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PROCEDURES FOR RADIOCHEMICAL ANALYSIS OF NUCLEAR REACTOR AQUEOUS SOLUTIONS

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OF NUCLEAR REACTOR AQUEOUS SOLUTIONS

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REVIEW NOTICE

FOREWORD

Man and his environment must be protected from the adverse effects of pesticides, radiation, noise and other forms of pollution, and the unwise management of solid waste. Efforts to protect the environment require a focus that recognizes the interplay between the components of our physical environment--air, water, and land. The National Environmental Research Centers provide this multidisciplinary focus through programs engaged in

> studies on the effects of environmental contaminants
> on man and the biosphere, and

> a search for ways to prevent contamination and to
> recycle valuable resources.

The current increase in the number of nuclear power stations requires expanded monitoring programs at the state and federal level to assure that radiation exposure of persons in the environment remain at an acceptably low level. The Environmental Protection Agency is therefore engaged in studies at operating nuclear power stations to provide information on environmental radiation and radioactivity levels and to evaluate monitoring programs. One aspect of these studies had been the collection, evaluation and, in some instances, modification of radiochemical analytical methods for measuring radionuclides in coolant and waste water at these stations. Presented in this manual are 38 methods that have been found appropriate for the commonly encountered radionuclides. This effort has been supported by the Office of Research and Monitoring, in cooperation with the Office of Radiation Programs, EPA.

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PREFACE

In the course of studies to evaluate potential health hazards from aqueous discharges at nuclear power stations during routine operations, the Radiochemistry and Nuclear Engineering Research Laboratory of the U. S. Environmental Protection Agency's National Environmental Research Center in Cincinnati has compiled and tested the radiochemical methods given in this manual. The composition of test solutions has ranged from mixtures of many radionuclides at microcuries per milliliter (μCi/ml) concentrations to barely detectable levels at picocuries per liter (pCi/l) concentrations. The substrate quality has ranged from highly deionized coolant water to waste solutions with high concentrations of salts and detergents.

The procedures in the front section of the manual are standard methods* which are applicable for separating and measuring these radionuclides in most reactor liquid wastes. Selected sections from each procedure have been reproduced verbatim from the standard text, with notes added at the end of each procedure to indicate where modifications were made or problems arose. Modifications were only employed to effect additional decontamination or to clarify the method for assuring uniformity in replicate analyses.

The methods in the second section have been compiled from information in analytical chemistry texts or from technical reports in the scientific literature. Many have been adapted from several sources, and all have been modified as deemed appropriate. Comparable procedures for barium, iodine, iron, manganese and tritium are to be found in both sections of the manual. These have been included with the other developed procedures, as personal preference, because they are simpler or more rapid than the ASTM methods and have been proven in comparable evaluations. All methods in this second section contain references to their origin and have explanatory notes when appropriate.

Method evaluation involved replicate analyses with reactor coolants, reactor wastes and specific tracer solutions as substrates. The criteria established for each method were chemical yields greater than 70%, decontamination factors at least 10^3, procedure time commensurate with the half life of the nuclide being separated, and ease of analysis. In general, the system followed for each radionuclide consisted of adding a standardized carrier to the test solution

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*ASTM Standards. Water; Atmospheric Analysis Part 23, American Society for Testing and Materials, Phila., Pa. 19103 (Oct. 1972).

to give about 20 mg as the final precipitate and stirring to effect complete interchange between the stable and radioactive components in the solution. Two of the procedures (neptunium and technetium) required non-isotopic carriers for yield determinations since standardized carriers are not available. For samples containing nuclides in several oxidation states, complete interchange with the stable carrier requires strong oxidative and/or reductive treatment during the initial steps of the procedure.

After concentrating the sample and purifying the nuclide by precipitation, evaporation, ion exchange, solvent extraction or distillation, the final precipitate is collected on a 2.8-cm glass fiber filter and washed with water and ethanol. Drying is effected either by oven heat or treatment with solvents and suction or both until a constant weight is obtained for chemical yield determination. The precipitate is prepared for counting by covering it with 0.01 mm mylar, and mounting it in a nylon ring and disc. The identification and activity level of the separated nuclide are confirmed by ingrowth and/or decay measurements, gamma-ray peak identification, and beta-particle absorption determinations. When required, repeated spectral analyses and decay measurements were made to identify and quantify the isotopes of the separated radionuclides (e.g., ^{134}Cs, ^{136}Cs and ^{137}Cs in the cesium chloroplatinate precipitate). The method capabilities and decontamination factors obtained for each procedure after replicate tests are given in Appendix C.2.

In the course of repetitive radiochemical analyses of reactor discharges, several problems were observed. These included incomplete purification (decontamination) of specific radionuclides in coolant water and reactor wastes; incomplete carrier-radionuclide exchange; loss of activity by adsorption on container or by volatility; and cross-contamination of separated fractions, particularly when very high- and low-level activity samples were analyzed simultaneously. Ultimately, the procedure to be selected and the modifications to be included are determined from experience. Activity loss on container walls, for example, is minimized (but not eliminated) by acidifying the sample at the source with conc. HNO_3 (1 volume acid to 10 volumes solution) and analyzing for all activities soon after collection. Radioiodine and carbon-14 analyses, however, are made on separate aliquots from an unacidified sample to prevent losing volatile fractions.

Many reactor-produced nuclides have half lives of less than one week and should be analyzed before much time has elapsed. The methods in this manual are applicable for the most frequently identified isotopes having a half life > 6 hr. To assist in performing

the maximum number of separations chronologically, a suggested order is included in Appendix C.3.

The users of this manual should be cautioned that, with the multitude of reactor and waste solutions generated, radionuclide and chemical compositions will vary and therefore require auxiliary treatment to effect desired decontamination. Although specific scavenges and repurification of the final precipitate have been effective in a few instances, no general approach can be recommended.

It is imperative that counter background and analyzer calibrations be monitored frequently to observe changes caused by contamination or electronic malfunction. In the laboratory, routine carrier standardizations and reagent purify checks are recommended and analytical capabilities should be confirmed by providing analysts with test samples and replicates for quality control. Routine carrier standardization involves the quantitative precipitation of aliquots in triplicate; weighing of the purified salt in the same geometrical configuration as the final precipitate in the procedure of concern; and repetition of the foregoing at intervals.

It is anticipated that for the nuclides discharged from light-water moderated nuclear power reactors today, the procedures in this manual will provide the analysts with a means for measuring specific radionuclides with some degree of confidence. As reactor types and operating procedures undergo changes, modifications to these methods may become necessary. Although this manual is primarily directed toward use of beta-particle counting with proportional or G-M counters and of gamma-ray spectrometry with NaI(Tl) detectors, Ge(Li) systems are becoming more widespread. The use of the latter, although somewhat more expensive, would minimize the need for much radiochemical separations except in the cases of pure beta emitters (^{14}C, ^{32}P, ^{35}S etc.). Readers are encouraged to submit comments on methods described in this manual and to indicate improvements which can be included in future revisions.

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SECTION I

A. ASTM Standard Methods

The full descriptive material for these five ASTM Standard Methods is not reproduced. The full Standard, including descriptive material, is obtainable from the American Society for Testing and Materials, 1916 Race St., Philadelphia, Pa. 19103. Reproduction of these Standards in this manual was through the permission of the Society.

Radioactive Barium — ASTM(D2038-68)

Principle of Method

Radioactive barium and added barium carrier are first precipitated from water to reduce the sample volume, then chemically purified, and finally counted with a gamma counter or beta particle detector. The main purification step is the repeated precipitation of barium chloride from a cold hydrochloric acid-ether mixture, and scavenging with ferric hydroxide. A final precipitation of barium sulfate is made and the chemical yield is computed by comparing the weight of the precipitate to the amount of carrier added originally. The recovery of radioactive barium is assumed to be equal to the chemical yield.

Reagents (Note 1)

Ammonium hydroxide solution (1:1)
Barium nitrate, carrier solution (19 g per liter)
Ethyl alcohol (95 per cent)
Ethyl ether
Ferric nitrate, carrier solution (72 g per liter)
Hydrochloric acid (sp gr 1.19)
Hydrochloric acid-ether mixture
Lanthanum nitrate, carrier solution (30.4 g per liter)
Sodium carbonate solution (106 g per liter)
Sulfuric acid solution (1:4)

Procedure

1. Add to the sample in a centrifuge tube, or a beaker in the case of a large sample, 1 ml of barium carrier solution and mix. Heat to near boiling. Then add an excess of Na_2CO_3 solution (Note 2), heat to boiling, and let stand for 5 min until precipitation of $BaCO_3$ is complete. Separate this precipitate by centrifugation, or by decanting and centrifugation in the case of a large sample.

2. Dissolve the carbonate precipitate in 1 ml of water and 4 drops of concentrated HCl (sp gr 1.19) and transfer the solution to a 40-ml

centrifuge tube. Add 10 ml of ice cold hydrochloric acid-ether mixture (Note 3) and cool in an ice bath for 5 min. Centrifuge the mixture and discard the supernate.

3. Dissolve the barium chloride ($BaCl_2$) in 1 ml of water and repeat the precipitation as described in step 2.

4. Dissolve the $BaCl_2$ in 2 ml of water, add 5 drops of both iron and lanthanum carriers and an excess of NH_4OH (1:1), and heat to precipitate the hydroxides. Centrifuge and discard the precipitate. Note the time of this step which removed any lanthanum daughter present. Complete the rest of the procedure, steps 5-7, in less than an hour.

5. Evaporate the supernate to 2 ml and add 10 ml of hydrochloric acid-ether reagent. Cool in an ice bath for 5 min and centrifuge to separate the precipitated $BaCl_2$.

6. Dissolve the $BaCl_2$ in 20 ml of water and add 3 ml of dilute sulfuric acid (1:4). Digest on a hot water bath for 5 min. Centrifuge the mixture and discard the supernate.

7. Transfer the precipitate to a tared quantitative filter paper using water. Wash with water, alcohol, and ether. Dry at $110^{\circ}C$ for 10 min, cool to room temperature, weigh as barium sulfate ($BaSO_4$), and mount for counting.

8. Count as soon as possible.

Calculation

Calculate the concentration, D, of radioactive barium in curies per liter as follows:

$$D = \frac{C}{2.22 \times 10^{12} \; EVR}$$

where:

C = net count rate, counts/min,
E = counter efficiency,
V = liters of sample used,
R = fractional chemical yield, and
2.22×10^{12} = conversion factor from disintegrations/min to curies.

Calculate the counter efficiency, E, for gamma-ray spectrometry as follows:

$$E = Fp$$

where:

F = fractional abundance of the gamma ray in gammas/disintegration, and
p = photopeak detection efficiency in counts/gamma ray.

Correct for the ingrowth of ^{140}La in samples containing ^{140}Ba as follows:

$$A_{La} = A_{Ba} \; \frac{e^{-0.693t_1/T_{Ba}} - e^{-0.693t_1/T_{La}}}{1 - T_{La}/T_{Ba}}$$

where:

A_{La} = lanthanum-140 activity present,

A_{Ba} = barium-140 activity present in step 4 (Note 4),

e = base of natural logarithms,

t_1 = elapsed time, in hours, from step 4 to counting time, and

T = half life of radioisotope, in hours.

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Calculate the decay correction for radioactive barium as follows:

$$A = A_o \, e^{-0.693t_2/T}$$

where:

t_2 = elapsed time, in hours, between sampling and counting.

Confirmation of ^{140}Ba Purity and Identification of Daughter Activities

1. Plot the gamma-ray spectrum of ^{140}Ba immediately after separation, then repeat after ^{140}La has grown in.
2. Count at 3-day intervals to measure the ingrowth of ^{140}La.
3. Beta-count weekly over a 30-day period to substantiate the 12.8 d half-life of ^{140}Ba.

Notes:
   1. The preparation of all reagents for this and the other ASTM procedures is listed in the back of Section I of this manual.
   2. An excess of reagent solution is that which assures that precipitation is complete.
   3. Caution. The hydrochloric acid-ether mixture should be prepared and stored in a fume hood. Naked flames must not be present.
   4. The ^{140}Ba activity, which is determined after step 8, should have no ^{140}La present if only 30 minutes has elapsed from the hydroxide scavenge (step 4) until counting time.

Radioactive Iodine (Distillation) — ASTM(D2334-68)

Principle of Method

This method is based on the separation of iodine from other activities by distillation of elemental iodine into cold carbon tetrachloride. To assure chemical interchange with the iodine carrier, an oxidation-reduction cycle is made. The iodide is oxidized to iodate with permanganate, reduced to iodide with bisulfite, and distilled over as free iodine in the presence of nitrite.

After washing the carbon tetrachloride with nitric acid, the iodine is reduced with bisulfite and back-extracted into water. Acidified silver nitrate solution is added to precipitate silver iodide. The chemical recovery is used as a measure of radiochemical recovery. Added decontamination from bromine activation product is afforded by the permanganate oxidation step. During this step elemental chlorine and bromine formed are distilled from the reaction flask and swept up the fume hood. High level radiobromine could be trapped by passing through a caustic solution, if desired.

The silver iodide precipitate is mounted for counting. Gamma counting of the purified iodine solution can be completed prior to precipitation of the silver iodide which is then used for determination of the chemical yield.

Reagents (Note 1)

Aerosol solution (1:100)
Carbon tetrachloride--Technical grade carbon tetrachloride (CCl_4)
Collodion solution (1:9)
Methyl orange indicator (0.5 g per liter)
Nitric acid solution (1:9)
Potassium iodide carrier solution (13.08 g per liter)
Potassium permanganate solution (saturated)
Silver nitrate solution (17 g per liter)
Sodium bisulfite solution (100 g per liter)
Sodium hydroxide solution (200 g per liter)
Sodium nitrite solution (100 g per liter)
Sulfuric acid (sp gr 1.84)
Sulfuric acid (1:9)
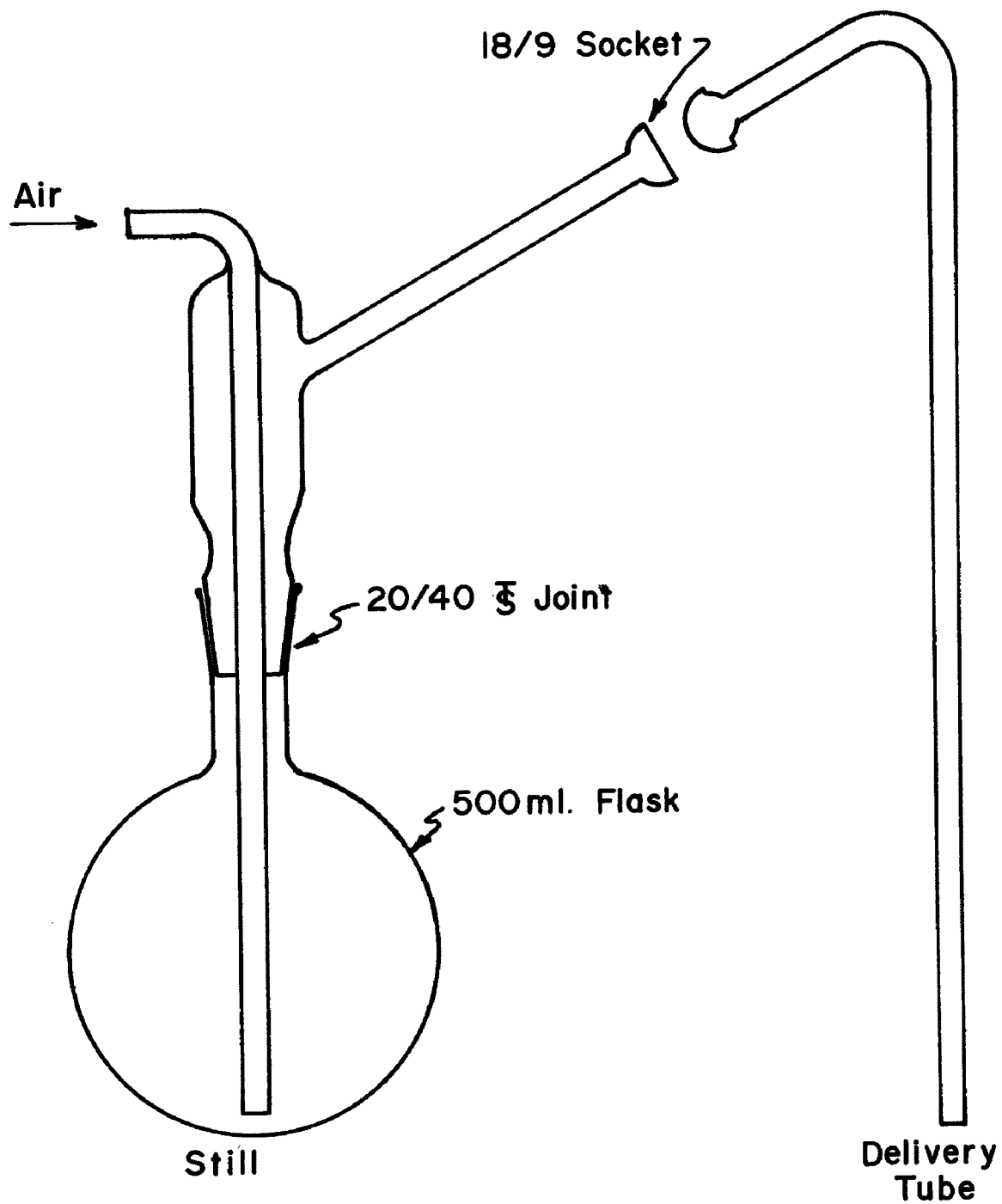
Figure 1. Distillation Apparatus for Iodine Analysis

Procedure

1. Take a sample aliquot which contains no more than 10^4 pCi of iodine and does not exceed 100 ml in volume.

2. Pipet 2.0 ml of KI carrier in the 500-ml distillation apparatus (Fig. 1). Add the sample, 2 drops of methyl orange indicator, and mix.

3. Adjust the pH to the end point with H_2SO_4 (1:9) or NaOH as required. [The color changes from yellow (basic) to red (acidic) or the reverse.]

4. Dilute the sample as required to about 70 ml. (Do not adjust the volume if it is already greater than 70 ml.)

5. Add 2 ml of concentrated H_2SO_4 (sp gr 1.84) for a 70-ml total volume or increase the amount to yield a final acid concentration of 1:35 for larger samples.

6. Add 3 ml of saturated $KMnO_4$. For volumes greater than 70 ml add 1 ml of saturated $KMnO_4$ for every 20 ml in the flask. A brown precipitate of manganese dioxide often forms at this step, but there should be sufficient permanganate to color the solution purple. If not, add permanganate solution until a permanent purple color remains.

7. Boil gently for 10 min. Cool to room temperature. (Bromine and chlorine are volatilized during boiling.)

8. Add $NaHSO_3$ solution dropwise while stirring until the purple color of permanganate and brown of iodine and manganese dioxide just disappear. (Continue stirring for an additional 5 min. if necessary).

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Avoid an excess of bisulfite. Add the reagent as rapidly as possible to avoid loss of iodine by volatilization.

9. Place 40 ml of CCl_4 in a 100-ml graduated cylinder. Place the cylinder in a 1-liter beaker used as an ice water bath and allow the CCl_4 to cool.

10. Place the top on the distilling apparatus and connect it to a delivery tube which has been placed in the CCl_4. Lubricate the ball socket joint with concentrated H_2SO_4 and clamp. Connect an air line to the inlet and adjust the flow rate to about 2 bubbles/sec.

11. Open the still and add about 2 ml of $NaNO_2$ solution. Close the still immediately.

12. Boil gently with a bunsen burner until all of the color in the still fades and then continue boiling for 1 min longer. Continue the air sparge for an additional 5 min.

13. Disconnect the delivery tube and rinse with water, catching the rinse in the CCl_4 trap.

14. Transfer the CCl_4 trap contents to a 250-ml separatory funnel. Drain the CCl_4 to a 250-ml beaker and discard the upper aqueous phase. Transfer the CCl_4 back into the separatory funnel. Rinse the beaker with 50 ml of HNO_3 (1:9) and add to the separatory funnel. Shake and let the phases separate.

15. Drain the CCl_4 back into the 250-ml beaker and discard the upper aqueous phase.

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16. Transfer the CCl_4 into the separatory funnel. Rinse the beaker with 50 ml of water and add to the separatory funnel. Add 3 to 5 drops of fresh $NaHSO_3$ as needed and shake until all color is gone from the organic phase.

17. Discard the CCl_4 to organic waste in a ventilated fume hood. The aqueous phase may be gamma-counted if desired.

18. Transfer the aqueous phase to the 250-ml beaker, add 1 ml of HNO_3 (1:9) and stir. Add 10 ml of the $AgNO_3$ solution and heat until the AgI precipitate coagulates.

19. Transfer the precipitate to a 100-ml glass centrifuge cone (Note 2) using water to rinse the beaker contents into the cone. Add 2 or 3 drops of the 1 per cent aerosol solution, centrifuge, and discard the supernate.

20. Wash the precipitate with 75 ml of water, add 2 or 3 drops of the 1 per cent aerosol solution, centrifuge, and discard the supernate.

21. Repeat the procedure given in step 20.

22. Transfer the precipitate to a tared counting dish (Note 3). Dry under an infra-red heat lamp.

23. Weigh the precipitate. Apply 4 or 5 drops of dilute collodion to fix the precipitate while counting and determine the count rate.

Calculation

Calculate the concentration, D, of the iodine isotopes in curies per liter as follows:

$$D = \frac{C}{2.22 \times 10^{12} \; EVR}$$

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where:

C = count rate, counts/min,
E = counter efficiency,
V = liters of sample used,
R = fractional chemical yield, and
2.22×10^{12} = conversion factor from disintegrations/min to curies.

Calculate the counter efficiency, E, for gamma-ray spectrometry as follows:

$$E = Fp$$

where:

F = fractional abundance of the gamma ray, gammas/disintegration, and
p = photopeak detection efficiency, counts/gamma ray.

Calculate decay corrections as follows:

$$A = A_o \, e^{-0.693t/T}$$

where:

A = activity at time t,
A_o = activity at time zero,
e = base of natural logarithms,
t = elapsed time in appropriate units, and
T = half life of radioisotope in same units as t.

Confirmation of ^{131}I Activity and Identification of Iodine Isotopes

1. Plot gamma-ray spectrum of separated sample immediately and after 6 hr, 24 hr, 2 d, 5 d, 1 week and 3 week intervals to identify ^{131}I ($t_{1/2}$ 8.06 d, 364 and 637 keV), ^{133}I ($t_{1/2}$ 20.9 hr, 530 keV), and ^{135}I ($t_{1/2}$ 6.7 hr, 1130, 1260 and 1710 keV) in the sample.
2. Beta-count the AgI planchet daily to measure decay and confirm half-life values for those isotopes present.

Notes:

1. The preparation of all reagents for this and the other ASTM procedures is listed in the back of Section I of this manual.
2. If 50-ml centrifuge tubes are used in this procedure, steps 19-23 can be performed as described except that only 20 ml of water will be required to wash the AgI precipitate.

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3. Since glass-fiber filters and the efficiency values for this geometry are available, the following procedural changes were made after step 21:
   a. Slurry the precipitate in 10 ml water, add 1 ml HNO_3 (1:9), stir and immediately transfer precipitate to a tared glass-fiber filter. Filter slowly at first to prevent loss.
   b. Wash precipitate on filter successively with 20 ml water containing a few ml HNO_3, 20 ml ethanol and 20 ml diethyl ether. Let dry with suction at least 10 minutes, then place in desiccator.
   c. Weigh, mount and store in dark until ready to count.*

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*Because glass fiber filters contain some ^{40}K beta particles and gamma rays, filter blanks as well as reagent blanks should be monitored at intervals. Reeve Angel glass fiber filters #934 AH, 2.8-cm dia, obtainable from any supply house, have been found to be satisfactory.

Radioactive Iron — ASTM(D2461-69)

Principle of Method

Radioactive iron and added iron carrier are separated from other activities by hydroxide precipitation, liquid-liquid extraction, and ion exchange. The separated iron is counted with a gamma counter or spectrometer, or a beta particle detector.

Reagents (Note 1)

Ammonium hydroxide (sp gr 0.90)
Anion exchange resin* (prepared ion-exchange column)
Ferric chloride, carrier solution (49 g per liter)
Hydrochloric acid (sp gr 1.19)
Hydrochloric acid (1:1)
Hydrochloric acid (1:19)
Hydrogen peroxide (30 per cent)
Nitric acid (sp gr 1.42)
Nitric acid-hydrofluoric acid mixture
Nitric acid-hydrogen peroxide mixture
Thenoyltrifluoroacetone (TTA)-Xylene (111 g per liter)
Xylene

Procedure

1. Make the sample just acidic with concentrated HCl (sp gr 1.19) and add 2 ml in excess. Add 1.00 ml of $FeCl_3$ carrier. Boil 2 min to ensure solution of all the iron (see ASTM Method D 1068, Test for Iron in Water.)

2. Add excess NH_4OH. (Note 2). Collect the precipitate in a centrifuge tube by initial settling (if large volume) and centrifugation. Discard the supernatant solution and wash the precipitate with 15 ml of water, discarding the wash.

3. Add to the precipitate 3 ml of water and 10 ml of concentrated

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*Dowex 1-X8 chloride-form resin, 50-100 mesh, obtainable from Bio-Rad Laboratories, Richmond, Calif., has been found to be satisfactory.

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HNO_3 (sp gr 1.42). Stir to dissolve and add 1 ml of H_2O_2. Mix.

4. In the following procedure, use a suitable extraction apparatus. A separatory funnel may be employed as usual, or a centrifuge tube may be used, removing unwanted phases by transfer pipet. Add 15 ml of TTA-xylene and extract for 5 min. Discard the aqueous (lower) phase. Wash the extract and vessel walls with several milliliters of water and discard the wash. If necessary for high decontamination, transfer the extract in this and the next three steps to clean vessels.

5. Add 15 ml of nitric acid-hydrogen peroxide mixture, shake 1 min, and discard aqueous phase.

6. Wash the extract with 15 ml of nitric acid-hydrofluoric acid mixture. Discard the aqueous phase.

7. Add 5 ml of concentrated HCl (sp gr 1.19). Mix until the organic phase is essentially decolorized. Discard the organic phase and wash the aqueous phase and vessel with several milliliters of xylene. Discard the xylene.

8. Evaporate just to dryness (do not bake), and take up in 20 ml of concentrated HCl (sp gr 1.19). Pass through the prepared resin in the column at a flow rate of 1 ml/min. Discard the effluent. Wash with 40 ml of concentrated HCl (sp gr 1.19).

9. Wash with 40 ml of HCl (1:1). Elute iron from the resin with 30 ml of water.

10. Precipitate with excess NH_4OH. Filter on ashless paper* designed for gelatinous precipitates. Dry and ignite to Fe_2O_3 in a porcelain crucible. Weigh to determine chemical yield.

11. Mount the Fe_2O_3 (Note 3) and count beta or gamma radiation.

Calculation

Calculate the concentration, D, of iron-59 in microcuries per milliliter as follows:

$$D = \frac{C}{2.22 \times 10^6 \ EVR}$$

where:

C = corrected count rate of sample, counts per minute per milliliter,
E = counter efficiency,
V = milliliters of sample used,
R = fractional chemical yield for the separation, and
2.22×10^6 = conversion factor from disintegrations per minute to microcuries.

Calculate the decay correction for iron-59 as follows:

$$A = A_o \ e^{-0.693t_d/T}$$

where:

A = activity at time of measurement,
A_o = activity at time zero, that is, reference time,
t_d = elapsed time, days, between measurement and reference time, and
T = half life of radioisotope, 44.6 d.

Confirmation of ^{59}Fe Activity and Identification of Iron Isotopes

1. Plot gamma-ray spectrum of separated sample to identify photopeaks of 44.6-d ^{59}Fe, 1095 keV and 1292 keV.
2. To identify the long-lived 2.7-yr ^{55}Fe isotope, the sample is counted on an x-ray proportional counter capable of resolving the ^{55}Fe photopeak from the adjacent ^{58}Co peak. If there is a possibility of small amounts of ^{58}Co being counted in the iron peak channels this will be revealed by repeated counting to detect the faster decaying ^{58}Co.

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*Whatman filter paper #41, or equivalent.

Notes:

1. The preparation of all reagents for this and the other ASTM procedures is listed in the back of Section I of this manual.
2. An excess of NH_4OH is added to assure completeness of the iron hydroxide precipitation.
3. Slurry the ignited Fe_2O_3 with a few ml water and transfer to a glass-fiber filter. Wash with water, alcohol and ether. Dry at 110°C for 10 min. Cool to room temperature, and mount for counting. Count beta or gamma radiation.

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Radioactive Manganese — ASTM(D2039-71)

Principle of Method

Radioactive manganese and the added carrier are first precipitated as manganese dioxide. A final gravimetric precipitation of manganese ammonium phosphate is used to compute the chemical yield of the process.

Reagents (Note 1)

Ammonium hydroxide solution (1:1)
Ammonium phosphate, monobasic ($NH_4H_2PO_4$)
Cobalt chloride, carrier solution (20 g per liter)
Ethyl alcohol (95 per cent)
Ethyl ether
Ferric chloride, carrier solution (49 g per liter)
Hydrogen peroxide (30 per cent)
Manganese chloride, carrier solution (36 g per liter)
Nitric acid (sp gr 1.42)
Potassium bromate ($KBrO_3$)
Potassium chromate, carrier solution (37.3 g per liter)

Procedure

1. Mix 1 ml of each of the carriers for manganese, cobalt, chromium, and iron in a centrifuge tube (or use an Erlenmeyer flask of suitable volume if a large sample must be taken) and add the sample.

2. Add 5 ml of concentrated HNO_3 (sp gr 1.42) and boil to remove chlorides until evolution of NO_2 ceases; then add 1 g of $KBrO_3$. (Note 2). Boil the mixture for 10 min and then cool.

3. Centrifuge the mixture and discard the supernate. Wash the precipitate of manganese dioxide with hot water acidified with HNO_3 until the wash water is colorless. (Note 3).

4. Dissolve the manganese dioxide in 1 ml of concentrated HNO_3 (sp gr 1.42) and one drop of H_2O_2, boil, and then add 1 ml of iron, chromium, and cobalt carriers.

5. Repeat the procedure described in steps 2 and 3. (Note 4).

6. Dissolve the manganese dioxide in 1 ml of concentrated HNO_3 (sp gr 1.42) and 1 drop of H_2O_2, boil, and then cool. Dilute with 5 ml of water.

7. Add 4 drops of iron carrier. Add NH_4OH (1:1) to precipitate the iron below a pH of 7. (Note 5). Boil and filter through a fast paper suitable for gelatinous precipitates. Discard the precipitate.

8. Dilute the solution to 15 ml and add 1 g of $NH_4H_2PO_4$. (Note 6). Boil until a crystalline precipitate forms. Cool in an ice bath for 10 min.

9. Filter onto a tared quantitative paper. Wash with water, ethyl alcohol, and ether.

10. Dry at $110^\circ C$ for 10 min. Weigh as manganese ammonium phosphate $[Mn(NH_4)PO_4 \cdot H_2O]$ and mount for counting.

Calculation

Calculate the concentration, D, of radioactive manganese in curies per liter as follows:

$$D = \frac{C}{2.22 \times 10^{12} \text{ EVR}}$$

where:

C = count rate of sample, in counts per minute,

E = counter efficiency,
V = liters of sample used,
R = fractional chemical yield for the separation, and
2.22×10^{12} = conversion factor from disintegrations per minute to curies.

Calculate the decay correction for radioactive manganese as follows:

$$A = A_o \, e^{-0.693t/T}$$

where:

A = activity at time t,
A_o = activity at time zero, in same units as A,
e = base of natural logarithms,
t = elapsed time, and
T = half life of isotope, in same units as t.

Confirmation of Purity and Identification of ^{54}Mn

1. Plot gamma-ray spectrum of separated sample to identify and quantify the 313-d ^{54}Mn photopeak photopeak (835 keV).
2. Repeat gamma spectrum measurement after 4 weeks to substantiate the manganese half life.

Notes:

1. The preparation of all reagents for this and the other ASTM procedures is listed in the back of Section I of this manual.
2. The $KBrO_3$ must be added slowly and in small increments.
3. Effective washing is accomplished with 15 ml portions of hot water acidified with 0.5 ml conc. HNO_3 (sp gr 1.42).
4. If cobalt contamination persists as a problem, another decontamination is suggested. This can be accomplished by repeating steps 2 and 3 of procedure another time.
5. $Fe(OH)_3$ precipitation begins at pH 5 and is complete at pH 6.
6. At this point, the $NH_4H_2PO_4$ is completely dissolved in the solution since the pH is below 7. To make the precipitation quantitative, the pH should be adjusted to 7 with 1:1 NH_4OH, then boiled and stirred to precipitate manganese ammonium phosphate.

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Tritium — ASTM(D2476-70)

Principle of Method

The scintillator solution, mixed with radioactive sample, is excited by the beta particles and emits light pulses by a molecular de-excitation process. The number of pulses per unit time is proportional to the quantity of activity present. Multiple solutes are used in the scintillator to provide the best combination of wavelength and pulse height for this application. These pulses are detected by two multiplier phototubes connected in coincidence and converted to electric signals. The amplified pulses are recorded and the count rate is measured. The efficiency of the system can be determined by use of prepared tritiated water standards having the same density and color as the sample.

