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Chemistry-Separation Processes
for Plutonium and Uranium

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LABORATORY RECORD
USA

MANUAL OF ANALYTICAL PROCEDURES

FOR THE

U235 RECOVERY PROCESS

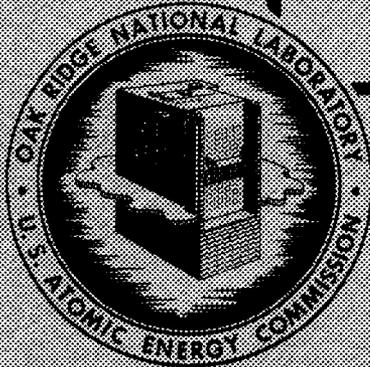
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Manual of Analytical Procedures for the U²³⁵
Recovery Process

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Edited by
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PREFACE

This manual of analytical procedures for the U²³⁵ Recovery Process comprises those methods which have been found most suitable for control of this process. Preliminary working copies of parts of this manual have been in use since 1947 during laboratory, semi-works, and pilot plant development of this process. No attempt is made in this manual to specify which samples will be analyzed by each procedure as this will probably be subject to change and should be the subject of separate documents.

The use of these procedures during the course of the development of the "25" process has resulted in strengthening of our confidence in these procedures and revision of many of them to increase their precision and applicability to radioactive samples. At the time this manual goes to press all methods included are felt to have been adequately tested with the possible exception of polarographic determination of uranium. While this is a well-recognized technique and has found considerable use at ORNL as a secondary uranium method, it has not found use as a routine method on which primary dependence for analytical control was based. Further studies on this subject will be made prior to the start-up time of the Arco operation.

The radiochemical procedures included are for those elements which are most commonly requested at ORNL. On the basis of Hanford experience it is felt that there will be little demand for radiochemical analysis when the plant operation becomes routine. Any further needs for radiochemical procedures can be satisfied by going to the references given on those included here.

We wish to thank all those at ORNL who have contributed to this manual of procedures and express special appreciation to Elvira K. Wilson and Helen P. Raaen

[REDACTED]

who have assembled and edited the procedures, to Dorothy Inman and Kathryn Odom who have typed the preliminary and final drafts of this manual, and to Peggy M. Carter for the preparation of the drawings used throughout.

I. IONIC METHODS

Methods Nos. 1-25

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TOTAL ACID IN HEXONE

Method No. 1

I. PRINCIPLE

The total acid present in hexone is determined by titration with standard sodium hydroxide to the methyl red end point and calculated as per cent acetic acid.

II. STATUS

The method is applicable to raw or treated hexone. Any impurity in hexone which reacts with NaOH will be calculated as acid. The accuracy and precision of the method have not been determined.

References:

1. Kolthoff, I. M., and Sandell, E. B., Textbook of Quantitative Inorganic Analysis, p. 552-4, MacMillan, New York (1948).

III. REAGENTS AND APPARATUS

A. Reagents

1. Standard Sodium Hydroxide Solution, approximately 0.1 N. Prepare from 1 N NaOH and standardize with potassium acid phthalate according to the procedure of Kolthoff and Sandell⁽¹⁾.
2. Methyl Red Indicator Solution, 0.2% in methanol-water. Prepare by dissolving 1 g of methyl red in 300 ml methanol and diluting to 500 ml with distilled water.
3. Methyl Alcohol, C₂H₅OH. Neutralize to the methyl red end point.

B. Apparatus

1. Pipets, volumetric, 20 and 25 ml capacities.
2. Flask, Erlenmeyer, 125 ml capacity.

IV. PROCEDURE

1. Pipet 20.0 ml hexone into a 125 ml Erlenmeyer flask.
- ~~SECRET~~

2. Add about 25 ml of methyl alcohol neutralized to methyl red.
3. Add about 25 ml of distilled water.
4. Mix until the solution is homogeneous.
5. Add 2 drops of methyl red indicator solution.
6. Titrate with standard sodium hydroxide solution to the first permanent appearance of a yellow color.

Calculations:

Let: A = normality of standard NaOH solution
 B = ml standard NaOH solution required for the titration
 C = ml of hexone titrated.

Also: 60.05 = mol. wt. of CH_3COOH , g

0.803 = density of hexone, g/ml

Then: Total acid in Hexone as CH_3COOH , per cent $\frac{A \times B \times 60.05 \times 100}{C \times 0.803 \times 1000}$

FREE ACID IN UNH SOLUTIONS OF LOW-LEVEL ACTIVITY

Method No. 2

I. PRINCIPLE

The free acid in UNH solutions is considered to be the same as total acidity. It is determined by titration with standard sodium hydroxide solution to the methyl red indicator end point after precipitation of the uranyl ion using a solution of 5% $K_4Fe(CN)_6$ in saturated KNO_3 . The total acidity is expressed as normality.

II. STATUS

The method is applicable to the analysis of UNH solutions of low-level activity. The error of the determination is reported to be less than 4%⁽¹⁾.

References:

1. Smith, D. M., "Determination of Free Nitric Acid in UNH," CC-1432 (April 24, 1944).
2. Kolthoff, I. M. and Sandell, E. B., Textbook of Quantitative Inorganic Analysis, p. 553, MacMillan, New York (1948).

III. REAGENTS AND APPARATUS

A. Reagents

1. Potassium Nitrate Solution, saturated. Prepare by dissolving 35 g KNO_3 in 85 ml of distilled water which has been neutralized with 0.1 N NaOH to the methyl red end point.
2. Potassium Ferrocyanide, 5% $K_4Fe(CN)_6$. Prepare by dissolving 5 g $K_4Fe(CN)_6$ in a small volume of saturated KNO_3 solution and dilute to 100 ml with the same KNO_3 solution.
3. Standard Sodium Hydroxide Solution, approximately 0.1 N. Prepare by dilution from 1 N stock reagent, available from Eimer and Amend,

Notes

- (a) For solutions which contain 48% UNH, use 20 ml of $K_4Fe(CN)_6$.
For lower UNH concentrations use smaller amounts as necessary.
- (b) A few drops of Aerosol solution will aid the centrifugation.
- (c) If the color of the solution is intense, use 5 drops of 0.04%
brom phenol blue instead of methyl red indicator.

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FREE ACID IN RADIOACTIVE UNH SOLUTIONS

Method No. 3

I. PRINCIPLE

Free acid is determined in radioactive UNH solutions after removing the interfering uranium. The uranium is complexed with potassium oxalate. The free acid is then titrated potentiometrically with sodium hydroxide. The determination is carried out at 1 to 3° C to repress dissociation of the uranium complex.

II. STATUS

The method is applicable to the analysis of radioactive UNH solutions for free acid, since the procedure is easily carried out behind a protective barrier. The accuracy and precision of the method have not been determined.

References:

1. Thomason, P. F., "Chemistry Division Quarterly Report for Period Ending Nov. 1948", ORNL-229 (Feb. 3, 1949).
2. Bennett, C. A., "Calculations of End Point in Potentiometric Analysis", HW-7737.
3. Kolthoff, I. M. and Sandell, E. B., Textbook of Quantitative Inorganic Analysis, Ch. XXXII, MacMillan, New York (1948).
4. Ibid, p. 553.
5. Kirk, P. L., Quantitative Ultramicro Analysis, p. 36, Wiley and Sons, New York (1950).

III. REAGENTS AND APPARATUS

A. Reagents

1. Standard Sodium Hydroxide Solution, approximately 1 N. Available from Eimer and Amend, 635 Greenwich St., New York. Check the normality reported by the supplier by titrating a sample of potassium acid phthalate (Ref. 4) with the solution.

~~SECRET~~

2. Standard Hydrochloric Acid Solution, approximately 1 N. Available from Eimer and Amend. Check the reported normality by titrating a sample of the acid solution with the standard sodium hydroxide solution.

3. Lead Nitrate Solution, 10% $\text{Pb}(\text{NO}_3)_2$. Prepare by dissolving 10 g $\text{Pb}(\text{NO}_3)_2$ in 100 ml distilled water.

4. Potassium Oxalate Solution, 25% $\text{K}_2\text{C}_2\text{O}_4$. Prepare by dissolving 25 g $\text{K}_2\text{C}_2\text{O}_4$ in 100 ml distilled water.

B. Apparatus

1. pH Meter, Beckman, Industrial Model M, provided with glass and calomel electrodes.

2. Stirrer, magnetic type, electric, provided with small stirrer cut from nickel wire.

3. Ice Bath.

4. Buret, micro, Kirk type, of 1 ml total capacity, calibrated (method of Kirk⁽⁵⁾ suggested.)

5. Pipet, micro, 200 λ capacity.

6. Pipet, volumetric, 1 ml capacity.

IV. PROCEDURE

1. From the estimated acidity of the sample determine what, if any, hydrochloric acid "spike" is required. If required, pipet it into the titration vessel.

2. Place the titration vessel and required apparatus behind a protective barrier.

3. Pipet 200 λ of the sample into the titration vessel and add a small magnetic stirring bar.

4. Place the vessel in the ice bath.

5. Start the magnetic stirrer.

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6. Pipet 1 ml of 25% $K_2C_2O_4$ solution into the titration vessel. The uranium should be precipitated. The total volume should be approximately 2 ml. This is critical.

7. After five minutes, stop the stirrer and lower the electrode assembly^(a) and the tip of the Kirk buret into the solution^(b).

8. Start the stirrer.

9. Titrate the acid potentiometrically with the standard NaOH solution, approximately 1 N, making the additions in 1 cm increments.

Calculations:

Locate the exact end point by use of the following equation:

$$\text{End point, ml std. NaOH solution added} = \frac{A - B}{2A - (B+C)} \times D$$

in which:

- A = maximum Δ pH
- B = Δ pH immediately preceding A
- C = Δ pH immediately following A
- D = increment of standard NaOH solution added in the vicinity of the end point, cm.

For example from the following data:

<u>Cm Std. NaOH Added in Vicinity of End Point</u>	<u>pH</u>	<u>Δ pH</u>
10	4.90	
11	5.00	0.16
12	5.16	
13	5.75	0.60
14	5.90	0.15

it is found that:

- A = 0.60
- B = 0.16
- C = 0.15
- D = 1.0 cm

Calculate the acidity (or basicity) of the sample as follows:

Let:

X = millequivalents of acid added = ml of acid added x N of acid

Y = millequivalents of base added = cm of base added x buret factor x N of base

Z = λ of sample.

Then:

For acid deficient samples:

$$\underline{N} \text{ of base in sample} = \frac{X - Y}{Z}$$

For acidic samples:

$$\underline{N} \text{ of acid in sample} = \frac{Y}{Z}$$

Notes

(a) Care must be used as the electrodes are easily broken if they touch the bottom of the titration vessel.

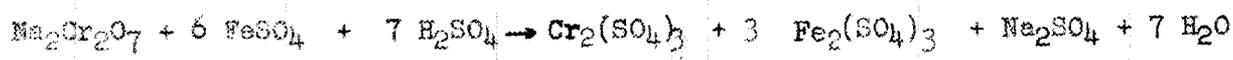
(b) The tip should be just below the surface of the liquid but not touching the electrodes.

OXIDIZING POWER OF SODIUM DICHROMATE SOLUTION

Method No. 4

I. PRINCIPLE

The oxidizing power of sodium dichromate solution is determined by the potentiometric titration of an aliquot with standard ferrous sulfate solution in sulfuric acid medium. The oxidizing power is reported as molarity. The reaction is as follows:



II. STATUS

Any other substance present in the dichromate solution which will oxidize ferrous sulfate will be reported as sodium dichromate molarity.

References:

1. Kolthoff, I. M., and Sandell, E. B., Textbook of Quantitative Inorganic Analysis, Chs. XXXVI and XXXVIII, MacMillan, New York (1948).
2. Bennett, C. A., "Calculations of End Point in Potentiometric Analysis", HW-7737.

III. REAGENTS AND APPARATUS

A. Reagents

1. Standard Ferrous Sulfate Solution, approximately 0.1 N FeSO_4 . Prepare by dissolving 13.9 g $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ in water containing 25 ml conc. H_2SO_4 . Dilute to 1 liter. Standardize daily against 0.1 N standard potassium dichromate solution. This solution is unstable.
2. Standard Potassium Dichromate Solution, 0.1000 N $\text{K}_2\text{Cr}_2\text{O}_7$. Prepare by weighing out 4.903 g of pure dry $\text{K}_2\text{Cr}_2\text{O}_7$, dissolve in water and dilute to exactly 1 liter.
3. Sulfuric Acid. 6 N. Prepare by adding 168 ml of 17.8 M (95% H_2SO_4) acid to a volume of water and dilute to 1 liter.

B. Apparatus

1. pH Meter, Beckman Industrial Model M, provided with a platinum and a tungsten electrode.
2. Stirrer, magnetic type, electric, provided with pyrex glass-sealed stirring bar 1 3/8 inches long X 3/8 inches diameter.
3. Buret, micro, 5 ml capacity, graduated in 0.01 ml. A Greiner or Kirk type is desirable.
4. Pipet, transfer type, 200 λ capacity.

IV. PROCEDURE

1. Pipet 200 λ of sample into a 50 ml beaker.
2. Dilute to approximately 10 ml with distilled water.
3. Add 10 ml 6 N H_2SO_4 .
4. Put a magnetic stirring bar into the solution and insert the electrode assembly.
5. Start the magnetic stirrer.
6. Lower the buret tip into the solution.
7. Titrate potentiometrically with standard $FeSO_4$ solution, approximately 0.1 N, adding the solution in 0.1 ml increments as the end point is approached.
8. Report the oxidizing power as molarity of sodium dichromate.

Calculations: Locate the exact end point of the titration by either (1) a plot of the volume (ml) of standard ferrous sulfate solution added as abscissa vs emf as ordinate (the inflection point of the curve indicates the end point) or (b) by using the following equation:

$$\text{End point, ml of standard } FeSO_4 \text{ added} = \frac{A - B}{2A - (B + C)} \times D$$

in which:

- A = maximum Δ emf, mv
 B = Δ emf immediately preceding A, mv
 C = Δ emf immediately following A, mv
 D = increment of standard $FeSO_4$ solution added in the vicinity of the end point, ml.

For example, from the following data:

<u>Ml Std. FeSO₄ Added in Vicinity of End Point</u>	<u>Emf, mv</u>	<u>Δ Emf, mv</u>
1.2	240	
1.3	240	0
1.4	20	220
1.5	15	5

it is found that:

A = 2.20 mv

B = 0.00 mv

C = 0.05 mv

D = 0.1 ml

The sign of the Δ emf is disregarded.

Calculate the oxidizing power of the sodium dichromate from the equation:

$$\text{Oxidizing power of dichromate, as } \underline{M} \text{ of Na}_2\text{Cr}_2\text{O}_7 = \frac{E \times F}{G \times 6}$$

in which:

E = ml standard FeSO₄ solution used

F = normality of standard FeSO₄

G = ml of sample.

TOTAL REDUCING NORMALITY OF AQUEOUS SOLUTIONS

Method No. 5

I. PRINCIPLE

The total amount of reducible material in a sample of aqueous solution is determined by its reaction with a measured excess of standard potassium dichromate. After the reaction is complete, the excess dichromate is titrated potentiometrically with standard ferrous sulfate.

II. STATUS

The method is applicable to aqueous solutions containing reducible material. The accuracy and precision of the method have not been determined. They are expected to vary with sample type.

References:

1. Kolthoff, I. M. and Sandell, E. B., Textbook of Quantitative Inorganic Analysis, Chs. XXXVI and XXXVIII, Macmillan, New York (1948).
2. Bennett, C. A., "Calculations of End Point in Potentiometric Analysis", HW-7737.

III. REAGENTS AND APPARATUSA. Reagents

1. Standard Potassium Dichromate Solution, 0.1000 N $K_2Cr_2O_7$. Prepare by weighing out 4.903 g of pure dry $K_2Cr_2O_7$, dissolve in water and dilute to exactly 1 liter.
2. Standard Ferrous Sulfate Solution, approximately 0.1 N $FeSO_4$. Prepare by dissolving 13.9 g $FeSO_4 \cdot 7H_2O$ in water containing 25 ml. of conc. H_2SO_4 . Dilute to 1 liter. Standardize daily against 0.1 N standard potassium dichromate solution. This solution is unstable.
3. Sulfuric Acid, 6 N. Prepare by adding 168 ml of 17.8 M (95% H_2SO_4) acid to a volume of water and dilute to 1 liter.

B. Apparatus

1. pH Meter, Beckman Industrial Model M, provided with a platinum and a tungsten electrode.
2. Stirrer, magnetic type, electric, provided with pyrex glass sealed stirring bar, 1 3/8 in. long x 3/8 in. diameter.
3. Buret, micro, 5 ml. capacity, graduated in 0.01 ml. A Greiner or Kirk type is desirable.
4. Pipet, transfer type, 200 μ capacity.

IV. PROCEDURE

1. Pipette 200 μ of sample into a 50 ml. beaker.
2. Dilute to approximately 10 ml with distilled water.
3. Add 10 ml. of 6 N H_2SO_4 .
4. Pipette into the beaker an excess of standard potassium dichromate solution, determined from the estimated reducing normality of the solution.
5. Place a magnetic stirring bar in the beaker and start the magnetic stirrer. Stir for five minutes.
6. Stop the stirrer; lower the electrode assembly and the tip of the buret into the solution.
7. Again start the stirrer.
8. Titrate the excess $K_2Cr_2O_7$ potentiometrically with the approximately 0.1 N standard ferrous sulfate solution, adding the solution in 0.1 ml increments as the end point is approached.

Calculations:

Locate the exact end point of the titration by either (1) a plot of the volume (ml) of standard ferrous sulfate solution added as abscissa vs emf as ordinate (the inflection point of the curve indicates the end point) or (2) by using the following equation:



End point, ml of standard FeSO₄ added =

$$\frac{A - B}{2A - (B + C)} \times D$$

in which:

- A = maximum Δ emf, mv
- B = Δ emf immediately preceding A, mv
- C = Δ emf immediately following A, mv
- D = increment of standard FeSO₄ solution added in the vicinity of the end point, ml.

For example, from the following data:

<u>ml Std. FeSO₄ Added in Vicinity of End Point</u>	<u>emf, mv</u>	<u>Δ emf, mv</u>
1.2	240	
1.3	240	0
1.4	20	220
1.5	15	5

it is found that:

- A = 220 mv
- B = 0 mv
- C = 5 mv
- D = 1 ml

The sign of the Δ emf is disregarded.

Calculate the total reducing normality of the sample from the equation:

$$\text{Total reducing normality} = \frac{(E \times F) - (G \times H)}{I}$$

in which:

- E = ml standard K₂Cr₂O₇ added
- F = normality of standard K₂Cr₂O₇ solution
- G = ml standard FeSO₄ used
- H = normality of standard FeSO₄ solution
- I = ml of sample

ISOBUTYLMETHYLCARBINOL IN HEXONE (ISOBUTYL METHYL KETONE)

AS REDUCING NORMALITY

Method No. 6

I. PRINCIPLE

The amount of isobutylmethylcarbinol present as an impurity in hexone is determined by its reduction of potassium dichromate. A sample of hexone is allowed to react with an excess of standard potassium dichromate in a nitric acid medium. The excess dichromate is then titrated with standard ferrous sulfate. The end point is detected by use of Ferroin indicator.

II. STATUS

The accuracy and precision of the method have not been determined. In addition to isobutylmethylcarbinol, any substances which reduce potassium dichromate, for example decomposition products of hexone, will be reported as reducing normality of hexone.

