ACNP-68505H

LA CROSSE BOILING WATER REACTOR

OPERATING MANUAL

VOLUME VIII: WATER CHEMISTRY

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under
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ALLIS-CHALMERS
Atomic Energy Division
6935 Arlington Road
Bethesda, Maryland 20014

DISCLAIMER

PREFACE

The Operating Manual for the La Crosse Boiling Water Reactor is being published in 11 volumes. This is Volume VIII: Water Chemistry (ACNP-68505H). The volumes that comprise the Operating Manual are listed below.

Volume I:	Integrated Plant Operation	(ACNP-68505A)
Volume II:	Reactor Process Systems	(ACNP-68505B)
Volume III:	Turbine Generator Systems	(ACNP-68505C)
Volume IV:	Instrumentation, Control and Electrical Distribution	(ACNP-68505D)
Volume V:	Service System	(ACNP-68505E)
Volume VI:	Refueling	(ACNP-68505F)
Volume VII:	Waste Collection and Treatment	(ACNP-68505G)
Volume VIII:	Water Chemistry	(ACNP-68505H)
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1. SAFETY

This section will describe in detail the safety needed in the laboratory. Principles of safe laboratory practices should be exercised at all times.

1.1 SAFE LABORATORY PRACTICES

The following summarizes the safe laboratory practices:

1. Personnel protective equipment such as eye protection, face shields, and gloves shall be used when necessary.

2. Rubber gloves shall be used when pouring acids, such as fuming nitric acid and hydrofluoric acid, or when handling radioactive material. Surgeon's gloves may be used when manual dexterity is required.

3. An acid- and alkaline-resistant laboratory coat shall be used in the laboratory at all times to protect the clothes and body from corrosive chemicals and radioactive contamination.

4. Smoking, eating and drinking are forbidden in the laboratory.

5. Avoid skin contact with and inhalation or ingestion of all chemicals.

6. Broken glassware shall be disposed of in a separate container.

7. The fume hood should be used when handling volatile or flammable chemicals.

8. Do not pick up small splinters of broken glass with the hands. Use a whisk broom and dust pan. Very small pieces may be picked up with a large piece of wet cotton or sticky paper.

9. Contaminated waste shall be segregated from clean debris.

10. When diluting strong acids, always add acid to the water slowly over a sink or vessel to contain any breakage or spillage. Rather than attempting to transfer acid directly from large stock bottles of reagents, it should first be transferred to a small beaker or reagent bottle.

11. Flammable liquids and corrosive, noxious, or vapor-producing chemicals shall not be poured in the sink but shall be stored in the containers provided. Acids and alkalis may be flushed down the sink with copious amounts of water for dilution, or else they should be neutralized before disposal.

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12. All reagent bottles and other containers of chemicals shall be clearly labeled. These shall not be filled to more than three-quarters of their capacity, thus allowing for expansion.

13. Never mix organic chemicals and acids except as specifically detailed in procedures.

14. Never pipette by mouth. Use a rubber bulb or equivalent to apply the suction.

15. All precautions used in handling corrosive and toxic chemicals shall also be observed with radioactive samples.

16. Mercury vapor is poisonous. Use trays to contain spills when working with mercury, and clean up all spillage.

17. Before analyzing primary coolant, the radiation levels shall be monitored to ascertain what precsutions must be taken.

18. Evaporations involving primary coolant must be performed in the fume hood.

19. Hands and clothing shall be monitored for contamination before leaving the laboratory.

1.2 SAFE LABORATORY TECHNIQUES

The following are the safe laboratory techniques and practices. They must be followed.

1.2.1 Evaporation

Evaporation in beakers and flasks should be made on a hot plate. To prevent "bumping" or excessive turbulence, a few glass beads may be added. Infra-red lamps may be used to evaporate small liquid samples in planchets. Solutions in centrifuge cones can be evaporated by placing a flame directly below the liquid level in the cone. The cone should be held with tongs, not with the fingers; and it should be continuously swirled to avoid overheating the liquid in any one place. This technique requires practice to avoid the loss of liquid. Evaporate organic solvents in a water bath under a fume hood. Solutions to be heated can be placed in a beaker half filled with water and placed on a hot plate.

1.2.2 Centrifuge Practice

When using the centrifuge, be sure that the cone containing the sample is counterbalanced by another tube containing the same level of liquid. The centrifuge should be thick-walled glass or plastic to allow the use of the highest speed on the centrifuge. Allow the

centrifuge to come to a stop by itself, unless it has a brake attachment which can be used with caution. Otherwise, the precipitate may become dislodged. If the precipitate becomes difficult to separate after centrifuging for 2 min, add a few drops of a wetting agent, which will remedy this problem.

1.2.3 Filtration

The final precipitate obtained from the radiochemical procedures is usually suction-filtered. The stainless-steel filtering apparatus is placed in a 500-ml sidearm flask through a one-hole rubber stopper. The flask is connected to an explosion-proof vacuum pump by means of a vacuum hose and an intermediate empty filtering flask, which is used as a liquid trap. The filter paper should be centered on the filter support. A few drops of water should be poured onto the filter to wet the filter. After this operation is completed, turn on the pump and pour the precipitate onto the filter. After washing the precipitate with ethyl alcohol and removing moisture with ether, the pump should remain on for approximately 30 sec. The top of the filtering apparatus is then removed with the vacuum pump still on. The pump is turned off, and the filter paper is removed with blunt-point forceps. (Blunt forceps should be used to prevent putting holes in the filter paper.)

2. STANDARDIZATION OF CARRIER SOLUTIONS

2.1 SUMMARY OF METHODS

The losses of a radioelement through the radiochemical procedure is determined by measuring the fractional recovery of the carrier element used. This requires the addition of a known amount of carrier element at the beginning of the analysis. To accomplish this, carrier solutions are prepared and standardized; and accurately measured volumes of the solutions are used.

2.2 APPARATUS

1. Normal laboratory glassware is required for this work.

2. Glass Fiber Filters of 1-in.-dia x 0.01-in. thickness should be used. Any similar filter will be suitable provided it retains fine precipitates adequately and maintains constant weight to ±0.0001 g during filtration and drying.

3. Filter Holder. The filter holder must hold the 1-in. filters rigidly in place during filtration.

NOTE: Care should be taken to clean the holder thoroughly between filtrations to prevent cross-contamination.

4. Desiccator. The desiccator must hold four 1-in.-dia filters similar to Fisher No. 8-615.

5. Oven. The oven should be of the gravity-convection type and able to supply uniform heat at 110 C to a ±0.5 C (Fisher No. 13-244-1 or equivalent).

6. Analytical Balance. It should be capable of weighing to the nearest 0.1 mg.

7. Muffle Furnace. It must be able to hold four crucibles and also must be designed for continuous operation at temperatures up to 900 C (1650 F). (Fisher No. 10-552 or equivalent.)

8. Refrigerator. It should be of the small laboratory type and designed to be explosion-proof.

9. Infra-Red Lamp. The infra-red lamp should be designed to adjust at various heights for evaporating solutions and drying precipitates. (Fisher No. 11-504-5V4 or equivalent.)

10. Centrifuge. A clinical centrifuge shall be used. The head should accommodate 50-ml centrifuge tubes.

2.3 REAGENTS AND MATERIALS

1. Purity of Reagents. Reagent-grade chemicals shall be used to prepare carriers. Unless otherwise indicated, all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society. Other reagents may be used, provided they are of sufficient purity to give the same accuracy.

2. Purity of Water. All water used in preparing the carriers and in standardization of these carriers shall be demineralized water and shall conform to the specification for Reagent Water (ASTM Designation D 1193).

3. Ethyl Alcohol. Either CP ethyl alcohol or denatured ethyl alcohol (denatured according to formula No. 30, Regulation No. 3 and its appendix, U.S. Bureau of Internal Revenue) shall be used for standardization of the carriers.

4. Cesium Chloride. Cesium chloride reagent No. C-24, purified, shall be used. It can be obtained from the Fisher Chemical Company.

5. Chloroplatinic Acid Reagent. Dissolve 7.3 g of hydrated chloroplatinic acid ($H_2PtCl_6 \cdot 6H_2O$) in 100 ml of water.

6. 6M Acetic Acid. Measure 40 ml concentrated acetic acid, and dilute it to 100 ml with water.

7. 6N Hydrochloric Acid. Measure 498 ml of 12.1N hydrochloric acid (concentrated), and dilute it to 1 liter with water.

8. 1N Hydrochloric Acid. Measure 83.0 ml of 12.1N hydrochloric acid (concentrated), and dilute it to 1 liter with water.

9. 2N Hydrochloric Acid. Measure 166 ml of 12.1N hydrochloric acid (concentrated), and dilute it to 1 liter with water.

10. 6N Nitric Acid. Measure 384 ml of 15.7N nitric acid (concentrated), and dilute it to 1 liter with water.

11. 4N Nitric Acid. Measure 256 ml of 15.7N nitric acid (concentrated), and dilute it to 1 liter with water.

12. 3M Ammonium Acetate. Dissolve 230 g of ammonium acetate ($NH_4C_2H_3O_2$) in water, and dilute to 1 liter with water.

13. Cupferron Reagent. Dissolve 6 g of the ammonium salt of nitroso-phenyl-hydroxylamine (cupferron) in 100 ml of water.

NOTE: Reagent is good for one week only, and it must be kept cool and stored in the dark.

14. 1.5M Sodium Chromate. Dissolve 243 g of sodium chromate (Na_2CrO_4), and dilute to 1 liter with water.

15. 0.1M Palladium Chloride. Dissolve 21.4 g of palladium chloride ($PdCl_2 \cdot 2H_2O$), and dilute to 1 liter with water.

16. 1.5N Sulfuric Acid. Measure 42 ml of 36.0N sulfuric acid (concentrated), and dilute to 1 liter with water.

17. 14.8N Ammonium Hydroxide. Concentrated ammonium hydroxide (NH_4OH).

18. 15.7N Nitric Acid. Concentrated nitric acid (HNO_3).

19. 12.1N Hydrochloric Acid. Concentrated hydrochloric acid (HCl).

20. (1-3) Hydrochloric Acid Solution. Measure 100 ml of concentrated hydrochloric acid (12.1N) (HCl), and dilute with 300 ml water.

21. The following additional chemicals are needed:

(a) saturated ammonium oxalate $(HN_4)_2C_2O_4$ solution
(b) thioacetamide
(c) saturated sodium bromate ($NaBrO_3$)
(d) saturated oxalic acid solution
(e) saturated barium nitrate solution

22. The following chemicals will be needed to prepare carriers:

(a) barium nitrate ($Ba(NO_3)_2$)
(b) cerium nitrate ($Ce(NO_3)_3 \cdot 6H_2O$)
(c) cobalt nitrate ($Co(NO_3)_2 \cdot 6H_2O$)
(d) potassium iodide (KI)
(e) iron chloride ($FeCl_3 \cdot 6H_2O$)
(f) potassium chloride (KCl)
(g) rubidium chloride (RbCl)

(h) strontium nitrate ($Sr(NO_3)_2 \cdot 4H_2O$)

(i) yttrium nitrate ($Y(NO_3)_3 \cdot 6H_2O$)

(j) zirconyl nitrate ($ZrO(NO_3) \cdot 2H_2O$)

(k) manganese dioxide (MNO_2)

(l) lanthanum nitrate ($La_2(NO_3)_3 \cdot 6H_2$))

(m) potassium dichromate ($K_2Cr_2O_7$)

(n) sodium fluoride (NaF)

(o) sodium tungstate ($Na_2WO_4 \cdot 2H_2O$)

(p) pure nickel metal powder

(q) pure copper metal

(r) sodium chloride (NaCl)

(s) ammonium chloride (HN_4Cl)

2.4 AMMONIUM CARRIER (10 mg/ml)

2.4.1 Procedure

1. Dissolve 2.9654 g ammonium chloride (NH_4Cl), and dilute it to 100 ml of solution.

2. Pipet accurately four 2-ml portions of the carrier solution into four separate 50-ml centrifuge tubes.

3. Dilute to 5 ml with 6N hydrochloric acid (HCl).

4. Add 1 ml of 5-percent chloroplatinic acid (H_2PtCl_6) and 5 ml of ethyl alcohol.

5. Place centrifuge tubes in an ice bath for 5 to 10 min.

6. Using suction, filter the precipitate onto a weighed glass fiber filter holder.

NOTE: The precipitate appearance will be a yellow-orange color precipitate.

7. Rinse the centrifuge tube with ehtyl alcohol, and pour the rinsings through the filter.

8. Wash the precipitate with approximately 10-ml ethyl alcohol and 10 ml of diethyl ether.

9. Weigh the filter and precipitate to the nearest 0.1 mg on an analytical balance.

10. Subtract the tare weight of the filter to obtain the weight of the precipitate.

11. Four standardizations of the carrier solution should be performed. The spread in results should be less than 0.5 percent.

2.4.2 Calculations

$$NH_4(mg/ml) = \frac{mg(ppt)(NH_4)_2PtCl_6(0.08128)}{ml\ (aliquot)}$$

2.5 BARIUM CARRIER (10 mg/ml)

2.5.1 Procedure

1. Dissolve 19.0 g of barium nitrate ($Ba(NO_3)_2$) in approximately 300 ml of water.

2. Dilute to 1 liter and shake for 1 or 2 min.

3. Pipet accurately four 5.0-ml portions of the carrier solution into four separate 250-ml beakers.

4. Dilute to approximately 100 ml.

5. Add 5ml of 6M acetic acid and 10 ml of 3M ammonium acetate.

6. Place beakers on a hot plate, and bring to a boil.

7. Add 5 ml of 1.5M sodium chromate (Na_2CrO_4) dropwise while stirring. Boil for 1 or 2 min with stirring.

8. Cool to room temperature; then, filter with suction the precipitate onto a weighed glass fiber filter placed in the filter holder.

9. Rinse the beaker with ethyl alcohol, and pour the rinsings through the filter.

10. Wash the precipitate with approximately 10-ml ethyl alcohol and 10 ml of diethyl ether.

11. Place the filter containing the precipitate in an oven, and dry at 110 C for 10 min. Cool in a desiccator for 10 min.

12. Weigh the filter and precipitate on an analytical balance to the nearest 0.1 mg.

13. Subtract the tare weight of the filter to obtain the weight of the precipitate.

14. Four standardizations of the carrier solution should be performed. The spread in results should be less than 0.5 percent.

2.5.2 Calculations

$$Ba(mg/ml) = \frac{(mg(ppt)BaCrO_4)\ (0.5421)}{ml\ (aliquot)}$$

2.6 CERIUM CARRIER (10 mg/ml)

2.6.1 Procedure

1. Dissolve 31.0 g of cerium nitrate ($Ce(NO_3)_3 \cdot 6H_2O$) in 200 ml of water.

2. Dilute to 1 liter, and shake for 1 or 2 min.

3. Pipet accurately four 5.0-ml portions of the carrier solution into four 100-ml beakers.

4. Dilute to approximately 20 ml with water.

5. Warm on a hot-water bath, and add about 50 ml of saturated ammonium oxalate ($(NH_4)_2C_2O_4$) solution (approximately 100 g in 1 liter).

6. Cool in an ice bath for approximately 15 min, and filter with a filter funnel using an 11-cm Whatman No. 42 filter paper.

7. Transfer the precipitate to a tared porcelain crucible, and dry under a heat lamp.

8. Cover and ignite for 10 min in a muffle furnace at 800 C.

9. Remove the cover, and continue the ignition for 30 min.

10. Cool and weigh the crucible and precipitate (CeO_2) on an analytical balance to the nearest 0.1 mg.

11. Place the crucible containing the precipitate in an oven, and dry at 110 C for 20 min.

12. Cool for 20 min in a desiccator; then, reweigh.

13. Repeat steps 11 and 12 until constant weight is obtained.

14. Four standardizations of the carrier solution should be performed. The spread in results should be less than 0.5 percent.

2.6.2 Calculations

$$Ce(mg/ml) = \frac{(mg(ppt)CeO_2)\ (0.8141)}{ml\ (aliquot)}$$

2.7 CESIUM CARRIER (10 mg/ml)

2.7.1 Procedure

1. Dissolve 12.5 g of cesium chloride in water, and dilute to 1 liter with water.

2. Pipet accurately four 5.0-ml portions of the carrier solution into a 50-ml centrifuge tube.

3. Adjust the volume to 10 ml in 6N hydrochloric acid (HCl).

4. Add 4 ml of chloroplatinic acid.

5. Stir for 1 or 2 min, and cool in a refrigerator for 10 min.

6. Filter with suction the precipitate onto a weighed glass fiber filter placed in the filter holder.

7. Rinse the centrifuge tube with ethyl alcohol, and pour the rinsings through the filter.

8. Wash the precipitate with approximately 10 ml ethyl alcohol and 10 ml of diethyl ether.

9. Place the filter containing the precipitate in an oven, and dry at 110 C for 30 min. Cool in a desiccator for 20 min.

10. Weigh the filter and precipitate on an analytical balance.

11. Subtract the tare weight of the filter to obtain the weight of the precipitate.

12. Repeat steps 9, 10, and 11 until constant weight is obtained.

13. Four standardizations of the carrier solution should be performed. The spread in results should be less than 0.5 percent.

2.7.2 Calculations

$$Cs(mg/ml) = \frac{(mg(ppt)Cs_2PtCl_6)\ (0.3945)}{ml\ (aliquot)}$$

2.8 CHROMIUM CARRIER (10 mg/ml) (Available from Fisher, Cat. No. So-C-184)

2.8.1 Procedure

1. Dissolve 28 g of potassium dichromate ($K_2Cr_2O_7$) in 200 ml of water.

2. Dilute to 1 liter with water, and shake for 1 or 2 min.

3. Pipet accurately four 2.0-ml portions of the carrier solution into four separate 50-ml centrifuge tubes.

4. Add 1 ml concentrated ammonium hydroxide (NH_4OH) and 15 ml of water.

5. Add 3 ml of saturated barium nitrate ($Ba(NO_3)_2$) solution to precipitate ($BaCrO_4$).

6. Filter with suction the precipitate onto a weighed glass fiber filter placed in the filter holder.

7. Rinse the 50-ml centrifuge with ethyl alcohol, and pour the rinsings through the filter.

8. Wash the precipitate with approximately 10 ml ethyl alcohol and 10 ml of diethyl ether.

9. Place the filter containing the precipitate in an oven, and dry at 110 C for 10 to 15 min. Cool in a desiccator for 10 to 15 min.

10. Weigh the filter and precipitate on an analytical balance to the nearest 0.1 mg.

11. Subtract the tare weight of the filter to obtain the weight of the precipitate.

12. Four standardizations of the carrier solution should be performed. The spread in results should be less than 0.5 percent.

2.8.2 Calculations

$$Cr(mg/ml) = \frac{(mg(ppt)BaCrO_4)\ (0.2053)}{ml\ (aliquot)}$$

2.9 COBALT CARRIER (10 mg/ml) (Available from Fisher, Cat. No. So-C-185)

2.9.1 Procedure

1. Dissolve 49.3 g of cobalt nitrate ($Co(NO_3)_2 \cdot 6H_2O$) in 200 ml of water.

2. Add 1 ml concentrated nitric acid (NHO_3), and dilute to 1 liter with water.

3. Pipet accurately four 5.0-ml portions of the carrier solution into four separate 50-ml centrifuge tubes.

4. Dilute to approximately 15 ml with water.

5. Add 2 ml of concentrated ammonium hydroxide (NH_4OH), and carefully saturate the solution with hydrogen sulfide (H_2S) gas.

6. Filter the cobalt monosulfide (CoS) onto a Whatman No. 42 filter paper, and wash with 5 ml of ammonia water.

7. Transfer the paper and precipitate to a tared porcelain crucible.

8. Dry under a heat lamp; cover with a porcelain cover, and ignite for approximately 10 min at 700 C.

9. Remove the cover, and continue the ignition for 30 min.

10. Cool and weigh the crucible and precipitate (Co_2O_3) on an analytical balance to the nearest 0.1 mg.

11. Place the crucible containing the precipitate in an oven, and dry at 110 C for 20 min.

12. Cool for 20 min in a desiccator, and reweigh.

13. Repeat steps 11 and 12 until constant weight is obtained.

14. Four standardizations of the carrier solution should be performed. The spread in results should be less than 0.5 percent.

2.9.2 Calculations

$$Co(mg/ml) = \frac{(mg(ppt)(Co_2O_3))\ (0.1253)}{ml\ (aliquot)}$$

2.10 COPPER CARRIER (mg/ml) (Available from Fisher, Cat. No. So-C-183)

2.10.1 Procedure

1. Dissolve 1.00 g (pure) copper metal in 25 ml concentrated nitric acid.

2. Dilute to 100 ml with water, and shake for 1 or 2 min.

NOTE: If the copper metal is weighed on an analytical balance to the nearest 0.1 mg, standardization will not be necessary.

2.11 FLUORIDE CARRIER (10 mg/ml)

2.11.1 Procedure

1. Dissolve 1.8 g of sodium fluoride (NaF) in 100 ml of water in a volumetric flask.

2. Shake for 1 or 2 min.

3. Pipet accurately four 2.0-ml portions of the fluoride carrier solution into four separate 50-ml centrifuge tubes.

4. Add 20 ml of lanthanum carrier.

5. Filter with suction the precipitate onto a weighed glass fiber filter placed in the filter holder.

NOTE: The precipitate appearance will be a white gelatinous precipitate.

6. Rinse the centrifuge tube with ethyl alcohol, and pour the rinsings through the filter.

7. Wash the precipitate with approximately 10 ml ethyl alcohol and 10 ml of diethyl ether.

8. Weigh the filter and precipitate on an analytical balance to the nesrest 0.1 mg.

9. Subtract the tare weight of the filter to obtain the weight of the precipitate.

10. Four standardizations of the carrier solution should be performed. The spread in results should be less than 0.5 percent.

2.11.2 Calculations

$$F(mg/ml) = \frac{(mg(ppt)NaF)\ (0.0726)}{ml\ (aliquot)}$$

2.12 IODINE CARRIER (10 mg/ml)

2.12.1 Procedure

1. Dissolve 13.1 g of potassium iodide (KI) in 200 ml of water.

2. Dilute to 1 liter with water, and shake to get into solution.

3. Pipet accurately four 5.0-ml portions of the carrier solution into four separate 100-ml beakers.

4. Acidify with 1 ml of concentrated hydrochloric acid (HCl).

5. Add about 2 ml of 0.1M (21.4g./1) palladium chloride ($PdCl_2$), to precipitate all the I.

6. Digest the precipitate on a hot plate for 1 hr.

7. Filter with suction the precipitate onto weighed glass fiber filters placed in the filter holder.

8. Rinse the beakers with ethyl alcohol, and pour the rinsings through the filters.

9. Wash the precipitates twice with about 5 ml of ethyl alcohol and twice with about 5 ml of diethyl ether.

10. Place the filters containing the precipitate in an oven, and dry at 110 C for 30 min. Cool in a desiccator for 20 min.

11. Weigh the filters and precipitate on an analytical balance to the nearest 0.1 mg.

12. Subtract the tare weights of the filters to obtain the weights of the precipitates.

13. The spread in results between the four standardizations should be less than 0.5 percent.

2.12.2 Calculations

$$I(mg/ml) = \frac{(mg(ppt)\ PdI_2)\ (0.7046)}{ml\ (aliquot)}$$

2.13 IRON CARRIER (10 mg/ml) (Available from Fisher, Cat. No. So-I-123)

2.13.1 Procedure

1. Dissolve 48.4 g of iron chloride ($FeCl_3 \cdot 6H_2O$) in 1N hydrochloric acid (HCl).

2. Dilute to 1 liter with 1N hydrochloric acid (HCl), and shake to mix.

3. Pipet four 5.0-ml portions of the iron carrier solution into four separate clean 100-ml beakers.

4. Add 1 ml of concentrated HCl to each beaker, and dilute to 20 ml with H_2O.

5. Add a small amount of filter paper pulp to each beaker.

6. Add two drops of concentrated nitric acid to each beaker to oxidize Iron (II) to Iron (III). Heat to boiling.

7. Add two drops of methyl orange.

8. Dilute one volume of concentrated ammonium hydroxide with two volumes of water, and filter with suction.

9. Add the ammonium hydroxide H_2O solution to the beakers until the iron solution becomes alkaline, as shown by a change of indicator color from red to yellow (about 6 ml).

10. Allow the precipitate to coagulate on the filter paper pulp for 20 min (no longer).

11. Wash and filter through Whatman No. 41 or 41H filter paper.

12. Wash with a solution of ammonium nitrate (10 g/liter) until the filtrate yields no precipitate when tested with $AgNO_3$ solution and nitric acid. (Treat a fresh portion of the filtrate with a few drops of HNO_3 and then with a few drops of $AgNO_3$ solution, approximately 5 g/100 ml.)

13. Transfer the paper and precipitate to a weighed porcelain crucible. Char off the paper carefully with a burner, using a minimum of heat. After charring, ignite in a muffle furnace for 1 hr at 700 C.

14. Cool and weigh the crucible and precipitate on an analytical balance to the nearest 0.1 mg.

15. Place the crucible and precipitate in an oven, and dry at 110 C for 20 min.

16. Cool for 20 min in a desiccator, and reweigh.

17. Repeat steps 15 and 16 until constant weight is obtained. The spread in results should be less than 0.5 percent.

2.13.2 Calculations

$$Fe(mg/ml) = \frac{(mg(ppt)Fe_2O_3)\ (0.6994)}{ml\ (aliquot)}$$

2.14 LANTHANUM CARRIER (10 mg/ml)

2.14.1 Procedure

1. Dissolve 15.6 g lanthanum nitrate ($La_2(NO_3)_3 \cdot 6H_2O$) in 200 ml of water.

2. Dilute to 1 liter with water, and shake for 1 or 2 min.

3. Pipet accurately four 5.0-ml portions of the carrier solution into four separate 50-ml centrifuge tubes.

4. Add 15 ml of water; place in a beaker half-filled with water, and heat on a hot plate to boiling.

5. While heating on the hot plate and stirring, add 15 ml of saturated oxalic acid.

6. Filter with suction the precipitate onto a weighed glass fiber filter placed in the filter holder.

7. Rinse the centrifuge tube with ethyl alcohol, and pour the rinsings through the filter.

8. Wash the precipitate with approximately 10 ml ethyl alcohol and 10 ml of diethyl ether.

9. Place the filter containing the precipitate in an oven, and dry at 110 C for 10 to 15 min. Cool in a desiccator for 15 min.

10. Weigh the filter and precipitate on an analytical balance to the nearest 0.1 mg.

11. Subtract the tare weight of the filter to obtain the weight of the precipitate.

12. Four standardizations of the carrier solution should be performed. The spread in results should be less than 0.5 percent.

2.14.2 Calculations

$$La(mg/ml) = \frac{mg(ppt)\ (La_2(C_2O_4)_3 \cdot 9H_2O)\ (0.3949)}{ml\ (aliquot)}$$

2.15 MANGANESE CARRIER (10 mg/ml) (Available from Fisher, Cat. No. So-M-72)

2.15.1 Procedure

1. Dissolve 16 g of manganese dioxide in 50 ml of concentrated hydrochloric acid (HCl) (12.1N).

NOTE: Heating may be necessary to dissolve.

2. Dilute to 1 liter with (1-3) hydrochloric acid solution (HCl), and shake for 1 or 2 min.

3. Pipet accurately four 5.0-ml portions of the carrier solution into four separate 50-ml centrifuge tubes.

4. Add 10 ml concentrated nitric acid (HNO_3) (15.7N) to each centrifuge tube.

5. Add 2 ml saturated sodium bromate ($NaBrO_3$) solution, and boil for 3 min by placing the centrifuge tubes into a beaker half-filled with water; then, place on a hot plate.

6. Filter with suction the precipitate onto a weighed glass fiber filter placed in the filter holder.

7. Rinse the centrifuge tube with ethyl alcohol, and pour the rinsings through the filter.

8. Wash the precipitate with approximately 10 ml ethyl alcohol and 10 ml of diethyl ether.

9. Place the filter containing the precipitate in an oven, and dry at 110 C for 10 to 20 min. Cool in a desiccator for 10 to 20 min.

10. Weigh the filter and precipitate on an analytical balance to the nearest 0.1 mg.

11. Subtract the tare weight of the filter to obtain the weight of the precipitate.

12. Four standardizations of the carrier solution should be performed. The spread in results should be less than 0.5 percent.

2.15.2 Calculations

$$Mn(mg/ml) = \frac{(mg(ppt)\ MnO_2)\ (0.6319)}{ml\ (aliquot)}$$

2.16 NICKEL CARRIER (10 mg/ml) (Available from Fisher, Cat. No. So-N-69)

2.16.1 Procedure

1. Dissolve 1.00 g (pure) nickel metal powder in 25 ml concentrated nitric acid,

2. Dilute to 100 ml with water, and shake for 1 or 2 min.

NOTE: If the nickel metal is weighed on an analytical balance to the nearest 0.1 mg, standardization will not be necessary.

2.17 POTASSIUM CARRIER (10 mg/ml) (Available from Fisher, Cat. No. So-P-350)

2.17.1 Procedure

1. Dry approximately 19 g of primary standard potassium chloride (KCl) salt at 110 C for 1 hr.

2. Store the dried salt in a glass-stoppered weighing bottle inside a desiccator.

3. Weigh the dried salt on an analytical balance to the nearest 0.1 mg.

4. Transfer the weighed salt to a 1-liter volumetric flask, and fill with water to the calibrated line.

5. Mix thoroughly for 5 or 10 min.

2.17.2 Calculations

Calculate the concentration as follows:

$$K(mg/ml) = \frac{(mg\ KCl)\ (0.5244)}{(1000\ ml)}$$

2.18 RUBIDIUM CARRIER (10 mg/ml)

2.18.1 Procedure

1. Dissolve 14.2 g of rubidium chloride (RbCl) in 500 ml of water.

2. Filter off any undissolved material, and dilute the filtrate to 1 liter.

3. Pipet accurately four 5.0-ml portions of the carrier solution into four separate 50-ml centrifuge tubes.

4. Adjust the volume to 10 ml with 6N hydrochloric acid (HCl).

5. Add 4 ml of chloroplatinic acid.

6. Stir for 1 or 2 min, and let stand for 10 min at 20 C.

7. Filter with suction the precipitate onto a weighed glass fiber filter placed in the filter holder.

8. Wash the precipitate three times with 5.0-ml portions of 6N hydrochloric acid (HCl).

9. Wash the precipitate with approximately 5 ml ethyl alcohol and 5 ml of diethyl ether.

10. Place the filter containing the precipitate in an oven, and dry at 110 C for 20 min. Cool in a desiccator for 20 min.

11. Weigh the filter and precipitate on an analytical balance to the nearest 0.1 mg.

12. Subtract the tare weight of the filter to obtain the weight of the precipitate.

13. Repeat steps 10, 11, and 12 until constant weight is obtained.

14. Four standardizations of the carrier solution should be performed. The spread in results should be less than 0.5 percent.

2.18.2 Calculations

$$Rb(mg/ml) = \frac{(mg(ppt)\ Rb_2PtCl_6)\ (0.2903)}{ml\ (aliquot)}$$

2.19 SODIUM CARRIER (10 mg/ml) (Available from Fisher, Cat. No. So-S-140)

2.19.1 Procedure

1. Dissolve 2.5420 g of sodium chloride (NaCl) in water.

NOTE: Sodium chloride crystals should be dried in an oven at 110 C for 1 hr prior to being used. Cool in a desiccator before weighing on an analytical balance.

2. Dilute to 100 ml with water, and shake for 1 or 2 min.

NOTE: This carrier need not be standardized if weighed accurately.

2.20 STRONTIUM CARRIER (10 mg/ml) (Available from Fisher, Cat. No. So-S-458)

2.20.1 Procedure

1. Dissolve 32.4 g of strontium nitrate ($Sr(NO_3)_2 \cdot 4H_2O$) in water.

2. Dilute to 1 liter with water, and shake for 1 or 2 min.

3. Pipet accurately four 5.0-ml portions of the carrier solution into four tared porcelain crucibles.

4. Add 500 (0.5 ml) of 1.5N sulfuric acid (H_2SO_4) solution.

5. With caution, carefully stir the mixture with a thin glass stirring rod.

6. While collecting the washings in the crucible, wash the stirring rod with a minimum quantity of water.

7. Evaporate to dryness under an infra-red heat lamp.

8. Ignite the crucibles in a muffle furnace at 500 C for 15 min.

9. Cool and weigh the crucibles and precipitates to the nearest 0.1 mg on an analytical balance.

10. Place the crucible containing the precipitate in an oven, and dry at 110 C for 20 min.

11. Cool for 20 min in a desiccator, and reweigh.

12. Repeat steps 10 and 11 until constant weight is obtained.

13. Four standardizations of the carrier solution should be performed. The spread in results should be less than 0.5 percent.

2.20.2 Calculations

$$Sr(mg/ml) = \frac{(mg(ppt)SrSo_4)\ (0.4525)}{ml\ (aliquot)}$$

2.21 TUNGSTEN CARRIER (10 mg/ml)

2.21.1 Procedure

1. Dissolve 1.8 g sodium tungstate ($Na_2WO_4 \cdot 2H_2O$) in water.

2. Dilute to 1 liter with water, and shake for 1 or 2 min.

3. Pipet accurately four 5.0-ml portions of the carrier solution into four separate 50-ml centrifuge tubes.

4. Add 10 ml concentrated nitric acid; place in a beaker half-filled with water, and heat on a hot plate. Boil for 10 min.

5. Filter with suction the precipitate onto an ashless filter paper.

6. Place the filter paper in a tared 40-ml porcelain crucible, and dry under a heat lamp.

7. Cover and ignite for 10 min in a muffle furnace at 800 C.

8. Remove the cover, and continue the ignition for 30 min.

9. Cool and weigh the crucible and precipitate (WO_3) on an analytical balance to the nearest 0.1 mg.

10. Place the crucible containing the precipitate in an oven, and dry at 110 C for 20 min.

11. Cool for 10 to 15 min in a desiccator, and reweigh.

12. Repeat steps 10 and 11 until constant weight is obtained.

13. Four standardizations of the carrier solution should be performed. The spread in results should be less than 0.5 percent.

2.21.2 Calculations

$$W(mg/ml) = \frac{(mg(ppt)WO_3)\ (0.7930)}{ml\ (aliquot)}$$

2.22 YTTRIUM CARRIER (10 mg/ml)

2.22.1 Procedure

1. Dissolve 43 g of yttrium nitrate ($Y(NO_3)_3 \cdot 6H_2O$) in 500 ml of water.

2. Add 5 ml of 6N nitric acid (HNO_3).

3. Dilute to 1 liter, and shake for 1 or 2 min.

4. Pipet accurately four 5.0-ml portions of the carrier solution into four separate 50-ml centrifuge tubes.

5. Add 10 ml of water, and heat to boiling.

6. While stirring, add 20 ml of saturated ammonium oxalate ($(NH_4)_2\ C_2O_4$).

7. Heat for 10 min in a hot-water bath, and then cool in an ice bath for 10 min.

8. Centrifuge the yttrium oxalate ($Y_2(C_2O_4)_3$), and decant the supernate.

9. Slurry the precipitate in 10 ml of water, and filter through a Whatman No. 40 filter paper.

10. Wash the precipitate with three 10-ml portions of water.

11. Transfer the precipitate to a tared porcelain crucible, and dry under a heat lamp.

12. Cover and ignite for 10 min in a muffle furnace at 800 C.

13. Remove the cover, and continue the ignition for 1 hr.

14. Cool and weigh the crucible and precipitate (Y_2O_3) on an analytical balance to the nearest 0.1 mg.

15. Place the crucible containing the precipitate in an oven, and dry at 110 C for 20 min.

16. Cool for 20 min in a desiccator, and reweigh.

17. Repeat steps 15 and 16 until constant weight is obtained.

18. Four standardizations of the carrier solution should be performed. The spread in results should be less than 0.5 percent.

