remains in solution at this hydroxide ion concentration.

(6) Gravity filter through Whatman No. 42 filter paper and wash the precipitate twice with 5 ml of warm 1 percent sodium hydroxide solution.

(7) To the combined filtrate and washes, add 5 mg of zirconium carrier and heat with stirring for about ten minutes.

(8) Repeat 3.2.3 step (6), collecting the filtrate and washes in a 125-ml separatory funnel.

(9) Add 5 ml of 10 percent sodium (tetra) ethylenediamine tetraacetate solution and adjust pH to abcut 6 with 2 to 3 ml of concentrated HCl.

NOTE: Beryllium hydroxide precipitates at this point.

(10) Add 1 ml of acetylacetone and shake for two or three minutes. Let stand for about ten minutes.

(11) Add 10 ml of chloroform to the separatory funnel and shake for two or three minutes.

NOTE: Beryllium acetylacetonate is soluble in chloroform.

(12) Allow the layers to separate and collect the lower chloroform layer in a 150-ml beaker.

(13) Repeat the extraction with 5 ml of chloroform and combine the lower chlorform layer with that obtained in 3.2.3 step (12).

(14) Add 5 ml of 6M HCl and evaporate to near dryness.

(15) Add 5 ml of aqua regia and evaporate to near dryness. Dissolve the residue in a minimum of distilled water.

(16) Add 5 ml of 4M ammonium chloride solution and dilute to about 50 ml.

(17) Heat the solution to 60 to 70°C.

(18) Add 20 to 30 percent excess 2 percent 8-hydroxyquinaldine solution dropwise with stirring. Adjust the pH to about 9 with 2M NH_4OH.

NOTE: Precipitation of $Be(C_{10}H_8NO)_2$.

(19) Digest the precipitate at 60 to 70°C for about thirty minutes.

(20) Filter the precipitate from the warm solution through a tared, pretreated Whatman No. 42 filter paper disc.

(21) Wash the precipitate several times with 30-ml portions of hot 1:100 NH_4OH and follow with a 30-ml distilled water wash.

(22) Dry in an oven at 110°C to constant weight. Weigh as $Be(C_{10}H_8NO)_2$. Record chemical yield, and γ count for Be^7 determination.

3.2.4 SULFUR SEPARATION AND PURIFICATION

(1) Evaporate the effluent and washings from 3.2.1 step (8) to dryness and dissolve in about 150 ml of distilled water.

(2) Adjust the pH to 1 with 6M HCl and heat the solution to boiling.

(3) Add about 5 ml of 10 percent barium chloride solution dropwise with stirring and then add 10 ml more of 10 percent barium chloride solution.

NOTE: Precipitation of barium sulfate.

(4) Digest the mixture on a hot plate for at least four hours.

(5) Filter the barium sulfate through a tared, pretreated, Whatman No. 542 filter paper disc, using a Millipore filter chimney and suction.

(6) Dry in an oven at 130°C to constant weight. Weigh as $BaSO_4$ and record chemical yield of sulfur to this point.

NOTE: The determination of sulfur yield at this point is not absolutely necessary. However, it provides a convenient check on the progress of the analysis.

(7) Grind the barium sulfate with about 10 to 20 times as much sugar charcoal in a mortar and transfer the mixture to a Coors No. 0 porcelain crucible containing a layer of sugar charcoal.

(8) Cover the barium sulfate-charcoal mixture with another layer of sugar charcoal to about 90 percent of the crucible volume and cover the crucible with a Vycor* cover.

(9) Heat the mixture over a Meker burner for about twenty minutes until a condensate is seen on the underside of the crucible cover.

(10) Continue ignition for ten minutes in a muffle furnace at 950 to 1000°C.

NOTE: Reduction of sulfate to soluble sulfide.

(11) Remove the mixture from the furnace, cool, and leach immediately with cold distilled water.

(12) Gravity filter the mixture through Whatman No. 42 filter paper, collecting the filtrate in a beaker containing 40 ml of 0.1 N iodine solution.

NOTE: Oxidation of sulfide to elemental sulfur.

(13) Continue leaching until the filtrate no longer gives a turbidity with 0.1 N iodine solution. Add more 0.1 N iodine solution, if needed. Discard sugar charcoal residue.

(14) Filter the mixture through a sintered glass filtering crucible of medium porosity.

(15) Wash the sulfur three times with 10 ml of 50 percent ethanol and with the use of a microburner, sublime the sulfur onto a Pyrex glass plate cooled with dry ice.

NOTE: Purification of sulfur.

(16) Allow the sulfur to harden for a few days in a desiccator. Scrape it from the glass plate into an agate mortar.

(17) Pulverize the sulfur to a fine powder using an agate mortar and pestle.

(18) Weigh as elemental S, record chemical yield, mount, and β^- count for S^{35} determination.

3.3 Sr^{89}, Sr^{90}, Rh^{102}, Ce^{141}, Ce^{144}, W^{181}, W^{185}, and Pb^{210} in Polystrene Filters

3.3.1 TUNGSTEN SEPARATION AND PURIFICATION

(1) Transfer the solution of 2.2.2 step (8), containing the following carriers in accurately known amounts: rhodium equivalent to about 3 mg Rh, tungsten equi-

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*Corning Glass Works, Corning, New York.

valent to about 5 mg W, bismuth equivalent to about 25 mg Bi, cerium equivalent to about 10 mg Ce, strontium equivalent to about 15 mg Sr, to a 150-ml beaker using dilute HCl and distilled water for the transfer. Dilute to 50 ml with distilled water.

> NOTE: The solution should also contain about 7 mg of thallium carrier and about 1 mg of tellurium carrier.

(2) Add 5 ml of concentrated HCl and 3 ml of concentrated HNO_3. Heat to incipient boiling.

(3) Add 3 ml of 10 percent cinchonine solution in 6M HCl and digest for at least one hour on a steam bath.

(4) Centrifuge the tungstic oxide, reserving the supernate in a 125-ml Erlenmeyer flask for bismuth, rhodium, strontium, and cerium.

(5) Wash the precipitate once with 6M HCl and centrifuge. Combine supernate with that of 3.3.1 step (4).

(6) Dissolve tungstic oxide with about 2 ml of concentrated NH_4OH and transfer the resulting solution to a platinum crucible.

(7) Evaporate to dryness and fuse with 2 to 3 g of solid sodium carbonate over a Meker burner.

(8) Cool the platinum crucible and place it, with contents, in a 250-ml beaker containing about 100 ml of distilled water. Digest over low heat for one hour.

> NOTE: Formation of soluble sodium tungstate.

(9) Filter the residue from 3.3.1 step (8) through Whatman No. 42 filter paper and wash with a 5 percent solution of sodium carbonate. Reserve the residue for strontium separation and purification.

(10) Neutralize the filtrate from 3.3.1 step (9) with concentrated HCl using phenolphthalein as an indicator. Add 50 ml of concentrated HCl and evaporate to dryness.

> NOTE: Dehydration of silica.

(11) Add about 250 ml of hot distilled water, 20 ml of concentrated HCl, 10 ml of concentrated HNO_3 and filter pulp. Bring the solution to an incipient boil and add 8 to 10 ml of 10 percent cinchonine solution in 6M HCl.

(12) Digest for two to three hours over low heat. Remove from heat and allow the sample to stand overnight for best results.

(13) Filter the tungstic oxide through Whatman No. 42 filter paper. Wash several times with cinchonine wash solution (1 ml of 10 percent cinchonine

solution in 6M HCl per 100 ml of distilled water) and transfer to a platinum crucible.

(14) Ignite over a Meker burner until all carbonaceous matter has been destroyed.

(15) Allow the crucible to cool and add 3 ml of concentrated HNO_3 and about 5 to 10 ml of 49 percent HF to the tungstic oxide-silica residue.

(16) Evaporate the sample to dryness on a sand bath.

NOTE: Removal of silica.

(17) Allow the platinum crucible to cool and add 1 ml of 6M sodium hydroxide solution dropwise. Wash down the walls of crucible with 2 to 3 ml of distilled water.

(18) Gently heat the crucible for about five minutes until the tungstic oxide has dissolved.

(19) Transfer the solution to a 40-ml centrifuge tube using distilled water in the transfer. Adjust the volume to about 15 ml with distilled water.

(20) Add 10 ml of concentrated HNO_3 and digest on a hot water bath for about two hours.

(21) Allow to cool, centrifuge, and discard supernate.

(22) Add 1 ml of 6M acetic acid and 2 ml of 6M ammonium acetate and adjust the pH to 5.5.

(23) Heat to 90°C on a sand bath and add 0.2 ml of 0.1 percent Aerosol OT solution.

(24) Add 2 ml of a 5 percent solution of 8-hydroxyquinoline in 2M acetic acid and stir for about two minutes.

(25) Cool the tungstic 8-hydroxyquinolate and filter through a tared, pretreated, Whatman No. 542 filter paper disc.

(26) Wash the precipitate several times with a wash solution consisting of 10 ml of 5 percent 8-hydroxyquinoline in 2M acetic acid and 50 ml of 6M ammonium acetate.

(27) Dry the sample at 110°C for thirty minutes and weigh as $WO_2(C_9H_6ON)_2$. Record chemical yield and x-ray count for W^{181} determination and β^- count for W^{185} determination.

3.3.2 RHODIUM SEPARATION AND PURIFICATION

(1) To the supernate from 3.3.1 step (4), add 10 to 20 ml concentrated HNO_3 and boil to completely destroy any excess cinchonine. Remove nitrogen oxides by heating to the evolution of SO_3 fumes.

(2) Add about 15 ml of distilled water, heat gently for several minutes, and transfer the mixture to a 40-ml centrifuge tube.

(3) Centrifuge and reserve the supernate in another 40-ml centrifuge tube. Wash the residue with about 5 ml of distilled water and again centrifuge. Combine this supernate with that reserved in the 40-ml centrifuge tube.

> NOTE: Residue is composed mainly of insoluble strontium sulfate and traces of silica.

(4) Combine the residue of 3. 3. 2 step (3) with the residue obtained in 3. 3. 1 step (9), using distilled water. Reserve for strontium determination.

(5) To the combined supernates of 3. 3. 2 step (3), add 2 ml of 5 percent sulfurous acid and 1 ml of 57 percent hydriodic acid (phosphorus-free) with vigorous stirring.

(6) Centrifuge and reserve the precipitate for bismuth separation and purification. Check the supernate for completeness of precipitation by the dropwise addition of 57 percent hydriodic acid.

(7) To the supernate from 3. 3. 2 step (6), add 10 ml of concentrated HCl and from 2 to 2. 5 ml of 57 percent hydriodic acid (phosphorus-free). Boil vigorously for about thirty minutes. Maintain the volume constant at about 20 ml by repeated additions of 6<u>M</u> HCl.