References:

1. Kolthoff, I. M., and Sandell, E. B., Textbook of Qualitative Inorganic Analysis, Ch. XXXVI, MacMillan, New York (1948).
2. Ibid, p. 494.

III. REAGENTS AND APPARATUS

A. Reagents

1. Standard Potassium Dichromate Solution, 0.1000 N $K_2Cr_2O_7$.
Prepare by weighing out 4.903 g of pure dry $K_2Cr_2O_7$, dissolve in water and dilute to exactly 1 liter.
2. Standard Ferrous Sulfate Solution, approximately 0.1 N $FeSO_4$.
Prepare by dissolving 13.9 g $FeSO_4 \cdot 7H_2O$ in water containing 25 ml of conc. H_2SO_4 . Dilute to 1 liter. Standardize daily against 0.1 N standard potassium dichromate solution. This solution is unstable.

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3. Ferroin (o-phenanthroline-ferrous sulfate) Indicator. Solution, 0.0125 M. Prepare by diluting 0.025 M stock solution with an equal volume of water.

Prepare a 0.025 M stock solution by dissolving 1.737 g $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ in 250 ml water and in this solution dissolve 14.85 g o-phenanthroline ($\text{C}_{12}\text{H}_8\text{N}_2 \cdot \text{H}_2\text{O}$). This stock solution is stable for at least one year.

4. Sulfuric Acid, 6 N H_2SO_4 . Prepare by adding 168 ml of 17.8 M (95% H_2SO_4) acid to a volume of water and dilute to 1 liter.

5. Nitric Acid, 5 N HNO_3 . Prepare by adding 325 ml of 15.4 M (69% HNO_3) acid to a volume of water and dilute to 1 liter.

B. Apparatus

1. Pipets, capacities of 5, 15, 20 and 25 ml.
2. Erlenmeyer flask, 125 ml capacity.
3. Buret, micro automatic, 5 ml capacity graduated in 0.01 ml.
4. Stop watch.

IV. PROCEDURE

1. Pipet 20 ml of the hexone into a 125 ml Erlenmeyer flask and add 5 ml of 0.1 N standard $\text{K}_2\text{Cr}_2\text{O}_7$ solution.
2. Add 25 ml of 5 N HNO_3 .
3. Shake for fifteen seconds^(a).
4. Let stand for five minutes^(a).
5. Shake for fifteen seconds^(a).
6. Let stand for ten minutes^(a).
7. Add 15 ml 6 N H_2SO_4 and three drops of Ferroin indicator.
8. Titrate immediately with standard FeSO_4 solution, approximately 0.1 N.

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Calculations:

Let:

- A = ml standard $K_2Cr_2O_7$ solution added
- B = normality of standard $K_2Cr_2O_7$ solution
- C = ml standard $FeSO_4$ solution used
- D = normality of standard $FeSO_4$ solution
- E = ml of hexone sample

Then:

$$\text{Reducing Normality of Hexone} = \frac{(A \times B) - (C \times D)}{E}$$

Note:

- (a) Time all shaking and sample standing intervals with a stop watch to insure complete reaction.

INORGANIC FLUORIDES - SPECTROPHOTOMETRIC METHOD WITH

"THORON" REAGENT

Method No. 7

I. PRINCIPLE

Fluoride ion diminishes the red color which is produced when "Thoron" reagent, 1-(*o*-arsonophenylazo)-2-naphthol-3, 6-disulfonic acid, is added to thorium nitrate solution. The color diminution is proportional to fluoride concentration. It is measured spectrophotometrically at a wave length of 545 μ .

II. STATUS

The method is applicable to the determination of inorganic fluorides in amounts ranging from 0 to 50 micrograms. The factors affecting the color stability of the thorium complex, as well as interferences and their elimination have been discussed in detail⁽¹⁾. The color is constant at pH between 0.2 and 1.0 and is stable at room temperature for approximately 24 hours in the absence of HClO_4 and 3 hours in its presence.

Two procedures are given, i.e. procedures to be used in the absence and presence of interferences. Aluminum and phosphorous are the chief interference in the fluoride reaction with the thorium complex. Steam distillation of a perchloric acid solution of the sample at special conditions frees the fluoride from interferences. The overall accuracy and precision of the method are approximately 4 and 2.5 per cent respectively. Beer's Law is not followed exactly.

References

1. Thomason, P. F., Perry, M. A. and Byerly, W. M., "Determination of Microgram Amounts of Thorium", Anal. Chem. 21, 1239 (1949).
2. Reed, S. A., Byrd, C. N. and Banks, C. V., "Preparation of the Disodium Salt of 1-(*o*-arsonophenylazo)-2-naphthol-3, 6-disulfonic acid ("Thoron") AEC-2565 (April 18, 1949).

~~SECRET~~

3. Horton, A. D., Thomason, P. F., and Miller, F. J., "Spectrophotometric Determination of Inorganic Fluorides", ORNL-839 (March 26, 1951).

4. Willard, H. H. and Winter, O. B., "Volumetric Method for the Determination of Fluorine", Ind. and Eng. Chem., Anal. Ed., 5, 7 (1933).

5. Kuney, J. H., "Perchloric Acid, Friend or Foe", Chem. and Eng. News, 25, 1658 (1947).

6. Chemical Safety Data Sheet SD-11, "Perchloric Acid Solution," preliminary, supplied by Manufacturing Chemists Assoc., 246 Woodward Bldg., Washington 5, D. C.

III. REAGENTS AND APPARATUS

A. Reagents

1. "Thoron" Reagent, 0.3% "Thoron", 1-(o-arsenophenylazo)-2-naphthol-3, 6 disulfonic acid. Synthesize "Thoron" (not commercially available) by the procedure of Reed, Byrd and Banks⁽²⁾. Purity and moisture content may vary from batch to batch; therefore, plot a standard curve to determine the purity of each batch of "Thoron" as described by Thomason, Perry and Byerly⁽¹⁾. From the determined purity of the "Thoron", calculate the milligrams required to give 100 ml of 0.3% solution and prepare the solution.

2. Standard Thorium Nitrate Solution, 100 γ Th/ml. Prepare a stock solution of approximately 10 mg Th/ml by dissolving 23.8 g. $\text{Th}(\text{NO}_3)_4 \cdot 4\text{H}_2\text{O}$ (Lindsay Light and Chemical Co., West Chicago, Illinois) in distilled water and diluting to 1 liter. Standardize by evaporating 10 ml aliquots to dryness and igniting (to ThO_2) at 1000°C to constant weight. Make a dilution of this solution with distilled water to obtain a standard thorium nitrate solution containing 100 γ Th/ml.

3. Standard Sodium Fluoride Solution, 10 γ F/ml. Prepare a stock solution of 100 γ F/ml by dissolving 0.2221 g. NaF in 1 liter distilled water. Prepare the standard solution by making a 1:10 dilution of the stock solution.

~~SECRET~~

4. Hydrazine Hydrate, 95% in H₂O, Eastman Kodak Co., Rochester, N. Y.,
Reagent No. 902.

5. Perchloric Acid, 70% HClO₄, C.P.

6. Hydrochloric Acid, conc. HCl, C.P.

7. Sodium Hydroxide, pellet, C.P.

8. Potassium Iodide, solid, C.P.

B. Apparatus

1. Fluoride Distillation Apparatus, see Apx. 1. Consists of:

(a) Steam generator

(1) flask

(2) flask heater, electric Cenco Hotcone[®], 115 v, 350 W.

(3) Condenser trap

(b) Modified Willard-Winter still.

(1) still pot

(2) condenser

(3) centrifuge tube, 15 ml capacity, graduated in 0.1 ml.

(4) still pot heater, electric, aluminum-jacketed, 40 mm

i.d., 95 mm o.d., 60 mm high.

(5) automatic temperature controller, Wheelco Model 224

TCB, used to regulate still pot temperature.

2. Spectrophotometer, Beckman Model B, provided with cells of 1 cm
light path.

3. Flasks, volumetric, 100 ml capacity.

4. Pipet, Mohr delivery, 1 ml capacity, graduated in 0.01 ml.

5. Pipet, volumetric, 1 ml capacity.

6. Pipets, micro volumetric, capacities 250 and 500 λ . The "Aba"
Model P 2030 automatic pipet, Arthur S. LaPine & Co., Catalogue MG, Cat. No.
M 9490, is convenient to use.

~~SECRET~~

7. Quartz chips, for still pot. Broken pieces of sand-finished, pure quartz tubing are suitable.

IV. PROCEDURE

A. In the Absence of Interfering Ions

1. Pipet 1 ml of standard thorium nitrate solution (100 μ /ml)^(a) into a 10 ml volumetric flask.
2. Add a volume of sample^(b) containing 10 to 50 μ F⁻.
3. Add 500 λ conc. HCl.
4. Rinse down the sides of the flask with distilled water.
5. Add 250 λ ^(c) of 0.3% "Thoron" solution.
6. Dilute to volume with distilled water and shake.
7. Prepare a reference solution of 500 λ of conc. HCl and 250 λ of 0.3% "Thoron" solution diluted to a 10 ml volume with distilled H₂O.
8. Allow the sample to stand 15 minutes^(d).
9. Transfer the sample and reference to matched spectrophotometer cells.
10. Determine the per cent transmittance of the sample against the reference on a Beckman Model "B" spectrophotometer at a wave length of 545 m μ on the open position.
11. Obtain the fluoride-values from a calibration curve^(e) prepared with the batch of "Thoron" being used, and report the value for the sample.

Calculation:

Let: A = quantity of fluoride in aliquot, as determined from calibration curve, μ

B = aliquot of sample, ml

Then:

$$\text{Fluoride in sample, } \mu/\text{ml} = \frac{A}{B}$$

~~SECRET~~

[REDACTED]

B. In the Presence of Interfering Ions

CAUTION: This procedure requires the use of perchloric acid, a reagent presenting an explosion hazard. Before proceeding, become thoroughly familiar with the possible hazard and the method of safely handling the reagent^(5 & 6). It is most important to avoid the formation of the anhydrous acid. The dehydrating agents, sulfuric acid and phosphorous pentoxide, can convert H_3PO_4 to the anhydrous acid. Contact with organic material or porous materials should be avoided. The distillation should be carried out in a fire-proof hood of special construction.

1. Place a few quartz chips in the distillation flask.
 2. Pipet a volume of sample containing 10 to 50 μF^- into the distillation flask.
 3. Seal the condenser into the flask with 70% $HClO_4$ as lubricant.
 4. Place receiver tip in a 15 ml centrifuge cone containing a NaOH pellet dissolved in approximately 1 ml distilled water.
 5. By means of a 1 ml Mohr pipet calibrated in 0.01 ml, add 0.75 ml of 70% $HClO_4$ thru the side arm (steam inlet) of the distillation flask.
 6. Heat the flask to $125^\circ C$, then introduce steam from the electrically-heated steam generator.
 7. Carry out the distillation between 125 and $135^\circ C$ until the volume of liquid in the centrifuge tube reaches 11.5 ml^(f).
 8. Neutralize the distillate, then acidify with 7 drops of conc. HCl.
 9. Add a few crystals of KI and let stand three minutes^(g).
 10. Add two drops of 85% hydrazine hydrate^(h), 1.5 ml standard thorium solution (100 $\mu Th/ml$)^(a) and 0.375 ml of 0.3% "Thoron" reagent.
 11. Dilute to 15 ml and allow the color⁽ⁱ⁾ to develop for 15 minutes.
- [REDACTED]

12. Prepare a reference solution containing only 0.375 ml of 0.3% "Thoron" reagent and 7 drops of HCl.

13. Determine the per cent transmittance of the sample against the reference solution using the Beckman spectrophotometer, model "B", at 545 m μ .

14. Obtain the fluoride value of the sample from the calibration curve^(j) (for samples containing impurities) prepared with the batch of "Thoron" in use.

Calculation:

Let: A = quantity of fluoride in sample aliquot as determined from calibration curve, δ

B = aliquot of sample analyzed, ml.

Then: Fluoride content of sample, δ /ml = $\frac{A}{B}$

Notes:

(a) The amount of standard thorium solution is critical and should be measured carefully.

(b) If the sample contains HNO₃, it should be neutralized with NaOH before the addition of other reagents.

(c) It is convenient to use an "Aba" Model D 2030 automatic micro pipet calibrated to deliver 250 λ .

(d) The color is stable for at least 24 hours.

(e) Prepare a calibration curve for use in the absence of interferences as follows. Use the standard NaF solution in place of the sample. Following Procedure A, determine the optical density of solutions containing from 0 to 50 δ F⁻ at 10 δ intervals. Plot the optical density values as ordinates versus F⁻ amounts as abscissa on semi-logarithmic paper. The curve does not follow Beer's Law. This curve must not be used for samples which have been distilled. A sample curve is shown in Apx. 2.

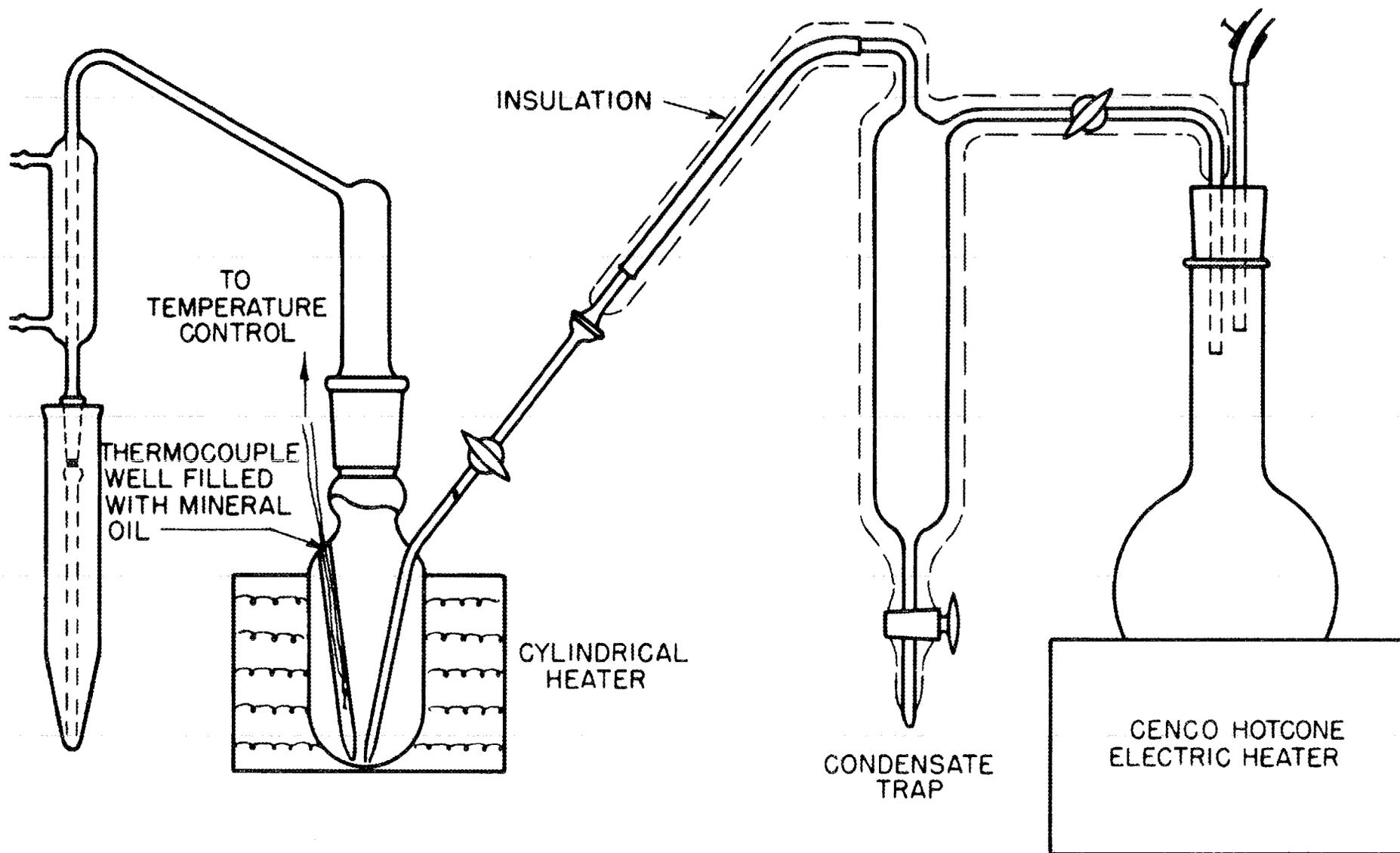
(f) The rate of distillation affects the results considerably. The collection of 11.5 ml of distillate in approximately 15 minutes is recommended.

(g) The KI is added to remove the Cl_2 which may form from $HClO_4$ decomposition.

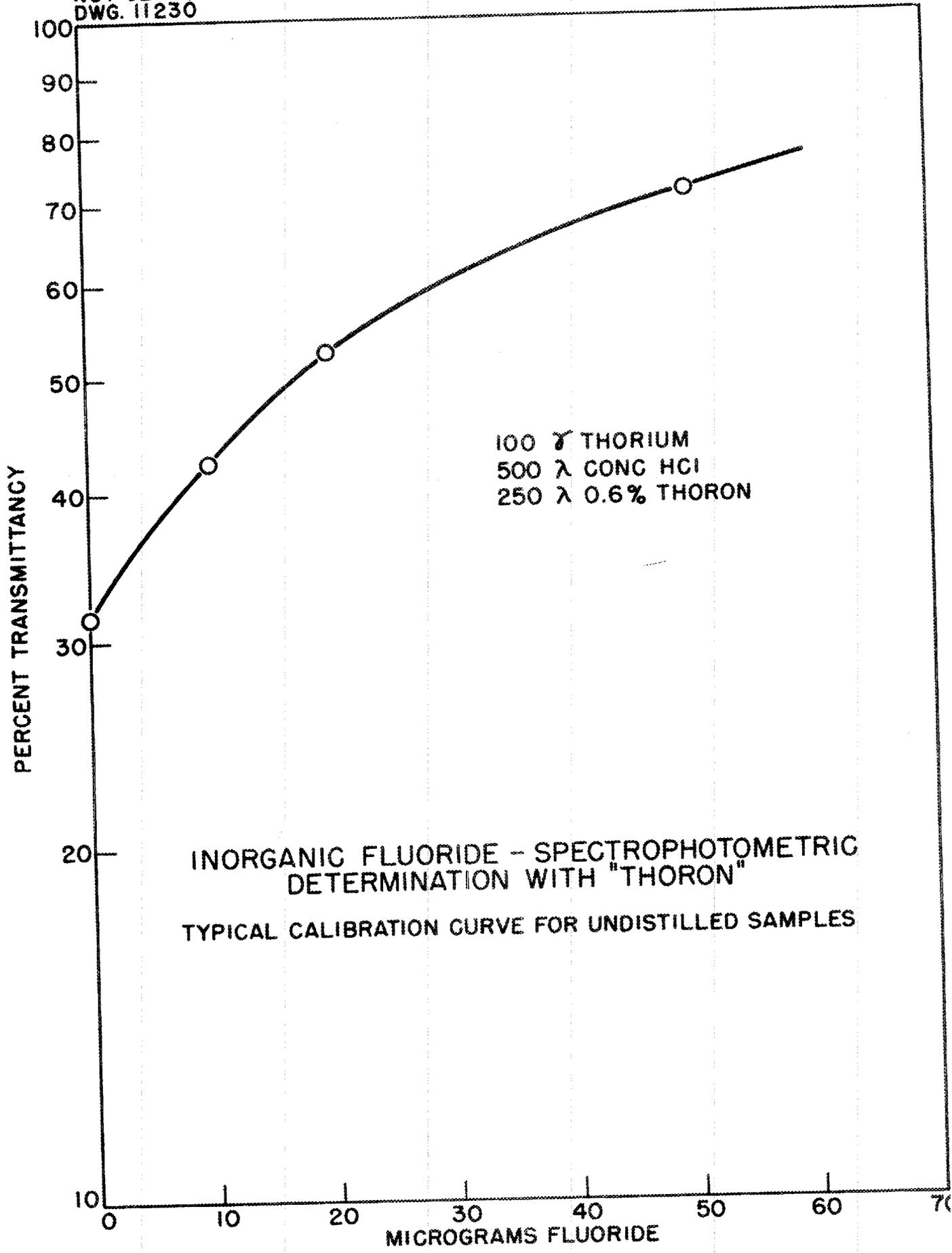
(h) The hydrazine hydrate reduces the excess KI.