2.22.2 Calculations

$$Y(mg/ml) = \frac{(mg(ppt)\ Y_2O_3)\ (0.7875)}{ml\ (aliquot)}$$

2.23 ZIRCONIUM CARRIER (10 mg/ml)

2.23.1 Procedure

1. Dissolve 41.135 g of zirconyl nitrate ($ZrO(NO_3)_2 \cdot 8H_2O$) in approximately 300 ml of water. Add sufficient nitric acid (HNO_3) to make the solution 4N in HNO_3 (approximately 100 ml of 16N HNO_3).

2. Filter and make the filtrate up to a volume of 1 liter using 4N HNO_3. Shake to mix thoroughly.

3. Pipet accurately four 5.0-ml portions of the carrier solution into 125-ml beakers.

4. Adjust each beaker to approximately 20 ml, using concentrated HCl.

5. Add 50 ml of 16-percent mandelic acid solution to each beaker, and dilute them to 100 ml with reagent water.

6. Heat solutions slowly to 85 C, and maintain this temperature for 20 min.

7. Filter and wash each sample using a hot solution of 2-percent HCl and 5-percent mandelic acid.

8. Transfer the filters and precipitate to tared porcelain crucibles, and ignite for 1 hr at 700 C.

9. Cool and weigh the crucibles and precipitate (ZrO_2) on an analytical balance to the nearest 0.1 mg.

10. Place the crucibles in an oven, and dry at 110 C for 20 min.

11. Cool for 20 min in a desiccator, and reweigh.

12. Repeat steps 10 and 11 until a constant weight is obtained.

13. Spread in results should be less than 0.5 percent.

2.23.2 Calculations

$$Zr(mg/ml) = \frac{(mg(ppt)ZrO_2)\ (0.7402)}{ml\ (aliquot)}$$

3. COUNTING TECHNIQUES AND DATA HANDLING

This section will provide a working knowledge of how to analyze and report data intelligently. Also, this section will aid in understanding how the methods of statistics may be applied to data obtained from Sec. 5, Radiochemistry Procedures.

3.1 COUNTING ERRORS, USING STANDARD DEVIATION

The standard deviation is the basis of all error calculation in radiation counting.

$$\delta = \sqrt{\frac{(x - \bar{x})^2}{n - 1}}$$

Where:

δ = standard deviation

x = any one count

$\bar{x}$ = average of all counts

n = number of observations

For Example:

Observation	x	$\lvert x - \bar{x} \rvert$	$(x - \bar{x})^2$
1	1069	5	25
2	1128	54	2916
3	1017	57	3249
4	1023	51	2601
5	1082	8	64
6	1090	16	256
7	1030	44	1936
8	1118	44	1936
9	1094	20	400
10	1088	14	196
	$\sum x = 1079$		$\sum (x - \bar{x})^2 = 13579$
	$\bar{x} = 1074$		

Therefore:

$$\delta = \sqrt{\frac{13579}{9}} = \sqrt{1509} = 38.84 \text{ c/min} = 39 \text{ c min}^{-1}.$$

Therefore, the true count rate R and the standard deviation of that count rate R is 1074 c min^{-1} ± the standard deviation of 39 c min^{-1}.

3.2 CONFIDENCE LEVELS

In the example mentioned above, if we say that the true count rate R = 1074 c min^{-1} ± 39 c min^{-1}, we have assigned an error of 1 standard deviation. Statistical principles show that the distribution of errors for a random process such as radioactive decay follows a bell-shaped distribution curve. If we assign an error of 1 standard deviation to the observed count rate, the true count rate will on the average lie within the quoted error limits for 68 percent of the time. If we assign an error of 1.96 standard deviations, the true count rate will lie within the stated error limits for 95 percent of the time. It should be pointed out that, as long as you understand the probabilities connected with the error you quote, you may use any number of standard deviations you wish.

The relationship between the number of standard deviations and the probability that the true number lies within the error limits quoted is summarized as follows:

Name of confidence	Probability that the true number lies within the quoted error limits	Number of standard deviations used (σ)
Standard devia.	0.67	1
95%	0.95	2

It is considered good practice in radiation counting to use the two sigma error (95 percent confidence level). If you use the two sigma error consistently, and if the equipment you are using is truly reproducible, you can be confident that the true numbers lie within the quoted error limits 95 percent of the time.

3.3 CHI-SQUARED TEST

When a counter and its electronic components are operating properly, the accuracy in determining the counting rate of a source is limited by the random nature of the disintegration process. If the equipment is not working properly, repeated counts on the same sample will be such that, on the average, counts will be outside the Chi-square limits.

Chi-square is defined as follows:

$$\text{Chi-square} = \frac{\sum (X_i - \bar{X})^2}{\bar{X}}$$

where:

X_i = observed count for each determination

$\bar{X}$ = mean count (average).

The following chart shows the allowed limits of Chi-square for different numbers of determinations.

ALLOWED LIMITS OF CHI-SQUARE BEYOND WHICH IT IS 99 PERCENT CERTAIN THAT STATISTICAL REPRODUCIBILITY IS LACKING

Number of Determinations	Chi-Square Limits
5	0.3 - 13
10	2 - 22
15	4 - 29
20	7 - 36
30	14 - 50

CAUTION: Replicate counts should be made with the same sample and not on supposedly duplicate samples.

Below is an example of Chi-square test where 10 counts were taken:

Determination	X_i	$X_i - \bar{X}$	$(X_i - \bar{X})^2$
1	1069	- 5	25
2	1128	+54	2916
3	1017	-57	3249
4	1023	-51	2601
5	1082	+ 8	64
6	1090	+16	256
7	1030	-44	1936
8	1118	+44	1936
9	1094	+20	400
10	1088	+14	196
	$\sum X_i = 10739$		$\sum (X_i - \bar{X})^2 = 13,579$

$$\bar{X} = \frac{10739}{10} = 1074$$

$$\text{Chi-square} = \frac{\sum (X_i - \bar{X})^2}{\bar{X}} = \frac{13,579}{1074} = 12.6 \text{ for 10 determinations.}$$

For 10 determinations, the Chi-square limits are 2-22, since the above example indicated 12.6 for 10 determinations. Therefore, there is no evidence of any statistical non-reproducibility in the example.

3.4 PLATEAU DETERMINATION

A plateau is determined by increasing the voltage; the count rate will increase rapidly and then approach a constant value. Further voltage increases result in only slight increases in counting rate; therefore, this region is called the plateau. The end of the plateau is indicated by a second rapid counting rate increase as the region of continuous discharge is reached.

3.4.1 Procedure

Place a Cs-137 or Pu-239 DEF source in the proportional counter, and adjust the high voltage to the point where the counting begins. This is called the standard voltage. Obtain 1-min counts at 50-v increments. See Fig. 3.1 for an example type plateau curve for a flow-type proportional counter.

CAUTION: Do not increase the voltage above the second (Beta plateau on Fig. 3.1) increase in count rate.

3.5 COUNTING EFFICIENCY

In order to relate count rates to a disintegration rate, all measurements should be converted to a common base. This base is the absolute disintegration rate of standard calibrated sources. The ratio of the count rate obtained to the disintegration rate of the source is known as the counting efficiency.

3.5.1 Proportional Counters

Place the beta or alpha standard in the sample drawer, and count for 10 min or longer until at least 10,000 counts have been accumulated.

NOTE: For the beta standard, set the voltage on the beta plateau; and for the alpha standard, set the voltage on the alpha plateau. See Sec. 3.4 on plateau determination for further information.

Divide the net counts by the time counted.

NOTE: Net counts means total counts minus the background counts.

Then divide the counts per minute by the disintegration rate of the standard.

NOTE: The disintegration rate of the standard should be corrected for decay since standardization.

3.5.1.1 Example. As an example, a carbon-14 standard with a disintegration rate of 1.1×10^4 disintegration per minute gives 16,870 counts in 10 min. The counter background is 12 counts per minute.

$$\text{Net counts per minute} = \left(\frac{16,870}{10}\right) - (12)$$

$$\text{Net cpm} = 1675$$

Therefore, the counting efficiency is: $\text{eff.} = \frac{1675}{1.1 \times 10^4} = \underline{0.152}$

3.5.2 Gamma-Ray Counting

Gamma rays are measured by a scintillation counter. Gamma rays from a test sample enter a detector crystal (e.g., Na I (Tl) Sodium iodide crystal), transferring all or portions of its energy to it. The crystal then emits light flashes, the number of which is proportional to the energy the crystal received from the sample emitting gamma rays. By the use of suitable light-sensitive devices and electronic apparatus, a pulse is obtained which is related to the disintegration rates of the radionuclides in the sample.

There are two ways to identify an unknown radionuclide by gamma-ray counting type technique. The first method is repeated counting over a period of time, and plotting a decay curve on semilog paper of the count rate vs. time, which will determine the half life of the radionuclide. The second method to identify the unknown is to examine the gamma-ray energy of the radionuclide.

It is desirable to calibrate the multi-channel analyzer so that there is a convenient factor which will convert channel number to Mev (Million electron volts) or Kev (Kilo electron volts).

To determine the counter efficiency over a range of energies, it is necessary to follow the procedure as outlined below:

1. Place the following gamma-ray standards, one at a time, at various distances; and count for a few minutes until at least 10^4 counts have been accumulated.

Nuclide	Energy of Gamma-Ray (Mev)
Hg-203	0.279
Bi-207	0.569
Cs-137	0.661
Y-88	0.898
Bi-207	1.064
Co-60	1.17
Na-22	1.27
Co-60	1.33
Na-24	1.37
Y-88	1.84
Bi-208	2.61
Na-24	2.76

2. Divide the net counts by the time counted.

NOTE: Net counts means total counts minus the background counts.

3. To determine the efficiency factor, divide the counts per minute of the standard by the disintegration rate of the standard.

NOTE: The disintegration rate of the standard should be corrected for decay since standardization.

3.5.2.1 Example. As an example, a cesium-137 standard with a disintegration rate of 2.0×10^4 disintegration per minute gives 14,800 counts in 10 min. The counter background is 22 counts per minute.

The area under the 0.661 photopeak is determined by summing individual channel data over the entire photopeak region (0.661 Mev Cs-137).

Therefore, the counting efficiency for Cs-137 0.661 Mev is:

$$\text{Net counts per minute} = \frac{14,800}{10} - (22)$$

$$\text{Net cpm} = 1458$$

$$\text{Counter Eff.} = \frac{1458}{2.0 \times 10^4} = 7.29 \times 10^{-2}$$

3.6 DATA REPORT

All sampling, separation and counting data should be reported on LACBWR Form-41 or -55. All of the columns may not be needed for every analysis. The one that is needed should be filled in.

3.7 DETERMINATION OF HALF-LIFE ($t_{1/2}$)

The time interval required for a radioisotope to decay to half its original activity is called the half life. It may be calculated from:

$$t_{1/2} = \frac{0.693}{\lambda}$$

where:

λ = decay constant for the specific radioisotope.

Therefore to determine the half life, count the sample at 1-min intervals. If there does not appear to be a significant difference between successive determinations, count every 10 min. If after three or more 10-min counts no significant difference has been observed, use longer periods of time until there is about 5 to 10 percent decrease in activity between successive counts. Using semi-log paper, plot the net count rate (background has been subtracted) on the logarithmic ordinate and the time on the linear abscissa. If a single radionuclide is present, a straight line will be observed, as shown in Fig. 3.2. If two radionuclides are present, a straight line will not be observed but a curve with two components as shown in Fig. 3.3 will be observed. If there are more than two radionuclides, this method will not be too accurate, necessitating a radiochemical separation to determine accurately the radionuclides present. Once the half-life is determined, a tentative identification of the nuclide on a single and a two-component unknown sample may be made using the General Electric chart of the nuclides or a similar type chart. More positive identification can be made from the beta and gamma energies as determined by a Feather analysis, radiochemical separation and a gamma spectrum.

3.8 RADIOACTIVE DECAY CORRECTIONS

To correct to the initial activity A_o, the procedure should be followed:

Divide the elapsed time between counting and sampling by the half-life of the radionuclide which has been determined by using the method mentioned in Sec. 2. Using Fig. 3.4 and knowing the number of $t_{1/2}$ (half-life) that the sample has decayed, the value (A/A_o) fraction of activity remaining can be read off the logarithmic ordinate of Fig. 3.4.

Divide the activity by the A/A_o value to obtain the initial activity.

To more clearly explain this, a typical problem is performed below:

A sample was taken from the reactor system on January 1 (0600 hr), and the separated sample was counted for I-131 (1000 c min^{-1}) on January 7 (0600 hr).

The half-life of I-131 - 8.05 days time from sampling to counting time - 6 days.

Therefore divide:

$$\frac{t}{t_{1/2}} = \frac{6 \text{ days}}{8.05 \text{ days}} = 0.746$$

Using Fig. 3.4, read on the abscissa 0.746 and find A/A_o on the logarithmic ordinate (see Fig. 3.4 for illustration).

$$A/A_o = 0.59$$

The activity at sampling time is:

$$\frac{1000 \text{ c min}^{-1}}{0.59} = \underline{1695 \text{ min}^{-1}}$$

Using a slide rule, the sample problem above can be solved by multiplying λ times t and reading the LL02 scale for the $e^{-\lambda t}$ value. For example:

Where $A = A_o e^{-\lambda t}$

$1000 \text{ cpm} = A_o e^{-(0.0862)(6.0 \text{ days})}$

$$\lambda = \frac{0.693}{8.05 \text{ days}} \qquad \lambda = 0.0862$$

Therefore, using a slide rule, place 1 on the C scale over the D scale 862 and then, moving the hairline to 6 on the C scale, read the LL02 scale. The reading should be 0.596.

3.9 FEATHER ANALYSIS

This type analysis identifies the beta energy or energies of an unknown radioactive sample. To identify the unknown sample by its beta energies, the following procedure should be

followed. Place the sample in the proportional flow counter or under the G-M counter and count for 10 min with no absorber and with aluminum absorbers of approximately 5 to 3500 mg/cm^2 thicknesses. (Background should be subtracted for each measurement.)

CAUTION: To carry out these measurements, the aluminum absorbers are to be placed as near to the counting tube as possible to minimize scattering effects.

Calculate the total absorber for each measurement by adding to the aluminum absorber the thickness in mg/cm^2 of the counting tube window and the air between the sample and the counting tube.

NOTE: This is equal to the distance in cm times the density of air in mg/cm^2 at the ambient temperature, pressure and humidity. (This information can be found in the Handbook of Chemistry and Physics for these densities. Normally this correction is made when extreme accuracy is necessary.)

Using semi-log paper, plot the count rate on the logarithmic ordinate vs. the absorber on the linear abscissa as shown on Fig. 3.5, and the maximum range is taken as the absorber thickness at which the curve flattens out to the constant background.

See Fig. 3.6 for the beta particle range energy curve.

LACBWR 41

ANALYZER

DATA

SHEET

SAMPLE _____ GAIN _____ CONTAINER _____

DATE _____ ZERO _____ SOURCE DIST. _____

TIME _____ KEV/CHANNEL _____ ABSORBER _____

VOLTAGE _____ LIVE MINUTES _____ EFFICIENCY _____

CALIBRATION _____ MEV PEAK IN CHANNEL _____ AT _____ HOURS

BACKGROUND: (CORRECTED , NOT CORRECTED)

0 8 16 24 32 40 48 56 64 72 80 88 96 104 112 120 128 136 144 152 160 168 176 184 192 200 208 216 224 232 240 248 256

L-55

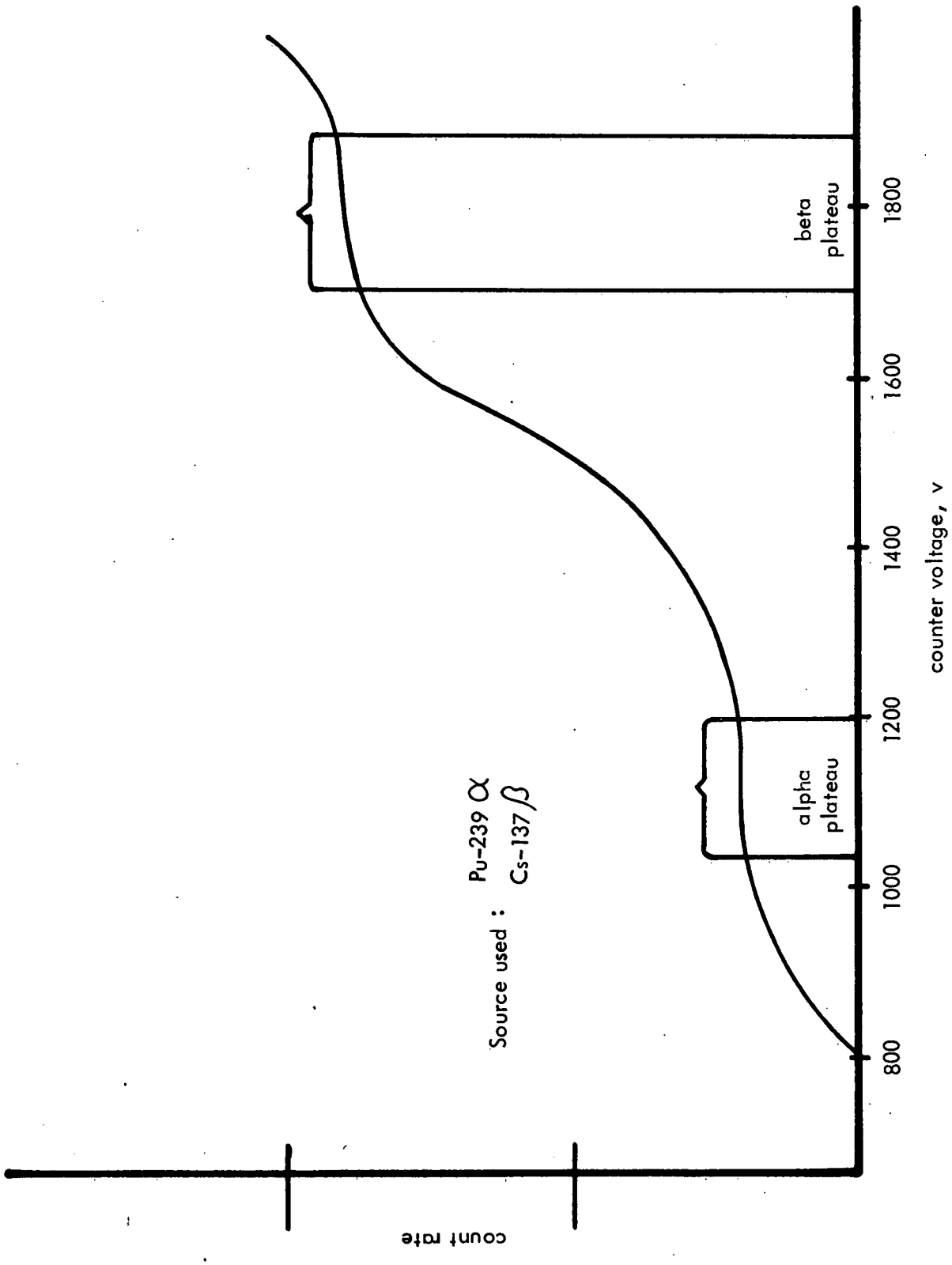
SAMPLE NUMBER	LOCATION-SAMPLE POINT	ANALYSIS-REQUESTED

SAMPLING: DATE _____ TIME _____ TEMPERATURE OF SAMPLE _____ APPEARANCE OF SAMPLE _____
ACTIVITY AT CONTACT _____ SAMPLE LOCATION FLOWRATE _____ SAMPLE LOCATION TEMP. _____
SIGNATURE OF SAMPLER _____

SEPARATION-DATA: DATE _____ TIME _____ WT. OF FILTER & SAMPLE _____ WT. OF FILTER _____
SAMPLE WT. _____ CARRIER ADDED _____ G.F. _____ CHEMICAL YIELD _____
ALIQUOT _____ TOTAL VOLUME _____ SEPARATION PERFORMED BY _____

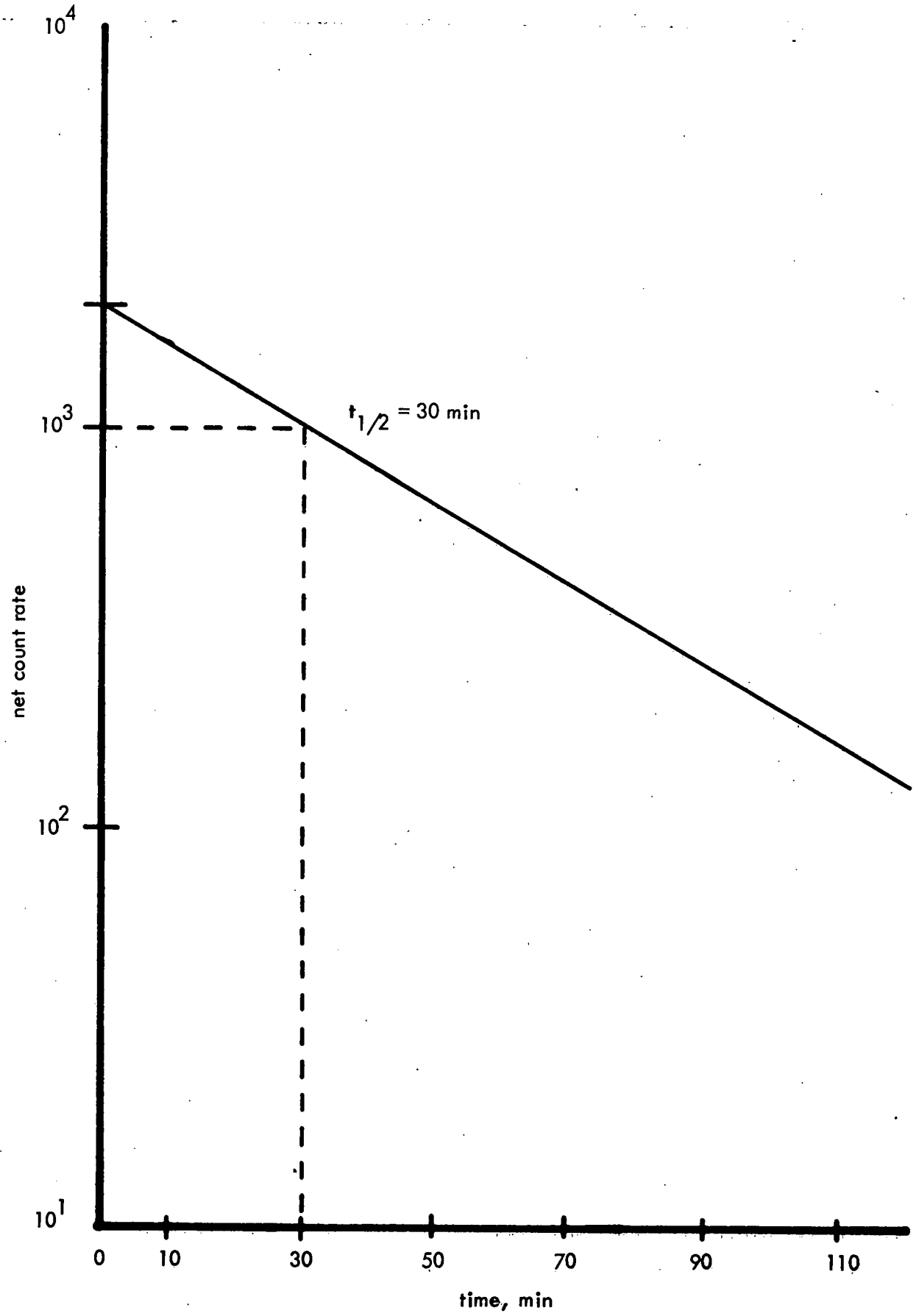
COUNTING - DATA: INSTRUMENT _____ COUNTING PERFORMED BY _____

ISOTOPE	DATE	TIME	COUNTING TIME	COUNTS	CPM	BKG. CPM	NET CPM	EFF.	GAMMA ABUND.	DECAY FACTOR	DPM	CONC. (μCi/ml)



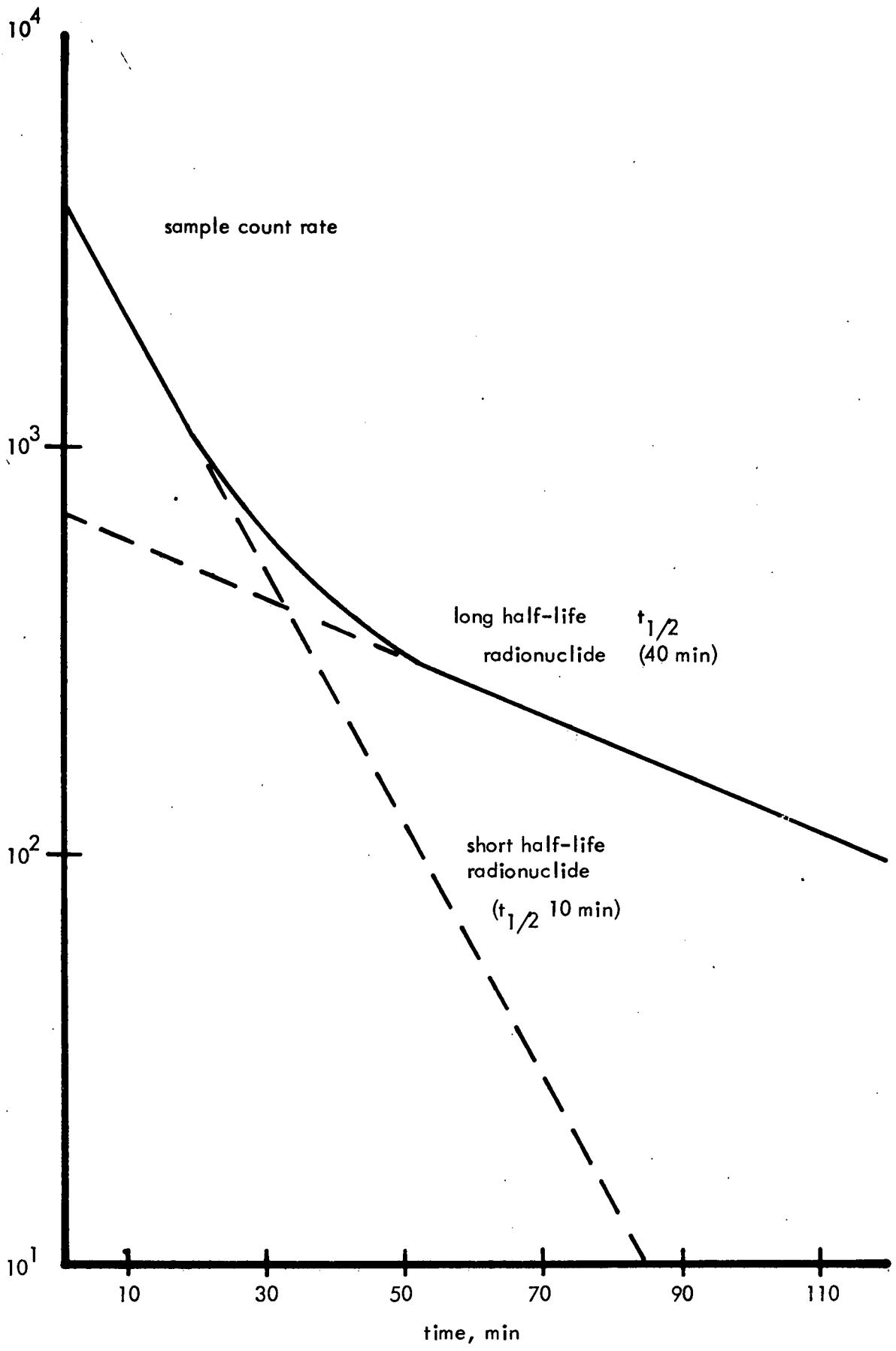
COUNTING RATE VS. COUNTER VOLTAGE FOR A FLOW-TYPE PROPORTIONAL COUNTER

FIG. 3.1



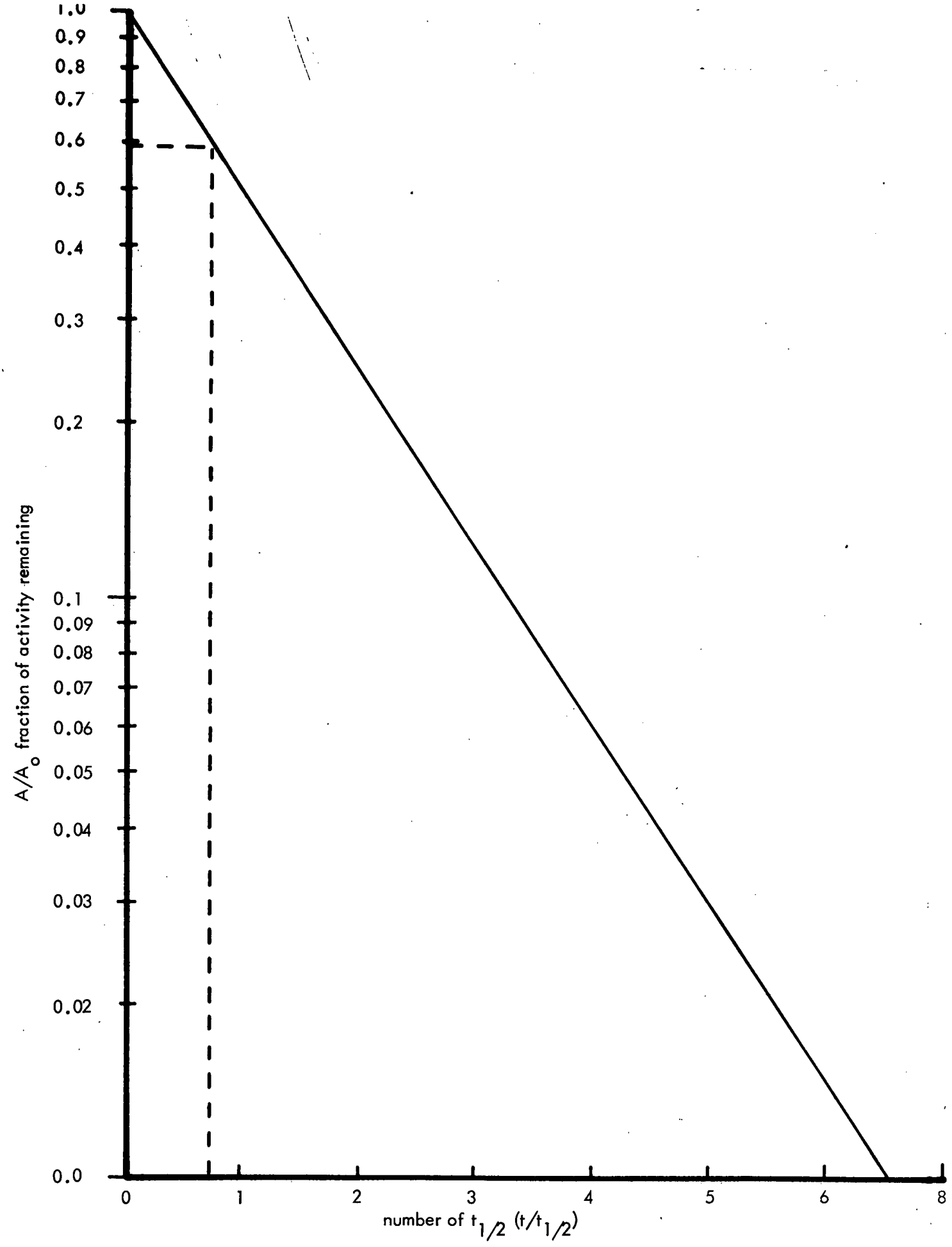
SINGLE RADIONUCLIDE DECAY

FIG. 3.2



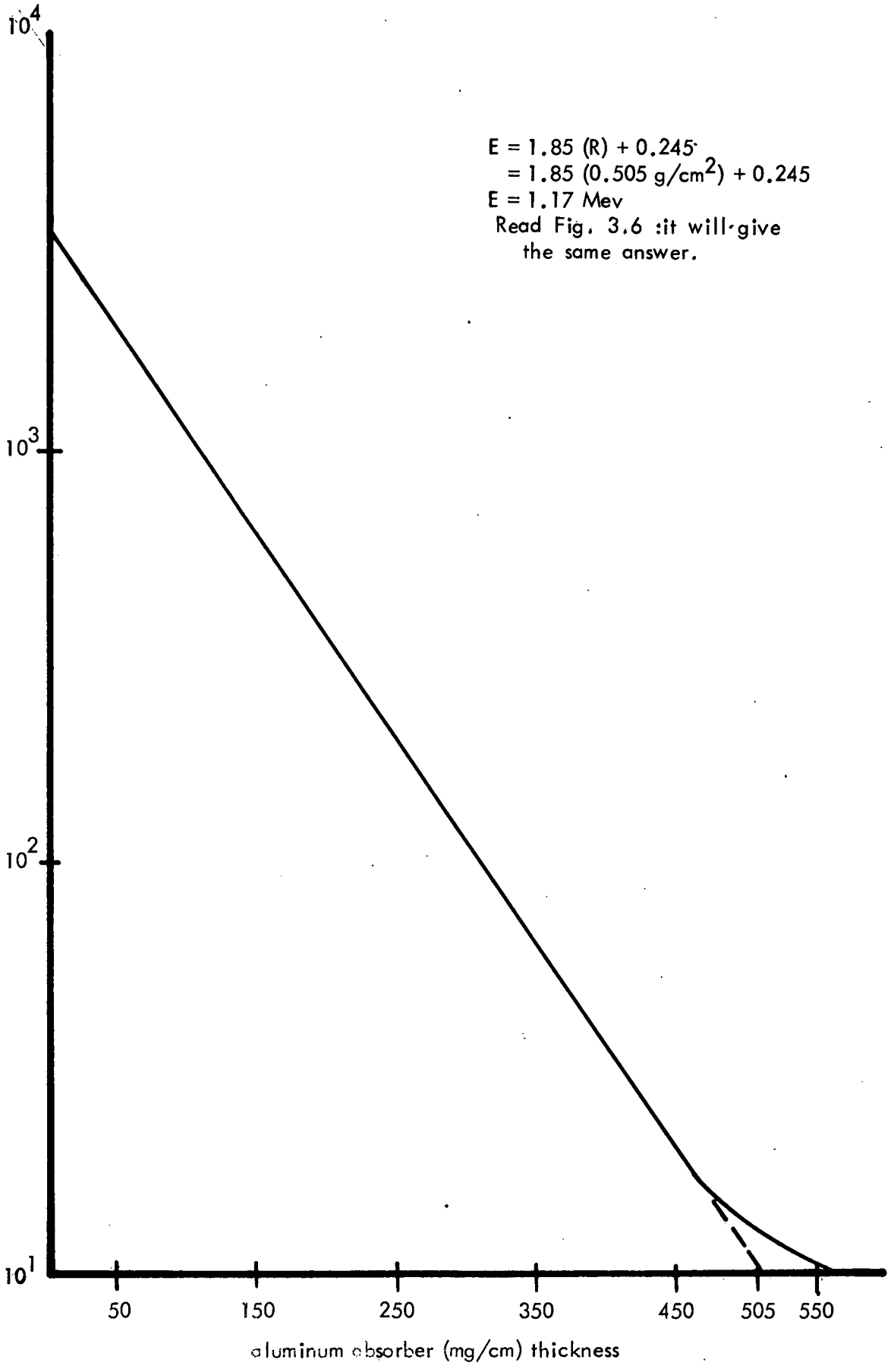
SAMPLE COUNT RATE

FIG. 3.3



RADIOACTIVE DECAY CORRECTION

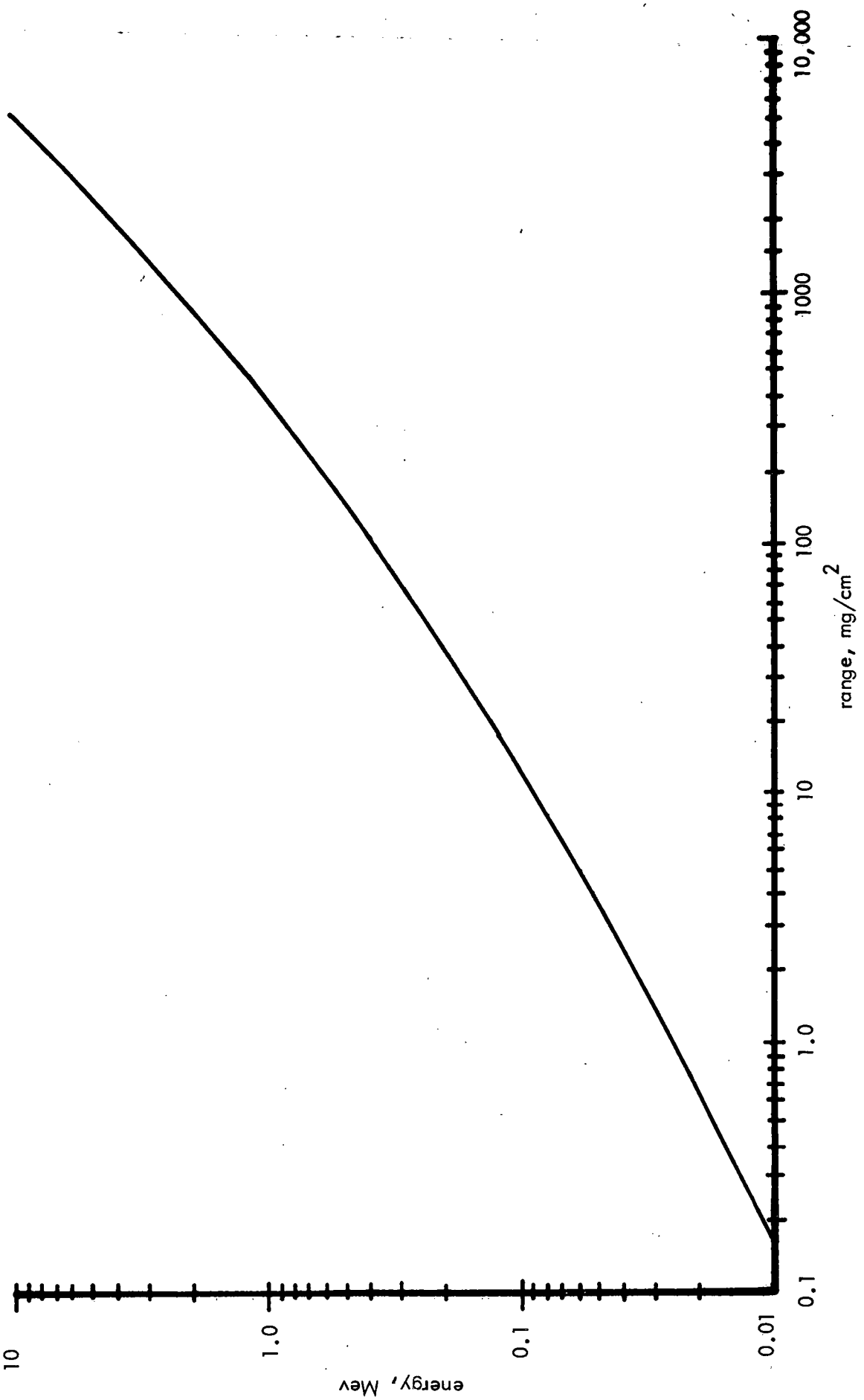
FIG. 3.4



$E = 1.85 (R) + 0.245$
$= 1.85 (0.505 \text{ g/cm}^2) + 0.245$
$E = 1.17$ Mev
Read Fig. 3.6 :it will give the same answer.