> NOTE: Precipitation of rhodium iodide.

(8) Allow the precipitated rhodium iodide to stand for a few minutes then centrifuge for ten minutes.

(9) Transfer the supernate to a 125-ml Erlenmeyer flask. Wash the precipitate with about 10 ml of 6M HCl.

(10) Centrifuge, combine the supernate with that of 3. 3. 2 step (9), and reserve for strontium separation and purification.

(11) To the rhodium iodide precipitate of 3. 3. 2 step (8), add 2 ml of concentrated HCl and 0. 5 to 1 ml of 30 percent hydrogen peroxide dropwise with gentle heating until solution is effected.

> NOTE: Further addition of 30 percent hydrogen peroxide may be required for complete solution.

(12) Evaporate the solution to about 1 ml by careful boiling.

(13) Cool slightly and dilute with distilled water to about 15 ml.

(14) Cautiously add 3 ml of a saturated solution of sodium nitrite with stirring.

(15) After effervescence has ceased, heat on a water bath for ten minutes with occasional stirring.

> NOTE: Formation of soluble sodium rhodonitrite complex.

(16) Add 0.1 ml of ferric carrier, stir, and digest on a water bath for one minute. Centrifuge and discard the precipitate.

NOTE: Ferric hydroxide scavenge.

(17) To the supernate, add 0.2 ml of lanthanum carrier, 0.2 ml of phenolphthalein indicator solution, and enough 1M sodium hydroxide to make the solution just alkaline.

(18) Digest the lanthanum hydroxide for one minute on a water bath. Centrifuge, transfer the supernate to another 40-ml centrifuge tube, and discard the precipitate.

NOTE: Rare earth scavenge.

(19) Acidify the supernate by the addition of 0.1 ml of 3M HCl.

(20) Add 2 ml of a saturated solution of potassium nitrate with vigorous stirring until precipitation occurs.

NOTE: Precipitation of potassium rhodonitrite.

(21) Digest the precipitate on a water bath for at least fifteen minutes.

(22) Cool, centrifuge, and discard the supernate.

(23) Dissolve the precipitate with 2 to 3 ml of 6M HCl and gentle heating. Continue heating and evaporate to dryness.

(24) Cool and dissolve the residue in 3 to 4 ml of 0.1M HCl.

(25) Pass the solution through a prepared Dowex I-X10 anion-exchange column (see Figure 2).

NOTE: For preparation of column, see 7.3 Rhodium Column.

(26) Wash with 1 to 2 ml of 0.1M HCl. Discard effluent and washings.

(27) Elute the rhodium with 15 ml of concentrated HCl, collecting the eluate in a 125-ml Erlenmeyer flask.

(28) Add 0.1 ml of tellurium carrier to the eluate from 3.3.2 step (27) and reduce the volume to about 10 ml by boiling.

(29) Cool and add 1 ml of 57 percent hydriodic acid (phosphorus-free). Transfer the mixture to a 125-ml separatory funnel containing 15 ml of 4-methyl-2-pentanone which has been previously equilibrated with 1 ml of 57 percent hydriodic acid (phosphorus-free) and 5 ml of 6M HCl. Use about 5 ml of 6M HCl in the transfer.

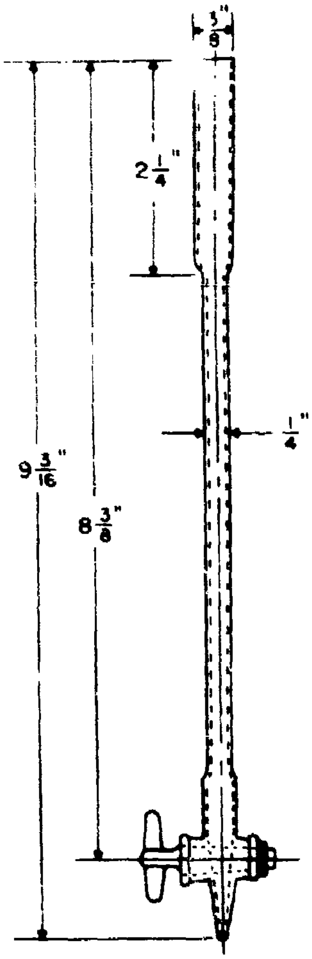

Figure 2. Ion Exchange Column 2

(30) Shake vigorously for two minutes and allow the mixture to stand for ten minutes.

NOTE: Removal of traces of silver and tellurium activities.

(31) Carefully collect the lower aqueous phase in a 125-ml Erlenmeyer flask and carefully boil for fifteen to twenty minutes. Maintain the volume at about 10 ml by the addition of 6$\underline{M}$ HCl.

NOTE: Care must be exercised to prevent spattering due to traces of 4-methyl-2-pentanone present.

(32) Cool and transfer the rhodium iodide to a 40-ml centrifuge tube, using 6M HCl in the transfer. Reserve the flask for use in subsequent steps.

(33) Centrifuge and discard supernate.

(34) Wash the precipitate with 5 to 10 ml of 6M HCl and again centrifuge. Discard the supernate.

(35) Transfer the rhodium iodide to the flask form 3. 3. 2 step (32) using distilled water i the transfer. Reserve the centrifuge tube for use in subsequent steps.

(36) Add 1 ml of concentrated H_2SO_4 and boil until iodine fumes cease to evolve.

(37) Cool, wash down the walls of the flask with 3 ml of distilled water, and add 1 ml of concentrated HCl. Boil for a few minutes until reddish color of rhodium chloride is apparent.

(38) Carefully add 1 ml of concentrated HNO_3 and 1 ml of 60 to 70 percent perchloric acid. Boil to fumes of SO_3.

(39) Transfer the hydrated rhodium sulfate to the centrifuge tube from 3. 3. 2 step (35) using a minimum amount of distilled water in the transfer and again boil to fumes of SO_3.

(40) Cool and transfer to an electroplating cell of approximately 3 ml capacity (see Figure 3), using distilled water to effect the transfer. Wash centrifuge tube with distilled water and transfer to cell.

NOTE: The plating cell should be filled to about 85 percent of capacity.

(41) Rhodium is electroplated onto a tared platinum disc (3/8-inch diameter, 0.001-inch thick) by electrolysis at about 75 milliamperes for about 16 hours (see Figure 4).

(42) Remove the platinum disc from the plating cell. Rinse with distilled water, followed by an ethanol rinse.

(43) Dry at 110°C for fifteen minutes, cool, and weigh as elemental Rh.

(44) Record chemical yield and x-ray count for Rh^{102} determination.

3. 3. 3 STRONTIUM SEPARATION AND PURIFICATION; YTTRIUM MILKING

(1) Ignite the residue from 3. 3. 1 step (9) in a platinum crucible.

(2) To the supernate of 3. 3. 2 step (10), carefully add about 10 ml of concentrated HNO_3. Gentle heating may be necessary to initiate the reaction which is somewhat violent.

NOTE: Oxidation of iodide to iodine.

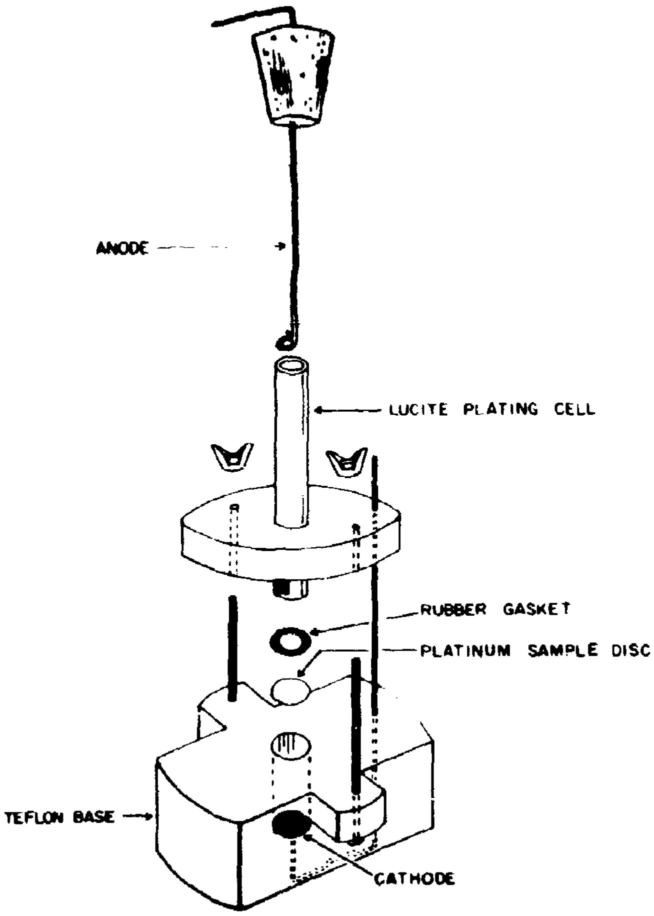

Figure 3. Electroplating Cell (Approximate sizes)

(3) After the initial reaction has subsided, boil to fumes of SO_3 to remove all traces of iodine.

(4) Add about 1 ml of distilled water and transfer to the platinum crucible of 3.3.3 step (1).

(5) Evaporate to dryness on a sand bath and gently heat over an open flame until SO_3 fumes cease to evolve.

(6) Add about 2.5 g of solid sodium carbonate and fuse over a Meker burner. Transfer the homogeneous melt to a muffle furnace at 900°C and continue heating for fifteen minutes.

NOTE: Conversion of strontium and cerium to carbonates and/or oxides.