(i) The color does not change appreciably in 3 hours.

(j) When standard NaF solutions are distilled from $HClO_4$ and then assayed, the results are higher than those obtained from duplicate samples analyzed without distillation⁽³⁾. Prepare a calibration curve for use with distilled samples as follows: Use the standard NaF solution in place of the sample. Following Procedure B, determine the per cent transmittance of solutions containing from 0 to 50 γ F^- at 10 γ intervals. Plot the optical density values as ordinates versus F^- amounts as abscissae on semi-logarithmic paper. The curve does not follow Beer's Law. Although this curve can be used for determining F^- concentrations of 0 to 50 γ , the most sensitive portion of the curve is in the range of 0 to 20 γ F^- where an average increase of 1 γ F^- produces an average decrease of 0.083 in optical density. A typical curve is shown in Apx. 2.



FLUORIDE DISTILLATION APPARATUS



[REDACTED]

ORNL HIGH-SENSITIVITY RECORDING POLAROGRAPH

Method No. 8

I. PRINCIPLE AND GENERAL DISCUSSION OF POLAROGRAPHIC ANALYSIS

The polarographic method is based on the interpretation of a current-voltage curve that is obtained when a solution containing a reducible or oxidizable ion is electrolyzed in a cell containing a dropping mercury electrode and a reference electrode which remains unpolarized during the electrolysis. From the current-voltage curves both a qualitative and a quantitative analysis may be made since the half-wave potential is characteristic for a specific ion, and the height of the diffusion current is proportional to the concentration of the ion.

In general, the concentration of the reducible ion in the test solutions ranges from 10^{-4} to 10^{-2} M and there is also present in the solution an inert electrolyte which acts as a supporting electrolyte. The concentration of the inert electrolyte should be at least fifty times the concentration of the reducible or oxidizable ion although the exact concentration is not critical and is usually about 0.1 M. The function of the supporting electrolyte is to carry the current in the bulk of the solution without appreciable transfer of the reducible ion. The current then is limited solely by the rate of diffusion of the reducible ion in the layer immediately surrounding the cathode, and hence is called the "diffusion current".

In most cases the solutions must be freed from dissolved oxygen because it is reduced at the dropping mercury electrode giving waves which interfere with those of many other elements. This may be accomplished by either bubbling oxygen-free nitrogen through the solution, or, in neutral or alkaline solutions, the oxygen may be removed by adding sodium sulfite. The solution is made about 0.1% in sodium sulfite.

[REDACTED]

In some cases polarograms of metal ions show maxima which interfere with the measurement of the diffusion current. These maxima can usually be eliminated by the addition of a surface active agent such as gelatin, methyl cellulose, or a dye, e.g. methyl red. The amount of agent to add depends on the particular agent; however, the usual concentration of the maxima suppressor is about 0.01%⁽¹⁾.

Polarography is readily adaptable to the analysis of radioactive materials because few manipulations are necessary in the course of analysis. However, in the case where the material is extremely radioactive the size of the sample must be severely limited and one must use micro techniques or one must analyze very dilute solutions with more conventional polarographic cells (1 to 10 ml).

Because of the difficulties involved in using micro apparatus and techniques behind barricades, a high sensitivity recording polarograph⁽²⁾ was designed which would be applicable to analyzing very dilute solutions in the range of 10^{-6} M or less.

The design of this polarograph, which was unavailable commercially, permits diffusion currents in the order of 5×10^{-3} microamperes to be recorded on a Brown recorder and measured with a good degree of accuracy.

References:

1. Kolthoff, I. M., and Lingane, J. J., Polarography, Interscience, New York, (1941).
2. Kelley, M. T., Miller, H. H., and Davenport, W. H., Jr. "Chemistry Division Quarterly Progress Report for Period Ending March 31, 1950. Part II, Analytical Chemistry. A Polarograph for Analysis of Very Dilute Solutions (10^{-6} M)", p. 24, ORNL-686.

II. DESCRIPTION OF THE INSTRUMENT CONTROLS

A. Span Potential

The span potential control sets the voltage range which the bridge will cover. The span voltmeter is usually set at one volt, in which case the bridge starts at zero volts and traverses through a one volt span at its maximum travel.

B. Initial Potential

The initial potential control determines the potential applied to the polarographic cell when the bridge is at zero and is indicated by the span voltmeter. Whether the initial potential is positive or negative depends upon the Reverse Switch. This initial potential control may be used to start a polarogram at any potential other than zero in order to eliminate running the bridge slide wire over the complete range. This control may also be used to cover a voltage range above one volt when the span voltmeter is set at one volt. For example, the half-wave potential of the cobaltous ion in 0.1 M pyridine - 0.1 M pyridinium chloride is -1.1 v. The most convenient setting of the span voltmeter is 1.0 v and of the initial voltmeter 0.85 v, in which case the zero position on the bridge would correspond to -0.85 v and would cover an additional one volt or to -1.85 v. As can be seen only about half of the bridge would have to be covered to completely record the wave.

C. Reverse Switch on the Initial Potential Control:

Ordinarily, this switch is left in the normal position in which case the sign of the potential impressed on the bridge is negative. By turning the switch to the reverse position, the potential on the bridge becomes positive. If the switch is in the reverse position, the initial potential on the bridge is positive and the bridge will traverse in a negative direction the span of voltage indicated on the span voltmeter.

D. Bridge Motor Switch

The bridge is started at the zero position and has an emf as determined by the span and initial voltmeters. The bridge motor switch simply starts the motor drive of the helipot. The bridge is equipped with a friction clutch mechanism so that it is returned to zero by simply turning the indicator knob to zero.

E. Brown Recorder Switch

In the "ON" position this switch starts the chart operating as

well as activates the motor which drives the recording pen.

F. Zero Control

The zero control is used to determine the position of the recording pen on the Brown chart with no applied potential. This control may also be used to buck out or eliminate reduction waves of ions that reduce before the ion being analyzed, provided the concentration of the undesired ion is not too great.

G. R-Compensator

When the polarograph is operated at high sensitivities the so-called "condenser current" assumes very great importance. This current is made up of the charges on each drop due to the charging of the electrical double layer as a capacitor. This current is of the order of 0.2 microampere, and in all polarograms where the diffusion current approaches this value it must be considered. This condenser current starts at a negative value at zero potential, decreases almost linearly to zero at the "electrocapillary zero potential" for mercury (about 0.5 volt) and then increases in a positive direction at a rate somewhat different from that prior to the electrocapillary zero. In practice this condenser current results in a considerable positive slope to the residual current portion of the curve so that the measurement of diffusion current becomes difficult. This effect can be nullified by applying a compensating current which increases with potential in a negative direction. A device for this purpose constitutes the so-called R-compensator of this instrument.

For practical operation, the position at which the R-compensator is set may be determined in one of the two ways. First, an aliquot of supporting electrolyte is placed in the cell and deaerated. With the other controls (span and initial voltmeters, sensitivity, etc.) in their proper settings, the curve is started. The R-compensator is adjusted until the curve is approximately parallel

to the voltage axis. This setting of the compensator will be approximately the same when the sample is polarographed. The alternate method of determining the position is to run a polarogram of the sample and to adjust the R-compensator until the residual current portion of the curve is parallel to the voltage axis.

At the highest sensitivities the shape of the curve may be different from the conventional shape in that the diffusion plateau may not be parallel to the residual current portion of the curve. In this case the method of measuring the curve to determine the height of the diffusion current is assumed to correct for the odd shape of the curve. This method was explained above.

H. Sensitivity Switch

The sensitivity switch determines the span of the wave on the Brown Recorder chart and is set in the position which will give the maximum wave height that can be drawn on the chart. The sensitivity is expressed in microamperes per full scale of the chart.

I. Damping Control

Again at high sensitivities, the magnitude of the oscillations drawn on the recorder caused by formation of the mercury drop in the electrode become so large that it is necessary to decrease the size of these oscillations. This is done by using the damping control. However, if the oscillations are completely damped out the curve drawn does not represent the true diffusion current, hence the damping used should be the minimum consistent with good recording of the curves. It is important not to change the damping control between the two curves of a standard addition analysis.

III. METHOD OF DETERMINING THE HEIGHT OF THE DIFFUSION CURRENT

In drawing the curves it is assumed that the average of the oscillations is the true current. On that assumption the midpoints of the oscillations are

measured and a line drawn through two points in the straightest portion of the residual curve. The same thing is done in the limiting current region and in this case the two lines may or may not be parallel.

A line is then drawn through the approximate position of the $E_{1/2}$, through the midpoints of the oscillations, until this line crosses both the previous lines. A line perpendicular to the voltage axis is dropped from the point where the two lines cross at the top of the wave to the point where it crosses the line representing the residual current. The distance between the point where the perpendicular line crosses the residual line and the point where the line drawn through the $E_{1/2}$ crosses the residual curve line is measured along the residual line and at one half the distance another perpendicular line to the voltage axis is drawn up through the $E_{1/2}$ until it crosses the line representing the diffusion current. The height of the diffusion current is measured from the points where the perpendicular line through the $E_{1/2}$ crosses the residual curve line and the diffusion curve line.

IV. OPERATING PROCEDURE

1. Place test solution in the cell and start deaeration by bubbling oxygen-free nitrogen through the solution.
2. Set span potential at desired potential (usually one volt).
3. Adjust initial potential to desired potential if necessary.
4. Set bridge at zero.
5. Adjust sensitivity control to the position that will give a full wave on the Brown chart. (This is determined by trial method.)
6. If a high sensitivity is being used, turn on the R-compensator and adjust as previously described.
7. After the solution has been deaerated, remove the nitrogen tube to a position above the solution.

8. Turn on the chart on the Brown and adjust the pen to about position 10 on the chart by the zero control.
9. If the oscillations are large adjust the damping control so that the oscillations are approximately 10 mm high.
10. After the Brown Recorder and solution reach equilibrium, as indicated by a pen drawing a straight line on the chart, turn on the Bridge motor and mark the beginning point on the chart.
11. Record the polarogram until the straight line diffusion current portion of the wave extends for at least 0.1 volt.

MERCURY - POLAROGRAPHIC DETERMINATION

Method No. 9

I. PRINCIPLE

A current-voltage curve is registered as an increasing emf is slowly and continuously applied to a polarizable electrode (mercury dropping from a capillary) relative to a reference electrode (saturated calomel) joined to the system by a KCl-agar bridge. The reduction of the ion, contained in a supporting electrolyte that is many times as concentrated, is indicated by a "wave", i.e., an increase in current to a limiting value, the height of which is a measure of the quantity, of the reducible substance. The potential at which the wave attains half its height after correction for the residual current of the supporting medium is characteristic for the reducible ion. This potential is called the half-wave potential.

Both mercuric and mercurous ions reduce at zero potential at the dropping mercury electrode versus the saturated calomel electrode; therefore, no residual curve is obtained for the polarogram. However, Kolthoff and Lingane have found that both ions yield well-defined diffusion currents that are directly proportional to the concentration⁽¹⁾.

II. STATUS

This method is applicable to the determination of mercury in concentrations of 20 to 100 γ /ml in solutions containing uranium. Since the half-wave potential of the uranyl ion is -0.18 volt it does not interfere with the mercury determination. By using relatively large concentrations of mercury, approximately 20 to 100 γ /ml, it has been found that, at the sensitivities at which these curves are run, the residual current is negligible, therefore the height of the current is proportional to the concentration. A typical polarogram is shown in Apx. 2.

The use of a recording polarograph, especially the ORNL polarograph designed by M. T. Kelley^(2, 3), is advised.

Further detailed information regarding the theory of polarography and the polarographic determination of mercury is given in the references.

References:

1. Kolthoff, I. M., and Lingane, J. J., Polarography, p. 251, Interscience, New York (1941).
2. "ORNL High-Sensitivity Recording Polarograph", Method No. 8, this manual.
3. "Chemistry Division Quarterly Progress Report for period ending March 31, 1950. Part II, Analytical Chemistry. A Polarograph for Analysis of Very Dilute Solutions (10^{-6} M)", M. T. Kelley, H. H. Miller, W. H. Davenport, Jr., p. 24, ORNL-686

III. REAGENTS AND APPARATUS

A. Reagents

1. Agar-KCl Solution for use in salt bridge. Prepare by dissolving 30 g KCl in 100 ml distilled water. Heat the solution and dissolve 3 g Agar in it.
2. Ammonium Chloride, sat. NH_4Cl . Prepare by adding about 500 g NH_4Cl to 1 liter of distilled water.
3. Ammonium Hydroxide, sat. NH_4OH .
4. Copper, strip.
5. Standard Mercuric Nitrate, 2.0 mg Hg (II)/ml in 0.1 N HNO_3 . Prepare by dissolving 2⁺ 0.005 g of mercury, redistilled analytical reagent grade, in 6.25 ml conc. HNO_3 . Add approximately 2 ml H_2O to aid dissolving, then dilute to one liter.
6. Mercurous Chloride (calomel), solid Hg_2Cl_2 , analytical reagent grade.
7. Methyl Red Indicator Solution, 0.2% in 60% $\text{C}_2\text{H}_5\text{OH}$. Prepare by dissolving 1 g methyl red indicator in 300 ml $\text{C}_2\text{H}_5\text{OH}$ and diluting to 500 ml with distilled water.

8. Nitrogen, water-pumped.

9. Sulfuric Acid, 6 N (3 M) H_2SO_4 . Prepare by adding 168 ml conc. H_2SO_4 to about 500 ml distilled water and diluting to 1 liter with distilled water.

B. Apparatus

1. Polarograph, ORNL High-Sensitivity Recording is recommended. See Reference 2 and 3.

2. Dropping Mercury Electrode. See Apx. 1. Construct from Sargent barometric tubing, 5 inch length, sealed to a mercury reservoir designed to provide a constant Hg level. The mercury dropping time of this arrangement at full height should be the optimum 3 to 5 seconds when immersed in water at room temperature. See Method No. 10, Ref. 2 for instructions and care of the electrode.

3. Saturated Calomel Electrode. Prepare by grinding approximately 50 g $HgCl$ (calomel) with approximately 50 g Hg. Place the mixture in a 250 ml Erlenmeyer flask fitted with a two-hole stopper. Add approximately 200 ml of a saturated KCl solution to the $HgCl$ - Hg mixture. Add Hg to cover the bottom of the flask. Seal a small piece of platinum wire into a small glass tube and fill the tube with mercury. Place this in the flask so that the Pt tip is in contact with the mercury pool. Connect the other end of the electrode (Hg in the tube) to the anode of the polarograph with a lead from a platinum wire dipping in the mercury. Use only platinum in contact with the mercury to prevent contamination of the mercury. Measure the resistance of the entire cell circuit from the mercury reservoir to the S.C.E. with a conductivity bridge. This should be less than 5000 ohms. If greater, replace the KCl-Agar bridge.

4. Reduction Cell. Prepare from a $\$ 40/25$ ball joint. Cut the female part of the joint off and seal it at the cut end to give a cell of about 2-1/2 inch length. Cut the male part off to about a 1 inch length and fit it with a four-hole No. 5 rubber stopper. Provide the cell with a clamp.

5. KCl-Agar Salt Bridge. Prepare by drawing the hot KCl-Agar solution up into a length of Tygon tubing by use of a large hypodermic syringe.

6. Nitrogen Gas Wash Train, consisting of four gas wash bottles each containing 200 ml of equal amounts of saturated NH_4Cl and conc. NH_4OH with a few strips of copper immersed in solution. Place 6 N H_2SO_4 and methyl red indicator in a fifth wash bottle to absorb NH_3 from the previous bottles. The indicator will turn yellow when the H_2SO_4 has been neutralized and should be replaced. Place glass wool in a sixth bottle, to serve as a moisture trap and connect this bottle to the reduction cell.

IV. PROCEDURE

1. Raise the mercury reservoir to full height on the ring stand and pipet an aliquot of the sample containing 20 to 100 γ Hg (II)/ml in 0.1 M HNO_3 into the reduction cell.
2. Bubble scrubbed nitrogen through the solution for ten minutes.
3. Set the span potential at 1.0 volt.
4. Set the sensitivity scale at 2 microamperes.
5. Set the damp control so that the oscillations are about 10 to 15 mm high when the cell is connected.
6. Set the slide wire at zero.
7. Remove the nitrogen inlet tube from the solution to a position just above the solution.
8. Disconnect the calomel electrode.
9. Adjust the zero knob of the polarograph so that the pen reads approximately 10 on the chart.
10. Wait until a straight line has been drawn. This forms the base line.
11. Connect the calomel electrode.

12. Record the polarogram until the chart has traveled approximately two inches.
13. Stop the recorder.
14. Determine the diffusion current and calculate the Hg (II) concentration of the sample.