TYPICAL TYPE OF β-RAY ABSORPTION CURVE

FIG. 3.5



BETA PARTICLE RANGE ENERGY CURVE

FIG. 3.6

4. WATER CHEMISTRY METHODS

Section 4 is a collection of water chemistry procedures for determining constituents in reactor steam and water. The methods specified for these analyses were chosen on the basis of accuracy and simplicity. They have been taken from ASTM and from other various established methods used throughout the industry.

4.1 APPARATUS FOR WATER CHEMISTRY PROCEDURES

1. Beckman Zero-Matic pH meter and necessary electrodes.

2. Conductivity Bridge Model RC-16B2 with Dip Cell No. Cel-A-002.

3. Spectrophotometer-Beckman Model DU with 1 cm, 5 cm, 10 cm cells and Bausch and Lomb Spectronic 20 with 1 cm cells.

4. Millipore type HA filter 47 mm.

5. One-liter stainless steel filter holder.

6. A desiccator similar to Fisher Model No. 8-650.

7. A gravity convection type oven able to supply uniform heat at 110 C ± 0.5.

8. An analytical balance capable of weighing to the nearest 0.1 mg.

9. Two-inch diameter stainless steel planchets.

10. Oxygen Comparator III 0, 5, 10, 15, 20, 30 ppb.

11. Oxygen Comparator IV 10, 25, 50, 75, 150, 300 ppb.

12. Burrell gas analysis equipment.

13. Magnetic stirrer.

14. Hot plates.

15. Hydrometer Set 0.700 - 2.000 sp. gr.

16. Muffle Furnace designed for continuous operation at 1000 C.

17. Platinum crucible and cover.

18. Normal laboratory equipment and glassware.

19. Centrifuge.

20. Triple beam balance.

21. Heat lamps.

22. Vacuum pump.

23. Dissolved oxygen analyzer.

4.2 REAGENTS AND MATERIALS

4.2.1 Purity of Reagents

Reagent grade chemicals shall be used unless otherwise indicated; all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society. Other reagents may be used, provided they are of sufficient purity to give the same accuracy.

4.2.2 Purity of Water

The water used in making reagents and dilutions shall be plant demineralized water which has been distilled and run through the mixed bed demineralizer cartridge.

4.3 pH DETERMINATION (METHOD WC-1)

4.3.1 Summary of Method

The hydrogen ion concentration is indicated by a pH measurement which may be made with electrical instruments.

4.3.2 Reagents and Materials

A standard set of buffer solution pH-1-14 at 25 C is used.

4.3.3 Procedure

1. Slide rubber sleeve down to expose vent hole on the reference electrode. Rinse the electrodes with demineralized water and wipe dry.

NOTE: Instrument should have a warmup period of 15-30 min.

2. Standardize pH meter using standard buffer solutions whose pH value is close to that expected in the sample.

3. Immerse the electrodes in one buffer solution; depress READ button, and adjust the ASYMMETRY CONTROL to set the meter needle to exactly read the pH of the rating stated for the buffer solution.

4. Depress STANDBY button; remove electrodes; wash electrodes with demineralized water and wipe dry.

5. Repeat steps 2, 3, and 4 using a different buffer pH range.

6. Insert electrodes into sample, and let stand for a few minutes; depress READ button, and read pH on meter.

NOTE: Sample should be approximately at room temperature.

7. Cover vent hole upon completion of test.

4.3.4 Precautions

1. Leave the instrument connected to the power line except when it is not to be used for extended periods.

2. Depress STANDBY button when the instrument is not in use and whenever removing the electrodes.

3. It is essential to standardize the instrument at least daily with the buffer solution.

4. A new glass electrode should be soaked in water for several hours before use. If stored in water, it is ready for immediate use. Be certain the Calomel reference electrode is filled with saturated KCl solution and contains KCl crystals. The electrode may be temporarily stored in demineralized water. For long periods of storage, store in saturated KCl solution.

4.4 CONDUCTIVITY DETERMINATION (METHOD WC-2)

4.4.1 Summary of Method

A dip cell is immersed in the sample water, and the conductivity is read directly from a bridge type instrument.

4.4.2 Procedure

1. Connect the dip cell leads to the Nos. 1 and 2 terminals on top of the conductivity bridge.

2. Plug line core into 120-v outlet.

3. Transfer solution to be tested into a 250-ml Erlenmeyer flask.

4. Remove dip cell from storage flask, and place it in solution to be tested. Agitate to remove all air bubbles trapped in the cell casing. Immerse the cell at least 1/2 in. below the air vents.

NOTE: The cell is normally stored in a 250-ml Erlenmeyer flask of demineralized water.

5. Turn the switch to the on position, and allow about 1 min for warmup.

6. Measure the temperature of the solution with a thermometer. To correct the conductivity to 25 C (reference point temperature), apply the following formula:

$$\text{Cond.}_{25} = \frac{1}{R_t\,(1 + 0.025\,\Delta_t)}$$

Cond._{25} = Conductivity measured at 25 C.

R_t = Specific resistance at higher or lower temperature.

Δ_t = Difference in temperature between 25 C and the temperature of test solution when measured, taken as positive when temperature is above 25 C and taken as negative when the temperature is below 25 C.

7. Rotate dial control and multiplier range knob until the black segment of the electron ray tube reaches its widest opening. The bridge is now at balance. The conductance - resistance scale is read, and the reading is multiplied by the cell constant of the dip cell being used (currently 0.02). This reading in turn is multiplied by the multiplier range reading to determine the conductivity or resistance needed in step 6 above.

NOTE: Bridge current of either line frequency (50-60 cps) or 1000 cps can be selected by means of a toggle switch in upper left hand corner of the instrument panel.

4.4.3 Calculations

Direct reading from the instrument. See step 6 and step 7 of Sec. 4.4.2 for determining the conductivity of the sample.

4.5 CHLORIDE DETERMINATION (METHOD WC-3)

4.5.1 Summary of Method

The chloride ion reacts with the mercuric thiocyanate to produce thiocyanate ion to form red ferric thiocyanate. The intensity of the color, which is proportional to the concentration of the chloride ion, is measured photometrically at a wave length of 463 mμ using a 10-cm cell. This method is good in the range of 0.02 to 10 ppm chloride ion.

4.5.2 Reagents and Materials

1. Ferric Alum Solution. Dissolve 5.0 g of ferrous ammonium sulfate $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2$ in 20 ml of water. Add 38 ml of concentrated nitric acid, and boil to oxidize the iron and remove the oxides of nitrogen. Dilute to 100 ml with halide-free water.

2. Mercuric Thiocyanate, Methanol Solution (3 g per liter). Dissolve 0.30 g of mercuric thiocyanate in 100 ml of methanol. Store in amber bottles. Allow to stand for at least 24 hr before using.

CAUTION: Do not use if more than four weeks old.

3. Sodium Chloride Standard Solution (10 mg Cl per liter). Dry sodium chloride (NaCl) to constant weight at 105 C. Prepare a stock solution by dissolving exactly 1.649 g of the dry NaCl in water, and dilute to 1 liter. Prepare the standard solution as needed by diluting 10 ml of the stock to water with chloride free water. The resulting standard contains 10 mg of chloride ion per liter.

4. 15.7N Nitric Acid. Concentrated nitric acid (HNO_3).

4.5.3 Procedure

CAUTION: Soak all new glassware in hot (1-20) nitric acid (HNO_3) for several hours. To be certain that new glassware is conditioned for the test, run a chloride determination on halide-free water. After the run, rinse the glassware thoroughly. Soak the glassware in halide-free water between tests. Discard all glassware that appears etched or scratched.

1. Prepare series of reference standards by diluting suitable volumes of the standard chloride solution with halide-free water. The series should cover the range from 0.02 ppm to 10 ppm.

NOTE: The temperature of the solutions used for calibration must be the same as that of the sample tested.

2. Transfer 25 ml of sample to a glass-stoppered volumetric flask or bottle.

3. To each of the calibration standards and samples, add 5 ml of ferric solution and 2.5 ml of mercuric thiocyanate solution.

4. Shake thoroughly for 1 or 2 min, and allow to stand for 10 min.

5. Measure the intensity of the color formed using the DU Spectrophotometer. Resistor should be in Position No. 2.

NOTE: Adjust the zero setting of the spectrophotometer by using 25 ml of halide-free water prepared in accordance with steps 3 and 4 above.

4.5.4 Calculations

Prepare a calibration curve by plotting the readings on the photometer vs. the concentration of chloride. When the scale of the photometer reads directly in absorbance, plot the curve on rectilinear paper. When the scale reads in transmittance, it is convenient to plot the results on semi-log paper, using the single-cycle log axis to plot transmittance and the linear axis to plot concentrations.

4.6 IRON DETERMINATION (METHOD WC-4)

4.6.1 Summary of Method

Iron is determined photometrically as the orange-red complex at about pH 4.0. Measurement is made at 510 mμ on the DU spectrophotometer using a 1-cm cell.

4.6.2 Reagents and Materials

1. 6N Hydrochloric Acid. Measure 498 ml of (12.1N) Hydrochloric Acid, and dilute to 1 liter with water.

2. 4N Hydrochloric Acid. Measure 332 ml of (12.1N) Hydrochloric Acid, and dilute to 1 liter with water.

3. Hydroxylamine Hydrochloride Solution. Dissolve 10 g of hydroxylamine hydrochloride ($NH_2OH \cdot HCl$) in a small quantity of water, and dilute to 100 ml. This solution is stable for several months.

4. Orthophenanthroline (1-10-Phenanthroline) Solution. Dissolve 0.1 g of the orthophenanthroline in 10 ml of ethyl alcohol, and dilute to 100 ml with water. The solution should be discarded if it darkens.

5. Acetate Buffer Solution. Dissolve 50 g of ammonium acetate, $NH_4C_2H_3O_2$ in 50 ml of demineralized water. Add 100 ml of Glacial Acetic acid, and dilute to 500 ml with water.

6. 3N Ammonium Hydroxide. Measure 202 ml of concentrated (14.8N) ammonium hydroxide (NH_4OH), and dilute to 1 liter with water.

7. Standard Iron Solution (1 ml = 0.1000 mg Fe). Weigh 0.1000 g of electrolytic "iron wire for standardizing," and place in a 50-ml beaker. Dissolve in 20 ml of 4N hydrochloric acid (HCL) while heating gently on a hot plate. Transfer to a 1-liter volumetric flask, using water, and dilute to 1 liter with water.

8. 10 ppm Iron Standard Solution. Measure accurately 10 ml of the Standard Iron solution, and dilute to 100 ml with water. (Use volumetric flask for this operation.)

4.6.3 Procedure

1. Pipet 1, 5, 10, and 50 ml aliquots of the C-10 iron standard solution into separate 250-ml Erlenmeyer flasks. Also, prepare a blank with no iron standard added.

NOTE: The iron solution aliquots represents iron concentrations of 0.10, 0.50, 1.0, and 5.0 ppm respectively.

2. To each sample add 1 ml of 6N hydrochloric acid (HCl); boil on a hot plate for 5 min, and cool in a water bath.

3. To each sample add 1 ml of hydroxylamine hydrochloride, and mix by swirling the solution in the Erlenmeyer flasks for approximately 1 min.

4. Add 5 ml orthophenanthroline to each flask, and swirl flask to mix solution.

5. Add 5 ml acetate buffer to each flask.

6. Dropwise, add 3N ammonium hydroxide (NH_4OH) until a pH of 3.5 to 4.0 is reached or until the Congo-red indicator paper turns red.

7. Quantitatively transfer the samples to 100-ml volumetric flasks; dilute to volume mark with water, and shake for 1 or 2 min. Allow to stand for 15 min for full color development.

8. Read the transmittance on the DU Spectrophotometer at 510 mμ, using 1-cm cells.

9. Secure a fresh sample (sample needed to be analyzed for iron content), and pipet a 50-ml aliquot into a 250-ml Erlenmeyer flask.

NOTE: Prepare samples for analysis as follows:

(a) Primary water: none.

(b) Crud: fume aliquot to eliminate all interfering acids.

NOTE: If allowed to bake, black MnO_2 precipitates. Add some demineralized water plus 6N hydrochloric acid (HCl) plus one drop of 30-percent hydrogen peroxide to reduce the manganese. Boil off the peroxide. Manganese concentration should not exceed 2 mg/25 ml final volume.

10. Repeat steps 2, 3, 4, 5, 6, and 7 above.

11. Repeat step 8 and obtain Fe concentration from curve produced in Sec. 4.6.4.

4.6.4 Calculations

1. Plot the readings from step 8 of Sec. 4.6.3 vs. concentration of iron (ppm in 100 ml) on semi-log paper.

NOTE: This plot should be a straight line.

$$\text{Total iron (ppm)} = \text{standard curve reading (ppm)} \cdot \frac{(100\ \text{ml})}{\text{SAMPLE VOLUME (ml)}}$$

4.7 SUSPENDED SOLIDS DETERMINATION (METHOD WC-5)

4.7.1 Summary of Method

The suspended solids are determined by filtering the sample through a Millipore filter.

4.7.2 Procedure

1. Dry a Millipore type HA filter in an oven at 110C ± 5 C for 2 min.

2. Place the filter in a desiccator and cool.

3. Weigh the filter to the nearest 0.10 mg on the analytical balance.

4. Repeat steps 1, 2, and 3 until constant weight is obtained.

5. Place the filter in the 1-liter stainless-steel filter holder.

6. Measure 1000 ml of the sample using a graduated cylinder and then vacuum filter through the filter holder.

CAUTION: The filtrate should be collected in a clean 1000-ml filter flask. Also, save the filtrate for further analysis.

7. Remove the filter and dry in an oven at 110 ± 5 C and repeat steps 2, 3, and 4.

4.7.3 Calculations

$$\text{Suspended Solids (ppm)} = \frac{1000\ (W_2 - W_1)}{V}$$

where:

W_1 = initial weight of filter in mg.

W_2 = final weight of filter plus suspended solids in mg.

V = volume of samples in milliliters.

4.8 DISSOLVED SOLIDS DETERMINATION (METHOD WC-6)

4.8.1 Summary of Method

The dissolved solids are determined by evaporation of a known volume of a filtered sample from procedure WC-5 in a stainless-steel planchet.

4.8.2 Procedure

1. The filtrate collected in step 6 of Sec. 4.7.2 of the WC-5 method is used to determine dissolved solids.

2. Clean a stainless-steel planchet by washing carefully in cleaning solution or a good detergent cleaning compound. Rinse thoroughly with demineralized water and acetone.

3. Dry in oven at 105-110 C for 20 min. Cool in desiccator until dish is at room temperature. Weigh dish to nearest 0.10 mg on the analytical balance.

NOTE: Handle planchet only with tongs to avoid grease from hands.

4. Evaporate a 1000-ml sample to nearly dryness on a low heat in a 1500-ml beaker. A ribbed watch glass should be placed over the planchet to exclude dust during evaporation. Quantitatively transfer to the tared planchet, and evaporate to dryness under a heat lamp.

5. Transfer the planchet to an oven set at 110 C ± 5 C and dry for 20 min. Cool in desiccator.

6. Determine weight of planchet plus residue to the nearest 0.10 mg on the analytical balance.

4.8.3 Calculations

$$\text{Total solids (ppm)} = \frac{1000\ (W_2 - W_1)}{V}$$

where:

W_1 = initial weight of planchet in mg.

W_2 = final weight of planchet in mg.

V = volume of samples in milliliters.

4.9 TOTAL SOLIDS DETERMINATION (METHOD WC-7)

4.9.1 Summary of Method

The total solids are determined by evaporation of a known volume of sample in a stainless-steel planchet.

4.9.2 Procedure

1. Clean a planchet by washing carefully in cleaning solution or a good detergent cleaning compound. Rinse thoroughly with demineralized water.

2. Dry and place in oven at 105-110 C for several hours. Cool in desiccator until planchet is at room temperature. Weigh dish to nearest 0.10 mg on the analytical balance.

NOTE: Handle planchet only with tongs to avoid grease from hands.

3. Pipet a sample into an evaporating dish, and evaporate almost to dryness on a low heat. A ribbed watch glass should be placed over the evaporating dish to exclude

dust during evaporation. Transfer to planchet, and evaporate to dryness under a heat lamp (1 hr).

NOTE: To evaporate large volume samples, an Evaporator Feeder can be used.

4. Transfer the planchet to an oven set at 105-110 C, and continue to heat for 20 min. Cool in desiccator.

5. Determine weight of planchet plus residue to the nearest 0.10 mg on the analytical balance.

4.9.3 Calculations

$$\text{Total solids (ppm)} = \frac{1000\ (W_2 - W_1)}{V}$$

where:

W_1 = initial weight of planchet in mg.

W_2 = final weight of planchet in mg,

V = volume of samples in milliliters.

4.10 DISSOLVED OXYGEN IN WATER (METHOD WC-8A)

4.10.1 Summary of Method

Dissolved oxygen reacts under alkaline conditions with the indigo carmine solution to produce a color change from yellow-green through red to blue and blue-green. The result of each test can be determined by comparison of color developed in the sample with a color comparator.

NOTE: This method is applicable to water containing 0-30 ppb and 0-300 ppb of dissolved oxygen, using two separate comparators.

4.10.2 Reagents and Materials

1. 12.1N Hydrochloric Acid. Concentrated hydrochloric acid (HCl).

2. (1-99) Hydrochloric Acid. Mix 1 volume of concentrated hydrochloric acid with 99 volumes of water.

3. Indigo Carmine Solution. Dissolve 0.18 g of 100-percent indigo carmine and 2.0 g of dextrose (or glucose) in 50 ml of water. Add 750 ml of glycerin, and mix thoroughly.

NOTE: The solution is usable for at least 30 days if stored in a refrigerator.

CAUTION: The stock solution deteriorates rapidly if allowed to stand in a lighted room at ambient temperature in an ordinary reagent bottle.

4. Potassium Hydroxide Solution. Dissolve 530 g of potassium hydroxide (KOH) in water, and dilute to 1 liter with water.

NOTE: Store in refrigerator.

5. Indigo Carmine. Potassium Hydroxide Reagent: mix four parts by volume of indigo carmine solution with one part of potassium hydroxide solution. Mix solution for several minutes.

NOTE: Allow the reagent to stand undisturbed until the initial red color changes to lemon yellow.

CAUTION: Keep in a dark cool place. Prepare a fresh solution daily.

4.10.3 Procedure

1. Mount a buret directly above the BOD bottle neck so that the buret tip dips into the overflowing sample to a depth of about 1/2 in.

2. Fill the buret with indigo carmine-potassium hydroxide reagent to about 1 ml above the zero mark.

3. Drain the buret to the zero mark into the overflowing sample, and allow the sample to flush for 1 min longer.

4. Remove the sample tubing gently so as not to introduce air bubbles, and quickly introduce 0.8 ml of indigo carmine-potassium hydroxide reagent from the buret into the sample if a 60-ml Nessler-type tube is used.

NOTE: If a BOD bottle is used, add 4 ml of the reagent.

5. Raise the buret above the sample vessel; and immediately stopper the vessel firmly with a rinsed glass stopper, being careful to exclude air bubbles.

6. Invert the vessel several times to mix.

NOTE: A color indicative of the dissolved oxygen concentration will develop.

4.10.4 Calculations

1. Place the sample vessel on a white surface, and match its color with the Oxygen Comparator III or IV.

2. Equivalent dissolved oxygen can be read using the values recorded on each comparator.

CAUTION: Colors should be matched as soon as possible after mixing the reagent and sample, since the colors are not stable for more than 30 min and air leakage may cause a change in color.

4.11 DISSOLVED OXYGEN IN WATER (METHOD WC-8B)

4.11.1 Summary of Method

The sample is collected in a 250-ml gas sampling tube. The free iodine liberated in an amount equivalent to the oxygen in the sample is titrated with thiosulfate using starch as an indicator.

NOTE: This method is applicable to water containing more than 0.02 ppm of dissolved oxygen.

4.11.2 Reagents and Materials

1. Manganous Sulfate Solution. Dissolve 364 g of manganous sulfate ($MnSO_4 \cdot H_2O$) in water; filter, and dilute to 1 liter with water.

2. Potassium Iodide (Alkaline Solution). Dissolve 700 g of potassium hydroxide (KOH) in sufficient water to make approximately 700 ml of solution in a 1-liter volumetric flask (cool to room temperature). Dissolve 150 g of iodate-free potassium iodide (KI) in 200 ml of water, and mix with the KOH solution in the volumetric flask. Dilute to 1 liter with water, and shake for 1 or 2 min.

CAUTION: Store solution in a dark, rubber-stoppered bottle.

3. (0.1N) Sodium Thiosulfate Standard Solution. This can be purchased from Fisher as a certified standard, Cat. No. So-S-368. It is standardized against National Bureau of Standards Potassium Dichromate.

4. (3-1) Sulfuric Acid. Pour carefully 750 ml of concentrated sulfuric acid (H_2SO_4) into 250 ml of water in a beaker which is placed in a sink. Cool to room temperature; transfer to a 1-liter volumetric flask, and dilute to 1 liter with water.

5. Starch Indicator. This indicator is available from Fisher, Cat. No. So-S-408.

4.11.3 Procedure

1. Add 2 ml of alkaline potassium iodide solution to the tube extension. Slowly open the stopcocks, and let the reagent flow into the sample tube. Allow no air into the tube. Close the stopcocks, and mix by inverting the tube.

2. Add 2 ml of manganous sulfate solution in the manner described in step 1. Mix thoroughly, and allow the precipitate to settle.

3. Add 2 ml of sulfuric acid solution in the manner described in step 1. Mix until all the precipitate has dissolved.

CAUTION: Steps 1 through 3 should be completed within 15 min after sampling.

4. Drain the sample, which shall be at a temperature not above 70 F, into a clean casserole; and add 10 drops of starch-indicator solution.

5. Titrate with 0.1N $Na_2S_2O_3$ to the disappearance of the blue, starch iodine color, rinsing the tip of the buret in the sample after each addition as the end point approaches.

CAUTION: Titration should be completed within 30 min after sampling.

4.11.4 Calculations

Calculate the dissolved oxygen content of the sample, in parts per million, as follows:

$$\text{Dissolved oxygen, ppm} = \frac{8000\ NS}{V}$$

where:

N = normality of the $Na_2S_2O_3$ solution.

S = ml of $Na_2S_2O_3$ solution required for titration.

V = ml of sample used.

4.12 DISSOLVED OXYGEN DETERMINATION IN WATER (METHOD WC-8C)

To determine dissolved oxygen content in water using Delta Scientific Model 106 Dissolved Oxygen Analyzer, consult the directions provided with the instrument.

4.13 OFF-GAS DETERMINATION (METHOD WC-9)

4.13.1 Summary of Method

In the analysis of a gaseous mixture of absorption and oxidation methods, the components of the mixture are determined by a systematic measurement of changes in gas volume using the Burrell equipment. These volume changes are affected by the successive removal of certain components from the mixture by treatment with absorbing reagents and by subjecting the combustible components to oxidation. Carbon dioxide is absorbed in Disorbent (Potassium Hydroxide). Oxygen is absorbed in Oxsorbent (Chromous Chloride). Hydrogen is oxidized by passing through heated copper oxide. Nitrogen is determined by difference after all other components have been removed.

4.13.2 Burrell Setup Procedure

1. Fill the buret and gas reservoir with aqueous salt solution. Add enough to the leveling bottle so that the buret may be filled completely and still have salt solution remaining in the leveling bottle. Add drop of phenol red for visual aid.

2. Fill the pipettes by opening the pipette to the atmosphere through the manifold. Remove the rubber stopper and gas bags; then, pour the solution into the rear compartment. Close the manifold stopcock; inflate the bag a little, and replace the stopper. The first pipette is for the determination of carbon dioxide and is filled with Disorbent solution. The second pipette is for illuminants and is filled with Lusorbent. The third pipette is for oxygen and is filled with Oxsorbent.

> NOTE: Oxsorbent takes up oxygen very rapidly. It is necessary to first fill the pipette and partially fill the expansion bag with an oxygen-free gas. Direct a stream of the gas upon the Oxsorbent as it is being poured into the pipette, and immediately replace the stopper and expansion bag.

3. Next bring the liquid in each pipette up to within 1/8 in. below the stopcock by opening each pipette in turn to the buret and carefully lowering the leveling bottle.

4. To test the apparatus for leaks, lower the buret leveling bottle; draw in about 100 ml of air, and open the buret to the manifold. Turn the end stopcock on the manifold to seal, and raise the leveling bulb to the top of the support rod. A leak in any stopcock or rubber connection is indicated by the liquid rising in the buret. Drop the gas reservoirs and note whether, upon standing, the liquid drops in any of the pipettes, thus indicating a leak in the rubber connections.

5. Electric Heaters. The first operation is to stabilize the copper oxide and catalyst heaters at the proper temperature. Plug in the Perma-Therm heaters, and in 10-20 min they will be ready.

6. Filling Capillaries with Nitrogen.

(a) The manifold, copper oxide, and catalyst tubes should be filled with nitrogen before the analysis is started.

(b) To prepare the nitrogen, draw about 30 ml of pure air into the buret; and remove the oxygen by passing the air into the Oxsorbent until no further absorption takes place.

(c) After sweeping the manifold and tubes with nitrogen, open the oxidation tubes to the manifold.

(d) Establish the nitrogen therein at atmospheric pressure by leveling the confining liquid in the leveling bottle and buret.

(e) When level, close the oxidation tubes and manifold, and discharge the nitrogen from the buret.

7. Volume of Sample.

(a) In general, the best procedure is to take as large a sample as may be conveniently handled throughout the various stages of the analysis. Errors will be of less magnitude than if a small sample is used. With a 100-ml sample, the volume of each component determined is equal to the percentage of that component.

(b) When aqueous salt solution is used as the confining liquid, a little more than 100 ml of the sample is drawn into the buret. The buret stopcock is closed, and the sample is allowed to stand for 1 min to permit the confining liquid to drain down the sides of the buret. The leveling bottle is elevated until the confining liquid in the buret is exactly 100 ml, thus placing the gas under a slight positive pressure. The connecting tubing is then pinched securely between the thumb and forefinger, and the buret stopcock is opened to the atmosphere momentarily, thus bringing the 100 ml of gas in the buret to atmospheric pressure. When aqueous salt solution is used as the confining liquid, the sample should be allowed to stand in the buret for 1 min prior to each reading. This insures a uniform time for drainage down the side of the buret.

4.13.3 Procedure - Off-Gas Determination

1. Carbon Dioxide by Absorption.

(a) Raise the buret leveling bottle slightly, thus putting the gas in the buret under slight pressure. This prevents any liquid from the pipette being pulled into the manifold.

(b) Then, turn the manifold stopcock to connect to the pipette; continue raising the buret leveling bottle until the confining fluid reaches the top of the buret and all the gas has been passed into the pipette.

(c) Lower the buret leveling bottle, bringing the gas back into the buret.

(d) Repeat steps (b) and (c) above.

(e) The last time the gas is returned to the buret, bring the level of the potassium hydroxide solution to the reference point on the capillary stem of the pipette.

(f) Close the pipette stopcock, and read the buret.

(g) The gas should be passed twice more into the potassium hydroxide pipette as a check. If the reading is the same as before, all of the carbon dioxide has been removed, and the operator may proceed with the analysis. If more than six passes are required to get complete absorption, the solution should be changed.

(h) The volume after absorption of carbon dioxide subtracted from the initial volume of sample equals the volume of carbon dioxide.

2. Oxygen by Absorption.

(a) Next, pass the gas twice into the pipette containing chromous chloride, and read the buret.

(b) Pass the gas once more to make sure that all the oxygen has been removed and read the buret.

(c) The volume after absorption of oxygen subtracted from the volume after absorption of carbon dioxide is equal to the volume of oxygen in the sample.

3. Hydrogen by Oxidation with Copper Oxide.

(a) Place the leveling bottle on the top of the platform, and regulate the flow of gas by means of the buret stopcock.

(b) Permit the gas to flow through the copper oxide tube at about 10 ml per minute.

(c) When all the gas has passed through the copper oxide tube, draw the gas back into the buret by way of the copper oxide tube at the same flow rate.

(d) Four such double passes through the copper oxide tube generally suffice to completely oxidize the hydrogen.

(e) If a high concentration of hydrogen exists, additional passes may be necessary.

(f) Continue passes until two identical readings are obtained.

(g) Draw the sample back into the buret through the copper oxide tube, and read the buret.

(h) Any contraction in volume is due to the oxidation of hydrogen and is equal to the volume of hydrogen in the sample.

4. Nitrogen.

Any gas remaining in the buret at this stage is due to the nitrogen in the sample.

NOTE: At the completion of the analysis, and before permitting the heater to cool, open the copper oxide tube to the atmosphere through the manifold, and also close the reservoir stopcock.

4.13.4 Caution

1. Errors may be introduced by the reagents becoming exhausted. The operator, by check analysis and by keeping a record of the amount of gas a reagent has absorbed, may avoid this possibility.

2. Incomplete absorption caused by insufficient contact with the reagent may be eliminated by repeating passes until constant readings are obtained.

3. The solutions must not be allowed to pass into the main manifold header. Wash out the header periodically with acidulated water, even though it has not been apparent that any solution has entered.

4. Keep stopcocks (Silicon type) greased to avoid leaks, and be sure that all rubber connections are sound.

5. Before making a final analysis of a gas that differs appreciably in composition from the gas previously analyzed, pass a sample through the solution in the regular manner in order to bring the solutions into equilibrium with the new sample.

6. Radioactive gases should be vented to exhaust and analyzed under a fume hood or equivalent.

4.14 CHROMATE DETERMINATION (METHOD WC-10)

4.14.1 Summary of Method

When potassium iodide solution is added to an acidified water sample containing hexavalent chromium (chromates), free iodine is released in proportion to the chromate originally present. The amount of iodine is determined by titration with standard sodium thiosulfate. Starch solution is used as the indicator, since it produces a blue starch iodine complex in the presence of free iodine. The end point of the titration is marked by the disappearance of this blue color, which is an indication that all the free iodine has been consumed. Sodium acetate and EDTA are added before the titration to complex interferences and to prevent them from reacting.

4.14.2 Reagents and Materials

1. 0.1N Sodium Thiosulfate Solution. This standard solution can be purchased from Fisher Scientific Company.

2. Hydrochloric Acid Solution. Measure 100 ml of concentrated (12.1N) hydrochloric acid, and add 100 ml of water.

3. Sodium Acetate Powder. Fisher Chemical Catalog No. S-209.

4. Ethylenediamine Tetraacetic Acid. Fisher Chemical Catalog No. E-478.

5. Concentrated Potassium Iodide. This solution can be purchased from Fisher Scientific Company. Excess solid should be present.

6. Starch Indicator Solution. Fisher Chemical Catalog No. So-S-408.

4.14.3 Procedure

1. Measure 50 ml of filtered sample in a graduate, and pour into casserole.

2. Stir while adding 5 ml of 1:1 hydrochloric acid and 10 drops of concentrated potassium iodide solution.

NOTE: Allow the solution to set for 2 min. The solution will turn to a color which may vary from amber to rust red, depending upon the chromate concentration present in the sample.

3. Add approximately 5 g of sodium acetate powdered and approximately 0.2 g EDTA. (See item 4 in Sec. 4.14.2.)

4. Stir for 1 or 2 min. Allow the solution to set for 5 min.

5. Start titrating solution in casserole with 0.1N sodium thiosulfate until the color weakens to a straw yellow color.

6. Stop titrating at this point, and add 10 drops of starch indicator. The solution will then turn a deep blue or blue-black.