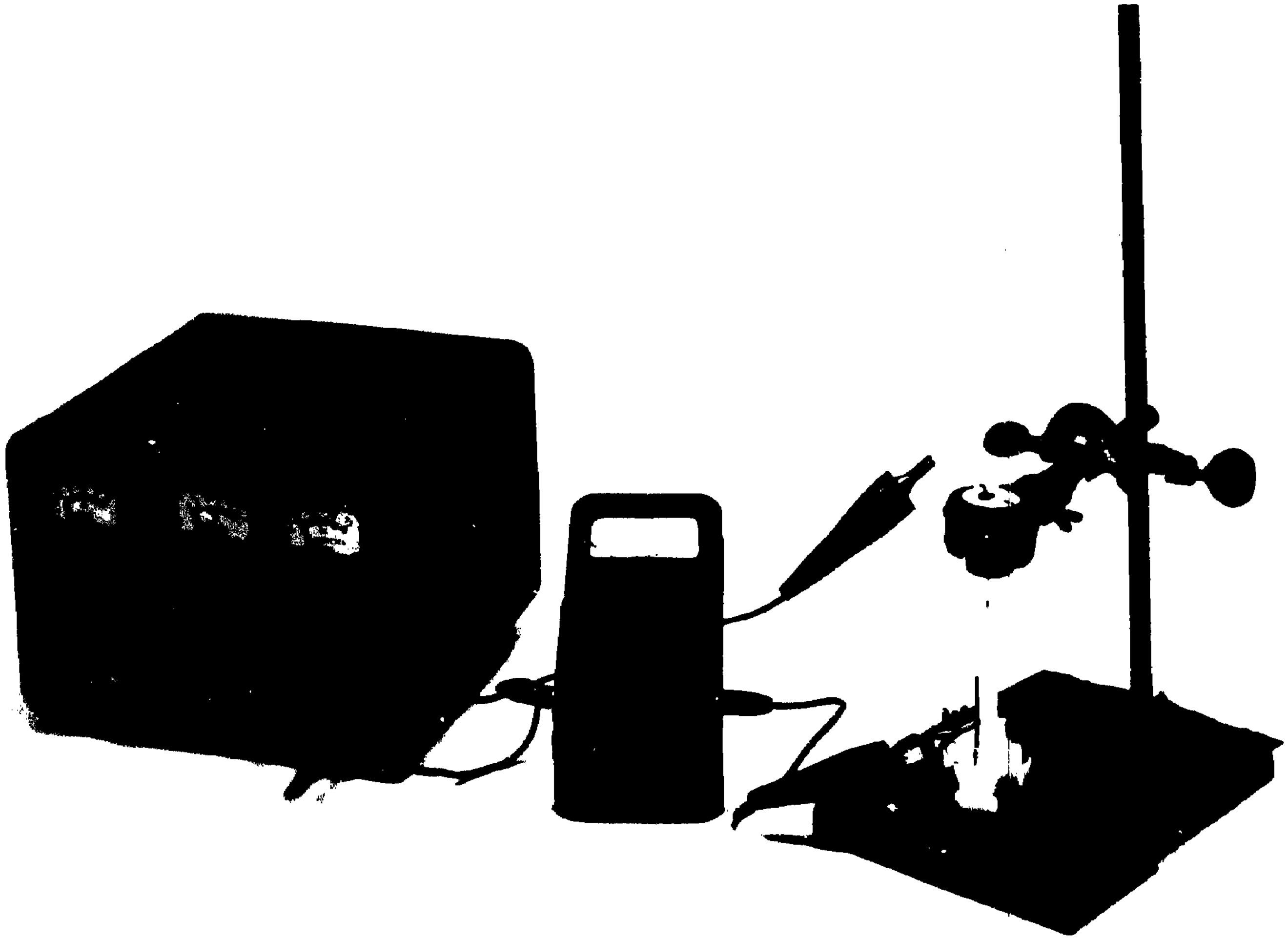

Figure 4. Electrolysis Apparatus, Complete

(7) Remove the platinum crucible from the muffle furnace, allow to cool, and place it and contents into a 250-ml beaker containing about 100 ml of hot distilled water.

(8) When the fused mass has loosened sufficiently, remove it from the crucible and wash the crucible thoroughly with distilled water, adding the washings to the beaker along with the removed mass. Digest over low heat with occasional stirring for about one hour.

(9) Cool and filter through Whatman No. 42 filter paper. Wash the residue with about three 10-ml portions of 5 percent sodium carbonate solution. Discard the filtrate and washings.

(10) Dissolve the strontium carbonate present in the residue on the filter paper with about 15 ml of 6M HCl. Reserve the filter paper and insoluble residue for cerium separation and purification.

NOTE: Separation of strontium.

(11) To the filtrate from 3.3.3 step (10) contained in a 250-ml beaker, add 20 ml of concentrated HCl and evaporate to dryness.

NOTE: Dehydration of silica.

(12) Add another 10 ml of concentrated HCl, gently heat for five minutes, add 100 ml of distilled water, and bring to an incipient boil.

NOTE: Dissolution of strontium salts.

(13) Gravity filter through Whatman No. 40 filter paper, washing the filter paper and any residue with several 5-ml portions of 5 percent HCl. Discard the residue.

(14) Evaporate the filtrate to about 15 ml.

(15) Add 90 ml of fuming HNO_3 (90 percent) and stir with the use of a mechanical stirrer for forty-five minutes.

(16) Cool in an ice bath, centrifuge, discard the supernate, wash the strontium nitrate precipitate with 5 ml of fuming HNO_3 (90 percent), and again centrifuge.

(17) Discard supernate and dissolve the strontium nitrate in about 5 ml of distilled water and evaporate to dryness.

(18) Dissolve the strontium nitrate with 12 ml of distilled water, add 40 ml of fuming HNO_3 (90 percent), and stir until strontium nitrate precipitates.

(19) Cool in an ice bath, centrifuge, and discard the supernate.

(20) Dissolve the strontium nitrate in 5 ml of distilled water and adjust the pH to 8 with concentrated NH_4OH.

(21) Add 0.1 ml of ferric carrier and stir until ferric hydroxide precipitates.

(22) Centrifuge and discard the ferric hydroxide precipitate.

(23) Adjust the volume to about 20 ml with distilled water and heat to incipient boiling.

(24) Add 10 ml of a saturated solution of sodium carbonate with stirring.

(25) Cool and filter through a tared, pretreated Whatman No. 542 filter paper disc using suction.

(26) Wash with two 10-ml portions of 5 percent sodium carbonate solution and two 10-ml portions of distilled water.

(27) Dry at 110°C to constant weight, weigh as $SrCO_3$, and record the chemical yield to this point.

(28) Dissolve the strontium carbonate off the filter paper disc using 6M HNO_3, collecting the resulting solution in a 40-ml centrifuge tube.

(29) Add exactly 1.0 ml of standardized strontium carrier, equivalent to 265 mg of $SrCO_3$/ml.

> NOTE: Additional strontium carrier is necessary in order to employ a thick solid sample technique for β-counting [Libby, (1957), Suttle and Libby (1955)].

(30) Add about 20 mg of barium carrier and about 5 mg of ferric carrier.

(31) Proceed with 3.1.1 steps (8) to (28) and 3.1.2 steps (1) to (15).

3.3.4 CERIUM SEPARATION AND PURIFICATION

(1) Ignite the filter paper and residue from 3.3.3 step (10) in a platinum crucible.

(2) Cool and add 2 ml of concentrated H_2SO_4 and 10 ml of 49 percent HF.

(3) Heat on a sand bath to fumes of SO_3 to insure silicon fluoride removal.

(4) Transfer the mixture to a 100-ml beaker using distilled water. Add 10 ml of concentrated HCl and 10 ml of concentrated HNO_3.

> NOTE: Dissolution of insoluble oxides.

(5) Boil to fumes of SO_3.

(6) Cool, centrifuge, and transfer the supernate to another 40-ml centrifuge tube.

> NOTE: Discard the insoluble residue.

(7) Adjust the pH to 10 with concentrated NH_4OH, cool, and centrifuge. Discard the supernate.

(8) Proceed with 3. 1. 5. 1 steps (9) and (10) and 3. 1. 5. 2 steps (1) to (14).

3. 3. 5 BISMUTH SEPARATION AND PURIFICATION

(1) Dissolve the iodides from 3. 3. 2 step (6) in 1 to 2 ml of 6M HNO_3 and heat until iodine is removed. Centrifuge and discard any residue that may remain.

(2) Transfer the resulting clear supernate to a 125-ml Erlenmeyer flask using a minimum of 6M HNO_3 rinses.

(3) Evaporate just to dryness over an open flame. Add 5 ml of concentrated HCl and again evaporate to dryness.

(4) Add 20 ml of 3M HCl and about 0. 5 g of hydrazine sulfate and heat to boiling.

(5) Add 1 ml of a saturated solution of sulfur dioxide and continue to boil, making three or four successive 1-ml additions of the saturated solution of sulfur dioxide. Boil for about five minutes.

(6) Gravity filter the mixture into a centrifuge tube using Whatman No. 40 filter paper. Wash the flask and precipitate with a dilute solution of sulfur dioxide. Discard the precipitate.

NOTE: The dilute solution of sulfur dioxide may be prepared by diluting a saturated solution of sulfur dioxide with an equal quantity of distilled water.

(7) Make the filtrate basic by the dropwise addition of concentrated NH_4OH. Add 1 ml in excess and cool in an ice bath.

(8) Centrifuge and discard the supernate.

(9) Dissolve the bismuth hydroxide in a minimum amount of 6M HNO_3 and transfer the resulting solution to a 250-ml beaker. Dilute to about 100 ml with distilled water.

(10) Add 6M NH_4OH until the solution is slightly turbid, then add 20 ml of a freshly prepared saturated solution of ammonium carbonate.

(11) Heat to boiling, cool, test for completeness of precipitation, filter using a Millipore filter chimney, a Whatman No. 542 filter disc, filter pulp, and suction. Wash the beaker and precipitate with several 5-ml portions of 0. 5 percent ammonium carbonate solution.

(12) Transfer the precipitate and paper to a tared porcelain crucible and then to a cold muffle furnace. Raise temperature gradually to 600°C and ignite for two hours.

(13) If, upon ignition, some of the bismuth oxide (yellow) has been reduced to elemental bismuth (silver or red), dissolve the mixture in 1 to 2 ml of 8M HNO_3, carefully evaporate to dryness on a hot plate, transfer to a cold muffle furnace, and ignite as before.

(14) Cool, weigh as Bi_2O_3, and record the chemical yield at this point.

(15) Dissolve the yellow bismuth oxide in a minimum amount of 8M HNO_3 with heating and transfer the resulting solution to a 800-ml beaker using several distilled water rinses. Dilute with distilled water to about 200 ml.

(16) Add exactly 1.0 ml of standardized bismuth carrier, equivalent to 100 mg of Bi_2O_3.

> NOTE: Additional bismuth carrier is necessary in order to employ a thick solid sample technique for β^- counting [Libby, (1957), Suttle and Libby (1955)].

(17) Add about 20 mg of antimony, tellurium, and zirconium, and about 10 mg of cerium holdback carriers.

(18) Dilute to about 500 ml with distilled water, adjust the pH to 4 to 5, heat to boiling, and gas with H_2S for twenty minutes while cooling in an ice bath.

(19) Filter through No. 42 Whatman filter paper using pulp and suction. Wash the precipitate with 1 percent HCl solution saturated with H_2S. Discard the supernate.

(20) Transfer the precipitate, filter paper, and pulp to a 250-ml beaker.

(21) Add 20 ml of ammonium sulfide solution (about 12 percent as sulfidic sulfur). Macerate the paper and pulp thoroughly.