Calculations:

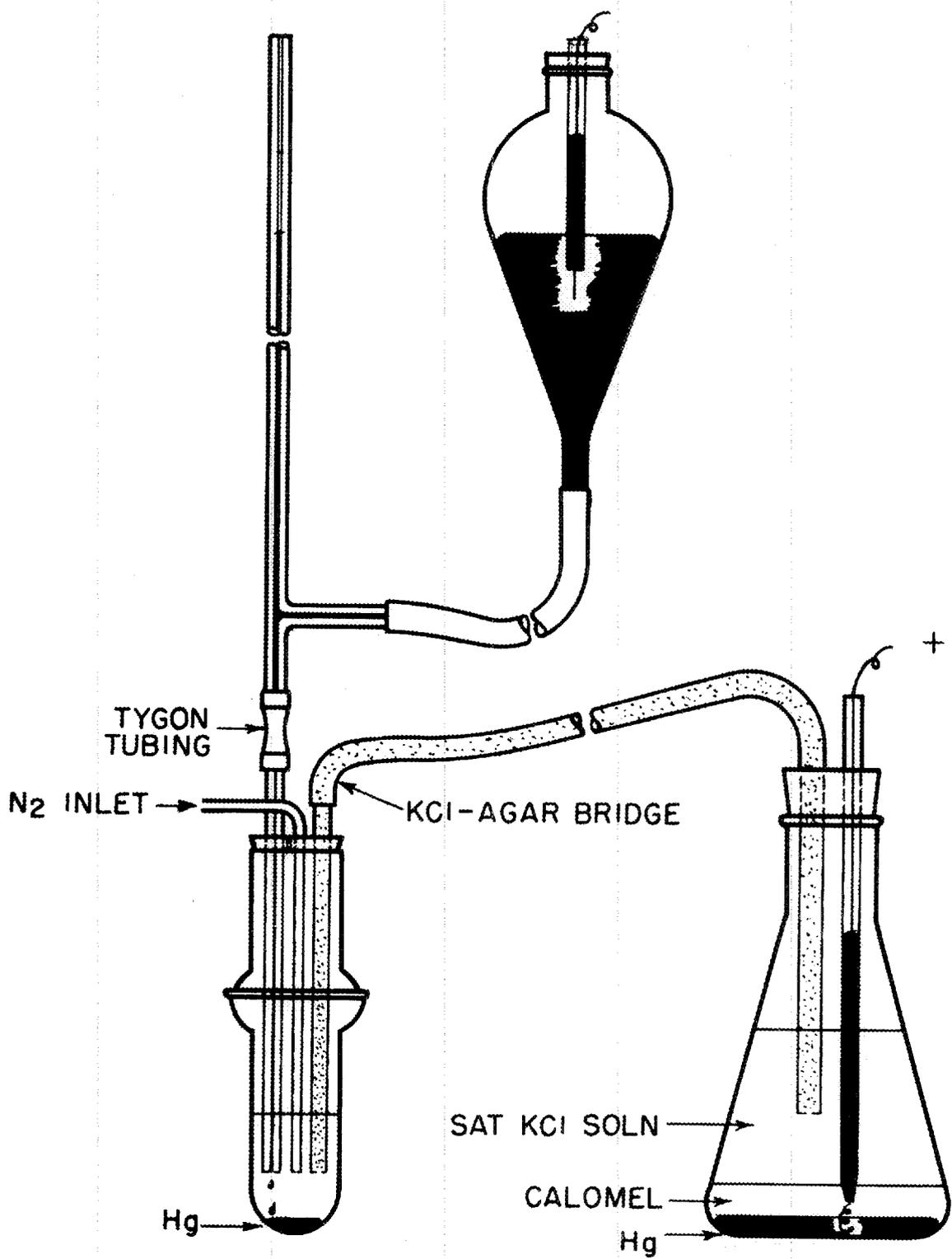
- Let: 100 = number of scale divisions for full chart
- A = sensitivity scale settings, μa
 - B = height of Hg (II) wave, scale divisions
 - C = diffusion current, $\mu\text{a} = A \times B$
 - D = γ Hg (II)/ml corresponding to C and determined from the calibration curve
 - E = sample dilution factor.

Then:

$$\text{Mercury (II) in sample, } \gamma/\text{ml} = D \times E.$$

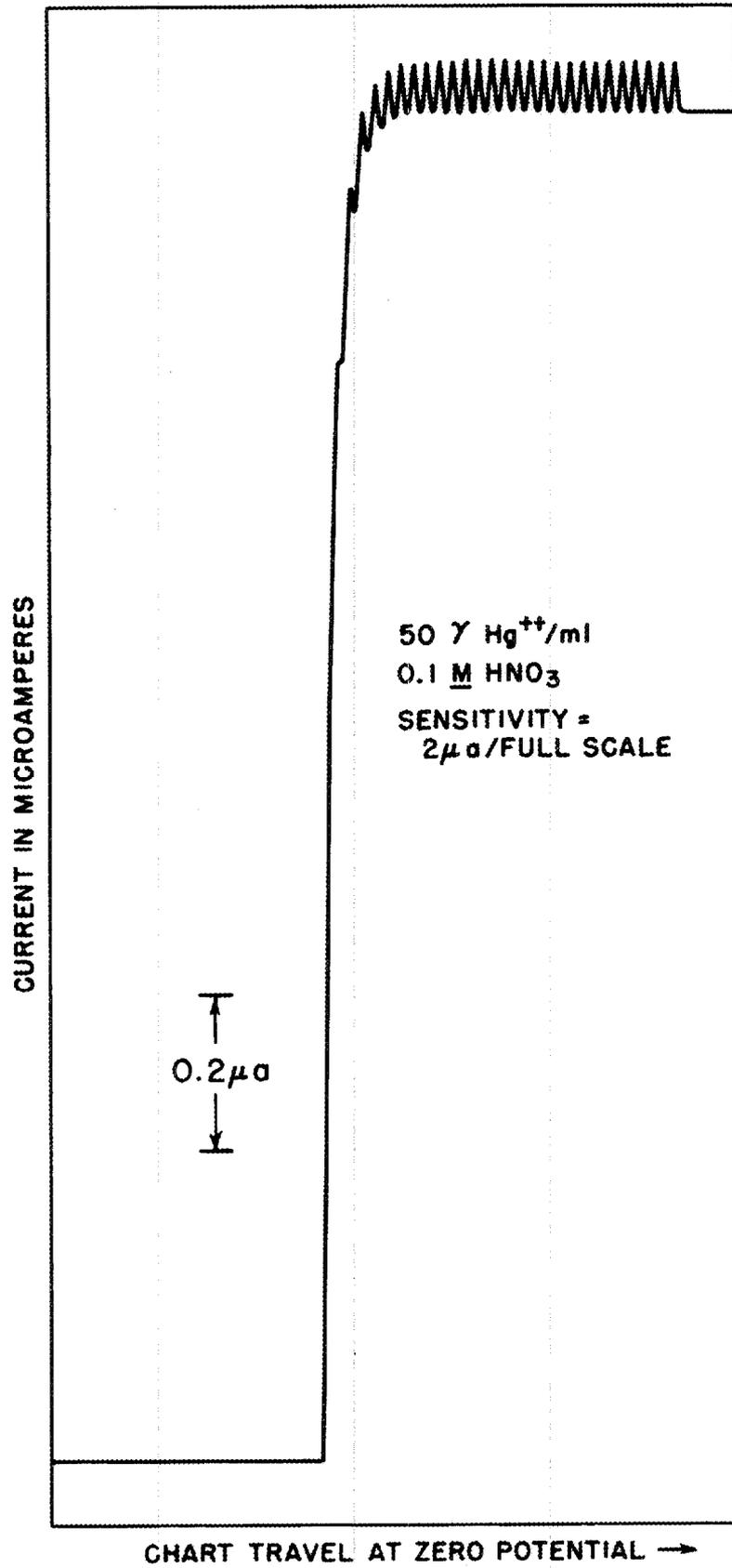
Preparation of Calibration Curve

Prepare a standard calibration curve in the following manner. From the standard mercuric nitrate stock solution, 2.0 γ Hg (II)/ml, prepare standard solutions containing 20, 40, 60 and 80 γ Hg (II)/ml in 0.1 M HNO_3 . Analyze 10.0 ml of each standard solution polarographically as described above, determining the diffusion current for each. Plot the results on rectangular coordinate graph paper, plotting the diffusion current, μa , as ordinate and concentration of mercury, γ/ml , as abscissa.



ELECTROLYSIS CELL ASSEMBLY

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TYPICAL POLAROGRAPH OF MERCURY (II)

URANIUM - POLAROGRAPHIC DETERMINATION BY STANDARD ADDITION

Method No. 10

I. PRINCIPLE

A current-voltage curve is registered as an increasing emf is slowly and continuously applied to a polarizable electrode (mercury dropping from a capillary) relative to a reference electrode (saturated calomel) joined to the system by a KCl-agar bridge. The reduction of the ion, contained in a supporting electrolyte that is many times as concentrated, is indicated by a "wave", i.e., an increase in current to a limiting value, the height of which is a measure of the quantity of the reducible substance. The potential at which the wave attains half its height after correction for the residual current of the supporting medium is characteristic for the reducible ion. This potential is called the half-wave potential.

The polarogram of the uranyl ion in dilute solutions of strong acids consists of a wave with a half-wave potential of -0.18 v and two coalesced waves with an apparent half-wave potential of -0.93 v (S.C.E.). It is with the first wave only that this method is concerned. It is due to reactions such as



The first half-wave potential is not appreciably affected by changes in acidity or salt concentration.

II. STATUS

This method is applicable to the determination of uranium in concentrations of 5 to 500 micrograms per ml in the presence of chromate and iron. The standard addition technique⁽¹⁾ is used. The supporting electrolyte is 0.1 M HCl. The height of the first polarographic wave has been shown by Tishkoff⁽⁴⁾ to be proportional to the concentration of the uranyl ion. A typical polarogram is shown in Apx. 2.

Interferences from Cr(VI) and Fe(III) are eliminated by boiling the sample with 1 ml of 10 per cent hydroxylamine hydrochloride. The dissolved oxygen in the

solution is removed before the polarogram is run by passing water-pumped, purified nitrogen through the solution for ten minutes.

The use of a recording polarograph is advised. The ORNL polarograph designed by M. T. Kelley⁽⁶⁾ is used in the ORNL analytical control laboratories and instructions for its use should be consulted.

Further detailed information regarding the theory of polarography and the polarographic determination of uranium is given in the references.

References

1. Kolthoff, I. M., and Lingane, J. J., Polarography p. 251, Interscience, New York (1941).
2. Rodden, C. J., Analytical Chemistry of the Manhattan Project, p. 586-610, McGraw Hill, New York (1950).
3. Strubl, R., "Polarographic Studies with the Dropping Mercury Kathode. Part LXXV. The Estimation of Uranium and Other Heavy Metals in the Excess of Iron", Czechoslov. Chem. Commun., 10, 466 (1938).
4. Tishkoff, G. H., "Polarographic Analysis of Uranium" AEC-D-2005 (October 20, 1944).
5. "ORNL High-Sensitivity Recording Polarograph", Method No. 8, this manual.
6. Chemistry Division Quarterly Progress Report for period ending March 31, 1950. Part II, Analytical Chemistry. "A Polarograph for Analysis of Very Dilute Solutions (10^{-6} M)", M. T. Kelley, H. H. Miller, W. H. Davenport, Jr., p. 24, ORNL-686.

III. REAGENTS AND APPARATUS

A. Reagents

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2. Ammonium Chloride, sat. NH_4Cl . Prepare by adding about 500 g NH_4Cl to 1 liter of distilled water.

3. Ammonium Hydroxide, sat. NH_4OH .
4. Copper, strip.
5. Hydroxylamine Hydrochloride Solution, 10% $\text{NH}_2\text{OH}\cdot\text{HCl}$. Prepare by adding 10 g of $\text{NH}_2\text{OH}\cdot\text{HCl}$ to 100 ml distilled water.
6. Hydrochloric Acid, 0.1 N HCl . Prepare by diluting 8.6 ml conc. (11.6 M) to 1 liter with distilled water.
7. Mercury, redistilled, analytical reagent grade.
8. Mercurous Chloride (calomel), solid HgCl_2 , analytical reagent grade.
9. Methyl Red Indicator Solution, 0.2% in 60% $\text{C}_2\text{H}_5\text{OH}$. Prepare by dissolving 1 g methyl red indicator in 300 ml $\text{C}_2\text{H}_5\text{OH}$ and diluting to 500 ml with distilled water.
10. Nitrogen, water-pumped.
11. Sulfuric Acid, 6 N (3 M) H_2SO_4 . Prepare by adding 168 ml conc. H_2SO_4 to about 500 ml distilled water and diluting to 1 liter with distilled water.
12. Standard Uranium Solution, 500 γ U/ml. Prepare a stock uranium solution containing approximately 10 mg U/ml by dissolving 21.09 g $\text{UO}_2(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$, adding 6.5 ml conc. HNO_3 and diluting to 1 liter with distilled water. Standardize in triplicate by evaporating 25 ml aliquots to dryness, igniting at 1000°C and weighing as U_3O_8 .

B. Apparatus

1. Polarograph, ORNL High-Sensitivity Recording is recommended. See Reference 5.
2. Dropping Mercury Electrode. See Apx. 1, Mtd. No. 9. Construct from Sarjent barometric tubing, 5 inch length, sealed to a mercury reservoir designed to provide a constant Hg level. The mercury dropping time of this arrangement at full height should be the optimum 3 to 5 seconds when immersed in water at room temperature. See reference 2, p. 591 for instructions and care of the electrode.

3. Saturated Calomel Electrode. Prepare by grinding approximately 50 g HgCl (calomel) with approximately 50 g Hg. Place the mixture in a 250 ml Erlenmeyer flask fitted with a two-hole stopper. Add approximately 200 ml of a saturated KCl solution to the HgCl - Hg mixture. Add Hg to cover the bottom of the flask. Seal a small piece of platinum wire into a small glass tube and fill the tube with mercury. Place this in the flask so that the Pt tip is in contact with the mercury pool. Connect the other end of the electrode (Hg in the tube) to the anode of the polarograph with a lead from a platinum wire dipping in the mercury. Use only platinum in contact with the mercury to prevent contamination of the mercury. Measure the resistance of the entire cell circuit from the mercury reservoir to the S.C.E. with a conductivity bridge. This should be less than 5000 ohms. If greater, replace the KCl-Agar bridge.

4. Reduction Cell. Prepare from a \$ 40/25 ball joint. Cut the female part of the joint off and seal it at the cut end to give a cell of about 2-1/2 inch length. Cut the male part off to about a 1 inch length and fit it with a four-hole No. 5 rubber stopper. Provide the cell with a clamp.

5. KCl-Agar Salt Bridge. Prepare by drawing the hot KCl-Agar solution up into a length of Tygon tubing by use of a large hypodermic syringe.

6. Nitrogen Gas Wash Train, consisting of four gas wash bottles each containing 200 ml of equal amounts of saturated NH₄Cl and conc. NH₄OH with a few strips of copper immersed in solution. Place 6 M H₂SO₄ and methyl red indicator in a fifth wash bottle to absorb NH₃ from the previous bottles. The indicator will turn yellow when the H₂SO₄ has been neutralized and should be replaced. Place glass wool in a sixth bottle, to serve as a moisture trap and connect this bottle to the reduction cell.

IV. PROCEDURE

1. Raise the mercury reservoir the full height on the ring standard and pipet 10.0 ml of the sample containing 5 to 200 γ U/ml in 0.1 M HCl into the cell^(a)

2. Bubble scrubbed nitrogen through the solution for five minutes^(b).
3. Set the span voltage at 1.0 volt and the sensitivity scale to 2.0 μ a for a sample containing approximately 100 γ U/ml. For more dilute solutions set the polarograph to a more sensitive scale in order to get a good measurable wave.
4. Set the slide wire at zero^(c).
5. Remove the nitrogen inlet tube from the solution^(d).
6. Turn on the recorder and the chart drive.
7. Adjust the zero knob^(e) of the polarograph so that the pen reads approximately 10 on the chart.
8. Adjust the damping control^(f) to obtain oscillations comparable to those shown in Apx. 2.
9. Start the polarogram by turning the motor switch on and/or engaging the clutch drive^(g) of the slide wire.
10. Mark the chart at the starting point.
11. Record the polarogram until the bridge indicator dial reads 4 (0.4 volt).
12. Stop the recorder.
13. Pipet 5.0 ml of a standard 500 γ U/ml solution^(h) into the cell and mix with the sample.
14. Bubble gas through the sample as before.
15. Record the polarogram as before on a sensitivity scale of 5.0 μ a.
16. Measure the height of each wave in divisions on the chart by the standard measuring technique and calculate the diffusion current⁽ⁱ⁾.
17. Calculate the concentration of uranium as follows:

Calculations

Let: V = aliquot of sample, ml

v = volume of standard uranium solution added to the reduction cell, ml

- i = diffusion current of sample aliquot, μa
 i_s = diffusion current of sample aliquot plus standard addition, μa
 Δi = increase in the diffusion current, μa

Then:

$$\text{Uranium in sample, } \gamma/\text{ml} = \frac{i v C_{\text{std}}}{\Delta i (V + v) + i v} = C.$$

Sample Calculation:

	Test Solution	Sensitivity Scale Setting, $\mu a/100$ scale div.	Wave Height, Scale Divisions	Diffusion Current, μa
1st Wave	Sample, 10 ml	2.0	62.5	1.25
2nd Wave	Sample, 10 ml (a) Standard, 5 ml	5.0	64.5	3.23

(a) 500 γ U(VI)/ml.

Then:

$$V = 10 \text{ ml}$$

$$v = 5 \text{ ml}$$

$$i = 1.25 \mu a$$

$$i_s = 3.23 \mu a$$

$$\Delta i = 1.98 \mu a$$

$$C_{\text{std}} = 500 \gamma \text{ U/ml}$$

And

$$C = \frac{1.25 \times 5.0 \times 500}{1.98 (10+5) + (1.25 \times 5)} = 86.92 \gamma/\text{ml}.$$

Notes

(a) If Cr(VI) or Fe(III) is present, boil the sample with 1 ml of 10% hydroxylamine hydrochloride solution and cool.

(b) For low concentrations of uranium, ten minutes degassing is required.

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(c) The slide wire with the clutch disengaged can be turned in either direction.

(d) Leave the nitrogen inlet tube above the surface of the liquid.

(e) Leave the R-compensator switch off unless solutions of very low concentrations (1 to 10 γ U/ml) are to be analyzed. (See polarograph instructions.)

(f) More damping to lessen the oscillation of the pen might be desirable with some solutions.

(g) For best accuracy the height of the wave after the standard addition should be approximately twice that of the original wave. The 5 ml of 500 γ U/ml standard addition is sufficient to obtain this increase with an original 10 ml sample of approximately 100 γ U/ml. The standard addition on more or less concentrated samples must be adjusted accordingly.

(h) See Sargent Model XII polarograph manual.

(i) Calculate the diffusion current of each wave as follows:

Let:

100 = number of scale divisions for full chart

A = diffusion current, μ a

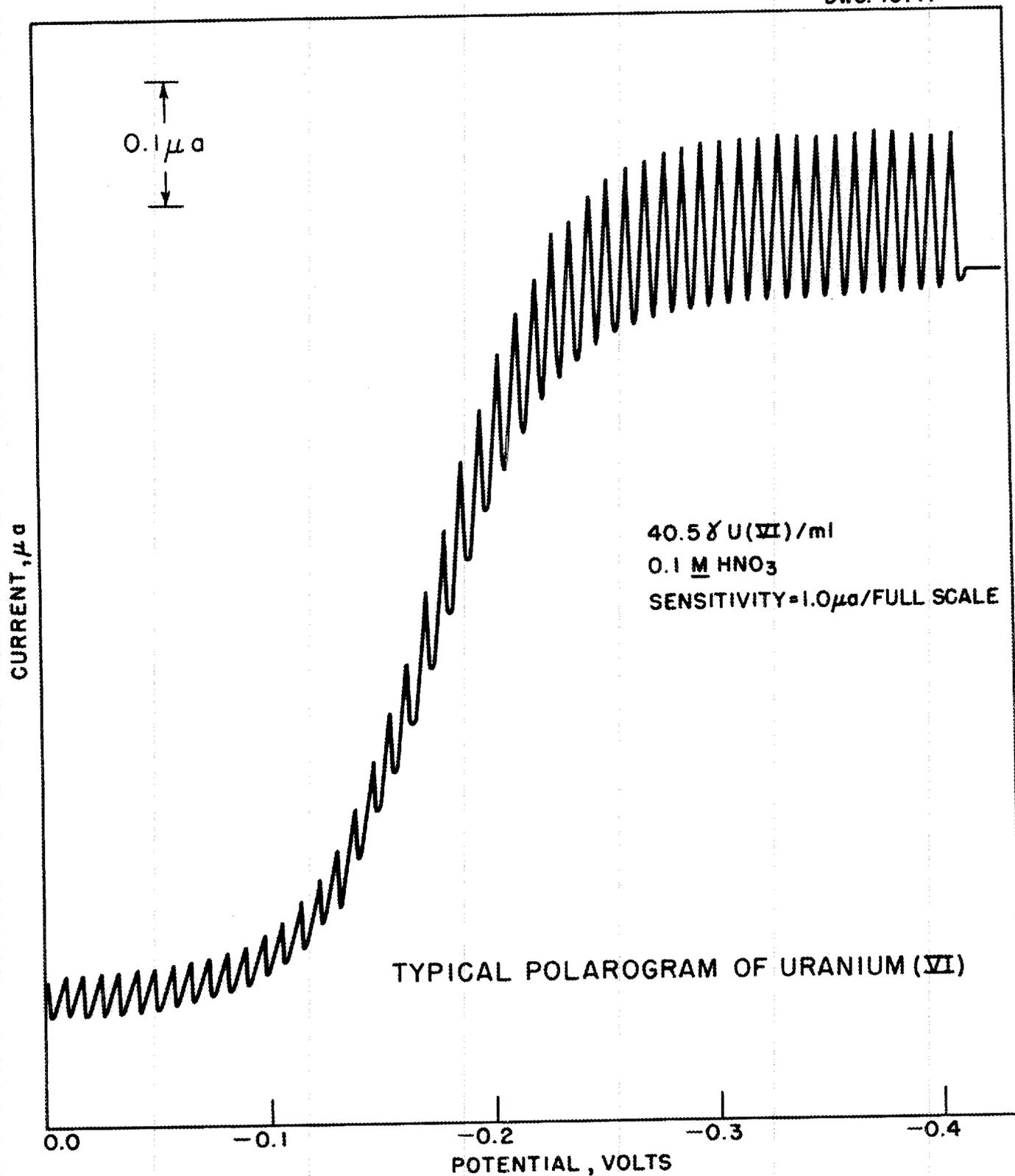
B = height of U(VI) wave in scale divisions

C = sensitivity scale setting, μ a.