Reagent

Scintillator stock solution (Note 1)

Procedure

1. Filter the sample through a membrane filter if turbid.

2. Distill the sample if ionizing radiation other than tritium is present. The distillate must be redistilled if any ionizing radiation other than tritium is carried over during the previous distillation. (Note 2).

3. Transfer a 5-ml sample aliquot into a sample vial and add 16 ml of previously standardized scintillator solution. Mix.

4. Prepare a blank having the same density and color as the sample using 5 ml of water.

5. Place the sample and blank in the counter and dark-adapt for 2 hr. (Note 3).

6. Count the sample for the length of time to give the desired

   reliability.

Calculation

The efficiency factor for the scintillator mixture (Note 4) is calculated as follows:

$$\text{Tritium activity,* } C = \frac{1}{V}\left(\frac{N}{t}-B\right)$$

where:

N = number counts accumulated,
B = background of blank, counts per minute (cpm),
C = net counts per minute per milliliter (cpm/ml),
t = time of counting, min, and
V = milliliters of test specimen used.

$$\text{Tritium efficiency (fraction), } E_{3_H} = \frac{C}{D}$$

where:

D = disintegration rate, disintegrations per minute per milliliter (dpm/ml)

$$\text{Tritium efficiency factor, } F(\mu Ci/cpm) = \frac{1}{E_{3_H} \times 2.22 \times 10^6}$$

where:

2.22×10^6 = conversion from disintegrations per minute to microcuries.

Calculate the tritium radioactivity in microcuries per milliliter as follows:

$$\text{Tritium activity, } A, (\mu Ci/ml) = FC$$

Confirmation of ^3H Activity

1. Determine the count rate for each sample, background and standard at two selected window settings. Compare the ratios for the ^3H

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*This is not "activity" but "cpm/ml".

standard with that for the samples to confirm that the activity being measured is tritium.

2. To make certain that the samples have been dark adapted, count at least three times until successive results are within 2 σ of each other.

Notes:

1. The preparation of this scintillation solution is described on page 30 of this manual. This solution is standardized as follows:

    > Transfer 16 ml of the scintillator stock solution into each of two 20-ml polyethylene sample vials. Pipet 4 ml of tritiated water standard solution containing 4000 to 5000 dpm/ml into one vial and 4 ml of water into the remaining vial. Mix. The latter will serve as a blank. Place the vials in position in the counter and dark-adapt for 2 hrs. Count the blank and standard and calculate the efficiency factor for the scintillator mixture as above. (If the sample vial is of such size as to contain 25 ml, use 20 ml of scintillator stock solution and 5 ml of the sample.)

2. As a general rule, all samples should be distilled to dryness for quantitative recovery and to decontaminate the tritium from other ionizing radiations that may be present. Any problems arising from the presence of iodine-131 in the aqueous samples can be eliminated by the addition of $AgNO_3$ and iodine carrier to the flask before distillation begins. In any event, the sample should be distilled carefully to guard against "bumping" and the physical carry-over of ionizing radiations other than tritium.

3. The same sample blank may be used for a number of samples provided the same scintillator solution is used for each and the blank has the same density and color as the samples.

4. Some scintillation mixtures are available which give lower background and higher counting efficiencies for ^3H. An example of such a stock solution, which is in use at this installation, is listed in the back of Section II of the manual (Appendix C.6).

B. Reagent Preparation — ASTM Standard Methods

I. Specifications

a. Reagent grade chemicals, or equivalent, as defined in ASTM Methods E-200, Preparation, Standardization, and Storage of Standard Solutions for Chemical Analysis*, shall be used in all tests.

b. Unless otherwise indicated, reference to water shall be understood to mean reagent water conforming to ASTM Specifications D1193, for Reagent Water, referee grade.

c. Radioactive purity shall be such that the measured radioactivity of blank samples does not exceed the calculated probable error of the measurement.

d. Carrier solutions are to be standardized in the manner prescribed in the Calibration and Standardization section of each procedure in the ASTM text. This requirement for quantitative chemical yield determination generally involves precipitation of aliquots of these solutions, in triplicate, in the same manner as the final precipitates in the respective procedures.

II. Reagents

Aerosol solution (1:100) - Add 1 ml of 25 per cent aerosol solution to 100 ml water and mix.

Ammonium hydroxide solution (1:1) - Mix 1 volume of concentrated ammonium hydroxide (NH_4OH, sp gr 0.90) with 1 volume of water.

Anion exchange resin - [For method ASTM - D2461-69] Make a slurry with water and transfer to a glass ion-exchange column [17 cm long by 0.9 cm I.D., with a 50-ml reservoir at the top and a 2-mm bore stopcock at the bottom] until a layer of resin

*ASTM Standards. Water; Atmospheric Analysis, Part 23, American Society for Testing and Materials, Phila., Pa. 19103 (Oct. 1972).

about 12 cm deep is formed. Wash with 50 ml of water and 50 ml of concentrated HCl (sp gr 1.19) before each use.

Barium nitrate, carrier solution (19 g per liter) - Dissolve 19 g of barium nitrate ($Ba(NO_3)_2$) in water, add 5 ml of concentrated HNO_3 (sp gr 1.42), and dilute to 1 liter. This solution will contain 10 g of Ba^{++} per liter.

Cobalt chloride, carrier solution (20 g per liter) - Dissolve 20 g of cobalt chloride ($CoCl_2.6H_2O$) in 100 ml of HCl (1:19), dilute to 1 liter and store in a polyethylene bottle. This solution will contain 5 g of Co^{++} per liter.

Collodion solution (1:9) - Dissolve 8 ml of collodion (USP) in a mixture of 48 ml of ethyl ether (anhydrous) and 24 ml of absolute ethanol.

Ferric chloride, carrier solution (49 g per liter) - Dissolve 49 g of ferric chloride ($FeCl_3.6H_2O$) in 100 ml of HCl (1:19), filter, and dilute to 1 liter. This solution will contain 10 g Fe^{+++} per liter. Standardize by precipitation of hydroxide, filtering, and igniting to ferric oxide (Fe_2O_3).

Ferric nitrate, carrier solution (72 g per liter) - Dissolve 72 g of ferric nitrate ($Fe(NO_3)_3.9H_2O$) in water containing 1 ml of concentrated nitric acid (HNO_3, sp gr 1.42) and dilute to 1 liter. This solution will contain 10 g of Fe^{+++} per liter.

Hydrochloric acid (1:1) - Mix 1 volume of concentrated hydrochloric acid (HCl, sp gr 1.19) with 1 volume of water.

Hydrochloric acid (1:19) - Mix 1 volume of concentrated hydro-
chloric acid (HCl, sp gr 1.19) with 19 volumes of water.

Hydrochloric acid - ether reagent - Slowly add 500 ml of concen-
trated hydrochloric acid (HCl, sp gr 1.19) to 100 ml of ethyl
ether and mix. Cool in an ice bath before using. [Prepare
and store this reagent in a fume hood. Naked flames must
not be present.]

Lanthanum nitrate, carrier solution (30.4 g per liter) - Dissolve
30.4 g of lanthanum nitrate ($La(NO_3)_3.6H_2O$) in water and
dilute to 1 liter. This solution will contain 10 g of La^{+++}
per liter.

Manganese chloride, carrier solution (36 g per liter) - Dissolve
36 g of manganese chloride ($MnCl_2.4H_2O$) in 1 liter of water
and store in a polyethylene bottle. This solution will
contain 10 g of Mn^{++} per liter.

Methyl orange indicator solution (0.5 g per liter) - Dissolve
0.05 g of methyl orange in water and dilute to 100 ml with
water.

Nitric acid solution (1:9) - Mix 1 volume of concentrated nitric
acid (HNO_3, sp gr 1.42) with 9 volumes of water.

Nitric acid-hydrofluoric acid mixture - Mix 1 volume of concen-
trated nitric acid (HNO_3, sp gr 1.42), 1 volume of hydro-
fluoric acid (HF, sp gr 1.19), and 98 volumes of water.

<u>Nitric acid - hydrogen peroxide mixture</u> - Mix 5 volumes of concentrated nitric acid (HNO_3, sp gr 1.42), 2 volumes of hydrogen peroxide (H_2O_2, 30%), and 13 volumes of water.

<u>Potassium chromate, carrier solution (37.3 g per liter)</u> - Dissolve 37.3 g of potassium chromate (K_2CrO_4) in 1 liter of water. This solution will contain 10 g of Cr^{+++} per liter.

<u>Potassium iodide, carrier solution (13.08 g per liter)</u> - Dissolve 13.08 g of potassium iodide (KI) in 500 ml of water and dilute to 1 liter. This solution will contain 10 g of I^- per liter.

<u>Potassium permanganate solution (saturated)</u> - Dissolve 65 g of potassium permanganate ($KMnO_4$) in 1 liter of warm water and let cool (solubility = 6.38 g per 100 ml at 20°C).

<u>Scintillator stock solution</u>* - (If prepared in the presence of daylight or fluorescent light, store in a dark place 2 days before use.) Dissolve 120 g of naphthalene, 0.05 g of p-bis (2-(5-phenyloxazolyl)) benzene (POPOP), and 4 g of 2,5-diphenyloxazole (PPO), in 1 liter of p-dioxane. Store in an amber-colored bottle. This solution must be standardized initially before use.

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*Scintillation grade reagents should be used in the preparation of the stock solution to assure sample stability in the counting vial for at least 3-4 weeks.

The solvent in the scintillation solution, p-Dioxane, is flammable and its vapors are toxic. Preparation of the scintillation solution should be carried out in a hood away from heat or flames.

Silver nitrate solution (17 g per liter) - Dissolve 17 g of silver nitrate (AgNO$_3$) in 300 ml of water and dilute to 1 liter.

Sodium bisulfite solution (100 g per liter) - Dissolve 10 g of sodium bisulfite (NaHSO$_3$) in 75 ml of water and dilute to 100 ml. Prepare a new solution when needed. Do not store for more than one week.

Sodium carbonate solution, saturated (212 g per liter) - Dissolve 212 g of sodium carbonate (Na$_2$CO$_3$) in water and dilute to 1 liter.

Sodium hydroxide solution (200 g per liter) - Dissolve 200 g of sodium hydroxide (NaOH) in 400 ml of water and dilute to 1 liter.

Sodium nitrite solution (100 g per liter) - Dissolve 10 g of sodium nitrite (NaNO$_2$) in water and dilute to 100 ml.

Sulfuric acid solution (1:4) - Slowly, with stirring, add 1 volume of concentrated sulfuric acid (sp gr 1.84) to 4 volumes of water.

Sulfuric acid solution (1:9) - Slowly, with stirring, add 1 volume of concentrated sulfuric acid (H$_2$SO$_4$, sp gr 1.84) to 9 volumes of water.

<u>Thenoyltrifluoroacetone (TTA) - Xylene (111 g per liter)</u> - Dissolve

111 g of TTA in xylene and dilute to 1 liter.

<u>Xylene, $C_6H_4(CH_3)_2$</u>: reagent grade.

SECTION II

A. Developed and Modified Methods

Radioactive Antimony

Principle of Method

Antimony carrier and appropriate scavenging carriers are added to the aqueous sample and impurities are removed by a basic sulfide precipitation. The antimony is collected as the sulfide in acid solution, and reduced to the metal for counting.

Procedure Time

4 samples - 5 hrs.

Reagents

Antimony carrier: 5 mg/ml
Cobalt carrier: 5 mg/ml
Ethanol, C_2H_5OH: 95%
Hydrochloric acid, HCl: 12 $\underline{N}$ (conc.)
Hydrogen sulfide, H_2S: gas
Iron, wire #36, analytical grade
Manganese carrier: 5 mg/ml
Sodium hydroxide, NaOH: 18 $\underline{N}$, 0.5 $\underline{N}$
Sulfuric acid, H_2SO_4: 36 $\underline{N}$ (conc.)
Thioacetamide, CH_3CSNH_2*: 5%

Procedure

1. To an aqueous sample (200 ml or less), add 2.0 ml antimony carrier and 1 ml each of cobalt and manganese holdback carriers (Note 1).

2. Make sample strongly basic (pH > 10) with 18 $\underline{N}$ NaOH and heat to boiling (Note 2).

3. Bubble in H_2S for 5 minutes to precipitate sulfides completely, filter while hot through Whatman #41 (or equivalent). Wash filter

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*If thioacetamide solution is preferred to hydrogen sulfide, 2 ml of the solution, with vigorous stirring, can be substituted in those steps requiring H_2S.

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paper with a few ml 0.5 $\underline{N}$ NaOH and discard filter paper.

4. Cool sample in an ice bath and neutralize by dropwise addition of 36 $\underline{N}$ H_2SO_4.

5. Make sample ~3 $\underline{N}$ in H_2SO_4 with 36 $\underline{N}$ H_2SO_4. (Note 3).

6. Heat to boiling, then bubble in additional H_2S for a few minutes.

7. Cool in an ice bath, centrifuge and discard supernatant.

8. Dissolve the antimony sulfide with 10 ml 12 $\underline{N}$ HCl and boil in a hot water bath for 15 min. to expel H_2S.

9. Add 5 ml water, 1 ml cobalt carrier and repeat steps 2-8.

10. Add 10 ml water and filter through Whatman #42 (or equivalent) into a graduated centrifuge tube. Wash residue with a few ml water and add to filtrate. Bring volume to 40 ml. Discard filter paper.

11. To filtrate add 225-250 mg iron wire. Heat in a boiling water bath, stirring occasionally until the reduction is complete and all the antimony has settled to the bottom of the tube. (This takes 45 min. - 1 hr.) Wash sides of tube with a few ml water and add 1 ml 12 $\underline{N}$ HCl. Stir well and continue heating about 10 min. to dissolve any residual iron. If necessary add another ml 12 $\underline{N}$ HCl to complete the dissolution.

12. Cool slightly, centrifuge and carefully discard supernatant.

13. Wash antimony with 20 ml water and 1 ml 12 $\underline{N}$ HCl. Heat and stir in a boiling water bath about 5 min. Cool slightly, centrifuge and carefully discard wash solution.

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14. Transfer to a tared glass-fiber filter with water and wash with successive portions of water and ethanol.

15. Dry in oven at $110^{\circ}C$ for 15 minutes, cool, weigh, mount and count.

Calculation

Calculate the concentration, D, of the antimony activity in picocuries per milliliter as follows:

$$D = \frac{C}{2.22 \times EVR}$$

where:

C = net count rate, counts/min,
E = counter efficiency,
V = milliliters of sample used,
R = fractional chemical yield, and
2.22 = conversion factor from disintegrations/min to picocuries.

Calculate the counter efficiency, E, for gamma-ray spectrometry as follows:

$$E = Fp$$

where:

F = fractional abundance of the gamma ray, gammas/disintegration, and
p = photopeak detection efficiency, counts/gamma ray.

Calculate decay corrections as follows:

$$A = A_o \, e^{-0.693t/T}$$

where:

A = activity at time t,
A_o = activity at time zero,
e = base of natural logarithms,
t = elapsed time from collection, and
T = half life of separated nuclide, in same units as t.

Confirmation of Purity of ^{124}Sb

1. Plot the gamma ray spectrum of the separated sample to identify the the ^{124}Sb photopeaks at 603 and 1692 keV.
2. Beta-count the planchets at 3-4 week intervals to measure decay and confirm the 60.2 d half life.
3. Frequent gamma spectral measurements will identify the other shorter-lived isotopes (2.7 d ^{122}Sb or 5.8 d ^{129m}Sb). The presence of the gamma photopeaks at 427, 599 and 634 keV will identify the longer-lived ^{125}Sb isotope ($t_{1/2}$ = 2.8 y).

Notes:

1. If the aqueous sample has significant ^{131}I activity, it will be necessary to modify the procedure to assure complete decontamination from the separated antimony fraction as follows:
   a. To 200 ml aqueous sample in a separatory funnel, add 2.0 ml antimony carrier and 1 ml each iodine, cobalt and manganese carriers. Add 5 ml 36 $\underline{N}$ H_2SO_4, stir well, then add 1 ml 1 $\underline{M}$ $NaNO_2$.
   b. Add 10 ml CCl_4, shake for 5-10 minutes. Discard the organic layer.
   c. To the aqueous layer add 0.5 ml iodine carrier, 0.5 ml 1 $\underline{M}$ $NaNO_2$ and 5 ml CCl_4. Shake for 5-10 minutes, discard the organic layer. Repeat.
   d. Wash aqueous layer twice with 5 ml CCl_4 and discard the organic washes.
   e. Add 2 drops 1 $\underline{M}$ $NaNO_2$. Stir and boil for a few minutes to remove excess NO_2.
   f. Proceed with step 2 of the Antimony procedure.
2. The sample must be strongly basic to ensure that antimony will stay in solution through the basic sulfide precipitation.
3. Depending on the sample aliquot taken for analysis, the adjustment to 3 $\underline{N}$ in H_2SO_4 at this point can be made as follows:
   a. Add 18 ml 36 $\underline{N}$ H_2SO_4 and dilute to 225 ml
   b. Add 13 ml 36 $\underline{N}$ H_2SO_4 and dilute to 150 ml
   c. Add 8.5 ml 36 $\underline{N}$ H_2SO_4 and dilute to 100 ml or
   d. Add 2.5 ml 36 $\underline{N}$ H_2SO_4 and dilute to 20 ml.

References:

1. Kleinberg, J., Ed., "Collected Radiochemical Procedures", LA-1721, 2nd ed., Los Alamos Scientific Laboratory, U. of Calif., 1958, pp. 156-162.
2. Pocze, L., et al., "Testing of Silver, Antimony, Zinc, Tin and Selenium Content in High Purity Coppers by Activation Analysis", Proc. Conf. Appl. Phys.-Chem. Methods Chem. Anal. Budapest 2, 270-5, 1966.

Radioactive Arsenic

Principle of Method

Arsenic carrier and appropriate holdback carriers are added to the acidified aqueous sample. The arsenic is collected as the sulfide in acid solution and reduced to the metal for counting.

Procedure Time

2 samples - 3 hrs.

Reagents

Aerosol solution: 1.5%
Arsenic carrier: 20 mg/ml
Cobalt carrier: 5 mg/ml
Ethanol, C_2H_5OH: 95%
Hydrochloric acid, HCl: 12 $\underline{N}$ (conc.), 6 $\underline{N}$
Hydrogen sulfide, H_2S: gas
Nitric acid, HNO_3: 16 $\underline{N}$ (conc.)
Perchloric acid, $HClO_4$: 70% (conc.)
Sodium hydroxide, NaOH: 2 $\underline{N}$
Stannous chloride, $SnCl_2.2H_2O$: freshly prepared reagent

Procedure

1. To an aqueous sample (100 ml or less), add 5 ml 16 $\underline{N}$ HNO_3, 1.0 ml

   arsenic carrier and 0.5 ml cobalt holdback carrier, and evaporate to

   dryness.

2. Add 10 ml 12 $\underline{N}$ HCl to residue and dissolve by heating and stirring

   on a hot plate. Transfer to a centrifuge tube with 12 ml 12 $\underline{N}$ HCl

   and make ~9 $\underline{N}$ in HCl by diluting to 30 ml.

3. Heat almost to boiling in a hot water bath and bubble in H_2S until

   precipitation of As_2S_5 is complete. Continue heating and stirring

   until precipitate has coagulated. Centrifuge and discard supernatant.

4. To the precipitate add 10 ml 2 $\underline{N}$ NaOH, stir in a hot water bath, filter through Whatman #41 (or equivalent) into a clean tube and discard filter paper.

5. Reprecipitate As_2S_5 by slowly adding 20 ml 12 $\underline{N}$ HCl. Heat and stir in a hot water bath and add additional H_2S to assure complete reprecipitation. Heat and stir to coagulate, cool, centrifuge and discard supernatant.

6. Stir precipitate in a hot water bath with 10 ml 12 $\underline{N}$ HCl. Add 5 ml water, centrifuge and discard supernatant.

7. To the precipitate, add 0.5 ml each of 16 $\underline{N}$ HNO_3 and 12 $\underline{N}$ HCl and 1 ml 70% $HClO_4$. Stir in hot water bath for 15 minutes, dry outside of centrifuge tube, then heat carefully over a burner for several minutes until dense white fumes appear. (Note 1).

8. Cool to room temperature, add 10 ml 6 $\underline{N}$ HCl and heat in a boiling water bath. Slowly add 15 ml freshly prepared stannous chloride solution, stirring and heating continuously until arsenic is precipitated and coagulated.

9. Add 2 drops aerosol solution, stir and rinse stirring rod and sides of the tube with 12 $\underline{N}$ HCl.

10. Let cool to room temperature, centrifuge and discard supernatant.

11. Wash with 15 ml ethanol and discard wash solution.

12. Transfer to tared glass-fiber filter with ethanol and wash with ethanol.

13. Dry 10 minutes in an oven, weigh rapidly to keep oxidation of

arsenic to a minimum, mount and count immediately.

Calculation

Calculate the concentration, D, of arsenic-76 in picocuries per milliliter as follows:

$$D = \frac{C}{2.22 \times EVR}$$

where:

C = net count rate, counts/min,
E = counter efficiency,
V = milliliters of sample used,
R = fractional chemical yield, and
2.22 = conversion factor from disintegrations/min to picocuries.

Calculate the counter efficiency, E, for gamma-ray spectrometry as follows:

$$E = Fp$$

where:

F = fractional abundance of the gamma ray, gammas/disintegration, and
p = photopeak detection efficiency, counts/gamma ray.

Calculate the decay correction for arsenic-76 as follows:

$$A = A_o \, e^{-0.693t/T}$$

where:

A = activity at time t,
A_o = activity at time zero,
e = base of natural logarithms,
t = elapsed time, in hours from collection, and
T = half life of ^{76}As in same units as t ($t_{1/2}$ = 26.4 h).

Confirmation of the Purity and Activity of ^{76}As

1. Plot the gamma-ray spectrum of the separated sample immediately to identify the predominant ^{76}As photopeak at 559 keV and to note the presence of photopeaks indicative of incomplete decontamination.

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2. Repeat the gamma measurement at 6-, 12-, and 24-hr intervals to corroborate the half life of ^{76}As.

Note:

1. It is essential that all HNO_3 be removed to eliminate interference with the conversion of arsenic to the metal. However, do not let sample go to dryness.

References:

1. Lingane, J. J., Analytical Chemistry of Selected Metallic Elements, (Reinhold, New York, N. Y. 1966) pp. 27-28.

2. Master Analytical Manual, Oak Ridge National Laboratory, USAEC Report TID-7015, Method 5-110600, 1957.

Carbon-14

Principle of Method

Carbon carrier in the form of sodium oxalate is added to an unacidified aqueous sample in a closed distillation apparatus. An oxidizing agent and acid are added to the sample to convert carbon compounds to CO_2. Air is slowly bubbled through the sample and heat is applied to transfer CO_2 into a flask that contains a basic $CaCl_2$ solution. The collected $CaCO_3$ is centrifuged, washed, transferred to a stainless steel planchet, weighed, and counted.

Procedure Time

1 sample - 1 hr.

Reagents

(Freshly boiled distilled water should be used in the preparation of the following reagents.)

Ammonium hydroxide, NH_4OH: 0.1 $\underline{N}$
Calcium chloride, $CaCl_2$: 1.5 $\underline{M}$
Carbon carrier, 0.1 $\underline{M}$ $Na_2C_2O_4$: 20 mg/ml (Note 1).
Potassium permanganate, $KMnO_4$: 0.5 $\underline{M}$
Sulfuric acid, H_2SO_4: 18 $\underline{N}$

Procedure

1. To an unacidified aqueous sample (200 ml or less) in a distilling flask (Fig. 2), add 1.0 ml carbon carrier. Close distillation apparatus. Connect a source of CO_2-free air to the flask and bubble gently through the solution (Note 2). Connect distilling outlet to a 200-ml receiving flask containing 100 ml 0.1 $\underline{N}$ NH_4OH and 1 ml 1.5 $\underline{M}$ $CaCl_2$ (60 mg Ca^{++}).

2. With the system closed, add 1 ml 0.5 $\underline{M}$ $KMnO_4$ and 5 ml 18 $\underline{N}$ H_2SO_4 through the separatory funnel to the distilling flask. Close
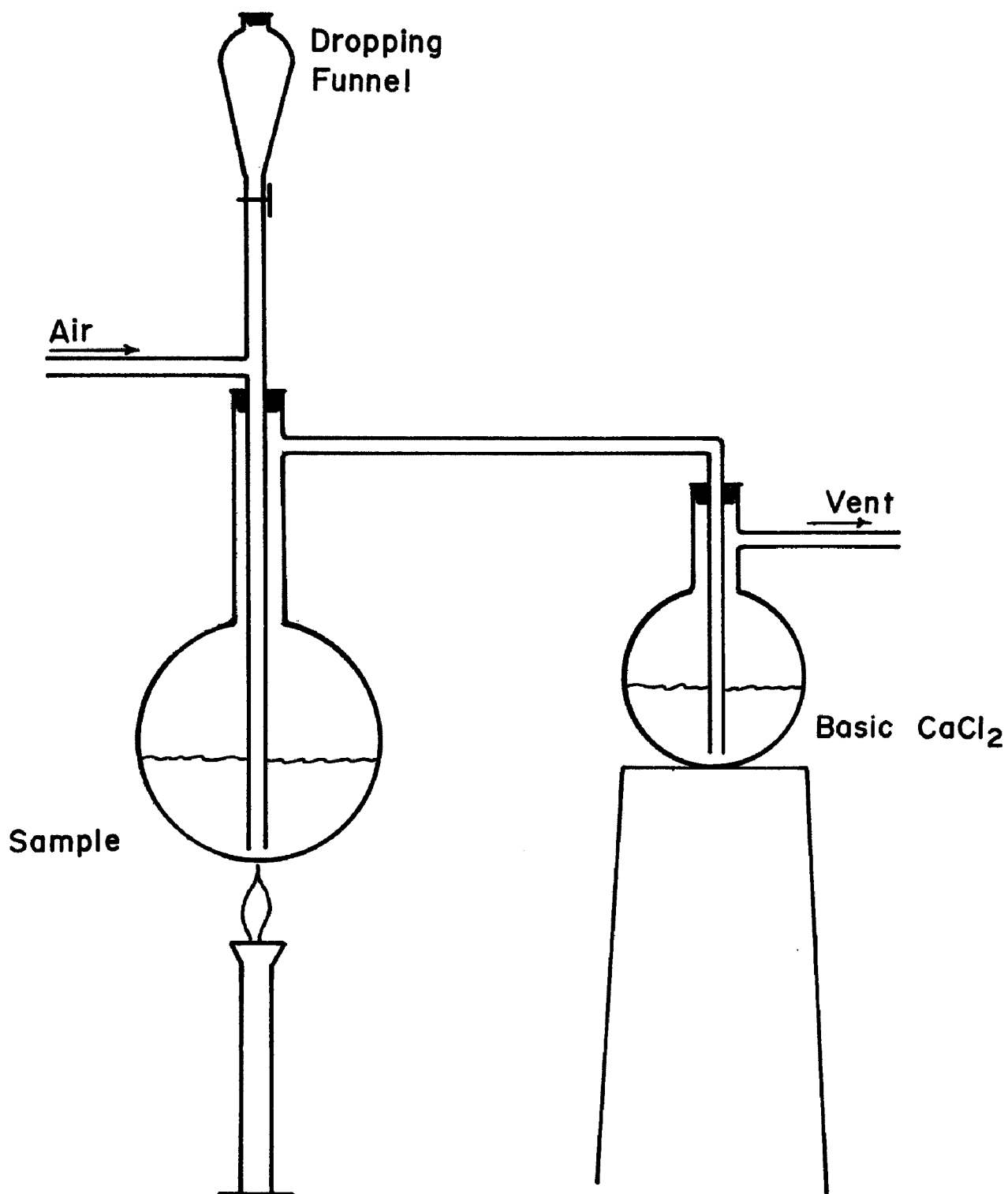
Figure 2. Distillation Apparatus for Carbon-14 Analysis

stopcock; swirl, and boil 30 minutes while bubbling air through the distilling flask into the receiving flask.

3. Transfer the precipitated $CaCO_3$ from the receiving flask to a centrifuge tube. Centrifuge and discard supernatant. (Note 3).

4. Wash precipitate twice with 15 ml portions of boiled distilled water and discard wash solutions.

5. Transfer quantitatively to a tared stainless steel planchet with 5 ml boiled distilled water.

6. Dry under infra-red lamp. Let cool and weigh. Compute chemical yield based on the total weight of $CaCO_3$ formed. Count with thin-window (< 2 mg/cm^2) beta counter.

Calculation

Calculate the concentration, D, of the carbon-14 activity in pico-curies per milliliter as follows:

$$D = \frac{C}{2.22 \times EVR}$$

where:

C = net count rate, counts/min,
E = counter efficiency,
V = milliliters of sample used,
R = fractional chemical yield, and
2.22 = conversion factor from disintegrations/min to picocuries.

Confirmation of Purity and Identification of ^{14}C (Note 4)

1. Ascertain if the activity is ^{14}C by counting the planchet with aluminum absorbers up to 25 mg/cm^2 and compare with a standard ^{14}C absorption curve (Fig. 3).
2. Decay counting for half-life corroboration is not practical (^{14}C $t_{1/2} = 5730$ y). A 3-month decay count, however, will demonstrate the absence of short-lived radioactive impurities.

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Figure 3. Absorption Curve for Carbon-14 ($Ca^{14}CO_3$ on s.s. planchet)
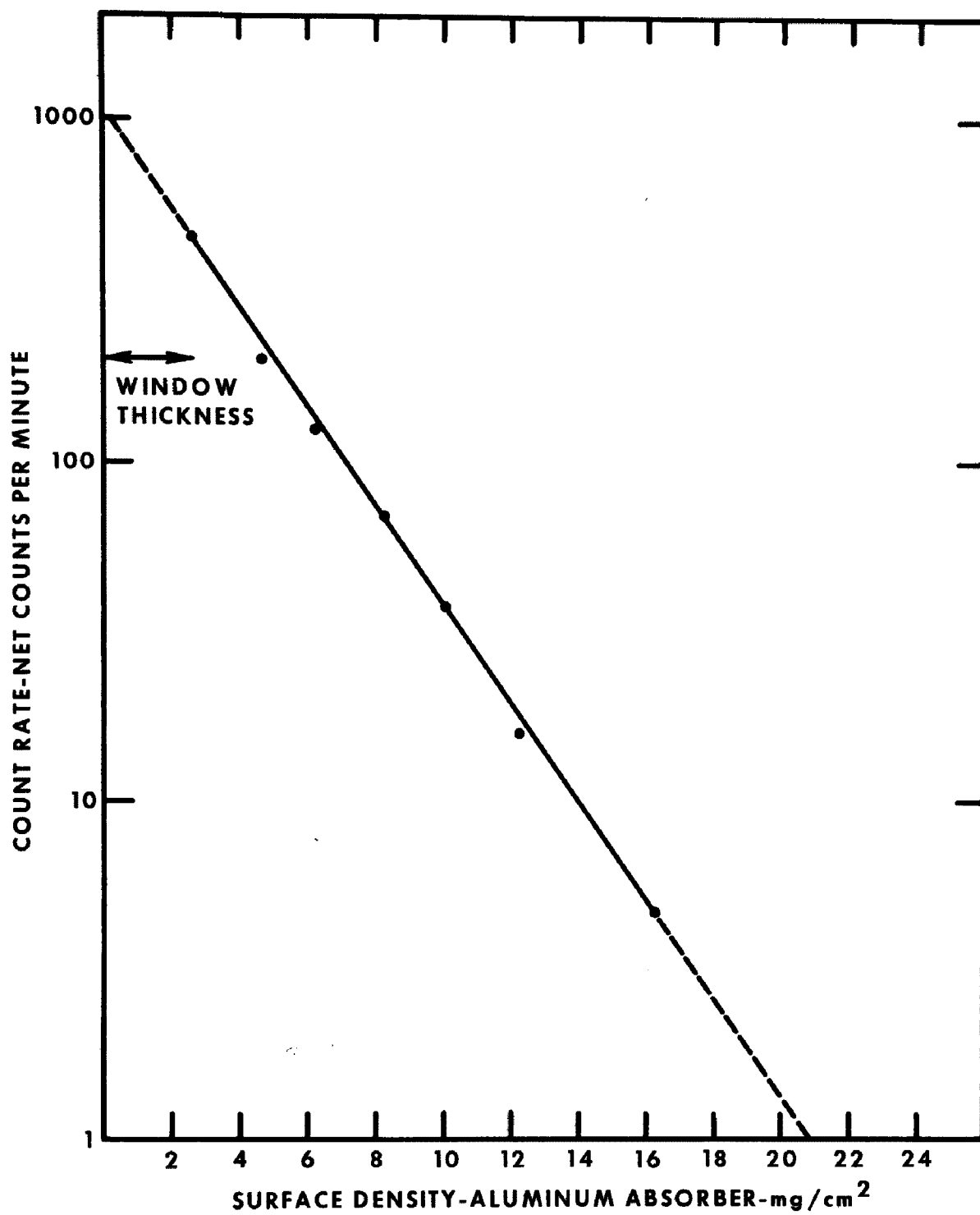2.5 mg/cm^2 Total Window Thickness Included

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Notes:

1. The $Na_2C_2O_4$ should be frequently standardized by replicate determinations. 1 ml 0.1 $\underline{M}$ $Na_2C_2O_4$ is equivalent to 20 mg $CaCO_3$, but the standardized value will include any CO_2 absorbed by the carrier solution upon standing.
2. A cylinder of oxygen can serve as an excellent source of CO_2-free air.
3. An alternate method for counting carbon-14 is by liquid scintillation*. At this point, the $CaCO_3$ precipitate is dried at 110°C overnight and cooled in a desiccator. Proceed as follows:
   a. Transfer quantitatively to a tared scintillation vial, add 450 mg Cab-o-sil, and suspend the mixture in 15 ml of a freshly prepared toluene scintillation solution. Agitate until uniform.
   b. Prepare a ^{14}C standard and a background sample in a similar manner.
   c. After determining optimum voltage and window settings, count at least three times to be certain the samples have been dark adapted.
4. If it is evident that another radionuclide contaminates the ^{14}C, the following corrective measures can be taken:
   a. Wash the $CaCO_3$ from the stainless steel planchet into a round bottom flask with boiled distilled water. Bring the volume to ~100 ml with boiled distilled water. Add the necessary holdback carrier (cobalt, manganese, etc.) and close the distilling system as before.
   b. Connect the distilling outlet to a 200-ml flask containing 100 ml 0.1 NH_4OH and 1 ml 1.5 $\underline{M}$ $CaCl_2$.
   c. With the system closed, add 2 ml 6 $\underline{N}$ HCl to the sample through the separatory funnel. Swirl. Boil gently for 15 minutes.
   d. Repeat the collection, washing, mounting, weighing and counting of $CaCO_3$ as before.