(22) Gravity filter through Whatman No. 42 filter paper. Wash thoroughly with a 10 percent ammonium sulfide solution and discard the filtrate.

(23) Transfer the bismuth sulfide precipitate and paper to a 250-ml beaker.

(24) Slowly add 60 ml of 8M HNO_3. Macerate the paper and digest on a hot plate with stirring until the bismuth sulfide has dissolved. An additional 60 ml of 8M HNO_3 may be required.

(25) Cool and dilute with 100 ml of hot distilled water.

(26) Filter off the paper pulp using suction and wash with 4M HNO_3. Transfer the filtrate to a 600-ml beaker.

> NOTE: Discard pulp and any insolubles.

(27) Dilute to about 300 ml with hot distilled water and add about 10 mg each of zirconium and palladium holdback carriers.

(28) Add 12 ml of 6M HCl and adjust the pH to about 4 with concentrated NH_4OH.

(29) Dilute to 500 ml with hot distilled water, heat on a hot plate, and hold at 90°C until bismuth oxychloride settles out.

(30) Filter with suction while hot through Whatman No. 42 filter paper and pulp. Wash the bismuth oxychloride with a warm 0.5 percent HCl solution and discard the filtrate.

(31) Dissolve the bismuth oxychloride off the paper with warm 6M HCl, using three portions of about 50 ml each and transfer the resulting solution to a 600-ml beaker.

(32) Repeat 3. 3. 5 step (27).

(33) Adjust the pH to about 4 with concentrated NH_4OH.

(34) Repeat 3. 3. 5 steps (29) and (30), recording the time after the final 0. 5 percent HCl wash as the time of separation t_s of Bi^{210} from Pb^{210}.

(35) Dissolve the bismuth oxychloride off the paper with warm 6M HCl using three 50-ml portions. Transfer solution to an 800-ml beaker.

(36) Add about 10 mg of zirconium and about 5 mg of cerium holdback carriers.

(37) Dilute to 500 ml with distilled water, heat to boiling, and gas with H_2S for twenty minutes while cooling the solution in an ice bath.

(38) Filter through Whatman No. 42 filter paper with pulp and suction. Wash the precipitate with 1 percent HCl solution saturated with H_2S. Discard the filtrate.

(39) Dissolve the bismuth sulfide precipitate off the paper with a minimum amount of warm 8M HNO_3.

(40) Transfer the solution to a 1000-ml beaker and dilute to 200 ml with distilled water.

(41) Add 6M NH_4OH (or concentrated NH_4OH) until the solution is slightly turbid.

(42) Add at least 20 ml of a freshly prepared saturated solution of ammonium carbonate.

(43) Heat to boiling, cool, and filter through Whatman No. 42 filter paper with pulp.

(44) Wash the precipitate with a 0. 5 percent ammonium carbonate wash solution. Check the filtrate for completeness of precipitation by adding more saturated ammonium carbonate solution and heating. Discard the filtrate when precipitation is complete.

(45) Transfer the precipitate, paper, and pulp to a weighed porcelain crucible.

(46) Place in a cold muffle furnace and ignite as in 3. 3. 5 step (12).

(47) Perform 3. 3. 5 step (13), if necessary.

(48) Cool and weigh as Bi_2O_3. Record the chemical yield based on the amount recovered in 3. 3. 5 step (14) plus that added in 3. 3. 5 step (16).

(49) β^- count for Bi^{210} determination.

3.4 Sr^{89}, Sr^{90}, W^{181}, and W^{185} in Precipitation Samples

3. 4. 1 TUNGSTEN SEPARATION AND PURIFICATION

(1) To the filtrate from 2. 1 step (5) add the following carriers in accurately known amounts: tungsten equivalent to about 50 mg of $WO_2(C_9H_6ON)_2$ and strontium equivalent to about 260 mg of $SrCO_3$.

(2) Evaporate the sample on a hot plate almost to dryness.

(3) Add 10 ml of concentrated HCl, digest for 10 minutes using a watch glass cover, remove cover, and evaporate to dryness. Do not bake.

NOTE: Precipitation of hydrous tungstic oxide.

(4) Transfer the tungstic oxide to a 40-ml centrifuge tube, using about 20 ml of 2M HCl in the transfer, and digest in a steam bath for ten minutes.

(5) Centrifuge while still hot. Decant and reserve the supernate in a 40-ml centrifuge tube for strontium separation and purification.

(6) Transfer the precipitate from 3.4.1 step (5) to a platinum crucible using a minimum amount of 2M NH_4OH in the transfer.

(7) Evaporate slowly to dryness and fuse with 3 g of solid sodium carbonate over a flame.

(8) To the platinum crucible, add a small amount of distilled water as soon as possible and transfer the contents to a 40-ml centrifuge tube.

(9) Digest in a steam bath, maintaining the volume at about 15 ml.

NOTE: Solution is hastened by breaking up the fused mass with a stirring rod.

(10) Cool, centrifuge, and decant the supernate into a 150-ml beaker.

(11) Add about 10 ml of distilled water to the residue, heat to boiling, cool, and centrifuge again.

(12) Add the supernate from 3.4.1 step (11) to that of 3.4.1 step (10) and discard any residue.

(13) Acidify the combined supernates from 3.4.1 step (12) with 6M HNO_3 and add 5 ml excess of concentrated HNO_3.

NOTE: Effervescence occurs.

(14) Add 5 ml of concentrated HCl and heat gradually to boiling.

(15) Dilute to about 75 ml with hot distilled water.

(16) Add 5 ml of cinchonine solution, heat, and stir for fifteen minutes.

(17) Cool to about 25°C and allow to stand for thirty minutes.

(18) Filter the tungstic oxide by gravity filtration, using Whatman No. 42 filter paper without washing. Discard filtrate.

(19) Dissolve the precipitate remaining in the beaker and on the filter paper from 3.4.1 step (18) with hot 6M NH_4OH.

(20) Collect the resulting solution in a 150-ml beaker, washing the filter paper thoroughly with a minimum amount of 6M NH_4OH.

(21) Discard the filter paper and any insoluble residue.

(22) Adjust the pH of the ammoniacal solution to about 8 with 6M HCl.

(23) Add about 0.3 ml of 1 percent Aerosol OT solution and heat to boiling.

(24) Remove solution from the heat source and add dropwise about 2 ml of a 4 percent alcoholic solution of 8-hydroxyquinoline with stirring.

> NOTE: Alcohol may boil off violently when added to the hot solution.

(25) Acidify the solution to a pH of about 5 using 2M acetic acid and stir until a precipitate forms.

> NOTE: Scratching the sides of beaker with stirring rod aids in the precipitation.

(26) Digest on a hot plate for one minute and allow to stand at about 25°C for thirty minutes.

(27) Filter the precipitate through a Whatman No. 542 filter paper disc, using a Millipore filter chimney and suction. Use distilled water for the transfer.

(28) Wash with several portions of distilled water followed by several hot distilled water washes.

(29) Add about 0.2 ml of 0.1 percent agar solution during the final stages of the filtering process to act as a binder.

(30) Dry at 110°C to constant weight. Cool, weigh as $WO_2(C_9H_6ON)_2$, record chemical yield, x-ray count for W^{181}, and β^- count for W^{185} determination.

3.4.2 STRONTIUM SEPARATION AND PURIFICATION, YTTRIUM MILKING

(1) Evaporate the supernate from 3.4.1 step (5) to 8 ml.

(2) Cool and slowly add 31 ml of fuming HNO_3 (90 percent) to precipitate strontium nitrate.

(3) Set in an ice bath, with occasional stirring, for twenty minutes.

(4) Centrifuge at high speed for ten minutes and discard supernate.

(5) Dissolve the precipitate in 5 ml of distilled water and carry out 3.1.1 steps (5) to (28) and 3.1.2 steps (1) to (15).

3.5 Na^{22}, P^{32}, Sr^{89}, Sr^{90}, and Ba^{140} in IPC Filter Samples

3.5.1 SODIUM SEPARATION AND PURIFICATION

(1) To the solution from 2.3.1 step (6), 2.3.2 step (7), or 2.3.3 step (6), add concentrated NH_4OH until the solution is just basic. The solution should contain the following carriers in accurately known amounts: barium equivalent to 125 mg

$BaCl_2 \cdot H_2O$, phosphorus equivalent to 30 mg $Mg_2P_2O_7$, sodium equivalent to 20 mg NaCl, and strontium equivalent to 270 mg $SrCO_3$, and approximately 20 to 30 mg ferric carrier.

> NOTE: Vycor glassware and Teflon stirring rods are used to minimize introduction of sodium from soft glass.

(2) Heat to boiling and add 20 ml of a saturated solution of ammonium carbonate and digest for fifteen minutes.

(3) Cool, centrifuge, and reserve the supernate. Wash the precipitate with 0. 5 percent ammonium carbonate solution.

(4) Centrifuge and combine the washings with the supernate of 3. 5. 1 step (3).

(5) Reserve the precipitate for subsequent separations.

(6) To the supernate from 3. 5. 1 step (3), add concentrated HCl to a pH less than 1 and evaporate to about 20 ml.

(7) Add 0. 2 ml of ferric carrier and make barely basic with concentrated NH_4OH and add 0. 3 ml in excess.

(8) Centrifuge and transfer the supernate to a 400-ml beaker.

(9) Dissolve the ferric hydroxide in a minimum of 6$\underline{M}$ HNO_3 and combine the solution with the supernates from 3. 5. 1 step (4).

(10) To the supernate from 3. 5. 1 step (8), add 1 ml of concentrated HCl and evaporate to near dryness.

(11) Cool and add 1 ml of 6$\underline{M}$ ammonium acetate and 220 ml of sodium precipitating reagent to precipitate $NaMg(UO_2)_2(C_2H_3O_2)_9 \cdot 6.5\ H_2O$.

(12) Stir at high speed for twenty minutes using a magnetic stirrer and stirring bar.

(13) Harvest the precipitate into a 10-ml centrifuge tube discarding the supernate.

(14) Wash the precipitate with 20 ml of sodium wash solution, centrifuge, and discard the supernate.

(15) Dissolve the precipitate with a minimum amount of concentrated HCl, dilute to 15 ml with distilled water, and repeat 3. 5. 1 step (7).

(16) Centrifuge and transfer the supernate to a 40-ml centrifuge tube, discarding the ferric hydroxide precipitate.

(17) To the supernate from 3. 5. 1 step (16), add enough concentrated HCl to make the solution 3$\underline{M}$.

(18) Add 5 mg of cupric carrier and gas with H_2S for five minutes.

(19) Centrifuge and transfer the supernate to a 150-ml beaker, discarding the precipitate.

(20) Evaporate the supernate to dryness and continue heating over a Meker burner until dense white fumes cease to evolve.