Then:

$$A = B \times C.$$

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URANIUM - POTENTIOMETRIC TITRATION WITH FERRIC SULFATE

Method No. 11

I. PRINCIPLE

The uranium in a solution originally containing tri- and quadrivalent uranium is determined accurately by measurement of the titer between the two end points indicated by changes in the potential of a platinum-calomel electrode system during addition of ferric ion to the solution.

II. STATUS

This method is applicable to the analysis of solutions containing either natural or U₂₃₅-enriched uranium. Chrome alum solution is reduced to chromous ion in a Jones reductor, and then transferred to the uranium solution in order to reduce the uranium. The reduced uranium is then titrated potentiometrically with ferric sulfate. The first end point is reached when all of the uranium is oxidized from the (III) to the (IV) valence state, which is indicated by an inflection of the galvanometer of approximately 100 mv. The excess chromous ion is simultaneously reoxidized so that the chromous is not involved in the second end point. A second end point is reached when all of the uranium is oxidized from the (IV) to (VI) state. The difference in the end points is the titer value. The titration is made at a temperature of 90°C under a CO₂ atmosphere.

A special titrimeter is employed which utilizes a 10 ml hypodermic syringe in the reagent delivery system. The volume of reagent consumed is obtained from a Veeder-Root counter geared to the manual syringe drive.

Nitrate, fluoride and large amounts of phosphate interfere with this titration. Iron, chromium, nickel, cadmium, manganese and aluminum do not interfere but molybdenum, tungsten, copper, and tin must be absent. The interference of vanadium is stoichiometric and may be corrected after separate determination of this element. Titanium introduces a third end point, but

no error results if all three are detected. The analysis of synthetic uranium solutions by this method has been made to an accuracy within $\pm 0.3\%$.

References

1. Nettle, G. J., Casto, C. C., Orlemann, E. F., Grimes, W. R., and Larson, C. E., "Potentiometric Titration of Uranium with Ferric Sulfate", MDDC-1123 (May 29, 1947)
2. Widing, R. A. and Farquharson, J., "An Automatic Potentiometric Titrimeter", AECD-2836 (Dec. 23, 1949).

III. REAGENTS AND APPARATUS

A. Reagents

1. Carbon Dioxide Gas, cylinder.
2. Chrome Potassium Alum Solution, $10\% \text{Cr}_2(\text{SO}_4)_3 \cdot \text{K}_2\text{SO}_4 \cdot 24 \text{H}_2\text{O}$.
Prepare by dissolving 10 g of the alum and diluting to 100 ml with distilled water. Unstable, therefore prepare daily.
3. Standard Ferric Sulfate Solution, approximately 0.1 N. Prepare by dissolving 28.1 g $\text{Fe}_2(\text{SO}_4)_3 \cdot \text{X} \text{H}_2\text{O}$ (assume $\text{X} = 9$) in 100 ml conc. H_2SO_4 and dilute (USE CAUTION) to 1 liter with distilled water. Allow the solution to stand 18 to 24 hours, then siphon it into the storage bottle (See Apx. 1 & 2) and remove air bubbles from the titration system.

The calibration of the syringe-type burette serves as an indirect method of standardizing the ferric sulfate solution (see Section III B-1).

4. Sulfuric Acid, conc. and 7.5% (v/v).
5. Standard Uranous Sulfate Solution, 1.13 mg U/ml. Prepare as follows. Weigh to ± 0.1 mg a 4 g sample of U_3O_8 (99.95% reagent, MS-ST). Transfer the sample quantitatively to a 500 ml flat-bottom flask fitted with a reflux condenser. Add 120 ml conc. H_2SO_4 and 10 ml conc. HCl. Place on a hot plate, heat strongly for 45 minutes, and add distilled water drop by drop through the top of the reflux condenser, swirling the flask between each

addition of the water. The green uranous sulfate should have dissolved. Transfer the solution quantitatively to a 1 liter flask and make up to volume with distilled water.

6. Mercuric Chloride Solution, 2%. Prepare by dissolving 20 g HgCl_2 and diluting to 1 liter with distilled water.

7. Zinc Metal, granular, 20 to 30 mesh.

B. Apparatus

1. Special Potentiometric Titrimeter, assembly manually operated, illustrated in Apx. 1 and 2. The assembly consists of the following parts:

- (a) Crank mechanism, geared to syringe plunger.
- (b) Counter, five figure, Veeder-Root type.
- (c) Buret, hypodermic syringe-type, 10 ml capacity.
- (d) Reservoir for $\text{Fe}_2(\text{SO}_4)_3$ Reagent.

(e) Reaction Cell consisting of:

- (1) beaker, spoutless, 300 ml capacity
- (2) platinum electrode, made from 20 gauge wire
- (3) calomel electrode, external, Beckman type
- (4) reagent inlet
- (5) CO_2 inlet
- (6) thermometer

(f) Heater and Controls. Jacket-type heater attached thru a Variac to a Wheelco Temperature Controller, supplied by Wheelco Instruments Co., Chicago, Ill.

(g) Magnetic Stirrer, and glass-covered stirring bar magnet.

(h) Potentiometer, Rubicon, supplied by the Rubicon Co., Philadelphia, Pa.

Calibrate the titrimeter in terms of the counter turns equivalent to 1 mg of uranium as follows, in triplicate, for each batch of $\text{Fe}_2(\text{SO}_4)_3$ prepared. Pipet a 25 ml aliquot of the standard uranous sulfate solution into the 300 ml reaction cell and carry out the potentiometric titration with ferric sulfate according to the procedure described in this method. This calibration procedure assumes constant bore diameter of the syringe-type buret:

Calculations

Let: A = total mg U in aliquot of standard uranous sulfate
 titrated
 B = counter number at second end point
 C = counter number at first end point

Then:

$$\text{Counter turns equivalent to 1 mg U} = \frac{B - C}{A}$$

Make a daily check of the apparatus in the above manner.

2. Jones Reductor. Make by sealing a small stopcock to a glass tube approximately 15 x 120 mm. Place a glass wool plug at the bottom and fill with distilled water. Prepare a zinc amalgam by adding 300 ml of 2% mercuric chloride (or nitrate) solution and 1 to 2 ml conc. HNO_3 to 300 g of pure 20 to 30 mesh Zn in a beaker. Stir the mixture for 5 minutes, then decant the solution and wash two or three times by decantation. Wash the reductor with 2% H_2SO_4 , then with distilled water. Always have the reductor filled with water when it is not in use.

IV. PROCEDURE

1. If the submitted samples contain nitric acid, add sulfuric acid and fume.
2. Bring aluminum heating jacket up to operating temperature of 100 to 115° C.
3. Adjust CO_2 flow to approximately 2 bubbles per second.

4. Pipet a suitable aliquot (approximately 100 mg uranium) into a 300 ml spoutless beaker.
5. Cover the beaker with a watch glass and heat the solution to boiling.
6. While the sample is heating, prepare a chromous solution as follows:
 - a. After rinsing Jones Reductor with 7.5% sulfuric acid wash, allow the wash solution volume to approach the bed of amalgam.
 - b. Add 5 to 8 ml of 10% chrome potassium alum solution to the reductor followed by approximately 15 ml of acid wash.
 - c. Allow the reduced chromous solution to descend to the glass wool plug at the base of the reductor then close the stopcock. Check to see that the amalgam is covered by acid wash.
7. When the sample is at a boil, move the titration beaker under the Jones reductor, cover with the rubber stopper, and pass the chromous solution into the sample.
8. Place the beaker into the aluminum heater.
9. Cover with the rubber cap, placing the heated platinum wire into position(a).
10. Attach the electrodes to the proper leads (b).
11. Allow the temperature as shown on the thermometer to go to $90 \pm 1^\circ\text{C}$.
12. Lower the burette assembly into the proper hole.
13. Titrate with ferric sulfate to the first end point.^(c) Record counter number.
14. Reverse the polarity and titrate to second end point^(d). Record counter number.

Calculations

A. Natural Uranium Samples

- Let: A = counter number at second end point
 B = counter number at first end point
 C = number of counter turns equivalent to 1 mg uranium
 D = total volume of sample, ml
 E = aliquot of sample taken for analysis, ml

Then:

Natural uranium content of sample, per cent

$$= \frac{A - B}{C} \times \frac{D}{E} \times 100 = F$$

B. U₂₃₅ - Enriched Samples

- Let: G = decimal per cent U₂₃₅ in sample
 H = decimal per cent U₂₃₈ in sample
 I = composite atomic weight of enriched uranium, g
 = (G x 235.12) + (H x 238.14)

Then:

Natural uranium content of enriched sample, per cent =

$$F \times \frac{I}{238.07 \text{ g}}$$

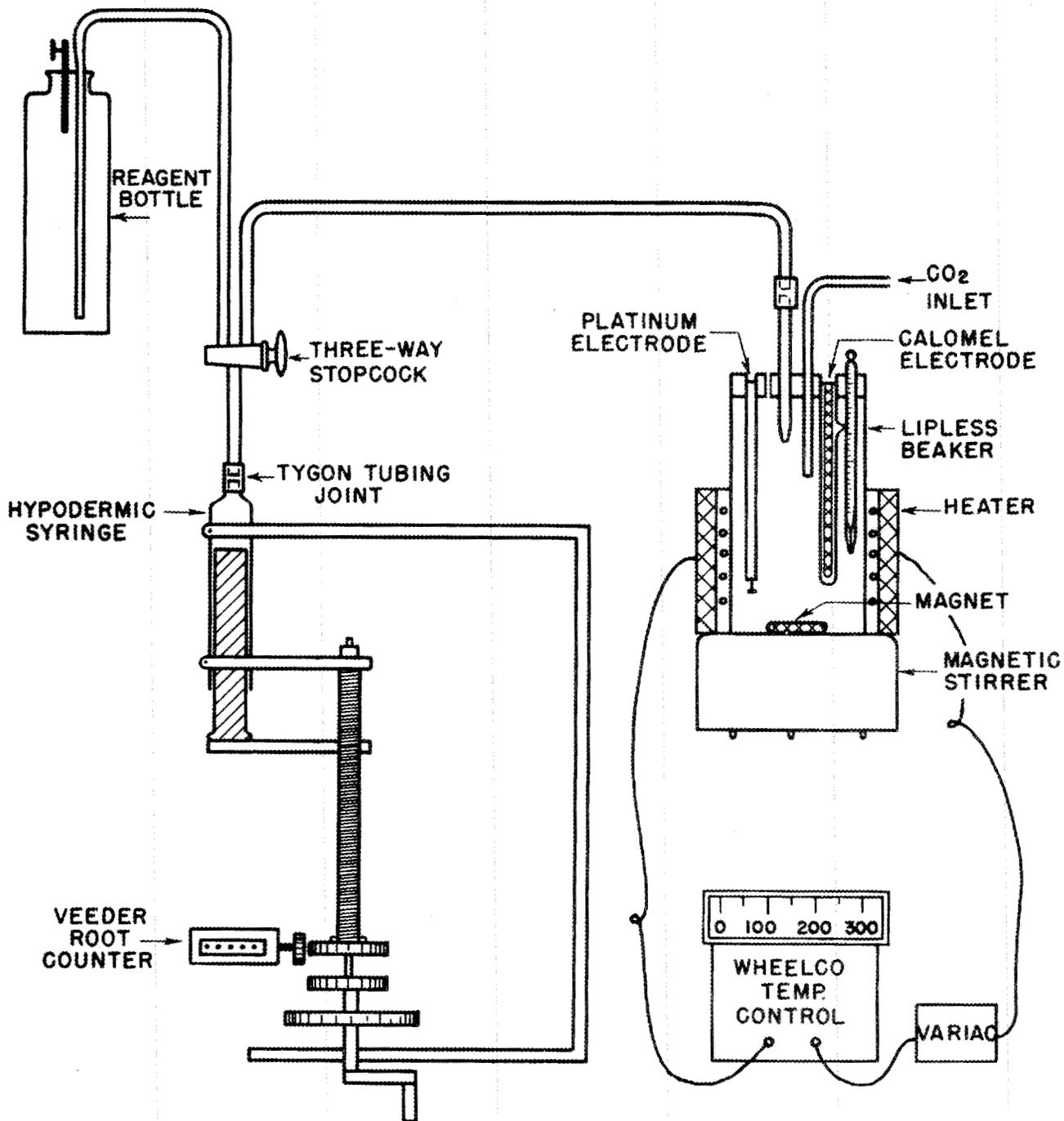
Notes:

- (a) The platinum wire should be heated to red heat between titrations.
- (b) The platinum electrode is connected to the negative pole of the potentiometer, and the calomel electrode is connected to the positive pole.
- (c) The excess chromous ion is oxidized to Cr(III) so that the chromous is not involved in the second end point.
- (d) This end point is marked by a similar inflection of the galvanometer but differing in degree. When approaching the second end point, add the ferric sulfate rapidly until a reading of 200 millivolts is obtained, whereupon

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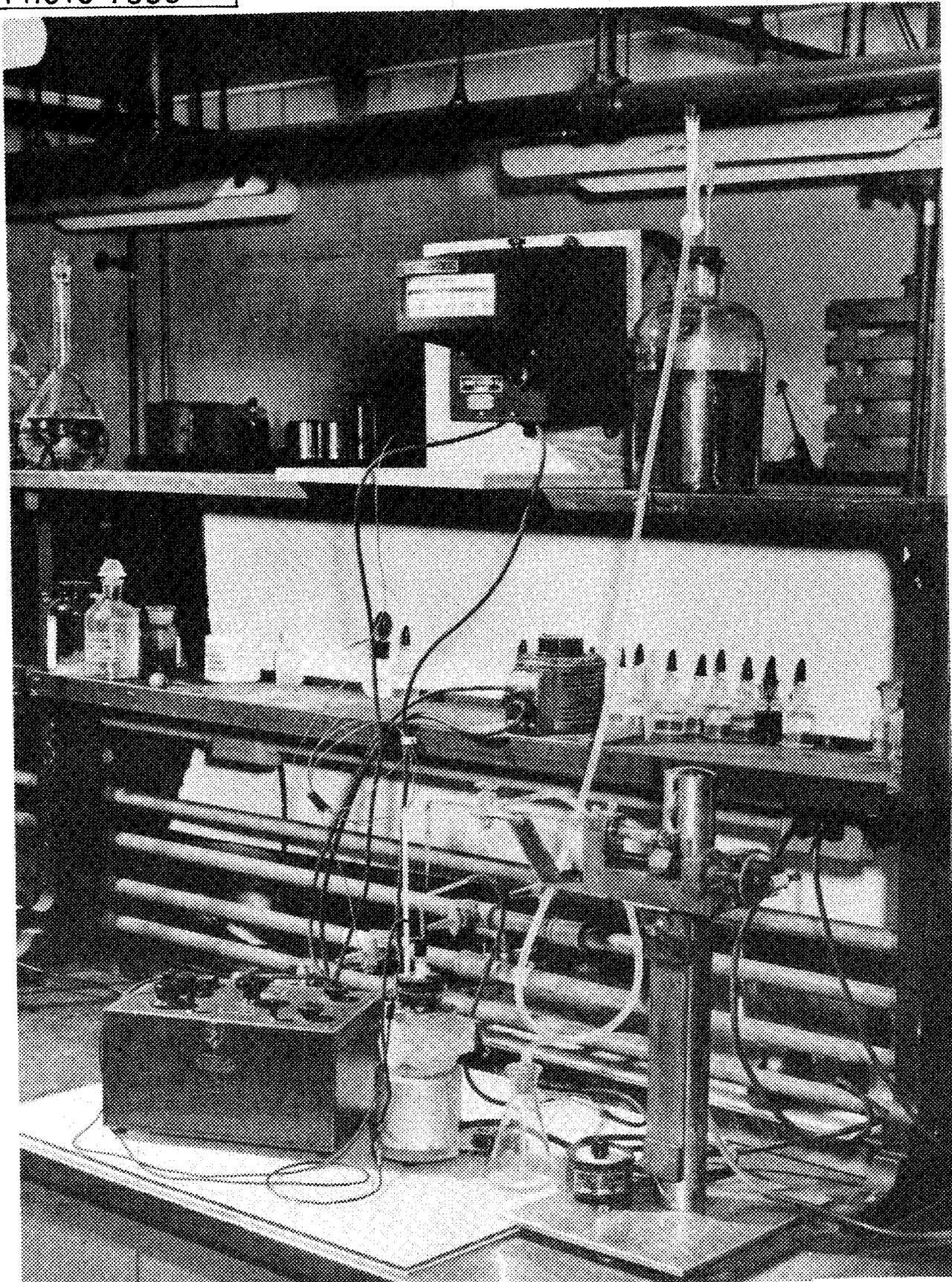
add the titrant in discrete increments, each addition equal to 2 numbers on the counting dial. Make readings on the galvanometer after each addition. The end point will occur close to 300 millivolts and can be calculated by noting the sharpest break in millivolt readings.



TITRIMETER ASSEMBLY FOR POTENTIOMETRIC
TITRATION OF URANIUM WITH $\text{Fe}_2(\text{SO}_4)_3$

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ASSEMBLY FOR POTENTIOMETRIC
TITRATION OF URANIUM WITH $\text{Fe}_2(\text{SO}_4)_3$

URANIUM - FLUOROMETRIC DETERMINATION

Method No. 12

I. PRINCIPLE

The fluorescence properties of uranium when exposed to ultraviolet light are intensified by fusion with some solids such as sodium fluoride. The fluorescence method is the most sensitive of all available methods for the determination of trace quantities of uranium.

Solutions containing microgram uranium concentrations are pipetted onto sodium fluoride pellets, dried, fused, and the fluorescence of the fused cake under ultraviolet illumination is measured with a fluorophotometer of special design.

II. STATUS

Rodden⁽¹⁾ gives a comprehensive discussion of the fluorometric method for determining uranium. It contains information on quenching, interfering elements, flux materials, fluorescence standards and apparatus. The analyst will find this reference most helpful. The method is reported to detect as little as 10^{-10} g of uranium. The accuracy of the method, however, is likely not better than 85 per cent.