7. Resume the titration, adding 0.1N sodium thiosulfate dropwise until the absence of the starch-iodine blue color.

NOTE: The specific color of the end point may vary depending upon what other substances are present in the sample. Hence, the solution should be titrated to the absence of the starch-iodine blue color and not to a colorless end point.

8. To check the end point, add another 5 drops each 1:1 hydrochloric acid and potassium iodide solution. If no blue color reappears, the buret reading is used in the calculation. However, if a color change does occur, continue titrating as in step 6 above.

4.14.4 Calculations

Buret reading in ml per 50-ml sample x 77.4 = ppm of chromate as chromate (CrO_4).

NOTE: The buret reading in ml, per 50 ml sample:

(a) x 108 = ppm chromate as sodium chromate (Na_2CrO_4).
(b) x 6.3 = grains per gallon of chromate as sodium chromate (Na_2CrO_4).
(c) x 77.4 = ppm of chromate as chromate (CrO_4).
(d) x 34.675 = ppm of chromium.
(e) x 196.3 = ppm of $K_2Cr_2O_7$.

4.15 BORON DETERMINATION (METHOD WC-11A)

4.15.1 Summary of Method

In the presence of boron, a solution of carmine or carminic acid in concentrated sulfuric acid changes from bright red to a bluish red or blue, depending on the concentration of boron present. The ions commonly found in water do not interfere with this method. Samples should be stored in polyethylene bottles or in boron-free glassware. The transmittance of the colored solution is measured with the DU Spectrophotometer using a 1-cm cell at a wavelength of 585 mμ.

4.15.2 Reagents and Materials

1. Standard Boric Acid Solution. Dissolve 0.5719 g of boric acid crystals in water, and dilute to 1000 ml. (1.00 ml equals 0.100 mg boron.)

CAUTION: Since boric acid crystals lose weight on drying at 105 C, a reagent meeting reagents and materials specifications should be used, and it should be kept tightly stoppered to prevent absorption of air mixture.

2. 12.1N Hydrochloric Acid. Concentrated hydrochloric acid (HCl).

3. 36.0N Sulfuric Acid. Concentrated sulfuric acid (H_2SO_4).

4. Carmine Solution. Dissolve 0.92 g of carmine N.F. 40 or carminic acid in 1 liter of H_2SO_4.

4.15.3 Procedure

1. Pipet 1.0, 2.0, 5.0, and 10.0 ml of the standard boric acid solution into separate 100-ml volumetric flasks. Also prepare a blank with no boric acid standard added.

NOTE: The boric acid solution aliquots represent boron concentrations of 1, 2, 5, and 10 ppm respectively.

2. Dilute to 100 ml with water.

3. Measure 2 ml of each solution, and transfer each into clean dry 50-ml volumetric flasks.

4. Add two drops of concentrated hydrochloric acid (HCl),

5. Pipet 10 ml of concentrated sulfuric acid (H_2SO_4) into each flask.

NOTE: Allow sufficient time for drainage of sulfuric acid (H_2SO_4) from the side walls of the flasks.

6. Swirl the solution with caution, and allow solutions to cool to room temperature.

7. Pipet 10 ml of carminic acid solution into each flask. Stopper and shake for 1 or 2 min.

CAUTION: Incomplete mixing in this step can cause bubbles to be present when the solution is transferred to the DU-Cells. This can be a serious source of error.

8. Allow the solutions to stand for 1 hr, and read the transmittance on the DU-Spectrophotometer at 585 mμ.

9. Secure a fresh sample (needed to be analyzed for boron content), and pipet 2 ml of the 100-ml sample into a clean dry 50-ml volumetric flask.

10. Repeat steps 4, 5, 6, 7, and 8 above.

NOTE: Carry a reagent blank throughout the entire procedure.

11. Read boron concentration in ppm from the standard curve mentioned in step 1 of Sec. 4.15.4 (below).

4.15.4 Calculations

1. Plot transmittance vs. ppm on semi-log paper from readings obtained from step 8 above.

CAUTION: Since the carmine reagent deteriorates, the standard curve should be checked daily.

4.16 BORON DETERMINATION (METHOD WC-11B)

4.16.1 Summary of Method

The concentration of boron in sodium pentaborate decahydrate can be determined by using a hydrometer to measure the specific gravity.

4.16.2 Procedure

1. Collect a sample of the sodium pentaborate decahydrate solution in the 1000-ml graduated cylinder.

2. Maintain the temperature of the sample at 80 F by means of a hot plate or water bath.

3. Place the hydrometer in the sample, and record the specific gravity.

4. Determine the concentration (w/o) of sodium pentaborate decahydrate from Fig. 4.1, which plots the relationship of concentration vs. specific gravity of sodium pentaborate decahydrate at 80 F.

4.16.3 Calculations

Convert the concentration (w/o) determined in step 4 of Sec. 4.16.2 as follows:

$$\text{boron}^{\text{natural}}\ (\text{ppm}) = (\text{w/o})\ (10^4)\ (0.183)$$

$$\text{boron}^{10}\ (\text{ppm}) = \text{ppm boron}^{\text{natural}} \times (0.1960)$$

4.17 COPPER DETERMINATION (METHOD WC-12)

4.17.1 Summary of Method

This method is based on the measurement of the intensity of the yellow color of the cuprous complex of 2-9 dimethyl - 1, 10 - phenanthroline (neo-cuproine). Full development of the color takes place over the pH range from 2.3 to 9.0. However, a buffer phase is used to produce an aqueous phase with a pH of 4.0 to 6.0. The copper is reduced with hydroxylamine hydrochloride, and the pH of the solution is adjusted with a sodium citrate solution. The cuprous ion is then reacted with neo-cuproine, and the yellow complex is extracted with chloroform. The method follows Beer's Law up to a concentration of 5 ppm Cu. The transmittance is measured at 457 mμ on the DU-Spectrophotometer using a 1-cm cell.

4.17.2 Reagents and Materials

1. 14.8N Ammonium Hydroxide. Concentrated ammonium hydroxide (NH_4OH).

2. Copper, Standard Solution (1 ml = 0.02 mg Cu). Weigh out 0.200 g of electrolytic copper. Place it in a 250-ml beaker under a hood; add 3 ml of water and 3 ml of HNO_3, and cover the beaker with a watch glass. After the metal has completely dissolved, add 1 ml of H_2SO_4 (sp. gr. 1.84), and heat on a hot plate just short of complete

dryness. Do not bake the residue. Cool the residue; wash down the sides of the beaker and the bottom of the watch glass; and again evaporate the solution nearly to dryness to expel the HNO_3. Cool the residue; dissolve it in water, and dilute the solution to 1 liter. Make the standard as needed by diluting 100 ml of the prepared solution to 1 liter with water. One milliliter of the standard contains 0.02 mg Cu or, when diluted to 50 ml with water, it represents a 0.4 ppm Cu solution.

3. 12.1N Hydrochloric Acid. Concentrated hydrochloric acid (HCl).

4. Hydroxylamine Hydrochloride Solution (200 g/l). Dissolve 40 g of hydroxylamine hydrochloride (NH_2OH HCl) in water, and dilute to 200 ml.

5. Neo-Cuproine Solution (1 g/l). Dissolve 0.1 g of neo-cuproine (2, 9 - dimethyl - 1, 10 - phenanthroline) in 50 ml of isopropyl alcohol. Dilute the solution to 100 ml with water.

6. 15.7N Nitric Acid. Concentrated nitric acid (HNO_3).

7. Sodium Citrate Solution (250 g/l). Dissolve 250 g of hydrated sodium citrate ($Na_3C_6H_5O_7 \cdot 2H_2O$) in water, and dilute to 1 liter. Add 10 ml of $NH_2OH \cdot HCl$ solution and 10 ml of neo-cuproine solution. Extract copper impurities in the solution with 50 ml of $CH Cl_3$, discarding the chloroform layer.

8. 36N Sulfuric Acid. Concentrated sulfuric acid (H_2SO_4).

9. Isopropyl Alcohol.

10. Chloroform ($CH Cl_3$).

4.17.3 Procedure

1. Prepare a series of standard copper solutions by pipetting 1, 2, 5, and 10-ml aliquots into 125-ml Squibb separatory funnels. Also prepare a blank with no copper standard added. Add 0.1 ml of hydrochloric acid (HCl), and dilute to 50 ml with water.

2. Add 5 ml of hydroxylamine hydrochloride NH_2OH:HCl solution, and shake for 30 sec.

3. Add 10 ml of sodium citrate solution, and shake for 30 sec.

4. Add 10 ml of neo-cuproine solution, and shake for 30 sec.

5. Add 30 ml of chloroform, and shake vigorously for 30 sec.

6. Allow the funnel to stand 5 min to permit the aqueous and chloroform layers to separate.

7. Drain the chloroform layer into a dry flask, and repeat step 5 with 20 ml of chloroform.

8. Combine the chloroform extracts in a volumetric flask, and dilute to 50 ml with isopropyl alcohol.

9. Read the percent transmittance on the DU-Spectrophotometer at 457 mμ using 1-cm cells.

10. Secure a fresh sample (sample needed to be analyzed for copper content), and pipet a 50-ml aliquot of the sample into a 125-ml Squibb separatory funnel. Add 1 ml of concentrated HCl to the 50-ml aliquot.

11. Repeat steps 2, 3, 4, 5, 6, 7, and 8 above.

12. Repeat step 9, and obtain copper concentration from curve produced on step 1 of Sec. 4.17.4.

CAUTION: If the water contains interfering substances such as organic matter, sulfide, or chromium (when ratio of Cr to Cu is 5 to 1), the following preliminary sample treatment is required:

13. Transfer 100 ml of the acidified sample to a 250-ml beaker.

14. Add 1 ml of sulfuric acid (H_2SO_4) and 5 ml of nitric acid (HNO_3).

15. In a fume hood, evaporate carefully on a hot plate to dense white sulfur trioxide fumes.

16. If solution remains colored, repeat the treatment with an additional 5 ml of nitric acid (HNO_3).

17. If organic matter is difficult to destroy, repeat the treatment with 5 ml of HNO_3 and 5 ml of hydrogen peroxide (H_2O_2).

18. Evaporate the solution to complete dryness.

19. Rinse the sides of the beaker and watch glass with water.

20. Evaporate to dryness again, and expel all nitric acid HNO_3.

21. Add about 80 ml of water to the residue; bring to a boil; cool, and if turbid, filter.

22. Adjust pH to 4 to 6 by dropwise addition of 3N NH_4 OH using range pH paper.

23. Add 0.2 ml of hydrochloric acid (HCl), and dilute to 100 ml in a volumetric flask with demineralized water.

24. Pipet a 50-ml aliquot into a 125-ml Squibb separatory funnel.

25. Repeat steps 11 and 12.

4.17.4 Calculations

1. Plot the reading from step 9 of Sec. 4.17.3 vs. concentration of copper on semi-log paper.

4.18 HARDNESS DETERMINATION (METHOD WC-13)

4.18.1 Summary of Method

Hardness in water is caused principally by the elements calcium and magnesium and sometimes by iron and aluminum. Total hardness is determined by titration at pH 10.0 with a standardized solution of the disodium salt of ethylenediamine tetraacetic acid (Versene). Eriochrome Black T is used as the indicator. Magnesium reacts with the indicator to form a wine-red complex. Calcium is completely converted to a colorless complex by the titrating solution before the magnesium is removed from its complex with the indicator. The end point is reached when the blue color of the indicator is visible with no trace of the wine-red color of the magnesium complex. Since calcium will not cause a color change with the indicator, magnesium is added to the titrating solution to insure formation of the wine-red color when titrating samples contain calcium but no magnesium. The interference of copper and iron, up to 10 ppm, is eliminated by the addition of sodium sulfide.

4.18.2 Reagents and Materials

1. Buffer Solution. Add 67.5 g of ammonium chloride (NH_4Cl) in 380 ml of water. Add 570 milliliters of concentrated ammonium hydroxide.

2. Sodium Sulfide Solution. Dissolve 45 g of sodium sulfide ($Na_2S \cdot 9H_2O$) in 100 milliliters of water.

3. Eriochrome Black T Indicator. Dissolve 0.025 g of dye in 50 milliliters of water. This reagent will not keep indefinitely; dispose of unused reagent and make fresh every two weeks.

4. Sodium Ethylenediamine Tetraacetate Solution. Purchase from Fisher Scientific Company (Cat. No. So-S-221).

5. Standard Titrating Solution. Add 0.1 g of magnesium chloride ($MgCl_2 \cdot 6H_2O$) to sodium (Di) Ethylenediamine Tetraacetate Solution (1 ml = 1 mg $CaCO_3$ Standard Solution).

CAUTION: Store solution in a plastic bottle.

6. Standard Hard Water. This Calcium Carbonate Standard (1 ml = 1 mg $CaCO_3$) may be purchased from Harleco (Catalog No. 12442). Oven-dry several grams of calcium carbonate crystals ($CaCO_3$) at 105 C for several hours (overnight should be sufficient). Transfer to a desiccator, and cool for 30 min. Weigh 1.00 g of dry calcium carbonate crystals into a 500-ml Erlenmeyer flask. Add (1-1) hydrochloric acid (HCl) until all the calcium carbonate ($CaCO_3$) has been dissolved. Add 200 ml of water, and boil for a few minutes to expel CO_2. Cool; add a few drops of methyl red indicator, and adjust to the intermediate orange color (pH 5.3) by addition of 3N ammonium hydroxide (NH_4OH) and (1-1) hydrochloric acid (HCl) as required. Transfer quantitatively to a liter volumetric flask and dilute to 1 liter with water.

NOTE: This standard contains 1.000 mg $CaCO_3$ in each milliliter, which represents 1000 ppm.

4.18.3 Procedure

1. Measure accurately 100 ml of sample, and transfer it to a 250-ml Erlenmeyer flask.

2. Add 1 ml of buffer solution.

3. Add 3 drops of sodium sulfide solution.

4. Add 2 drops of Eriochrome Black T Indicator, and stir for 1 or 2 min.

5. While stirring the solution, titrate slowly with standard titrating solution, using a microburet.

NOTE: Titrate until the wine-red color disappears and a blue color remains.

4.18.4 Calculations

$$\text{Total hardness as ppm Ca } CO_3 = \frac{(\text{ml titrating solution})\ (1000)}{(\text{volume of sample, ml})}$$

4.19 PHOSPHATE DETERMINATION (METHOD WC-14)

4.19.1 Summary of Method

Orthophosphate reacts with ammonium molybdate in an acid medium to form a phosphomolybdate which, in turn, is reduced to a molybdenum blue complex with stannous chloride. This color intensity is proportional to the phosphate concentration of the sample.

4.19.2 Reagents and Materials

1. Phosphate, Standard Solution (1 ml = 0.1 mg PO_4). Dissolve 0.1433 g of oven-dried potassium dihydrogen phosphate (KH_2PO_4) in water, and dilute to 1 liter in a volumetric flask.

2. Ammonium Molybdate-Sulfuric Acid Solution. Add 310 ml of concentrated sulfuric acid (H_2SO_4) to about 600 ml of water. To this, add 15 g of ammonium molybdate. Cool and dilute to 1 liter with water.

3. Stannous Chloride Solution. Dissolve 2.38 g of stannous chloride ($SnCl_2$-$2H_2O$) in 25 ml of concentrated hydrochloric acid (HCl).

CAUTION: Filter if turbid. Add a layer of pure mineral oil 5-mm thick over the surface of the solution to minimize oxidation.

NOTE: The reagent can also be preserved several weeks by adding mossy tin and storing it in a refrigerator.

4.19.3 Procedure

1. Prepare a series of standard phosphate solutions to cover the range from 0 to 25 ppm. Prepare the standards by diluting suitable volumes of phosphate solution (1 ml - 0.1 mg PO_4) to 100 ml with water. One milliliter of phosphate solution (1 ml - 0.1 mg PO_4) diluted to 100 ml with water produces a standard containing 1.0 ppm of phosphate.

2. Add 4 ml of ammonium molybdate-sulfuric acid solution to each sample, and mix.

3. Add 1 ml of stannous chloride solution to each sample, and mix for 1 or 2 min.

4. Read immediately.

5. Measure the absorbance at 620 mμ with a spectrophotometer, using water as the reference sample. Plot the absorbance values obtained as ordinates, and plot the corresponding phosphate concentrations as abscissas.

6. Transfer 100 ml of clear sample into an Erlenmeyer flask.

NOTE: Filter with suction if suspended matter is present into an Erlenmeyer flask. If the sample contains more than 25 ppm PO_4, use a correspondingly smaller sample.

7. Repeat steps 2 through 5 above.

4.19.4 Calculations

Calculate the concentration of phosphate, in parts per million, as follows:

$$\text{phosphate, ppm} = C\,\frac{100}{S}$$

where:

C = parts per million phosphate ion indicated by the calibration curve for the determined color absorbance, and

S = milliliters of sample.

4.20 SULFATE DETERMINATION (METHOD WC-15A)

4.20.1 Summary of Method

Sulfate ion is converted to a barium sulfate suspension under controlled conditions. Glycerin solution and a sodium chloride solution are added to stabilize the suspension and minimize interferences. The resulting turbidity is determined with the DU-Spectrophotometer using 5-cm cells at a wavelength of 380 to 400 mμ. This procedure is directly applicable over the range of 10 to 100 ppm of sulfate ion ($SO_4^{=}$).

4.20.2 Reagents and Materials

1. Barium Chloride Solution ($BaCl_2 \cdot 2H_2O$). 118 g/liter.

2. Glycerol Solution. 250 ml H_2O to 250 ml of glycerol.

3. Sodium Chloride Solution. 240 g/l. Dissolve 240 g of NaCl in water containing 20 ml of concentrated HCl, and dilute to 1 liter.

4. Sulfate Standard Solution. 0.1 mg/ml $SO_4^=$. Dissolve 0.1479 g of dry anhydrous sodium sulfate (Na_2SO_4) in water, and dilute to 1 liter in a volumetric flask.

4.20.3 Procedure

1. Plot a calibration curve by adding 0, 2.0, 5.0, 10.0, 15.0, 20.0, 30.0, 40.0, and 50.0 ml of standard sulfate solution to separate 50-ml volumetric flasks, and dilute to the mark with water. The solutions will have sulfate ion concentrations of 0, 4, 10, 20, 30, 40, 60, 80, and 100 ppm respectively.

2. Filter sample if turbid, and adjust the temperature between 15 and 30 C.

3. Transfer to a 250-ml beaker.

4. Add 10 ml of glycerol solution and 5 ml of NaCl solution, and swirl to mix.

5. Fill the sample cell with sample solution, and place in cell compartment to zero the instrument.

6. Pour the sample solution from the cell back into the beaker.

7. Add, with stirring on the magnetic stirrer, 2.5 ml of $BaCl_2 \cdot 2H_2O$ solution.

8. Stir for 1 min; then, let stand for 4 min, and stir again for 15 sec.

9. Fill the sample cell as before, and read immediately.

10. Secure a fresh sample, and pipet 50 ml into a 250-ml beaker; then, proceed as in steps 2, 3, 4, 5, 6, 7, and 8.

11. Repeat step 9 and obtain the $SO_4^=$ concentration from the curve produced in step 1 of Sec. 4.20.4.

4.20.4 Calculations

1. Plot the reading from step 9 of Sec. 4.20.3 vs. concentration of $SO_4^=$ (ppm) on semi-log paper.

4.21 SULFATE DETERMINATION (METHOD WC-15B)

4.21.1 Summary of Method

Sulfate ion is precipitated and weighed as barium sulfate after removal of silica and other insoluble matter. This method is applicable to samples containing approximately 20 to 100 ppm of sulfate ion ($SO_4^{=}$). It can be extended to higher or lower ranges by adjusting the sample size.

4.21.2 Reagents and Materials

1. 14.8N Ammonium Hydroxide. Concentrated ammonium hydroxide (NH_4OH).

2. Barium Chloride Solution. Dissolve 118 g of barium chloride ($BaCl_2 \cdot 2H_2O$) in water, and dilute to 1 liter.

3. (1-9) Hydrochloric Acid. Mix 1 volume of concentrated hydrochloric acid (HCl) with 9 volumes of water.

4. (48 Percent) Hydrofluoric Acid. Concentrated hydrofluoric acid (HF).

5. Methyl Orange Indicator. Dissolve 0.05 g of methyl orange in 100 ml of water.

6. 15.7N Nitric Acid. Concentrated nitric acid (NHO_3).

7. Picric Acid. Saturated aqueous solution.

8. Silver Nitrate Solution. Dissolve 10 g of silver nitrate ($AgNO_3$) in water, and dilute to 100 ml.

9. 36N Sulfuric Acid. Concentrated sulfuric acid (H_2SO_4).

4.21.3 Procedure

1. Filter the sample, using a fine filter paper.

2. Measure into a clean beaker a quantity of the clear filter sample containing sulfate ion equivalent to 10 to 50 mg of barium sulfate ($BaSO_4$).

NOTE: Adjust the volume by evaporation or dilution with water to approximately 200 ml.

3. Add a few drops of methyl orange, and adjust the acidity of the sample by adding (1-9) hydrochloric acid (HCl) until the red end point is reached.

4. Add 10 ml of (1-9) hydrochloric acid (HCl) in excess.

5. Add 10 ml of saturated picric acid solution, and boil the sample for 5 min.

NOTE: Faster precipitation and coarse precipitate is obtained when using saturated picric acid.

6. After boiling the sample for 5 min, slowly add 5 ml of hot barium chloride ($BaCl_2$) solution.

NOTE: Stir the sample vigorously while adding the ($BaCl_2$) solution.

CAUTION: Keep the temperature just below boiling until the liquid has become clear and the precipitate has settled out completely.

7. Filter the suspension of barium sulfate ($BaSO_4$) on a fine, ashless filter paper, and wash the precipitate with hot water until the washings are substantially free of chlorides, as indicated by testing the last portion of the washings with $AgNO_3$ solution.

NOTE: Discontinue washing when no more than a faint opalescence is produced in the test.

8. Place the filter paper and contents in a tared platinum crucible.

9. Ash the filter paper without flaming by use of a torch.

10. Ignite the residue at 800 C for 1 hr, or until it is apparent that all carbon has been consumed.

11. Cool and add a drop of concentrated sulfuric acid (H_2SO_4) and a few drops of hydrofluoric acid (HF).

12. Place on a hot plate, and evaporate under a hood to expel silica as silicon tetrafluoride (SiF_4).

13. Reignite at 800 C.

14. Cool in a desiccator, and weigh the crucible and precipitate ($BaSO_4$) on an analytical balance to the nearest 0.1 mg.

4.21.4 Calculations

1. Calculate the concentration of sulfate ion ($SO_4^{=}$) in parts per million, as follows:

$$\text{sulfate } (SO_4^{=}) \text{ ppm} = \frac{(W)\ (411,500)}{S}$$

where:

W = grams of $BaSO_4$.

S = milliliters of sample.

4.22 SILICA DETERMINATION (METHOD (WC-16)

4.22.1 Summary of Method

This method covers the determination of soluble silica in the range from 50 to 1000 ppb. This method is based on the reaction of soluble silica with molybdate ion to form a greenish-yellow complex which in turn is converted to a blue complex by reduction with 1-amino-2-napthol-4-sulfonic acid. Phosphate interference is eliminated by the use of oxalic acid. Iron, if present in large amounts, also interferes. The concentration of silica is determined by measuring the transmittance on the DU-Spectrophotometer at a wavelength of 815 mμ using 1-cm cells or Spectronic 20, 700 mμ.

4.22.2 Reagents and Materials

CAUTION: All reagents should be stored in polyethylene bottles.

1. Amino-Napthol-Sulfonic Acid. Dissolve 0.5 g of 1-amino-2-napthol-4-sulfonic acid in 50 ml of solution containing 1 g of sodium sulfite (Na_2SO_3). After dissolving, add the solution to 100 ml of a solution containing 30 g of sodium hydrogen sulfite ($NaHSO_3$). Make up to 200 ml with demineralized water, and store solution in a dark, plastic bottle.

CAUTION: Prepare a fresh solution every two weeks.

2. Ammonium Molybdate Solution (100 g/l). Dissolve 10 g of ammonium paramolybdate $(NH_4)_6\ Mo_7O_{24} - 4H_2O$ in 100 ml of water.

3. Hydrochloric Acid (1:1). Mix 1 volume of concentrated HCl with 1 volume of demineralized water.

4. Oxalic Acid Solution (100 g/l). Dissolve 10 g of oxalic acid ($H_2C_2O_4 \cdot 2H_2O$) in 100 ml of water.

5. Silica Standard Solution (1 ml = 1 mg SiO_2). Dissolve 4.732 g of sodium metasilicate ($Na_2SiO_3 \cdot 9H_2O$) in water, and dilute it to 1 liter with demineralized water. Check the concentration of this solution gravimetrically. (See Sec. 4.22.5.) Pipette 3 ml of standard silica solution into a 1000-ml volumetric flask, and dilute it to mark with demineralized water. This solution contains 3 ppm SiO_2 and is used as a working solution.

4.22.3 Procedure

1. From the 3-ppm working solution, prepare a series of standards by pipetting aliquots of 1.0, 5.0, 10.0, and 15.0 ml into polyethylene graduated mixing cylinders. Also, prepare a blank with no silica standard added.

NOTE: The silica working solution aliquots represents silica concentration of 0.06, 0.30, 0.60, and 0.90 ppm respectively.

2. Dilute each sample to the 50-ml mark.

3. Add 1 ml of (1-1) hydrochloric acid solution and 2 ml of ammonium molybdate solution; mix, and allow to stand exactly 5 min.

4. Add 1.5 ml of oxalic acid reagent; mix well, and allow to stand exactly 1 min.

5. Add 2 ml of amino-napthol-sulfonic acid. Mix well, and allow to stand for 10 min for full color development.

6. Read the transmittance on the DU-Spectrophotometer at 815 mμ, using 1-cm cells.

7. Secure a fresh sample (sample needed to be analyzed for silica content), and transfer 50 ml of this sample to a polyethylene graduated cylinder.

8. Repeat steps 3, 4, and 5 above.

9. Prepare a blank by using 50 ml of demineralized water, and repeat step 8 above.

10. Repeat step 6, and obtain concentration of silica as SiO_2 directly from curve produced in step 1 of Sec. 4.22.4.

4.22.4 Calculations

1. Plot percent transmittance vs. ppb on semi-log paper.

NOTE: This plot should be a straight line.

4.22.5 Gravimetric Silica Determination (Method WC-16A)

This method is used to check the concentration of silica standard solution method WC-16 gravimetrically.

4.22.5.1 Procedure.

1. Pipet 5 ml from the method WC-16 silica standard solution into a 150-ml beaker.

2. Add 5 ml of concentrated hydrochloric acid.

3. Evaporate the sample to dryness on a water bath with periodic additions of the three 5-ml portions of concentrated hydrochloric acid.

4. Dry the evaporated residue in an oven at 110 C for 1 hr.

5. Add 5 ml of concentrated hydrochloric acid, and then add 50 ml of water to the dried residue in the beaker.

6. Warm the beaker and contents and stir to dissolve or suspend all the residue. Filter the warm solution through an ashless, medium filter paper.

7. Wash the residue on the filter paper 15 times with (1-49) hydrochloric acid and then with several washings of water.

CAUTION: Cover the funnel containing the filter paper and its residue with a clean watch glass, and reserve it for later ignition.

8. Return the filtrate to the original evaporating beaker; evaporate to dryness on a water bath with periodic addition of two 5-ml portions of concentrated hydrochloric acid.

9. Dry, and repeat the filtration and washing steps 2 through 7, using a second funnel and filter paper.

10. Place both filter papers with their dehydrated residue in a tared platinum crucible, and dry under a heat lamp.

11. Cover and ignite for 10 min in a muffle furnace at 1000 to 1200 C.

12. Remove the cover, and continue the ignition for 30 min.

13. Cool in a desiccator, and weigh the crucible and precipitate on an analytical balance to the nearest 0.1 mg.

14. Repeat steps 12 and 13 until a constant weight is obtained.

15. Add several drops of concentrated sulfuric acid (H_2SO_4) and 5 ml of hydrofluoric acid (HF) to the weighed residue in the crucible, and evaporate to dryness on a low-temperature hot plate.

16. Reignite the residue by repeating steps 12, 13, and 14.

4.22.5.2 Calculations. Calculate the concentrations of silica, in ppm, as follows:

$$SiO_2, \text{ ppm} = \frac{(W_1 - W_2)\ (1000)}{V}$$

where:

W_1 = weight of crucible and sample residue, in milligrams after first ignition (step 14).

W_2 = weight of crucible and sample residue, in milligrams after treatment with HF and reignition (step 16).

V = milliliters of sample used from WC-16 method.

4.23 CHROMIUM DETERMINATION (METHOD WC-17)

4.23.1 Summary of Method

The sample is oxidized by acid treatment, followed by potassium permanganate treatment. A color is developed in acid solution with 1,5 diphenylcarbazide. This color (reddish-purple complex) is measured by means of a DU-Spectrophotometer at 540 mμ using 1-cm cells.

4.23.2 Reagents and Materials

1. (1-1) Ammonium Hydroxide. Mix 1 volume of concentrated ammonium hydroxide (NH_4OH) with 1 volume of water.

2. 15.7N Nitric Acid. Concentrated (low chromium content) nitric acid.

NOTE: Reagent grade nitric acid frequently may contain sufficient chromium to interfere in this method. It may be purified by distillation in all-glass equipment.

CAUTION: Such a distillation often may need to be repeated.

3. Potassium Dichromate Standard Solution (1 ml - 0.5 ppm). Dissolve 1.414 g of potassium dichromate ($K_2Cr_2O_7$) in water, and dilute to 1 liter with water. Pipet 10 ml of this solution into a 1-liter volumetric flask, and dilute to the liter mark. One milliliter of this finally-diluted solution corresponds to 0.5 ppm chromium in a 10-ml sample.

4. Potassium Permanganate Solution. Dissolve 3.16 g of potassium permanganate ($KMnO_4$) in water, and dilute to 1 liter with water.

5. Diphenylcarbazide Solution. Add 4.0 g of phthalic anhydride to 80 ml of ethanol (95 percent), and shake for 1 or 2 min. Add 0.5 g of 1,5-diphenylcarbazide, and dilute to 100 ml with ethanol (95 percent). Shake occasionally to dissolve the phthalic anhydride.

CAUTION: This solution is stable for about 6 mos if stored in a cool, dark place.

NOTE: New calibration curves should be prepared at least monthly.

6. 12.1N Hydrochloric Acid. Concentrated hydrochloric acid (HCl).

7. Sodium Dihydrogen Phosphate Solution. Dissolve 138 g of sodium dihydrogen phosphate (NaH_2PO_4) in water, and dilute to 1 liter with water.

8. 36N Sulfuric Acid. Concentrated sulfuric acid (H_2SO_4).

9. (1-49) Sulfuric Acid. Mix 1 volume of concentrated sulfuric acid (H_2SO_4), cautiously and while stirring, with 49 volumes of water.

10. Wash Acid. Mix 50 ml of concentrated nitric acid with 150 ml of concentrated hydrochloric acid, and add 200 ml of water.

4.23.3 Procedure

CAUTION: All glassware should be rinsed in wash acid solution and then rinsed with water before use.

1. Pipet accurately 2, 4, 6, 10, 15, and 20 ml of the diluted standard solution into six separate 100-ml volumetric flasks, and dilute to the mark. Pipet 10 ml of water for use in preparing the reference solution.

NOTE: 10 ml of these dilutions carried through the procedure represents chromium concentrations of 0.05, 0.1, 0.15, 0.25, 0.4, and 0.5 ppm respectively.

2. Secure a fresh sample (10 ml) of solution needed to be analyzed for chromium content.

NOTE: If reducing impurities are absent, hexavalent chromium may be determined directly by omitting steps 3 through 10. Add 13 ml of (1-49) sulfuric acid H_2SO_4, and proceed as described in step 11. (If a standard solution is used, proceed directly to step 11.)

3. Add 5 ml of concentrated nitric acid and evaporate just to dryness.

CAUTION: Do not bake.

4. Cool, and add an additional 5 ml of concentrated nitric acid, followed by 2 ml of concentrated sulfuric acid H_2SO_4.

5. Evaporate to fumes; then, heat gently for 1 min.

NOTE: If the residue is discolored by organic matter, cautiously add 2 ml of concentrated H_2SO_4 to reduce fumes, and repeat treatment as often as necessary. It may be necessary to add more concentrated sulfuric acid (H_2SO_4) to prevent the mixture from becoming dry.

6. Cool the solution; then, add 17 ml of water and neutralize with (1-1) ammonium hydroxide NH_4OH.

7. Add 13 ml of (1-49) sulfuric acid H_2SO_4. Swirl and, if necessary, warm to achieve solution.

8. Filter through fine filter paper, and wash the filter three times with 5 ml portions of water. Filtrate and washings should be collected in a 250-ml beaker.

9. Add 12 drops of potassium permanganate ($KMnO_4$) solution. Place on a hot plate on low heat for 20 min. If the pink color disappears, add an additional 12 drops of potassium permanganate ($KMnO_4$) solution to maintain a slight excess.

10. Add 3 drops of concentrated hydrochloric acid, and heat the solution until the color of the potassium permanganate ($KMnO_4$) disappears.

NOTE: If any turbidity or precipitate is present at this point, clarify by centrifuging.

11. Transfer the solution to a 50-ml volumetric flask, and add 2 ml of the 1.5 diphenylcarbazide solution. Shake for 1 or 2 min, and let stand for 1 min.

12. Add 5.0 ml of sodium dihydrogen phosphate (NaH_2PO_4) solution, and let stand at least 5 min but not more than 30 min. Dilute to the 50-ml mark, and shake for 1 or 2 min.

13. Read the percent transmittance on the DU-Spectrophotometer at 540 mμ using 1-cm cells.

NOTE: The spectrophotometer should be balanced at 100-percent transmittance using the blank water solution.

14. The chromium concentration in ppm is read directly from the calibration curve produced by following Sec. 4.23.4.

4.23.4 Calculations

1. Plot percent transmittance vs. ppm chromium on semi-log paper from step 13 of Sec. 4.23.3.

4.24 NICKEL DETERMINATION (METHOD WC-18)

4.24.1 Summary of Method

This method is based on the formation of a wine-red color complex of nickel with ammoniacal dimethylglyoxime in the presence of iodine. The color is measured directly with the DU-Spectrophotometer at a wavelength of 530 mμ, using a 1-cm cell.

4.24.2 Reagents and Materials

1. Ammonium Citrate Solution. Dissolve 500 g of citric acid monohydrate in 576 ml of concentrated ammonium hydroxide (NH_4OH); cool, and dilute to 1 liter with water.

NOTE: Filter solution through a fine filter paper before using the solution.

2. (1-1) Ammonium Hydroxide. Mix 1 volume of concentrated ammonium hydroxide (NH_4OH) with 1 volume of water.

NOTE: Filter solution through a fine filter paper before using the solution.

3. Dimethylglyoxime Ammoniacal Solution. Dissolve 1 g of dimethylglyoxime in 500 ml concentrated ammonium hydroxide, and dilute to 1 liter with water.

CAUTION: Prepare fresh every two weeks.

NOTE: Filter solution.

4. Iodine Solution (12.7 g/l). Dissolve 6.35 g of iodine in a solution of 75 g of potassium iodide (KI) in 60 ml of water, and dilute to 500 ml with water.

CAUTION: Store solution in a stoppered dark bottle.

5. Nickel Solution (1 ml = 0.02 mg Ni). Dissolve 1.000 g of nickel (99.9 percent Ni) in 10 ml of warm concentrated nitric acid (HNO_3). Boil to expel nitrous oxide fumes, and dilute to 500 ml in a volumetric flask. Dilute 50 ml of this solution to 1000 ml in a volumetric flask, and finally dilute 50 ml of this solution to 250 ml in a volumetric flask.