Reference:

1. Rodden, C. J., Ed., Analysis of Essential Nuclear Reactor Materials (Div. Tech. Inf. USAEC, 1964) p. 561.

*Rapkin, E., "Measurement of $^{14}CO_2$ by Scintillation Techniques", Packard Technical Bulletin #7, Packard Instrument Co., La Grange, Ill., 1962.

Radioactive Cerium

Principle of Method

Cerium carrier is added to the aqueous sample, which is evaporated to dryness, taken up in concentrated HCl and passed through a mixed anion resin column. (Note 1). Manganese is scavenged from the effluent, and the cerium is precipitated as $Ce(IO_3)_4$ for counting.

Procedure Time

2 samples - 6 hrs.

Reagents

Anion Exchange Resins
    Dowex 1-X8 (100-200 mesh)
    Dowex 2-X8 (20-50 mesh)
Cerium carrier: 5 mg/ml
Cobalt carrier: 5 mg/ml
Ethanol, C_2H_5OH: 95%
Hydrochloric acid, HCl: 12 $\underline{N}$ (conc.), 6 $\underline{N}$
Hydrogen peroxide, H_2O_2: 30%
Manganese carrier: 5 mg/ml
Nitric acid, HNO_3: 16 $\underline{N}$ (conc.)
Potassium bromate, $KBrO_3$: solid
Potassium iodate, KIO_3: prepared reagent
Potassium iodate wash solution, KIO_3: prepared reagent

Procedure

1. To an aqueous sample (100 ml or less), add 1.0 ml cerium carrier, 0.5 ml 6 $\underline{N}$ HCl and evaporate to dryness.

2. Prepare a mixed anion exchange resin column as follows:

    Individually equilibrate 10 g Dowex 1-X8 anion resin (100-200 mesh) and 10 g Dowex 2-X8 anion resin (20-50 mesh) with 50 ml 12 $\underline{N}$ HCl each. Into a glass column, 0.9 cm (I.D.) x 30 cm, slurry Dowex 2-X8 to a height of 5 cm, then add the Dowex 1-X8 resin.

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3. Dissolve residue in 10 ml 12 $\underline{N}$ HCl and add 1 drop H_2O_2 to reduce the cerium to the cerous (+3) state.

4. Add 1 ml cobalt carrier to the solution, stir well. Pass over column at a rate of 0.25 ml/min. Collect effluent in a beaker.

5. Wash column with 15 ml 12 $\underline{N}$ HCl and add wash to effluent in the beaker.

6. Evaporate effluent almost to dryness to remove chlorides. Do not bake. Dissolve residue in 50 ml water, add 0.5 ml manganese carrier and 2.5 ml 16 $\underline{N}$ HNO_3.

7. Heat to boiling and slowly add 1 g $KBrO_3$. Boil until MnO_2 coagulates. Cool, centrifuge, and filter supernatant through Whatman #42 (or equivalent), into a clean beaker. Wash filter paper with a few ml water, and discard filter paper.

8. Heat solution to boiling and add a pinch of $KBrO_3$ to assure complete oxidation to the ceric (+4) state.

9. Add 20 ml KIO_3 solution, stir and boil until the $Ce(IO_3)_4$ coagulates. Cool, centrifuge and discard supernatant.

10. Wash precipitate twice with 15 ml KIO_3 wash solution and discard washings.

11. Transfer to a tared glass-fiber filter with KIO_3 wash solution.

12. Wash with successive portions of KIO_3 wash solution, water and ethanol.

13. Dry in oven at 110°C for 15 minutes, cool, weigh, mount and count.

Calculation

Calculate the concentration, D, of the cerium activity in pico-curies per milliliter as follows:

$$D = \frac{C}{2.22 \times EVR}$$

where:

C = net count rate, counts/min,
E = counter efficiency,
V = milliliters of sample used,
R = fractional chemical yield, and
2.22 = conversion factor from disintegrations/min to picocuries.

Calculate the counter efficiency, E, for gamma-ray spectrometry as follows:

$$E = Fp$$

where:

F = fractional abundance of the gamma ray, gammas/disintegration, and
p = photopeak detection efficiency, counts/gamma ray.

Calculate decay corrections as follows:

$$A = A_o e^{-0.693t/T}$$

where:

A = activity at time t,
A_o = activity at time zero,
e = base of natural logarithms,
t = elapsed time from collection, and
T = half life of separated nuclides, in same units as t.

Confirmation and Identification of Cerium Isotopes

1. Plot the gamma-ray spectrum of the separated sample to identify the ^{141}Ce photopeak at 145 keV, the ^{143}Ce photopeak at 293 keV, and/or the ^{144}Ce photopeak at 134 keV.
2. Beta count the planchets at 2-week intervals to measure decay and confirm the 32.5 d half life of ^{141}Ce, the 33 hr half life of ^{143}Ce, and/or the 284 d half life of ^{144}Ce.

Note:

1. A mixed anion resin is employed because, from a 12 $\underline{N}$ HCl solution, ruthenium and molybdenum are strongly adsorbed on Dowex 1; niobium is quantitatively adsorbed on Dowex 2; protactinium and zirconium are adsorbed equally well on either resin, whereas Ce^{+3} passes quantitatively into the effluent.

Reference:

1. Albu-Yaron, Ana, Mueller, D. W. and Settle, A. D., Jr., "Chemical Separation of Cerium Fission Products from Microgram Quantities of Uranium", Anal. Chem. 41, 1351, August 1969.

Radioactive Cesium

Principle of Method

Cesium carrier is added to the aqueous sample. The cesium is collected as the phosphomolybdate and purified as Cs_2PtCl_6 for counting.

Procedure Time

4 samples - 5 hrs.

Reagents

Ammonium phosphomolybdate, $(NH_4)_3PMo_{12}O_{40}$: prepared reagent
Calcium chloride, $CaCl_2$: 3 $\underline{M}$
Cesium carrier: 10 mg/ml
Chloroplatinic acid, $H_2PtCl_6.6H_2O$: 0.1 $\underline{M}$
Ethanol, C_2H_5OH: 95%
Hydrochloric acid, HCl: 12 $\underline{N}$ (conc.), 6 $\underline{N}$, 1 $\underline{N}$
Sodium hydroxide, NaOH: 6 $\underline{N}$

Procedure

1. To an aqueous sample (1000 ml or less), add 1.0 ml cesium carrier, and enough 12 $\underline{N}$ HCl to make the solution ~0.1 $\underline{N}$ HCl.

2. Slowly add 1 g ammonium phosphomolybdate and stir for 30 minutes, using a magnetic stirrer. Allow precipitate to settle for at least 4 hours, and discard supernatant. (Note 1).

3. Slurry precipitate into a centrifuge tube. Centrifuge and discard supernatant.

4. Wash precipitate with 20 ml 1 $\underline{N}$ HCl, and discard wash solution.

5. Dissolve precipitate by dropwise addition of 3-5 ml 6 $\underline{N}$ NaOH. Heat over a flame for several minutes to remove ammonium ions. (Moist pH paper turns green as long as NH_3 vapors are evolved.) Dilute to 20 ml with water.

6. Add 10 ml 3 $\underline{M}$ CaCl$_2$ and adjust to pH 7 with 6 $\underline{N}$ HCl to precipitate CaMoO$_4$. Stir, centrifuge and filter supernatant through Whatman #41 (or equivalent) into a 50 ml centrifuge tube.

7. Wash the precipitate remaining in the centrifuge tube with 10 ml water; filter through the same filter paper, and combine the wash with the filtrate. Discard filter paper.

8. Add 2 ml 0.1 $\underline{M}$ H$_2$PtCl$_6$ and 5 ml ethanol. Cool and stir in ice bath for 10 minutes.

9. Transfer to a tared glass-fiber filter with water. Wash with successive portions of water, 1 $\underline{N}$ HCl and ethanol.

10. Dry, cool, weigh, mount and count.

Calculation

Calculate the concentration, D, of the cesium activity in pico-curies per milliliter as follows:

$$D = \frac{C}{2.22 \times EVR}$$

where:

C = net count rate, counts/min,
E = counter efficiency,
V = milliliters of sample used,
R = fractional chemical yield, and
2.22 = conversion factor from disintegrations/min to picocuries.

Calculate the counter efficiency, E, for gamma-ray spectrometry as follows:

$$E = Fp$$

where:

F = fractional abundance of the gamma ray, gammas/disintegration, and
p = photopeak detection efficiency, counts/gamma ray.

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Calculate decay corrections as follows:

$$A = A_o \, e^{-0.693t/T}$$

where:

A = activity at time t,
A_o = activity at time zero,
e = base of natural logarithms,
t = elapsed time from collection, and
T = half life of separated nuclide, in same units as t.

Confirmation of Purity of ^{134}Cs, ^{136}Cs and ^{137}Cs, and Identification of Cesium Isotopes

1. Plot the gamma-ray spectrum of the separated sample. The main ^{134}Cs photopeaks are at 605 keV and 796 keV; the main ^{136}Cs photo-peaks are at 818 keV and 1050 keV; and the ^{137}Cs photopeak is at 662 keV.
2. Repeat gamma spectral measurements at 1-week intervals to measure decay of the ^{136}Cs ($t_{1/2}$ = 13 d).
3. Beta count at 1-month intervals to measure decay and confirm half-life value for ^{134}Cs (2.07 yr).

Note:

1. If a small volume sample is analyzed, it is possible to transfer the solution directly to a centrifuge tube and there would be no need for lengthy settling time.

Reference:

1. Finston, H. L. and Kinsley, M. T., "The Radiochemistry of Cesium", AEC Rept. NAS-NS-3035 (1961).

Radioactive Chromium

Principle of Method*

Chromium carrier (Cr^{+3}) and appropriate holdback carriers are added to the acidified aqueous sample. Chromium is oxidized to the chromate (Cr^{+6}), and impurities are removed by nitric acid evaporations (to volatilize radioiodine) and cation exchange. The chromium is precipitated as $BaCrO_4$ for counting.

Procedure Time

2 samples - 5 hrs.

Reagents

Cation exchange resin
 Dowex 50W-X8 (100-200 mesh)
Ammonium chloride, NH_4Cl: 10%
Ammonium hydroxide, NH_4OH: 1 $\underline{N}$
Barium nitrate, $Ba(NO_3)_2$: 10%
Cesium carrier: 10 mg/ml
Chromium carrier: 10 mg/ml as Cr^{+3}
Cobalt carrier: 5 mg/ml
Ethanol, C_2H_5OH: 95%
Hydrochloric acid, HCl: 12 $\underline{N}$ (conc.)
Iron carrier: 10 mg/ml
Nitric acid, HNO_3: 16 $\underline{N}$ (conc.)
Sodium hypochlorite, NaOCl: 5%
Sodium metaperiodate, $NaIO_4$: solid

Procedure

1. To an aqueous sample (100 ml or less), add 1 ml 16 $\underline{N}$ HNO_3, 1.0 ml chromium carrier and 0.1 ml each of iron, cobalt and cesium holdback carriers. Mix well and evaporate sample to dryness (do not bake).

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*This procedure was developed by Robert Lieberman, Analytical and Radiochemistry Research Section, EERF, Montgomery, Alabama 36101.

2. Prepare a cation exchange resin column as follows:

   Slurry Dowex 50W-X8 resin (100-200 mesh) with water and transfer to a column 2.5 cm (I.D.) x 30 cm until a layer 8 cm deep is formed. Wash column with 100 ml water and pass 100 ml 10% NH_4Cl through the column. Wash column with another 100 ml water. (Note 1).

3. Cool the residue from step 1. Add 25 ml 16 $\underline{N}$ HNO_3 and evaporate to dryness. Repeat.

4. Slurry residue with 35 ml water. Heat to boiling and add 50 ml water.

5. Add 1 ml 5% NaOCl and continue heating for 5 minutes.

6. Add 1 ml 16 $\underline{N}$ HNO_3 and evaporate sample to approximately 75 ml. [Sample should have a bright yellow color at this stage.] Cool.

7. Pass the solution over the cation exchange resin column at a rate of 2 ml/min and collect effluent in a 250 ml beaker.

8. Wash the column with 100 ml water and add this wash to the effluent from step 7.

9. Adjust the sample to pH 5 with 1 $\underline{N}$ NH_4OH, add 2 ml 10% $Ba(NO_3)_2$ and stir for 1 hour to precipitate barium chromate. Allow precipitate to settle and discard the clear supernatant.

10. Slurry the precipitate into a centrifuge tube with 15 ml water. Centrifuge and discard supernatant.

11. Wash the precipitate with 20 ml water and discard wash solution.

12. Transfer to a tared glass-fiber filter with water. Wash with successive portions of water and ethanol.

13. Dry, cool, weigh, mount and count.

Calculation

Calculate the concentration, D, of the chromium activity in pico-curies per milliliter as follows:

$$D = \frac{C}{2.22 \times EVR}$$

where:

C = net count rate, counts/min,
E = counter efficiency,
V = milliliters of sample used,
R = fractional chemical yield, and
2.22 = conversion factor from disintegrations/min to picocuries.

Calculate the counter efficiency, E, for gamma-ray spectrometry as follows:

$$E = Fp$$

where:

F = fractional abundance of the gamma ray, gammas/disintegration, and
p = photopeak detection efficiency, counts/gamma ray.

Calculate decay corrections as follows:

$$A = A_o \, e^{-0.693t/T}$$

where:

A = activity at time t,
A_o = activity at time zero,
e = base of natural logarithms,
t = elapsed time from collection, and
T = half life of ^{51}Cr in same units as t, ($t_{1/2}$ = 27.8 d).

Confirmation of Purity of ^{51}Cr Activity and Measurement of Activity

1. Plot the gamma-ray spectrum of the separated sample. The ^{51}Cr photopeak is at 320 keV.
2. Repeat gamma spectral measurement at 1-month intervals to measure decay and confirm the purity of the ^{51}Cr.

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Note:

1. The cation resin is regenerated by passing 200 ml 12 $\underline{N}$ HCl through the column. It is then prepared for subsequent use by washing with 100 ml water, followed by 100 ml 10% NH_4Cl and a final wash with 100 ml water.

Reference:

1. Pijck, J., "Radiochemistry of Chromium", AEC Rept. NAS-NS-3007, 1964.

Radioactive Cobalt and Cadmium

Principle of Method

Cobalt and cadmium carriers are added to the aqueous sample and collected as insoluble hydroxides. The cobalt is precipitated and purified as $K_3Co(NO_2)_6$ for counting; cadmium is precipitated as the sulfide in acid solution and purified as $Cd(OH)_2$ for counting.

Procedure Time

4 samples - 8 hrs.

Reagents

Acetic acid, CH_3COOH: 8 $\underline{N}$
Ammonium acetate buffer, $(CH_3COOH-CH_3COONH_4)$: pH 5.0
Cadmium carrier: 20 mg/ml
Cobalt carrier: 5 mg/ml
Ethanol, C_2H_5OH: 95%
Hydrochloric acid, HCl: 12 $\underline{N}$ (conc.), 2 $\underline{N}$
Hydrogen peroxide, H_2O_2: 30%
Hydrogen sulfide, H_2S: gas
Potassium hydroxide, KOH: 6 $\underline{N}$
Potassium nitrite wash solution: (1:100)
Potassium nitrite, KNO_2: solid
Nitric acid, HNO_3: 16 $\underline{N}$ (conc.), 6 $\underline{N}$
Sodium hydroxide, NaOH: 6 $\underline{N}$, 2 $\underline{N}$
Thioacetamide, CH_3CSNH_2*: 5%

Procedure

1. To an aqueous sample (100 ml or less), add 1.0 ml each of cobalt

    and cadmium carriers.

2. Slowly add at least 2 drops H_2O_2 and 6 $\underline{N}$ KOH until precipitation

    of hydrous oxides is complete. Heat to coagulate, cool, centrifuge

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*If thioacetamide solution is preferred to hydrogen sulfide, 2 ml of the solution, with vigorous stirring, can be substituted in those steps requiring H_2S.

and discard supernatant. (Note 1).

3. Dissolve precipitate in 5 ml 8 $\underline{N}$ acetic acid and 2 drops H_2O_2 with heating. Dilute to 15 ml with water, add 5 ml ammonium acetate buffer solution (pH 5) and heat to boiling in a water bath. Carefully add 5 g KNO_2 in small increments, with stirring. Continue boiling until gas evolution ceases and the potassium cobaltinitrite precipitate coagulates and settles. Cool, centrifuge, and filter supernatant containing the cadmium through Whatman #42 (or equivalent). Discard filter paper. Reserve the supernatant for the cadmium purification, steps 11 through 18.

4. Wash cobalt precipitate with 10 ml water and discard wash solution.

5. Dissolve precipitate with 1-2 ml 12 $\underline{N}$ HCl by heating and stirring until the solution is a clear blue.

6. Dilute to 10 ml and add at least 2 drops H_2O_2 and 6 $\underline{N}$ KOH until hydrous oxide precipitation is complete. Heat to coagulate, cool, centrifuge and discard supernatant.

7. Dissolve the precipitate in 5 ml 8 $\underline{N}$ acetic acid and 2 drops H_2O_2 by heating in a boiling water bath. Dilute to 15 ml with water, add 5 ml ammonium acetate buffer solution, heat to boiling and carefully add 5 g KNO_2 in small increments with stirring. Continue boiling until gas evolution ceases and the potassium cobaltinitrite precipitate settles. Cool at least 30 minutes, centrifuge and discard supernatant.

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8. Wash precipitate with 15 ml KNO_2-wash solution and discard wash solution.

9. Transfer to a tared glass-fiber filter with water. Wash with successive portions of water and ethanol.

10. Dry, cool, weigh, mount and count cobalt activity.

11. To the supernatant from step 3, add 6 $\underline{N}$ NaOH until the precipitation is complete. Stir in a water bath for a few minutes and let the precipitate settle. Centrifuge and discard supernatant.

12. Dissolve the precipitate with 1 ml 12 $\underline{N}$ HCl, dilute to 50 ml and heat almost to boiling.

13. Bubble in H_2S for one minute to precipitate CdS. Cool, centrifuge and discard supernatant.

14. To the precipitate add 15 ml 2 $\underline{N}$ NaOH and stir in water bath for 15 minutes.

15. Cool, centrifuge and discard supernatant. Wash precipitate with 20 ml water and discard wash solution.

16. Dissolve precipitate with 2 ml 6 $\underline{N}$ HNO_3 with heating and add 10 ml water (Note 2).

17. Add 6 $\underline{N}$ NaOH until $Cd(OH)_2$ precipitate forms. Cool and filter through a tared glass-fiber filter. Wash with successive portions of water and ethanol.

18. Dry, cool, weigh, mount and count the cadmium activity.

Calculations

I. Cobalt isotopes

Calculate the concentration, D, of cobalt-57, cobalt-58 and cobalt-60 in picocuries per milliliter as follows:

$$D = \frac{C}{2.22 \times EVR}$$

where:

C = net count rate, counts/min,
E = counter efficiency,
V = milliliters of sample used,
R = fractional chemical yield, and
2.22 = conversion factor from disintegrations/min to picocuries.

Calculate the counter efficiency, E, for gamma-ray spectrometry for each cobalt isotope as follows:

$$E = Fp$$

where:

F = fractional abundance of the gamma ray, gammas/disintegration, and
p = photopeak detection efficiency, counts/gamma ray.

Calculate the decay correction for the cobalt isotopes as follows:

$$A = A_o\, e^{-0.693t/T}$$

where:

A = activity at time t,
A_o = activity at time zero,
e = base of natural logarithms,
t = elapsed time from collection, and
T = half life of separated nuclide, in same units as t.

Confirmation and Identification of Cobalt Isotopes

1. Plot gamma-ray spectrum of separated sample immediately to identify the ^{57}Co (122 keV), ^{58}Co (511 keV and 810 keV) and ^{60}Co (1173 keV, 1332 keV and the 2505 keV sum) photopeaks.

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2. Repeat the gamma measurement after 2 and 4 weeks to observe the decay of the shorter-lived isotopes.
3. Beta count the planchet immediately and at 1-month intervals to corroborate the half lives of ^{58}Co (270 d) and ^{60}Co (5.26 yr). (Note 3).

II. Cadmium isotopes

Calculate the concentration, counter efficiency and decay correction for cadmium-109 and cadmium-115m in picocuries per milliliters as shown above for cobalt isotopes.

Confirmation and Identification of Cadmium Isotopes

1. Plot the gamma ray spectrum of the separated sample to identify the ^{109}Cd photopeak at 88 keV and the ^{115m}Cd photopeak at 485 keV.
2. Beta count the planchet at 2-week intervals to measure decay and confirm the 43 d half life of ^{115m}Cd and/or the 453 d half life of ^{109}Cd.

Notes:

1. More H_2O_2 may be needed if H_2O_2 is not absolutely fresh or if the sample contains reducing reagents. An excess of H_2O_2 will not hinder the analysis.
2. If any undissolved residue remains at this point, the solution should be filtered and the clear supernatant transferred to a clean centrifuge tube.
3. The ^{40}K beta in $K_3Co(NO_2)_6$ will add approximately 10 dpm per 20 mg separated precipitate, and this background must be taken into consideration during the beta-decay counting.

References:

1. Lingane, J. J., Lingane, P. J. and Morris, M. D., Anal. Chim. Acta, 29, 10 (1963).
2. Lingane, J. J., ibid, 31, 315 (1964).

Radioactive Cobalt and Nickel

Principle of Method

Cobalt and nickel carriers are added to the aqueous sample and precipitated as insoluble hydroxides. The cobalt is separated and purified as $K_3Co(NO_2)_6$ for counting. The nickel is reprecipitated as the hydroxide, purified with dimethylglyoxime and collected as the hydroxide dissolved in caproic acid. To measure ^{63}Ni, the solution is mixed with scintillation solution and counted in a liquid scintillation spectrometer.

Procedure Time

2 samples - 8 hrs.

Reagents

Anion exchange resin
  Dowex 1-X8 (20-50 mesh)
Acetic acid, CH_3COOH: 8 $\underline{N}$
Ammonium acetate buffer, $(CH_3COOH-CH_3COONH_4)$: pH 5.0
Ammonium hydroxide, NH_4OH: 15 $\underline{N}$ (conc.)
Caproic acid, $CH_3(CH_2)_4COOH$
Chloroform, $CHCl_3$
Cobalt carrier: 5 mg/ml
Dimethylglyoxime, $(CH_3C:NOH)_2$: 1% in C_2H_5OH
Ethanol, C_2H_5OH: absolute (99.5%), 95%
Hydrochloric acid, HCl: 12 $\underline{N}$ (conc.), 4 $\underline{N}$
Hydrogen peroxide, H_2O_2: 30%
Lanthanum carrier: 10 mg/ml
Nickel carrier: 5 mg/ml
Nitric acid, HNO_3: 16 $\underline{N}$ (conc.), 6 $\underline{N}$
Potassium hydroxide, KOH: 6 $\underline{N}$
Potassium nitrite wash solution: (1:100)
Potassium nitrite, KNO_2: solid
Scintillation solution (toluene), prepared reagent
Sodium citrate, $Na_3C_6H_5O_7 \cdot 2H_2O$: 10%
Sodium hydroxide, NaOH: 6 $\underline{N}$

<u>Procedure</u>

1. To an aqueous sample (100 ml or less), add 1.0 ml each of cobalt and nickel carriers.

2. Proceed with steps 2-10, of the Cobalt and Cadmium procedure, page 61, to separate and purify the cobalt. Reserve the supernatant from step 3, Cobalt and Cadmium procedure for nickel purification.

3. Prepare an anion column equilibrated on the Cl^- cycle as follows: Slurry Dowex 1-X8 (20-50 mesh) resin with water and transfer to a column 1.0 cm (I.D.) x 20 cm until a layer 10 cm deep is formed. Wash column with 25 ml water and 50 ml 12 $\underline{N}$ HCl before each use.

4. To the supernatant containing the nickel activity, add 6 $\underline{N}$ KOH until precipitation of nickel hydroxide is complete. Heat to coagulate, cool, centrifuge and discard supernatant.

5. Wash precipitate with 20 ml water and discard wash solution.

6. Dissolve precipitate by warming in 2 ml 12 $\underline{N}$ HCl. Add 5 ml 12 $\underline{N}$ HCl and pass solution over the anion resin column previously equilibrated with 50 ml 12 $\underline{N}$ HCl. Wash column with 10 ml 12 $\underline{N}$ HCl and collect entire effluent in a 100 ml beaker. (Note 1).

7. Evaporate effluent almost to dryness and transfer to a centrifuge tube with a little water. Add 1 ml lanthanum carrier, 10 ml water and make solution basic with excess 15 $\underline{N}$ NH_4OH. Centrifuge, decant supernatant into a 500 ml separatory funnel and discard precipitate.

8. Mix 5 ml 10% sodium citrate and 10 ml 1% dimethylglyoxime with solution in separatory funnel. Extract the nickel dimethylglyoximate into chloroform by shaking for 5 minutes with 300 ml chloroform. Drain chloroform layer into a beaker and discard aqueous phase. (Perform extraction in hood.)

9. Pour chloroform layer into a clean separatory funnel and wash twice with 50 ml portions of water containing 0.5 ml 15 $\underline{N}$ NH_4OH. Drain chloroform layer into a beaker, discard the wash solution and return the chloroform to the separatory funnel.

10. Add 25 ml 4 $\underline{N}$ HCl to chloroform and extract nickel into HCl solution by shaking 5 minutes. Discard chloroform layer and drain aqueous phase into a 100 ml beaker.

11. Evaporate solution to dryness (do not bake), cool, add 10 ml 16 $\underline{N}$ HNO_3 and evaporate to dryness again. Cool, take up residue in 4 ml 12 $\underline{N}$ HCl and transfer to a centrifuge tube with a little water. (Note 2).

12. Make solution basic with 6 $\underline{N}$ NaOH to precipitate nickel hydroxide, centrifuge and discard supernatant.

13. Dissolve precipitate with 1-2 ml 12 $\underline{N}$ HCl and dilute to 5 ml with water.

14. Add 15 $\underline{N}$ NH_4OH until solution is strongly basic, then add 5-10 ml 1% dimethylglyoxime to precipitate nickel dimethylglyoximate. Stir, centrifuge and discard supernatant.

15. Wash with a mixture of 15 ml water and 15 ml 95% ethanol and discard wash solution.

16. Slurry precipitate with 95% ethanol on a tared stainless steel planchet. Dry, cool and weigh for chemical yield determination and beta measurement in gas flow counter. (Note 3).

17. Dissolve precipitate with 1-2 ml 12 $\underline{N}$ HCl, add 10 ml 16 $\underline{N}$ HNO$_3$ and evaporate to dryness. Repeat with an additional 5 ml 16 $\underline{N}$ HNO$_3$. Dissolve residue with 5 ml 12 $\underline{N}$ HCl and evaporate to dryness. Repeat with an additional 5 ml 12 $\underline{N}$ HCl. Transfer to centrifuge tube by rinsing beaker with a few ml 12 $\underline{N}$ HCl followed by a little water. Heat to dissolve, and filter if any residue remains.

18. Make solution basic with 6 $\underline{N}$ NaOH to precipitate nickel hydroxide, centrifuge and discard supernatant.

19. Wash precipitate with a few ml water added to a few ml 95% ethanol. Centrifuge and discard wash solution.

20. Dissolve precipitate in 1 ml caproic acid and add 3 ml absolute ethanol. Transfer to a low-K glass liquid scintillation vial containing 16 ml toluene scintillation solution. Shake well and dark-adapt sample prior to counting.

21. Prepare background and [63]Ni standard samples in a similar manner and count alternately at predetermined settings. (Note 4).

Calculations

I. Cobalt isotopes

Calculate the concentration, D, of cobalt-57, cobalt-58 and cobalt-60 in picocuries per milliliter as follows:

$$D = \frac{C}{2.22 \times EVR}$$

where:

C = net count rate, counts/min,
E = counter efficiency,
V = milliliters of sample used,
R = fractional chemical yield, and
2.22 = conversion factor from disintegrations/min to picocuries.

Calculate the counter efficiency, E, for gamma-ray spectrometry for each cobalt isotope as follows:

$$E = Fp$$

where:

E = fractional abundance of the gamma ray, gammas/disintegration, and
p = photopeak detection efficiency, counts/ gamma ray.

Calculate the decay correction for the cobalt isotopes as follows:

$$A = A_o\, e^{-0.693t/T}$$

where:

A = activity at time t,
A_o = activity at time zero,
e = base of natural logarithms,
t = elapsed time from collection, and
T = half life of separated nuclide in same units as t.

Confirmation and Identification of Cobalt Isotopes

1. Plot gamma-ray spectrum of separated sample immediately to identify the ^{57}Co (122 keV), ^{58}Co (511 keV and 810 keV) and ^{60}Co (1173 keV, 1332 keV and the 2505 keV sum) photopeaks

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2. Repeat the gamma measurement after 4 weeks to observe the decay of the shorter-lived isotopes.

3. Beta count the planchet immediately and at 1-month intervals to corroborate half lives of ^{58}Co (71 d), ^{57}Co (270 d) and ^{60}Co (5.26 yr).

II. Nickel-63

    a. Gas-flow beta counter

Calculate the concentration, D, of nickel-63 in picocuries per milliliter as follows:

$$D = \frac{C}{2.22 \times EVR}$$

where:

C = net count rate, counts/min,
E = counter efficiency,
V = milliliters of sample used,
R = fractional chemical yield, and
2.22 = conversion factor from disintegrations/min to picocuries.

    b. Liquid scintillation analyzer

Calculate the concentration, D, of nickel-63 in picocuries per milliliter as follows:

$$\frac{S-B}{2.22 \times EVR}$$

where:

S = counts/min accumulated in sample,
B = background of blank in counts/min,
V = milliliters of sample used,
R = fractional chemical yield as determined in step 16, and
2.22 = conversion factor from disintegrations/min to picocuries.

Confirmation of ^{63}Ni Activity

A. Gas-flow beta counter

1. Determine the activity of ^{63}Ni by counting the stainless steel planchet with aluminum absorbers up to 10 mg/cm^2 and compare with a standard ^{63}Ni absorption curve (Fig. 4).
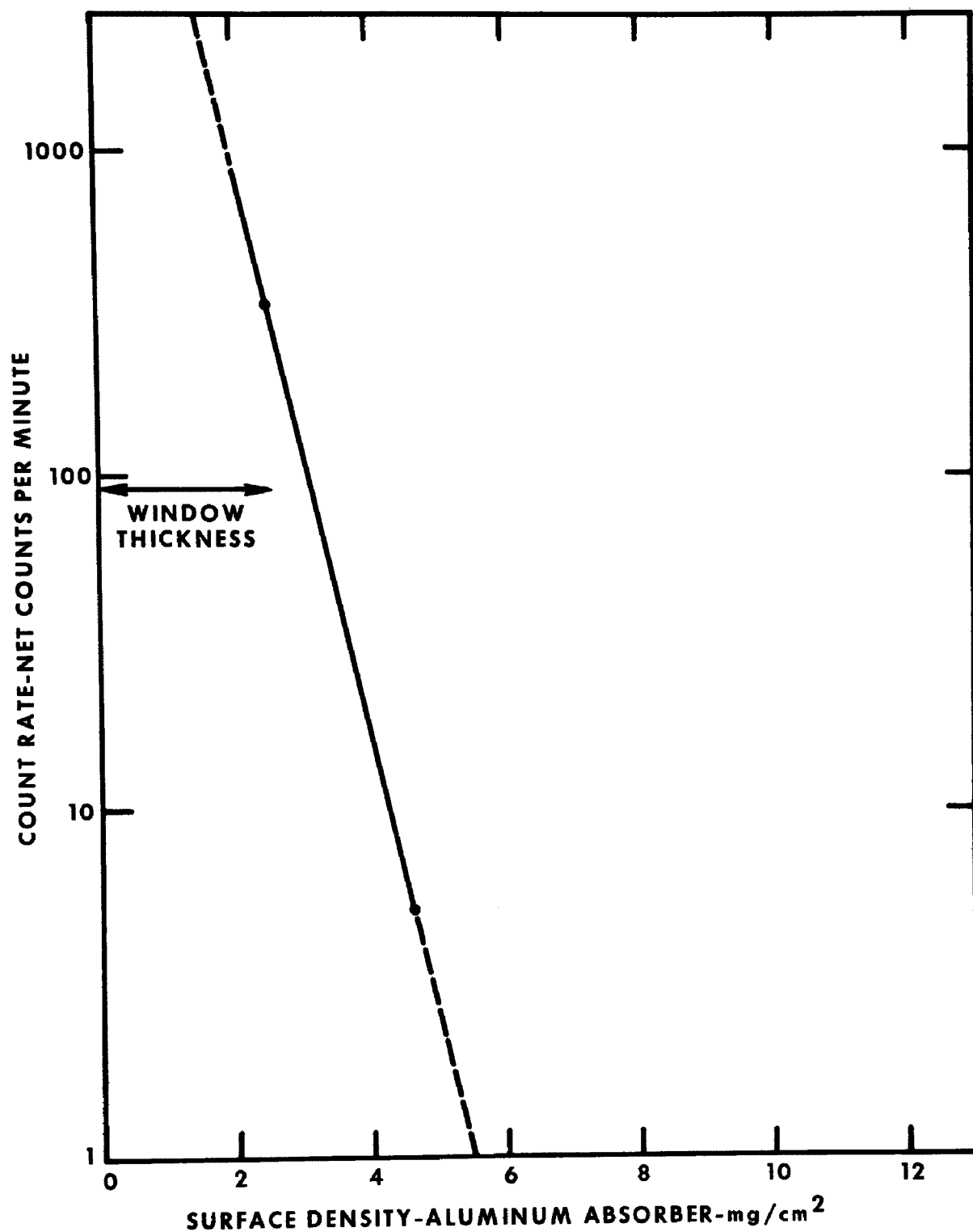
Figure 4. Absorption Curve for Nickel-63 Analysis (^{63}NiDMG on s.s. planchet) 2.5 mg/cm^2 Total Window Thickness Included

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2. Decay count over a period of 3 months to demonstrate the absence of short-lived radioactive impurities.