If the submitted samples contain interfering elements, or high levels of radioactivity, uranium is extracted with tributylphosphate - "Varsol" solutions. Samples submitted in an organic medium are usually free enough of impurities so that aliquots of the samples can be pipetted directly onto the sodium fluoride pellets and fused.

References

1. Rodden, C. J. Analytical Chemistry of the Manhattan Project, p 122-135 and 565-573, McGraw-Hill, New York, (1950).
2. Northrup, M. A., "Fluorescence Bead Test for Uranium in Minerals", Ind. Eng. Chem., Anal. Ed., 17, 664 (1945).

III. REAGENTS AND APPARATUS

A. Reagents

1. Sodium Fluoride, solid NaF, giving a low fluorescence blank when tested by the procedure below, and being easily formed into pellets. Variation within a single vendor's material is often noticeable and each batch must be tested.

2. Nitric Acid, 12 N HNO₃. Prepare by diluting 780 ml conc. (15.4 M) to 1 liter with distilled water.

3. Tributyl Phosphate Solution, approximately 25% TBP in "Varsol". Prepare by diluting 250 ml (C₄H₉)₃PO₄, commercial grade, to 1 liter with "Varsol", supplied by oil companies.

4. Standard Uranium Solution, 1γ U/ml. Prepare a stock solution of uranyl nitrate containing 10.00 mg U/ml by dissolving 21.09 g UO₂(NO₃)₂·6H₂O, adding 6.5 ml conc. HNO₃ and diluting to 1 liter with distilled water. Standardize the solution gravimetrically in triplicate by evaporating 25 ml aliquots to dryness and igniting at 1000° C and weighing as U₃O₈.

5. "Permanent" Uranium Fluorescence Standard. Prepare from uranium soft glass, available from Corning Glass Co., Corning, N. Y., by grinding the uranium glass and mixing it with ground soft glass. Fuse the mixture in a platinum button on the multiple burner fusion device. Attempt to prepare a standard which will read approximately 15 mv on a 2 - 2 sensitivity setting. Reserve position No. 2 of the Fluorophotometer for this standard.

B. Apparatus

1. Fluorophotometer, Model Q-1165 constructed by ORNL Instrument Division and to be described in a forthcoming report by M. T. Kelley. See Apx. 2.

2. Multiple Burner Fusion Device, constructed by ORNL Instrument Division and described in their drawings numbered D-4421, C-4422, D-4423, C-4424, D-4425, D-4427, D-5478 and B-5492. See Apx. 1.

The temperature of the first two burners on the fusion device

should be 1000° C and the last 800° C. Fusion time should be two 1.5 minute periods.

3. Pelletizer, for forming NaF pellets. Described in ORNL Instrument Division drawing No. C-9202. See Apx. 1.
4. Platinum "Buttons", milled. See Apx. 1.
5. "Lucite" Carrier, tray for holding platinum buttons containing fused pellets and provided with a cover. See Apx. 1.
6. Magnetic Stirrer, type supplied by Fisher Scientific Co. Equip with a "Lucite" cover containing holes into which the four inch test tubes can rest. Use pieces of nickel wire as stirrers for the liquids contained in the test tubes.
7. Infra-red Lamp.
8. Test Tubes, four inch length.
9. Pipets, volumetric, 1 ml capacity.
10. Pipets, micro, 5 to 500 λ capacities.
11. Forceps, provided with platinum tips.

IV. PROCEDURE

A. Extraction of Uranium from Interfering Elements

If the sample is believed to contain interfering elements, extract the uranium as follows; performing the analysis in duplicate.

1. Pipet an aliquot (approximately 0.5 γ U) of the sample into a small test tube containing a magnetic stirrer (Ni wire).
2. Dilute to 500 λ with distilled water.
3. Add 500 λ of 12 N HNO_3 .
4. Pipet in 1.0 ml of 25% TBP in "Varsol".
5. Prepare two blanks by pipeting the following into small test tubes containing magnetic stirrers: 500 λ distilled water, 500 λ 12 N HNO_3 and 1.0 ml 25% TBP in "Varsol".

6. Place all the tubes in the "Lucite" holder on top of the magnetic stirrer.

7. Stop the stirrer and allow the phases to separate.

B. Preparation of the NaF Pellet for Fluorescence Measurement

1. By use of the pelletizer place 300 mg of NaF into each of twelve platinum buttons.

2. Pipet a suitable aliquot of the blank, sample, or of the organic phase if the Procedure A was used, directly onto the NaF pellet, in triplicate.

3. Dry the button for five minutes under an infra-red lamp.

4. Using a pair of platinum-tipped forceps place each button on one of the spindles of the fusion device.

5. After each button is fused place it into a "Lucite" carrier for protection from contamination until the uranium fluorescence can be read.

C. Measurement of Uranium Fluorescence

1. Plug the Fluorophotometer, Model Q-1165, into the controlled voltage line.

2. Approximately thirty minutes before reading samples, turn on the ultraviolet light switch at the left of the instrument panel and then the high voltage switch at the right of the panel.

3. Rotate the carrier of the Fluorophotometer and insert a series of sodium fluoride fused blanks into the numbered slots, leaving the first hole clean and vacant.

4. Rotate the No. 1 empty slot to the measurement position. Set the coarse sensitivity indicator at "2" and the fine sensitivity indicator at "0". Check to see whether the galvanometer reads "0". If not, adjust the zero knob until it does.

5. Turn the fine sensitivity knob to the 1 position and adjust the dark current to give a reading of '0' on the galvanometer.

6. Read each blank against the open No. 1 slot and record the reading for each. Turn the high voltage switch off. Average the readings for the blanks. Pick the blank that gives a reading as close as possible to the average of the series and place this in the No. 1 slot. Use this blank in reading a series of samples. Discard the rest.

7. Place the samples to be read in the Nos. 3 - 22 positions in the carrier and rotate into the instrument. With the carrier in the No. 1 position repeat Steps 4 and 5.

8. Rotate the "permanent" fluorescence standard, placed in the No. 2 slot, to the measurement position. Turn the fine sensitivity knob to read 1. Check to see that the galvanometer reading is the accepted reading for the standard. If not, re-zero the instrument. If this does not correct it, and if the reading is off more than ± 2 divisions, have an instrument man check the instrument.

9. Now rotate the samples in turn to the measurement position. Adjust the coarse and fine sensitivity knobs until the galvanometer reading lies between 10 and 25, in which range the highest accuracy is obtained. If it is necessary to switch from one coarse sensitivity to another, re-balance the dark current.

10. Record the coarse and fine sensitivity adjustments and the galvanometer reading.

11. Turn off the high voltage switch immediately after making the measurements.

12. For the blank and the samples, multiply the galvanometer scale reading, mv, by the factor specified for the particular combination of sensitivities used. The factors are supplied with the instrument. From the calibration curve (Part E) and the calculations below determine the amount of uranium in the sample.

Calculations

- Let: A = scale reading for blank, mv, x scale factor for blank
B = scale reading for sample aliquot, mv, x scale factor for sample
C = correct scale reading for sample aliquot, mv = B - A
D = γ of uranium corresponding to C (determined from the calibration curve)
E = aliquot of sample analyzed, ml.

Then:

$$\text{Uranium in sample, } \gamma/\text{ml} = \frac{D}{E}$$

D. Cleaning of Platinum Buttons

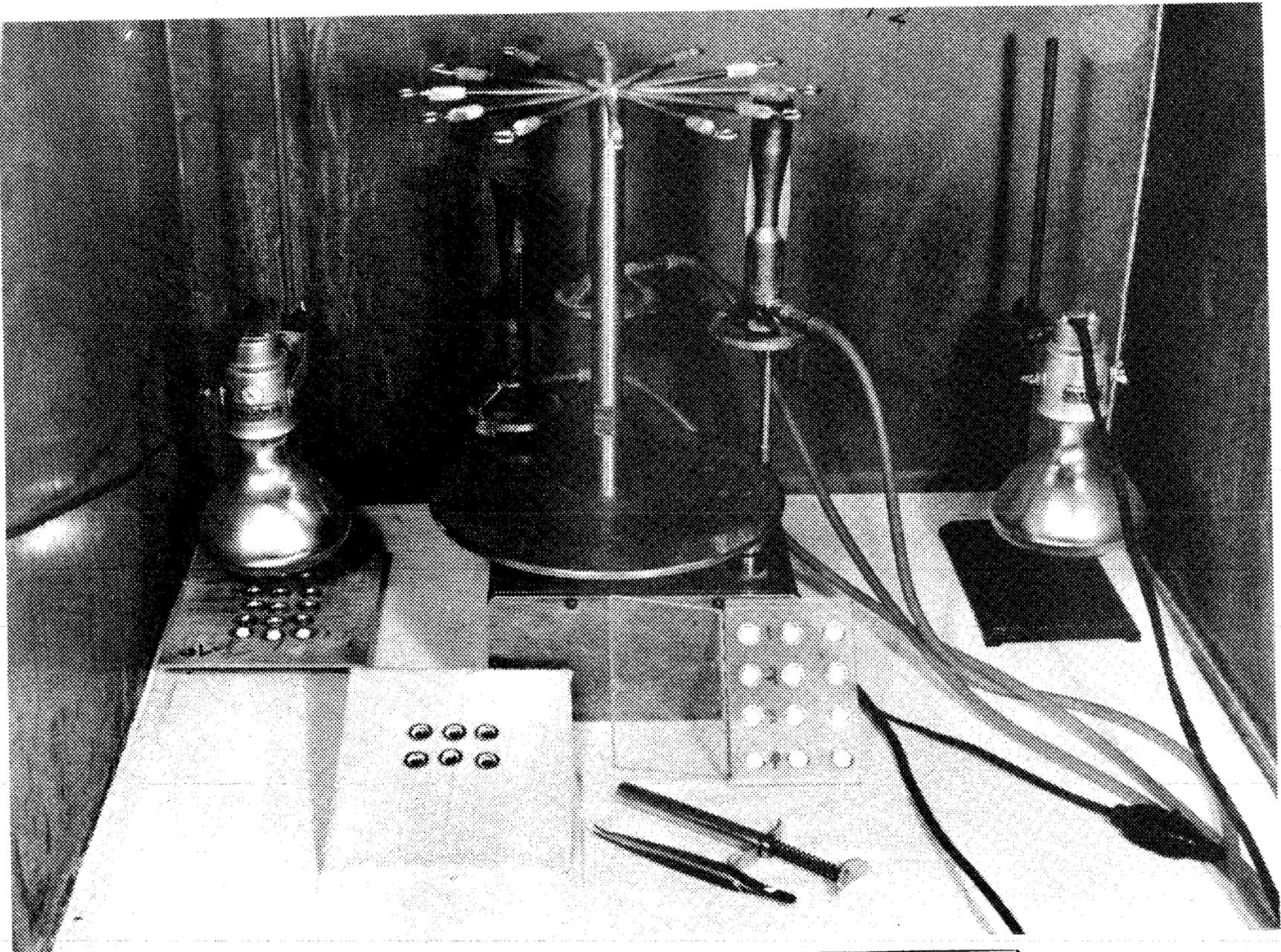
Clean the platinum buttons after each use as follows:

1. Boil in conc. HNO_3 for not less than thirty minutes. An hour is adequate.
2. Rinse thoroughly with distilled water.
3. Boil in conc. H_2SO_4 for not less than one hour.
4. Rinse thoroughly in distilled water and dry with Kleenex.

E. Preparation of Calibration Curve

Prepare a standard calibration curve by analyzing 10, 25, 50, 100 and 200 λ aliquots of the standard uranium solution, 17 U/ml, and reading the plates against a blank of NaF according to the procedure described above. Plot the number of millivolts as ordinate against the milligramma of uranium as abscissae on three cycle log-log graph paper (Dietzgen No. 340-L33). A typical calibration curve is shown in Apx. 3.

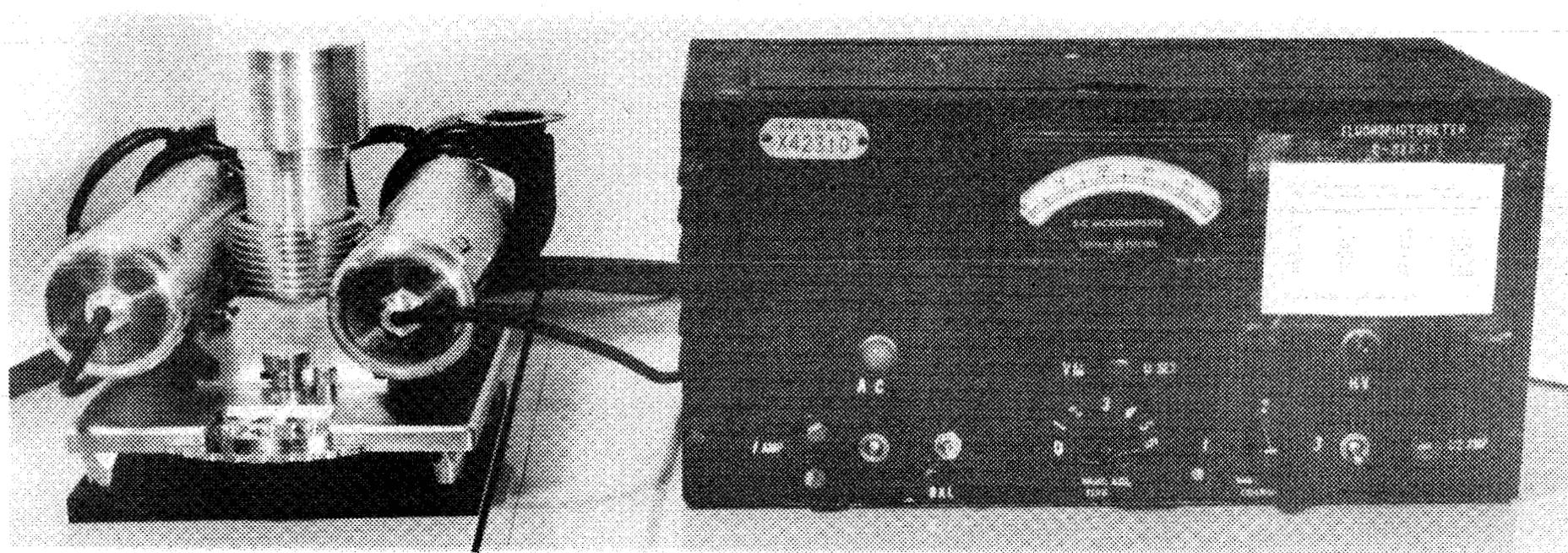
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FUSION APPARATUS FOR FLUORO-
PHOTOMETRIC DETERMINATION OF URANIUM

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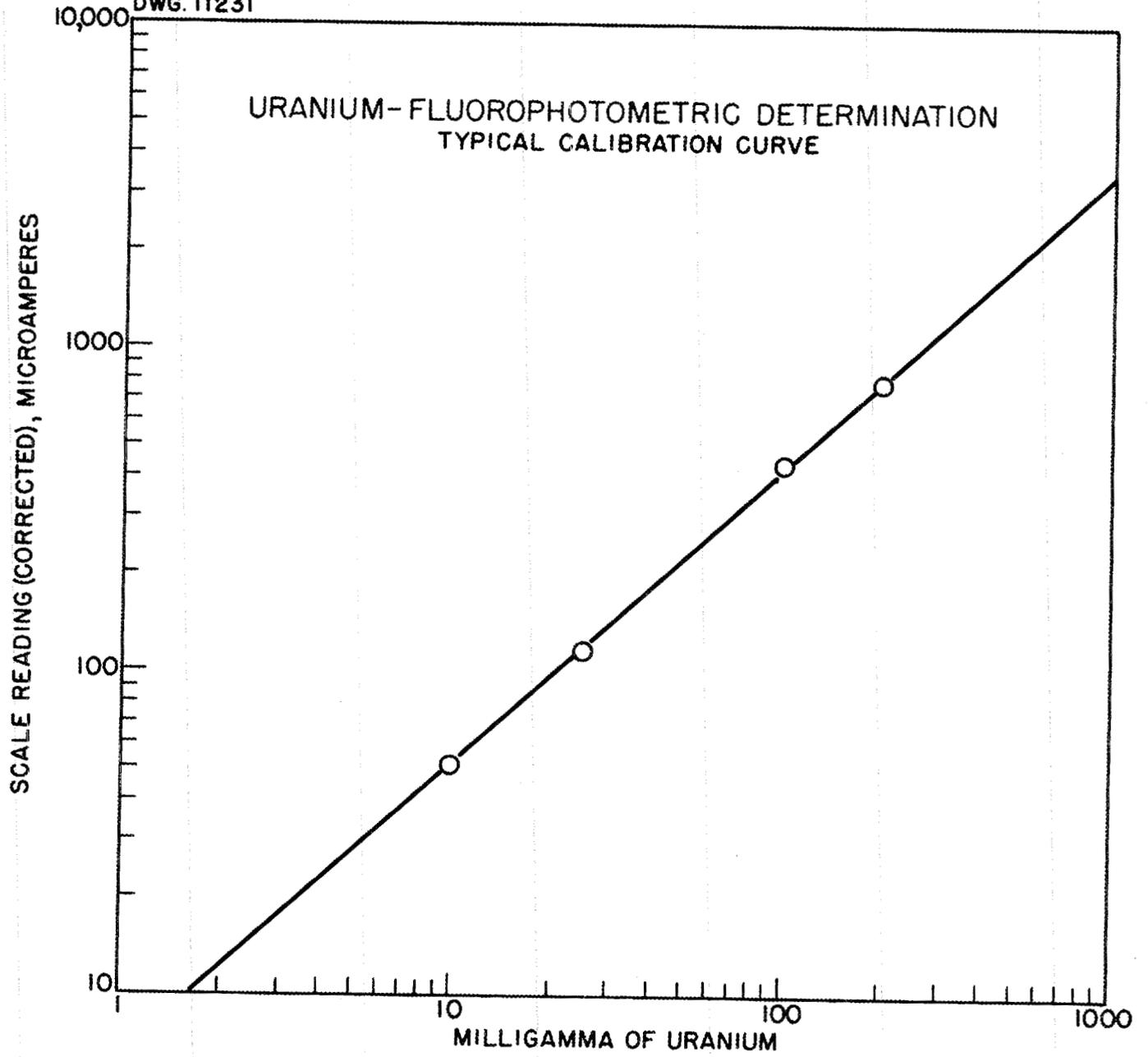
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FLUOROPHOTOMETER

12-APX. 2
6-1-51

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URANIUM - AMMONIUM THIOCYANATE SPECTROPHOTOMETRIC METHOD

Method No. 13

I. PRINCIPLE

Uranium (VI) and ammonium thiocyanate react in solution to form a yellow-colored complex. This complex is used under specified conditions as a basis for determining uranyl ion. The intensity of the yellow color is measured against a reference solution using a spectrophotometer.

II. STATUS

The method is suitable for the determination of U(VI) in the range of 100 to 1000 γ . It has the advantages of no interference from carbonate ion and of tolerating up to about 2 mg Fe(III). The red color of Fe(III) thiocyanate complex, which increases the absorption of light at the wave length used, is prevented from forming by the addition of SnCl₂. The pH of the solution in which the color is developed should be below 1.0 but the acid concentration not greater than 12 millequivalents. Interferences from metal ions, organic and mineral acids are discussed in the references ^(1 and 2). The time factor is important. The accuracy of the method is \pm 3%.

References:

1. Currah, J. E., and Beamish, F. E., "Colorimetric Determination of Uranium with Thiocyanate", Anal. Chem. 19, 609 (1947).
2. Nutting, L. A., "Uranium Spectrophotometric Determination Using Ammonium Thiocyanate", Collection of Laboratory Procedures for Ionic Analysis Group, files of L. T. Corbin, ORNL.