(21) Dissolve the residue in water and transfer to a 40-ml centrifuge tube.

(22) Evaporate the solution to dryness and dissolve the residue in about 0.5 ml of distilled water.

NOTE: A small amount of concentrated HCl may be required to effect complete solution.

(23) Add 20 ml of concentrated HCl-ethyl ether (1:1) reagent. Cool in an ice bath with vigorous stirring.

NOTE: Precipitation of sodium chloride.

(24) Centrifuge and discard the supernate.

(25) Dissolve the sodium chloride in a minimum amount of water and reprecipitate sodium chloride with 20 ml of concentrated HCl-ethyl ether reagent as in 3.5.1 step (23).

(26) Centrifuge and discard the supernate.

(27) Suspend the precipitate in 10 ml of cold absolute ethanol and filter through a pretreated, tared Whatman No. 542 filter paper disc using suction, a Millipore filter chimney, and cold absolute ethanol as a transfer agent

(28) Dry in an oven at 110°C for ten minutes, cool in a desiccator, weigh as NaCl, record chemical yield, and determine Na^{22} using a $\gamma - \gamma$ coincidence counter.

3.5.2 PHOSPHORUS SEPARATION AND PURIFICATION

(1) Dissolve the precipitate from 3.5.1 step (5) in a minimum amount of $6\underline{M}$ HNO_3 and evaporate to near dryness.

(2) Dissolve the residue in 6 ml of distilled water and add 24 ml of fuming HNO_3 (90 percent).

(3) Cool in an ice bath for twenty minutes with occasional stirring.

(4) Centrifuge and transfer the supernate to a beaker along with the dissolved $Fe(OH)_3$ from 3.5.1 step (9) and reserve.

(5) Dissolve the precipitate from 3.5.2 step (4) with 5 ml of distilled water and add 19 ml of fuming HNO_3 (90 percent).

(6) Repeat 3.5.2 step (3).

(7) Centrifuge and combine the supernate with that of 3.5.2 step (4) and reserve the precipitate for barium and strontium separation and purification.

(8) Evaporate the combined supernates from 3.5.2 step (4) to 5 ml.

(9) Add 5 ml of distilled water, 5 ml of concentrated HNO_3, 1 drop of 1 percent Aerosol OT solution, and 5 ml of ammonium molybdate reagent. Heat on a water bath for five minutes.

NOTE: Precipitation of ammonium phosphomolybdate.

(10) Centrifuge and wash the precipitate twice with 20 ml of 2 percent ammonium nitrate solution, containing a few drops of 1 percent Aerosol OT solution. Discard the washings.

> NOTE: The supernate may be used for beryllium analysis if required.

(11) Continue with 3.2.2 steps (12) to (31).

3.5.3 STRONTIUM SEPARATION AND PURIFICATION

(1) Dissolve the precipitate from 3.5.2 step (7) in 15 ml of distilled water. Add 5 mg of ferric carrier and bubble in ammonia gas until ferric hydroxide is precipitated.

(2) Centrifuge, discard precipitate, and repeat ferric hydroxide scavenge two more times.

(3) Add 0.2 ml 0.1 percent methyl red solution and then add 6<u>M</u> HNO_3 to a light pink color.

(4) Heat to incipient boiling in a water bath and then add 0.4 ml of 1 percent Aerosol OT solution with stirring.

(5) Add 3 ml of 1.5<u>M</u> sodium chromate dropwise with stirring.

(6) Digest for ten minutes, with stirring, centrifuge, and reserve precipitate for barium separation and purification.

(7) To the supernate, add 5 mg of barium carrier, digest in a water bath, centrifuge, and discard the precipitate.

(8) Make the supernate barely basic with concentrated NH_4OH.

(9) Continue with 3.1.1 steps (17) to (28) and 3.1.2 steps (1) to (15).

3.5.4 BARIUM SEPARATION AND PURIFICATION

(1) Dissolve the barium chromate precipitate from 3.5.3 step (6) in 10 ml of hot 2<u>M</u> HCl. Cool and carefully add 30 ml of fresh HCl-ether reagent (5:1).

(2) Cool in an ice bath for five minutes with stirring. Centrifuge and discard supernate.

(3) Dissolve precipitate in a minimum amount of water. Add 5 mg of ferric carrier and make basic with 6<u>M</u> NH_4OH.

(4) Centrifuge and discard precipitate.

> NOTE: Filter if necessary to remove traces of ferric hydroxide.

(5) Evaporate the supernate to 2 to 3 ml and reprecipitate barium chloride with 30 ml of HCl-ether reagent (5:1) cool in an ice bath, centrifuge, and discard supernate.

NOTE: Record the time since this is separation of Ba^{140} from La^{140}.

(6) Filter through a Whatman No. 542 filter paper disc, using a Millipore filter chimney and suction.

(7) Use three 5-ml portions of absolute ethanol, containing 3 to 5 drops of concentrated HCl in the transfer.

(8) Wash the barium chloride with three 5-ml portions of anhydrous ethyl ether.

(9) Transfer precipitate and filter paper disc to a vacuum desiccator.

(10) Evacuate for two minutes, slowly release suction, evacuate for five minutes, and again slowly release suction.

(11) Weigh as $BaCl_2 \cdot H_2O$ to constant weight, record chemical yield, and β^- count for Ba^{140} determination.

3.6 Cd^{109} and Ag^{110} in IPC Filter Samples

3.6.1 SILVER SEPARATION AND PURIFICATION

(1) The solution from 2.3.3 step (6) containing an accurately known amount of cadmium carrier equivalent to about 5 mg of Cd is evaporated to incipient dryness. (Rhodium, strontium, manganese, and cerium carriers in accurately known amounts may also be present should these nuclide determinations be desired).

NOTE: Silver carrier is not added due to the presence of chloride ion, which would precipitate silver chloride. About 5 mg of zirconium carrier is also present as a holdback. About 7 mg of thallium and 1 mg of tellurium carriers are also present, if rhodium is being determined.

(2) Wash down the sides of the beaker with about 5 ml of concentrated HNO_3 and again evaporate to incipient dryness.

NOTE: Removal of chloride ion.

(3) Repeat 3.6.1 step (2) two more times, adding about 0.2 ml of 30 percent hydrogen peroxide, if necessary.

NOTE: The addition of 30 percent hydrogen peroxide may be required to prevent precipitation of manganese dioxide if manganese carrier has been added.

(4) Add 10 ml of 6M HNO_3 and heat gently to dissolve any salts.

NOTE: Dropwise addition of 30 percent hydrogen peroxide may be necessary to effect complete solution.

(5) Remove the solution from the hot plate and add an accurately known quantity of silver carrier equivalent to about 10 mg.

NOTE: Silver chloride should not precipitate at this point.

(6) Boil gently for about five minutes and transfer the solution to a 40-ml centrifuge tube.

(7) Adjust the volume to about 15 ml with 6M HNO_3 and then add about 0.5 ml of 0.1 percent Aerosol OT solution.

(8) Bring the solution to a boil and add 1 ml of 1M HCl.

NOTE: Precipitation of silver chloride.

(9) Heat gently to coagulate the precipitate, centrifuge, and reserve the supernate in a 125-ml Erlenmeyer flask for cadmium separation and purification.

NOTE: The supernate also contains those carriers present in 3.6.1 step (1).

(10) Dissolve the silver chloride in 2 ml of concentrated NH_4OH and dilute to 15 ml with distilled water.

NOTE: Gentle heating will aid in the dissolution.

(11) Add 2 to 3 mg of ferric carrier and centrifuge. Transfer supernate to a 40-ml centrifuge tube and discard the precipitate.

NOTE: Ferric hydroxide scavenge.

(12) Add 1 ml of a saturated solution of ammonium sulfide to the supernate and stir vigorously.

NOTE: Precipitation of silver sulfide.

(13) Centrifuge and discard the supernate.

(14) Add 1 ml of concentrated HNO_3 to the precipitate and heat carefully until dissolution is effected.

(15) Dilute the solution to about 20 ml with distilled water.

(16) Bring the solution to a boil and add 1 ml of 1M HCl.

(17) Heat gently to coagulate the precipitate, centrifuge, and discard the supernate.

(18) Repeat 3.6.1 steps (10) to (14).

(19) Add 6M NaOH until the solution is alkaline and a precipitate is produced, then add about 0.3 ml in excess.

(20) Centrifuge and discard the supernate.

(21) Dissolve the precipitate in about 0.2 ml of concentrated H_2SO_4 and then evaporate to dryness.

(22) Cool and dissolve the residue in 20 ml of distilled water.

(23) Add 1 ml of 2M iodic acid, centrifuge, and discard supernate.

NOTE: Precipitation of silver iodate.

(24) Dissolve the precipitate in about 0.4 ml of concentrated NH_4OH. Wash down the sides of the centrifuge tube with about 1 ml of distilled water.

NOTE: If any sulfur residue is present, centrifuge and discard it.

(25) Add about 0.3 ml of concentrated H_2SO_4 and about 0.3 ml of distilled water.

NOTE: Reprecipitation of silver iodate.

(26) Filter the precipitate through a pretreated, tared Whatman No. 542 filter paper disc, using a Millipore filter chimney and suction.

(27) Wash the precipitate with three 3-ml portions of 95 percent ethanol.

(28) Dry in an oven at 110°C for fifteen minutes. Cool, weigh as $AgIO_3$, record chemical yield, and γ count for Ag^{110} determination.

3.6.2 CADMIUM SEPARATION AND PURIFICATION

(1) Evaporate the supernate from 3.6.1 step (9) almost to dryness.

(2) Add about 3 ml of concentrated HCl and again evaporate almost to dryness.

(3) Repeat 3.6.2 step (2) two more times to insure complete removal of oxides of nitrogen.

(4) Dissolve the residue with 2 ml of concentrated HCl and gentle warming.

(5) Dilute the resulting solution to about 15 ml with distilled water and transfer to a 40-ml centrifuge tube.

(6) Add 2 ml of 6 percent sulfurous acid with vigorous stirring followed by the addition of 1 ml of 57 percent hydriodic acid (phosphorus-free).

NOTE: Tellurium and thallium iodide scavenge. Steps (6) to (18) of this section are carried out only if rhodium carrier is present. If no rhodium carrier is present, the residue from 3.6.2 step (3) contained in a 125-ml Erlenmeyer flask is used, proceeding with 3.6.2 step (19).

(7) Centrifuge and discard the precipitate.

(8) To the supernate, add 10 ml of concentrated HCl and about 2 ml of 57 percent hydriodic acid (phosphorus free).

(9) Boil vigorously for about twenty minutes maintaining the volume constant at about 20 ml by repeated additions of 6M HCl.