B. Liquid scintillation spectrometer

1. Determine the count rate for each sample, background and standard at two selected window settings. Compare the ratios for the ^{63}Ni standard with that for the samples to confirm that the activity being measured is nickel-63 (half life 92 y).
2. To make certain that the samples have been dark-adapted, count at least three times until successive results are within 2 σ differences of each other.

Notes:

1. Any cobalt interference is removed by anion exchange separation of its chloride complex.
2. Steps 13-17 are included to prepare the purified nickel dimethylglyoxime for beta particle counting and chemical yield determination. These steps can be omitted if chemical yield determination is not desired.
3. Steps 17-20 must be performed quantitatively if the chemical yield determined in step 16 is to be used in the calculation.
4. The samples are counted alternately with standard ^{63}Ni and background samples to nullify errors produced by aging of the scintillation medium or instrument drift.

Reference:

1. Gleit, C. E. and Dumot, J., Int. J. Appl. Radiat. 12, 1-2, 66 (1961).

Radioactive Copper and Technetium

Principle of Method

Copper carrier and appropriate holdback carriers are added to an acidified aqueous sample and both copper and technetium are precipitated as sulfides. After dissolving the precipitate, the technetium is separated from the copper by cation exchange purification and coprecipitated with copper carrier as CuS for counting. The copper is eluted from the resin column, reduced to Cu^+ with Na_2SO_3, and precipitated as CuSCN for counting.

Procedure Time

2 samples - 6 hrs.

Reagents

Cation exchange resin
    Dowex 50W-X8 (100-200 mesh)
Ammonium hydroxide, NH_4OH: 15 $\underline{N}$ (conc.), 2 $\underline{N}$
Cesium carrier: 10 mg/ml
Cobalt carrier: 5 mg/ml
Copper carrier: 20 mg/ml
Ethanol, C_2H_5OH: 95%, 20%
Hydrochloric acid, HCl: 12 $\underline{N}$ (conc.), 6 $\underline{N}$, 0.5 $\underline{N}$
Iron carrier: 10 mg/ml
Nitric acid, HNO_3:   16 $\underline{N}$ (conc.), 6 $\underline{N}$
Potassium thiocyanate, KSCN: 0.75 $\underline{M}$
Potassium thiocyanate wash solution: (1:200)
Silver carrier: 20 mg/ml
Sodium sulfite, Na_2SO_3:   solid
Sulfuric acid, H_2SO_4:   36 $\underline{N}$ (conc.), 3 $\underline{N}$
Thioacetamide, CH_3CSNH_2:   5%

Procedure

1. To an aqueous sample (100 ml or less), acidified with 6 $\underline{N}$ HNO_3, add

   1.0 ml copper carrier and 1 ml silver carrier.

2. Heat nearly to boiling and add 1 ml 0.5 $\underline{N}$ HCl dropwise while

   stirring. Digest until AgCl precipitates. Cool, filter through

Whatman #42 (or equivalent) into a clean beaker. Discard filter paper.

3. To filter add 0.5 ml each cobalt, iron and cesium carriers, neutralize with 15 $\underline{N}$ NH_4OH, then add enough 36 $\underline{N}$ H_2SO_4 to make the solution 3 $\underline{N}$ in H_2SO_4. Heat to near boiling and add dropwise, with stirring, 2 ml 5% thioacetamide. Digest on the hot plate and stir until the copper and technetium sulfides coagulate. Cool, centrifuge and discard supernatant.

4. Wash precipitate with 10 ml 3 $\underline{N}$ H_2SO_4 containing a few drops 5% thioacetamide and discard wash solution.

5. Dissolve precipitate in 1 ml 16 $\underline{N}$ HNO_3 by stirring and heating in a boiling water bath until solution is clear green and only a small amount of light colored residue remains. Add 5 ml water and filter through Whatman #41 (or equivalent) into a clean centrifuge tube. Wash the residue with a few ml water, add wash water to filtrate, and discard filter paper.

6. Add 3 ml 15 $\underline{N}$ NH_4OH and dilute to 15 ml. Pour solution over a previously prepared Dowex 50W-X8 (100-200 mesh) cation resin column 1 cm (I.D.) x 6 cm in depth which has been equilibrated with 50 ml 2 $\underline{N}$ NH_4OH.

7. Collect the technetium fraction effluent at 1 ml/min in a centrifuge tube. Wash column with 10 ml 2 $\underline{N}$ NH_4OH, collect in same tube and proceed with the technetium purification. The resin column containing the copper fraction is set aside until step 12.

8. Neutralize effluent with 36 $\underline{N}$ H_2SO_4. Make the solution 3 $\underline{N}$ in

   H_2SO_4 by adding 2.5 ml 36 $\underline{N}$ H_2SO_4 and diluting to 30 ml. Add

   0.5 ml copper carrier, heat to near boiling and add dropwise, with

   stirring 2 ml 5% thioacetamide to precipitate copper sulfide which

   carries the technetium activity. Digest in a water bath and stir

   until the precipitate coagulates. Cool, centrifuge and discard

   supernatant.

9. Wash precipitate with 10 ml 3 $\underline{N}$ H_2SO_4 containing a few drops 5%

   thioacetamide and discard wash solution.

10. Transfer to a tared glass-fiber filter with water. Wash with

    successive portions of water and ethanol.

11. Dry, cool, weigh, mount and count the technetium activity.

12. Elute copper from resin column with 15 ml 6 $\underline{N}$ HCl and collect in

    a beaker. Wash column with 10 ml 6 $\underline{N}$ HCl and add to beaker.

13. Evaporate to dryness. Slurry with 5 drops 6 $\underline{N}$ HCl and transfer to

    a centrifuge tube with 30 ml water.

14. Heat in a boiling water bath and reduce the Cu^{++} to Cu^{+} by adding

    Na_2SO_3 in small increments (a few grains on the tip of a spatula

    each time) with stirring until the solution is colorless and smells

    of SO_2. Add 1 ml 0.75 $\underline{M}$ KSCN and stir until CuSCN has coagulated.

    Cool, centrifuge and discard supernatant.

15. Wash with 10 ml KSCN-wash solution in which a few grains of Na_2SO_3

    have been dissolved, and discard wash solution.

16. Transfer to a tared glass-fiber filter with a few ml KSCN-wash solution. Wash 3 times with 5 ml 20% ethanol.

17. Dry, cool, weigh, mount and count the copper activity.

Calculations

I. Copper-64

Calculate the concentration, D, of copper-64 in picocuries per milliliter as follows:

$$D = \frac{C}{2.22 \times EVR}$$

where:

C = net count rate, counts/min,
E = counter efficiency,
V = milliliters of sample used,
R = fractional chemical yield, and
2.22 = conversion factor from disintegrations/min to picocuries.

Calculate the counter efficiency, E, for gamma-ray spectrometry as follows:

$$E = Fp$$

where:

F = fractional abundance of the gamma ray, gammas/disintegration, and
p = photopeak detection efficiency, counts/gamma ray.

Calculate the decay correction for ^{64}Cu as follows:

$$A = A_o \, e^{-0.693t/T}$$

where:

A = activity at time t,
A_o = activity at time zero,
e = base of natural logarithms,
t = elapsed time from collection, and
T = half life of the separated nuclide, in same units as t.

Confirmation of Purity and Identification of ^{64}Cu

1. Plot the gamma-ray spectrum of the separated sample immediately to identify the ^{64}Cu photopeak (511 keV) and verify the purity of the separation.
2. Repeat the gamma measurement daily for a week to follow decay of the photopeak.
3. Beta count the planchet at 2-, 6-, 12-, 24- and 48-hr intervals to corroborate the 12.8-hr half life.

II. Technetium-99m

Calculate the concentration, D, of ^{99m}Tc in picocuries per milliliter as follows:

$$D = \frac{C}{2.22 \times EVR}$$

where:

C = net count rate, counts/min,
E = counter efficiency,
V = milliliters of sample used,
R = fractional chemical yield for the separation (Note 1), and
2.22 = conversion factor from disintegrations/min to picocuries.

Calculate the counter efficiency, E, for gamma-ray spectrometry as follows:

$$E = Fp$$

where:

F = fractional abundance of the gamma ray, gammas/disintegration, and
p = photopeak detection efficiency, counts/gamma ray.

Calculate the decay correction for ^{99m}Tc as follows:

$$A = A_o \, e^{-0.693t/T}$$

where:

A = activity at time t,
A_o = activity at time zero,
e = base of natural logarithms,
t = elapsed time from collection, and
T = half life of ^{99m}Tc, in same units as t.

Confirmation of Purity and Identification of ^{99m}Tc

1. Plot the gamma-ray spectrum of the separated sample immediately and again in 4 hours to identify the ^{99m}Tc photopeak (140 keV) and to follow its decay.
2. Gamma scan the planchet after 24 hours to verify the 6.0-hr half life of ^{99m}Tc.

Note:

1. The chemical yield for ^{99m}Tc (step 11), does not account for any losses that may occur in the first seven steps. Studies with long-lived ^{99}Tc have indicated that > 95% of the technetium activity was present in the resin effluent. Analysts should determine their own average tracer loss and incorporate it in the calculations.

References:

1. Master Analytical Manual, Oak Ridge National Laboratory, USAEC Rept. TID-7015, Method 5-11230, 1957.
2. Anders, E., "The Radiochemistry of Technetium", USAEC Rept., NAS-NS-3021, 1960.
3. Kolthoff, I. M. and Sandell, E. B., Textbook of Quantitative Inorganic Analysis, (Macmillan, New York, N. Y., 1952) p. 671.

Radioactive Iodine

Principle of Method

Iodide carrier and appropriate holdback carriers are added to the sample. The sample is acidified, and iodine is distilled into caustic solution. The distillate is acidified and the iodine is extracted into CCl_4. After back extraction, the iodine is purified as AgI for counting.

Procedure Time

2 samples - 6 hrs.

Reagents

Ammonium hydroxide, NH_4OH: 15 $\underline{N}$ (conc.)
Carbon tetrachloride, CCl_4
Cobalt carrier: 5 mg/ml
Diethyl ether, $(C_2H_5)_2O$: anhydrous
Ethanol, C_2H_5OH: 95%
Iodide carrier: 20 mg/ml
Nitric acid, HNO_3: 16 $\underline{N}$ (conc.), 4 $\underline{N}$, 0.2 $\underline{N}$
Silver nitrate, $AgNO_3$: 0.1 $\underline{M}$
Sodium bisulfite, $NaHSO_3$: 1 $\underline{M}$
Sodium hydroxide, NaOH: 0.5 $\underline{N}$
Sodium nitrite, $NaNO_2$: 1 $\underline{M}$
Sulfuric acid, H_2SO_4: 12 $\underline{N}$
Tartaric acid, $C_4H_6O_6$: 50%

Procedure

1. To an unacidified aqueous sample (100 ml or less), in a 250 ml round bottom flask, add 15 ml 50% tartaric acid, 1.0 ml iodide carrier and 1 ml cobalt holdback carrier. Mix well, cautiously add 15 ml cold 16 $\underline{N}$ HNO_3 and close the distillation apparatus (Note 1).

2. Distill at least 15 minutes into 15 ml 0.5 $\underline{N}$ NaOH. Cool and transfer the NaOH solution to a 60 ml separatory funnel. Discard the solution in the round bottom flask.

3. Adjust the solution to slightly acid with 1 ml 12 $\underline{N}$ H_2SO_4 and oxidize with 1 ml 1 $\underline{M}$ $NaNO_2$. Add 10 ml CCl_4 and shake for 5-10 minutes. Draw off organic layer into a clean 60 ml separatory funnel containing 2 ml 1 $\underline{M}$ $NaHSO_3$.

4. Add 5 ml CCl_4 and 1 ml 1 $\underline{M}$ $NaNO_2$ to the original separatory funnel containing the aqueous layer and shake for 5-10 minutes. Combine the organic fraction with that in the separatory funnel in step 3.

5. Repeat step 4 and discard the aqueous layer.

6. Shake separatory funnel thoroughly until CCl_4 layer is decolorized, allow phases to separate and transfer aqueous layer to a centrifuge tube.

7. Add 2 ml 1 $\underline{M}$ $NaHSO_3$ to separatory funnel which has the CCl_4 and shake for several minutes. When the phases separate, combine this aqueous layer with that in centrifuge tube from step 6.

8. Add 1 ml water to separatory funnel and shake for several minutes. When the phases separate, add aqueous layer to the same centrifuge tube. Discard organic layer.

9. To the combined aqueous fractions, add 2 ml 0.1 $\underline{M}$ $AgNO_3$ plus 4 ml HNO_3. Stir for 1 minute then allow to stand 30 minutes at room temperature to coagulate silver iodide. Centrifuge at high speed for 10 minutes. Carefully decant and discard supernatant.

10. Pipet 5 ml 15 $\underline{N}$ NH_4OH into the centrifuge tube and stir thoroughly for several minutes. Heat carefully while stirring until boiling

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begins. Centrifuge at high speed for 10 minutes. Carefully

decant and discard supernatant.

11. Slurry precipitate in 10 ml water, add 1 ml 4 $\underline{N}$ HNO_3, stir and

immediately transfer precipitate to tared glass-fiber filter.

Filter slowly at first to prevent loss.

12. Wash precipitate on filter successively with 20 ml 0.2 $\underline{N}$ HNO_3,

20 ml ethanol and 20 ml diethyl ether. Let dry with suction at

least 10 minutes. Store in desiccator.

13. Weigh, mount and store in light-tight container until ready to

count.

Calculation

Calculate the concentration, D, of the iodine radioisotopes in picocuries per milliliter as follows:

$$D = \frac{C}{2.22 \text{ x } EVR}$$

where:

C = net count rate, counts/min,
E = counter efficiency,
V = milliliters of sample used,
R = fractional chemical yield, and
2.22 = conversion factor from disintegrations/min to picocuries.

Calculate the counter efficiency, E, for gamma-ray spectrometry as follows:

$$E = Fp$$

where:

F = fractional abundance of the gamma ray, gammas/disintegration, and
p = photopeak detection efficiency, counts/gamma ray.

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Calculate decay corrections as follows:

$$A = A_o \, e^{-0.693t/T}$$

where:

A = activity at time t,
A_o = activity at time zero,
e = base of natural logarithms,
t = elapsed time from collection, and
T = half life of separated nuclide, in same units as t.

Confirmation of Activity and Identification of Iodine Isotopes

1. Plot gamma-ray spectrum of separated sample immediately and after 6 hr, 24 hr, 2 d, 5 d, 1 week and 3 week intervals to identify 8.06-d ^{131}I (364, 637 and 284 keV), 20.9-hr ^{133}I (530 and 850 keV), and 6.7-hr ^{135}I (1130, 1260 and 1710 keV).
2. Beta-count the AgI planchet daily to measure and confirm half-life values for those isotopes present.

Note:

1. A distillation apparatus such as shown in Figure 1 (page 8) or equivalent can be used. It should consist of a round bottom flask fitted with a ground-glass joint that allows for a source of air to be bubbled into the sample, and has a delivery tube on the other end that extends into a caustic trap.

Reference:

1. Kleinberg, J. and Cowan, G. A., "The Radiochemistry of Fluorine, Chlorine, Bromine and Iodine", AEC Rept. NAS-NS-3005, 1960.

Radioactive Iron

Principle of Method

Iron carrier and the appropriate holdback carrier are added to the acidified aqueous sample. Iron is extracted into trioctylphosphine oxide and back extracted into dilute perchloric acid. After double precipitation of the hydrous oxide to separate it from impurities, the iron is precipitated as the alcohol-washed $Fe(OH)_3 \cdot 2H_2O$ for counting.

Procedure Time

2 samples - 4 hrs.

Reagent

Acetone, $(CH_3)_2CO$: anhydrous
Ammonium hydroxide, NH_4OH: 15 $\underline{N}$ (conc.), 1 $\underline{N}$
Cobalt carrier: 5 mg/ml
Ethanol, C_2H_5OH: 95%
Hydrochloric acid, HCl: 12 $\underline{N}$ (conc.), 6 $\underline{N}$
Indicator, methyl red: 0.1%
Iron carrier: 10 mg/ml
Perchloric acid, $HClO_4$: 1 $\underline{N}$
Pyridine, C_5H_5N
Trioctylphosphine oxide, $(C_8H_{17})_3PO$: 20% in xylene

Procedure

1. To an acidified aqueous sample (100 ml or less), add 1.0 ml iron

   carrier and 0.5 ml cobalt carrier and dilute or concentrate to

   20 ml. Transfer to a 125 ml separatory funnel (Note 1).

2. Add 50 ml 6 $\underline{N}$ HCl and 10 ml 20% trioctylphosphine oxide in xylene.

   Shake 5 min. and discard the bottom aqueous layer.

3. Wash with 10 ml 6 $\underline{N}$ HCl and discard wash solution

4. Back extract iron for 2 min. with 10 ml 1 $\underline{N}$ $HClO_4$ and transfer acid

   phase to a centrifuge tube.

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5. Repeat step 4 with a second 10 ml portion of 1 $\underline{N}$ HClO$_4$ and add the acid phase to the same centrifuge tube. Discard the organic layer.

6. Heat in a boiling water bath to drive off excess xylene. Cool to room temperature.

7. Add 2 drops methyl red indicator and a few ml 15 $\underline{N}$ NH$_4$OH until color just begins to change. Complete precipitation of iron by adding 1 $\underline{N}$ NH$_4$OH just to the permanent color change.

8. Stir in the hot water bath until the precipitate coagulates and settles readily. Centrifuge and discard supernatant. (Note 2).

9. Dissolve precipitate in 1.0 ml 6 $\underline{N}$ HCl with heating. Dilute to 20 ml with water, add 1 ml pyridine, stir well and heat in a water bath until precipitation is complete. (Note 3).

10. Cool, centrifuge and discard supernatant.

11. Wash precipitate with ~20 ml water. Centrifuge and discard the wash solution.

12. Break up the gelatinous precipitate with the tip of a thin stirring rod and a few drops of ethanol. Transfer to a tared glass-fiber filter with ethanol. Wash twice with ethanol and once with acetone, adding each portion just as the traces of the last addition have gone through the filter. Let air go through the filter for a few minutes.

13. Dry in an oven, cool in a desiccator and weigh to a constant weight. Mount, cover with 0.005 mm mylar and count.

Calculation

Calculate the concentration, D, of iron-59 in picocuries per milliliter as follows:

$$D = \frac{C}{2.22 \times EVR}$$

where:

C = net count rate, counts/min,
E = counter efficiency,
V = milliliters of sample used,
R = fractional chemical yield, and
2.22 = conversion factor from disintegrations/min to picocuries.

Calculate the counter efficiency, E, for gamma-ray spectrometry as follows:

$$E = Fp$$

where:

F = fractional abundance of the gamma ray, gammas/disintegration, and
p = photopeak detection efficiency, counts/gamma ray.

Calculate the decay correction for iron-59 as follows:

$$A = A_o \, e^{-0.693t/T}$$

where:

A = activity at time t,
A_o = activity at time zero,
e = base of natural logarithms,
t = elapsed time from collection,
T = half life of separated nuclide in same units as t.

Confirmation of ^{59}Fe Activity and Identification of Iron Isotopes

1. Plot gamma-ray spectrum of separated sample to identify photopeaks of 44.6-d ^{59}Fe (1099 and 1291 keV).
2. To identify and quantify the 2.7-yr ^{55}Fe, the sample is counted on an x-ray proportional counter capable of resolving the 5.90 keV ^{55}Fe photopeak from the adjacent 6.40 keV ^{58}Co peak. (Note 4).

Notes:

1. The sample should be acidified with 1 ml 12 $\underline{N}$ HCl per 50 ml solution since extraction efficiency is lowered if nitric acid is present.

2. For a sample containing significant cobalt activity, the following modification should be followed at this point:

    a. wash precipitate with ~20 ml water. Centrifuge and discard wash solution.

    b. dissolve precipitate with 1 ml 6 $\underline{N}$ HCl and heat. Dilute to 20 ml with water.

    c. add 1 ml pyridine, stir well and heat in a water bath to coagulate. Cool, centrifuge and discard supernatant.

    d. wash with ~20 ml water. Centrifuge and discard wash solution.

    e. dissolve precipitate with 1 ml 6 $\underline{N}$ HCl and heat. Dilute to 20 ml with water and add 1 ml cobalt holdback carrier. Place in a 125 ml separatory funnel.

    f. repeat Iron procedure steps 2-8.

3. Use pyridine in a hood.

4. This technique is especially useful if any radiocobalt still remains even after completing the procedure modification suggested in Note 2. If there is a possibility of small amounts of ^{58}Co being counted in the ^{55}Fe channels, this will be revealed by delayed counting to detect the faster decaying ^{58}Co.

References:

1. Nielsen, J. M., "The Radiochemistry of Iron", USAEC Rept. NAS-NS-3017, 1960.

2. Lingane, J. J. and Kerlinger, H., "Polarographic Determination of Nickel and Cobalt", Ind. Chem., Anal. Ed., $\underline{13}$, 77, 1941.

Radioactive Lanthanum
plus
Trivalent Rare Earths and Yttrium

Principle of Method

Lanthanum carrier and appropriate scavenging carriers are added to the acidified aqueous sample and impurities are removed by cobaltinitrite and iodate precipitations. The lanthanum is collected as the hydroxide and purified as $La_2(C_2O_4)_3 \cdot 8H_2O$ for counting.

Procedure Time

4 samples - 6 hrs.

Reagents

Acetic acid, CH_3COOH: 8 $\underline{N}$
Ammonium acetate buffer, $(CH_3COOH-CH_3COONH_4)$: pH 5.0
Boric acid, H_3BO_3: saturated
Cerium carrier: 5 mg/ml
Cobalt carrier: 5 mg/ml
Ethanol, C_2H_5OH: 95%
Hydrochloric acid, HCl: 6 $\underline{N}$
Hydrofluoric acid, HF: 48% (conc.)
Hydrogen peroxide, H_2O_2: 30%
Iodic acid, HIO_3: 0.35 $\underline{M}$
Lanthanum carrier: 10 mg/ml
Nitric acid, HNO_3: 16 $\underline{N}$ (conc.)
Oxalic acid, $H_2C_2O_4$: saturated
Potassium hydroxide, KOH: 6 $\underline{N}$
Potassium nitrite, KNO_2: solid
Sodium bromate, $NaBrO_3$: 0.5 $\underline{M}$
Sodium hydroxide, NaOH: 18 $\underline{N}$
Strontium carrier: 20 mg/ml

Procedure

1. To an aqueous sample (100 ml or less), add 1 ml 16 $\underline{N}$ HNO_3, 1.0 ml lanthanum carrier, and 1 ml each of cerium, cobalt and strontium carriers. Stir to mix well.

2. Slowly add at least 2 drops H_2O_2 and 6 $\underline{N}$ KOH until precipitation of

hydrous oxides is complete. Heat to coagulate, cool, centrifuge and discard supernatant.

3. Dissolve precipitate in 5 ml 8 $\underline{N}$ acetic acid and 2 drops H_2O_2 with heating. Dilute to 15 ml with water, add 5 ml ammonium acetate buffer solution (pH 5) and heat to boiling in a water bath. Carefully add 5 g KNO_2 in small increments, with stirring. Continue boiling until gas evolution ceases and the potassium cobaltinitrite precipitate settles.

4. Cool, centrifuge and filter supernatant through Whatman #42 (or equivalent), into a polypropylene tube containing 5 ml 16 $\underline{N}$ HNO_3. Discard filter paper.

5. Slowly add 20 drops HF, stir and let the fluoride precipitate settle for 5 minutes. Centrifuge and discard supernatant.

6. Wash twice with 20 ml water and discard wash solutions.

7. Dissolve precipitate with 1 ml sat. H_3BO_3 and 8 ml 16 $\underline{N}$ HNO_3. Add 4 ml 0.5 $\underline{M}$ $NaBrO_3$ to oxidize cerous to ceric ion and stir for 1 minute.

8. Add 20 ml 0.35 $\underline{M}$ HIO_3 slowly, with stirring. Cool in an ice bath for 5 minutes. Centrifuge, transfer supernatant to a glass centrifuge tube and discard precipitate.

9. Make basic with 5-10 ml 18 $\underline{N}$ NaOH to precipitate lanthanum and the rare earth hydroxides. Stir and cool for 5 minutes. Centrifuge and discard supernatant.

10. Wash precipitate with 30 ml water and discard the wash solution.

11. Dissolve precipitate with 1 ml 6 $\underline{N}$ HCl and add 15 ml water. Heat in a water bath, add 15 ml sat. $H_2C_2O_4$ with stirring and digest for a few minutes.

12. Cool, centrifuge and discard supernatant.

13. Wash precipitate with 15 ml hot water and discard wash solution.

14. Transfer to a tared glass-fiber filter with water. Wash with successive portions of water and ethanol.

15. Dry, cool, weigh, mount and count.

Calculations

    Calculate the concentration, D, of lanthanum-140 and/or the trivalent rare earths and yttrium* in picocuries per milliliter as follows:

$$D = \frac{C}{2.22 \text{ x EVR}}$$

where:

C = net count rate, counts/min,
E = counter efficiency,
V = milliliters of sample used,
R = fractional chemical yield, and
2.22 = conversion factor from disintegrations/min to picocuries.

    Calculate the counter efficiency, E, for gamma-ray spectrometry as follows:

$$E = Fp$$

*These nuclides include:		$T_{1/2}$					
	^{90}Y		64.0	hr		no gammas	
	^{91}Y		59	d			1210 keV
	^{93}Y		10.3	hr	297,	940 and	1900 keV
	^{147}Nd		11	d	91,	533 and	319 keV
	^{152}Eu		12.7	y	122,	344 and	1408 keV
	^{154}Eu		16	y	123,	724 and	1278 keV
	^{143}Pr		13.6	d		no gammas	
	^{147}Pm		2.6	y		no gammas	

where:

F = fractional abundance of the gamma ray, gammas/disintegration, and
p = photopeak detection efficiency, counts/gamma ray.

Calculate activity decay corrections as follows:

$$A = A_o \, e^{-0.693t/T}$$

where:

A = activity at time t,
A_o = activity at time zero,
e = base of natural logarithms,
t = elapsed time from collection, and
T = half life of the separated nuclide, in same units as t.

Confirmation of Purity and Identification of [140]La, the Trivalent Rare Earths and Yttrium*

1. Plot the gamma-ray spectrum of the separated sample immediately and again at daily intervals to identify the main [140]La photopeaks (1596 keV, 487 keV, 329 keV and 815 keV) and follow decay.

2. If other photopeaks are present, determine whether they represent trivalent rare earth peaks or are due to incomplete procedure decontamination. A distinct gamma photopeak at 1210 keV would suggest the presence of 59-d half life [91]Y. The measurement and identification of this nuclide can be confirmed by following photopeak decay at 2-week intervals.

3. If the planchet contains only photopeaks for [140]La, beta count at 2-day intervals to corroborate the [140]La half-life (40.2 hr). After 1 month, beta count to ascertain if [147]Pm activity is present (2.6 y $t_{1/2}$, no γ radiation).

Reference:

1. Stevenson, P. C. and Nervik, W. E., "The Radiochemistry of the Rare Earths, Scandium, Yttrium and Actinium", USAEC Rept. NAS-NS-3020, 1961.

*If yttrium isotopes, ^{90}Y, [91]Y or [93]Y, are believed to be present, the yttrium procedure, p. 151, should be performed on an acidified aliquot for verification.

Radioactive Manganese

Principle of Method

Manganese carrier and appropriate scavenging carriers are added to the acidified aqueous sample and impurities are removed by cobalti-nitrite and hydroxide precipitations. The manganese is purified as $MnNH_4PO_4 \cdot H_2O$ for counting.

Procedure Time

4 samples - 3 hrs.

Reagents

Acetic acid, CH_3COOH: 8 $\underline{N}$
Ammonium acetate buffer ($CH_3COOH-CH_3COONH_4$): pH 5.0
Ammonium hydroxide, NH_4OH: 6 $\underline{N}$
Ammonium phosphate, $NH_4H_2PO_4$: solid
Chromium carrier: 10 mg/ml as $Cr_2O_7^=$
Cobalt carrier: 5 mg/ml
Hydrogen peroxide, H_2O_2: 30%
Iron carrier: 10 mg/ml
Manganese carrier: 5 mg/ml
Nitric acid, HNO_3: 16 $\underline{N}$ (conc.)
Potassium hydroxide, KOH: 6 $\underline{N}$
Potassium nitrite, KNO_2: solid

Procedure

1. To an aqueous sample (100 ml or less), add 1 ml 16 $\underline{N}$ HNO_3, 1.0 ml manganese carrier and 0.5 ml each of cobalt, chromium and iron carriers. Stir to mix well.

2. Slowly add at least 2 drops H_2O_2 and 6 $\underline{N}$ KOH until precipitation of hydrous oxides is complete. Heat to coagulate, cool, centrifuge and discard supernatant.

3. Wash precipitate with ~20 ml water and discard wash solution.

4. Dissolve precipitate with 5 ml 8 $\underline{N}$ CH_3COOH and 2 drops H_2O_2 with heating. Dilute to 15 ml with water, add 5 ml ammonium acetate buffer solution (pH 5) and heat to boiling in a water bath. Carefully add 5 g KNO_2 in small increments, with stirring. Continue boiling until gas evolution ceases, and the precipitate of potassium cobaltinitrite settles. Cool, centrifuge and filter the supernatant through Whatman #42 (or equivalent) into a clean centrifuge tube. Discard filter paper.

5. Repeat steps 2 and 3.

6. Dissolve the precipitate with 1 ml 16 $\underline{N}$ HNO_3 and 1 drop H_2O_2.

7. Add 5 ml water, 0.5 ml iron carrier and heat almost to boiling. Adjust the pH to just below 7 with 6 $\underline{N}$ NH_4OH, stirring rapidly to effect precipitation of $Fe(OH)_3$.

8. Filter, while hot, through Whatman #41 (or equivalent) into a clean centrifuge tube. Discard precipitate.

9. Dilute to 15 ml with water, add 1 g $NH_4H_2PO_4$ and bring the solution nearly to boiling. Adjust to pH 7 with 6 $\underline{N}$ NH_4OH and stir until the crystalline precipitate manganese ammonium phosphate $[Mn(NH_4)PO_4.H_2O]$ forms.

10. Cool in an ice bath for 10 min., transfer to a tared glass-fiber filter, wash with successive portions of water and ethanol.

11. Dry, cool, weigh, mount and count.

Calculation

Calculate the concentration, D, of radioactive manganese in picocuries per milliliter as follows:

$$D = \frac{C}{2.22 \times EVR}$$

where:

C = net count rate, counts/min,
E = counter efficiency,
V = milliliters of sample used,
R = fractional chemical yield, and
2.22 = conversion factor from disintegrations/min to picocuries.

Calculate the counter efficiency, E, for gamma-ray spectrometry as follows:

$$E = Fp$$

where:

F = fractional abundance of the gamma ray, gammas/disintegration, and
p = photopeak detection efficiency, counts/gamma ray.

Calculate decay corrections as follows:

$$A = A_o \, e^{-0.693t/T}$$

where:

A = activity at time t,
A_o = activity at time zero,
e = base of natural logarithms
t = elapsed time from collection, and
T = half life of separated nuclide, in same units as t.

Confirmation of Purity and Identification of ^{54}Mn

1. Plot gamma-ray spectrum of separated sample to identify and quantify the 313 d ^{54}Mn photopeak (835 keV).
2. Repeat gamma spectrum measurement after 4 weeks to substantiate the manganese half life.