4.24.3 Procedure

1. From the nickel solution prepare a series of standards by pipetting aliquots of 1.0, 2.0, 5.0, 10.0, and 25.0 ml into separate 100-ml volumetric flasks. Also prepare a blank with no nickel standard added.

NOTE: The nickel standard solution aliquots represent nickel concentrations of 0.4, 0.8, 2.0, 4.0, and 10.0 ppm respectively. The blank represents 0.0 ppm nickel.

2. Add water to make a volume of 50 ml.

3. Add 10 ml of ammonium citrate solution and 5 ml of iodine solution to each volumetric flask.

4. Add 20 ml of ammoniacal dimethylglyoxime solution, and dilute to 100 ml with water.

5. Mix well, and allow to stand for 10 min for full color development.

6. Read the transmittance on the DU-Spectrophotometer at 530 mμ, using 1-cm cells.

NOTE: The spectrophotometer should be balanced to 100-percent transmittance using the blank solution prepared in step 1 of Sec. 4.24.3.

7. Secure a fresh sample (sample needed to be analyzed for nickel content), and transfer two 50-ml portions of the sample into separate 100-ml volumetric flasks.

8. Repeat step 3 above for both flasks.

9. For one of the flasks, repeat steps 4 and 5 above.

10. To the second flask, add 20 ml of (1-1) ammonium hydroxide (NH_4OH); then, dilute to 100 ml with water, and repeat step 5.

NOTE: Use this solution as the blank solution.

11. Repeat step 6 above.

NOTE: Read step 9 solution, and use step 10 solution as the blank solution.

12. The nickel concentration in ppm is read directly from the calibration curve produced on step 1 of Sec. 4.24.4.

4.24.4 Calculations

Plot transmittance vs. ppm nickel on semi-log paper from step 6 of Sec. 4.24.3.

NOTE: This plot should be a straight line.

4.25 NITRITE DETERMINATION (METHOD WC-19)

4.25.1 Summary of Method

This test is based upon the determination of the nitrite content of a sample titration in an acid medium with a standard oxidizing agent, potassium permanganate. The persistance of a definite pink color for 1 min is taken as the end point.

4.25.2 Reagents and Materials

Potassium Permanganate 0.01N, Sulfuric Acid 5-percent solution.

4.25.3 Procedure

1. Measure a 10-ml sample in a graduate; cool to room temperature.

2. Transfer to a casserole.

3. Add 3 ml of 5-percent H_2SO_4 solution.

4. Add the 0.01N $KMnO_4$ dropwise with constant stirring until a pink color starts to persist.

5. At this point, add 1 ml of 0.01N $KMnO_4$ at a time with constant stirring.

6. Continue to add the 0.01N $KMnO_4$ at the rate of 1 ml until a definite pink color persists for 1 min.

NOTE: The time interval (1 min) should be measured with a second hand or a stopwatch.

4.25.4 Calculations

$$\text{ppm nitrite as } NO_2 = \text{ml of } 0.01N\ KMnO_4 \times \frac{230}{\text{ml of sample}}$$

4.26 NITRATE DETERMINATION (METHOD WC-20)

4.26.1 Summary of Method

A chloroform solution of brucine alkaloid and sulfuric acid added to the sample produces a yellow color, the intensity of which is proportional to the amount of nitrate ion present. The intensity of the color is measured at 470 mμ by means of a spectrophotometer.

4.26.2 Interfering Substances

1. Nitrite ion interferes with the determination in proportion to its concentration in the sample.

2. The following amounts of various inorganic substances may be present without causing interference in tests for nitrate ion:

Ion	Concentration (ppm)
Fe^{++}, Fe^{+++}	250
OH^- (NaOH)	85
NH_4^+	65
Ca^{++}	100
Mg^{++}	60
Cl^- (NaCl)	1000
SO_3^{--}	50
PO_4^{---}	200
PO_3^-	40
SiO_2	200

3. Satisfactory results can be obtained with up to 100 ppm of organic matter present.

4.26.3 Reagents and Materials

1. Brucine Alkaloid Solution. Dissolve 5 g of pure brucine alkaloid crystals in about 20 ml of chloroform, and dilute to 100 ml with chloroform.

NOTE: Brucine is very poisonous and should be handled with care.

2. Potassium Nitrate, Standard Solution. Dry KNO_3 in an oven at 105 C for 24 hr. Weigh out 1.631 g; dissolve in about 20 ml of reagent water; and dilute to 1 liter with reagent water in a volumetric flask. One ml of this solution is equal to 1 mg of nitrate ion.

3. Sulfuric Acid. Concentrated.

4.26.4 Procedure

1. Prepare a series of standards by diluting 0, 5, 10, 15, 20, 30, 40, and 50-ml portions of the KNO_3 solution to 1 liter with reagent water in separate volumetric flasks. These solutions will have nitrate ion concentrations of 0, 5, 10, 15, 20, 30, 40, and 50 ppm respectively.

NOTE: A calibration curve must be prepared independently for each photometer.

2. Plot transmittance vs. ppm nitrate on semi-log paper.

3. Pipet 5.0-ml portions of the sample to be analyzed into each of two clean, dry 50-ml beakers.

4. To one sample, add 0.2 ml of brucine alkaloid solution.

5. To both samples, add 10 ml of H_2SO_4. Add the H_2SO_4 slowly, and mix it thoroughly.

6. To the sample not treated with brucine, add 10 ml of reagent water. Swirl to mix; cool to room temperature, and transfer a portion of the sample to the photometer cell. Use this cell to adjust the Spectronic 20 to 100-percent transmittance at 470 mμ wavelength.

7. When the brucine-treated sample has stood for at least 3 min but not longer than 10 min, add 10 ml of reagent water; mix; and cool to room temperature. Transfer to a photometer cell as before, and determine the reading. Read the nitrate ion content equivalent to the photometer reading from the calibration curve.

NOTE: In the range of nitrate concentration from 0 to 50 ppm, an accuracy of 0.5 ppm can be obtained. Samples above 50 ppm should be diluted with reagent water and the result multiplied by the proper factor.

4.27 COPPER DETERMINATION (METHOD WC-21)

4.27.1 Summary of Method

This method is based on the measurement of the intensity of the yellow color of the cuprous complex of 2,9 dimethyl-1, 10-phenanthroline (neo-cuproine). Full development of the color takes place over the pH range from 2.3 to 9.0. However, a buffer phase is used to produce an aqueous phase with a pH of 4.0 to 6.0. The copper is reduced with hydroxylamine hydrochloride, and the pH of the solution is adjusted with a sodium acetate solution. The cuprous ion is then reacted with neo-cuproine, and the yellow complex is extracted with chloroform. The method follows Beer's Law up to a concentration 1000 ppb Cu. The transmittance is measured at 457μ on the DU-Spectrophotometer, using a 10-cm cell.

4.27.2 Reagents and Materials

1. Chloroform Solvent. Mix 9 volumes of chloroform ($CHCl_3$) with 1 volume of isopropyl alcohol.

2. Copper Standard Solution (1 ml ~ 2μ g Cu). Weigh out 0.200 g of electrolytic copper. Place it in a 250-ml beaker under a hood; add 3 ml of water and 3 ml of

HNO_3, and cover the beaker with a watch glass. After the metal has completely dissolved, add 1 ml of H_2SO_4 (sp. gr. 1.84) and heat on a hot plate just short of complete dryness. Do not bake the residue. Cool the residue; wash down the sides of the beaker and the bottom of the watch glass; and again evaporate the solution nearly to dryness to expel the HNO_3. Cool the residue; dissolve it in water, and dilute the solution to 1 liter. Take 100 ml of the prepared solution, and dilute it to 1 liter with water. This solution has a concentration of 0.02 mg/ml Cu. Take 100 ml of this solution, and dilute it to 1 liter with water. One ml of this standard solution contains 2 μg of Cu or, when diluted to 250 ml with water, it contains 8 ppb Cu.

3. Hydrochloric Acid (sp. gr. 1.19). Concentrated hydrochloric acid (HCl).

4. Hydroxylamine Hydrochloride Solution (200 g/liter). Dissolve 40 g of hydroxylamine hydrochloride ($NH_2OH \cdot HCl$) in water, and dilute to 200 ml.

5. Isopropyl Alcohol. Copper-free.

6. Neo-Cuproine Solution (1 g/liter). Dissolve 0.1 g of neo-cuproine (2, 9-dimethyl-1, 10-phenanthroline) in 50 ml of isopropyl alcohol. Dilute the solution to 100 ml with water.

7. Sodium Acetate Solution (275 g/liter). Dissolve 55 g of sodium acetate trihydrate ($NaC_2H_3O_2 \cdot 3H_2O$) in water, and dilute to 200 ml. Add 10 ml of $NH_2OH \cdot HCl$ solution and 10 ml of neo-cuproine solution. Extract copper impurities in the solution with 50 ml of $CHCl_3$, discarding the chloroform layer.

4.27.3 Procedure

1. Prepare a series of standard copper solutions by pipetting 1, 2, 5, 10, and 15-ml aliquots into separate 250-ml volumetric flasks. Also, prepare a blank with no copper standard added. Add 0.4 ml of hydrochloric acid (HCl), and dilute to mark with water.

2. Transfer to 500-ml separatory funnels.

3. Add 1 ml of $NH_2OH \cdot HCl$ solution, and shake for 30 sec.

4. Add 10 ml of $NaC_2H_3O_2$ solution, and shake for 30 sec.

5. Add 4 ml of neo-cuproine solution, and shake for 30 sec.

6. Add 25 ml of chloroform solvent, and shake for 1 min.

7. Allow the funnel to stand 5 min to permit aqueous and chloroform layers to separate.

8. Drain the chloroform layer into a dry 125-ml Erlenmeyer flask, and repeat step 6 with 15 ml of chloroform.

9. Combine chloroform extractions in 125-ml Erlenmeyer flask, and dilute to 50 ml with isopropyl alcohol.

10. Read the percent transmittance on the DU-Spectrophotometer at 457 μ, using 10-cm cells.

11. Secure a fresh sample, and add 250 ml to a 500-ml separatory funnel. Add 1 ml of concentrated HCl.

12. Repeat steps 3, 4, 5, 6, 7, 8, and 9 above.

13. Repeat step 10, and obtain the copper concentration from the curve produced from the previous data.

4.27.4 Calculations

Plot the readings from step 10 above vs. ppb copper on semi-log paper.

NOTE: The precision for the method is:

$S_T = 0.008 \times +0.9$, where:

S_T = precision in ppb

X = concentration of copper in sample in ppb.

4.28 HYDRAZINE DETERMINATION (METHOD WC-22)

4.28.1 Summary of Method

This method is based on the intensity of the yellow-red complex ion formed when Para-Dimethylaminobenzaldehyde is added to a sample containing Hydrazine. The transmittance is read on a spectrophotometer at a wavelength of 458 mμ using 1-cm cells. This method is good for the range of from 0.01 to 0.24 ppm.

4.28.2 Reagents and Materials

1. 6N Hydrochloric Acid.

2. Para-Dimethylaminobenzaldehyde Solution. Dissolve 4.0 g of para-dimethylaminobenzaldehyde in a solution consisting of 200 ml of methyl alcohol (CH_3OH) and 20 ml of concentrated HCl. Store in a dark bottle. It is good for two weeks.

3. Hydrazine, Standard Solution (1 ml = 0.1 mg N_2H_4). Dissolve 0.3276 g of hydrazine dihydrochloride ($N_2H_4 \cdot 2HCl$) in a solution of 100 ml of water and 10 ml of concentrated HCl. Dilute with water to 1 liter in a volumetric flask, and mix.

4.28.3 Procedure

NOTE: Hydrazine reacts rapidly with oxygen in the air when the solution is alkaline; it is necessary that 2 ml of 6N HCl be added to the sample bottle before the sample is collected.

1. Prepare a 1-ppm hydrazine working solution by diluting 1 ml of the Hydrazine Standard with water in a 100-ml volumetric flask.

2. Pipet 2 ml of 6N HCl into each of five 100-ml graduated mixing cylinders.

3. Pipet 0, 1, 5, 10, and 50-ml aliquots of the working solution into the mixing cylinders; these represent 0, 0.01, 0.05, 0.1, and 0.5 ppm respectively.

4. Dilute each cylinder to 100 ml with water.

5. Carefully pipet 5 ml of para-dimethylaminobenzaldehyde into each cylinder.

6. Stopper and mix contents of each cylinder, and let stand 10 min for full color development.

7. Read on the spectrophotometer at 458 mμ, and plot the transmittance vs. concentration on semi-log paper.

8. Secure a fresh 100-ml sample that has been properly acidified.

9. Pipet a portion into a 100-ml mixing cylinder, and dilute to 100 ml if necessary so that the concentration will fall within the standard curve.

10. Repeat steps 5, 6, and 7 above, and obtain the hydrazine concentration.

4.28.4 Calculations

$$\text{Hydrazine (ppm)} = \frac{\text{concentration from curve} \times 100}{\text{volume of sample used}}$$

4.29 GRAVIMETRIC CHLORIDE DETERMINATION (METHOD WC-23)

4.29.1 Summary of Method

Chloride ion is precipitated from an acidified solution with silver nitrate. The precipitate is collected and weighed on a millipore filter. The method is applicable for greater than 1 mg of chloride ion in a liter of solution.

4.29.2 Reagents and Materials

1. Concentrated Nitric Acid.

2. Silver Nitrate Solution (50 g/l). Dissolve 5 g of silver nitrate ($AgNO_3$) in 100 milliliters of chloride-free water, and store in a brown bottle.

4.29.3 Procedure

1. Wash all glassware and equipment with dilute nitric acid and chloride-free water.

2. Place a washed and dry 47-mm millipore filter in a 1-liter filter funnel.

3. Acidify the sample with about 5 ml of HNO_3, and mix well.

4. Transfer a known volume of the sample to the 1-liter filter funnel, and filter with suction into a clean 1-liter filter flask.

5. Wash with water, and save filtrate and all washes.

6. Quantitatively transfer filtrate and washes to a 1500-ml beaker, and add 5 ml of silver nitrate solution.

7. Remove and discard the millipore filter, and wash the funnel thoroughly.

8. Weigh a washed and dried filter on the analytical balance to the nearest 0.1 mg, and place it in the filter funnel.

9. Filter the solution derived from step 6 through the filter funnel; then, wash the beaker and funnel with water, using a wash bottle.

10. Remove the filter carefully, and transfer it to a 2-in. dia planchet. Dry the filter for 30 min at 110 C.

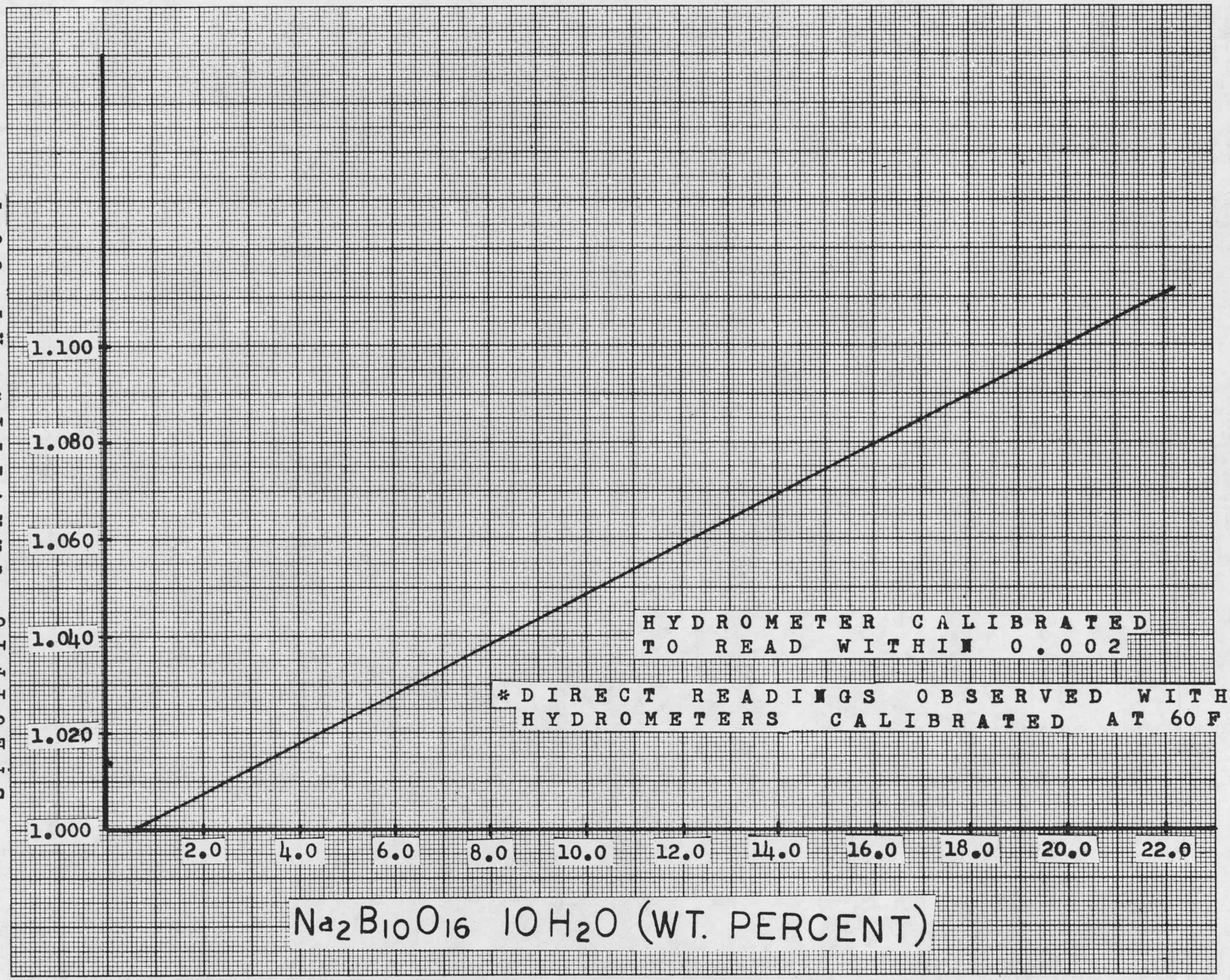
11. Cool in a desiccator, and weigh to the nearest 0.1 mg on the balance.

4.29.4 Calculations

$$\text{ppm } Cl^- = \frac{\text{mg of ppt} \times 0.24737}{V}$$

Where:

V = sample volume (from step 4) in liters.



CONCENTRATION VS. SPECIFIC GRAVITY OF SODIUM PENTABORATE AT 80F

FIG. 4.1

5. RADIOCHEMISTRY PROCEDURES

5.1 RADIOCHEMISTRY METHODS

This section is a collection of radiochemical procedures for determining the activity of selected radioisotopes. The method specified for each isotope was chosen on the basis of simplicity of the chemical operations involved, the time required for completion, and the required degree of decontamination (based on the distribution of activity released from UO_2 fuel elements to the coolant) from other radioisotopes expected to be present.

The manipulations and techniques of radiochemistry and analytical chemistry are similar except for the final determination. In analytical chemistry analysis, the element is identified by weight of precipitate, by titration, or by transmission or absorption of light. In a radiochemical analysis, the unknown is isolated by performing a series of chemical separations that are specific for the radionuclide to be assayed. Therefore, the unknown in radiochemical analysis is determined by the energy and disintegration rate of its radiation.

5.2 APPARATUS

1. Normal laboratory glassware is required.

2. Glass Fiber Filters. Filters must be 1-in. dia x 0.01-in. thick. Must retain fine precipitates adequately, and must maintain constant weight to ±0.01 mg during filtration and drying.

3. Filter Holder. The filter holder must hold the 1-in. dia filters rigidly in place during filtration.

4. Desiccator. The desiccator must hold four 1-in. dia filters similar to those of Fisher Cat. No. 8-615.

5. Oven. The oven should be of the gravity-convection type and able to supply uniform heat at 110 C to a ±0.5 C.

6. Gamma-Ray Spectrometer. A sodium iodide scintillation detector assembly connected to the appropriate amplifier and pulse height analyzer.

7. Analytical Balance. Capable of weighing to the nearest 0.1 mg.

8. Resin Column. A 1-cm buret cut to a length of about 35 cm.

9. Centrifuge. A clinical centrifuge shall be used. The head should accommodate 50-ml centrifuge tubes.

10. Proportional Counting System. A proportional detector connected to appropriate amplifier and scaler type system.

11. Evaporator Feeder. Able to evaporate large volume samples onto a planchet.

12. Infra-Red Lamp.

5.3 REAGENTS AND WATER PURITY

5.3.1 Purity of Reagents

Reagent grade chemicals shall be used to prepare reagents. Unless otherwise indicated, all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society. Other reagents may be used, provided they are of sufficient purity to give the same accuracy.

5.3.2 Purity of Water

All water used in preparing the reagents and in standardization of these reagents shall be demineralized water from the LACBWR demineralized water system, further purified by distillation and ion exchange through the laboratory system.

5.4 IODINE (METHOD NO. RC-1)

5.4.1 Summary of Method

The iodine isotopes are separated from the mixed fission product mixture by oxidizing to I_2 with nitrate and extracting into carbon tetrachloride (CCl_4). The iodine is reduced to iodide and extracted into sulfurous acid solution. This oxidation-reduction is repeated once more, and the iodide is precipitated as palladium iodide (PdI_2) for weighing and determining the total disintegration rate of I-131 and I-133.

5.4.2 Reagents and Materials

1. Ethyl Alcohol. Either CP ethyl alcohol or denatured ethyl alcohol (denatured according to Formula No. 30, Regulation No. 3 and its Appendix, U.S. Bureau of Internal Revenue) shall be used.

2. 2M Sodium Carbonate. Dissolve 21 g of sodium carbonate (Na_2CO_3) in 100 ml of water.

NOTE: Heat to get complete dissolution.

3. 1M Hydroxylamine Hydrochloride. Dissolve 7 g hydroxylamine hydrochloride ($NH_2OH \cdot HCl$) in 100 ml water. Store in cool place.

4. 1N Nitric Acid (HNO_3). Measure 64 ml of 15.7N nitric acid (HNO_3), and dilute to 1 liter with water.

5. 0.1M Palladium Chloride. Dissolve 21.4 g of palladium chloride ($PdCl_2 - 2H_2O$), and dilute to 1 liter with water.

6. Iodine Carrier (10 mg/ml). See Sec. 2.10 on standardization of carrier.

7. These additional chemicals are needed:

(a) carbon tetrachloride (CCl_4)

(b) sulfurous acid (H_2SO_3)

(c) sodium nitrite ($NaNO_2$), solid

(d) sodium hypochlorite (about 5 percent)

8. 15.7N Nitric Acid. Concentrated nitric acid.

5.4.3 Procedure

1. To the sample of the primary water (50 ml or adjust to 50 ml), add 2 ml of standardized iodine carrier.

2. Add 5 ml of 2M sodium carbonate (Na_2CO_3) and 15 ml of 5-percent sodium hypochlorite (5.25-percent household bleach is satisfactory). Heat to boiling, and cool.

3. Transfer to a 250-ml separatory funnel, and add 25 ml of carbon tetrachloride (CCl_4).

4. Acidify by addition of concentrated nitric acid (about 10 ml).

5. Add 15 ml of 1M hydroxylamine hydrochloride ($NH_2OH \cdot HCl$), and shake separatory funnel until the brown color leaves the aqueous layer. (Blue color will develop in the CCl_4 phase.)

CAUTION: Relieve gas pressure which is built up during the shaking operation. With stopper inserted in the separatory funnel, turn over and open the stopcock.

6. If no color develops in either phase, repeat step 4 until blue-purple color appears in the CCl_4 phase. (Shake separatory during this operation.)

7. Transfer the CCl_4 layer to a clean separatory flask; and wash the original aqueous layer twice more with 25 ml of carbon tetrachloride, 5 ml of nitric acid and 3 ml of hydroxylamine hydrochloride. Combine all extracts in the original separatory flask. Discard the aqueous layers as radioactive waste.

8. Add 2 ml of 1N nitric acid and 5 ml of sulfurous acid (H_2SO_3) to the combined carbon tetrachloride washes from step 7.

9. Shake and transfer aqueous layer to a clean separatory flask.

10. Wash the CCl_4 phase twice more, using 5 ml of 1N HNO_3 and 5 ml of H_2SO_3. Combine all aqueous phases, and discard the organic (CCl_4) layer.

11. Add 25 ml of carbon tetrachloride to the flask containing the aqueous phases, and cautiously add solid sodium nitrite ($NaNO_2$) by using a spatula; shake separatory funnel until the brown color leaves the aqueous layer (as shown by blue color in the CCl_4 phase).

CAUTION: Relieve the gas pressure that is built up during the shaking operation.

12. If no color appears in either phase, repeat step 11 until blue color appears in the organic phase. Transfer CCl_4 phase to clean separatory flask.

13. Repeat step 11, and discard the aqueous layer.

14. Add 10 drops of 1N nitric acid, 10 ml of H_2O and 2 ml of sulfurous acid (H_2SO_3) to the combined CCl_4 layers.

15. Shake, and transfer the aqueous layer to a clean 50-ml beaker.

16. Wash the CCl_4 phase twice more, using the same mixture as for step 14.

17. Combine washes in the 50-ml beaker.

NOTE: Discard the CCl_4 layer.

18. Heat the combined washes to boiling (for at least 2 min) to drive off SO_2.

19. Add about 3 ml of palladium chloride ($PdCl_2$) solution to precipitate the palladium iodide (PdI_2).

20. Digest the precipitate on a hot plate for 1 hr.

21. Filter with suction the precipitate onto a weighed glass fiber filter placed in the filter holder.

22. Rinse the beaker with ethyl alcohol, and pour the rinsings through the filter.

23. Wash the precipitate with approximately 10 ml of ethyl alcohol and 10 ml of diethyl ether.

24. Place the filter containing the precipitate in an oven, and dry at 110 C for 30 min. Cool in a desiccator for 15 min.

25. Weigh the filter and precipitate on an analytical balance to the nearest 0.1 mg.

26. Subtract the tare weight of the filter to obtain the weight of the precipitate.

27. Mount the filter on a suitable holder, and radioassay the precipitate with a gamma-ray spectrometer.

5.4.4 Calculations

Only the 9.05-day half-life I-131 and the 21-hr half-life I-133 are counted. Both are beta and gamma emitters and may be determined by selectively counting either beta or gamma.

1. Plot the gamma spectrum.

2. Determine the disintegration rate of the 21-hr I-133 by integrating the area under the 0.53-Mev photo peak.

3. Determine the disintegration rate of the 8.05-day I-131 by determining the area under the 0.364-Mev photo peak.

4. The disintegration rate of I-131 and -133 is calculated using the equation:

$$\text{dpm/ml} = \frac{C}{(V)(E)(Fy)}$$

where

C = Counts per minute for I-131 and -133 each, corrected for background counts and extrapolated back to sampling time.

E = Counting efficiency.

NOTE: This factor should include the fractional abundance of the gamma ray and the photo-peak detection efficiency.

Fy = Fractional chemical yield for the separation.

V = Volume of sample in ml.

5.5 ION EXCHANGE SEPARATION PROCEDURE FOR NICKEL, MANGANESE, COBALT, COPPER AND IRON (METHOD RC-2)

5.5.1 Summary of Method

This method is based on the fact that, except for Ni^{++}, these ions form complex metal-chloride ions with the Cl^- present on the resin. Ni^{++} has no affinity for the resin and passes through the resin. The remaining complex ions can be eluted by reducing the molarity of the HCl solutions and collected quantitatively as separate solutions for analysis.

5.5.2 Apparatus

Resin Column. Use a 1-cm dia buret cut to a length of about 35 cm.

5.5.3 Reagents

1. (1-2) Acetic Acid. Mix 1 volume of 17.4N glacial acetic acid with 2 volumes of water.

2. 14.8N Ammonium Hydroxide. Concentrated ammonium hydroxide (HN_4OH). For dilutions use 67.5 ml times the desired N diluted to 1 liter.

3. Cobalt Carrier. 10 mg/ml.

4. Nickel Carrier. 10 mg/ml.

5. Manganese Carrier. 10 mg/ml.

6. Copper Carrier. 10 mg/ml.

7. Iron Carrier. 10 mg/ml.

8. 12.1N Hydrochloric Acid. Concentrated HCl. For dilutions use 83 ml times the desired normality diluted to 1 liter.

9. 10N Potassium Hydroxide Solution. Dissolve 561 g of KOH in water, and dilute to 1 liter.

10. Solid Potassium Nitrite. (KNO_2).

11. 1-20 Potassium Hydroxide Solution. Dilute 1 volume of 10N KOH with 20 volumes of water.

12. 36N Sulfuric Acid. Concentrated H_2SO_4. For dilutions use 28 ml times the desired normality diluted to 1 liter.

13. Ethyl Alcohol. Either CP ethyl alcohol or denatured ethyl alcohol (denatured according to formula No. 30, Regulation No. 3 and its appendix, U.S. Bureau of Internal Revenue) shall be used with these methods.

14. Saturated Sodium Bromate Solution. Dissolve 40 g of sodium bromate ($NaBrO_3$) in 100 ml of water.

15. Diethyl Ether.

16. 1 Percent Dimethylglyoxime. Purchased from Fisher Scientific Co., Cat. No. 50-D-52.

17. 2 Percent Benzoin Oxime. Dissolve 2 g of benzoin oxime in 98 ml of ethyl alcohol.

18. 15.7N Nitric Acid. Concentrated HNO_3. For dilutions use 64 ml times the desired normality diluted to 1 liter.

19. Methyl Orange Indicator.

20. Ammonium Nitrate Solution. Dissolve 1 g of NH_4NO_3 in water, and dilute to 100 ml.

21. Silver Nitrate Solution. Dissolve 5 g of $AgNO_3$ in water, and dilute to 100 ml.

22. Dowex 1x8, 100-200 mesh anion exchange in chloride form.

5.5.4 Resin Preparation

Add about 50 ml of new Dowex 1x8, 100-200 mesh resin (in the Cl^- form) to a 150-ml graduated beaker. Add sufficient demineralized water to cover resin, and stir. Filter

resin through a Whatman No. 41 filter paper to wash, and transfer back to 150-ml beaker. Add enough concentrated HCl to cover resin, and stir. Prepare a column by placing a small ball of glass wool into a buret about 1-cm dia and 35-cm long. Slurry the resin into the column; open the stopcock and catch the eluate in a beaker. Never allow the level of the liquid to get below the level of the resin. Pass 75 ml more of concentrated HCl through the column to condition the resin. If the column is not to be used immediately, add about 5 to 10 ml of concentrated HCl to cover resin, and wrap a piece of Parafilm securely over the top of the column to prevent evaporation.

5.5.5 Procedure

1. Add 2 ml each of Mn and Fe carriers and 1 ml each of Co, Ni, and Cu carriers to the sample in a 125-ml Erlenmeyer flask.

2. Add 20 ml of concentrated nitric acid (16NHNO$_3$), and evaporate to near dryness.

3. Add 10 ml of concentrated hydrochloric acid (12N HCl), and again evaporate to near dryness.

4. Add 10 ml of 12N HCl, and again evaporate to near dryness.

5. Cool the residue; pick it up with a polyethylene dropper; and transfer it to the conditioned column with a minimum of 12N HCl.

6. Elute transfer solution to just above the resin, and collect eluate in a 150-ml beaker.

7. Use 12N HCl, and pass 25 ml through the column. Collect eluate in same beaker used in step 6.

8. Label, and save for nickel analysis.

9. Use 8N HCl, and pass 30 ml through the column. Collect eluate in a clean 150-ml Erlenmeyer flask.

10. Label, and save for manganese analysis.

11. Use 4N HCl, and pass 30 ml through the column. Collect eluate in a clean 150-ml beaker.

12. Label, and save for cobalt analysis.

13. Use 2.5N HCl, and pass 30 ml through the column. Collect eluate in a clean 150-ml beaker.

14. Label, and save for copper analysis.

15. Use 0.5N HCl, and pass 30 ml through the column. Collect eluate in a clean 150-ml beaker.

16. Label, and save for iron analysis.

5.5.6 Nickel Analysis

1. To the nickel eluted in step 8 of Sec. 5.5.5, add 14.8N NH_4OH to pH=8.

2. Add 15 ml of 1 percent dimethylglyoxime solution.

3. Filter the precipitate with suction onto a weighed glass fiber filter placed in the glass filter holder.

4. Rinse the beaker with water, and pour the rinsings through the filter.

5. Wash the precipitate with approximately 10 ml of water.

6. Place filter containing the precipitate in an oven, and dry at approximately 110 C for 30 min. Cool in a desiccator for 20 min.

7. Weigh the filter and precipitate on an analytical balance to the nearest 0.1 mg.

8. Subtract the tare weight of the filter to obtain the weight of the precipitate.

9. Mount the filter in a 2-in.-dia stainless steel planchet, and count on the gamma analyzer.

5.5.6.1 Calculations. Chemical yield for Ni $= \frac{0.2032 \times \text{mg of ppt}}{\text{ml of carrier added}}$. The nickel characteristics are as follows:

Isotope	Half-Life	γ Energy - Mev	
Nickel 57 (Ni-57)	36 hr	1.38	(72 Percent)
		1.75	(14 Percent)
		1.92	(14 Percent)
Nickel 65 (Ni-65)	2.56 hr	1.48	(25 Percent)
		1.114	(15.8 Percent)

Calculations are performed in the following manner:

1. Determine the disintegration rate for Ni-57 by determining the area under the 1.38-Mev photo peak.

2. Determine the disintegration rate for Ni-65 by determining the area under the 1.48-Mev photo peak.

3. The disintegration rate of Ni-57 and -65 is calculated using the equation:

$$\text{dpm/ml} = \frac{\text{cpm}}{(V)\,(E)\,(Fy)}$$

where

cpm = Counts per minute for Ni-57 and -65 each, corrected for background and extrapolated back to sampling time.

E = Counting efficiency.

NOTE: This factor should include the fractional abundance of the gamma ray and the photo-peak detection efficiency.

Fy = Fractional chemical yield for the separation.

V = Sample volume in ml.

4. Plot a decay curve on semi-log paper of the corrected cpm vs. time.

NOTE: A decay curve should be taken over a period of several hours. (Ni-57 should be followed for one week, counting at a minimum of one time a day; Ni-65 should be counted at a minimum of every 2 hr for a period of 24 hr and extrapolated back to sampling time.)

5.5.7 Manganese Analysis

1. To the manganese eluted in step 10 of Sec. 5.5.5, add 5 ml of concentrated nitric acid, and evaporate to about 5 ml on a hot plate.

2. Add 2 ml of saturated sodium bromate solution, and boil for 3 min to precipitate manganese dioxide (MnO_2), which is brown.

3. Cool and filter the precipitate onto a weighed glass fiber filter with suction in a glass filter tower.

4. Rinse the Erlenmeyer flask with 20 ml of water, and pour the rinsings through the tower.

5. Wash the precipitate with 10 ml of ethyl alcohol and 10 ml of diethyl ether.

6. Place the filter containing the precipitate in an oven, and dry at 110 C for 30 min. Cool in a desiccator for 20 min.

7. Weigh the filter and precipitate on an analytical balance to the nearest 0.1 mg.

8. Subtract the tare weight of the filter to obtain the weight of the precipitate.

9. Mount the filter in a 2-in.-dia planchet, and count immediately on an Internal Proportional Counter.

5.5.7.1 Calculations. Chemical yield for $Mn = \frac{(0.6320)\ (\text{mg of ppt})}{\text{ml of carrier added}}$.

Only the 2.6-hr half-life Mn-56 and the 314-day half-life Mn-54 are to be studied.