NOTE: Precipitation of rhodium iodide.

(10) Centrifuge and transfer the supernate to a 125-ml Erlenmeyer flask.

NOTE: Rhodium is removed, since it interferes with the cadmium sulfide separation.

(11) Wash the precipitate with about 10 ml of 6M HCl, combining the washings with the supernate of 3.6.2 step (10).

(12) Reserve the precipitate for rhodium purification. [See 3.3.2 step (11).]

(13) Very carefully add about 5 ml of concentrated HNO_3 to the supernate from 3.6.2 step (10).

(14) Very gently warm the solution to initiate the reaction. After effervescence ceases, evaporate the solution to incipient dryness.

(15) If the iodine has not been completely removed, add more concentrated HNO_3 to the residue and again evaporate to incipient dryness.

(16) Add 5 to 10 ml of concentrated HCl to the residue and evaporate almost to dryness.

(17) Wash down the sides of the flask with 6M HCl and again evaporate almost to dryness.

(18) Repeat 3.6.2 steps (16) and (17) two more times.

(19) Dissolve the residue in about 20 ml of 0.2M HCl, using gentle heat. About 0.3 ml of 30 percent hydrogen peroxide may be used to aid in dissolution.

NOTE: If hydrogen peroxide is used, boil the solution for a few minutes to remove any excess.

(20) Cool the solution and transfer it to a 40-ml centrifuge tube, using about 4 ml of distilled water in the transfer.

(21) Saturate the solution with H_2S for about three minutes, centrifuge, and reserve the supernate for subsequent analysis depending upon carriers present in 3.6.1 step (1).

NOTE: Precipitation of cadmium sulfide.

(22) Dissolve the precipitate in 5 ml of 6M HCl, add about 1 mg of palladium carrier, heat to boiling, and saturate the solution with H_2S.

NOTE: Precipitation of palladium sulfide. Cadmium sulfide does not precipitate at this pH.

(23) Allow the precipitate to stand for about five minutes and then gravity filter through Whatman No. 42 filter paper into a clean 40-ml centrifuge tube.

NOTE: Discard precipitate.

(24) Evaporate the filtrate to dryness, cool, and dissolve the residue in 15 ml of distilled water.

(25) Add about 1 mg of ferric carrier and 1 ml of 6M ammonium acetate.

NOTE: Basic ferric acetate scavenge.

(26) Boil the mixture, centrifuge, and discard the precipitate.

(27) To the supernate, add 1 ml of 6M ammonium acetate.

(28) Boil the mixture and add about 1 mg more of ferric carrier.

(29) Centrifuge, discard precipitate, and transfer supernate to a 40-ml centrifuge tube.

(30) Add 1 ml of 6M HCl and saturate the solution with H_2S.

NOTE: Precipitation of cadmium sulfide.

(31) Centrifuge and discard the supernate.

(32) Repeat 3.6.2 steps (22) to (31).

(33) Dissolve the precipitate in 1 ml of 6M HCl and evaporate to dryness.

(34) Wash down the sides of the centrifuge tube with a minimum amount of distilled water and add about 0.5 ml of concentrated H_2SO_4.

(35) Heat the mixture until fumes of SO_3 are evolved.

(36) Cool and wash down the sides of the centrifuge tube with a minimum amount of distilled water.

(37) Again heat the mixture until the cadmium salts begin to appear.

NOTE: Do not heat to dryness.

(38) Cool and dissolve the precipitate in about 0.5 ml of distilled water.

(39) Add 6M sodium hydroxide until the solution is just alkaline to phenolphtalein.

NOTE: Precipitation of cadmium hydroxide.

(40) Cautiously add 10 percent potassium cyanide solution dropwise until the precipitate just dissolves, avoiding an excess.

NOTE: Formation of $Cd(CN)_4^{-2}$.

(41) Transfer the solution to an electroplating cell of approximately 3-ml capacity (see Figure 3), using distilled water to effect the transfer. To the cell, also add about 0.2 ml of 0.03 percent gelatin solution.

NOTE: The volume of liquid in the cell should be about 85 percent of full capacity.

(42) Cadmium is electroplated onto a tared platinum disc (3/8-inch diameter, 0.001-inch thick) by electrolysis at 10-15 milliamperes for three hours (see Figure 4).

(43) Remove the anode while the current is still on and then remove the platinum disc from the plating cell.

(44) Wash the platinum disc with several portions of distilled water followed by several portions of 95 percent ethanol.

(45) Dry in an oven at 105°C for ten minutes. Cool, weigh as elemental Cd, record chemical yield, and x-ray count for Cd^{109}.

3.7 Mn^{54}, Sr^{89}, Sr^{90}, Zr^{95}, Ce^{141}, and Ce^{144} in Polystyrene Filters and Impactor Samples, Alternative Method

3.7.1 STRONTIUM SEPARATION AND PURIFICATION; YTTRIUM MILKING

(1) Evaporate the solution from 2.2.1 step (6), 2.4.1 step (4), or 2.4.2 step (9), containing the following carriers in accurately known amounts: cerium equivalent to about 65 mg $Ce(IO_3)_4$, strontium equivalent to about 265 mg $SrCO_3$.

manganese equivalent to about 15 mg MnO_2, and zirconium equivalent to about 70 mg of ZrO_2, to about 5 ml in a 150-ml beaker.

(2) Add about 5 ml of concentrated HNO_3 and evaporate to near dryness.

(3) Wash down the walls of the beaker with concentrated HNO_3 and repeat 3.7.1 step (2) twice.

NOTE: Destruction of organic matter.

(4) Add 4 ml of concentrated HCl, 1 ml of concentrated HNO_3, and a few ml of distilled water. Heat gently until solution is effected.

NOTE: The addition of 0.2 to 0.3 ml of 30 percent hydrogen peroxide may be necessary to effect complete dissolution.

(5) Adjust volume to about 50 ml with distilled water and add about 0.5 ml of 30 percent hydrogen peroxide.

(6) Adjust the pH to 10 or 11, using concentrated NH_4OH.

NOTE: Precipitation of hydroxides of manganese, zirconium, and cerium.

(7) Gently heat the mixture for about three minutes and allow it to cool for ten minutes.

NOTE: Readjust pH to 10 or 11 with concentrated NH_4OH if necessary.

(8) Centrifuge and transfer the supernate to a 250-ml beaker.

NOTE: If the supernate is not colorless, add about 0.3 ml of 30 percent hydrogen peroxide and repeat 3.7.1 step (7).

(9) Wash the precipitate with a 1 percent solution of NH_4OH, centrifuging and combining the washes with the supernate of 3.7.1 step (8).

(10) Dissolve the precipitate in a minimum amount of $6\underline{M}$ HCl.

(11) Add about 0.3 ml of 30 percent hydrogen peroxide and repeat 3.7.1 steps (6) to (9).

(12) Reserve the precipitate for subsequent analysis.

(13) Acidify the solution from 3.7.1 step (8) with concentrated HCl and evaporate until salting out occurs.

(14) Remove mixture from heat source and cautiously add 10 to 20 ml of concentrated HNO_3.

(15) When the reaction has subsided, evaporate to incipient dryness.

(16) Repeat 3. 7. 1 steps (14) and (15).

NOTE: Removal of excess ammonium chloride is necessary to ensure a satisfactory strontium yield.

(17) Dissolve the residue of 3. 7. 1 step (15) in about 5 ml of 4$\underline{M}$ HCl, using a little heat if necessary.

(18) Transfer the resulting solution to a 40-ml centrifuge tube, using distilled water in the transfer.

(19) Make the solution alkaline to phenolphthalein indicator, using 6$\underline{M}$ sodium hydroxide.

(20) Heat the solution to boiling and add 10 ml of a saturated solution of sodium carbonate with stirring.

NOTE: Precipitation of strontium carbonate.

(21) Digest the mixture in a hot water bath for thirty minutes to ensure complete precipitation.

(22) Cool, centrifuge, and test the supernate for completeness of precipitation. Discard supernate.

(23) Dissolve the precipitate in 5 ml of 6$\underline{M}$ HNO_3.

(24) Proceed with 3. 1. 1 steps (5) to (28) and 3. 1. 2 steps (1) to (15).

3. 7. 2 MANGANESE SEPARATION AND PURIFICATION

(1) Dissolve the precipitate from 3. 7. 1 step (12), using about 3 ml of 6$\underline{M}$ HCl and about 0. 4 ml of 30 percent hydrogen peroxide.

NOTE: Gentle heat may be necessary to effect complete solution.

(2) Transfer the solution to a 150-ml beaker using distilled water in the transfer.

(3) Evaporate the solution to near dryness and add about 5 ml of concentrated HNO_3.

(4) Repeat 3. 7. 2 step (3) two more times.

NOTE: Removal of chloride ion.

(5) To the residue, add about 40 ml of concentrated HNO_3 and boil until oxides of nitrogen have been removed.

NOTE: About 0.3 ml of 30 percent hydrogen peroxide may be necessary to effect complete solution. Boil off excess peroxide, if used.

(6) Cover the beaker with a watch glass and cautiously add 1 to 2 g of potassium chlorate in small increments, replacing the watch glass after each addition of potassium chlorate.

NOTE: This precipitation of manganese dioxide is best carried out while the mixture is at a brisk boil.

(7) Remove the beaker from the heat source and wash the watch glass with cold distilled water, collecting the washings in the beaker.

(8) Cool the mixture in an ice bath for about ten minutes.

(9) Centrifuge and reserve the supernate in a 250-ml beaker for zirconium and cerium separation.

(10) Wash the precipitate with 10 to 15 ml of distilled water, centrifuging and adding the washings to the supernate of 3.7.2 step (9).

(11) Proceed with 3.1.4 steps (10) to (44).

3.7.3 ZIRCONIUM AND CERIUM SEPARATION

(1) Evaporate the supernate from 3.7.2 step (9) until salting out occurs.

(2) Wash the walls of the beaker with 6M HCl, cautiously add about 10 ml of concentrated HCl, and then evaporate to near dryness.

(3) Repeat 3.7.3 step (2).

(4) Add about 5 ml of concentrated HCl and heat gently.

(5) Cool, centrifuge, and decant the supernate into a 40-ml centrifuge tube.

(6) Wash the precipitate with about 3 ml of 6M HCl and centrifuge.

(7) Add the washings to the supernate of 3.7.3 step (5) and discard the precipitate.

NOTE: If the precipitate shows a yellow discoloration, repeat 3.7.3 steps (6) and (7).

(8) Cautiously adjust the pH of the supernate from 3.7.3 step (5) to 10 with concentrated NH_4OH.

NOTE: Precipitation of zirconium and cerium hydroxides.