Reference:

1. Lingane, J. J., Analytical Chemistry of Selected Metallic Elements, (Reinhold, New York, N. Y. 1966) pp. 48-49.

Radioactive Molybdenum

Principle of Method

Molybdenum carriers and appropriate scavenging carriers are added to the aqueous sample. Impurities are removed by a double hydroxide scavenge followed by sample evaporation. The molybdenum is extracted into diethyl ether, back extracted into water, precipitated with α-benzoinoxime and ashed to MoO_3 for counting.

Procedure Time

2 samples - 6 hrs.

Reagents

α-Benzoinoxime: 2% in ethanol
Cobalt carrier: 5 mg/ml
Diethyl ether, $(C_2H_5)_2O$: anhydrous, equilibrated with 6 $\underline{N}$ HCl
Ethanol, C_2H_5OH: 95%
Hydrochloric acid, HCl: 12 $\underline{N}$ (conc.), 6 $\underline{N}$
Hydrogen peroxide, H_2O_2: 30%
Iron carrier: 10 mg/ml
Molybdenum carrier: 10 mg/ml
Nitric acid, HNO_3: 16 $\underline{N}$ (conc.), 1 $\underline{N}$, 0.2 $\underline{N}$
Potassium hydroxide, KOH: 6 $\underline{N}$
Sodium bromate, $NaBrO_3$: 1.5 $\underline{M}$
Tellurium carrier: 10 mg/ml

Procedure

1. To an aqueous sample (100 ml or less), add 2.0 ml molybdenum carrier and 0.5 ml each tellurium and cobalt carriers. Evaporate to dryness, cool and slurry residue with 10-20 ml water.

2. Slowly add at least 2 drops H_2O_2 and 6 $\underline{N}$ KOH until precipitation of cobalt hydrous oxide is complete. Heat to coagulate, filter while hot through Whatman #41 (or equivalent), and collect filtrate in a clean beaker. Discard filter paper.

3. Add 0.5 ml cobalt carrier and 2 drops H_2O_2 to the filtrate. Heat nearly to boiling, stir, filter while hot through Whatman #41 (or equivalent), and collect filtrate in a clean beaker. Discard filter paper.

4. Evaporate filtrate almost to dryness and add 5 drops each of iron carrier and 1.5 $\underline{M}$ $NaBrO_3$.

5. Adjust volume to 15 ml and add 0.5 ml cobalt carrier. Transfer to a 200 ml separatory funnel with 15 ml 12 $\underline{N}$ HCl to make solution ~6 $\underline{N}$ in HCl.

6. Shake for 15 minutes with 100 ml diethyl ether which was equilibrated with 6 $\underline{N}$ HCl. After the layers separate, discard the bottom aqueous layer.

7. Wash the ether twice with 2 ml 6 $\underline{N}$ HCl and discard the wash layers.

8. Back extract molybdenum three times with three 10 ml portions of water, combining the aqueous fractions in a beaker. Discard the ether layer.

9. Add 2 ml 16 $\underline{N}$ HNO_3, 0.5 ml cobalt holdback carrier and 10 ml α-benzoinoxime solution. Stir for 5 minutes, centrifuge and discard supernatant.

10. Wash with 15 ml 0.2 $\underline{N}$ HNO_3 and discard wash solution.

11. Slurry precipitate with a few ml water and filter through Whatman #42 (or equivalent). Complete the transfer with a few ml 1 $\underline{N}$ HNO_3. Discard filtrate.

12. Dry precipitate at 110°C for 15 minutes. Transfer to a platinum crucible and ash for 1 hour at 550°C to convert molybdenum to MoO_3.

13. Cool and transfer to a tared glass-fiber filter with water. Wash with successive portions of water and ethanol.

14. Dry, cool, weigh, mount and count.

Calculation

Calculate the concentration, D, of molybdenum-99 in picocuries per milliliter as follows:

$$D = \frac{C}{2.22 \times EVR}$$

where:

C = net count rate, counts/min,
E = counter efficiency,
V = milliliters of sample used,
R = fractional chemical yield, and
2.22 = conversion factor from disintegrations/min to picocuries.

Calculate the counter efficiency, E, for gamma-ray spectrometry as follows:

$$E = Fp$$

where:

F = fractional abundance of the gamma ray, gammas/disintegration, and
p = photopeak detection efficiency, counts/gamma ray.

Calculate the decay correction for molybdenum-99 as follows:

$$A = A_o \, e^{-0.693t/T}$$

where:

A = activity at time t,
A_o = activity at time zero

e = base of natural logarithms,

t = elapsed time from collection, and

T = half life of molybdenum-99 in same units as t $(t_{1/2} = 66.3$ hr).

Confirmation of Purity and Identification of Molybdenum-99

1. Plot the gamma-ray spectrum of the ashed precipitate soon after separation to identify any contaminating gamma emitters and the main ^{99}Mo photopeaks (181 and 740 keV).

2. Gamma scan at 2- or 3-day intervals to observe the 66.3 hr decay of the 740 keV ^{99}Mo photopeak. The presence of ^{99}Mo can also be corroborated by following the ingrowth of the 6.0 hr ^{99m}Tc daughter at 140 keV (abundance 90%). Any calculations based on the 140 keV peak, has to consider the 181 keV ^{99}Mo peak (abundance 7%).

3. Two days after separation, ^{99}Mo-^{99m}Tc equilibrium is nearly complete, and the 66.3 hr half life of ^{99}Mo can be corroborated by beta counting the planchet at 3-day intervals.

Reference:

1. Scadden E. M. and Ballou, N. E., "The Radiochemistry of Molybdenum", USAEC Rept. NAS-NS-3009, 1960.

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Neptunium

Principle of Method

Cerium carrier is added to the acidified aqueous sample, and is scavenged along with rare earth fission products by a fluoride precipitation in an oxidized solution while neptunium remains in solution. Lanthanum carrier and appropriate holdback carriers are added, and neptunium is collected on the lanthanum fluoride precipitate under reduced conditions. The neptunium is purified by a double hydroxide precipitation and is carried on $La(OH)_3$ for counting.

Procedure Time

2 samples - 3 hrs.

Reagents

Acetone, $(CH_3)_2CO$: anhydrous
Ammonium hydroxide, NH_4OH: 15 $\underline{N}$ (conc.), 1 $\underline{N}$
Boric acid, H_3BO_3: saturated
Cerium carrier: 5 mg/ml
Cesium carrier: 10 mg/ml
Cobalt carrier: 5 mg/ml
Ethanol, C_2H_5OH: 95%
Hydrochloric acid, HCl: 12 $\underline{N}$ (conc.), 6 $\underline{N}$
Hydrofluoric acid, HF: 48% (conc. ~30 $\underline{N}$), 1 $\underline{N}$
Indicator, phenolphthalein: 1%
Iron carrier: 10 mg/ml
Lanthanum carrier: 10 mg/ml
Manganese carrier: 5 mg/ml
Nitric acid, HNO_3: 16 $\underline{N}$ (conc.), 6 $\underline{N}$
Sodium bromate, $NaBrO_3$: 1.5 $\underline{M}$ (freshly prepared)
Sodium sulfite, Na_2SO_3: 1 $\underline{M}$
Zirconium carrier: 10 mg/ml

Procedure

1. To an aqueous sample (50 ml or less), add 2 ml 16 $\underline{N}$ HNO_3, 3 drops

   cerium carrier and evaporate to dryness. (Do not bake.)

2. Slurry with 2 ml 6 $\underline{N}$ HNO_3 and transfer to a polypropylene tube with

water to a volume of 10 ml. Add 1 drop cerium carrier and 1.5 ml

freshly prepared 1.5 $\underline{M}$ NaBrO$_3$. (Note 1). Digest and stir for

20 minutes in a water bath maintained at 95°C.

3. Cool to room temperature and make ~3 $\underline{N}$ in HF by adding 1.5 ml 48%

   HF (~30 $\underline{N}$) dropwise while stirring and diluting to 15 ml. Centri-

   fuge at least 10 min. (Note 2).

4. Destroy most of the bromates by adding 1-2 ml 12 $\underline{N}$ HCl dropwise and

   stirring in a boiling water bath until solution is clear. Cool

   slightly and add 15 ml freshly prepared 1 $\underline{M}$ Na$_2$SO$_3$. Add 1.0 ml

   lanthanum carrier and one drop each cobalt, manganese, iron,

   zirconium and cesium holdback carriers. Stir a few minutes in a

   boiling water bath.

5. Cool to room temperature and make ~3 $\underline{N}$ in HF by adding 3 ml 48% HF.

   Stir well during the addition of the HF, then allow the precipitate

   to settle.

6. Centrifuge at high speed at least 5 minutes and discard supernatant.

7. Wash with a solution containing 5 ml 1 $\underline{N}$ HNO$_3$, 5 ml 1 $\underline{N}$ HF and

   10 drops 1 $\underline{M}$ Na$_2$SO$_3$ and discard wash solution.

8. Dissolve fluorides with 1 ml sat. H$_3$BO$_3$ and 1 ml 16 $\underline{N}$ HNO$_3$. Dilute

   to 10 ml and make basic with 15 $\underline{N}$ NH$_4$OH to phenolphthalein end

   point. Add an additional 2 ml 15 $\underline{N}$ NH$_4$OH, and stir in a hot water

   bath until precipitate is well coagulated. Cool, centrifuge and

   discard supernatant. (Note 3).

9. Dissolve precipitate with 1-2 ml 6 $\underline{N}$ HCl, and dilute to 10 ml.
Filter through Whatman #41 (or equivalent) into a clean glass
centrifuge tube. Reprecipitate lanthanum hydroxide with 15 $\underline{N}$
NH_4OH as in step 8. Centrifuge and discard supernatant.

10. Wash precipitate with 10 ml $\underline{N}$ NH_4OH and discard wash solution.

11. Transfer to a tared glass-fiber filter with 1 $\underline{N}$ NH_4OH. Wash twice
with 10 ml ethanol and twice with 10 ml acetone.

12. Dry at 110°C for 30 minutes, cool, weigh, mount and count.

Calculation

Calculate the concentration, D, of the ^{239}Np in picocuries per
milliliter as follows:

$$D = \frac{C}{2.22 \times EVR}$$

where:

C = count rate, counts/min,
E = counter efficiency for ^{239}Np,
V = milliliters of sample used,
R = fractional chemical yield, and
2.22 = conversion factor from disintegrations/min to picocuries.

Calculate the counter efficiency, E, for gamma-ray spectrometry
as follows:

$$E = FP$$

where:

F = fractional abundance of the gamma rays, gammas/disintegration, and
p = photopeak detection efficiency, counts/gamma ray.

Calculate decay corrections as follows:

$$A = A_o \, e^{-0.693t/T}$$

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where:

A = activity at time t,
A_o = activity at time zero,
e = base of natural logarithms,
t = elapsed time from collection, and
T = half life of ^{239}Np in same units as t ($t_{1/2}$ = 2.34 d).

Confirmation of Purity and Identification of ^{239}Np

1. Plot the gamma-ray spectrum of the activity immediately after separation to identify any contaminating gamma emitters.
2. Gamma scan at 1-day intervals to observe the decay of predominant ^{239}Np photopeaks (106 keV, 228 keV and 278 keV).
3. Beta count the planchet daily to record the decay and corroborate the 2.34-d half life of ^{239}Np.

Notes:

1. Prepare only enough 1.5 $\underline{M}$ NaBrO$_3$ and 1 $\underline{M}$ Na$_2$SO$_3$ for each analysis.
2. Care must be taken to make the procedure quantitative, through step 3 and the first part of step 4, because no carrier is added for neptunium up to the point of addition of lanthanum carrier in step 4. The cerium fluoride precipitate can be dissolved and gamma scanned to make certain no neptunium was lost.
3. Further decontamination can be accomplished by adding one drop each of the holdback carriers and reprecipitating lanthanum fluoride under reducing conditions after dissolving the first lanthanum hydroxide precipitate, as follows:
   a. Dissolve hydroxide in 1-2 ml 6 $\underline{N}$ HCl and dilute to 10 ml with water.
   b. Add 10 ml 1 $\underline{M}$ Na$_2$SO$_3$ and 1 drop each of the cobalt, manganese, iron, zirconium and cesium holdback carriers. Stir for a few minutes in a boiling water bath.
   c. Repeat steps 5-8.

References:

1. Seaborg, G. T. and Katz, J. J., Eds., Radiochemical Studies: The Actinide Elements, Nat'l Nucl. Energy Series, Div. IV, 14A (McGraw-Hill, New York, N. Y., 1954) pp. 574-577.
2. Prakash, S., Advanced Chemistry of Rare Elements, (Chemical Publishing Co., Inc., New York, N. Y., 1967) pp. 777-778.

Radioactive Phosphorus

Principle of Method

Phosphorus carrier and appropriate scavenging carriers are added to the acidified aqueous sample and impurities are removed by a double hydroxide precipitation. The phosphorus is precipitated as $MgNH_4PO_4$ for counting.

Procedure Time

4 samples - 4 hrs.

Reagents

Ammonium hydroxide, NH_4OH: 15 $\underline{N}$ (conc.), 1 $\underline{N}$
Cobalt carrier: 5 mg/ml
Diethyl ether, $(C_2H_5)_2O$: anhydrous
Ethanol, C_2H_5OH: 95%
Hydrochloric acid, HCl: 12 $\underline{N}$ (conc.), 6 $\underline{N}$
Hydrogen peroxide, H_2O_2: 30%
Indicator, methyl red: 0.1%
Magnesia mixture: prepared reagent
Manganese carrier: 5 mg/ml
Nitric acid, HNO_3: 6 $\underline{N}$
Phosphorus carrier: 5 mg/ml
Potassium hydroxide, KOH: 6 $\underline{N}$
Silver carrier: 20 mg/ml
Zirconium carrier: 10 mg/ml

Procedure

1. To an aqueous sample (200 ml or less), add 1 ml 6 $\underline{N}$ HNO_3, 1.0 ml

   phosphorus carrier and 0.5 ml each cobalt, zirconium, silver and

   manganese carriers.

2. Slowly add at least 2 drops H_2O_2 and 6 $\underline{N}$ KOH until precipitation of

   hydrous oxides is complete. Heat to coagulate and filter while hot

   through Whatman #41 (or equivalent). Discard filter paper.

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3. To the filtrate add 2 drops cobalt and zirconium carriers and 2 drops H_2O_2. Heat to coagulate and filter while hot through Whatman #41 (or equivalent). Discard filter paper.

4. Acidify the filtrate with 12 $\underline{N}$ HCl and boil a few minutes to remove excess H_2O_2. Cool in an ice bath.

5. Add 3 ml magnesia mixture and neutralize to methyl red end point with 15 $\underline{N}$ NH_4OH to precipitate $MgNH_4PO_4$. Let stand 2 minutes then add 3 ml excess 15 $\underline{N}$ NH_4OH. Centrifuge and discard supernatant.

6. Wash the precipitate with 10 ml 1 $\underline{N}$ NH_4OH and discard wash solution.

7. Dissolve precipitate with 1 ml 6 $\underline{N}$ HCl. Transfer to an ice bath, add 10 ml water and 3 ml magnesia mixture and neutralize to methyl red end point with 15 $\underline{N}$ NH_4OH. Let stand 2 minutes then add 3 ml excess 15 $\underline{N}$ NH_4OH. Centrifuge and discard supernatant.

8. Repeat steps 6 and 7 using only 1 ml magnesia mixture.

9. Wash the precipitate with 10 ml 1 $\underline{N}$ NH_4OH and discard wash solution.

10. Transfer to a tared glass-fiber filter with 1 $\underline{N}$ NH_4OH. Wash with successive portions of 1 $\underline{N}$ NH_4OH, ethanol and ether.

11. Dry, cool, weigh, mount and count.

Calculation

Calculate the concentration, D, of phosphorus-32 in picocuries per milliliter as follows:

$$D = \frac{C}{2.22 \times EVR}$$

where:

C = net count rate, counts/min,
E = counter efficiency,
V = milliliters of sample used,
R = fractional chemical yield, and
2.22 = conversion factor from disintegrations/min to picocuries.

Calculate the decay correction for ^{32}P ($t_{1/2}$ = 14.3 d) as follows:

$$A = A_o \, e^{-0.693t/T}$$

where:

A = activity at time t,
A_o = activity at time zero,
e = base of natural logarithms,
t = elapsed time from collection, and
T = half life of ^{32}P, in same units as t.

Confirmation of Purity and Identification of ^{32}P

1. Plot the gamma-ray spectrum of the separated sample to ascertain whether any gamma photopeaks from impurities are present.
2. Beta count the planchet at 1-week intervals to corroborate the 14.3 d half-life of the phosphorus activity.

References:

1. Bowen, H. J. M. and Gibbons, D., Radioactivation Analysis (Oxford University Press, London, 1963) p. 222.
2. Kolthoff, I. M. and Sandell, E. B., Textbook of Quantitative Inorganic Analysis (Macmillan, New York, N. Y., 1952) pp. 316 and 379.

Radioactive Ruthenium

Principle of Method

Ruthenium carrier and the appropriate holdback carrier are added to a sample in a special distillation flask. In acid solution, in the presence of a strong oxidant, the ruthenium is converted to the tetroxide, distilled into caustic, and reduced to the metal for counting.

Procedure Time

4 samples - 3 hrs.

Reagents

Cobalt carrier: 5 mg/ml
Diethyl ether, $(C_2H_5)_2O$: anhydrous
Ethanol, C_2H_5OH: 95%
Hydrochloric acid, HCl: 12 $\underline{N}$ (conc.), 6 $\underline{N}$
Magnesium metal, Mg: solid
Phosphoric acid, H_3PO_4: 44 $\underline{N}$ (conc.)
Potassium permanganate, $KMnO_4$: 0.5 $\underline{M}$
Ruthenium carrier: 10 mg/ml
Sodium hydroxide, NaOH: 6 $\underline{N}$

Procedure

1. To an aqueous sample (100 ml or less) in a special ruthenium distillation flask (Fig. 5), add 2.0 ml ruthenium carrier and 1 ml cobalt holdback carrier.

2. Connect the ruthenium still to an air inlet, and insert the distilling end into a centrifuge tube containing 15 ml 6 $\underline{N}$ NaOH in an ice bath.

3. To distillation flask add 3 ml 44 $\underline{N}$ H_3PO_4 and 3 ml 0.5 $\underline{M}$ $KMnO_4$, and immediately close system.

AIR INLET →

5-mm ID TUBING

9.2 cm

9 cm

GROUND
GLASS
JOINT $\overline{S}\frac{24}{40}$

13.8 cm

30 cm

125-ml
← FLORENCE
FLASK

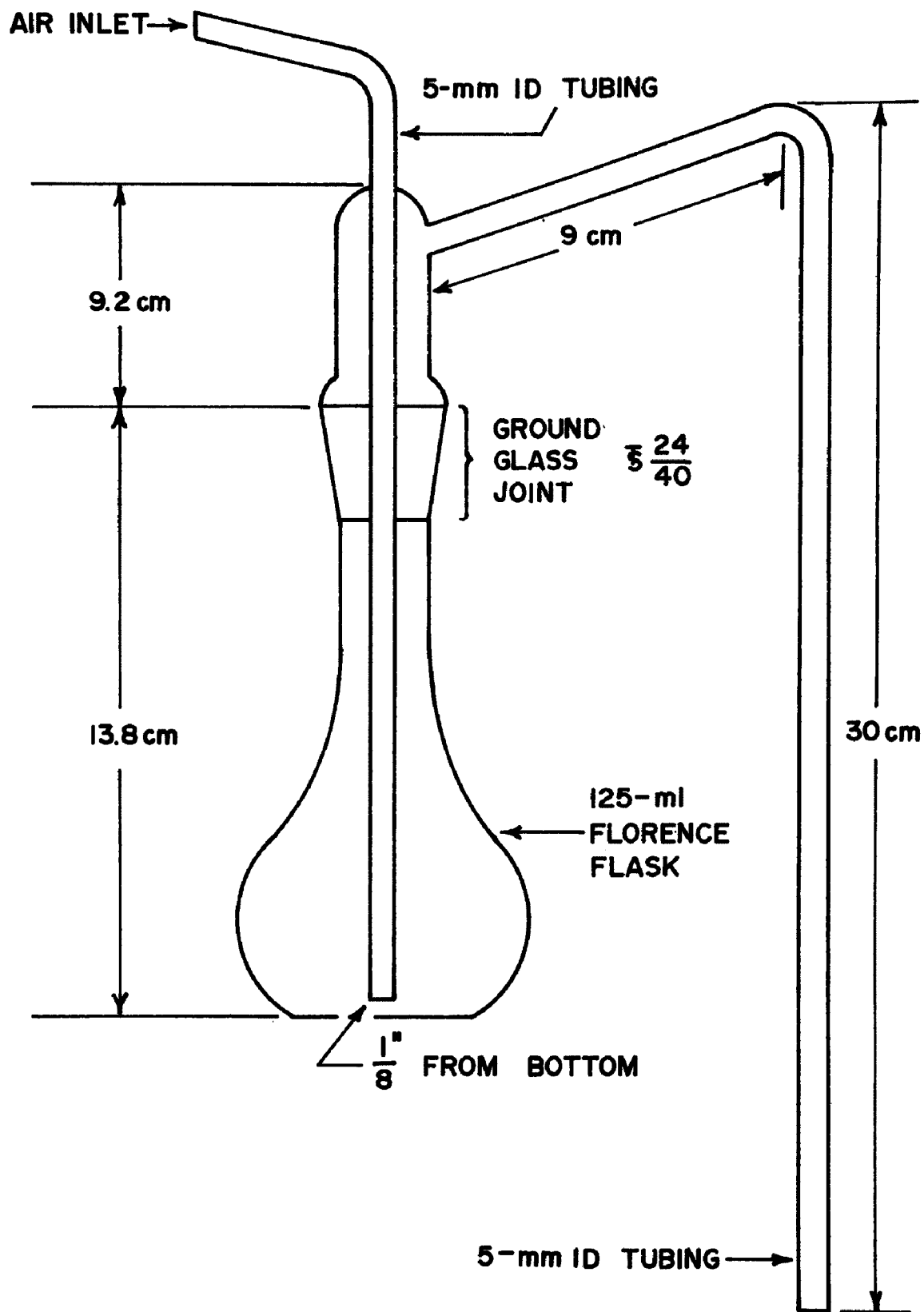$\frac{1''}{8}$ FROM BOTTOM

5-mm ID TUBING →

Figure 5. Distillation Apparatus for Ruthenium Analysis

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4. Pass air gently through system to drive volatile ruthenium into the NaOH solution. (Note 1).

5. Gently heat to boiling and continue heating for 10-15 minutes. Turn off air, disconnect apparatus and discard contents of still.

6. Add 3-5 ml ethanol to distillate, stir, boil to precipitate RuO_2 and cool. Centrifuge and discard supernatant.

7. Suspend precipitate in 10 ml water containing 1 ml 6 N NaOH. Boil, cool, centrifuge and discard supernatant.

8. Dissolve precipitate in 2 ml 6 N HCl, heating gently in a water bath to aid dissolution.

9. Add 10 ml water and slowly add 100-200 mg magnesium metal in small portions, adding each portion when the previous addition has been oxidized.

10. Boil until ruthenium metal has completely precipitated. Wash walls of tube with a few drops of 12 N HCl and add additional HCl to dissolve residual magnesium. Cool, centrifuge and discard supernatant.

11. Transfer precipitate to a tared glass-fiber filter with 15 ml water. Wash with successive portions of water, ethanol and ether.

12. Dry, cool, weigh, mount and count.

Calculation

Calculate the concentration, D, of radioactive ruthenium in pico-curies per milliliter as follows:

$$D = \frac{C}{2.22 \times EVR}$$

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where:

C = net count rate, counts/min,
E = counter efficiency,
V = milliliters of sample used,
R = fractional chemical yield, and
2.22 = conversion factor from disintegrations/min to picocuries.

Calculate the counter efficiency, E, for gamma-ray spectrometry as follows:

$$E = Fp$$

where:

F = fractional abundance of the gamma ray, gammas/disintegration, and
p = photopeak detection efficiency, counts/gamma ray.

Calculate the decay correction for radioactive ruthenium as follows:

$$A = A_o \, e^{-0.693t/T}$$

where:

A = activity at time t,
A_o = activity at time zero,
e = base of natural logarithms,
t = elapsed time from collection, and
T = half life of separated nuclides, in same units as t.

Confirmation of Purity and Identification of Ruthenium Isotopes

1. Plot the gamma-ray spectrum of the separated sample. The ^{106}Ru (^{106}Rh) photopeaks are at 512 keV and 620 keV; the ^{103}Ru photopeaks are at 497 keV and 610 keV.
2. The ^{106}Ru (^{106}Rh) and the ^{103}Ru photopeaks are distinguished by differing relative intensities of gamma rays at approximately 500 and 600 keV. These ratios, previously determined with standardized tracer solutions, can indicate if either of these ruthenium isotopes is present alone.
3. Beta-count the planchet at 1-month intervals to measure decay and confirm the half-life values for the isotope(s) present: ^{103}Ru, 39.7 d; ^{106}Ru,1.0 yr.

Note:

1. If ruthenium activity, which could be present in several oxidation states in reactor effluents, is not completely interchanged with the carrier solution, discrepancies between radiochemical and chemical yield determinations will result. Treatment parameters (boiling, distilling etc.) to remedy this situation are mentioned in reference 2.

Reference:

1. Wyatt, E. I. and Rickard, R. R., "The Radiochemistry of Ruthenium", USAEC Rept. NAS-NS-3029, 1961.
2. Kahn, B. and Reynolds, S. A., "Determination of Radionuclides in Low Concentrations in Water", Jour. AWWA, 50, 613, 1958.

Radioactive Silver

Principle of Method

Silver carrier and the appropriate scavenging carrier are added to the aqueous sample. After silver is collected as the hydrous oxide, impurities are removed by a cobaltinitrite precipitation. The silver is precipitated as AgCl for counting.

Procedure Time

4 samples - 3 hrs.

Reagents

Acetic acid, CH_3COOH: 8 $\underline{N}$
Ammonium acetate buffer, $(CH_3COOH-CH_3COONH_4)$: pH 5.0
Cobalt carrier: 5 mg/ml
Ethanol, C_2H_5OH: 95%
Hydrochloric acid, HCl: 0.5 $\underline{N}$
Hydrogen peroxide, H_2O_2: 30%
Nitric acid, HNO_3: 1 $\underline{N}$
Potassium hydroxide, KOH: 6 $\underline{N}$
Potassium nitrite, KNO_2: solid
Silver carrier: 20 mg/ml

Procedure

1. To an unacidified aqueous sample (200 ml or less), add 1.0 ml silver carrier and 1 ml cobalt carrier. (Note 1). Evaporate to about 30 ml.

2. Slowly add at least 2 drops H_2O_2 and 6 $\underline{N}$ KOH until precipitation of the black hydrous oxides of silver and cobalt is complete. Heat to coagulate, cool, centrifuge and discard supernatant.

3. Wash precipitate with 20 ml water and discard wash solution.

4. Dissolve precipitate in 5 ml 8 $\underline{N}$ CH_3COOH and 2 drops H_2O_2 with heating. Dilute to 15 ml with water, add 5 ml ammonium acetate buffer solution (pH 5) and heat to boiling in a water bath. Carefully add 5 g KNO_2 in small increments, with stirring. Continue boiling until gas evolution ceases and the precipitate settles. Cool, centrifuge and filter the supernatant containing the silver into a clean centrifuge tube through Whatman #42 (or equivalent). Discard filter paper.

5. Boil filtrate until all brown nitric oxide fumes are released, and dilute to 40 ml with water.

6. Add 1 drop 1 $\underline{N}$ HNO_3 and 6 drops 0.5 $\underline{N}$ HCl to the warm solution. Continue stirring and heating until the coagulated AgCl settles, and supernatant is clear. Test supernatant for completeness of precipitation with one more drop 0.5 $\underline{N}$ HCl.

7. Cool in an ice bath, centrifuge and discard supernatant.

8. Wash with 20 ml water and discard wash solution.

9. Transfer to a tared glass-fiber filter with water. Wash with successive portions of water and ethanol.

10. Dry, cool, weigh, mount and count (Note 2).

Calculation

Calculate the concentration, D, of the ^{110m}Ag in picocuries per milliliter as follows:

$$D = \frac{C}{2.22 \times EVR}$$

where:

C = net count rate, counts/min,
E = counter efficiency,
V = milliliters of sample used,
R = fractional chemical yield, and
2.22 = conversion factor from disintegrations/min to picocuries.

Calculate the counter efficiency, E, for gamma-ray spectrometry as follows:

$$E = Fp$$

where:

F = fractional abundance of the gamma ray, gammas/disintegration, and
p = photopeak detection efficiency, counts/gamma ray.

Calculate decay corrections as follows:

$$A = A_o e^{-0.693t/T}$$

where:

A = activity at time t,
A_o = activity at time zero,
e = base of natural logarithms,
t = elapsed time from collection in days, and
T = half life of the ^{110m}Ag (253 d).

Confirmation of Purity and Identification of ^{110m}Ag

1. Plot the gamma-ray spectrum of the AgCl precipitate to verify the ^{110m}Ag photopeaks at 658 keV, 885 keV, 937 keV, 764 keV and 1384 keV and identify any contaminating gamma emitters (Note 2).
2. Beta count the sample after 2 months and 6 months to confirm the 253-d half life of ^{110m}Ag.

Notes:

1. The aqueous sample must not contain chlorides. If the sample contains chlorides, it should be evaporated to dryness, the residue taken up in 10 ml 16 $\underline{N}$ HNO_3, evaporated to dryness again and taken up in 30 ml H_2O. Dilute NH_4OH should be added to neutralize the sample before the silver and cobalt carriers are added.

2. If cobalt activity is still present in the AgCl precipitate, wash the precipitate from the glass-fiber filter into a beaker with a minimum of water. Heat and add 15 $\underline{N}$ NH_4OH to dissolve. Add 0.5 ml cobalt carrier and repeat steps 2-10.

Reference:

1. Lingane, J. J., <u>Analytical Chemistry of Selected Metallic Elements</u> (Reinhold, New York, N. Y., 1966) pp. 48, 99.

Radioactive Strontium and Barium

Principle of Method

The strontium and barium carriers are added to the aqueous sample, collected as insoluble carbonates, and separated from most of the calcium as nitrates. Impurities are removed by an hydroxide scavenge. The barium is precipitated as the chromate and purified as $BaSO_4$ for counting; the strontium is purified as $SrCO_3$ for counting.

Procedure Time

4 samples - 6 hrs.

Reagents

Ammonium acetate buffer, $(CH_3COOH-CH_3COONH_4)$: pH 5.0
Ammonium hydroxide, NH_4OH: 15 $\underline{N}$ (conc.), 6 $\underline{N}$
Barium carrier: 20 mg/ml
Ethanol, C_2H_5OH: 95%
Hydrochloric acid, HCl: 6 $\underline{N}$, 1 $\underline{N}$
Indicator, methyl red: 0.1%
Iron chloride, $FeCl_3$: 0.1 $\underline{M}$
Nitric acid, HNO_3: 16 $\underline{N}$ (conc.), 6 $\underline{N}$, 1 $\underline{N}$
Oxalic acid, $H_2C_2O_4$: saturated
Sodium carbonate, Na_2CO_3: 1.5 $\underline{M}$
Sodium chromate, Na_2CrO_4: 0.5 $\underline{M}$
Sodium hydroxide, NaOH: 6 $\underline{N}$
Strontium carrier: 20 mg/ml
Sulfuric acid, H_2SO_4: 12 $\underline{N}$
Yttrium carrier: 10 mg/ml

Procedure

1. To an aqueous sample (1000 ml or less), add 1.0 ml of strontium and barium carriers.

2. Make basic with 6 $\underline{N}$ NaOH and heat to boiling.

3. Add 5 ml 1.5 $\underline{M}$ Na_2CO_3, stir, digest, cool, centrifuge and discard supernatant.

4. Wash precipitate with 15 ml water and discard wash solution.

5. Dissolve precipitate with 1 ml 6 $\underline{N}$ HNO$_3$.

6. Add 25 ml 16 $\underline{N}$ HNO$_3$, stir and cool in an ice bath 5 min.

7. Centrifuge, discard supernatant and let drain a few minutes.
    (Note 1).

8. Dissolve precipitate with 10 ml water and add 0.5 ml 0.1 $\underline{M}$ FeCl$_3$.

9. Heat to near boiling in water bath and add 6 $\underline{N}$ NH$_4$OH dropwise until

    Fe(OH)$_3$ precipitates.

10. Cool, centrifuge and transfer supernatant to a clean centrifuge
    tube. Discard precipitate. Record time as beginning of yttrium
    ingrowth. (Complete steps 11-18 without delay, to minimize
    ingrowth of ^{90}Y.)

11. Add 3 drops methyl red indicator, and adjust pH to near 5 with a
    few drops 1 $\underline{N}$ HCl. (Color change is from yellow to red.)

12. Add 5 ml ammonium acetate buffer solution and heat in water bath.

13. Slowly add 1 ml 0.5 $\underline{M}$ Na$_2$CrO$_4$. Stir, heat, centrifuge. Transfer
    supernatant to a clean centrifuge tube. Save precipitate for
    step 19.

14. Add 2 ml 15 $\underline{N}$ NH$_4$OH to the supernatant, heat in water bath, and
    slowly add, with stirring, 5 ml 1.5 $\underline{M}$ Na$_2$CO$_3$. Digest for a few
    minutes, cool, centrifuge and discard supernatant.