Calculations are as follows:

1. Count on an IPC every 2 hr until the decay curve for Mn-56 can be determined.

2. Plot the decay curve, and extrapolate back to sampling time.

3. Determine the disintegration rate for Mn-56 by using the equation:

$$\text{dpm/ml} = \frac{\text{cpm}}{(V)\ (E)\ (Fy)}$$

where

cpm = Counts per minute of sample minus background extrapolated back to sample time.

E = IPC counting efficiency.

V = Sample volume in ml.

Fy = Fractional chemical yield for the separation.

4. After a minimum of 20 hr, count the sample in the gamma analyzer to determine the Mn-54 activity.

5. The count rate of 290-day half-life Mn-54 is found by determining the area under the 0.835-Mev photo peak.

6. The disintegration rate of the Mn-54 can be determined by using the formula:

$$dpm/ml = \frac{cpm}{(V)\ (E)\ (Fy)}$$

where

cpm = Counts per minute of sample minus background.

V = Sample volume in ml.

E = Counter efficiency.

NOTE: This factor should include the fractional abundance of the gamma ray and the photo-peak detection efficiency.

Fy = Fraction chemical yield for the sample separation.

7. Correct the sample for decay by referring to page 89 in the Decay Correction Factors Handbook, or use formula:

$$A = A_o\ e^{-0.693\ t/T_{1/2}}$$

5.5.8 Cobalt Analysis

1. Evaporate the cobalt eluted in step 12 of Sec. 5.5.5 to near dryness in the beaker. Add 1 ml of 6N HCl.

2. Transfer with about 10 ml of water to a 50-ml centrifuge tube.

3. Add 10N KOH solution dropwise to the solution until a precipitate forms. Then, add 2 ml in excess.

4. Place the centrifuge tube in a water bath, and boil for about 15 min.

5. Cool and centrifuge for 2 min, and discard the supernate to radioactive waste.

6. Wash the precipitate with 10 ml of 1 to 10 dilution of 10N KOH solution, and discard the washings to waste.

7. Dissolve the precipitate in 10 ml of 6N acetic acid, and dilute to 20 ml with water.

8. Add 1 g of potassium nitrite (KNO_2), and heat to from 50 to 60 C.

9. Swirl frequently until the reaction ceases (approximately 45 min). Color should be yellow at this time.

10. Cool in an ice bath for 30 min.

11. Filter the precipitate with suction onto a weighed glass fiber filter placed in the glass filter tower.

12. Rinse the centrifuge tube with ethyl alcohol, using a polyethylene dropper; and transfer the rinsings to the tower.

13. Wash the precipitate with 10 ml of ethyl alcohol and 10 ml of diethyl ether.

14. Place the filter containing the precipitate in an oven, and dry at 110 C for 30 min. Cool in a desiccator for 20 min.

15. Weigh the filter and precipitate on an analytical balance to the nearest 0.1 mg.

16. Subtract the tare weight of the filter to obtain the weight of the precipitate.

17. Mount the filter in a 2-in.-dia planchet, and count on the gamma analyzer.

5.5.8.1 Calculations. Chemical yield for Ni $= \frac{0.1253 \times \text{mg of ppt}}{\text{ml of carrier used}}$.

The cobalt activity characteristics are as follows:

Isotope	Half-Life	γ Energy - Mev	
Cobalt 58 (Co-58)	71 days	0.808	(100 Percent)
Cobalt 60 (Co-60)	5.27 years	1.17	(100 Percent)
		1.33	(100 Percent)

1. Determine the disintegration rate for Co-58 by determining the area under the 0.808-Mev photo peak.

2. Determine the disintegration rate for Co-60 by determining the area under the 1.33-Mev photo peak.

3. The disintegration rate of Co-58 and Co-60 is calculated by using the equation:

$$dpm/ml = \frac{cpm}{(V)\ (E)\ (Fy)}$$

where

cpm = Counts per minute for Co-58 and Co-60 each, corrected for background and for decay.

E = Counting efficiency.

NOTE: This factor should include the fractional abundance of the gamma ray and the photo-peak detection efficiency.

Fy = Fractional chemical yield for the separation.

V = Sample volume in ml.

5.5.9 Copper Analysis

1. Evaporate the copper eluted in step 14 of Sec. 5.5.5 to near dryness on a hot plate.

2. Add 5 ml of 2N HCl to the residue.

3. Add concentrated NH_4OH dropwise until the solution is deep blue.

4. Heat to about 80 C, and add 3 ml of 2 percent benzoin oxime solution.

5. Filter the precipitate with suction onto a weighed glass fiber filter placed in the glass filter tower.

6. Rinse the beaker with water, and transfer it to the tower.

7. Wash the precipitate with 5 ml of water and 10 ml of hot ethyl alcohol.

8. Place the filter containing the precipitate in an oven, and dry at 110 C for 30 min. Cool in a desiccator for 20 min.

9. Weigh the filter and precipitate on the analytical balance to the nearest 0.1 mg.

10. Subtract the tare weight of the filter to obtain the weight of the precipitate.

11. Mount the filter in a 2-in.-dia planchet, and count on the gamma analyzer.

5.5.9.1 Calculations. Chemical yield for Cu $= \frac{0.2202 \times \text{mg of ppt}}{\text{ml of carrier added}}$.

The copper activity is primarily composed of 12.8-hr half-life Cu-69.

1. Determine the disintegration rate by determining the area under the 0.51 Mev annihilation peak for Cu-64.

2. The disintegration rate of Cu-64 is calculated by using the equation:

$$\text{dpm/ml} = \frac{\text{cpm}}{(V)\,(E)\,(Fy)}$$

where

cpm = Counts per minute, corrected for background and decay.

E = Counting efficiency.

NOTE: This factor should include the photo-peak detection efficiency and annihilation abundance.

Fy = Fractional chemical yield for the separation.

V = Sample volume in ml.

5.5.10 Iron Analysis

1. To the iron eluted in step 16 of Sec. 5.5.5 add a small volume of filter-paper pulp solution.

2. Add 2 drops of concentrated HNO_3 to oxidize the Iron (II) to Iron (III).

3. Heat to boiling, and add 2 drops of methyl orange indicator.

4. Add 5N NH_4OH (filtered) to the iron solution until it becomes alkaline, as shown by a color change from red to yellow (approximately 6 ml).

5. Allow the precipitate to coagulate on the macerated filter pulp and settle for 20 min (no longer).

6. Wash and filter through Whatman No. 41 filter paper.

7. Continue washing with a solution of ammonium nitrate (1 g/100 ml) until the filtrate yields no precipitate with $AgNO_3$ and nitric acid. (Treat a fresh portion of the filtrate with a few drops of HNO_3 and then with a few drops of $AgNO_3$ solution.)

8. Transfer the paper and precipitate to a weighed porcelain crucible.

9. Char off the paper carefully with a minimum of heat, using a burner.

10. After the paper is burned off, ignite the crucible in the muffle furnace for 1 hr at 700 C. The precipitate is FE_2O_3.

11. Cool in a desiccator for 20 min, and weigh the crucible and precipitate on the analytical balance to the nearest 0.1 mg.

12. Subtract the tare weight of the crucible to obtain the weight of the precipitate.

13. Mount the precipitate by transferring it to a 2-in.-dia planchet, and count it on the gamma analyzer.

5.5.10.1 Calculations. Chemical yield $= \frac{0.6994 \times \text{mg of ppt}}{\text{ml of carrier added}}$.

The iron activity characteristics are as follows:

Isotope	Half-Life	γ Energy - Mev	
Iron 59	45 days	1.290	(44 Percent)
		1.102	(56 Percent)

1. Determine the disintegration rate for Fe-59 by determining the area under the 1.29-Mev photo peak.

2. The disintegration rate of Fe-59 is calculated by using the equation:

$$dpm/ml = \frac{cpm}{(V)\,(E)\,(Fy)}$$

where

cpm = Counts per minute for Fe-59, corrected for background and decay.

E = Counting efficiency.

NOTE: This factor should include the fractional abundance of the gamma ray and the photo-peak detection efficiency.

Fy = Fractional chemical yield for separation.

V = Sample volume in ml.

3. Correct the sample for decay by referring to page 78 in the Decay Correction Factors Handbook.

5.6 GROSS ALPHA ACTIVITY (METHOD RC-3)

5.6.1 Summary of Method

The coolant shall be analyzed by evaporating a sample of it on a stainless steel planchet and counting on a proportional counter to determine gross alpha activity.

5.6.2 Reagents and Materials

Concentrated nitric acid (15.7N) (HNO_3).

5.6.3 Procedure

1. Add 5 ml concentrated (15.7N) nitric acid (HNO_3) to 500 ml of primary coolant in an evaporator feeder. (See Fig. 5.1.)

2. Using an evaporator feeder, evaporate the 500 ml derived from step 1 above onto a 2-in.-dia stainless steel planchet.

3. Count on the proportional flow counter.

5.6.4 Calculations

1. Count for 1 hr at the alpha voltage setting.

2. Correct for a 1-hr planchet background, and calculate μc/ml as:

$$\mu c/ml = \frac{C}{2.22 \times 10^6 \, (E) \, (V)}$$

where

C = Alpha count rate in net counts per minute.

E = Counter efficiency.

V = Volume of original sample in ml.

2.22×10^6 = Conversion factor from disintegrations per minute to micro curies.

5.7 CESIUM METHOD (METHOD RC-4)

5.7.1 Procedure

1. To the sample to be analyzed add a known amount of standardized Cs carrier and about 5 mg each of Rb, Ba, Sr, and Fe carriers. (A higher yield is obtained if all reagents are kept in an ice bath.) Add 12N NaOH until the solution is just basic; then, add 1 ml of 2M Na_2CO_3. Centrifuge, and discard the precipitates.

A 10-ml sample is used for Cs-138 analyses; for Cs-137 analyses 500 ml is usually evaporated to dryness after carrier is added. The dried solids are then picked up with 10 ml of H_2O.

2. Carefully acidify the solution with glacial actic acid, keeping the final volume to 15 ml or less. Stir to eliminate the CO_2 from the solution. Add 3 to 5 ml of HI-BiI_3 reagent (10 g of BiI_3 per 50 ml of 55-percent HI); cool in ice bath for 2 min, and stir vigorously to initiate precipitation. Centrifuge and discard supernate.

3. Wash the precipitate with 8 to 10 ml of a mixture of 1 ml 2N HCl and 7 ml of cold H_2O. Centrifuge, and discard the wash. Add 2 drops of 12N NaOH and 5 ml of H_2O to the precipitate. Centrifuge and transfer the supernate to a clean centrifuge cone.

4. Add 3 ml of concentrated HNO_3, and heat with caution to expel I_2. Use caution when adding HNO_3 to the solution to oxidize I to free I_2. The solution should be clear after boiling.

5. Place in an ice bath, and allow to cool for a few minutes. Add 7 drops of 10-percent H_2PtCl_6, and then add 15 to 20 ml of ethanol. Stir intermittently for 2 min.

6. Slurry precipitate onto a tared 2.5-cm filter paper, and wash with 5 ml of H_2O and 5 ml of ethanol. Dry in an oven at 110 C, and weigh.

5.8 STRONTIUM AND BARIUM METHOD (METHOD RC-5)

5.8.1 Summary of Method

Barium and strontium are separated from fission product mixtures by precipitation with fuming nitric acid. Barium is separated from strontium as the chromate in buffered acetic acid solution, and strontium is precipitated as strontium oxalate.

NOTE: The only important alkaline earth fission products are barium and strontium.

5.8.2 Reagents and Materials

1. Ethyl Alcohol. Either CP ethyl alcohol or denatured ethyl alcohol (denatured according to formula No. 30, Regulation No. 3 and its appendix, U.S. Bureau of Internal Revenue) shall be used for standardization of the carriers.

2. Standardized Strontium Carrier. See Sec. 2 of this volume on Standardization of Carriers.

3. Standardized Barium Carrier. See Sec. 2 on Standardization of Carriers.

4. Lanthanum Carrier. Dissolve 31 g in 1000 ml of water.

5. Iron Carrier (Unstandardized). Dissolve 1 g of iron metal powder in 50 ml of concentrated hydrochloric acid (HCl) plus 50 ml water.

6. 6M Ammonium Hydroxide (NH_4OH). Measure 400 ml of concentrated ammonium hydroxide (NH_4OH) (14.8M), and dilute to 1 liter with water.

7. 6M Nitric Acid (HNO_3). Measure 384 ml of concentrated nitric acid (15.7N) (HNO_3), and dilute to 1 liter with water.

8. 6M Acetic Acid. Measure 200 ml concentrated acetic acid ($HC_2H_3O_2$)(17.4N), and dilute to 500 ml with water.

9. 1.5M Sodium Chromate (Na_2CrO_4). Dissolve 243 g of sodium chromate (Na_2CrO_4) in water, and dilute to 1 liter with additional water.

10. 6M Ammonium Acetate. Dissolve 230 g of ammonium acetate ($NH_4C_2H_3O_2$) in water, and dilute to 500 ml with additional water.

11. Concentrated Ammonium Hydroxide. Normality of concentrated reagent is 14.8N.

5.8.3 Procedure

1. To a 50-ml glass centrifuge tube, add 2 ml of standardized strontium carrier, 2 ml of standardized barium carrier, and 2 ml of unstandardized lanthanum.

NOTE: Sample size should be chosen to contain 2000 to 6000 strontium beta counts per minute at 2π geometry.

2. Add 30 ml of red fuming nitric acid (HNO_3), and stir for 1 to 2 min.

NOTE: While performing step 2, the sample should be cooled in an ice bath.

3. Centrifuge for 2 min, and discard supernate to a plastic waste bottle at least half-full of water.

4. Dissolve the precipitate in about 4 ml of water, and add 15 ml of red fuming nitric acid (HNO_3). (Cool in an ice bath during this operation.)

NOTE: To effect a complete solution when dissolving the precipitate, heating may be necessary.

5. Repeat step 3 above.

6. Dissolve precipitate in 5 to 10 ml of water, and add approximately 1 ml iron carrier (unstandardized) and 2 ml 6M ammonium hydroxide (NH_4OH).

NOTE: $Fe(OH)_3$ scavenging precipitation is made to remove contaminating activities.

7. Centrifuge and decant supernate to a new glass 50-ml centrifuge tube. Discard the precipitate.

NOTE: Note date and time when this step is performed. Date and time are necessary to make correction in calculation for yttrium-90 growth.

8. Neutralize supernate to alk-acid paper by adding 6M nitric acid (NHO_3) dropwise.

9. Add 1 ml 6M acetic acid and 2 ml ammonium acetate.

10. Heat to incipient boiling; while stirring, add 1 ml of 1.5M sodium chromate (Na_2CrO_4).

NOTE: Barium is separated from strontium as the chromate. Strontium remains in solution.

11. Centrifuge for 2 min, and decant supernate to a new clean glass centrifuge tube.

12. Save the precipitate from step 11; rinse the centrifuge tube with ethyl alcohol, and pour the rinsings onto a weighed glass fiber filter placed in the filter holder.

13. Wash the precipitate with approximately 10 ml ethyl alcohol and 10 ml of diethyl ether.

14. Place the filter containing the precipitate in an oven, and dry at 110 C for 20 min. Cool in a desiccator for 10 to 15 min.

15. Weigh the filter and precipitate on an analytical balance to the nearest 0.1 mg.

16. Subtract the tare weight of the filter to obtain the weight of the precipitate.

17. Mount the filter on a suitable holder.

18. With a gamma-ray spectrometer, radioassay the precipitate.

19. To the clear supernate obtained from step 11, add 2 ml of concentrated ammonium hydroxide (NH_4OH).

20. Heat to incipient boiling and, while stirring, slowly add 5 ml saturated ammonium oxalate $(NH_4)_2C_2O_4$.

NOTE: Strontium is precipitated as strontium oxalate ($Sr_2C_2O_4$-H_2O) and is weighed as such.

21. Filter with suction the precipitate onto a weighed glass fiber filter placed in the filter holder, and repeat steps 13, 14, 15, 16, and 17 above.

22. Carry out a beta count using the Proportional Flow Counting System.

5.8.4 Calculations

The barium activity is primarily composed of 83-min half-life Ba-139 and 12.8-day half-life Ba-140 activities. Both are beta and gamma emitters. For the Ba-139 determination, count every 15 min for 1-1/2 hr by following the 0.165-Mev gamma photo peak. For the Ba-140 determination, if Ba-139 is present, begin counting one day after purification from step 10. Then, wait for two weeks, and count daily thereafter for 5 to 10 days.

1. Plot the gamma spectrum.

2. Determine the disintegration rate by determining the area under the 0.165-Mev photo peak for Ba-139.

3. On semi-log paper, plot a decay curve of the corrected counts per minute vs. time.

NOTE: The counting rate of Ba-139 at sampling time is obtained by extrapolating the 83-min decay curve back to sampling time.

4. To determine the contribution of 12.8-day half-life Ba-140 to the sample, allow the sample to equilibrate with its 40-hr half-life La-140 daughter over a period of two weeks. Then, count daily for five days. The count taken one day after separation may be computed because a lanthanum holdback carrier was used in the separation part of the procedure. (See Fig. 5.2 for the curve on Ba-140 decay and growth of La-140 activity.)

5. The disintegration rate of both Ba-139 and Ba-140 is calculated using the equation:

$$\text{dpm} - \text{ml} = \frac{C}{(V)\,(E)\,(Fy)}$$

where

C = Counts per minute corrected for background counts.

V = Factor for volume of sample.

E = Counting efficiency.

Fy = Yield factor.

6. To determine strontium-90, see method RC-6, Sec. 5.9.

5.9 STRONTIUM-90 (METHOD RC-6)

5.9.1 Summary of Method

The precipitated sample of strontium oxalate monohydrate from procedure RC-5 is disintegrated with fuming nitric acid after addition of the yttrium carrier. Strontium and yttrium are co-precipitated as a mixture of oxalate and carbonate salts by the addition of excess sodium carbonate. The precipitate is ignited, then dissolved in nitric acid, and then precipitated as yttrium hydroxide. The yttrium hydroxide is dissolved and finally precipitated as yttrium oxalate for weighing and counting.

NOTE: This method should be used if high purification is required.

5.9.2 Reagents and Materials

1. Ammonium Hydroxide (14.8N). Concentrated ammonium hydroxide (NH_4OH).

2. Ethyl Alcohol. Either CP ethyl alcohol or denatured ethyl alcohol (denatured according to formula No. 30, Regulation No. 3 and its appendix, U.S. Bureau of Internal Revenue) shall be used for this method.

3

3. Ammonium Oxalate Solution ($(NH_4)_2C_2O_4 \cdot H_2O$). Saturated solution.

4. Hydrochloric Acid Solution (1-1). Mix 1 volume of concentrated (12N) hydrochloric acid (HCl) with 1 volume of water.

5. Nitric Acid Solution (2-3). Mix 2 volumes of concentrated (15.7N) nitric acid (HNO_3) with 3 volumes of water.

6. Sodium Carbonate Solution. Dissolve 212 g of sodium carbonate (Na_2CO_3) in water, and dilute to 1 liter with additional water.

7. Strontium Carrier. Refer to Sec. 2 of this volume on standardization of carrier.

8. Yttrium Carrier. Refer to Sec. 2 on standardization of carrier.

9. The following additional chemicals are needed:

(a) ethyl ether
(b) (red) fuming nitric acid
(c) sodium carbonate (Na_2CO_3), solid.

5.9.3 Procedure

1. Place the filter containing the strontium oxalate precipitate in a 25-ml beaker.

2. Add 2.0 ml of standardized yttrium carrier.

3. Add 10 ml of fuming nitric acid (HNO_3), and evaporate to near dryness.

NOTE: After evaporating to near dryness, cool beaker to room temperature.

4. Add 2 ml of fuming nitric acid (HNO_3), and evaporate to near dryness.

5. Add carefully 10 ml of the saturated sodium carbonate (Na_2CO_3) solution and 1 g of solid sodium carbonate (Na_2CO_3).

6. Boil for 5 min on a hot plate, and cool to room temperature.

7. Filter the solution through a fine filter paper. After filtering the solution, wash the precipitate with water.

8. Transfer the filter paper containing the precipitate toa porcelain crucible, and ignite at 700 C for 1 hr in a muffle fumace.

9. Carefully dissolve the residue in nitric acid (2-3) (HNO_3), and transfer to a 100-ml beaker with 20 ml of water.

10. Repeat step 6.

11. Add concentrated ammonium hydroxide (NH_4OH) dropwise until yttrium hydroxide precipitates. Add 5 ml in excess, and transfer to a 50-ml centrifuge tube.

12. Centrifuge and discard the supernate.

13. Wash the precipitate twice with 10 ml of water, and repeat step 12 between each wash.

NOTE: Record the date and time after washing precipitate twice.

14. Dissolve the precipitate in (2-3) nitric acid (HNO_3). Add 2 ml of the strontium carrier solution, and repeat steps 11, 12, and 13.

15. Dissolve the precipitate in 2 ml of (1-1) hydrochloric acid (HCl); dilute to 15 ml with water, and transfer to a 50-ml beaker.

16. Heat the solution to near-boiling, and add 20 ml of saturated ammonium oxalate solution. Continue heating for 10 min, and then cool in an ice bath.

17. Filter with suction the precipitate onto a weighed glass fiber filter placed in the filter holder.

18. Rinse the beaker with ethyl alcohol, and pour the rinsings through the filter.

19. Wash the precipitate with approximately 10 ml ethyl alcohol and 10 ml of diethyl ether.

20. Place the filter containing the precipitate in an oven, and dry at 110 C for 20 min. Cool in a desiccator for 20 min.

21. Weigh the filter and precipitate on an analytical balance to the nearest 0.1 mg.

22. Subtract the tare weight of the filter to obtain the weight of the precipitate.

23. Mount the filter on a suitable holder.

24. Count the yttrium oxalate precipitate on the Proportional Flow Counting System.

5.9.4 Calculations

1. Calculate the concentration D of radioactive yttrium-90 (Y-90) in micro curies per cc as follows:

$$D = \frac{C}{2.22 \times 10^6 (E)(V)(R_1)(R_2)}$$

where

C = Beta count rate in net counts per minute.

E = Beta counter efficiency in counts per disintegration.

V = Volume of original sample in cc.

R_1 = Fractional chemical yield for the separation of yttrium (from step 23).

2.22×10^6 = Conversion factor from disintegrations per minute to micro curies.

R_2 = Fractional chemical yield for the separation of strontium given in Method RC-5, Sec. 5.8.

2. Calculate the decay correction for Y-90 as follows:

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

where

A = Activity at time sample is counted for yttrium.

A_o = Activity at time of separation of yttrium from strontium (step 13).

t = Elapsed time between counting and separation of yttrium from strontium from step 13.

T = Half-life of yttrium in same unit as t.

3. Calculate the activity of strontium-90 (Sr-90) from the growth and separation of yttrium-90 at the beginning of the decay period of Sr-90 as follows:

$$A_o = A \left(\frac{1}{1 - e^{-0.693\, t/T}} \right)$$

where

A_o = Sr-90 activity at the beginning of the decay period of Sr-90.

A = Y-90 activity at the time yttrium is separated from Sr-90 in step 13.

t = Sr-90 decay period as determined by step 13 in same unit as T.

T = Half-life of Sr-90.

5.10 CHROMIUM PROCEDURE (METHOD RC-7)

5.10.1 Summary of Method

Chromium is oxidized to chromate, scavenged with iron hydroxide ($Fe(OH)_3$) to remove impurities, and then precipitated as $BaCrO_4$.

5.10.2 Reagents and Materials

1. Chromium Carrier (10 mg/ml). See Sec. 2 of this volume on standardization of carriers.

2. Barium Nitrate (Saturated Solution). Dissolve 10 g barium nitrate in 100 ml of water.

NOTE: Excess solid should be present.

3. 1M Ammonium Acetate. Dissolve 7.7 g of ammonium acetate in 100 ml of water.

4. Iron Carrier (10 mg/ml). See Sec. 2 of this volume on standardization of carrier.

5. 3N Potassium Hydroxide. Dissolve 88 g in 500 ml of water.

6. Potassium Bromate ($KBrO_3$). Solid crystals.

7. 12.1N Hydrochloric Acid. Concentrated HCl.

8. 15N Ammonium Hydroxide. Concentrated NH_4OH.

5.10.3 Procedure

1. Add 2 ml chromium and iron carrier to the sample to be analyzed for chromium-51. Use a 50-ml centrifuge tube.

2. Add approximately 0.2 g potassium bromate ($KBrO_3$).

3. Place the centrifuge tube in a beaker of boiling water to assure oxidation of chromium to chromate. Fifteen minutes required.

4. Add 3N KOH to a pH of 10. Heat to coagulate the ppt of iron hydroxide.

5. Centrifuge and decant the liquid containing chromate to a 50-ml centrifuge tube. Discard the precipitate to radioactive waste.

6. Add 5 ml 1M ammonium acetate and 5 ml of saturated $Ba(NO_3)_2$. Swirl to mix.

7. Centrifuge for 2 min, and discard supernate to radioactive waste.

8. Dissolve the $BaCrO_4$ in 10 ml of water and 6N HCl; dilute to 30 ml, and reprecipitate with 5 ml 1M ammonium acetate and 5 ml of saturated $Ba(NO_3)_2$.

9. Add a few drops of dilute ammonium hydroxide.

10. Filter with suction the precipitate onto a weighed glass fiber filter placed in the filter holder.

11. Rinse the centrifuge tube with ethyl alcohol, and pour the rinsings through the filter.

12. Wash the ppt with 2- to 5-ml portions of ethyl alcohol and 2- to 5-ml portions of diethyl ether.

13. Place the filter containing the precipitate in an oven, and dry at 110 C for 1 hr. Cool in desiccator for 20 min.

14. Weigh the filter, and precipitate on an analytical balance to the nearest 0.1 mg.

15. Subtract the tare weight of the filter to obtain the weight of the precipitate.

16. Mount the filter in a 2-in.-dia stainless steel planchet, and radioassay the precipitate with a gamma-ray spectrometer.

5.10.4 Calculations

The chromium activity is primarily composed of 27.8-day half-life chromium-51.

1. Determine the disintegration rate by determining area under the 0.32-Mev photo peak for Cr-51.

2. The disintegration rate of chromium-51 is calculated using the equation:

$$\text{dpm-ml} = \frac{C}{(V)\,(E)\,(Fy)}$$

where

C = Counts per minute, corrected for background counts and extrapolated back to sampling time.

E = Counting efficiency.

Fy = Fractional chemical yield for the separation

V = Volume of sample in ml.

3. $\text{Chemical yield} = \frac{(\text{mg/ppt})\,(0.2053)}{\text{aliquot}}$

5.11 SODIUM-24 (METHOD RC-8)

5.11.1 Summary of Method

Sodium is separated as the chloride after scavenging the solution with strontium, lanthanum, and iron carriers.

5.11.2 Reagents and Materials

1. Sodium Carrier (10 mg/ml). Refer to Sec. 2 on standardization of carriers.

2. Strontium Carrier (10 mg/ml). Refer to Sec. 2 on standardization of carriers.

3. Lanthanum Carrier (10 mg/ml). Refer to Sec. 2 on standardization of carriers.

4. Iron Carrier (10 mg/ml). Refer to Sec. 2 on standardization of carriers.

5. Saturated Ammonium Carbonate Solution. Dissolve 35 g $(NH_4)_2CO_3 \cdot H_2O$ in 100 ml of water.

NOTE: Excess solids should be present.

6. 12.1N Hydrochloric Acid. Concentrated hydrochloric acid (HCl).

7. Ether.

5.11.3 Procedure

1. Add sample to be analyzed for sodium to a 250-ml beaker.

2. Add 2 ml sodium carrier to the coolant sample, and evaporate on a hot plate to about 25 ml.

3. Transfer to a 50-ml centrifuge tube, and add 5 drops each of strontium, lanthanam, and iron carriers.

4. Add a saturated ammonium carbonate solution dropwise until no more iron hydroxide forms.

NOTE: This iron hydroxide, when formed, will be a brown gelatinous precipitate.

5. Centrifuge for 2 min, and transfer the supernate to a 125-ml Erlenmeyer flask.

6. Add 2 ml concentrated hydrochloric acid (HCl), and evaporate to dryness using a hot plate.

7. Dissolve the residue with 2 ml of water and, using 10 ml of concentrated hydrochloric acid (HCl), transfer the dissolved solution to a 50-ml centrifuge tube.

8. Cool the centrifuge in an ice bath and, with vigorous stirring, add 10 ml ether. Continue to stir for 1 to 2 min.

9. Centrifuge for 2 min, and discard the supernate to radioactive waste.

10. Dissolve the white precipitate in 2 ml of water, and add 10 ml of concentrated hydrochloric acid (HCl).

11. Repeat step 8.

12. Filter with suction the precipitate onto a weighed glass fiber filter placed in the filter holder.

13. Rinse the centrifuge tube with ethyl alchol, and pour the rinsings through the filter.

14. Wash the precipitate with approximately 10 ml ethyl alcohol and 10 ml of diethyl ether.

15. Place the filter containing the precipitate in an oven, and dry at 110 C for 10 to 15 min. Cool in a desiccator for 10 to 15 min.

16. Weigh the filter and precipitate on an analytical balance to the nearest 0.1 mg.

17. Subtract the tare weight of the filter to obtain the weight of the precipitate.

18. Mount the filter on a suitable holder.

19. With a gamma-ray spectrometer, radioassay the precipitate.

5.11.4 Calculations

The sodium activity is primarily composed of 15-hr half-life sodium-24 (Na-24).

1. Determine the disintegration rate by determining area under the 2.75-Mev photo peak for Na-24.

2. On semi-log paper, plot a decay curve of the corrected counts per minute vs. time.

NOTE: A decay curve should be taken over a period of several hours (sample should be counted at a minimum of one time a day over a period of four days) and extrapolated back to sampling time.

3. The disintegration rate of Na-24 is calculated using the equation:

$$\text{dpm-ml} = \frac{C}{(V)\,(E)\,(Fy)}$$

where

C = Counts per minute, corrected for background counts and extrapolated back to sampling time.

E = Counting efficiency.

Fy = Fractional chemical yield for the separation.

V = Volume of sample in ml.

5.12 RADIOACTIVE OFF-GAS ANALYSES (METHOD RC-9)

5.12.1 Summary of Method

The off-gases are sampled in a counting bottle which is placed directly on the sodium iodide crystal connected to a gamma-ray spectrometer. Gamma-ray count rates are taken at various time intervals.

5.12.2 Apparatus

Counting Cell. See Fig. 5.3. The cell should be made of high vacuum glass.

5.12.3 Procedure

1. Off-gas is sampled into an evacuated glass Merinelli counting bottle and placed on the sodium iodide crystal.

2. With a gamma-ray spectrometer, radioassay the off-gas sample.

5.12.4 Calculations

1. Record gamma count at time intervals.

2. Plot the gamma spectrum.

3. Plot a decay curve of the count rate vs. time on semi-log paper. Identify isotopes from their half-lifes. You should be alert for 110-min half-life A-41 from activation of air and noble gas fission products and their daughters: 9-hr half-life Xe-135; 18-min half-life Rb-88; and 32-min half-life Cs-138.

It is suggested that time intervals for counting should be every 15 min for the first hour; then every 30 min for the next 3 hr; then, once every 8 hr for the next 24 hr.

5.13 GROSS BETA GAMMA ACTIVITY (METHOD RC-10)

5.13.1 Summary of Method

A sample of the coolant shall be analyzed by evaporating a sample on a stainless-steel planchet and counting on a proportional counter to determine gross beta gamma activity.

5.13.2 Procedure

1. Using an evaporator feeder (see Fig. 5.1), evaporate 500 ml of the coolant onto a 2-in.-dia stainless-steel planchet.

2. Count on the proportional flow counter.

5.13.3 Calculations

1. Count for 1 hr at the beta-voltage setting.

2. Correct for a 1-hr planchet background, and calculate $\mu c/ml$ as:

$$\mu c/ml = \frac{C}{(2.22 \times 10^6)\,(E)\,(V)}$$

where

C = Beta gamma count rate in net counts per minute.

E = Counter efficiency.

V = Volume of original sample in ml.

2.22×10^6 = Conversion factor from disintegrations per minute to micro curies.

5.14 ZIRCONIUM-95 (METHOD RC-11)

5.14.1 Summary of Method

Zirconium is precipitated as the mandelate, weighed, and counted on a gamma-ray spectrometer. Sodium, barium, and lanthanum carriers are added as scavengers.

5.14.2 Reagents and Materials

1. 4N HNO_3. Measure 256 ml of 15.7N concentrated nitric acid, and dilute to 1 liter with reagent water.

2. Zirconium Carrier (10 mg/ml). Refer to Sec. 2 on standardization of carrier solutions.

3. 16-Percent Mandelic Acid Solution. Dissolve 160 g of mandelic acid in 840 ml of water.

4. 2-Percent HCL - 5-Percent Mandelic Acid Solution. Measure 930 ml of reagent water, and add 20 ml of concentrated HCl and 50 g of mandelic acid.

5. Sodium, Barium, and Lanthanum Carriers. Refer to Sec. 2 on standard carrier solutions.

5.14.3 Procedure

1. Add 2 ml each of zirconium, sodium, barium, and lanthanum standard carriers to the sample to be analyzed.

2. Adjust the sample to approximately 10 ml by evaporation.

3. Adjust the sample to approximately 20 ml by adding concentrated HCl.

4. Add 50 ml of 16-percent mandelic acid solution to the sample, and dilute to 100 ml with reagent water.

5. Heat sample slowly to 85 C, and maintain this temperature for 20 min.

6. Filter and wash the sample, using a hot solution of 2-percent HCl, and 5-percent mandelic acid. Discard filtrate as radioactive waste.

7. Transfer the filter and precipitate to a porcelain crucible, and ignite for 1 hr at 700 C.

8. Cool and transfer the precipitate to a tared 2-in-dia planchet, and weigh on an analytical balance to the nearest 0.1 mg.

9. Subtract the tare weight of the planchet to obtain the weight of the precipitate.

10. Mount the filter on a suitable holder, and radioassay the precipitate with a gamma-ray spectrometer.

5.14.4 Calculations

The zirconium activity may consist of 65-day half-life zirconium-95 and 17-hr zirconium-97.

1. Determine the disintegration rate by determining the area under the 0.76-Mev photo peak for Zr-95.

2. Determine the disintegration rate by determining area under the 1.15-Mev photo peak for Zr-97.

3. The disintegration rate of Zr-95 and Zr-97 may be determined using the equation:

$$dpm/ml = \frac{C}{(V)\,(E)\,(Fy)}$$

where

C = Counts per minute, corrected for background and extrapolated back to sample time.

E = Counting efficiency.

Fy = Yield factor.

V = Volume of sample in ml.

4. If the sample is not counted within one day from the time of radiochemical separation, a correction for the Nb-95 daughter should be made as set forth in Fig. 5.4.

5.15 FLUORINE-18 AND NITROGEN-13 (METHOD RC-12)

5.15.1 Summary of Method

The disintegration rate of Fluorine-18 and Nitrogen-13 is determined by integrating under the 0.51-Mev annihilation photo peak and plotting the decay curve. N-13 has a 10-min half-life, and F-18 has a 1.87-hr half-life.

5.15.2 Procedure

Add 1000 ml of primary water to a 1-liter Marinelli beaker, and count on the gamma analyzer. Determine the area under the 0.51-Mev annihilation photo peak, and plot the decay curve of this peak. Count often enough to obtain an accurate curve for the 10-min N-13 during the first hour after sampling. Continue to count for 4 to 6 hr to determine the decay curve for F-18. Extrapolate back to time of sample to determine the contribution of each isotope to the activity.

5.15.3 Calculations

$$\mu Ci/cc = \frac{C}{(V)\,(E)\,(2.22 \times 10^{6})}$$

where:

C = Counts per minute, corrected for background and extrapolated back to sampling time.