(9) Digest the precipitate, cool, and centrifuge. Discard the supernate.

(10) Dissolve the precipitate in 10 ml of concentrated HCl.

(11) Proceed with 3.1.5.1 steps (6) to (20) and 3.1.5.2 steps (1) to (14).

4. PREPARATION OF CARRIER SOLUTIONS

a. Antimony carrier. Carefully add 5.5 ml of $SbCl_5$ to 250 ml of concentrated HCl and cautiously dilute to 500 ml with distilled water.

b. Barium carrier. Dissolve 14.3 g of $Ba(NO_3)_2$ in enough distilled water to make 500 ml.

c. Beryllium carrier. Dissolve 46.0 g of $Be(NO_3)_2 \cdot 3H_2O$ in enough distilled water to make 1000 ml.

d. Bismuth carrier. Dissolve 58.0 g of $Bi(NO_3)_3 \cdot 5H_2O$ in a sufficient quantity of concentrated HNO_3 and dilute to 1000 ml with distilled water.

e. Cadmium carrier. Dissolve 13.7 g of $Cd(NO_3)_2 \cdot 4H_2O$ in a sufficient quantity of distilled water. Slightly acidify the solution with HCl and add enough distilled water to make 500 ml.

f. Cerium carrier. Dissolve 15.5 g of $Ce(NO_3)_3 \cdot 6H_2O$ in enough distilled water to make 500 ml.

g. Copper carrier. Dissolve 13.4 g of $CuCl_2 \cdot 2H_2O$ in enough distilled water to make 500 ml.

h. Ferric carrier. Dissolve 48.4 g of $FeCl_3 \cdot 6H_2O$ in enough 1<u>M</u> HCl to make 1000 ml.

i. Lanthanum carrier. Dissolve 3.1 g of $La(NO_3)_3 \cdot 6H_2O$ in enough distilled water to make 100 ml.

j. Manganese carrier. Dissolve 18.0 g of $MnCl_2 \cdot 4H_2O$ in enough 1 percent HCl to make 500 ml.

k. Niobium carrier. Fuse 0.7 g of Nb_2O_5 with about 3 g of potassium bisulfate. Leach the cooled melt with 80 ml of a saturated solution of oxalic acid with the aid of gentle heat and stirring. Cool and gravity filter through Whatman No. 42 filter paper. Dilute the filtrate to 100 ml with saturated oxalic acid solution.

l. Palladium carrier. Dissolve 1.7 g of $PdCl_2$ in about 60 ml of concentrated HCl. Carefully dilute the resulting solution to 100 ml with distilled water.

m. Phosphorus carrier. Dissolve 17.0 g of $(NH_4)_2HPO_4$ in enough distilled water to make 500 ml.

n. Rhodium carrier. Dissolve 1.0 g of $Rh(NO_3)_3 \cdot 2H_2O$ in enough distilled water to make 200 ml.

o. Silver carrier. Dissolve 7.9 g of $AgNO_3$ in a sufficient amount of distilled water. Slightly acidify the solution with HCl and dilute to 500 ml with distilled water.

p. Sodium carrier. Dissolve an accurately known amount of NaCl (about 25.4 g) in enough distilled water to make 1000 ml.

q. Strontium carrier. Dissolve 185 g of $Sr(NO_3)_2$ in enough distilled water to make 500 ml.

r. Sulfur carrier. Dissolve 39 g of K_2SO_4 in enough distilled water to make 1000 ml.

s. Tellurium carrier. Dissolve 1.7 g of Na_2TeO_3 in enough distilled water to make 100 ml. Filter.

t. Thallium carrier. Carefully dissolve 1.0 g of Tl_2O_3 in about 50 ml of concentrated HCl and dilute with enough distilled water to make 100 ml.

u. Tungsten carrier. Dissolve 17.9 g of $Na_2WO_4 \cdot 2H_2O$ in enough distilled water to make 1000 ml.

v. Yttrium carrier. Place 31 g of Y_2O_3* in an 800-ml beaker. Slowly add 150 ml of concentrated HCl. Cover beaker with a watch glass, place in an ice bath, and allow to stand overnight. If solution has not been effected the next day, add 50 ml more of concentrated HCl and stir. Use of gentle heat and stirring may be necessary to effect complete solution. Cool and dilute with distilled water to 500 ml.

w. Zirconium carrier. Dissolve 3.1 g of $ZrO_2(NO_3)_2 \cdot 2H_2O$ in a sufficient amount of distilled water. Add about 0.5 ml of concentrated HNO_3 to the resulting solution and then dilute to 200 ml with distilled water.

5. STANDARDIZATION OF CARRIER SOLUTIONS

5.1 Barium Carrier

(1) To each of three 5.0-ml portions of carrier solution in 250-ml beakers, add 75 ml of HCl-ether reagent (5:1).

(2) Cool in a cold water bath for about 15 minutes while stirring.

NOTE: Maximum yield obtained at about 5°C.

(3) Filter through a pretreated, tared, sintered glass crucible of medium porosity with suction using three 5-ml portions of absolute ethanol for the transfer.

(4) Wash precipitate with three 5-ml portions of absolute ethanol containing 4 percent HCl.

(5) Wash precipitate with three 5-ml portions of anhydrous ethyl ether and place crucible in a vacuum desiccator.

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*Lindsay Chemical Div., American Potash and Chemical Corp., West Chicago, Illinois.

(6) Evacuate the desiccator for two minutes, release suction, and evacuate again for five minutes.

NOTE: Release suction slowly to prevent rapid influx of air.

(7) Repeat desiccation to constant weight and weigh precipitate as $BaCl_2 \cdot H_2O$.

5.2 Beryllium Carrier

(1) To each of three 5.0-ml portions of carrier solution contained in 150-ml beakers, add 5 ml of 4M ammonium chloride and 5 ml of 10 percent sodium tartrate solution.

(2) Dilute to 50 ml with distilled water and heat to 60 to 70°C.

(3) Adjust pH to about 9 with 2M NH_4OH.

(4) Add dropwise, with stirring, 20 to 30 percent excess of the calculated amount of 2 percent 8-hydroxyquinaldine solution required to completely precipitate the beryllium present.

NOTE: 8-hydroxyquinaldine is also known as 8-hydroxy-2-methylquinoline, 2-methyl-8-quinolinol, or 2-methyl oxine, having the empirical formula $C_{10}H_9NO$.

(5) Digest the precipitate at 60 to 70°C for about thirty minutes.

(6) Filter the precipitate through a pretreated, tared, sintered glass crucible of medium porosity with suction using 1:100 NH_4OH in the transfer.

(7) Wash with several portions of 1:100 NH_4OH and dry at 110°C to constant weight and weigh as $Be(C_{10}H_8NO)_2$.

NOTE: The precipitate is yellow and crystalline and exhibits a bright green fluorescence when viewed under short-wave ultraviolet light.

5.3 Bismuth Carrier

(1) Place each of three 10.0-ml portions of carrier solution into 400-ml beakers.

(2) Dilute to 200 ml with distilled water.

(3) Add 6M NH_4OH until the solution is slightly turbid, then add 20 ml of a freshly prepared saturated solution of ammonium carbonate.

(4) Heat to boiling, cool, test for completeness of precipitation, and filter through Whatman No. 42 filter paper, using filter paper pulp and suction. Effect transfer with 0.5 percent ammonium carbonate solution.

(5) Wash precipitate with 0. [illegible] percent ammonium carbonate solution and transfer precipitate, paper, and pulp to a tared porcelain crucible.

(6) Place crucible and contents in a cold muffle furnace and gradually raise temperature to 600°C.

(7) Continue ignition at 600°C for two hours.

(8) Cool and weigh as Bi_2O_3.

NOTE: If, after ignition, some of the yellow bismuth oxide has been reduced to silver or red bismuth metal, dissolve in a minimum of 1:1 HNO_3, evaporate to dryness on a hot plate, transfer to a cold muffle furnace, and ignite as before.

5.4 Cadmium Carrier

(1) Evaporate each of three 5.0-ml portions of the carrier solution contained in 100-ml beakers to dryness.

NOTE: Do not allow salts to bake.

(2) Dissolve the residue in 20 ml of distilled water.

(3) Add 2 ml of 3<u>M</u> ammonium chloride solution.

(4) Add 2 ml of 1.5<u>M</u> dibasic ammonium phosphate dropwise while stirring and boiling.

(5) Discontinue heating and allow the mixture to cool to room temperature.

(6) Filter through a pretreated, tared, sintered glass crucible of medium porosity.

(7) Wash the precipitate with several portions of distilled water followed by several portions of 95 percent ethanol.

(8) Dry in an oven at 110°C for thirty minutes, cool, and weigh as $CdNH_4PO_4 \cdot H_2O$.

5.5 Cerium Carrier

(1) To each of three 2.0-ml portions of carrier solution contained in 250-ml beakers, add 10 ml of concentrated HNO_3.

(2) Add 20 ml of 0.35<u>M</u> iodic acid and immerse in an ice bath.

(3) Add 2 ml of a saturated solution of sodium bromate and digest in a steam bath for ten minutes.

NOTE: Precipitation of ceric iodate.

(4) Cool in an ice bath for ten minutes, with stirring.

(5) Filter the precipitate through a pretreated, tared, sintered glass crucible of fine porosity.

(6) Wash with several portions of iodate wash solution (0.18M iodic acid in 10 percent HNO_3).

(7) Dry in an oven at 110°C to constant weight and weigh as $Ce(IO_3)_4$.

5.6 Manganese Carrier

(1) Transfer three 2.0-ml portions of carrier solution into 150-ml beakers and add 100 ml of distilled water.

(2) Add 2 g of solid ammonium chloride and 1 ml of 1.5M dibasic ammonium phosphate.

NOTE: If a precipitate forms here, add enough 1M HCl to dissolve it.

(3) Bring the solution to a boil and, while stirring, add 1:1 NH_4OH dropwise until complete precipitation is effected.

(4) Continue boiling until the precipitate loses its flocculent appearance and appears crystalline.

(5) Discontinue heating and add about 0.5 ml of 1:1 NH_4OH.

(6) Cover beaker with a watch glass and cool in an ice bath for two hours with occasional stirring.

NOTE: A slight excess of NH_4OH should be present as evidenced by its odor.

(7) Gravity filter the precipitate through Whatman No. 42 filter paper and wash with a 10 percent solution of ammonium nitrate, made slightly alkaline by the addition of NH_4OH.

(8) Continue washing until chloride ion has been completely removed.

NOTE: Presence of chloride ion will cause reduction of manganese during ignition.

(9) Ignite over a Meker burner and continue ignition in a muffle furnace at 1000°C.

(10) Cool and weigh as $Mn_2P_2O_7$.