15. Dissolve precipitate with 5 ml 1 $\underline{N}$ HCl, add 10 ml water and repeat
    step 14.

16. Wash the strontium carbonate precipitate with 20 ml water, and discard wash solution.

17. Slurry the precipitate with a minimum of water and transfer to a tared stainless steel planchet. Dry under infra-red lamps.

18. Cool, weigh and count immediately. Store planchet for suitable time for yttrium-90 ingrowth. (Note 2).

19. Dissolve precipitate from step 13 with 2 ml 6 $\underline{N}$ HCl and dilute to 10 ml. Heat in water bath several minutes.

20. Slowly add 2 ml 12 $\underline{N}$ H_2SO_4 dropwise, with stirring, to precipitate $BaSO_4$.

21. Centrifuge and discard supernatant. Record this time as the beginning of ^{140}La ingrowth.

22. Wash precipitate twice with 15 ml water and discard wash solutions.

23. Transfer to a tared glass-fiber filter with water. Wash with successive portions of water and ethanol.

24. Dry, cool, weigh, mount and count both beta and gamma activity. Record date and time of counting.

Yttrium Separation

25. After the period for ^{90}Y ingrowth, slurry the precipitate on the planchet with 2 ml water and transfer to a centrifuge tube with the aid of a rubber policeman. To make the transfer quantitative, wash the residue from the planchet with a small amount of 1 $\underline{N}$ HNO_3. Dissolve the precipitate in the tube with sufficient 1 $\underline{N}$ HNO_3, and dilute with water to 10 ml.

26. Add 1.0 ml yttrium carrier and stir.

27. Boil to expel dissolved carbon dioxide; cool to room temperature.

28. Replace in water bath and make basic with 2-3 ml 15 $\underline{N}$ NH$_4$OH. Stir and digest until the yttrium hydroxide precipitation is complete.

29. Cool, centrifuge, and decant supernatant into a 100-ml beaker. Record time of separation. This is the end of yttrium-90 ingrowth and the beginning of yttrium-90 decay.

30. Dissolve precipitate in 1 ml 1 $\underline{N}$ HNO$_3$ and dilute with water to 10 ml.

31. Reprecipitate yttrium by dropwise addition of 15 $\underline{N}$ NH$_4$OH.

32. Centrifuge, combine supernatant with solution in the 100-ml beaker (step 29).

33. Repeat steps 30, 31 and 32. Save the combined supernatants in the beaker for strontium activity and gravimetric yield determination, step 41.

34. Dissolve the Y(OH)$_3$ precipitate from step 32 with 2 ml 1 $\underline{N}$ HNO$_3$ and dilute to 5 ml with water.

35. Slowly add 5 ml sat. H$_2$C$_2$O$_4$, with stirring, and digest in hot water bath for 10 minutes.

36. Cool in an ice bath to room temperature.

37. Centrifuge and discard supernatant.

38. Wash precipitate twice with 10 ml hot water and discard wash solutions.

39. Filter the yttrium oxalate on a tared glass-fiber filter. Wash with hot water and ethanol.

40. Dry, cool, weigh, mount and count the ^{90}Y.

41. Warm the combined supernatant solution from step 33, add 5 ml 1.5 $\underline{M}$ Na_2CO_3 and digest for 10 minutes.

42. Cool, centrifuge and discard supernatant.

43. Wash the $SrCO_3$ with 15 ml water and discard wash solution.

44. Slurry with a few ml water and transfer quantitatively to a tared stainless steel planchet. Dry under infra-red lamps.

45. Cool, weigh and count immediately.

Calculations:

I. ^{89}Sr and ^{90}Sr (beta activity):

   1. ^{90}Y cpm (corrected) $= \dfrac{cpm}{A \times B_1 \times C}$

   2. ^{90}Sr cpm $= {}^{90}Y$ cpm (corrected) $\times \dfrac{D}{E}$

   3. ^{90}Y cpm $= \dfrac{{}^{90}Y \text{ cpm (corrected)} \times G \times B_2}{E}$

   4. ^{89}Sr cpm $= (R - {}^{90}Sr \text{ cpm} - {}^{90}Y \text{ cpm}) \dfrac{1}{F}$

   5. ^{90}Sr activity $= \dfrac{{}^{90}Y \text{ cpm (corrected)}}{E \times 2.22 \times I \times V}$

   6. ^{89}Sr activity $= \dfrac{{}^{89}Sr \text{ cpm}}{H \times 2.22 \times I \times V}$

where:

A = Decay factor for ^{90}Y
B_1 = Ingrowth factor of ^{90}Y from time of strontium purification to yttrium separation
B_2 = Ingrowth factor of ^{90}Y from time of yttrium separation to time of total strontium count
C = Yttrium yield
D = ^{90}Sr efficiency for counter in which radiostrontium is counted
E = ^{90}Y efficiency for counter in which ^{90}Y is counted

F = Decay factor for ^{89}Sr from sample collection to counting time
G = ^{90}Y efficiency for counter in which radiostrontium is counted
H = Efficiency for ^{89}Sr
I = Strontium yield
R = Observed count rate of total radiostrontium fraction (step 18 or 45)
V = Sample volume

II. ^{140}Ba (beta activity)*:

$$^{140}\text{Ba activity (pCi/ml)} = \frac{A}{[B \times C \times D]\,[E + (F \times G \times H)]}$$

where:

A = Net cpm
B = Sample volume (ml)
C = Barium chemical yield
D = Correction factor $e^{-\lambda t}$ for ^{140}Ba decay, where t is the time, in hours, from sample collection to time of counting if λ is in hr^{-1}

E = Efficiency for counting ^{140}Ba $\frac{(cpm)}{(pCi)}$

F = Efficiency for counting ^{140}La $\frac{(cpm)}{(pCi)}$

G = Correction factor $1-e^{-0.017t}$ for the degree of equilibrium attained, where t is the time, in hours, from the barium separation to the time of counting
H = The ratio of ^{140}La to ^{140}Ba when the mixture is in transient equilibrium (1.153).**

Confirmation of Purity of ^{90}Sr, ^{90}Y and ^{140}Ba Activities

1. Immediately plot the gamma-ray spectrum of each separated product to identify the short-lived 9.7-hr ^{91}Sr in the SrCO$_3$ precipitate, and any contaminating gamma-ray emitters in either precipitate. If the sample is analyzed soon after collection, the 9.7-hr ^{91}Sr photopeaks may be discernible at 1025, 748 and 645 keV.
2. Repeat the gamma measurement of the ^{140}Ba over a period of a week to observe the ingrowth of the ^{140}La daughters.

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* "Radioassay Procedures for Environmental Samples", Env. Health Series, BRH, Public Health Service Publication 999-RH-27, Jan. 1967.

**Based on the ^{140}Ba half life of 12.8 d and the ^{140}La half life of 40 hrs.

3. Beta count the planchet over a 2-week interval to check the ^{90}Y decay and the ingrowth of ^{90}Sr-^{90}Y and ^{140}Ba-^{140}La.

Notes:

1. If excess calcium is present in the sample, steps 5, 6 and 7 should be repeated as often as is necessary to remove all the calcium.
2. The counting result, immediately ascertained, represents the strontium activity (^{90}Sr + ^{89}Sr) plus an insignificant fraction of the ^{90}Y that has grown in from the separated ^{90}Sr. To determine the ^{89}Sr and ^{90}Sr with a greater precision, the planchet should be stored at least two weeks so that the ^{90}Sr-^{90}Y activity will be in equilibrium. At this point, steps 25-45 are to be performed on the precipitate in the planchet.

Reference:

1. Hahn, R. B. and Straub, C. P., "Determination of Radioactive Strontium and Barium in Water", J. Am. Water Works Assn. 47, 335 (April 1955).

Radioactive Sulfur

Principle of Method

Sulfur carrier and appropriate holdback carriers are added to the aqueous sample. After sulfides are oxidized to sulfates, impurities are removed by an hydroxide scavenge. The sulfur is purified as $NH_2C_6H_4C_6H_4NH_2 \cdot H_2SO_4$ for counting.

Procedure Time

2 samples - 5 hrs.

Reagents

Ammonium hydroxide, NH_4OH: 15 $\underline{N}$ (conc.), 1 $\underline{N}$, 0.1 $\underline{N}$
Benzidine hydrochloride, $NH_2C_6H_4C_6H_4NH_2 \cdot 2HCl$: 2%
Cadmium carrier: 20 mg/ml
Cobalt carrier: 5 mg/ml
Copper carrier: 20 mg/ml
Ethanol, C_2H_5OH: 95%
Hydrogen peroxide, H_2O_2: 30%
Hydrogen peroxide - Ammonium hydroxide solution: (5:1)
Indicator, phenolphthalein: 1%
Iron carrier: 10 mg/ml
Manganese carrier: 5 mg/ml
Phosphorus carrier: 5 mg/ml
Sulfur carrier: 3 mg/ml as $S^=$
Zinc carrier: 5 mg/ml
Zirconium carrier: 10 mg/ml

Procedure

1. To an unacidified aqueous sample (200 ml or less), add 1.0 ml sulfur carrier, and 0.1 ml (2 drops) each of cadmium, cobalt, copper, iron, manganese, phosphorus and zinc holdback carriers (Note 1).

2. Oxidize the $S^=$ to $SO_4^=$ by slowly adding 10 ml $H_2O_2 - NH_4OH$ (5:1) solution. Evaporate to complete dryness.

3. Slowly add 5 ml H_2O_2-NH_4OH solution to residue to avoid spattering, and evaporate to complete dryness.

4. Slurry residue with a few drops of H_2O_2 and add 15 ml water. (Loosen with a rubber policeman if necessary.) Heat for a few minutes to dissolve sulfates, and cool.

5. Filter residue through Whatman #41 (or equivalent), wash with 5 ml water and combine wash solution and filtrate. Discard filter paper.

6. Add 0.1 ml each of zirconium, cobalt and iron carriers, adjust to pH 6.5 with 0.1 $\underline{N}$ NH_4OH and add 3 drops H_2O_2. Heat and stir until all H_2O_2 is boiled away and precipitate is coagulated. Cool to room temperature.

7. Filter through Whatman #41 (or equivalent) into a centrifuge tube. Discard filter paper.

8. Add 2-3 drops phenolphthalein indicator and adjust to end point with 1 $\underline{N}$ NH_4OH. Cool in ice bath and add 2 ml benzidine hydrochloride. Stir, settle, centrifuge and discard supernatant.

9. Wash precipitate with 20 ml water and discard wash solution.

10. Transfer to a tared glass-fiber filter with water. Wash with successive portions of water and ethanol.

11. Dry, cool, weigh, mount using 0.25 mil mylar and count.

Calculation

Calculate the concentration, D, of sulfur-35 in picocuries per milliliter as follows:

$$D = \frac{C}{2.22 \times EVR}$$

where:

C = net count rate, counts/min,
E = counter efficiency,
V = milliliters of sample used,
R = fractional chemical yield, and
2.22 = conversion factor from disintegrations/min to picocuries.

Calculate decay corrections as follows:

$$A = A_o \, e^{-0.693t/T}$$

where:

A   = activity at time t,
A_o = activity at time zero,
e   = base of natural logarithms,
t   = elapsed time in days, and
T   = half life of ^{35}S (87.2 d).

Confirmation of the Purity and Activity of ^{35}S

1. Plot gamma-ray spectrum of the separated sample to assure complete decontamination from interfering radionuclides. If contaminated, the analysis should be repeated with appropriate scavenging steps and holdback carriers.
2. Beta count the planchet several times over a 30-day period to confirm the 87.2-d half life.

Note:

1. It is imperative that these carriers were not prepared in the sulfate form to assure accurate calculation of chemical yield.

References:

1. Leddicotte, G. W., "The Radiochemistry of Sulfur", Nuclear Science Series, NAS-NS-3054, Nat'l Res. Council, USAEC, 1962.
2. Elinson, S. V. and Petrov, K. I., Analytical Chemistry of Zirconium and Hafnium (Ann Arbor-Humphrey Science Publishers, Ann Arbor, Michigan, 1969) p. 47.

Radioactive Tantalum and Niobium

<u>Principle of Method</u> (Note 1)

Tantalum, niobium and zirconium carriers are added to the acidified aqueous sample and collected as phosphates. The zirconium is precipitated as the fluorozirconate, leaving tantalum and niobium in solution. The tantalum is extracted into MIBK, back extracted into water and purified as Ta_2O_5 for counting; niobium is precipitated as the basic hydroxide and purified by ashing as Nb_2O_5 for counting.

<u>Procedure Time</u>

     2 samples - 8 hrs. (Zr-Nb time) + 2 hrs.

<u>Reagents</u>

        Acetone, $(CH_3)_2CO$: anhydrous
        Ammonium hydroxide, NH_4OH: 15 $\underline{N}$ (conc.), 6 $\underline{N}$
        Ammonium nitrate, NH_4NO_3: 2%
        Cobalt carrier: 5 mg/ml
        Hydrofluoric acid, HF: 5 $\underline{N}$
        Indicator, phenolphthalein: 1%
        Methyl isobutyl ketone, $C_6H_{12}O$, (MIBK)
        Niobium carrier: 10 mg/ml
        Nitric acid, HNO_3: 16 $\underline{N}$ (conc.), 1 $\underline{N}$
        Oxalic acid, $H_2C_2O_4$: saturated
        Tantalum carrier: 10 mg/ml
        Zirconium carrier: 10 mg/ml

<u>Procedure</u>

1. To an aqueous sample (200 ml or less), add 5 ml 16 $\underline{N}$ HNO_3, 1 ml sat. $H_2C_2O_4$, 2.0 ml each of tantalum, zirconium and niobium carriers and 1 ml cobalt holdback carrier. Stir. Follow the procedure for zirconium and niobium (p. 159) from step 2 through step 13.

2. Wash the mixed niobium-tantalum precipitate with 10 ml hot 2% NH_4NO_3, and discard wash solution.

3. Dissolve precipitate in 0.5 ml 5 $\underline{N}$ HF plus 5 ml 1 $\underline{N}$ HNO$_3$. Add 5 ml MIBK and stir with a polypropylene rod for 2 minutes. Transfer to a polypropylene separatory funnel. Drain aqueous phase into a polypropylene tube and transfer organic layer to a 60 ml glass separatory funnel. Add 5 ml MIBK to the aqueous phase and stir with a polypropylene rod for 2 minutes. Transfer to the polypropylene separatory funnel. Combine organic layer with that in the glass separatory funnel. Save aqueous phase which contains niobium for step 9.

4. Back extract organic phase twice with 5 ml portions of water, collecting aqueous phases in a centrifuge tube. Discard organic layer.

5. Add 2-3 drops phenolphthalein indicator and adjust to the end point with 15 $\underline{N}$ NH$_4$OH to precipitate Ta$_2$O$_5$. Digest in a hot water bath 5-10 minutes. Centrifuge and discard supernatant.

6. Wash precipitate with 10 ml hot 2% NH$_4$NO$_3$ and discard wash solution.

7. Transfer to a tared glass-fiber filter with 10 ml acetone.

8. Dry, cool, weigh, mount and count precipitate as Ta$_2$O$_5$.

9. To supernatant from step 3, add 2-3 drops phenolphthalein indicator and make basic with 15 $\underline{N}$ NH$_4$OH to precipitate Nb$_2$O$_5$. Digest in a hot water bath 5-10 minutes. Centrifuge and discard supernatant.

10. Wash precipitate with 10 ml hot 2% NH$_4$NO$_3$ and discard wash solution.

11. Slurry with water and filter through Whatman #42 (or equivalent).

Transfer filter paper to a porcelain crucible, dry and heat in furnace for 1 hour at $800^{\circ}C$. (Note 2).

12. Cool, and transfer to a tared glass-fiber filter with water. Wash with successive portions of water and ethanol.

13. Dry, cool, weigh, mount and count as Nb_2O_5.

Calculations

I. Tantalum

Calculate the concentration, D, of tantalum-182 in picocuries per milliliter as follows:

$$D = \frac{C}{2.22 \times EVR}$$

where:

C = net count rate, counts/min,
E = counter efficiency,
V = milliliters of sample used,
R = fractional chemical yield, and
2.22 = conversion factor from disintegrations/min to picocuries.

Calculate the counter efficiency, E, for gamma-ray spectrometry as follows:

$$E = Fp$$

where:

F = fractional abundance of the gamma ray, gammas/disintegration and
p = photopeak detection efficiency, counts/gamma ray.

Calculate the decay correction for the tantalum isotopes as follows:

$$A = A_o \, e^{-0.693t/T}$$

where:

A = activity at time t,
A_o = activity at time zero,
e = base of natural logarithms,
t = elapsed time from collection, and,
T = half life of separated nuclides in same units as t.

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Confirmation of Purity and Identification of Tantalum Isotopes

1. Plot the gamma-ray spectrum of the separated sample to identify the major ^{182}Ta photopeaks (1220, 1120 and 68 keV), the major ^{183}Ta photopeaks (246, 354 and 108 keV) and verify the purity of the separation. The presence of other photopeaks may indicate contamination, necessitating repetition of the analysis with additional holdback carriers and scavenging.
2. Repeat gamma measurement and beta counting at 1-week intervals to follow decay of the photopeaks and corroborate the half lives of ^{183}Ta (5.1 d) and ^{182}Ta (115 d).

II. Niobium (see page 162).

Notes:

1. Combining this procedure with the zirconium-niobium procedure (P. 159) makes it possible to analyze for zirconium, niobium and tantalum on one aliquot.
2. To prevent flash ignition which would cause loss of unashed filter paper and activity, the dried crucible should be put into the cold muffle as the temperature is raised to 800°C. After an hour at this temperature the crucible is carefully removed and allowed to cool.

References:

1. Faye, G. M. and Inman, W. R., Res. Rept. MD-210, Canadian Dept. of Mines and Tech. Surveys, Aug. 1957.
2. Steinberg, E. P., "The Radiochemistry of Niobium and Tantalum", AEC Rept. NAS-NS-3039, 1961.

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Radioactive Tellurium

Principle of Method*

Tellurium carrier is added to the acidified aqueous sample. Impurities are removed by a double hydroxide scavenge. The tellurium salts are collected in acid solution and reduced to the metal for counting.

Procedure Time

4 samples - 8 hrs.

Reagents

Dextrose, $C_6H_{12}O_6$: anhydrous
Ethanol, C_2H_5OH: 95%
Hydrochloric acid, HCl: 12 $\underline{N}$ (conc.)
Iron carrier: 10 mg/ml
Potassium hydroxide, KOH: 6 $\underline{N}$
Nitric acid, HNO_3: 16 $\underline{N}$ (conc.)
Tellurium carrier: 10 mg/ml

Procedure

1. To an aqueous sample (200 ml or less), add 1 ml 12 $\underline{N}$ HCl and 2.0 ml

   tellurium carrier. Evaporate to damp dryness. (Do not bake.)

2. Slurry the salts with 1 ml 12 $\underline{N}$ HCl, add 25 ml water and transfer

   to a centrifuge tube.

3. Add 0.5 ml iron carrier and make strongly basic with 3-4 ml 6 $\underline{N}$

   KOH. Digest in a water bath until $Fe(OH)_3$ coagulates. Cool and

   centrifuge. Transfer supernatant to a beaker.

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*This procedure was developed by Robert Lieberman, Analytical and Radiochemistry Research Section, EERF, Montgomery, Alabama 36101.

4. Wash precipitate with 15 ml water and add wash to supernatant in beaker. Discard precipitate.

5. Repeat steps 3 and 4, omitting the 6 $\underline{N}$ KOH.

6. Acidify supernatant with 1-2 ml 12 $\underline{N}$ HCl and evaporate to damp dryness. (Do not bake.)

7. Slurry the salts with 1 ml 12 $\underline{N}$ HCl and 25 ml water. Add 1 g dextrose to reduce the tellurium to the metal, and stir until completely dissolved. Heat gently, if necessary.

8. Make the mixture strongly basic with 3-4 ml 6 $\underline{N}$ KOH and heat to boiling for 10 minutes to coagulate the tellurium metal.

9. Cool and transfer to a centrifuge tube. Centrifuge and discard supernatant.

10. Slurry the precipitate with 5 ml 12 $\underline{N}$ HCl. Dilute to 25 ml with water, stir, centrifuge and discard supernatant.

11. Dissolve the precipitate in 2 ml 16 $\underline{N}$ HNO_3 and transfer to a beaker with a few ml water. Evaporate to damp dryness. (Do not bake.)

12. Repeat steps 7 through 10.

13. Transfer to a tared glass-fiber filter with water. Wash with successive portions of water and ethanol.

14. Dry, cool, weigh, mount and count.

Calculation

Calculate the concentration, D, of the ^{129}Te or ^{132}Te activities in picocuries per milliliter as follows:

$$D = \frac{C}{2.22 \times EVR}$$

where:

C = net count rate, counts/min,
E = counter efficiency,
V = milliliters of sample used,
R = fractional chemical yield, and
2.22 = conversion factor from disintegrations/min to picocuries

Calculate the counter efficiency, E, for gamma-ray spectrometry as follows:

$$E = Fp$$

where:

F = fractional abundance of the gamma ray, gammas/disintegration, and
p = photopeak detection efficiency, counts/gamma ray.

Calculate decay corrections as follows:

$$A = A_o \, e^{-0.693t/T}$$

where:

A = activity at time t,
A_o = activity at time zero,
e = base of natural logarithms
t = elapsed time from collection, in same units as T, and
T = half life of separated nuclides, ^{129}Te ($t_{1/2}$ 34.1 d) or ^{132}Te ($t_{1/2}$ 78 h).

Confirmation of Purity of ^{129}Te and ^{132}Te and Measurement of Activity

1. Plot the gamma-ray spectrum of the separated sample. The ^{129}Te photopeak is at 455 keV; the ^{132}Te photopeak is at 230 keV. (At equilibrium, the 523 keV, 668 keV, and 773 keV photopeaks of the 2.3-hr ^{132}I daughter of ^{132}Te will be present.)

2. Repeat the gamma measurement after 2 days to observe the decay of the shorter-lived (^{132}Te) isotope.

3. Beta count the sample immediately after separation and at 2-day intervals to corroborate the half life of ^{132}Te and of ^{129}Te.

Reference:

1. Leddicotte, G. W., "The Radiochemistry of Tellurium", AEC Rept. NAS-NS-3038, 1961.

Radioactive Tin

Principle of Method

Tin carrier and appropriate scavenging carriers are added to the acidified aqueous sample and collected as mixed sulfides. Impurities are removed by an hydroxide scavenge. The tin is precipitated with cupferron and ignited to SnO_2 for counting.

Procedure Time

2 samples - 8 hrs.

Reagents

Antimony carrier: 5 mg/ml
Ammonium hydroxide, NH_4OH: 15 $\underline{N}$ (conc.)
Bromine water: saturated
Cupferron: $C_6H_9N_3O_2$: 6%
Hydrochloric acid, HCl: 12 $\underline{N}$ (conc.), 3 $\underline{N}$
Hydrogen peroxide, H_2O_2: 30%
Hydrogen sulfide, H_2S: gas
Iron carrier: 10 mg/ml
Nickel, powdered
Nitric acid, HNO_3: 16 $\underline{N}$ (conc.)
Sodium hydroxide, NaOH: 6 $\underline{N}$
Tin carrier: 10 mg/ml

Procedure

1. To an aqueous sample (50 ml or less), add 12 $\underline{N}$ HCl to adjust the sample to 4 $\underline{N}$ HCl. (For a 50 ml sample, this is accomplished by the addition of 25 ml 12 $\underline{N}$ HCl.) Add 2.0 ml tin carrier and 1 ml antimony carrier. Heat and stir approximately 30 minutes. (Note 1).

2. Add 30-40 mg powdered Ni, and continue heating and stirring at least 15 min to reduce Sn^{+4} to Sn^{+2}.

3. Filter through Whatman #41 (or equivalent) into a clean beaker and discard filter paper.

4. Add 2 ml bromine water, neutralize with 15 $\underline{N}$ NH_4OH, then make 1 $\underline{N}$ in HCl. (For a 50 ml sample this is accomplished by adding 4.6 ml 12 $\underline{N}$ HCl). Heat to boiling in a water bath and saturate with H_2S at least 3 min to precipitate a mixture of tin and antimony sulfides. Cool in an ice bath, centrifuge and discard supernatant.

5. Dissolve precipitate in 3 ml 12 $\underline{N}$ HCl and 1 drop H_2O_2. Boil off excess peroxide and add a few ml water. Neutralize with 15 $\underline{N}$ NH_4OH then make 2.5 $\underline{N}$ in HCl. (For a 10 ml sample this is accomplished by adding 2.5 ml 12 $\underline{N}$ HCl.)

6. Heat to boiling and saturate with H_2S to precipitate antimony sulfide. Filter while hot through Whatman #41 (or equivalent) into a clean beaker. Wash precipitate with a little 3 $\underline{N}$ HCl and discard filter paper.

7. Add 2 ml bromine water to filtrate, neutralize with 15 $\underline{N}$ NH_4OH, then make 1 $\underline{N}$ HCl. Heat to boiling in a water bath and saturate with H_2S at least 3 min to precipitate tin sulfide. Cool in ice bath, centrifuge and discard supernatant.

8. Dissolve precipitate in 2 ml 12 $\underline{N}$ HCl and 1 drop H_2O_2 and heat. Add a few ml water and continue heating to remove excess peroxide. Dilute to 15 ml.

9. Add 0.5 ml iron carrier. Stir in water bath and add 6 $\underline{N}$ NaOH until basic, then add 2 drops more to precipitate $Fe(OH)_3$ and leave tin

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in solution. Filter through Whatman #41 (or equivalent) into a clean centrifuge tube. Discard filter paper.

10. Add 5 ml 6% cupferron and chill in an ice bath.

11. Add 12 $\underline{N}$ HCl dropwise until precipitate of tin cupferrate no longer dissolves. Stir well and continue to chill.

12. Filter through Whatman #42 (or equivalent) and wash well with water. Discard filtrate.

13. Transfer filter paper to a porcelain crucible and dry in oven at about 110°C.

14. Char cautiously with low heat, then ignite over a Meker burner (or muffle) at high heat (about 700°C), under oxidizing conditions for 45 min. Let cool.

15. Moisten with 2 drops 16 $\underline{N}$ HNO_3. Let dry carefully on a hot plate with very low heat, then reignite over a Meker burner (or muffle) for 15 min. Place in a desiccator to cool.

16. Transfer to a tared glass-fiber filter with water. Wash with successive portions of water and ethanol.

17. Dry, cool, weigh, mount and count.

Calculation

Calculate the concentration, D, of the tin isotopes in picocuries per milliliter as follows:

$$D = \frac{C}{2.22 \times EVR}$$

where:

C = net count rate, counts/min,
E = counter efficiency,

V = milliliters of sample used,
R = fractional chemical yield, and
2.22 = conversion factor from disintegrations/min to picocuries.

Calculate the counter efficiency, E, for gamma-ray spectrometry as follows:

$$E = Fp$$

where:

F = fractional abundance of the gamma ray, gammas/disintegration, and
p = photopeak detection efficiency, counts/gamma ray.

Calculate the decay correction for the specific tin isotope as follows:

$$A = A_o \, e^{-0.693t/T}$$

where:

A = activity at time t,
A_o = activity at time zero,
e = base of natural logarithms,
t = elapsed time from collection, and
T = half life of the tin isotope in the same unit as t.

Confirmation of Purity and Identification Tin Isotopes

1. Plot the gamma-ray spectrum of the separated sample to identify the photopeaks of ^{113}Sn (255 keV, $t_{1/2}$ 113 d) and of ^{123}Sn (1080 keV, $t_{1/2}$ 125 d) and verify the purity of the separation.
2. Beta count the separated planchet at 30-d intervals to substantiate the half life of the tin isotope that is present.

Note:

1. The volume should be kept constant during the heating in steps 1 and 2 by adding water as needed to maintain the 4 $\underline{N}$ HCl concentration.

References:

1. Meinke, W. Wayne, Ed., Chemical Procedures Used in Bombardment Work at Berkeley, UCRL-432, U. of Calif., 1949.
2. Bowen, H. J. M. and Gibbons, D., Radioactivation Analysis, (Oxford University Press, London, 1963) p. 250.
3. Lingane, J. J., Analytical Chemistry of Selected Metallic Elements (Reinhold, New York, N. Y., 1966) p. 105.

Tritium

Principle of Method (Note 1)

The aqueous sample is distilled to dryness to effect quantitative transfer of tritium to the distillate and to remove interfering radionuclides and quenching materials. A portion of the distillate is mixed with scintillation solution and counted in a liquid scintillation spectrometer. Standard tritium and background samples are prepared and counted alternately, to nullify errors produced by aging of the scintillation medium or instrument drift.

Procedure Time

1 sample - 2 hrs.

Reagents

Scintillation solution (dioxane): prepared reagent
Tritium, ^{3}H: standard tracer solution

Procedure

1.. Distill an unacidified aqueous sample (50 ml or less) to dryness and collect the distillate in a dry flask. (Note 2).

2. Pipette 16 ml scintillation solution into a 25 ml scintillation vial.

3. Pipette 4 ml sample distillate into scintillation vial, cap tightly and shake until thoroughly mixed.

4. Prepare a background sample consisting of 4 ml low-tritium water and 16 ml scintillation solution in same manner as sample.

5. Prepare a standard consisting of 16 ml scintillation solution and 4 ml water, containing a standard concentration of tritium activity, in same manner as sample.

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6. Dark-adapt and cool sample, background and standard solutions in instrument freezer to prepare for counting. (Note 3).

7. In normal counting operation, tritium is counted with a window setting where the figure of merit is at maximum. (Note 1). The high voltage is set to obtain the peak counting efficiency in the window.

Calculation

Calculate the concentration, D, of the tritium activity in picocuries per milliliter as follows:

$$D = \frac{C}{2.22 \times EV}$$

where:

C = net count rate, counts/min,
E = efficiency for measuring ^3H in liquid scintillation spectrometer,
V = milliliters of sample used,
2.22 = conversion factor from disintegrations/min to picocuries.

Calculate the efficiency, E, for measuring ^3H in the liquid scintillation spectrometer as follows:

$$E = \frac{Y}{S}$$

where:

Y = counts/min determined by counting standard tritium sample (step 5) at the optimum instrument settings, and
S = standard tritium activity (dpm/ml) as rated by NBS or equivalent, corrected for decay.

Calculate the decay correction for the tritium activity as follows:

$$A = A_o\, e^{-0.693t/T}$$

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where:

A   = activity at time t,
A$_o$ = activity at time of collection or from the date the standard was rated,
e   = base of natural logarithms,
t   = elapsed time from collection or from the date the standard was rated,
T   = half life of tritium (12.3 yr).

Confirmation of Purity and Identification of the Tritium Activity

1. Determine the count rate for each sample, background and standard. Three successive results which are within 2σ of each other assure that the vials have been dark adapted.
2. With a 2-channel spectrometer, one window is set to give the best figure of merit and the other is set as an impurity screen. The ratios of the activity for the ^{3}H standard and for the distilled samples should be the same at the two window settings. If not, the samples must be redistilled to remove interfering ionizing radiations and prepared for counting again.

Notes:

1. This procedure is similar to the ASTM standard method described on page 23, but since it employs a different scintillation solution which has been found to give a better "Figure of Merit",* it has been included in this manual.
2. As a general rule, all samples should be distilled to dryness for quantitative recovery of tritium and to remove interfering radionuclides. Iodine-131 in aqueous samples can be eliminated by adding stable iodine and $AgNO_3$ to the flask before the distillation.
3. The freezer temperature must be maintained above 2°C or, in time, the solution will begin to solidify. If an ambient temperature liquid scintillation spectrometer is employed, the vial must be dark-adapted, usually 24-48 hrs, before counting begins.

Reference:

1. Butler, F. E., "Determination of Tritium in Water and Urine", Anal. Chem. 33, 409, 1961.

* Figure of Merit = $\dfrac{S^2 \ (Efficiency)^2}{B \ (Background)}$

Radioactive Tungsten

Principle of Method

Tungsten carrier is added to a basic aqueous sample and collected as tungstic acid. Impurities are removed by hydroxide and basic sulfide scavenges. The tungsten is reprecipitated as tungstic acid and purified as $WO_2(C_9H_6ON)_2$ for counting.

Procedure Time

2 samples - 4 hrs.

Reagents

Acetic acid, CH_3COOH: 17.4 $\underline{N}$ (glacial)
Ammonium hydroxide, NH_4OH: 15 $\underline{N}$ (conc.)
Ethanol, C_2H_5OH: 95%
8-hydroxyquinoline, C_9H_7NO: 5% in CH_3COOH
Hydrogen sulfide, H_2S: gas
Iron carrier: 10 mg/ml
Molybdenum carrier: 10 mg/ml
Nitric acid, HNO_3: 16 $\underline{N}$ (conc.)
Sodium acetate buffer, $(CH_3COOH-CH_3COONa)$: pH 5.0
Sulfuric acid H_2SO_4: 36 $\underline{N}$ (conc.)
Tartaric acid, $C_4H_6O_6$: 50%
Tungsten carrier: 10 mg/ml
Zirconium carrier: 10 mg/ml

Procedure

1. To an aqueous sample (200 ml or less) made slightly basic (pH 7-9) with 15 $\underline{N}$ NH_4OH, add 2.0 ml tungsten carrier and stir. Add 30 ml 16 $\underline{N}$ HNO_3 and bring to vigorous boil to precipitate tungstic acid.