V = Volume of sample in ml.

E = Counting efficiency for 0.51-Mev photo peak.

5.16 IRON-55 AND -59 (METHOD RC-13)

5.16.1 Summary of Method

Benzene sulfinic acid reacts with iron (III) salts to form a precipitate which is insoluble in dilute mineral acids. The precipitate is iron (III) benzene sulfinate, and it is stable at temperatures up to 130 C.

5.16.2 Reagents and Materials

1. Benzene Sulfinic Acid. Dissolve 4 g of benzene sulfinic acid sodium salt ($C_6H_5SO_2Na \cdot 2H_2O$) in 100 ml of water.

2. Iron Carrier. 10 mg/ml.

3. Concentrated HCl.

4. Concentrated Ammonium Hydroxide.

5.16.3 Procedure

1. Pipet 20 ml of sample into a 40-ml centrifuge tube.

2. Add 1 ml of standard iron carrier.

3. Adjust pH to 1-3 with HCl or NH_4OH.

4. Heat tube in a water bath to about 50 C.

5. Add 10 ml of benzene sulfinic acid solution, and digest for 10 min at 70 C.

6. Remove from water bath, and allow to set for 15 min.

7. Filter with suction onto a tared Whatman No. 542 filter.

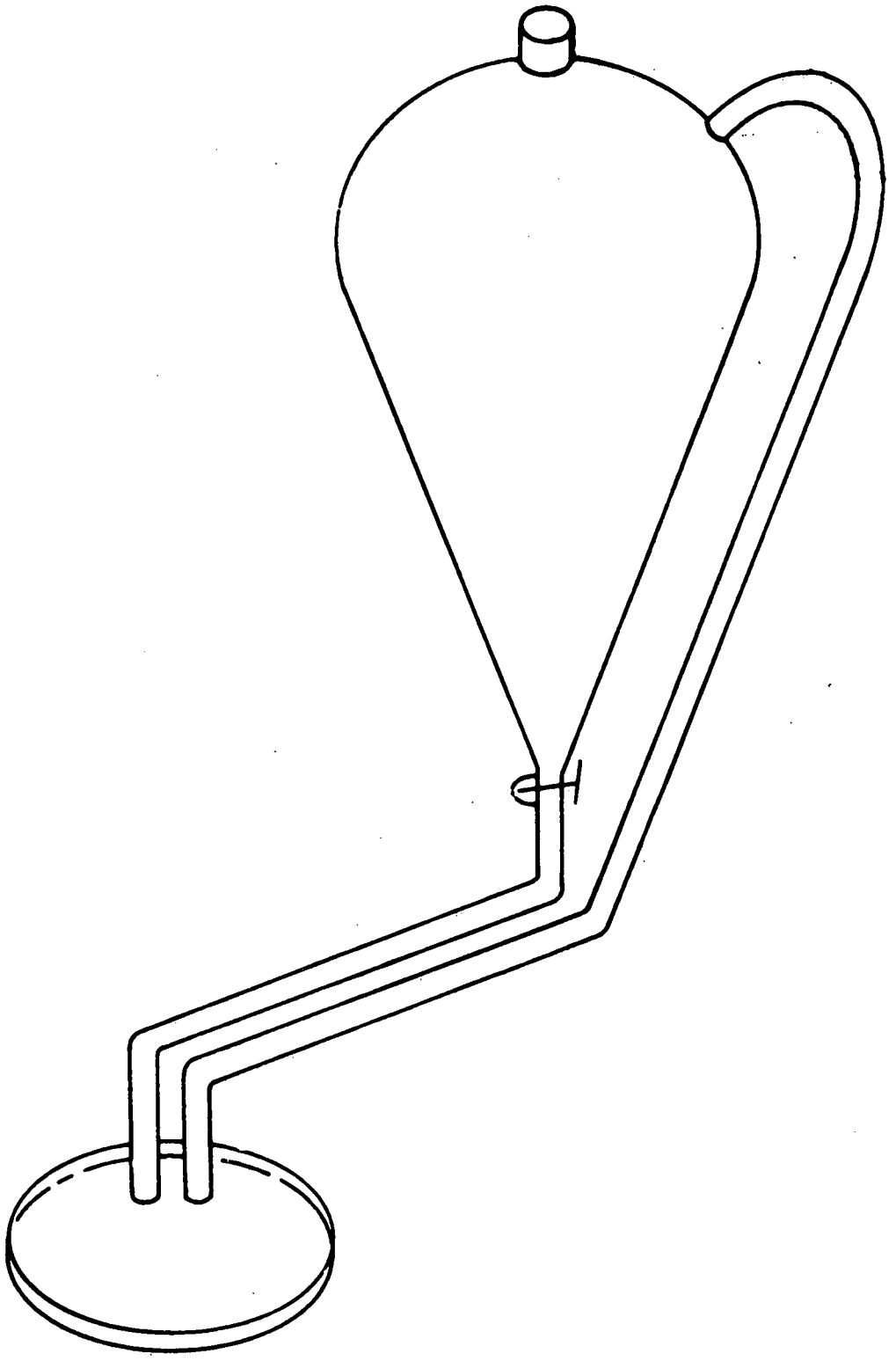
8. Transfer, and wash with 10 ml of 0.1 N HCl.

9. Dry for 1 hr at 110 C. Cool in a desiccator, and weigh as iron (III) benzene sulfinate, $Fe(C_6H_5SO_3)$. (G.F. = 0.1165.)

10. Count on the gamma analyzer.

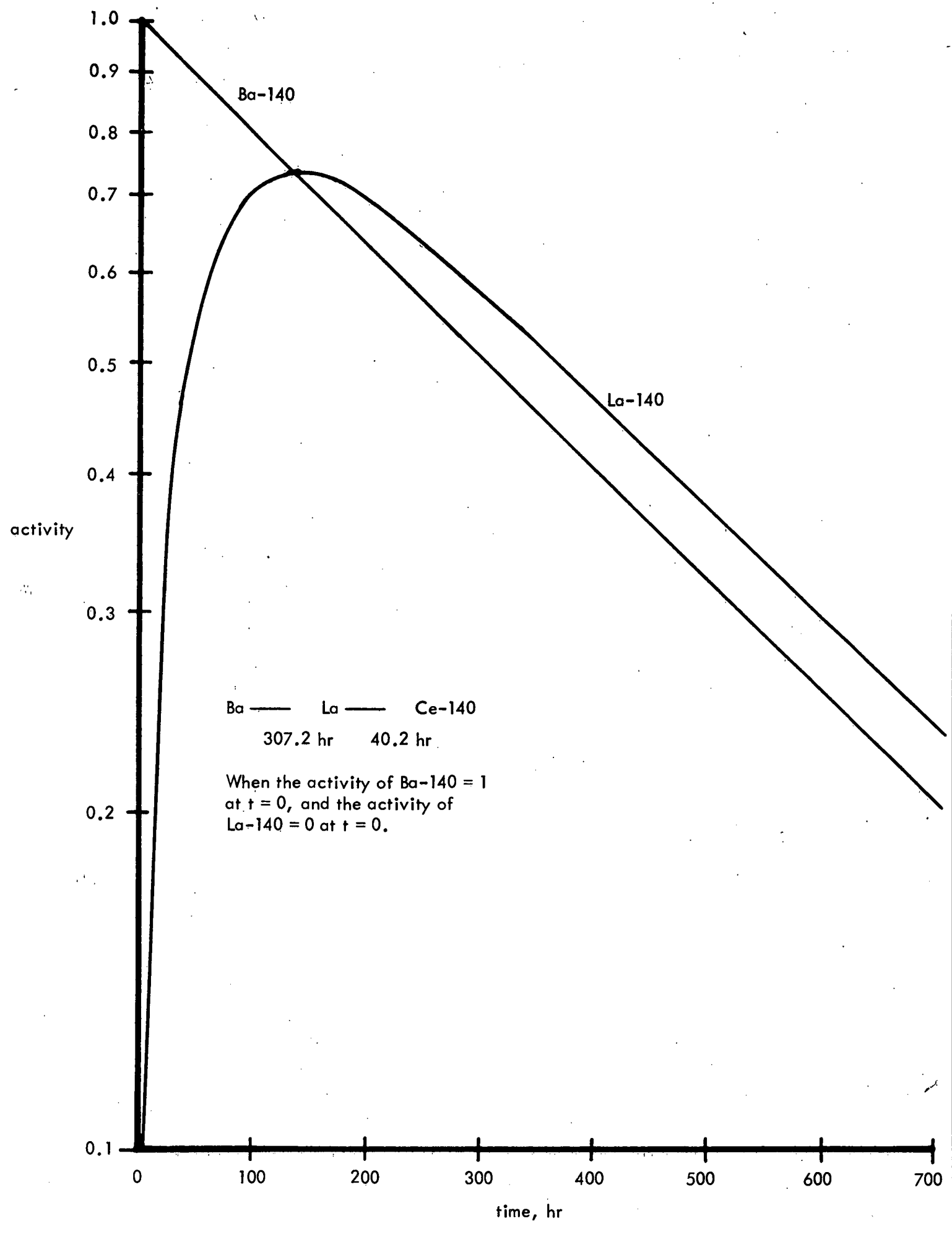
5.16.4 Calculations

$$\text{Chemical yield} = \frac{0.1165 \times \text{mg of ppt}}{\text{mg of carrier added}}$$



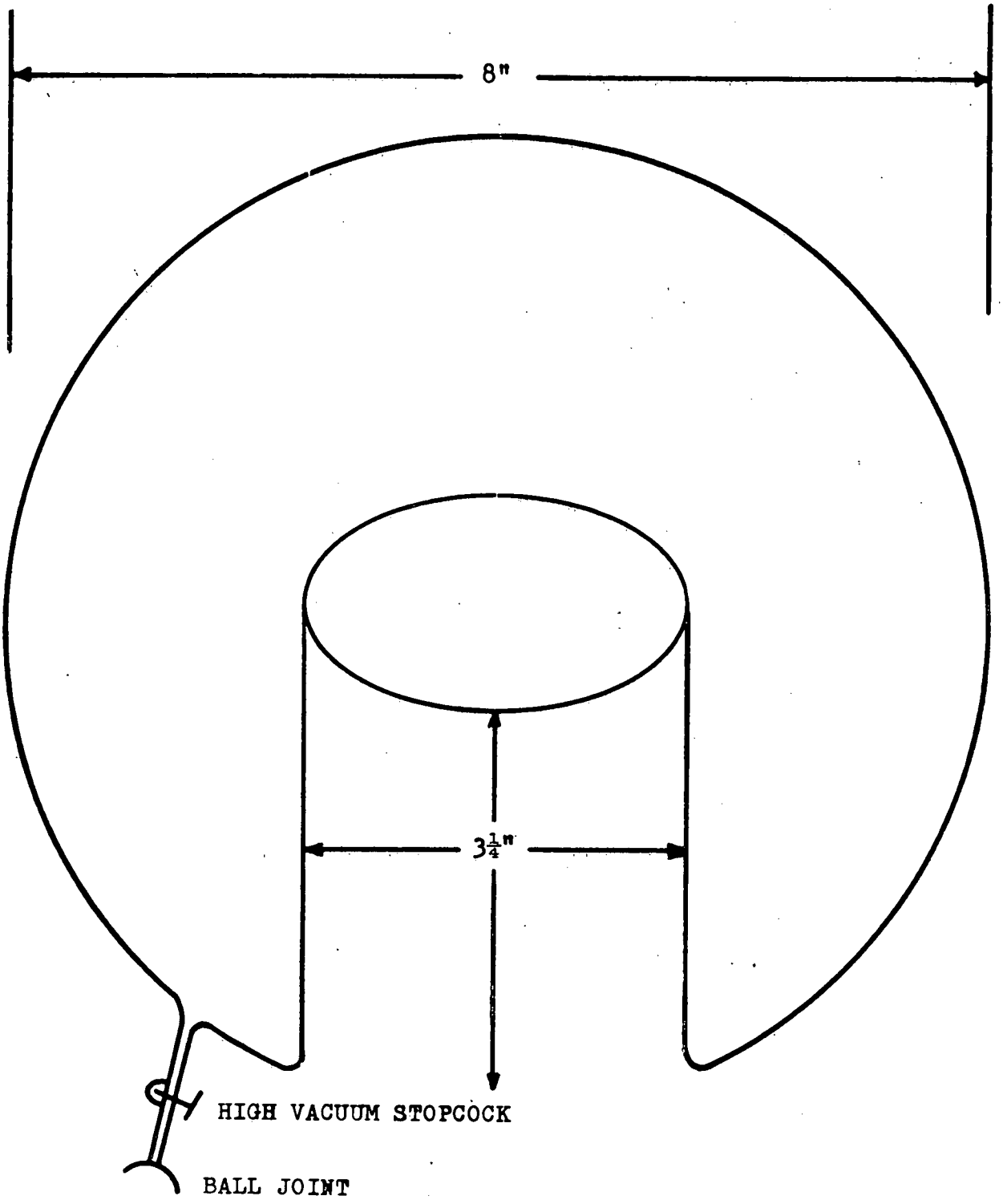
EVAPORATOR FEEDER

FIG. 5.1



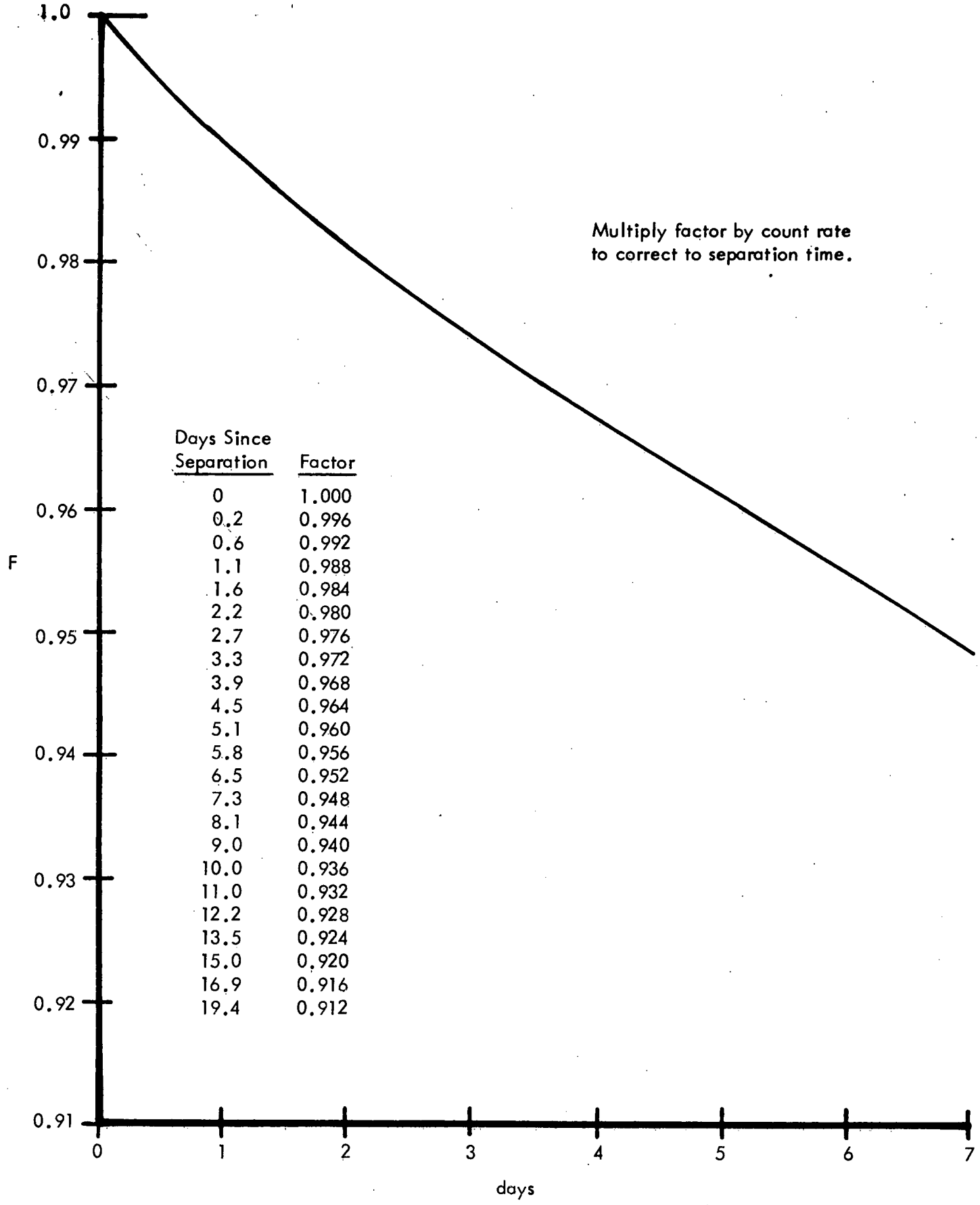
DECAY OF Ba-140 AND GROWTH OF La-140 ACTIVITY

FIG. 5.2



RADIOACTIVE GAS COUNTING CHAMBER

FIG. 5.3



Days Since Separation	Factor
0	1.000
0.2	0.996
0.6	0.992
1.1	0.988
1.6	0.984
2.2	0.980
2.7	0.976
3.3	0.972
3.9	0.968
4.5	0.964
5.1	0.960
5.8	0.956
6.5	0.952
7.3	0.948
8.1	0.944
9.0	0.940
10.0	0.936
11.0	0.932
12.2	0.928
13.5	0.924
15.0	0.920
16.9	0.916
19.4	0.912

CORRECTION FOR Nb-95 GROWTH IN Zr-95 AFTER SEPARATION

FIG. 5.4

6. DISSOLUTION METHODS

This section is a collection of dissolution procedures for quantitative removal of sorbed activity from ion exchange resins and for the dissolution of insoluble corrosion products which flake off metal surfaces and are transported through the cooling system. The dissolution methods have been selected on the basis of the effectiveness and the simplicity of the chemical operations involved.

6.1 ION EXCHANGE RESIN DISSOLUTION (METHOD D-1)

6.1.1 Summary of Method

Quantitative removal of sorbed activity from ion exchange resins is most effectively accomplished by completely destroying organic resin with the concurrent dissolution of all ionic activity in the reactant solution. Hot concentrated sulfuric acid is effective in degrading the resin so that subsequent oxidation with hot concentrated nitric acid (HNO_3) results in complete resin dissolution.

It should be noted that recovery of I_2 activity from resin samples requires the use of Method D-2, covered in Sec. 6.2 of this volume.

6.1.2 Apparatus

1. Hot plate.
2. Three 600-ml beakers.
3. Transfer pipettes with rubber bulb attached (as required).

6.1.3 Reagents and Materials

1. Concentrated nitric acid (15.7N).
2. Concentrated sulfuric acid (36.0N).
3. Standardized carriers for each of the isotopes to be analyzed.

6.1.4 Procedure

1. Weigh to the nearest 0.01 g approximately 5 g of air-dried resin to be analyzed, and place it in a 600-ml beaker.

NOTE: Perform the dissolution in triplicate in a fume hood.

2. Add 20 mg of standardized carrier for each of the isotopes undergoing analysis.

3. Add 2 ml of concentrated nitric acid (HNO_3), and cover the beaker with a watch glass.

4. Place beakers on a hot plate, and evaporate to dryness.

CAUTION: Use low heat to evaporate to dryness.

5. When the sample is dry, turn the hot plate temperature control to the HIGH position, and char the resin.

6. Cool, and add 50 ml of concentrated sulfuric acid (H_2SO_4).

7. Place on the hot plate, and heat to dense white fumes.

8. Keeping the sample on the hot plate, add concentrated nitric acid (HNO_3) carefully by allowing the HNO_3 to run slowly from a transfer pipette down the side of the beaker.

CAUTION: Excess splashing should be avoided by keeping the temperature of the sulfuric acid solution just slightly above the boiling point of the nitric acid (HNO_3).

NOTE: The black mixture will slowly clear. The final solution should be perfectly clear except for insoluble sulfate precipitates such as barium or strontium.

For each gram of resin, 20 to 30 ml of concentrated nitric acid (HNO_3) should be sufficient.

6.1.5 Calculations

There are no calculations involved in this procedure.

6.2 IODINE EXTRACTED FROM ION-EXCHANGE RESIN (METHOD D-2)

6.2.1 Summary of Method

During the specific determination of radioactive metal nuclides, the resin is generally destroyed. (See Sec. 6.1 covering the D-1 Method.) The severity of this process, which is used to destroy the resin, would result in a complete loss of iodine activities. Therefore, a separate sample of resin should be used for iodine analyses. The iodine

activity is removed by oxidation to the molecular state and extraction into carbon tetrachloride. The iodine is finally precipitated as PdI_2 for weighing and counting.

6.2.2 Apparatus

1. Normal laboratory glassware is required for this work.

2. Glass Fiber Filter. A filter 1-in.-dia x 0.01-in. thick should be used. Any similar filter will be suitable provided it retains fine precipitates adequately and maintains constant weight to ±0.1 mg during filtration and drying.

3. Filter Holder. The filter holder must hold the 1-in. filters rigidly in place during filtration.

NOTE: Care should be taken to clean the holder thoroughly between filtrations to prevent cross-contamination.

4. Desiccator. The desiccator must hold four 1-in.-dia filters similar to Fisher Cat. No. 8-615.

5. Oven. The oven should be of the gravity-convection type and able to supply uniform heat at 110 C to a ±0.5 C (Fisher Cat. No. 13-244-1 or equivalent).

6. Analytical Balance. It should be capable of weighing to the nearest 0.1 mg.

7. Gamma-Ray Spectrometer. A sodium iodide scintillation detector assembly connected to the appropriate amplifier and pulse height analyzer.

8. The following additional supplies are needed:

(a) One separatory funnel, 1000-ml Squibb type.
(b) Two separatory funnels, 125-ml Squibb type.
(c) One 50-ml beaker.
(d) One 10-ml graduated cylinder.
(e) One 100-ml beaker.
(f) One separatory funnel, 60-ml Squibb type.

6.2.3 Reagents and Materials

1. Purity of Reagents. Reagent grade chemicals shall be used to prepare reagents. Unless otherwise indicated, all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society. Other reagents may be used, provided they are of sufficient purity to give the same accuracy.

2. Purity of Water. All water used in preparing the reagents and in diluting the samples shall be demineralized water and shall conform to the Specification for Reagent Water (ASTM Designation D 1193).

3. Ethyl Alcohol. Either CP ethyl alcohol or denatured ethyl alcohol (denatured according to formula No. 30, Regulation No. 3 and its appendix, U.S. Bureau of Internal Revenue) shall be used for standardization of the carriers.

4. 2M Sodium Carbonate. Dissolve 21 g sodium carbonate (Na_2CO_3) in 100 ml of water.

5. 1M Hydroxylamine Hydrochloride. Dissolve 7 g hydroxylamine hydrochloride (NH_2OH-HCl) in 100 ml water.

NOTE: Store in cool place.

6. 1N Nitric Acid (HNO_3). Measure 64 ml of 15.7N nitric acid (HNO_3), and dilute to 1 liter with water.

7. 0.1M Palladium Chloride. Dissolve 21.4 g of palladium chloride ($PdCl_2$-$2H_2O$), and dilute to 1 liter with water.

8. 2M Sodium Carbonate (Na_2CO_3). Dissolve 105 g sodium carbonate (Na_2CO_3), and dilute with 500 ml water.

9. These additional chemicals are needed:

(a) Carbon tetrachloride (CCl_4).
(b) Concentrated nitric acid (HNO_3).
(c) Standardized iodine carrier (10 mg/ml).
(d) Sulfurous acid (H_2SO_3).
(e) Sodium nitrite ($NaNO_2$) (solid).
(f) Sodium hyprochlorite (5 percent) (NaClO).

6.2.4 Procedure

1. To a 100-ml beaker containing 2 ml of standardized iodine carrier and 10 ml of 2M sodium carbonate (Na_2CO_3), add 5 g of air-dried resin.

NOTE: Sodium carbonate (Na_2CO_3) keeps the solution alkaline to prevent the formation and subsequent loss of I_2.

2. Add 1 ml of 5-percent sodium hyprochlorite (NaClO) solution; place in a hot water bath, and stir vigorously.

3. Cool the solution, and then transfer the solution to a 60-ml separatory funnel.

4. To separate I-131, use Method RC-1. (See steps 4 through 29 in Sec. 5.1.4.)

6.2.5 Calculations

Only the 8.05-day I-131 will be present. Analyze I-131 data as stated in Method RC-1. (See Sec. 5.1.5 of this volume.)

6.3 DISSOLUTION OF CRUD (METHOD D-3)

6.3.1 Summary of Method

The crud consists of insoluble corrosion products that flake off metal surfaces and are transported through the cooling system. The crud is transferred to a porcelain crucible (Coors No. 1 or 2), ignited over a burner, fused in pyrosulfate dissolved in a hydrochloric acid media, and diluted to appropriate volume. After the crud is put into solution, the dissolved crud is then radioassayed for various isotopes.

6.3.2 Apparatus

1. Normal laboratory glassware is required for this work.

2. The following equipment will be needed:

   (a) One porcelain crucible, Coors No. 1 or 2.
   (b) One gas burner (Fisher-type burner preferred).
   (c) One 150-ml beaker.
   (d) One crucible tongs.
   (e) One 50-ml graduated cylinder.
   (f) One hot plate.
   (g) One 50-ml volumetric flask.

6.3.3 Reagents and Materials

1. Reagent grade chemicals shall be used to prepare reagents. Unless otherwise indicated, all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society. Other reagents may be used provided they are of sufficient purity to give the same accuracy.

2. Purity of Water. All water used in preparing the reagents and in diluting the samples shall be demineralized water and shall conform to the Specification for Reagent Water (ASTM Designation D 1193).

3. 6M Hydrochloric Acid (HCl). Measure 100 ml of concentrated (12M) hydrochloric acid (HCl), and dilute with 100 ml water.

4. Solid potassium pyrosulfate ($K_2S_2O_7$).

6.3.4 Procedure

1. Place the filter paper containing the crud in a porcelain crucible.

2. Ignite over the gas burner. Use a low flame until filter paper is completely charred. Then, turn up gas burner to a medium flame, and ignite for 10 min.

NOTE: This operation should be performed in a fume hood.

3. Cool porcelain crucible, and add just enough solid potassium pyrosulfate ($K_2S_2O_7$) to cover the sample.

4. Heat over the gas burner until a cherry red melt is formed.

NOTE: This operation should be performed in a fume hood.

5. Cool the platinum crucible, and add 20 ml of 6M hydrochloric acid (HCl).

6. Heat gently on a hot plate until the solid has loosened.

7. After the solid has loosened, transfer to a 150-ml beaker, and boil until the solid has completely dissolved.

NOTE: Add 6M hydrochloric acid (HCl) if necessary.

8. Cool and dilute the solution to 50 ml with water.

NOTE: If Mn-56 is to be determined, use two 25-ml aliquots.

6.3.5 Calculations

There are no calculations involved in this procedure.

2. Purity of Water. All water used in preparing the reagents and in diluting the samples shall be demineralized water and shall conform to the Specification for Reagent Water (ASTM Designation D 1193).

3. 6M Hydrochloric Acid (HCl). Measure 100 ml of concentrated (12M) hydrochloric acid (HCl), and dilute with 100 ml water.

4. Solid potassium pyrosulfate ($K_2S_2O_7$).

6.3.4 Procedure

1. Place the filter paper containing the crud in a porcelain crucible.

2. Ignite over the gas burner. Use a low flame until filter paper is completely charred. Then, turn up gas burner to a medium flame, and ignite for 10 min.

NOTE: This operation should be performed in a fume hood.

3. Cool porcelain crucible, and add just enough solid potassium pyrosulfate ($K_2S_2O_7$) to cover the sample.

4. Heat over the gas burner until a cherry red melt is formed.

NOTE: This operation should be performed in a fume hood.

5. Cool the platinum crucible, and add 20 ml of 6M hydrochloric acid (HCl).

6. Heat gently on a hot plate until the solid has loosened.

7. After the solid has loosened, transfer to a 150-ml beaker, and boil until the solid has completely dissolved.

NOTE: Add 6M hydrochloric acid (HCl) if necessary.

8. Cool and dilute the solution to 50 ml with water.

NOTE: If Mn-56 is to be determined, use two 25-ml aliquots.

6.3.5 Calculations

There are no calculations involved in this procedure.

7. SCHEDULE FOR WATER AND RADIOCHEMISTRY ANALYSES

7.1 LACBWR SAMPLING SYSTEM

The LACBWR Sampling System provides the means by which the various reactor and generator plant auxiliary systems can be sampled. The sampling program has been designed to supplement plant operating instrumentation.

7.1.1 Operational Uses of Routine Sampling

Routine sampling of the reactor and generator plant auxiliary systems enables the plant chemist to:

1. Maintain chemical control within the limits specified in the contract and as dictated by good water chemistry control practice to achieve optimum water quality for the protection of plant equipment.

2. Establish baseline water chemistry and radiochemistry data for use in the detection and interpretation of abnormal conditions.

3. Calibrate and check station operating instruments.

4. Determine that activation of the system corrosion products from structural materials does not exceed expected values.

5. Achieve efficiency for and provide operational information on the purification demineralizers systems.

7.1.2 Chemical Testing to Detect Abnormal Conditions

In addition to the normal control procedures such as pH, conductivity, and chloride used to determine whether chemical control is operating as designed, the system provides a means for conducting the following chemical tests for gathering a history of plant operation on which to base the detection and interpretation of abnormal conditions:

7.1.2.1 Total Iron and Copper. Determining the level of copper in the reactor coolant, feedwater, and full-flow condensate systems enables the plant chemist to establish a material balance and to detect abnormal corrosion behavior of components in these systems. Total iron determines the relative rate of total system corrosion, and total copper determines the rate of condenser tubing corrosion.

7.1.2.2 Dissolved Oxygen. Determining the dissolved oxygen concentration in the reactor coolant, feedwater, and full-flow condensate systems enables the plant chemist to detect air inleakage and to better understand plant corrosion, with special interest focused on reactor components subject to chloride stress corrosion cracking.

7.1.2.3 Total Solids. Determining the total solids concentration of the reactor coolant, feedwater, and full-flow condensate systems enables the chemist to better understand overall plant corrosion behavior and to detect condenser inleakage.

7.1.2.4 Silica. Determining the silica concentration of the feedwater, main steam, and the virgin and condensate storage tanks enables the chemist to establish a material balance, to detect condenser inleakage, to insure proper makeup water quality, and the minimization of SiO_2 carryover and turbine blade buildup.

7.1.2.5 Radionuclide Separation. Determining which of the following radionuclides are present in the reactor coolant will establish the concentration and types of corrosion-erosion products present in the coolant and also in the failed fuel elements.

The following chart lists the typical radionuclides present in water reactor coolant:

Coolant Activation Products		Fission Products		Activated Corrosion Products	
Radionuclide	Half-Life	Radionuclide	Half-Life	Radionuclide	Half-Life
N-16	7.35 sec	I-134	58.0 min	Mn-56	2.58 hr
N-13	10.0 min	I-135	6.70 hr	Ni-65	2.56 hr
Ar-41	110.0 min	I-133	21.0 hr	Cu-64	12.9 hr
F-18	112.0 min	I-131	8.05 days	W-187	24.0 hr
Na-24	15.0 hr	Cs-139	9.5 min	Cr-51	27.8 days
		Cs-138	32.2 min	Fe-59	45.0 days
		Cs-137	30 yr	Zr-95	65 days
		Ba-139	83 min	Co-58	71 days
		Ba-140	12.8 days	Co-60	5.27 yr
		Sr-91	9.7 hr	Mn-54	314 days
		Sr-92	2.7 hr		
		Sr-89	50.4 days		
		Sr-90	27.7 yr		
		Zr-95	65 days		
		Mo-99	66 hr		
		Xe-133	5.27 days		
		Xe-135	9.2 hr		
		Xe-135m	15 min		
		Kr-85	10.4 yr		

7.2 SAMPLING POINTS

7.2.1 Reactor Purification

The reactor purification system can be sampled at two points: the influent and effluent streams.

The influent sample connection, located upstream of the cation and mixed bed ion exchanger and downstream of valve 51-24-007, consists of a 1/2-in. stainless steel pipe and two normally-closed 1/2-in. stainless steel globe valves (51-23-001 and 51-23-002).

The effluent sample connection, which is located upstream of valves 51-24-014 and 51-24-016 and downstream of the cation and mixed bed ion exchanger of valve 51-24-013, consists of a 1/2-in. stainless steel pipe and two normally-closed 1/2-in. stainless steel globe valves (51-23-003 and 51-23-004).

Both sample connections terminate at elevation 642 ft 9 in.

7.2.2 Overhead Water Storage Tank

The overhead water storage tank sample point, which is located upstream of the locked closed 3-in. drain valve (69-24-002) above the main floor, consists of a 1/2-in. carbon steel pipe and a 1/2-in. globe valve (69-23-001). The sample connection terminates at elevation 701 ft 0 in.

7.2.3 Boron Injection

The Boron Injection System can be sampled at two points: the storage tank and the pump suction line.

The storage tank sample connection is located downstream of the tank and upstream of the locked-open 3-in. gate valve (60-24-002). Both sample points are located at elevation 667 ft 0 in.; and each consists of a 1/2-in. stainless steel pipe and a 1/2-in. globe valve (60-23-001 tank sample, 60-23-002 pump suction line sample).

The pump suction of the auto control valve (60-25-001) line sample point is useful in detecting any crystallization of the sodium pentaborate in the suction line.

7.2.4 Shield Cooling

The Shield Cooling System sample point, located on the shield cooling pump discharge header upstream of the shield cooling filter, consists of a 1/2-in. carbon steel pipe and 1/2-in. globe valve (59-23-002).

The sample connection terminates at elevation 621 ft 0 in.

7.2.5 Fuel Storage Well

The Fuel Storage Well System can be sampled at two points at elevation 642 ft 9 in. One sample point is located upstream of the filter and downstream of the skimmer and overhead storage tank connections (58-23-003). The other sample point is located on the return line, immediately upstream of the fuel storage well (58-23-002).

Each sample connection consists of a 1/2-in. stainless steel pipe and a normally-closed 1/2-in. globe valve (58-23-002 and 58-23-003 respectively).

7.2.6 Component Cooling Water

The Component Cooling Water System sample point, located on the component cooling water pump discharge header, consists of a 1/2-in. carbon steel pipe and 1/2-in. globe valve (57-23-003) at elevation 640 ft 0 in. in the Generator Plant.

7.2.7 Liquid Waste

The Liquid Waste Disposal System can be sampled at the following eight points:

1. Each of the two 6000-gal retention tanks (1A and 1B) has a bottom sample connection consisting of 1-in. carbon steel pipe and a 1-in. bronze globe valve (54-23-006 "1A" and 54-23-007 "1B"). Both sample connections terminate at elevation 621 ft 0 in.

2. The 3000-gal waste water storage tank has a bottom sample connection consisting of a 1-in. carbon steel pipe and a 1-in. bronze globe valve (54-23-008).

3. The 4500-gal waste water storage tank has a bottom sample connection consisting of a 1-in. carbon steel pipe and 1-in. bronze globe valve (54-23-009) which terminates outside the shielding wall surrounding the tank.

4. The evaporator feed tank has a bottom sample connection consisting of 1/2-in. stainless steel pipe, which is extended outside the shielding wall, and the 1/2-in. stainless steel globe valve (54-23-013).

5. The 1-gpm waste evaporator has a bottom sample connection consisting of 1-in. stainless steel pipe and a 1-in. stainless steel extended stem ball valve (54-23-011).

6. The spent resin tank has a bottom sample connection consisting of 1/2-in. stainless steel pipe extended outside the shield wall, and the 1/2-in. stainless steel ball valve (54-23-014).