III. REAGENTS AND APPARATUSA. Reagents

1. Standard Uranium (VI) Solution, 1 mg U (VI)/ml. Prepare a stock solution to contain approximately 10 mg U (VI)/ml by dissolving 21.09 g

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$UO_2(NO_3)_2 \cdot 6H_2O$ in 1 liter of distilled water. Standardize the stock solution by evaporating 25 ml aliquots to dryness and igniting to U_3O_8 at $1000^\circ C$. Prepare the standard uranium solution by dilution from the stock solution.

2. Ammonium Thiocyanate Solution, 8 M NH_4SCN . Prepare by dissolving 608.96 g NH_4SCN in distilled water and diluting to 1 liter.

3. Stannous Chloride Solution, 10% $SnCl_2$. Dissolve 50 g $SnCl_2$ in distilled water and dilute to 500 ml.

4. Hydrochloric Acid, conc. HCl.

B. Apparatus

1. Spectrophotometer, Beckman Model "B", supplied with a matched set of cells, 1 cm light path.

2. Flasks, volumetric, 25 ml capacity.

3. Pipet, volumetric, 5 ml capacity.

V. PROCEDURE

1. Pipet a suitable sample aliquot (200 to 1000 γ U(VI)) into a 25 ml volumetric flask.

2. Add 5 drops of conc. HCl and mix^(a).

3. Dilute to a volume of 15 ml.

4. Pipet 5 ml 8 M NH_4SCN into the flask^(b).

5. Add dropwise enough 10% $SnCl_2$ solution to cause a permanent disappearance of the red color.

6. Dilute to the 25 ml volume with distilled water and shake the flask until the solution is homogeneous.

7. Measure the per cent transmittance of the sample with a Beckman Model B spectrophotometer at a wave length of 380 m μ , using as a reference liquid^(c) contained in a matched cell, a blank of reagents.

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8. Determine the quantity of U(VI) in the sample aliquot analyzed by reference to a calibration curve^(d). Calculate the concentration of uranium in the sample.

Calculations:

Let: A = quantity of U (VI) in sample aliquot, as determined from calibration curve, γ

B = aliquot of sample analyzed, ml

Then: U (VI) in sample, $\gamma/\text{ml} = \frac{A}{B}$

Notes:

(a) The pH should be at a value below 1.0 but the acid concentration should not be greater than 12 millequivalents. A low concentration of acid fails to keep the stannous chloride from hydrolyzing, and excess acid will decompose the ammonium thiocyanate leading to a false intensification of color.

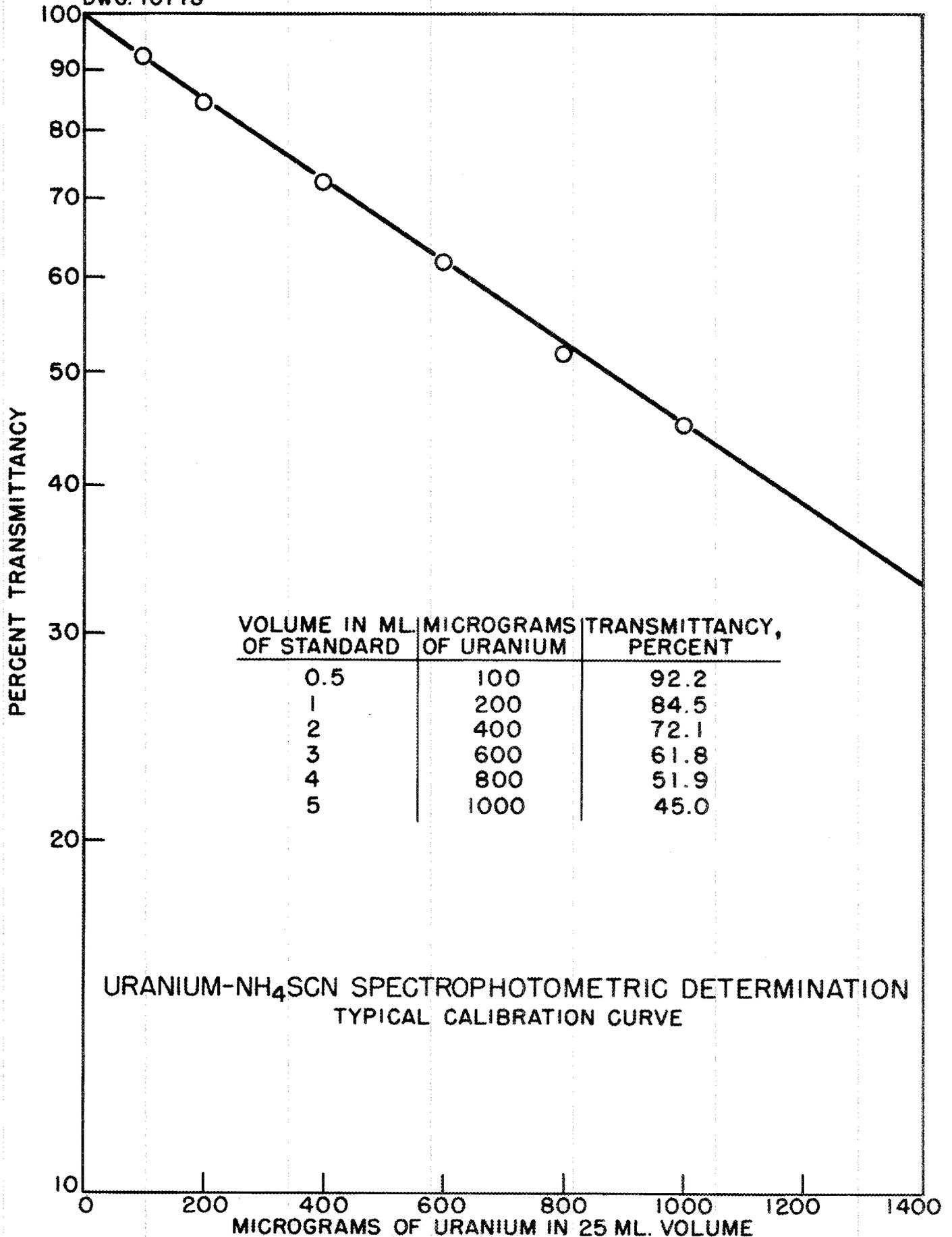
(b) The volume is quite critical. It has been shown in a similar method⁽²⁾ that a $\pm 2.0\%$ error in volume leads to approximately a $\pm 3.0\%$ error in the uranium value.

The SnCl_2 should be added after the NH_4SCN thereby preventing the reduction of Hg(II) to Hg_2 by the SnCl_2 .

(c) The reference solution contains all reagents but no sample. A single reference solution is stable for an hour and all readings of one series of analyses should be made within this time.

(d) Prepare a calibration curve by following the procedure above to determine the per cent transmittancies of solutions containing from 100 to 1000 γ U (VI) at 200 γ intervals. Using semi-logarithmic paper plot the per cent transmittance values on the logarithmic and the γ of U (VI) on the linear scale. A typical calibration curve is shown in Apx. 1.

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DIETHYL ETHER EXTRACTION OF URANIUM

Method No. 14

I. PRINCIPLE

The solubility of uranyl nitrate in diethyl ether permits the separation of uranium from many other elements. Complete conversion of the original sample to its nitrate prior to extraction is a primary requisite.

II. STATUS

A batch procedure is described by which quantities of uranium up to 400 mg can be separated from interfering elements and radioactivity by diethyl ether extraction. The uranium content of the extract can then be determined by any accepted method. A gravimetric method is not recommended because other elements are extracted to some extent. Rodden⁽¹⁾ gives an excellent discussion of interferences in the ether extraction of uranium and the most satisfactory methods of analyzing the ether extract according to the interferences present. This discussion should be read.

References:

1. Rodden, C. J., Analytical Chemistry of the Manhattan Project, p. 36, McGraw Hill, New York (1950).
2. "Ethyl Ether", Chemical Safety Data Sheet SD-29, available from Manufacturing Chemists Assoc., Washington, D. C.

III. REAGENTS AND APPARATUS

A. Reagents

1. Aluminum Nitrate, 2.3 M $\text{Al}(\text{NO}_3)_3$. Prepare by dissolving 431.41 g $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ in distilled water and dilute to 500 ml with distilled water.
2. Diethyl Ether, $(\text{C}_2\text{H}_5)_2\text{O}$, C.P. anhydrous.
3. Ferrous Sulfamate, 3 N. Prepare in the laboratory by reacting an excess of iron filings with the required amount of sulfamic acid.

When the reaction is complete filter and standardize the filtrate with standard ceric sulfate solution.

4. Nitric Acid, 0.1 N HNO_3 . Dilute 6.5 ml of 15.4 M acid (69% HNO_3) to 1 liter with distilled water.

B. Apparatus

1. Extraction Apparatus, shown in Apx. 1 and consisting of:
 - (a) Stripping funnel, 125 ml capacity
 - (b) Extraction column
 - (c) Ether reservoir
2. Pipets, 10 ml, and -micro, 250 λ capacities
3. Flask, volumetric 25 ml

IV. PROCEDURE

CAUTION - The use of diethyl ether in this experiment presents a fire and explosion hazard. For instructions on its safe handling see Reference 2.

Preparation of Extraction Apparatus

Before starting a series of extractions, clean the column with 1:1 HNO_3 and rinse it with distilled water. Clean the stripping funnel, wipe the stopcock dry and regrease it with silicone stopcock grease. When running duplicate samples, do not dismantle the column; drain the first sample from the column, rinse the column twice with distilled water and proceed with Step 4 of the extraction.

Extraction

1. Close the stopcock on the stripping funnel, pipet in 10 ml of 0.1 N HNO_3 and attach the flask to the column with a clamp.
2. Fill the section of the column below the fritted disk with ether.
3. Check the ether line from the reservoir to the column and remove any bubbles.
4. Add 10 ml of 2.3 M $\text{Al}(\text{NO}_3)_3$ thru the top of the column.

5. In the analysis of samples containing plutonium, add 250 λ of 3 N ferrous sulfamate.
6. Pipet the specified sample aliquot (approximately 500 λ U) into the extraction column.
7. Fill the extraction column to just below the sidearm with 2.3 M $\text{Al}(\text{NO}_3)_3$ solution.
8. Open the stopcocks on the ether reservoir and on the sidearm of the stripping flask. A gentle suction on the stripping flask is usually necessary to start the flow of ether through the column. Care must be exercised in removing the vacuum to prevent the stripping solution from being sucked back into the extraction section.
9. Continue the flow of ether until 100 ml has been caught in the stripping flask.
10. Turn the stopcock on the stripping flask to a closed position and then turn off the stopcock on the ether reservoir.

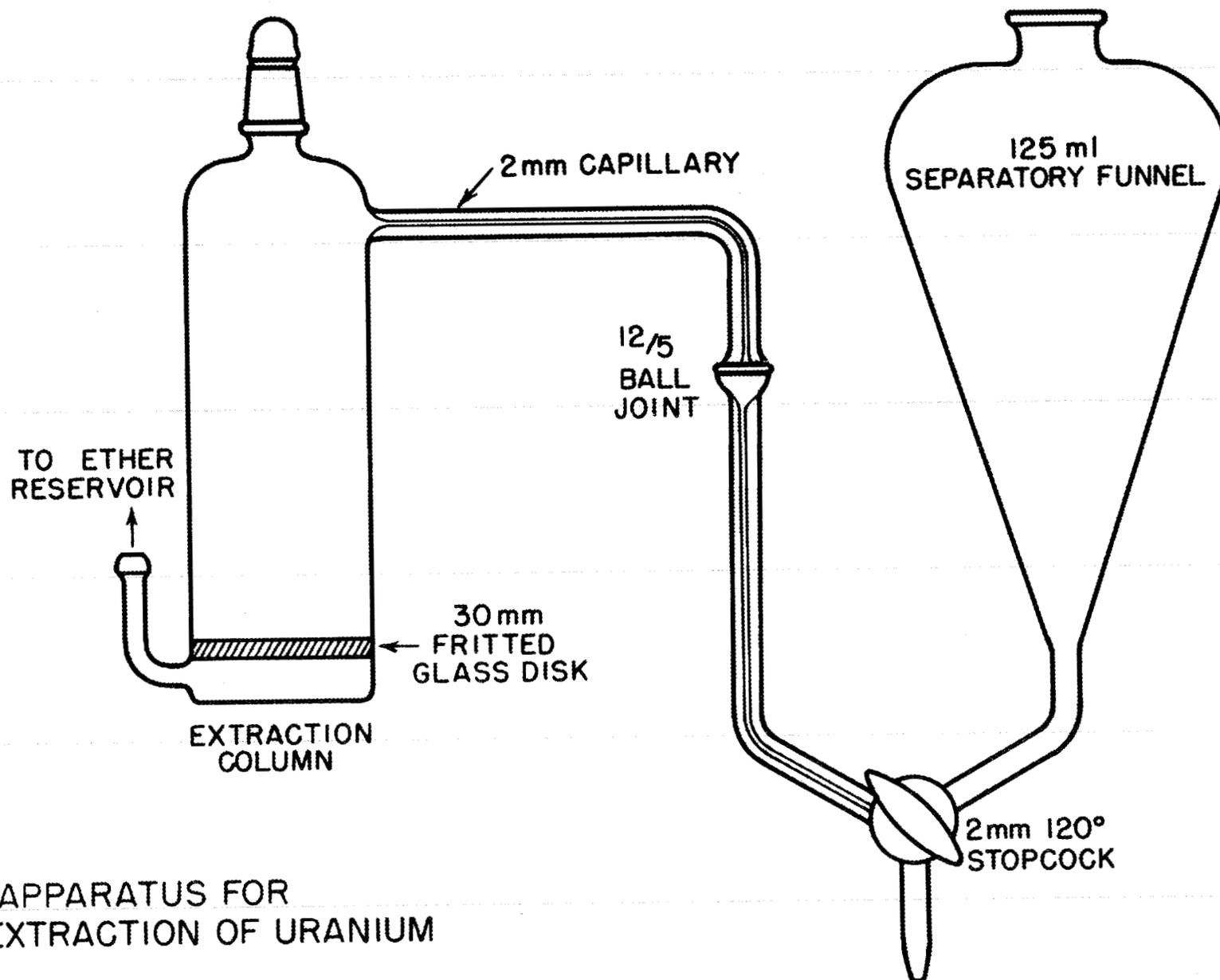
Stripping:

1. Remove the stripping flask from the extraction column and stopper it.
2. Shake for 4 to 5 minutes, remove the stopper carefully from time to time to relieve any internal pressure that has been built up.
3. Allow the phases to separate.
4. Drain the lower phase into a 25 ml volumetric flask.
5. Add 5 ml of 0.1 N HNO_3 and repeat steps 2 through 4.
6. Discard the ether through the top of the flask, rinse the flask with 5 ml of distilled water. Add this rinse to the solution in the 25 ml volumetric flask.
7. Heat the flask carefully and with constant stirring in a beaker of boiling water until all of the ether has evaporated.

8. Cool the flask to room temperature and dilute to volume with distilled water.

9. Proceed with the method of analysis for U as specified.

NOT CLASSIFIED
DWG. 10719



APPARATUS FOR
ETHER EXTRACTION OF URANIUM

14-APX. 1
6-1-51

II. RADIOCHEMICAL METHODS

Methods Nos. 26-50

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METHODS AND TECHNIQUES OF RADIOCHEMICAL ACTIVITY ANALYSIS

Method No. 26

I. PRINCIPLES

There are two fundamentally different types of radiochemical analyses. The first, radiometric analysis, involves the determination of the weight of an element by measurement of its radioactivity, with previous knowledge of specific activity. In this manner the weight of U present in a mixture could be determined by isolating the U free from other radioactive elements and counting the alpha activity. This method is closely analogous to colorimetric and volumetric determinations. The second type of radiochemical analysis, activity analysis, involves the determination of the radioactivity due to a given element in a mixture of radioactive elements. The results may be expressed as absolute activity or in terms of percentage of the total mixed activities due to the element in question. In the determination of the activity associated with an element, one is generally not concerned with the weight of inactive isotopes of the element present.

It is not usually feasible to isolate quantitatively for measurement the submicroscopic amounts of a radio element which occur in the samples which we ordinarily must work upon. In general a carrier technic is employed. To the sample a known amount of the desired element is added as an inactive carrier. By ordinary chemical methods the element is then separated from the mixture and purified. The active atoms accompany the inactive, and the activity in the final precipitate is determined. The amount of carrier recovered is measured and the chemical yield of the fraction of atoms, active and inactive, recovered in the chemical manipulations is then used to correct the observed activity of the final precipitate to 100% recovery.

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The addition of inactive isotopes of the same element is not possible for the radiochemical determination of such activities as elements 43 and 61, since no inactive isotopes are known to exist. Under these circumstances one must either develop a procedure and technique which gives quantitative (or reproducible and known) recovery or use a closely similar element as carrier, such as Re for element 43, and assume that carrier and tracer are recovered with efficiency.

II. EXPERIMENTAL TECHNIQUE

A. General Discussion

The laboratory technique employed is essentially that used in modern qualitative analysis. Reagents are usually dispensed from small pipette-type dropping bottles. Most operations are performed in 50 ml glass or lusteroid centrifuge tubes, and centrifugation is used instead of filtration whenever possible. A clinical style centrifuge is preferred. The activity sought is, if possible, isolated as a precipitate which can be weighed directly without ignition. The precipitate is collected on a 5/8 inch filter circle with the aid of a small Hirsch funnel and washed with alcohol and ether. Further drying is obtained by use of a vacuum desiccator or drying oven at 110° C.

In general, a separate sample is taken for the determination of each element. A systematic analysis has been worked out for the determination of most of the fission products in a single sample (W. H. Sullivan et al, CC-765, June, 1943), but this method of approach has several disadvantages. The presence of carriers for all the elements makes purifications more difficult as a rule, since greater contamination of precipitates occurs. A

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systematic analysis is also less convenient if only one or two elements are to be determined and requires more time, as the beginning of some procedures must wait upon the completion of others. The abundance of material usually available for sampling makes recourse to systematic analysis unnecessary in most process work.

In development of the procedures described in this manual, efforts have been made to provide separations which are as nearly quantitative as possible. Completeness of recovery has been sacrificed in a number of operations, however, for the sake of increased speed and high purity of the final precipitate.

B. Choice of Sample Size

It is desirable to take a sample for analysis such that the final mounted precipitate will give a count in the range of 500 to 9,000 cts/min. Low counts are inaccurate and time consuming to measure. Very high counting rates are complicated by instrumental imitations (coincidence errors, etc.). The choice of sample size depends on the gross activity of the sample and the anticipated percentage of constituent to be determined. From past experience it is often possible to estimate fairly well the proper range of sample size if the gross is known and the type of solution is familiar. It is usually desirable as the first step in the examination of a sample to measure the gross beta and gamma activity to see how much dilution, if any, is to be required.

For samples consisting of or derived from UNH or bombarded metal, the following tables may serve as a guide to the relative distribution of activities among the several fission elements.