2. Digest at near boiling for 10-15 minutes on hot plate; cool, centrifuge and discard supernatant.

3. Dissolve in 6 drops 15 $\underline{N}$ NH_4OH and dilute to 15 ml with water. Add

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2 drops each iron and zirconium carriers, centrifuge and transfer supernatant to a centrifuge tube. Discard precipitate.

4. Add 1 ml 50% tartaric acid, 0.5 ml 36 $\underline{N}$ H_2SO_4 and 0.5 ml molybdenum carrier. Heat in water bath, bubble in H_2S and stir vigorously for at least 2 minutes. Filter while hot through Whatman #41 (or equivalent). Wash centrifuge tube with 2-3 ml hot water, pour through filter paper and combine with filtrate. Discard filter paper.

5. To filtrate add 10 ml 16 $\underline{N}$ HNO_3 and digest the tungstic acid precipitate in water bath for 10 minutes. Cool, centrifuge and discard supernatant.

6. Repeat steps 3, 4, and 5.

7. Dissolve the precipitate with 6 drops 15 $\underline{N}$ NH_4OH and transfer to a 125 ml Erlenmeyer flask with 15 ml water. Add 6 drops glacial CH_3COOH, 10 ml sodium acetate buffer and heat to boiling. Add 1 ml 5% 8-hydroxyquinoline in CH_3COOH, dropwise, boil for 30 seconds and let cool 5 minutes.

8. Transfer to a tared glass-fiber filter with water. Wash with successive portions of water and ethanol.

9. Dry, cool, weigh, mount and count immediately.

Calculation

Calculate the concentration, D, of tungsten-185 and tungsten-187 in picocuries per milliliter as follows:

$$D = \frac{C}{2.22 \times EVR}$$

where:

C = net count rate, counts/min,
E = counter efficiency,
V = milliliters of sample used,
R = fractional chemical yield,
2.22 = conversion factor from disintegrations/min to picocuries.

Calculate the counter efficiency, E, for gamma-ray spectrometry for ^{187}W as follows:

$$E = Fp$$

where:

F = fractional abundance of the gamma rays, gammas/disintegration, and
p = photopeak detection efficiency, counts/gamma ray.

Calculate the decay correction for the tungsten isotopes as follows:

$$A = A_o \, e^{-0.693t/T}$$

where:

A = activity at time t,
A_o = activity at time zero,
e = base of natural logarithms,
t = elapsed time from collection, and
T = half life of separated nuclide, in same units as t.

Confirmation of Purity and Identification of Tungsten Isotopes

1. Plot the gamma-ray spectrum of the sample immediately after separation to identify the 618 and 686 keV photopeaks of ^{187}W ($t_{1/2}$ 24 h). Daily gamma spectral analysis is required to corroborate the 24-hr half life and confirm the presence of ^{187}W.
2. If other photopeaks are present, indicative of gamma impurities, the analysis should be repeated immediately with the necessary holdback carriers and scavenge steps included.
3. Beta count the separated sample at 2-week intervals to follow the decay of ^{185}W ($t_{1/2}$ 75 d, no gamma rays, average beta energy 124 keV).

Reference:

1. Kleinberg, J., Ed., "Collected Radiochemical Procedures", LA-1721, 2nd ed., Los Alamos Scientific Laboratory, U. of Calif., 1954, pp. 191-196.

Radioactive Yttrium

Principle of Method

Yttrium carrier and appropriate holdback carriers are added to the acidified aqueous sample. The yttrium is collected as the fluoride to separate it from most of the impurities. After purification by an hydroxide precipitation and extraction into tributyl phosphate, the yttrium is precipitated as $Y_2(C_2O_4)_3 \cdot 7H_2O$ for counting.

Procedure Time

2 samples - 4 hrs.

Reagents

Ammonium hydroxide, NH_4OH: 15 $\underline{N}$ (conc.)
Boric acid, H_3BO_3: saturated
Cobalt carrier: 5 mg/ml
Ethanol, C_2H_5OH: 95%
Hydrochloric acid, HCl: 6 $\underline{N}$
Hydrofluoric acid, HF: 48% (conc.), 5 $\underline{N}$
Nitric acid, HNO_3: 16 $\underline{N}$ (conc.)
Oxalic acid, $H_2C_2O_4$: saturated
Tributyl phosphate, (TBP): equilibrated with 16 $\underline{N}$ HNO_3
Yttrium carrier: 10 mg/ml
Zirconium carrier: 10 mg/ml

Procedure

1. To an aqueous sample (200 ml or less), add 1.0 ml yttrium carrier, 1 ml 16 $\underline{N}$ HNO_3 and evaporate to 20 ml.

2. Transfer to polypropylene tube with a few ml water. Add 4 ml 16 $\underline{N}$ HNO_3, 2 ml each of cobalt and zirconium carriers and mix well. Add 5 ml conc. HF to precipitate yttrium fluoride, stir several minutes, centrifuge and discard supernatant.

3. Dissolve precipitate in 2 ml sat. H_3BO_3 and 2 ml 16 $\underline{N}$ HNO_3. Dilute

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to 10 ml with water, add 2 ml zirconium and cobalt carriers and mix
well. Add 2 ml conc. HF to reprecipitate yttrium fluoride, stir
several minutes, centrifuge and discard supernatant.

4. Wash precipitate with 10 ml 5 $\underline{N}$ HF and carefully discard wash
solution.

5. Dissolve precipitate in 2 ml sat. H_3BO_3 and 2 ml 16 $\underline{N}$ HNO_3. Dilute
to 10 ml with water. If turbid, centrifuge and discard residue.
Add 15 $\underline{N}$ NH_4OH with stirring until precipitation of yttrium
hydroxide is complete. Centrifuge and discard supernatant.

6. Dissolve precipitate with 50 ml 16 $\underline{N}$ HNO_3 and transfer to a 125 ml
separatory funnel. Add 10 ml equilibrated tributyl phosphate (TBP)
and extract 5 min. Transfer the bottom aqueous layer to another
separatory funnel, add 10 ml equilibrated TBP and repeat the
extraction two more times. Combine the three organic fractions in
the same funnel. Discard the aqueous layer.

7. Wash organic layer with 30 ml 16 $\underline{N}$ HNO_3 and discard wash solution.

8. Back extract three times with 10 ml portions of water and combine
the aqueous fractions in a 50 ml centrifuge tube. Discard the
organic layer.

9. Add 15 $\underline{N}$ NH_4OH to precipitate yttrium hydroxide. Stir, centrifuge
and discard supernatant.

10. Dissolve precipitate in 2 ml 6 $\underline{N}$ HCl and dilute to 15 ml with
water. Heat in water bath and add 20 ml sat. $H_2C_2O_4$ to precipitate
yttrium oxalate. Digest for 10 minutes and cool in an ice bath.

11. Centrifuge and discard supernatant.

12. Transfer to a tared glass-fiber filter with water. Wash with

successive portions of water and ethanol.

13. Dry, cool, weigh, mount and count.

Calculation

Calculate the concentration, D, of the yttrium activity in pico-curies per milliliter as follows:

$$D = \frac{C}{2.22 \times EVR}$$

where:

C = net count rate, counts/min,
E = counter efficiency,
V = milliliters of sample used,
R = fractional chemical yield, and
2.22 = conversion factor from disintegrations/min to picocuries.

Calculate the counter efficiency, E, for gamma-ray spectrometry as follows:

$$E = Fp$$

where:

F = fractional abundance of the gamma ray, gammas/disintegration, and
p = photopeak detection efficiency, counts/gamma ray.

Calculate decay corrections as follows:

$$A = A_o \, e^{-0.693t/T}$$

where:

A = activity at time t,
A_o = activity at time zero,
e = base of natural logarithms,
t = elapsed time from collection, in same units as T, and
T = half life of separated nuclides ^{90}Y ($t_{1/2}$ 64.0 h), ^{91}Y ($t_{1/2}$ 58.8 d) and ^{93}Y ($t_{1/2}$ 10.3 h).

Confirmation of Yttrium Purity and Identification of Yttrium Isotopes

1. Plot the gamma-ray spectrum of the separated sample to identify and quantify the 10.3-h ^{93}Y (267 and 940 keV) and the 58.8-d ^{91}Y (1210 keV). The presence of other photopeaks indicates contamination and necessitates repeat of the analysis with appropriate scavenges and holdback carriers.
2. Gamma scan again in 5 days to measure the decay of ^{93}Y, and substantiate the longer-lived yttrium isotope (1210 keV).
3. Beta count the planchet at daily intervals to confirm the presence of the pure beta ^{90}Y and to corroborate the ^{91}Y half life.

Reference:

1. Kleinberg, J., Ed., "Collected Radiochemical Procedures", LA-1721, 2nd ed., Los Alamos Scientific Laboratory, U. of Calif., 1954, pp. 104-107.

Radioactive Zinc

Principle of Method

Zinc carrier and appropriate scavenging carriers are added to the acidified aqueous sample and impurities are removed by basic hydroxide and acid sulfide precipitations. The zinc is collected as zinc mercuric thiocyanate and purified as $Zn(C_{10}H_6NO_2)_2 \cdot H_2O$ for counting.

Procedure Time

2 samples - 4 hrs.

Reagents

Acetic acid, CH_3COOH: 1 $\underline{N}$
Acetone, $(CH_3)_2CO$: anhydrous
Ammonium hydroxide, NH_4OH: 6 $\underline{N}$
Ammonium mercuric thiocyanate, NH_4HgSCN: prepared reagent
Antimony carrier: 5 mg/ml
Cobalt carrier: 5 mg/ml
Ethanol, C_2H_5OH: 95%
Hydrogen peroxide, H_2O_2: 30%
Hydrogen sulfide, H_2S: gas
Indicator, phenolphthalein: 1%
Iron carrier: 5 mg/ml
Manganese carrier: 5 mg/ml
Nitric acid, HNO_3: 16 $\underline{N}$ (conc.)
Oxalic acid, $H_2C_2O_4$: 10%
Quinaldic acid solution, $C_{10}H_7NO_2 \cdot 2H_2O$: prepared reagent
Silver carrier: 5 mg/ml
Sodium hydroxide, NaOH: 6 $\underline{N}$, 0.5 $\underline{N}$
Sulfuric acid, H_2SO_4: 36 $\underline{N}$ (conc.), 6 $\underline{N}$, 1 $\underline{N}$
Zinc carrier: 5 mg/ml

Procedure

1. To an aqueous sample (100 ml or less), add 1 ml 16 $\underline{N}$ HNO_3, 1.0 ml

   zinc carrier and 1 ml each of antimony, cobalt, iron, manganese and

   silver carriers.

2. Slowly add at least 2 drops H_2O_2 and make sample strongly basic

(> pH 13) with 6 $\underline{N}$ NaOH. Heat and stir until the excess H_2O_2 is boiled off and the mixed hydrous oxide precipitate settles readily.

3. Cool to room temperature and filter through Whatman #41 (or equivalent) into a graduated beaker. Wash the residue with 5-10 ml 0.5 $\underline{N}$ NaOH and add wash to the filtrate in the beaker. Discard filter paper.

4. Evaporate the solution to less than 50 ml, and neutralize with 6 $\underline{N}$ H_2SO_4. Make solution 3 $\underline{N}$ in H_2SO_4 by adding 4.2 ml 36 $\underline{N}$ H_2SO_4 and diluting to 50 ml with water.

5. Heat nearly to boiling and bubble in H_2S to precipitate Sb_2S_3. (Note 1).

6. Cool in an ice bath, filter through Whatman #41 (or equivalent) into a clean beaker, wash with a few ml 1 $\underline{N}$ H_2SO_4 and discard filter paper.

7. Boil off excess H_2S and cool in an ice bath. Add 1 ml 10% oxalic acid, 5 ml NH_4HgSCN reagent and stir in the ice bath until precipitation is complete (about 15 minutes).

8. Transfer to a centrifuge tube, centrifuge and discard supernatant.

9. Add 0.5 ml 16 $\underline{N}$ HNO_3 to dissolve precipitate and place in a boiling water bath. Stir and heat until all brown fumes are gone and the solution is clear.

10. Add 5 ml water and neutralize to a phenolphthalein end point with 6 $\underline{N}$ NH_4OH.

11. Add 5 ml 1 $\underline{N}$ CH_3COOH and 2 ml quinaldic acid solution, stir well

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and heat in a water bath until the precipitate has settled. Cool, centrifuge and discard supernatant.

12. Repeat steps 9, 10 and 11.

13. Wash with water containing a few ml 1 $\underline{N}$ CH_3COOH. Centrifuge and discard wash solution.

14. Transfer to a tared glass-fiber filter with water.

15. Wash once with water and twice with ethanol and acetone.

16. Dry, cool, weigh, mount and count as $Zn(C_{10}H_6NO_2)_2 \cdot H_2O$.

Calculation

Calculate the concentration, D, of ^{65}Zn in picocuries per milliliter as follows:

$$D = \frac{C}{2.22 \times EVR}$$

where:

C = net count rate, counts/min,
E = counter efficiency,
V = milliliters of sample used,
R = fractional chemical yield, and
2.22 = conversion factor from disintegrations/min to picocuries.

Calculate the counter efficiency, E, for gamma-ray spectrometry as follows:

$$E = Fp$$

where:

F = fractional abundance of the gamma ray, gammas/disintegration, and
p = photopeak detection efficiency, counts/gamma ray

Calculate the decay correction for ^{65}Zn as follows:

$$A = A_o \, e^{-0.693t/T}$$

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where:

A   = activity at time t,
A_o = activity at time zero,
e   = base of natural logarithms,
t   = elapsed time from collection, and
T   = half life of separated nuclide in same units as t ($t_{1/2}$ = 245 d).

Confirmation of Purity and Identification of ^{65}Zn

1. Plot the gamma-ray spectrum of the separated sample soon after separation and at 30-day intervals to note presence of contaminating photopeaks and to identify the predominant ^{65}Zn photopeak (1115 keV).

Note:

1. If sulfide precipitate is not observed within 15 seconds, add a few ml water while the H_2S is being bubbled until a precipitate does form.

References:

1. Lingane, J. J., Analytical Chemistry of Selected Metallic Elements (Reinhold, New York, N. Y., 1966) pp. 48 and 131.
2. Bowen, H. J. M. and Gibbons, D., Radioactivation Analysis (Oxford University Press, London, 1963) p. 233.
3. Kolthoff, I. M. and Sandell, E. B., Textbook of Quantitative Inorganic Analysis, 3rd ed. (Macmillan, New York, N. Y., 1952) p. 93.

Radioactive Zirconium and Niobium

Principle of Method

Zirconium and niobium carriers are added to an acidified aqueous sample and collected as phosphates. The zirconium is precipitated as the fluorozirconate, reprecipitated with cupferron and ashed to ZrO_2 for counting; niobium is converted to a fluoride complex and purified by extraction into tributyl phosphate. After precipitation as the hydrous oxide, the niobium is ashed to Nb_2O_5 for counting.

Procedure Time

2 samples - 8 hrs.

Reagents

Acetone, $(CH_3)_2CO$: anhydrous
Ammonium hydroxide, NH_4OH: 15 $\underline{N}$ (conc.)
Ammonium nitrate, NH_4NO_3: 2%
Barium carrier: 20 mg/ml
Boric acid, H_3BO_3: saturated, 5%
Cerium carrier: 5 mg/ml
Cobalt carrier: 5 mg/ml
Cupferron, $C_6H_9N_3O_2$: 6%
Ethanol, C_2H_5OH: 95%
Hydrochloric acid, HCl: 12 $\underline{N}$ (conc.), 6 $\underline{N}$, 1 $\underline{N}$
Hydrofluoric acid, HF: 48% (conc.)
Niobium carrier: 10 mg/ml
Nitric acid, HNO_3: 16 $\underline{N}$ (conc.)
Oxalic acid, $H_2C_2O_4$: saturated
Petroleum ether
Phosphoric acid, H_3PO_4: 44 $\underline{N}$ (conc.)
Potassium bromate, $KBrO_3$: solid
Sulfuric acid, H_2SO_4: 36 $\underline{N}$ (conc.), 24 $\underline{N}$
Tributyl phosphate, $(H_3CCH_2CH_2CH_2O)_3PO$, (TBP)
Zirconium carrier: 10 mg/ml

Procedure

1. To an aqueous sample (200 ml or less), add 5 ml 16 $\underline{N}$ HNO_3, 1 ml

    saturated $H_2C_2O_4$, 2.0 ml each niobium and zirconium carriers

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and 1 ml cobalt holdback carrier. Stir. (Note 1).

2. Add 3 ml 44 $\underline{N}$ H_3PO_4, heat to boiling, stir for a few minutes and cool.

3. Decant clear supernatant and transfer precipitate with remaining solution to a polypropylene tube. Centrifuge and discard supernatant.

4. Wash precipitate with 20 ml 6 $\underline{N}$ HCl and discard wash solution.

5. Dissolve precipitate with 1 ml HF, add 10 ml water and 1 ml cerium carrier. Stir. Let stand 5 minutes, centrifuge and decant supernatant into a polypropylene tube. Discard precipitate.

6. Add 2 ml barium carrier, stir, centrifuge and decant supernatant containing niobium into a 150 ml beaker. Reserve the barium fluorozirconate precipitate for zirconium purification, step 18.

7. Add 2 ml sat. H_3BO_3 and 20 ml 16 $\underline{N}$ HNO_3 to supernatant solution and heat to boiling. Slowly add 1 g $KBrO_3$ and stir until fuming ceases. Continue stirring and heating until Nb_2O_5 coagulates.

8. Cool, transfer to a polypropylene centrifuge tube, centrifuge and discard supernatant.

9. Wash precipitate with 15 ml hot 2% NH_4NO_3, cool and discard wash solution.

10. Dissolve precipitate with 2 ml HF and 3 ml 24 $\underline{N}$ H_2SO_4 and add 1 ml cobalt carrier.

11. Add 5 ml TBP and stir for 2 minutes with a polypropylene rod.

Transfer to a polypropylene separatory funnel. When the layers separate, discard the bottom aqueous phase.

12. Transfer the organic layer to a polypropylene tube and add 5 ml petroleum ether. Cool in an ice bath and slowly add 5 ml 15 $\underline{N}$ NH_4OH. Stir for 2 minutes, remove from ice bath and transfer to a polypropylene separatory funnel. When layers separate, drain the bottom aqueous layer into a polypropylene tube and discard the organic layer.

13. Wash aqueous phase by stirring 1 minute with 4 ml petroleum ether. Centrifuge at high speed 1 minute. Decant and discard both organic and aqueous supernatants (Note 2).

14. Wash precipitate with 10 ml hot 2% NH_4NO_3 and discard wash solution.

15. Slurry precipitate with water and filter through Whatman #42 (or equivalent). Transfer to porcelain crucible, dry and heat in furnace for 1 hour at 800°C. (Note 3).

16. Cool and transfer to a tared glass-fiber filter with water. Wash with successive portions of water and ethanol.

17. Dry, cool, weigh, mount and count as Nb_2O_5.

18. Dissolve precipitate from step 6 with 5 ml water, 2 ml 5% H_3BO_3 and 3 ml 12 $\underline{N}$ HCl. Add 2 drops 36 $\underline{N}$ H_2SO_4, stir, cool and centrifuge. Decant supernatant into a glass centrifuge tube. Discard precipitate.

19. Dilute to 20 ml, cool in ice bath, add 2 ml 6% cupferron and stir

for a few minutes. Centrifuge and discard supernatant.

20. Wash precipitate with 10 ml 1 $\underline{N}$ HCl containing a drop of cupferron and discard wash solution.

21. Slurry precipitate with water and filter through Whatman #42 (or equivalent). Transfer to porcelain crucible, dry and heat in furnace for 1 hour at 800°C. (Note 3).

22. Cool and transfer to a tared glass-fiber filter with water. Wash with successive portions of water and ethanol.

23. Dry, cool, weigh, mount and count immediately as ZrO_2.

Calculation

Calculate the concentration, D, of the ^{95}Zr and ^{95}Nb in pico-curies per milliliter as follows:

$$D = \frac{C}{2.22 \text{ x EVR}}$$

where:

C = net count rate, counts/min,
E = counter efficiency,
V = milliliters of sample used,
R = fractional chemical yield, and
2.22 = conversion factor from disintegrations/min to picocuries.

Calculate the counter efficiency, E, for gamma-ray spectrometry as follows:

$$E = Fp$$

where:

F = fractional abundance of the gamma rays, gammas/disintegration for each nuclide, and
p = photopeak detection efficiency, counts/gamma ray for each nuclide.

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Calculate decay corrections as follows:

$$A = A_o \, e^{-0.693t/T}$$

where:

A = activity at time t,
A_o = activity at time zero,
e = base of natural logarithms,
t = elapsed time from collection, and
T = half life of separated nuclide, in same units as t, ^{95}Zr ($t_{1/2}$ 65 d), ^{95}Nb ($t_{1/2}$ 35 d).

Confirmation of Purity of ^{95}Nb and ^{95}Zr

1. Plot the gamma ray spectrum of the separated samples to identify the ^{95}Nb photopeak at 765 keV and the ^{95}Zr photopeaks at 724 and 756 keV. If the sample contains short-lived activities, and is analyzed soon after collection, the presence of 17-hr ^{97}Zr can be identified by its 747-keV photopeak in the ZrO_2 fraction.
2. Beta count the planchets at 1-month intervals to measure decay and confirm the ^{95}Nb and ^{95}Zr half lives. The calculation of the ^{95}Zr activity during these counting intervals must consider the ingrowth of the ^{95}Nb daughter into the purified ^{95}Zr precipitate.

Notes:

1. Oxalic acid must be present for complete exchange of zirconium and niobium carrier and activity. The solution should be stirred for at least 10 minutes.
2. Traces of TBP are removed from the aqueous phase by washing it with petroleum ether. After centrifugation, the niobium has precipitated as the hydrated oxide, leaving both the organic and aqueous phase.
3. To prevent flash ignition which would cause loss of unashed filter paper and activity, the dried crucible should be put into the cold muffle as the temperature is raised to 800°C. After an hour at this temperature the crucible is carefully removed and allowed to cool.

References:

1. Rodden, C. J., Ed., Analysis of Essential Nuclear Reactor Materials, (Div. Tech. Inf., USAEC, 1964) p. 680 and 685.
2. Steinberg, E. P., The Radiochemistry of Niobium and Tantalum, AEC Rept. NAS-NS-3039, 1961.

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B. Acknowledgments

C. Appendices

Appendix 1

Reactor Coolant Radionuclide Half-lives and Gamma-ray Energies as Reported in the Literature

Nuclide	Half life	Gamma Energies, MeV	Nuclide	Half life	Gamma Energies, MeV
^{227}Ac	21.8 y	1.29	^{242}Cm	163 d	0.044
^{106m}Ag	8.5 d	0.512, 0.616, 0.80	^{57}Co	270 d	0.122, 0.136
^{110m}Ag	253 d	0.658, 0.885, 0.937	^{58}Co	71.3 d	0.511, 0.811
^{241}Am	433 y	0.060	^{60}Co	5.26 y	1.173, 1.332
^{41}Ar	1.83 h	1.29	^{244}Cm	18.1 y	0.043
^{76}As	26.4 h	0.559, 0.657, 1.21	^{51}Cr	27.8 d	0.320
^{131}Ba	12.0 d	0.124, 0.216, 0.496	^{134}Cs	2.07 y	0.57, 0.605, 0.796
^{139}Ba	82.9 m	0.166	^{136}Cs	13.7 d	0.340, 0.818, 1.05
^{140}Ba	12.8 d	0.304, 0.438, 0.537	^{137}Cs	30.0 y	0.662
^{80}Br	17.6 m	0.511, 0.618	^{138}Cs	32.2 m	0.463, 1.01, 1.426
^{80m}Br	4.4 h	0.037	^{64}Cu	12.7 h	0.511
^{82}Br	35.4 h	0.554, 0.777, 1.044	^{152}Eu	12.7 y	0.122, 0.344, 1.408
^{83}Br	2.4 h	0.530	^{154}Eu	16 y	0.123, 0.248, 0.724
^{84}Br	6.0 m	0.44, 0.88, 1.46	^{155}Eu	1.81 y	0.087, 0.105
^{14}C	5730 y	---	^{18}F	110 m	0.511
^{109}Cd	1.26 y	0.088	^{55}Fe	2.7 y	x-ray
^{113m}Cd	14 y	0.265	^{59}Fe	44.6 d	1.095, 1.292
^{115}Cd	55 h	0.49, 0.53	^{72}Ga	14.1 h	0.630, 0.835
^{115m}Cd	43 d	0.485, 0.935, 1.29	^{3}H	12.4 y	---
^{141}Ce	32.5 d	0.145	^{181}Hf	42.5 d	0.346, 0.482
^{143}Ce	33 h	0.29, 0.668, 0.725	^{129}I	1.6×10^{7} y	0.040
^{144}Ce	284 d	0.134	^{131}I	8.06 d	0.364, 0.637

Nuclide	Half life		Gamma Energies, MeV	Nuclide	Half life		Gamma Energies, MeV
^{132}I	.2.3	h	0.668, 0.955	^{65}Ni	2.56	h	1.115, 1.481
^{133}I	20.9	h	0.53	^{239}Np	2.4	d	0.106, 0.228, 0.278
^{134}I	52.4	m	0.85, 0.89	^{32}P	14.3	d	---
^{135}I	6.7	h	1.13, 1.26, 1.71	^{233}Pa	27.0	d	0.31
^{115m}In	4.5	h	0.335	^{107}Pd	7×10^6	y	---
^{42}K	12.4	h	1.524	^{147}Pm	2.2	y	---
^{85}Kr	10.7	y	0.514	^{149}Pm	53	h	0.286
^{85m}Kr	4.4	h	0.150, 0.305	^{151}Pm	28	h	0.17, 0.340
^{87}Kr	78	m	0.403, 0.85, 2.57	^{86}Rb	18.7	d	1.077
^{88}Kr	2.8	h	0.196, 0.85, 1.55, 2.40	^{105}Rh	36	h	0.306, 0.319
^{140}La	40.2	h	0.487, 1.596	^{103}Ru	39.7	d	0.497, 0.610
^{54}Mn	313	d	0.835	^{106}Ru	368	d	0.512, 0.620
^{56}Mn	2.58	h	0.847, 1.811, 2.110	^{35}S	88	d	---
^{99}Mo	66.3	h	0.181, 0.740	^{120}Sb	5.8	d	0.200, 1.03, 1.17
^{13}N	10.0	m	0.511	^{122}Sb	2.7	d	0.564, 0.686
^{22}Na	2.6	y	0.511, 1.275	^{124}Sb	60.2	d	0.603, 1.691
^{24}Na	15.0	h	1.369, 2.754	^{125}Sb	2.8	y	0.427, 0.599
^{95}Nb	35	d	0.765	^{127}Sb	93	h	0.060, 0.25, 0.41
^{97}Nb	72	m	0.665	^{46}Sc	84	d	0.889, 1.120
^{147}Nd	11.1	d	0.091, 0.533	^{31}Si	2.6	h	1.26
^{57}Ni	1.5	d	0.511, 1.37	^{151}Sm	90	y	0.022
^{63}Ni	92	y	---	^{153}Sm	46.8	h	0.070, 0.103

Appendix 1 (Cont'd.)

Nuclide	Half life		Gamma Energies, MeV	Nuclide	Half life		Gamma Energies, MeV
^{89}Sr	51	d	---	^{133m}Xe	2.3	d	0.233
^{90}Sr	28.5	y	---	^{135}Xe	9.2	h	0.250, 0.61
^{91}Sr	9.7	h	0.645, 0.748, 1.025	^{138}Xe	17	m	0.160, 0.420
^{92}Sr	2.7	h	1.37	^{88}Y	107	d	0.898, 1.836
^{182}Ta	115	d	1.122, 1.189, 1.222	^{90}Y	64	h	---
^{183}Ta	5.1	d	0.108, 0.161, 0.246	^{91}Y	59	d	1.21
^{99}Tc	2.1 x 10^5	y	---	^{91m}Y	50	m	0.551
^{99m}Tc	6.0	h	0.140	^{93}Y	10.3	h	0.267, 0.94, 1.90
^{132}Te	78	h	0.228	^{65}Zn	244	d	0.511, 1.115
^{185}W	75	d	---	^{69m}Zn	14	h	0.439
^{187}W	24	h	0.479, 0.686	^{95}Zr	65	d	0.724, 0.757
^{131m}Xe	12	d	0.164	^{97}Zr	17.0	h	0.747
^{133}Xe	5.3	d	0.081				

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Appendix 2

Method Capabilities and Decontamination Factors

Nuclide	Minimum Detectable Limits, pCi/ml			Average chemical yield, %	Decontamination Factors***		
	Gamma ray*	Beta particles*	special case**		^{131}I	$^{58/60}$Co	^{110m}Ag
^{110m}Ag	0.04	0.02	---	75	10^3	10^3	---
^{76}As	0.1	0.02	---	60	10^2	10^3	10^3
^{140}Ba	0.1	0.01	---	75	10^4	10^3	10^4
^{14}C	---	0.03	---	90	10^2	10^3	10^4
^{115m}Cd	0.1	0.01	---	65	10^3	10^2	10^4
^{141}Ce	0.05	0.03	---	75	10^4	10^3	10^3
^{144}Ce	0.2	0.03	---	75	10^4	10^3	10^3
^{58}Co	0.05	---	0.03	75	10^3	---	10^3
^{60}Co	0.05	0.02	0.03	75	10^3	---	10^3
^{51}Cr	0.5	---	---	80	10^3	10^3	10^3
$^{134/137}$Cs	0.05	0.01	0.02	85	10^4	10^3	10^3
^{136}Cs	0.07	0.02	---	85	10^4	10^3	10^3
^{64}Cu	0.1	---	---	70	10^3	10^3	10^3
^{55}Fe	---	---	0.02	75	10^4	10^2	10^4
^{59}Fe	0.1	---	---	75	10^4	10^2	10^4
^{3}H	---	---	0.2	100	10^3	10^3	10^4
^{131}I	0.05	0.01	0.02	80	---	10^3	10^2
^{133}I	0.07	0.02	---	80	---	10^3	10^2
^{140}La	0.1	0.01	---	80	10^3	10^3	10^3
^{54}Mn	0.06	---	0.04	65	10^3	10^3	10^4
^{99}Mo	0.3	0.01	---	55	10^2	10^3	10^3

Appendix 2 (Cont'd.)

Nuclide	Minimum Detectable Limits, pCi/ml			Average chemical yield, %	Decontamination Factors***		
	Gamma ray*	Beta particles*	special case**		^{131}I	$^{58/60}$Co	^{110m}Ag
^{95}Nb	0.05	0.05	---	65	10^4	10^2	10^3
^{63}Ni	---	0.06	---	80	10^4	10^3	10^3
^{239}Np	0.15	0.01	---	90	10^4	10^4	10^4
^{32}P	---	0.01	---	85	10^2	10^3	10^3
^{103}Ru	0.05	0.01	---	85	10^3	10^3	10^3
^{106}Ru	0.2	0.01	---	85	10^3	10^3	10^3
^{35}S	---	0.05	---	80	10^3	10^2	10^3
^{124}Sb	0.04	0.02	---	90	10^3	10^3	10^3
^{113}Sn	0.1	---	---	75	10^3	10^3	10^3
^{89}Sr	---	0.05	---	80	10^4	10^4	10^4
^{90}Sr	---	0.01	---	80	10^4	10^4	10^4
^{182}Ta	0.08	0.02	---	50	10^3	10^3	10^3
^{99m}Tc	0.04	0.02	---	80	10^2	10^3	10^3
^{132}Te	0.06	0.02	---	65	10^2	10^2	10^3
^{185}W	---	0.03	---	50	10^3	10^3	10^3
^{91}Y	1.0	0.02	---	75	10^4	10^3	10^4
^{65}Zn	0.15	---	---	80	10^3	10^3	10^4
^{95}Zr	0.05	0.03	---	75	10^4	10^2	10^3

*These minimum detectable limits were calculated for each separation of a 100 ml aliquot and 100 min counting time. The precipitate, mounted on a nylon ring and disc was counted for γ activity on 10 x 10 cm NaI(Tl) detector, and for β activity in a low-background beta counter (~1 c/m bkgd). Although it is not always practical, lower limits can be obtained with larger sample volumes and longer counting time.

**For the special cases for a few selected nuclides, the limit for ^{3}H is based on a 4-ml aliquot counted 300 minutes in a liquid scintillation system; for ^{55}Fe, the value is derived from a 1000-minute count on the x-ray proportional counter; for the others, the limits are based on a 400-ml plastic container 10-cm dia. x 6.5-cm high counted for 300 minutes on the 10 x 10 cm NaI(Tl) detector.

***These four nuclides were the most resistant to complete decontamination in the course of analysis. No problem was ever encountered with the other nuclides present, and for them the decontamination factor would be $> 10^4$.