7. The water collection tank has a bottom sample connection consisting of 1-in. carbon steel pipe and the 1-in. bronze globe valve (54-23-005).

8. The 500-gal concentrated waste storage tank has a bottom sample connection consisting of 1-in. stainless-steel pipe and a 1-in. extended stem and handwheel diaphragm valve (54-24-012).

The evaporator and evaporator feed tank sample points terminate at a central sampling station located over a sample trough just outside the shield wall in the waste disposal building. The spent resin tank sample point will extend down into the basement. The water collection tank sample point will be located at the tank.

7.2.8 Gaseous Waste System

The Gaseous Waste System can be sampled at four points, two of which are for gaseous content, and two for condensed moisture.

The two 1600-ft^3 gas storage tanks located in the underground gas storage vault have a common bottom sample connection consisting of a 1/4-in. carbon steel pipe and 1/4-in. carbon steel globe valve (55-23-008). This bottom sample connection, together with tank drain valves (55-23-006 and -007), are used to sample the condensed moisture in the tanks.

In addition, each gas storage tank has a top sample connection consisting of a 1/4-in. carbon steel piping and 1/4-in. carbon steel needle valves (55-23-011, Tank No. "1B") and (55-23-010, Tank No. "1A"). These top sample connections are used to sample the gaseous contents of the tanks.

The two gaseous sample lines terminate in the entrance way to the concentrated waste tank in the basement of the waste disposal building.

7.2.9 Shutdown Condenser

The Shutdown Condenser can be sampled at two points: the shell side coolant and the condensate return.

The shell side sample connection, located upstream of drain valve (62-24-018), consists of a sample cooler, 1/2-in. carbon steel pipe, and 1/2-in. bronze globe valves (62-23-004).

7.2.10 Feedwater

The Feedwater System sample point, located at elevation 667 ft 0 in., consists of a sample cooler, 1/2-in. stainless-steel pipe, and two normally-closed 1/2-in. stainless-steel globe valves (65-23-001 and 65-23-002), which are located downstream of valve (65-23-001).

7.2.11 Main Steam

The Main Steam Sampling arrangement, located at elevation 667 ft 0 in., consists of an ASME sample nozzle, a throttling calorimeter, and a sample cooler.

The throttling calorimeter is used to measure steam quality.

The condensed steam leaving the sample cooler can be sampled via a 1-in. stainless-steel pipe and two 1-in. stainless-steel globe valves (64-23-001 and 64-23-002).

7.2.12 Full-Flow Condensate Demineralization

The Full-Flow Condensate Demineralization System can be sampled at four points: one common sample point in the influent stream and a separate sample point for each of the three mixed-bed demineralizers in the effluent stream.

The common influent sample connection is located on the condensate pump discharge header downstream of the conductivity element and upstream of the three demineralizers. It consists of a 1/2-in. carbon steel pipe and two 1/2-in. carbon steel globe valves located downstream of the extended stem handwheel effluent valves.

7.2.13 Demineralized Makeup and Well Water

The Demineralized Makeup and Well Water System can be sampled at three points.

The deep well water supply sample connection, located downstream of the deep well pumps and upstream of the cation exchanger, consists of a 1/2-in. line and a 1/2-in. globe valve.

The cation exchanger sample connection is located on the demineralizer effluent line, and it consists of a 1/2-in. line and a 1/2-in. globe valve.

The anion exchanger sample connection is located on the demineralizer effluent line, and it consists of a 1/2-in. line and a 1/2-in. globe valve.

7.3 RADIO AND WATER CHEMISTRY TESTS

The water chemistry limits shown on Table 7-1 are those recommended for normal plant operation. Normal operation is defined as operation with the plant turbine at 20 percent load or above. Radio and water chemistry tests shown without limits are those tests which are conducted to gain baseline operational data.

TABLE 7-1

RADIO AND WATER CHEMISTRY TESTS SCHEDULE
APPROACH TO FULL POWER, AND FULL POWER

System Description	Sample Valve Number	Analysis	Frequency	Limits	Method Number
1. Reactor Purification Influent Sample	51-23-002	pH	once/day	7.0 ± 0.5	WC-1
	51-23-001	Conductivity (μmhos-cm)	once/day	5.0	WC-2
		Chloride (ppm)	once/day	0.1	WC-3
		Dissolve oxygen (ppm)	once/day	2.0 ± 2	WC-8A
		Gross β-γ activity (μCi/ml)	once/day		RC-10
		Copper (ppm)	once/month		WC-12
		Iron (ppm)	once/2 months		WC-4
		Radiochemical iodine (μCi/ml)	once/week		RC-1
		Gross α activity (μCi/ml)	once/month		RC-3
		γ Ray spectrum of water	once/week		
		Dissolved solids (ppm)	once/month		WC-6
		Suspended solids (ppm)	once/month		WC-5
		Total solids (ppm)	once/month		WC-7
		Radiochemical manganese (μCi/ml)	once/6 months		RC-2
		Radiochemical cesium (μCi/ml)	once/6 months		RC-4
		Radiochemical strontium (μCi/ml)	once/6 months		RC-5
		Radiochemical iron (μCi/ml)	once/6 months		RC-2
		Radiochemical chromium (μCi/ml)	once/6 months		RC-7

Table 7-1 - Radio and Water Chemistry Tests Schedule
Approach to Full Power, and Full Power (cont'd)

System Description	Sample Valve Number	Analysis	Frequency	Limits	Method Number
I. Reactor Purification Influent Sample (cont'd)		Radiochemical sodium (μCi/ml)	once/6 months		RC-8
		Radiochemical cobalt (μCi/ml)	once/6 months		RC-2
		Radiochemical nickel (μCi/ml)	once/6 months		RC-2
		Radiochemical copper (μCi/ml)	once/6 months		RC-2
		Radiochemical zirconium (μCi/ml)	once/6 months		RC-11
		Radiochemical nitrogen (μCi/ml)	once/6 months		RC-12
		Radiochemical fluorine (μCi/ml)	once/6 months		RC-12
Effluent Sample	51-23-003	pH	once/day	7.0 ± 0.5	WC-1
	51-23-004	Conductivity (μmhos/cm)	once/day	5.0	WC-2
II. Overhead Water Storage Tank	69-23-001	pH	once/month		WC-1
		Conductivity (μmhos/cm)	once/month		WC-2
		Chloride (ppm)	once/month		WC-3
		Gross β-γ activity (μCi/ml)	once/month		RC-10
III. Boron Injection	60-23-001	Boron (w/o)	once/month	17.8 (min)	WC-11B

Table 7-1 - Radio and Water Chemistry Tests Schedule
Approach to Full Power, and Full Power (cont'd)

System Description	Sample Valve Number	Analysis	Frequency	Limits	Method Number
IV. Shield Cooling	59-23-002	pH	once/month		WC-1
		Total solids (ppm)	once/month		WC-7
		Gross β-γ activity (μCi/ml)	once/month		RC-10
		γ Ray spectrum of water	once/month		
		Chloride (ppm)	once/month		WC-3
		Chromate (ppm)	once/month		WC-10
V. Fuel Storage Well Upstream of Filter	58-23-003	pH	once/month		WC-1
		Conductivity (μmhos/cm)	once/month		WC-2
		Chloride (ppm)	once/month		WC-3
		Total solids (ppm)	once/month		WC-7
		Gross β-γ activity (μCi/ml)	once/month		RC-10
		γ Ray spectrum of water	once/month		
VI. Component Cooling Water	57-23-003	pH	once/month	9.0 - 10.5	WC-1
		Chromate (ppm)	once/month	300 - 400	WC-10
		Phosphate (ppm)	once/month	25 - 30	WC-14
		Total solids (ppm)	once/month	1000	WC-7
		Gross β-γ activity (μCi/ml)	once/month		RC-10
VII. Liquid Waste 6000-Gal Retention Tank 1A and Retention Tank 1B	54-23-006 54-23-007	pH	as required		WC-1
		Conductivity (μmhos/cm)	as required		WC-2
		Suspended solids (ppm)	as required		WC-5
		Total solids (ppm)	as required		WC-7
		Gross β-γ activity (μCi/ml)	as required		RC-10

Table 7-1 - Radio and Water Chemistry Tests Schedule
Approach to Full Power, and Full Power (cont'd)

System Description	Sample Valve Number	Analysis	Frequency	Limits	Method Number
VII. Liquid Waste 6000-Gal Retention Tank 1A and Retention Tank 1B (cont'd)		Gross α activity (μCi/ml)	as required		RC-3
		γ Ray spectrum of water	as required		
Waste Water Storage Tank: 3000-Gal and 4500-Gal	54-23-008	pH	as required		WC-1
	54-23-009	Conductivity (μmhos/cm)	as required		WC-2
		Suspended solids (ppm)	as required		WC-5
		Total solids (ppm)	as required		WC-7
		Gross β-γ activity (μCi/ml)	as required		RC-10
		Gross α activity (μCi/ml)	as required		RC-3
		γ Ray spectrum of water	as required		
Evaporated Water	54-23-013	pH	as required		WC-1
		Conductivity (μmhos/cm)	as required		WC-2
		Gross β-γ activity (μCi/ml)	as required		RC-10
		Total solids (ppm)	as required		WC-7
Waste Evaporator	54-23-011	pH	as required		WC-1
		Total solids (ppm)	as required		WC-7
		Gross β-γ activity (μCi/ml)	as required		RC-10

Table 7-1 - Radio and Water Chemistry Tests Schedule
Approach to Full Power, and Full Power (cont'd)

System Description	Sample Valve Number	Analysis	Frequency	Limits	Method Number
VII. (cont'd)					
Spent Resin Tank	54-23-014	γ Ray spectrum of resin which will indicate radionuclides to be analyzed	as required		RC-10
		Gross β-γ activity (μCi/ml)	as required		
Water Collection Tank	54-23-005	pH	as required		WC-1
		Conductivity (μmhos/cm)	as required		WC-2
		Gross β-γ activity (μCi/ml)	as required		RC-10
		γ Ray spectrum of water	as required		
500-Gal Concentrated Waste Tank	54-23-012	pH	as required		WC-1
		Gross β-γ activity (μCi/ml)	as required		RC-10
		γ Ray spectrum of water	as required		
Change Room Drain Tank	54-23-040	pH	as required		WC-1
		Conductivity (μmhos/cm)	as required		WC-2
		Suspended solids (ppm)	as required		WC-5
		Total solids (ppm)	as required		WC-7
		Gross β-γ (μCi/cc)	as required		RC-10
		γ Ray spectrum of water	as required		
		Gross α activity (μCi/ml)	as required		RC-3

Table 7-1 - Radio and Water Chemistry Tests Schedule
Approach to Full Power, and Full Power (cont'd)

System Description	Sample Valve Number	Analysis	Frequency	Limits	Method Number
VIII. Gaseous Waste Sample Condensed Moisture	55-23-008	Gross β-γ activity (μCi/ml)	as required		RC-10
	55-23-006	γ Ray spectrum of water	as required		
		Radiochemical iodine (μCi/ml)	as required		RC-1
Gaseous Content of Retention Tanks 1A and 1B	55-23-011	Gaseous activity (μCi/cc)	as required		RC-9
	55-23-010	γ Ray spectrum of gas	as required		
IX. Shutdown Condenser Shell Side	62-23-003	pH	twice/month		WC-1
	62-23-004	Conductivity (μmhos/cm)	twice/month		WC-2
		Total solids (ppm)	once/month		WC-7
		Chloride	once/month		WC-3
X. Feedwater	65-23-001	pH	3 times/week	7.0 ± 0.5	WC-1
	65-23-002	Conductivity (μmhos/cm)	3 times/week	1.0 ± 1.0	WC-2
		Chloride (ppm)	3 times/week	0.1 ± 0.1	WC-3
		Copper (ppb)	once/month	10	WC-12
		Iron (ppb)	once/2 months	50	WC-4
		Silica (ppb)	once/week	10	WC-16
		Dissolved oxygen (ppm)	once/week		WC-8A
		Dissolved solids (ppm)	once/week		WC-6
		Suspended solids (ppm)	once/week		WC-5
		Total solids (ppm)	once/week	0.15	WC-7
		Gross β-γ activity (μCi/ml)	once/month		RC-10

Table 7-1 - Radio and Water Chemistry Tests Schedule
Approach to Full Power, and Full Power (cont'd)

System Description	Sample Valve Number	Analysis	Frequency	Limits	Method Number
X. Feedwater (cont'd)		Gross α activity (μCi/ml)	once/month		RC-3
		γ Ray spectrum of water	once/month		
XI. Main Steam Condensed Sample	64-23-001	Chloride (ppm)	once/month		WC-3
	64-23-002	Conductivity (μmhos/cm)	once/month		WC-2
		Dissolved oxygen (ppm)	once/month		WC-8A
		Silica (ppm)	once/month		WC-16
		Copper (ppm)	once/month		WC-12
		γ Ray spectrum of water	once/month		
XII. Full Flow Condensate Demineralizer from Hotwell Condensate Pump	63-23-001	pH	once/day		WC-1
		Conductivity (μmhos/cm)	once/day		WC-2
		Chloride (ppm)	once/day		WC-3
		Copper (ppm)	once/week		WC-12
		Iron (ppm)	once/week		WC-4
		Silica (ppm)	once/week		WC-16
		Dissolved oxygen (ppm)	once/week		WC-8A
		Gross α activity (μCi/ml)	once/month		RC-3
		Gross β-γ activity (μCi/ml)	once/month		RC-10
		γ Ray spectrum of water	once/month		
		Dissolved solids (ppm)	once/month		WC-6
		Suspended solids (ppm)	once/month		WC-5
		Total solids (ppm)	once/month		WC-7

Table 7-1 - Radio and Water Chemistry Tests Schedule
Approach to Full Power, and Full Power (cont'd)

System Description	Sample Valve Number	Analysis	Frequency	Limits	Method Number
XII. (cont'd)					
Cation Regeneration	63-25-003	pH	as required		WC-1
Anion Regeneration	63-25-034	Conductivity (μmhos/cm)	as required		WC-2
		Suspended solids (ppm)	as required		WC-5
		Dissolved solids (ppm)	as required		WC-6
		Total solids (ppm)	as required		WC-7
		Gross β-γ activity (μCi/g)	as required		RC-10
		γ Ray spectrum of resin	as required		
Caustic Tank Inlet Sample	63-23-009	Conductivity (μmhos/cm)	as required		WC-2
		pH			WC-1
Service Tank Sampling	63-23-002	pH			WC-1
	63-23-003	Conductivity (μmhos/cm)	as required		WC-2
	63-23-004	Chloride (ppm)	as required		WC-3
		Copper (ppm)	as required		WC-12
		Iron (ppm)	as required		WC-4
		Silica (ppm)	as required		WC-16
		Dissolved oxygen (ppm)	as required		WC-8A
		Gross α activity (μCi/ml)	as required		RC-3
		Gross β-γ activity (μCi/ml)	as required		RC-10
		γ Ray spectrum of water	as required		

Table 7-1 - Radio and Water Chemistry Tests Schedule
Approach to Full Power, and Full Power (cont'd)

System Description	Sample Valve Number	Analysis	Frequency	Limits	Method Number
XII. (cont'd)					
Service Tank Sampling (cont'd)		Dissolved solids (ppm)	as required		WC-6
		Suspended solids (ppm)	as required		WC-5
		Total solids (ppm)	as required		WC-7
XIII. Virgin and Condensate Storage Tanks and Well Water		pH	once/month		WC-1
		Conductivity (μmhos/cm)	once/month		WC-2
		Chloride (ppm)	once/month		WC-3
		Silica (ppm)	once/month		WC-16
		Copper (ppm)	once/2 months		WC-12
		Iron (ppm)	once/2 months		WC-4
		Gross β-γ activity (μCi/ml)	once/month		RC-10
		Total solids (ppm)	once/month		WC-7
XIV. Hydraulic Valve Accumulator		pH	once/month	9.5 - 10.5	WC-1
		Chromate (ppm)	once/month	300 - 400	WC-10
		Phosphate (ppm)	once/month	25 - 30	WC-14
XV. Reactor Feed-water Pump Coupling 1A and 1B	98-23-007	pH	once/month		WC-1
	98-23-008	Chromate (ppm)	once/month	300 - 400	WC-10
XVI. Heating Boiler		pH	once/week		WC-1
		Hydrazine (ppm)	once/week		WC-22
		Iron	as required		WC-4
		Copper	as required		WC-12

APPENDIX A

SPECTROPHOTOMETRIC ANALYSIS

SPECTROPHOTOMETRIC ANALYSIS

A-1 PRINCIPLE AND INTRODUCTION

In order to provide a logical basis for measurement of the absorption of light, it is necessary to allow for losses by reflection and by scattering at the boundaries of the cell that contains the medium and also for the small losses caused by scattering within the medium itself. This correction is made by comparing the intensity I of the ray of light that has passed through the absorption cell that contains the sample with the intensity I_0 of the ray of light after it has passed through a medium of similar refractive index contained in an identical cell. The ratio $I/I_0 \times 100$ is then the percent transmittancy of the sample.

The absorption spectrum of a given medium can be expressed in the form of a graph of absorbency vs. wavelength. The shape of such a curve is more or less characteristic of the absorbing substance; however, the characteristics of the absorption spectrum also depend on several other factors, such as the thickness of the cell, the concentration of the absorbing substance, and--if the medium is a solution--the chemical nature of the solvent and of the solute. Some media will give smooth absorption curves without well-marked points of inflection; this property is termed "general absorption." Other curves will show maxima or minima; this property, which is more common, is termed "selective absorption." All substances exhibit absorption in some region of the electromagnetic spectrum. For example, benzene shows a complicated group of maxima and minima in the ultraviolet region, whereas water shows strong absorption in the near infrared. These extensive invisible regions of the spectrum can be investigated spectrophotometrically and are more significant in some fields of analytical chemistry than is the visible region itself.

A-2 TREATMENT OF DATA

The analytical chemist is concerned primarily with spectrophotometric data insofar as it will aid him in the identification of an unknown substance, or in carrying out a quantitative determination of a constituent.

For purposes of identification, a spectrum is obtained by plotting absorbency measurements vs. the wavelength in millimicrons at different wavelength settings. The curve is then compared with the absorption spectra of known substances. Identification is established when the absorption spectrum of the unknown can be superimposed on a known spectrum.

Quantitative determinations are preceded by the establishment of a calibration curve that is prepared by plotting absorbency (or extinction) as the ordinate vs. the concentration of the substance as the abscissa on rectilinear graph paper. The wavelength setting chosen for the standard curve is usually the wavelength of maximum absorption. The absorbency of the unknown is then measured, and the concentration is determined by reference to the standard calibration curve. A separate calibration curve is established for each spectrophotometer.

A-3 OPERATING INSTRUCTIONS FOR DU-SPECTROPHOTOMETER OPERATING CONTROLS - POWER SUPPLY

1. Power Switch

This two-position rotary switch turns the power supply on and off. In the on position this switch supplies power, through the multi-conductor cable, to the electronic circuitry of the spectrophotometer; this switch also supplies power, through the terminals on the output and of the power supply, to the tungsten lamp.

NOTE: Before turning the Power Switch on, always turn the Filament Temperature Switch off. After turning the Power Switch on, wait for 1 min before turning the Filament Temperature Switch from the off position.

2. Filament Temperature Switch

This eight-position rotary switch, used in conjunction with the Source Circuit Switch, controls operation of a hydrogen lamp or mercury lamp by determining its filament and anode voltages. In the off position, this switch removes all voltage from the socket. The off position is used when the spectrophotometer is operated without either the hydrogen lamp or the mercury lamp.

3. Source Circuit Switch

This two-position switch, used in conjunction with the Filament Temperature Switch, sets the anode voltage at the correct value for the hydrogen or mercury lamp.

4. Photomultiplier Gain Switch

This eleven-position rotary switch, functional only if the spectrophotometer is operated with the photomultiplier tube, adjusts the sensitivity of the multiplier phototube by changing the voltage applied to the dynodes.

In addition to an off position, this switch has ten operating positions. The full position provides maximum sensitivity. Clockwise rotation of the switch decreases the sensitivity. This switch is used as a coarse sensitivity adjustment for the sensitivity knob on the DU-Spectrophotometer.

5. Zero Suppression Switch

This six-position rotary switch applies a bucking voltage to compensate for background radiation effects in flame, fluorescence, or reflectance measurements.

6. Screen Bias Switch

This five-position rotary switch controls the screen-bias voltage on the 2532 tube in the amplifier circuit of the DU-Spectrophotometer.

Ordinarily, adjustment of this switch is required only infrequently, and then as a result of the tube aging or replacement. This switch is a coarse adjustment for the dark current control on the DU-Spectrophotometer.

7. Operation with Tungsten Lamp

To operate the DU-Spectrophotometer with the tungsten lamp, use the following procedure:

(a) Turn DU Shutter Switch off.

(b) Turn DU Tungsten Lamp Switch on.

(c) Turn DU Function Switch to the Check position.

(d) Turn power supply Power Switch on.

(e) Allow power supply to warm up for about 1 hr.

(f) Rotate the Wavelength Selector to set the desired wavelength.

(g) Push Phototube Positioning Knob in to select the red-sensitive phototube (above 625 mu.), or pull positioning knob out to select the blue-sensitive phototube.

(h) Make sure the load resistor in in position number 1.

(i) Select proper filter if one is required.

(j) Insert standard and sample cells in the cell holder, and place holder in the cell compartment. Replace compartment cover.

(k) Use Sample Positioning Knob to position the standard cell in the light path.

(l) Rotate Dark Current Control to zero meter needle.

(m) Turn Shutter Switch on.

(n) Rotate Slit Adjustment Control to approximately zero the meter needle or to set the desired slit width.

(o) Rotate the Sensitivity Control to accurately zero the meter needle.

(p) Turn Shutter Switchoff.

(q) Use Sample Positioning Knob to position the unknown sample cell in the light beam.

(r) Set Selector Switch to 1, or to 0.1 if the transmittance is less than 10 percent.

(s) Turn Shutter Switch on.

(t) Rotate Transmittance Control to zero the meter needle.

(u) Record the transmittance or absorbence reading.

(v) Turn Shutter Switch off.

(w) Use the Sample Positioning Knob to move the next unknown sample into the light beam, and repeat step (l) and steps (r) through (u); or repeat the preceding measurement procedures using the new sample and with controls set at a new wavelength or at new slit openings.

A-4 DESCRIPTION OF OPERATING CONTROLS

1. Absorption Cells and Holder

The front position in the cell holder should be used for the cell that contains the reference liquid. The cells should be marked so that they can always be used in the same position in the cell holder. The cells should be compared by filling them with demineralized water. Before use, the cells should be cleaned with distilled water or other suitable solvent. Do not use hot concentrated acids which might etch the polished surfaces. Remove the cells from the holder for cleaning and filling. Make sure the cells are seated properly in the cell compartment and that the knob is pushed in; then, replace the cover. Each cell can be moved into the light beam by pulling the slide knob to the appropriate stop.

2. Phototube Selection

The spectral range to be investigated determines the proper phototube to be used. The red-sensitive phototube is used above 625 mu and is in position when the knob is pushed in. The blue-sensitive phototube is used below 625 mu and is in position when the knob is pulled out as far as possible.

3. Filter Slide

The filter slide is located between the exit slit and the cell compartment, and it is operated by means of a knob on the front end. The front position knob, pushed in, is blank and is used in the range 400 to 1000 mu and also with the hydrogen lamp. The second position contains a red-purple filter and is used in the range 400 to 320 mu with the tungsten lamp. The third position is blank and may be fitted with special filters if needed.

4. Sensitivity Control

For best performance, it is recommended that the sensitivity knob be used one to three turns from its clockwise limit. The most accurate readings on the Transmittance Scale can be obtained with the sensitivity knob set between the clockwise limit and the midpoint. The accuracy is within 0.1 percent at the clockwise limit. Maximum photometric resolution is attained when the Sensitivity Control is rotated to its counterclockwise limit, since less light is required to zero the meter needle at 100 percent transmittance, thus permitting narrower slit widths to be used.

5. Wavelength Selector

This control adjusts the position of the quartz prism inside the monochromator and simultaneously rotates the calibrated Wavelength Scale. It is recommended that the wavelength settings be approached from the long wavelength end of the scale each time.

6. Tungsten Lamp Switch

This is a toggle switch located on the exterior of the lamp housing's back plate.

7. Selector Switch

This is the main instrument switch and controls the function of the DU-Spectrophotometer. The off position disconnects power to the spectrophotometer. The check position provides a rapid means of adjusting it at 100 percent transmittance without having to turn the Transmittance Control. When the switch is in the 1 position, the Transmittance Scale reads 0 to 110 percent transmittance and the Absorbance Scale reads infinity to 0. Setting the Selector Switch at 0.1 position expands the Transmittance Scale, permitting it to be used in making measurements on samples having less than 11 percent transmittance.

8. Shutter Switch

Passage of light from the cell compartment to the phototube is controlled by the Shutter Switch on the phototube housing. This switch must be off to adjust dark current. When the switch is in the on position, light transmitted through the sample reaches the phototube. Turn the switch gently from one position to the other.

9. Dark Current Control

Dark current is the current passing through the phototube and other circuit components when the phototube is not exposed to light. For accuracy of measurement, dark current must be balanced out of the circuit before each meter reading. The adjustment is made by turning the Shutter Switch off and bringing the meter needle to zero by rotating the Dark Current Control.

10. Phototube Load Resistor Switch

In the number 1 position, a 2000-megohm load resistor is equipped to be used with the tungsten, hydrogen, or mercury lamps. The 2 and 3 positions are reserved for special load resistors used in special applications.

11. Null Meter

This meter indicates electrical balance of the instrument during various measurement procedures, i.e., dark current adjustment, setting of the 100-percent reference point, etc.

12. Slit Adjustment Control

This rotary control adjusts the width of the curved bilateral entrance and exit slits simultaneously. The slits are continuously adjustable from 0.01 to 2 millimeters. Slit width settings are indicated on an accurately calibrated scale and should always be approached from the narrow width direction.

13. Transmittance Control

The transmittance control is used to balance the null meter at zero before reading the transmittance or absorbence of the sample. Positioning of the Selector Switch and the Sensitivity Control affects the sensitivity of the instrument and the readings of the calibrated Transmittance or Absorbence Scales.

APPENDIX B

USE AND CARE OF POLYETHYLENE

USE AND CARE OF POLYETHYLENE

B-1 PROPERTIES

Polyethylene absorbs water extremely slowly. It has been found that, after a sample of polyethylene had been allowed to stand in water at room temperature for 1 yr, the weight gained due to absorbed water was about 0.15 percent.

Polyethylene is relatively unreactive chemically. Concentrated caustic materials (such as ammonium hydroxide, potassium hydroxide, and sodium hydroxide) do not affect polyethylene. Potassium permanganate and hydrogen peroxide, at room temperature, do not attack it. Diluted acids, bases, and salt solutions have no corrosive action on it.

The temperature should be kept below 70 C. Concentrated HNO_3, carbon disulfide, bromine, acetone, ether, toluene, ethyl acetate, lubricating oil, and turpentine should not be stored in polyethylene containers.

B-2 CARE

Ordinary soap and water can be used to clean the surface of polyethylene.

APPENDIX C

NUCLEAR DATA MULTICHANNEL ANALYZER

NUCLEAR DATA MULTICHANNEL ANALYZER

C-1 INTRODUCTION

This equipment is used to qualitatively and quantitatively determine the radioactivity contained in a given sample of gamma-emitting radioisotopes. This is done by counting the sample, storing the counts in a memory section, reading out the counts (after some internal computations), and identifying the isotope by its characteristic spectrum.

C-2 DESCRIPTION OF EQUIPMENT

Basically, there are six pieces of equipment: the detector, the shield, the analyzer-computer, the scope, the integrator, and the printout unit. They are described below:

1. The detector is a 3-in. x 3-in. thallium-activated sodium iodide crystal coupled to a photomultiplier tube and kept in a light-tight container.

2. The shield is a 6-in. thick steel housing for the detector, and it has a roll-top cover to allow access to the detector. The internal cavity is 15 in. x 15 in. x 18 in. deep, and it is lined with about 1/8 in. of lead and 0.030 in. of stainless steel.

3. The analyzer-computer unit contains the amplifier, timer, 512 memory units, operational mode section, and controls for accessory units.

4. The scope is a Tektronix-503 oscilloscope; it serves as a visual display of the memory information, and it aids in operating the integrator.

5. The integrator contains the section used to reduce the data from the analyzer-computer memory into a more useful form.

6. The printout unit is an IBM typewriter modified to accept counting from the analyzer-computer and to print it out on paper.

C-3 OPERATING CONTROLS

1. Analyzer-Computer

(a) Analyze - Stop - Readout Switch

This switch permits the operator to stop any operation and to initiate either analysis or readout.

(b) Readout Mode Switches

These switches permit the operator to select the mode for data display, i.e., scope, paper, tape, typewriter, or plotter.

(c) Sub-Group Position Switches

These switches permit the operator to select the section of the memory into which the data will be stored during analysis.

(d) Group-Size Switches

These switches should be set in a position corresponding to the size group desired and with reference to the sub-group section selected.

(e) Ramp Slope Switch

This switch selects the number of channels over which the spectrum will be spread.

(f) Auto-Repeat Switch

This switch is to repeat counting of a sample after a previous count is printed. This operation clears the memory, and previous data is lost.

(g) Pen Calibration Switch

This switch is used to calibrate a logarithmic recorder.

(h) Live Time Control Switches

These switches are used to turn on the live timer and select the amount of time, from 1 to 800 min, that the sample is to be counted. The normal method of counting is with the live timer on.

(i) Overlap Switch

This switch allows data from one-half of the memory to be superimposed on data from the other half.

(j) Amplifier Controls

These controls are used to position photopeaks in the desired location to facilitate isotope identification.

(k) Energy Zero Position

This control permits the operator to position zero energy in zero channel.

(l) Input Selector Switch

This switch is used to select the means by which the counts from the detector enter the analyzer-computer.

2. Data Reduction Controls

(a) Group Interchange Switch

This switch transposes information from one-half of the memory to the other half. This operation must be done in the Stop mode to prevent loss of data from the memory.

(b) Multiplier Switch

This switch permits the operator to add or subtract various multiples of the data from the right half of the memory to data in the left half.

(c) Initiate Computer Cycle Switch

This switch initiates the addition or subtraction of data from the right half to the left half of the memory, and it is used in conjunction with the multiplier switch and the add-subtract switch. The readout mode must be in CRT, and the sub-group size must be in 0-511 position.

3. Integration Controls

(a) Off-All-Selected Switch

When in off position, this switch allows a point-by-point addition or subtraction from the right half to the left half of the memory. When in the All position, the integration of the right half is completed and the result has been deposited in the first channel of the memory. This channel, called the sum channel, must first be cleared of all other data. When in the selected position, a specific portion of the spectrum is integrated and deposited in the sum channel.

(b) Address Switches for Integration

These switches allow the portion of the spectrum that is of interest to be selected for integration. These switches are used in the selected position and while viewing the spectrum on the scope.

C-4 OPERATING PROCEDURES

1. Preliminary Setup

(a) Place the Analyze-Stop-Readout switch to Stop 1.
(b) Place the Normal-Auto Repeat switch to Normal.
(c) Place the Normal-Pen Calibration switch to Normal.
(d) Form of readout:

(1) Place the Type-Punch-Dump switch to Type.
(2) Place the Digital-Analog switch to Analog.
(3) Place the CRT-Pen switch to CRT.

(e) Place the Live Timer to On.
(f) Place time units to Minutes.
(g) Place the live time units switch at stop point to X 1. Place all other switches to left.
(h) Place Off-Overlap switch to Off.
(i) Place Add-Subtract switch to Add.
(j) Place Coincidence switch to Off.
(k) Place Input Selector switch to right.
(l) Computer Control:

(1) Place Group Interchange switch to left.
(2) Place Multiplier switch to X 1.

(m) Set Energy Zero Position dial to read 500.
(n) Set Amplifier Coarse Gain and Fine Gain to desired calibration.
(o) Integrator:

(1) Place Off-All-Selected switch to Off.
(2) At Address at Start Point, place all switches Down.
(3) At Address at End Point, place all switches Up.

(p) Place Window-Off switch on rear panel to Off.

2. 512: Channel Operation

(a) Sub-Group Position: 0-511. All others to left.
(b) Group Size: 512 points. All others to left.
(c) Channels per 3 v to 512.

3. 256: Channel Operation

(a) Sub-Group Position: 0-255 or 256-511 switch to right. All others to left.
(b) Group Size: 256 points. All others to left.
(c) Channels per 3 v to 256.

4. 128: Channel Operation

Sub-Group Position: 0-127 or 128-255 or 256-383 or 384-511 switch to right. All others to left.

5. 10 Kev/Channel Adjustment

The analyzer should be set up for 256: Channel Operation. A Cs-137 source with a 0.662 Mev gamma and a Co-60 source with 1.17 and 1.332 Mev gammas are used for this operation. Place the Cs-137 source on the detector, and count for 1 min. The operator can determine which way to move the gain controls to position the photopeak in channel 66.2. Increasing the gain shifts the photopeak to the right as viewed on the scope, and decreasing the gain has the opposite effect. With careful and repeated changes in the fine gain, it is possible to position this peak in the proper location. Next, the Co-60 source should replace the Cs-137 source and be counted for an appropriate time. This serves as a check, and the photopeaks of Co-60 should fall in channels 133.2 and 117.

6. Computer Operation

(a) Addition or Subtraction of One Spectrum from Another.

A spectrum counted in the 0-255 half of the memory includes natural background. This can be corrected for by counting the background in the 256-511 half of the memory for a time equal to that of the spectrum to be corrected. Then switch to Stop 1 position; switch from 256-511 to 0-511; switch from add to subtract; place multiplier on X1; place integrator in off position; place switch to readout and, with decade lines on, initiate computer cycle. The background corrected spectrum appears in the 0-255 half of the memory.

(b) Summation of All Counts in a Spectrum.

The first step is to correct the spectrum for background effects. Then, switch to Stop 1; switch from subtract to add; move integrator to All position; group the interchange; place switch to readout; erase the sum channel; and initiate computer cycle. The total counts in the spectrum appear in Channel 1.

(c) Integrate Under a Portion of Spectrum.

The first step is to correct the spectrum for background effects. Then, in the following order:

(1) Place control knob to Stop 1.
(2) Place Add-Subtract switch to Add.
(3) Move Integration switch to selected position.
(4) Place control knob to readout position.
(5) Set Integration switches to isolate peak.
(6) Place control knob to Stop 1.
(7) Switch the group interchange.
(8) Place control knob to readout.
(9) Erase the sum channel.
(10) Depress switch to initiate the computer cycle.
(11) Place control knob to Stop 1.
(12) Place Analog-Digital switch to Digital.
(13) Place control knob to readout (3 channels sufficient).
(14) Place control knob to Stop 1.
(15) Place Add-Subtract switch to Subtract.
(16) Place Digital-Analog switch to Analog.
(17) Place control knob to Readout.
(18) Depress switch to initiate computer.
(19) Place control knob to Stop 1.
(20) Place Integration switch to Off position.
(21) Place Add-Subtract switch to Add position.
(22) Switch the group interchange.
(23) Place control knob to readout position.
(24) Depress left erase if data is no longer needed. This procedure works best if the address switches on left are down to start and if the switches on right are up to start. The sum includes the first channel selected but not the last. The printer will operate when the analog-digital switch is in digital and the control knob has been switched to readout. Counting data should be printed out after subtracting the background and before performing any integration operations.

APPENDIX D

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REFERENCES CONSULTED FOR RADIO AND WATER CHEMISTRY METHODS (SECS. 4 AND 5)

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