5.7 Phosphorus Carrier

(1) To each of three 10.0-ml portions of carrier solution contained in 200 ml beakers, add 20 ml of magnesia mixture I, and a few drops of concentrated NH_4OH.

(2) Allow to stand for five minutes with occasional stirring, then add 10 ml of concentrated NH_4OH, with stirring.

(3) Cover the beaker with a watch glass and place in an ice bath and allow to stand overnight.

(4) Collect the precipitate on Whatman No. 42 filter paper, using suction, and wash with 10-ml portions each of 1:20 NH_4OH, 50 percent ethanol, and 95 percent ethanol.

(5) Transfer precipitate and filter paper to a tared porcelain crucible and ignite over a Meker burner.

(6) Cool, add a small amount of solid ammonium nitrate, and reignite over a Meker burner.

NOTE: Increase flame intensity in increments to prevent "popping".

(7) Finally place crucible and contents into a muffle furnace at about 700°C for two hours.

(8) Advance temperature to 1000°C and ignite for thirty minutes to constant weight.

(9) Cool in a desiccator and weigh as $Mg_2P_2O_7$.

5.8 Rhodium Carrier

(1) To each of three 1.0-ml portions of carrier solution contained in 40-ml centrifuge tubes, add 1 ml of concentrated H_2SO_4 and heat to fumes of SO_3.

(2) Cool and transfer to an electroplating cell of approximately 3 ml capacity (see Figure 3), using a minimum amount of water to effect the transfer.

(3) Electroplate rhodium onto a tared platinum disc (3/8-inch diameter, 0.001-inch thick) by electrolysis at about 75 milliamperes for about sixteen hours (see Figure 4).

(4) Remove the platinum disc from the cell, rinse with distilled water and with 95 percent ethanol.

(5) Dry in an oven at 110°C for fifteen minutes to constant weight.

(6) Cool and weigh as elementary Rh.

5.9 Silver Carrier

(1) To each of three 2.0-ml portions of carrier solution contained in 40-ml centrifuge tubes, add 1 ml of 2$\underline{M}$ iodic acid and stir vigorously.

NOTE: Test for completeness of precipitation.

(2) Collect the precipitate on a pretreated, tared, sintered glass crucible of medium porosity.

(3) Wash the precipitate with two 5-ml portions of 95 percent ethanol.

(4) Dry in an oven at 110°C for fifteen minutes to constant weight.

(5) Cool and weigh as $AgIO_3$.

5.10 Sodium Carrier

(1) chemical standardization is performed. An accurately weighed quantity of reagent grade sodium chloride is dissolved in an accurately known volume of distilled water and the amount of sodium per ml of solution is calculated.

5.11 Strontium Carrier

(1) To each of three 10.0-ml portions of carrier solution contained in 150-ml beakers, add about 60 ml of a saturated solution of ammonium carbonate.

(2) Digest on a hot plate at low heat for about thirty minutes with occasional stirring.

> NOTE: Test for completeness of precipitation by adding a few ml more of the saturated solution of ammonium carbonate.

(3) Filter through a pretreated, tared, sintered glass crucible of medium porosity and wash with three 5-ml portions of distilled water.

(4) Dry in an oven at 110°C for about one hour to constant weight.

(5) Cool in a desiccator and weigh as $SrCO_3$.

5.12 Sulfur Carrier

(1) To each of three 5.0-ml portions of carrier solution contained in 150-ml beakers, add 45 ml of distilled water.

(2) Adjust pH of solution to 1 using 6M HCl and heat nearly to boiling.

(3) Add 10 ml of 10 percent barium chloride solution with stirring.

(4) Digest on a hot plate for about one hour and allow to stand overnight at 25°C.

> NOTE: Precipitation of barium sulfate.

(5) Filter the precipitate, using Whatman No. 42 filter paper and suction.

(6) Wash precipitate with several 10-ml portions of distilled water.

(7) Transfer precipitate and filter paper to a porcelain crucible and ignite over a Meker burner for twenty minutes.

(8) Complete the ignition in a muffle furnace for about one hour at 800 ±50°C to constant weight.

(9) Cool in a desiccator and weigh as $BaSO_4$.

5.13 Tungsten Carrier

(1) To each of three 10.0-ml portions of carrier solution contained in 125-ml Erlenmeyer flasks, add 2 ml of glacial acetic acid and 8 ml of 6<u>M</u> ammonium acetate solution.

(2) Heat on a steam bath to about 80°C.

(3) Add a few drops of 1 percent Aerosol OT solution and 5 ml of 5 percent solution of 8-hydroxyquinoline in 2<u>M</u> acetic acid.

(4) Heat on a steam bath until the 8-hydroxyquinoline derivative of tungsten coagulates.

> NOTE: Coagulation may be aided by bringing the solution to a boil over an open flame.

(5) Filter the precipitate through a pretreated, tared, sintered glass crucible of medium porosity.

(6) Wash with three 5-ml portions of distilled water and one 5-ml portion of absolute ethanol.

(7) Dry the precipitate in an oven at 110°C for thirty minutes to constant weight.

(8) Cool in a desiccator and weigh as $WO_2(C_9H_6ON)_2$.

5.14 Yttrium Carrier

(1) To each of three 5.0-ml portions of carrier solution contained in 400-ml beakers, add 40 ml of 2M HCl and 40 ml of distilled water.

(2) Heat the solution to incipient boiling.

(3) Add hot 10 percent oxalic acid solution in 1-ml portions while stirring.

> NOTE: Avoid supersaturation.

(4) When the yttrium oxalate has been precipitated, add more hot 10 percent oxalic acid solution until the volume is twice that at the start of step (3).

(5) Digest on a hot plate at low for ten minutes and cool to room temperature.

(6) Filter the yttrium oxalate through a pretreated, tared, porous bottom porcelain crucible using suction.

(7) Ignite the crucible and precipitate at 800 ±25°C to constant weight.

(8) Cool in a desiccator and weigh as Y_2O_3.

5.15 *Zirconium Carrier*

(1) To each of three 5.0-ml portions of carrier solution, add 20 ml of distilled water.

(2) Adjust the pH to 10 with 1:1 NH_4OH.

NOTE: Precipitation of zirconium hydroxide.

(3) Allow the mixture to stand for about fifteen minutes.

(4) Gravity filter the mixture through Whatman No. 40 filter paper.

(5) Wash the precipitate with two portions of 1:100 NH_4OH.

(6) Transfer the filter paper and precipitate to a tared porcelain crucible and ignite over a Meker burner.

(7) Continue the ignition in a muffle furnace at 1200°C.

(8) Cool and weigh as ZrO_2.

6. SPECIAL REAGENTS

a. Ammonium molybdate reagent. Dissolve 100 g of ammonium molybdate tetrahydrate in 400 ml of distilled water and add 80 ml of concentrated NH_4OH.

b. Butanol-chloroform mixture, 10 percent. Mix 100 ml of 1-butanol (n-butyl alcohol) with 900 ml of chloroform.

c. Cinchonine solution, 10 percent. Dissolve 10 g of cinchonine in enough 1:1 HCl to make 100 ml.

d. Hydrochloric acid - ether reagent. Carefully mix 5 parts by volume of concentrated HCl to 1 part by volume of anhydrous ethyl ether.

e. 8-hydroxyquinaldine, 2 percent. Dissolve 2 g of 8-hydroxyquinaldine in 4 ml of glacial acetic acid and dilute with enough distilled water to make 100 ml. This solution is stable for about one week.

f. Iodine solution, 0.1 N. Dissolve 1.3 g of iodine crystals in 10 ml of distilled water in which 4 g of potassium iodide have been dissolved. Dilute to 100 ml with distilled water.

g. Magnesia mixture I. Dissolve 100 g of magnesium chloride hexahydrate and 200 g of ammonium chloride in a minimum amount of distilled water. Add about 0.5 ml of concentrated HCl and dilute with enough distilled water to make 1000 ml.

h. Magnesia mixture II. Dissolve 55 g of magnesium chloride hexahydrate and 140 g of ammonium chloride in a minimum amount of distilled water. Add 130 ml of concentrated NH_4OH and dilute with enough distilled water to make 1000 ml.

i. <u>Sodium precipitating reagent</u>. Dissolve 45 g of uranyl acetate dihydrate, 300 g of magnesium acetate tetrahydrate in 800 ml of distilled water containing 60 ml of glacial acetic acid. Dilute with enough distilled water to make 1000 ml. Add about 50 mg of sodium carrier and stir constantly for two hours. Allow the mixture to stand for several hours and filter using Whatman No. 42 filter paper and suction. Store the reagent in a polyethylene container.

j. <u>Sodium wash solution</u>. Combine 35 ml of glacial acetic acid, 405 ml of anhydrous ethyl acetate, and 460 ml of absolute ethanol in a polyethylene container.

k. <u>Sugar charcoal</u>. Place a quantity of granulated cane sugar in an evaporating dish and heat on a hot plate set at moderate temperature. Set up a 125-watt infrared heating lamp at about six inches from the surface of the sugar. Heat for about ninety minutes with intermittent mixing until a brownish-black mass of the desired consistency is produced. Reduce heat and continue heating until there is no appearance of smoke upon mixing. Cool the mixture, remove it from the evaporating dish, and pulverize using a porcelain mortar and pestle. Considerable experimentation is necessary in order to determine those heating conditions required to obtain a satisfactory sugar charcoal consisting of the optimum ratio of caramelized to carbonized sugar.

7. PREPARATION OF ION EXCHANGE COLUMNS

7.1 Zirconium Column

Place a wad of glass wool above the stopcock and add 20 ml of wet, settled, analytical-grade Dowex 1-X2 anion exchange resin (50 to 100 mesh) in the chloride form. After the resin settles in the column, pass 150 ml of concentrated HCl through at a flow rate not exceeding 3 ml per minute. Pass through 1 ml of niobium carrier and 100 ml of concentrated HCl. After use, the column may be regenerated by passing 250 ml of 0.5<u>M</u> HCl through the resin bed at a flow rate not exceeding 5 ml per minute.

7.2 Strontium Column

Place a wad of glass wool above the stopcock and add 25 ml of wet, settled, analytical-grade Dowex 50W-X8 cation exchange resin (100 to 200 mesh) in the hydrogen form. After the resin settles in the column, pass through 75 ml of 6<u>M</u> HCl. Then pass distilled water through until the excess acid is removed.

7.3 Rhodium Column

Place a wad of glass wool above the stopcock and add enough wet, settled, analytical-grade Dowex 1-X10 anion exchange resin (200 to 400 mesh) in the chloride form to measure about 3 to 4 cm in height when settled. Wash the resin bed with about 50 ml of distilled water.

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