Appendix 3

Suggested Order of Analyses for Aqueous Reactor Samples

1. Sodium
2. Iodine
3. Copper
4. Technetium
5. Tungsten
6. Strontium
7. Yttrium
8. Cerium
9. Zirconium
10. Arsenic
11. Neptunium
12. Lanthanum and Trivalent Rare Earths
13. Molybdenum
14. Tellurium
15. Antimony
16. Barium
17. Phosphorus
18. Chromium
19. Cesium
20. Niobium
21. Ruthenium
22. Iron
23. Sulfur
24. Manganese
25. Cobalt
26. Cadmium
27. Tantalum
28. Tin
29. Silver
30. Zinc
31. Nickel
32. Tritium
33. Carbon-14

Appendix 4

Efficiency Multiplication Factors for Gamma-ray Emitters
NaI(Tl) 4" x 4" cylindrical detector

Nuclide	Half life	Principal γ Energy, MeV	Abundance, %	Approximate Number of Channels*	Eff. Factor ** dpm/cpm Ring & Disc Geometry***
^{110m}Ag	253 d	0.658 + 0.68 + 0.706	96 + 16 + 19	59-72	6.4
^{41}Ar	1.83 h	1.27	99	115-148	11.4
^{76}As	26.4 h	0.559	43	49-62	5.5
^{77}As	38.7 h	0.239	2.5	17-30	3.0
^{133}Ba	10.7 y	0.302 + 0.356 + 0.382	91	25-42	3.6
^{140}Ba	12.8 d	0.537	34	43-56	5.2
^{140}Ba-^{140}La	12.8 d	1.60	96	149-170	12.6
^{82}Br	35.3 h	1.044	29	99-116	9.2
^{109}Cd	453 d	0.084	4	7-14	3.0
^{115}Cd	55 h	0.53 + 0.49	26 + 10	41-62	5.2
^{115m}Cd	43 d	0.935	1.9	87-100	8.1
^{141}Ce	32.5 d	0.145	48	9-18	3.2
^{143}Ce	33 h	0.293	46	23-34	3.4
^{144}Ce	284 d	0.134	11	9-18	3.2
^{57}Co	270 d	0.122 + 0.136	87 + 11	9-18	3.2
^{58}Co	71.3 d	0.810	99	71-90	7.3
^{60}Co	5.26 y	1.332	100	125-142	10.8
		2.54 (sum peak)	100	239-270	72.8
^{51}Cr	27.8 d	0.320	9	27-36	3.5
^{134}Cs	2.07 y	0.796 + 0.802	88 + 9	73-86	7.3

Appendix 4 (Cont'd.)

Nuclide	Half life	Principal γ Energy, MeV	Abundance, %	Approximate Number of Channels*	Eff. Factor ** dpm/cpm Ring & Disc Geometry***
^{136}Cs	13.7 d	1.05	82	97-110	9.0
^{137}Cs	30 y	0.662	85	59-74	6.2
^{64}Cu	12.7 h	0.511	38	41-62	5.2
^{59}Fe	44.6 d	1.10	56	103-116	9.4
^{131}I	8.06 d	0.364	82	31-40	3.8
^{133}I	20.9 h	0.53	90	40-62	5.2
^{135}I	6.7 h	1.72 + 1.80	30	157-186	13.6
^{85}Kr	4.4 h	0.15	74	9-18	3.3
^{140}La	40.2 h	1.60	96	149-170	12.6
^{54}Mn	313 d	0.835	100	73-90	7.6
^{56}Mn	2.58 h	0.847	99	75-98	7.7
^{99}Mo	66.3 h	0.140	7 + 90	9-18	3.2
		0.740 + 0.780	12 + 4	67-80	6.8
^{22}Na	2.6 y	1.275	100	111-132	9.5
^{24}Na	15.0 h	1.369	100	123-150	11.2
		2.754	100	259-290	19.5
^{95}Nb	35 d	0.765	100	69-82	7.0
^{147}Nd	11.1 d	0.533	13	43-58	5.3
^{57}Ni	1.5 d	1.37	86	129-146	11.2
^{239}Np	2.4 d	0.106 + 0.122	72	9-18	3.2
^{103}Ru	39.7 d	0.497	88	43-56	5.2

Appendix 4 (Cont'd.)

Nuclide	Half life	Principal γ Energy, MeV	Abundance, %	Approximate Number of Channels*	Eff. Factor** dpm/cpm Ring & Disc Geometry***
^{106}Ru-^{106}Rh	1.01 y	0.512	21	45-58	5.2
^{122}Sb	2.7 d	0.564	66	49-62	5.5
^{124}Sb	60.2 d	0.603 + 0.644 + ~0.72	97 + 7 + 14	53-78	5.9
^{125}Sb	2.71 y	0.427 + 0.463	41	37-48	4.1
^{91}Sr	9.7 h	1.025	30	93-110	8.8
^{182}Ta	115 d	1.12 + 1.19 + 1.23	90	107-126	9.8
^{99m}Tc	6.0 h	0.140	90	5-18	3.2
^{132}Te	78 h	0.230	91	17-28	3.4
		0.773	89	71-84	7.0
^{187}W	24 h	0.686 + 0.618	33	63-72	6.4
^{135}Xe	9.2 h	0.250	91	17-28	3.4
^{91}Y	59 d	1.21	0.3	111-128	10.1
^{93}Y	10.3 h	0.267	6.4	19-40	3.2
		0.947	2.3	85-104	8.3
^{65}Zn	244 d	1.115	49	103-116	9.4
^{95}Zr	65 d	0.724 + 0.756	44 + 54	65-81	7.0
^{97}Zr	17.0 h	0.743	94	65-78	6.9

*For a 10 x 10-cm NaI(Tl) detector with analyzer calibrated at 10 keV/channel.
**Efficiency multiplication factors have been calculated for other geometries:
1. Falcon container - 5-cm dia. x 6.5-cm high, 35 ml sample; the factor is 1.47 times the nylon ring and disc value.
2. Plastic container - 10-cm dia. x 6.5-cm high, 400 ml sample; the factor is 2.88 times the nylon ring and disc value.
***Plastic ring and disc in 1" diameter, molded of nylon. The precipitate is filtered on 2.8-cm fiber glass filter, covered with mylar (0.01 or 0.005 mm) and mounted for counting.

Appendix 5

Decay Correction Factors
Fractional Half Lives

	0.000	0.020	0.040	0.060	0.080
0.00	1.0000	0.9862	0.9727	0.9593	0.9461
0.10	0.9330	0.9202	0.9075	0.8950	0.8827
0.20	0.8706	0.8586	0.8467	0.8351	0.8236
0.30	0.8123	0.8011	0.7900	0.7792	0.7684
0.40	0.7579	0.7474	0.7371	0.7270	0.7170
0.50	0.7071	0.6974	0.6878	0.6783	0.6690
0.60	0.6598	0.6507	0.6417	0.6329	0.6242
0.70	0.6156	0.6071	0.5987	0.5905	0.5824
0.80	0.5743	0.5664	0.5586	0.5510	0.5434
0.90	0.5359	0.5285	0.5212	0.5141	0.5070
1.00	0.5000	0.4931	0.4863	0.4796	0.4730
1.10	0.4665	0.4601	0.4538	0.4475	0.4414
1.20	0.4353	0.4293	0.4234	0.4175	0.4118
1.30	0.4061	0.4005	0.3950	0.3896	0.3842
1.40	0.3789	0.3737	0.3686	0.3635	0.3585
1.50	0.3536	0.3487	0.3439	0.3392	0.3345
1.60	0.3299	0.3253	0.3209	0.3164	0.3121
1.70	0.3078	0.3035	0.2994	0.2952	0.2912
1.80	0.2872	0.2832	0.2793	0.2755	0.2717
1.90	0.2679	0.2643	0.2606	0.2570	0.2535
2.00	0.2500	0.2466	0.2432	0.2398	0.2365
2.10	0.2333	0.2300	0.2269	0.2238	0.2207
2.20	0.2176	0.2146	0.2117	0.2088	0.2059
2.30	0.2031	0.2003	0.1975	0.1948	0.1921
2.40	0.1895	0.1869	0.1843	0.1817	0.1792
2.50	0.1768	0.1743	0.1719	0.1696	0.1672
2.60	0.1649	0.1627	0.1604	0.1582	0.1560
2.70	0.1539	0.1518	0.1497	0.1476	0.1456
2.80	0.1436	0.1416	0.1397	0.1377	0.1358
2.90	0.1340	0.1321	0.1303	0.1285	0.1267
3.00	0.1250	0.1233	0.1216	0.1199	0.1183
3.10	0.1166	0.1150	0.1134	0.1119	0.1103
3.20	0.1088	0.1073	0.1058	0.1044	0.1029
3.30	0.1015	0.1001	0.0988	0.0974	0.0961
3.40	0.0947	0.0934	0.0921	0.0909	0.0896
3.50	0.0884	0.0872	0.0860	0.0848	0.0836
3.60	0.0825	0.0813	0.0802	0.0791	0.0780
3.70	0.0769	0.0759	0.0748	0.0738	0.0728
3.80	0.0718	0.0708	0.0698	0.0689	0.0679
3.90	0.0670	0.0661	0.0652	0.0643	0.0634
4.00	0.0625	0.0616	0.0608	0.0600	0.0591

Sample Calculation Sheet

SAMPLE #   <u>NUCLIDE</u> $T_{1/2}$ =

Sample description: Eff. Mult. Fac.
Collection date: Abundance:
Energy   Channels   Sample size:
Counting Geometry: Chemical yield:

$$\text{at } t_o: \quad \frac{pCi}{c/m} = \frac{\rule{3cm}{0.4pt}}{2.22X}$$

INSTRUMENT:

Scan #

Counting date

C = Counting time, _____, min.   Elapsed time, t

G = Gross cpm, _____, cpm $t/T_{1/2} = F =$

B = Bkgd cpm, _____, cpm   Decay factor = 2^{-F}

Net cpm = G - B   1 σ error = $\sqrt{\dfrac{G + B}{C}}$

                                                2 σ error = $2\sqrt{\dfrac{G + B}{C}}$

Appendix 6

Reagent Preparation

Distilled or deionized water should be used in the preparation of all reagents requiring water as the solvent.

I. <u>Carrier Solutions</u> - These solutions, prepared as the specific ion, are to be filtered and standardized prior to use. Some salts (cerium and lanthanum nitrate, for example) contain naturally radioactive impurities (Th), so reagent blanks should be prepared to ascertain instrument plus reagent background.

$\underline{Ag^+}$ - 20 mg/ml. Dissolve 3.150 g $AgNO_3$ in water and dilute to 100 ml. Store in the dark in a brown glass container.

$\underline{Ag^+}$ - 5 mg/ml. Dissolve 0.788 g $AgNO_3$ in water and dilute to 100 ml. Store in the dark in a brown glass container.

$\underline{As^{+5}}$ - 20 mg/ml. Dissolve 8.3 g $Na_2HAsO_4.7H_2O$ in water and dilute to 100 ml.

$\underline{Ba^{+2}}$ - 20 mg/ml. Dissolve 3.577 g $BaCl_2.2H_2O$ in water and dilute to 100 ml.

$\underline{Ce^{+3}}$ - 5 mg/ml. Dissolve 1.545 g $Ce(NO_3)_3.6H_2O$ in water and dilute to 100 ml.

$\underline{Cd^{+2}}$ - 20 mg/ml. Dissolve 5.489 g $Cd(NO3)_2.4H2O$ in water and dilute to 100 ml.

$\underline{Co^{+2}}$ - 5 mg/ml. Dissolve 2.469 g $Co(NO_3)_2.6H_2O$ in water and dilute to 100 ml.

$\underline{Cr^{+3}}$ - 10 mg/ml. Dissolve 5.1 g $CrCl_3.6H_2O$ in water and dilute to 100 ml.

$\underline{Cr^{+6}}$ - 10 mg/ml. Dissolve 2.8 g $K_2Cr_2O_7$ in water and dilute to 100 ml.

$\underline{Cs^+}$ - 10 mg/ml. Dissolve 1.267 g CsCl in water and dilute to 100 ml.

$\underline{Cu^{+2}}$ - 20 mg/ml. Dissolve 4.232 g $CuCl_2$ in water and dilute to 100 ml.

$\underline{Fe^{+3}}$ - 10 mg/ml. Dissolve 4.840 g $FeCl_3.6H_2O$ in water, add 1 ml 6 $\underline{N}$ HCl and dilute to 100 ml.

$\underline{I^-}$ - 20 mg/ml. Dissolve 2.616 g KI in water, add 2 drops Na_2SO_3 and dilute to 100 ml. Store in dark flask.

$\underline{La^{+3}}$ - 10 mg/ml. Dissolve 3.127 g $La(NO_3)_3.6H_2O$ in water and dilute to 100 ml.

Mn^{+2} - 5 mg/ml. Dissolve 1.801 g $MnCl_2.4H_2O$ in water and dilute to 100 ml.

Mo^{+6} - 10 mg/ml. Dissolve 1.840 g $(NH_4)_6Mo_7O_{24}.4H_2O$ in 1 ml 0.5 $\underline{M}$ $NaBrO_3$ and dilute to 100 ml with 6 $\underline{N}$ HCl.

Nb^{+5} - 10 mg/ml. Dissolve 5.2 g $K_8Nb_6O_{19}.16H_2O$ in 50 ml water, heat nearly to boiling and add 10 ml 16 $\underline{N}$ HNO_3 slowly with stirring. Continue heating and stirring for 2-3 minutes and centrifuge. Wash the precipitate three times with 10 ml hot 2% NH_4NO_3 solution. Add 40 ml sat. $H_2C_2O_4$ and heat with stirring until Nb_2O_5 dissolves. Cool and dilute to 200 ml. Filter if solution is not clear.

Ni^{+2} - 5 mg/ml. Dissolve 2.025 g $NiCl_2.6H_2O$ in water and dilute to 100 ml.

P^{+5} - 5 mg/ml. Dissolve 2.197 g KH_2PO_4 in water and dilute to 100 ml.

Ru^{+3} - 10 mg/ml. Dissolve 2.1 g $RuCl_3$ in 100 ml 0.1 $\underline{N}$ HCl.

S^{-2} - 3 mg/ml. Dissolve 2.247 g $Na_2S.9H_2O$ in water and dilute to 100 ml.

Sb^{+3} - 5 mg/ml. Dissolve 1.00 g powdered antimony in 60 ml 36 $\underline{N}$ H_2SO_4 by heating with a burner. Cool and add the dissolved antimony to 100 ml water. Make a quantitative transfer by rinsing flask with small portions of water. Dissolve the antimony sulfate with 15 ml 12 $\underline{N}$ HCl and dilute to 200 ml with water.

Sn^{+4} - 10 mg/ml. Dissolve 4.43 g $SnCl_4.5H_2O$ in 30 ml 12 $\underline{N}$ HCl by heating and stirring in a hot water bath. Cool, add 20 ml 12 $\underline{N}$ HCl and dilute to 150 ml with water. Filter if solution is not clear.

Sr^{+2} - 20 mg/ml. Dissolve 4.831 g $Sr(NO_3)_2$ in water and dilute to 100 ml.

Ta^{+5} - 10 mg/ml. Fuse 1.3 g Ta_2O_5 in a platinum crucible with 3-5 g of a K_2CO_3-KNO_3 mixture (Ratio 10:1). Heat at red heat over a flame until melt becomes clear and glassy. Cool, add cold water to crucible to loosen the melt and transfer to a beaker with a little water. Add an equal volume of 16 $\underline{N}$ HNO_3 to make solution 6 $\underline{N}$ in HNO_3, and heat until Ta_2O_5 reprecipitates. Wash the precipitate three times with 10 ml hot 2% NH_4NO_3 solution. Add 40 ml water and heat in a water bath. Add about 10 g solid $H_2C_2O_4$ until Ta_2O_5 dissolves. Cool and dilute to 100 ml. Filter if solution is not clear.

Te^{+4} - 10 mg/ml. Dissolve 1.0 g tellurium metal in 10 ml 16 $\underline{N}$ HNO_3 and evaporate to ~3 ml. Dissolve residue in 10 ml 12 $\underline{N}$ HCl and evaporate to ~3 ml. Dissolve residue again in 10 ml 12 $\underline{N}$ HCl and evaporate to ~3 ml. Slurry into a 100 ml volumetric flask and bring to volume with 3 $\underline{N}$ HCl.

W^{+6} - 10 mg/ml. Dissolve 1.795 g $Na_2WO_4.2H_2O$ in water and dilute to 100 ml.

Y^{+3} - 10 mg/ml. Dissolve 43.1 g $Y(NO_3)_3.6H_2O$ in 800 ml water, add 5 ml 6 $\underline{N}$ HNO_3 and dilute to 1 liter.

Zn^{+2} - 5 mg/ml. Dissolve 1.042 g $ZnCl_2$ in water and dilute to 100 ml.

Zr^{+4} - 10 mg/ml. Dissolve 3.53 g $ZrOCl_2.8H_2O$ in 0.1 $\underline{N}$ HCl and dilute to 100 ml with 0.1 $\underline{N}$ HCl.

II. <u>Acids and Inorganic Reagents</u>

Acetic acid, CH_3COOH, 17.4 $\underline{N}$. This is the concentrated (glacial) reagent; sp. gr. 1.06, 99.5%.

Acetic acid, 8 $\underline{N}$. Add 460 ml 17.4 $\underline{N}$ CH_3COOH to 500 ml water and dilute to 1 liter.

Acetic acid, 1.5 $\underline{N}$. Add 86 ml 17.4 $\underline{N}$ CH_3COOH to 800 ml water and dilute to 1 liter.

Acetic acid, 1 $\underline{N}$. Add 58 ml 17.4 $\underline{N}$ CH_3COOH to 800 ml water and dilute to 1 liter.

Ammonium acetate, 3 $\underline{M}$. Dissolve 231 g CH_3COONH_4 in 600 ml water and dilute to 1 liter.

Ammonium acetate buffer, pH 5.0. Mix 100 ml 1.5 $\underline{N}$ CH_3COOH and 100 ml 3 $\underline{M}$ CH_3COONH_4.

Ammonium chloride, 10%. Dissolve 10 g NH_4Cl in water and dilute to 100 ml.

Ammonium hydroxide, NH_4OH, 15 $\underline{N}$. This is the concentrated reagent; sp. gr. 0.9, 59%.

Ammonium hydroxide, 6 $\underline{N}$. Add 400 ml 15 $\underline{N}$ NH_4OH to 400 ml water and dilute to 1 liter.

Ammonium hydroxide, 2 $\underline{N}$. Add 135 ml 15 $\underline{N}$ NH_4OH to 500 ml water and dilute to 1 liter

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Ammonium hydroxide, 1 N. Add 68 ml 15 N NH$_4$OH to 500 ml water and dilute to 1 liter.

Ammonium hydroxide, 0.1 N. Add 100 ml 1 N NH$_4$OH to 500 ml water and dilute to 1 liter.

Ammonium mercuric thiocyanate (prepared reagent). Dissolve 3.15 g NH$_4$SCN and 2.71 g HgCl$_2$ in 100 ml water. Stir, filter and store in a brown bottle for no longer than one month.

Ammonium nitrate, 2%. Dissolve 2 g NH$_4$NO$_3$ in water and dilute to 100 ml.

Ammonium phosphate, monobasic, NH$_4$H$_2$PO$_4$, solid.

Ammonium phosphomolybdate (prepared reagent). Dissolve 100 g of molybdic acid (85% MoO$_3$) in a mixture of 240 ml of water and 140 ml 15 N NH$_4$OH. When solution is complete, filter, and add 60 ml of 16 N HNO$_3$. Mix 400 ml of 16 N HNO$_3$ and 960 ml of water. Allow both solutions to cool to room temperature. With constant stirring, add the ammonium molybdate solution to the nitric acid solution. Allow to stand for 24 hours. Filter through Whatman #42 filter paper. Discard the insoluble material.

Collect the filtrates in a 3-liter beaker and heat to 50°-55°C. Remove from heating unit. It is important that the solution is not heated above 55°C to avoid contamination of the precipitate with molybdic anhydride. Add 25 g of NaH$_2$PO$_4$ dissolved in 100 ml of water to the ammonium molybdate solution. Stir occasionally for 15 minutes and allow the precipitate to settle (approximately 30 minutes). Filter through Whatman #42 filter paper. Wash the precipitate with 1% potassium nitrate and finally with water. Dry the precipitate and paper at 100°C for 3 to 4 hours. Transfer the (NH$_4$)$_3$(PMo$_{12}$O$_{40}$) solid to a weighing bottle, and store in a desiccator.

Barium nitrate, 10%. Dissolve 10 g Ba(NO$_3$)$_2$ in water and dilute to 100 ml.

Boric acid, saturated. Dissolve 100 g H$_3$BO$_3$ in 1 liter boiling water.

Boric acid, 5%. Dissolve 5 g H$_3$BO$_3$ in 100 ml water.

Bromine water, saturated.

Calcium chloride, 3 M. Dissolve 330 g CaCl$_2$ in water and dilute to 1 liter.

Calcium chloride, 1.5 $\underline{M}$. Dissolve 165 g $CaCl_2$ in water and dilute to 1 liter.

Chloroplatinic acid, 0.1 $\underline{M}$. Dissolve 51.8 g $H_2PtCl_6 \cdot 6H_2O$ in water and dilute to 1 liter.

Hydrochloric acid, HCl, 12 $\underline{N}$. This is the concentrated reagent; sp. gr. 1.19, 37%.

Hydrochloric acid, 6 $\underline{N}$. Add 500 ml 12 $\underline{N}$ HCl to 400 ml water and dilute to 1 liter.

Hydrochloric acid, 4 $\underline{N}$. Add 336 ml 12 $\underline{N}$ HCl to 500 ml water and dilute to 1 liter.

Hydrochloric acid, 3 $\underline{N}$. Add 250 ml 12 $\underline{N}$ HCl to 500 ml water and dilute to 1 liter.

Hydrochloric acid, 1 $\underline{N}$. Add 84 ml 12 $\underline{N}$ HCl to 800 ml water and dilute to 1 liter.

Hydrochloric acid, 0.5 $\underline{N}$. Add 42 ml 12 $\underline{N}$ HCl to 900 ml water and dilute to 1 liter.

Hydrofluoric acid, HF, 48% (~30 $\underline{N}$). This is the concentrated reagent; sp. gr. 1.15.

Hydrofluoric acid, 5 $\underline{N}$. Add 17 ml 48% HF to 50 ml water and dilute to 100 ml. Store in polypropylene bottle.

Hydrofluoric acid, 1 $\underline{N}$. Add 3.5 ml 48% HF to 50 ml water and dilute to 100 ml. Store in polypropylene bottle.

Hydrogen peroxide, H_2O_2, 30%.

Hydrogen peroxide - Ammonium hydroxide solution, (5:1). Mix 50 ml H_2O_2 and 10 ml 15 $\underline{N}$ NH_4OH.

Hydrogen sulfide, H_2S, gas.

Iodic acid, 0.35 $\underline{M}$. Dissolve 61.6 g HIO_3 in water and dilute to 1 liter.

Iron chloride, 0.1 $\underline{M}$. Dissolve 27 g $FeCl_3 \cdot 6H_2O$ in water plus 2 ml 12 $\underline{N}$ HCl and dilute to 1 liter.

Iron, wire #36, analytical grade.

<u>Magnesia Mixture</u>. Dissolve 20 g NH_4Cl in water, add 10 g $MgCl_2$ and dilute to 100 ml.

<u>Magnesium metal, Mg, solid, ribbon</u>.

<u>Nickel, powdered, analytical grade</u>.

Nitric acid, HNO_3, 16 $\underline{N}$. This is the concentrated reagent; sp. gr. 1.42, 70%.

Nitric acid, 6 $\underline{N}$. Add cautiously 375 ml 16 $\underline{N}$ HNO_3 to 600 ml water and dilute to 1 liter.

Nitric acid, 4 $\underline{N}$. Add cautiously 250 ml 16 $\underline{N}$ HNO_3 to 700 ml water and dilute to 1 liter.

Nitric acid, 1 $\underline{N}$. Add 62 ml 16 $\underline{N}$ HNO_3 to 900 ml water and dilute to 1 liter.

Nitric acid, 0.2 $\underline{N}$. Add 12.5 ml 16 $\underline{N}$ HNO_3 to 900 ml water and dilute to 1 liter.

<u>Oxalic acid, 10%</u>. Dissolve 10 g $H_2C_2O_4$ in water and dilute to 100 ml.

<u>Oxalic acid, saturated</u>. Dissolve 150 g $H_2C_2O_4$ in 1 liter boiling water.

Perchloric acid, $HClO_4$, 70% (11.6 $\underline{N}$). This is the concentrated reagent; sp. gr. 1.67.

Perchloric acid, 1 $\underline{N}$. Dilute 85 ml 70% $HClO_4$ to 1 liter with water.

Phosphoric acid, H_3PO_4, 85% (44 $\underline{N}$). This is the concentrated reagent; sp. gr. 1.69.

Potassium bromate, $KBrO_3$, solid.

Potassium hydroxide, 6 $\underline{N}$. Dissolve 33.7 g KOH in water and dilute to 100 ml.

<u>Potassium iodate, prepared reagent</u>. Dissolve 100 g KIO_3 in 333 ml 16 $\underline{N}$ HNO_3 and dilute to 1 liter with water.

<u>Potassium iodate wash solution</u>. Dissolve 8 g KIO_3 in 50 ml 16 $\underline{N}$ HNO_3 and dilute to 1 liter with water.

Potassium nitrite, KNO_2, solid.

Potassium nitrite wash solution (1:100). Dissolve 10 g KNO_2 in water and dilute to 1 liter.

Potassium permanganate, 0.5 $\underline{M}$. Dissolve 7.9 g $KMnO_4$ in water and dilute to 100 ml.

Potassium thiocyanate, KSCN, 0.75 $\underline{M}$. Dissolve 7.29 g KSCN in water and dilute to 100 ml.

Potassium thiocyanate wash solution (1:200). Dilute 0.5 ml 0.75 $\underline{M}$ KSCN to 100 ml with water.

Silver nitrate, 0.1 $\underline{M}$. Dissolve 17 g $AgNO_3$ in water and dilute to 1 liter. Store in a dark container.

Sodium acetate, 3.6 $\underline{M}$. Dissolve 295.3 g CH_3COONa in water and dilute to 1 liter.

Sodium acetate buffer, pH 5.0. Mix 100 ml 1 $\underline{N}$ CH_3COOH and 100 ml 3.6 $\underline{M}$ CH_3COONa.

Sodium bisulfite, 1 $\underline{M}$. Dissolve 5.2 g $NaHSO_3$ in water and dilute to 50 ml. Prepare only as much as is needed.

Sodium bromate, 1.5 $\underline{M}$. Dissolve 11.5 g $NaBrO_3$ in water and dilute to 50 ml. Prepare only as much as needed.

Sodium bromate, 0.5 $\underline{M}$. Dissolve 76 g $NaBrO_3$ in water and dilute to 1 liter.

Sodium carbonate, 1.5 $\underline{M}$. Dissolve 160 g Na_2CO_3 in 600 ml water and dilute to 1 liter.

Sodium chromate, 0.5 $\underline{M}$. Dissolve 171.1 g $Na_2CrO_4 \cdot 10H_2O$ in 400 ml water and dilute to 1 liter.

Sodium citrate, 10%. Dissolve 10 g $Na_3C_6H_5O_7 \cdot 2H_2O$ in 100 ml water.

Sodium hydroxide, 18 $\underline{N}$. Dissolve 720 g NaOH in 500 ml water and dilute to 1 liter.

Sodium hydroxide, 6 $\underline{N}$. Dissolve 240 g NaOH in 800 ml water and dilute to 1 liter.

Sodium hydroxide, 2 $\underline{N}$. Dissolve 80 g NaOH in 800 ml water and dilute to 1 liter.

Sodium hydroxide, 0.5 $\underline{N}$. Dissolve 20 g NaOH in 800 ml water and dilute to 1 liter.

Sodium hypochlorite, NaOCl, 5%. This is ordinary liquid laundry bleach.

Sodium metaperiodate, $NaIO_4$, solid.

Sodium nitrite, 1 $\underline{M}$. Dissolve 69 g $NaNO_2$ in water and dilute to 1 liter.

Sodium oxalate, 0.1 $\underline{M}$. Dissolve 13.4 g $Na_2C_2O_4$ in water and dilute to 1 liter.

Sodium sulfite, Na_2SO_4, solid.

Sodium sulfite, 1 $\underline{M}$. Dissolve 12.6 g Na_2SO_3 in water and dilute to 100 ml.

Stannous chloride, prepared reagent. Dissolve 2.5 g $SnCl_2 \cdot 2H_2O$ in 15 ml 12 $\underline{N}$ HCl. Heat and stir until dissolved. Prepare only as much as is needed.

Sulfuric acid, H_2SO_4, 36 $\underline{N}$. This is the concentrated reagent; sp. gr. 1.84, 95-98%.

Sulfuric acid, 24 $\underline{N}$. Add cautiously, with stirring, 667 ml 36 $\underline{N}$ H_2SO_4 to 300 ml water and dilute to 1 liter.

Sulfuric acid, 18 $\underline{N}$. Add cautiously, with stirring, 500 ml 36 $\underline{N}$ H_2SO_4 to 400 ml water and dilute to 1 liter.

Sulfuric acid, 12 $\underline{N}$. Add cautiously, with stirring, 333 ml 36 $\underline{N}$ H_2SO_4 to 500 ml water and dilute to 1 liter.

Sulfuric acid, 6 $\underline{N}$. Add cautiously, with stirring, 167 ml 36 $\underline{N}$ H_2SO_4 to 500 ml water and dilute to 1 liter.

Sulfuric acid, 3 $\underline{N}$. Add cautiously, with stirring, 84 ml 36 $\underline{N}$ H_2SO_4 to 800 ml water and dilute to 1 liter.

Sulfuric acid, 1 $\underline{N}$. Add cautiously, with stirring, 28 ml 36 $\underline{N}$ H_2SO_4 to 800 ml water and dilute to 1 liter.

III. Organic Reagents

Acetone, $(CH_3)_2CO$, anhydrous.

Aerosol solution, 1.5%. Add 1.5 ml Aerosol OT (25%) to 23.5 ml water.

Benzidine hydrochloride, 2%. Dissolve 5 g $NH_2C_6H_4C_6H_4NH_2 \cdot 2HCl$ in 40 ml 1 $\underline{N}$ HCl and dilute to 250 ml with 50% ethanol. Keep refrigerated.

α-Benzoinoxime, 2%. Dissolve 2 g $C_{13}H_{12}O:C:NOH$ in 100 ml 95% ethanol.

Caproic acid, $CH_3(CH_2)_4COOH$.

Carbon tetrachloride, CCl_4.

Chloroform, $CHCl_3$.

Cupferron, 6%. Dissolve 6 g $C_6H_9N_3O_2$ in 100 ml water. Keep refrigerated.

Dextrose, $C_6H_{12}O_6$, anhydrous.

Diethyl ether, $(C_2H_5)_2O$, anhydrous.

Dimethylglyoxime, 1% in C_2H_5OH. Dissolve 1 g $(CH_3C:NOH)_2$ in 100 ml 95% ethanol.

1,4 Dioxane, $C_4H_8O_2$. Scintillation grade.

Ethanol, C_2H_5OH, absolute 99.5%.

Ethanol, C_2H_5OH, 95%.

Ethanol, 50%. Add 105 ml 95% C_2H_5OH to 95 ml water.

Ethanol, 20%. Add 42 ml 95% C_2H_5OH to 158 ml water.

8-Hydroxyquinoline, 5% in CH_3COOH. Dissolve 5 g C_9H_7NO in 100 ml 1.5 $\underline{N}$ CH_3COOH.

Methyl isobutyl ketone, $C_6H_{12}O$ (MIBK).

bis-MSB, (p-bis-(methylstyryl)-benzene), scintillation grade.

Naphthalene, $C_{10}H_8$, solid.

Petroleum ether.

POPOP, (1,4-di[2-(5 phenyloxazolyl)] benzene).

PPO, (2,5-Diphenyloxazole).

Pyridine, C_5H_5N.

Quinaldic acid solution, prepared reagent. Dissolve 2 g $C_{10}H_7NO_2 \cdot 2H_2O$ in 50 ml ethanol, add 4 ml 6 $\underline{N}$ NaOH and filter if undissolved residue remains. Dilute to 100 ml with water and store in the refrigerator.

Scintillation solution (dioxane). Mix thoroughly 7 g PPO, 1.5 g bis-MSB and 120 g naphthalene in 1 liter 1,4-dioxane.

Scintillation solution (toluene). Mix thoroughly 4 g PPO, 0.1 g POPOP in 1 liter toluene.

Tartaric acid, 50%. Dissolve 50 g $C_4H_6O_6$ in water and dilute to 100 ml.

Thioacetamide, CH_3CSNH_2: solid

Thioacetamide, 5%. Dissolve 2.5 g CH_3CSNH_2 in 50 ml water, and filter before using.

Toluene, $C_6H_5CH_3$, reagent grade.

Tributyl phosphate, $(H_3CCH_2CH_2CH_2O)_3PO$, (TBP).

Trioctylphosphine oxide, $(C_8H_{17})_3PO$. Dissolve 20 g trioctyl-phosphine oxide in 100 ml xylene.

Xylene, $C_6H_4(CH_3)_2$, reagent grade.

IV. Indicators and Ion Exchange Resins

Methyl red, 0.1%. Dissolve 0.1 g methyl red in 100 ml 95% ethanol.

Phenolphthalein, 1%. Dissolve 1 g phenolphthalein in 50 ml 95% ethanol and add 50 ml water.

Ion Exchange Resins

Dowex 50 W-X8, cation resin, 20-50 mesh, 100-200 mesh, ionic form H^+.

Dowex 1-X8, anion resin, 20-50 mesh, 100-200 mesh, ionic form Cl^-.

Dowex 2-X8, anion resin, 20-50 mesh, ionic form Cl^-.

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