Table 1

Percentage Distribution of Beta Activity
In Active UNH After Various Periods of Cooling*
(10-11 mg Total Absorption)

<u>Element</u>	<u>10 d</u>	<u>30 d</u>	<u>120 d</u>	<u>365 d</u>
Ba	10	9	0.5	-
Sr	9	18	23	11
Zr	3.3	7	12	7.5
Cb	0.3	1.2	3	0.4
Ru	1.3	2.6	3	4.5
Te	3.0	1.0	0.6	0.1
Mo	1.7	0.1	-	-
Cs	0.1	0.2	0.8	2.2
I**	3.0	1.4	-	-
Y	8.5	17	23	6.4
Ce	9	16	31	67
La	14	13	0.5	-
Pr-Nd-61	7.5	8	0.5	0.7
93	21	0.1	-	-

*The relative importance of the natural (UX) activity of the U depends upon both the age of the material and the intensity of bombardment.

**Relatively large amounts of I are easily lost. Dissolved metal is usually lower in I content than bombarded UNH.

Table 1 shows the percentage distribution of beta activity among 93 and the fission elements in metal or UNH bombarded for relatively long periods of time (10-100d) and cooled various lengths of time. The data are derived from Brady and Coryell (CC-643) and Rubinson, Metcalf, Seiler, Steinberg and Winsberg (CC-2658). All the experimental work was done with 10-11 mg total absorber and,

in the second study, negligible amounts of self-scattering. The backscattering contribution in each study was less than that associated with the standard watchglass mounting technic. It should be remembered, too, that the activity distribution is somewhat a function of bombardment time. For these reasons the data should not be expected to agree exactly with experimental findings using the methods in this manual, but the relative orders of magnitude should agree.

In Table 2 is given an estimate of the approximate percentage distribution of effective gamma activity for the same material as in Table 1. Most of the data has been adapted from CC-643 (counting through 1.9 g of Pb) and CC-2658 (counting with the sample between 1.7 g slabs of Al).

Table 2

Percentage Distribution of Effective Gamma Activity in Active UNH After Various
Periods of Cooling

<u>Element</u>	<u>10 d</u>	<u>30 d</u>	<u>120 d</u>	<u>365 d</u>
La + Nd	60	39	4	0.01
Zr	14	27	32	21
Cb	6	23	48	46
Ce	2	4	9	23
Ru	3	5	7	3.7
Te	8	1.0	0.1	0.02
Cs	0.1	0.1	0.5	5.5
I	2	1.0	-	-

Since those data were taken before adoption of the standard "gamma sandwich", the results differ somewhat from what would be obtained now. The observed gamma counts contained a substantial contribution due to Bremsstrahlungen and scattered beta radiation. An effort has been made in preparing the table to allow for this and it is hoped that the values given are not seriously far from truth. The distribution of 10d was calculated from a number of discordant sources and has been adjusted to the writer's prejudice by free application of interpolation, extrapolation and intuitive weighting.

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C. Mounting and Counting the Sample

Counting of beta and gamma activities is done by means of a standard thin windowed Geiger-Muller counter with scaling circuit and recorder. The technic is quite similar to that described in MCC 1602. Samples are chosen, if possible, to give counts satisfactory for measurement on the second shelf of the standard counting arrangement. Liquid samples are evaporated to dryness on 1 inch watch glasses for mounting. The evaporation is best done with the aid of a radiant heater mounted above the watch glass, because heating from above causes less spattering than heating from below. When solutions containing H_2SO_4 or H_3PO_4 are to be evaporated, a crystal of KNO_3 is added to the solution on the watch glass. This results in volatilization of HNO_3 during evaporation and leaves a non-hygroscopic residue of potassium salts.

Before counting, the watch glass is mounted on a stiff $3 \frac{1}{4}$ inch x $2 \frac{1}{2}$ inch card with a $1 \frac{1}{16}$ inch round hole in the center. The watch glass is placed on a flat surface, a 2 inch x 2 inch, thin cellophane sheet placed over it and the card pressed down from above so that the watch glass, now covered with the tightly stretched cellophane, rises through the hole. A 3 inch x 2 inch strip of gummed paper or Scotch tape is then placed on the bottom of the card, sealing the watch glass into place (Apx. 1). This method of mounting supplies firm support and good centering for the sample and prevents contamination of the counting equipment by loss of the sample.

D. Geometry

The observed counts obtained with both beta and gamma active samples are quite dependent on the geometry factor at which they are counted. Empirical factors may be used to convert counting rates from shelf to shelf. It should be noted, however, that these factors are not highly reliable since they vary with the hardness of radiation and the scattering in different types of mounting and should be used only for approximations unless a special study has been made. The geometry factor is determined by counting the so-called geometry standard, a

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mounted U or U_3O_8 sample which has been carefully compared with a UX sample of known absolute disintegration rate. There are small differences in shelf geometry from set to set depending on the height of the tube above the shelves. The following values approximate the conditions in use at the time of writing.

<u>Shelf</u>	<u>Geometry Factor</u>
1	31.1%
2	9.5
3	4.1
4	2.6

III. CORRECTIONS

A. Backscattering

The material on which a sample is mounted may affect profoundly the observed counting rate due to the phenomenon known as backscattering. Beta particles traveling in a downward direction are scattered (reflected) back upward into the counter window. The observed backscattering is a function of both the energy of the radiation and the atomic number of the scattering material.

Engelkemeir (MUC-NS No. 312) has given curves showing the increase in the counting rate of samples of various fission isotopes mounted on increasing thicknesses of mica. The maximum increase in counting rate is 10 to 15% for weak beta emitters and 10 to 20% with higher beta energy. The backscattering for various beta emitters mounted on "infinite" thicknesses or various backing materials is shown as a function of the atomic number of the mounting material. With moderately strong beta emitters (about 1 Mev.) the observed counting rate, with reference to zero backscattering as 1.00, were about 1.2, 1.35, 1.55, 1.70 and 1.80 for Be, Al, Cu, Cd, and Pb respectively.

It is seen, therefore, that it is necessary that different samples have the same sort of mounting in order that they may be compared. The complete elimination of backscattering is inconvenient and for most practical purposes unnecessary. It is sufficient to count all samples under identical conditions of

backscattering. Since liquid samples are mounted by evaporation on watch glasses, it is desirable to mount solid samples on watch glasses as well. It is most convenient to do this in the following manner.

The filter paper circle is first weighed on a small watch glass, the zero weight being taken as the weight of the two together. After filtration, washing, and drying with alcohol and ether, the filter with its precipitate is returned to the same watch glass for desiccator drying, weighing and mounting. If a precipitate is to be oven-dried it is easiest to put it in Hirsch and all. When dry, the paper is transferred to the watch glass which, being cool, can be weighed immediately. If a precipitate must be ignited before weighing, it is most simply done in an unweighed crucible. The crucible with the ignited residue is then weighed, the residue carefully transferred to a watch glass for mounting and the weight of mounted residue determined by reweighing the emptied crucible.

Instead of using weighed filter circles, one may transfer the dried precipitate from the filter paper to a weighed watch glass and weigh again. This saves time in preparing papers but may give a less even distribution of the solid over the watch glass.

B. Absorption

The amount of absorbing material between sample and counter is another factor which must be kept constant if samples are to be compared. Absorption in measurement of beta activity is measured in milligrams per square centimeter of absorber. Absorption in measurement of gamma activity is measured in grams per square centimeter of absorber. The absorber thicknesses will be reported as mg or g, unit area being understood. As a first approximation it is assumed that absorption depends only on the mass per unit area and that all substances are alike in this respect. This is not exactly true but for elements of relatively low atomic number (3-18) the error introduced is of little con-

sequence. The absorption of the counter window is usually about 3.5 mg, of the cellophane cover about 3 mg, and of the air 2.7 mg for the second shelf or 4.8 mg for the third shelf. Aside from the absorption due to the sample itself, the total effective absorption on the second and third shelves is about 9 and 11 mg respectively.

If an activity is mounted as a precipitate, the precipitate itself may contribute to the total absorption of the counting arrangement. This self-absorption could be corrected for as simply half the weight of precipitate per unit area were it not for the compensating effect of self-scattering. The solid matter in the precipitate acts as a scattering medium just as does the backing material, increasing the observed count. Engelkemeir and his associates have shown that if the same amount of activity is mounted with successively greater amounts of carrier precipitate, the observed count increases due to self-scattering, goes through a maximum and then falls as the self-absorption factor begins to be felt. Experiments by G. Sadowski and H. A. Mahlman have shown that on watch glasses, the rise may be of the order of 30% with the maximum usually between 15 and 20 mg of solid matter present. The magnitude of the effect depends on the beta energy, the density of the precipitate and whether the activity is deposited in or spread on the particles of solid. It is not possible to set up a simple uniform mounting arrangement so that all samples will have the same self-scattering and back-scattering contributions, but as a first approximation the following conventions may be employed. All liquid samples are evaporated on watch glasses with 20 mg of cerous nitrate to supply optimum self-scattering, and self-absorption comparable to the amounts of precipitate usually mounted. Solid samples are mounted on watch glasses as already described. With 10 to 30 mg of precipitate, the self-absorption correction is disregarded, being more than compensated by the self-scattering introduced. For precipitates weighing more than 30 mg, the weight in excess of 30 mg is considered in making correction for self-absorption. One-half

the excess weight of precipitate is divided by the area over which the solid is assumed to be uniformly spread and the result considered to be the effective self-absorption. For a five-eighths inch (16 to 17 mm diameter) filter paper, as commonly used in this work, the self-absorption of a uniformly spread precipitate is thus calculated to be almost exactly one-fourth of the total excess weight. The average weight of a mounted precipitate obtained by the procedures in this manual is between 20 and 30 mg which would make the effective total absorption for a mounted sample about 10 mg. If the absorption curve of the mounted activity is known in the region between 0 and 50 mg, it is not difficult to correct the observed count to any chosen standard total absorption for comparison with other samples. If the actual absorption is less than the chosen standard amount, aluminum absorbers may be added on top of the sample to bring the total absorption up to the standard amount and the sample counted directly. T. B. Novey and N. Elliott (CC-1204) have shown that the relative positions of the sample and absorber affect the counting rate. Absorbers placed very close to the sample give greatly augmented scattering analogous to self-scattering.

For the purposes of these analyses, the standard total absorption is taken as 30 mg/sq. cm. for beta counting. Thus, for every sample, the total absorption due to window, cellophane, air, and self-absorption is calculated and enough aluminum placed on top to bring the total to 30 mg for counting. The original gross beta sample is counted under the same conditions. It is seen that the use of this much absorber results in the relatively complete screening out of weak beta radiation such as that of $^{35}\text{d Cb}$. This is not as serious as it might appear, as these very soft beta particles do not constitute a source of danger or trouble, and are therefore not of practical concern. It is, in fact, desirable in most work to eliminate the effect of soft beta radiations as they are very sensitive to small variations in the total absorption. If, for some reason, an activity characterized by very soft beta radiation is to be

determined, the absorption of all samples involved is reduced to a minimum.

The absorption of a given counter window is usually determined by the maker and posted on the shield containing the counter. The absorption of air is 2.1 mg between each shelf and about 0.6 mg between the first shelf and the counter window. The absorption due to the cellophane used for covering samples should be determined by weighing a sheet of measured area. Scotch tape, if used for direct covering of samples, should be standardized in the same way.

C. Coincidence

The efficiency of a Geiger-Muller counter falls off at high counting rates resulting in the observed count being lower than the true. The error (coincidence error) may be determined experimentally for a given counter and corrections applied. For self-quenched circuits, the correction is approximately 0.5% per thousand counts per minute and for Neher-Harper quenched circuits, 1.5% per thousand counts per minute. The correction is added to the observed count before subtracting background and should always be made. For a discussion see MCC 1602. A simple method of determining coincidence corrections has been described by R. P. Metcalf in CP-2582.

D. Standard

The counts obtained from day to day on a standard sample with a given counter are found to vary up and down within a range greater than is expected from statistical considerations. To make all counts comparable, they must be normalized to a standard. A standard sample should be counted at least twice each day on a given counter and all counts taken should then be multiplied by the factor necessary to bring the observed count of the standard sample to the accepted value. Thus, if the chosen standard (on the shelf for which it has been made) counts 5150 cts/min while the accepted value is 5300 cts/min, all counts taken at that time should be multiplied by the factor (5300/5150).

E. Yield

The employment of the carrier technique permits an estimation of the chemical yield from the radiochemical activity analysis. The quantity of carrier recovered is measured. The chemical yield of the fraction of atoms, active and inactive, recovered in the chemical manipulations is then used to correct the observed activity of the final precipitate to 100% recovery.

The following ruthenium determination is a typical example: A solution of mixed activities has a total beta activity of 453,600 cts/min/ml. To 1.00 ml of sample is added 20.0 mg of Ru and by appropriate chemical manipulations the Ru is isolated and purified. The final precipitate of metallic Ru weighs 18.0 mg and given 4950 cts/min. The chemical yield is therefore 90% and the count, corrected for chemical yield, is 5500 cts/min/ml or 1.20% of the total beta activity

F. Decay

It is frequently necessary to know the activity of a constituent at some time other than the analysis time. If the half life of the constituent is known, the correction may be made using the radioactive decay law.

$$\log A = \log A_0 - \left(\frac{0.301}{T_{\frac{1}{2}}} \right) t$$

where A is the activity at any time, A_0 is the activity at analysis time, $T_{\frac{1}{2}}$ the half life and t, the time difference in the same units. The following graphical method is very convenient if many corrections are to be made.

Appendix 3 gives the table of the correction factor, F, in the equation

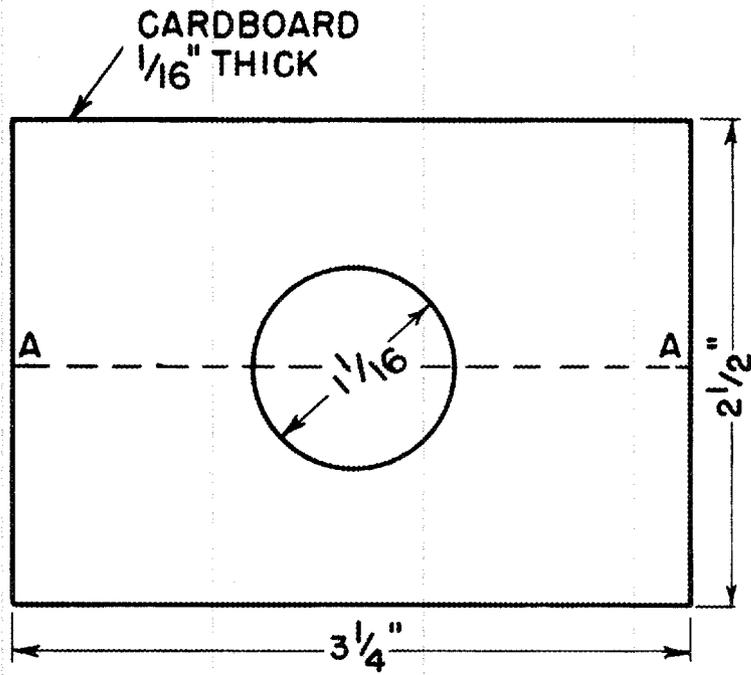
$$(\text{activity at comparison time}) = (\text{activity at analysis time}) \times (F),$$

against the number of half lives elapsed between the comparison time and analysis time, which is assumed to be later. If the analysis time is earlier than the comparison time, the factor, F, is divided into instead of multiplied by the

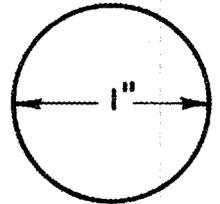
activity at analysis time. The basis of the method lies in the fact that all activities decay by the same fraction in the same number of half-lives (see CN-1312). If an activity being determined has an active daughter, the activity due to the daughter may also have to be considered. If the half-lives in question are long, the error over a period of a few hours may be negligible. If the half-life of the daughter is quite short, it is usually most convenient to count the sample when the daughter is grown into the equilibrium with the parent.

IV. REPORTING OF RESULTS

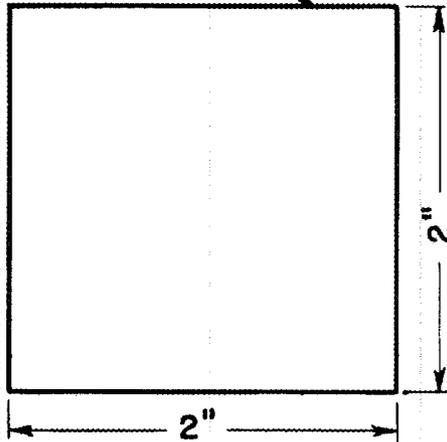
The result of a radiochemical activity analysis is conveniently reported as counts per minute per μg or ml of the starting sample or in terms of percentage of total beta or gamma activity of the mixture. With many analyses to be run, the report form shown in Apx. 2, has been found most convenient. It is printed on standard 4 x 6 in. filing cards which are easily handled and stored. The two columns are for duplicate samples. On the card the abbreviations CCC, CCB, CCS, and CCY are the counts corrected for coincidence, background, standard and yield respectively.



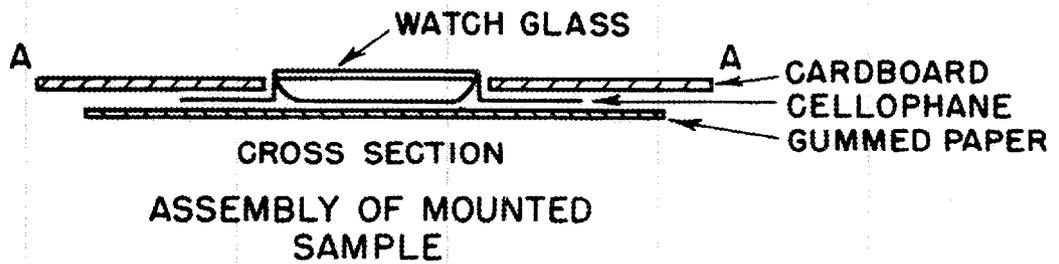
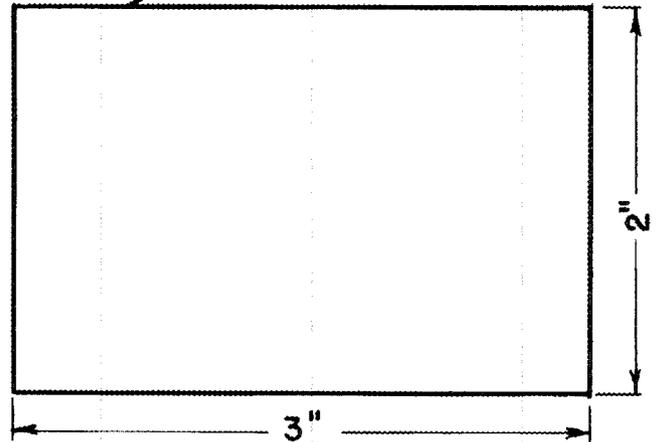
WATCH GLASS



CELLOPHANE (THIN)



GUMMED KRAFT PAPER



MOUNTING TECHNIQUE

APPENDIX 2

FORM FOR REPORTING ACTIVITY ANALYSIS DATA

(FRONT)

	#1	#2	
Carrier (mg)			Sample No. _____
Gross (g)			Constituent _____
Tare (g)			Begun: _____
Net (mg)			F. Sep. _____
% Yield			
Volume			Cir. _____
Day & Hr.			Geom. _____
Final R.			Abs. _____
Initial R.			GB _____ BB _____
Difference			
Residual			Std: C/M _____
Minutes			CCC _____
C/M			CCB _____
CCC			
CCB			
CCS			
CCY			
C/M/V			

(BACK)

REMARKS:

Analyzed by: _____

Ctd. by: _____

Calculated by: _____

Checked by: _____

DECAY OF A RADIOELEMENT

F = Fraction Remaining

Half-Lives	F	Half-Lives	F	Half-Lives	F	Half-Lives	F
0	1.000	1.10	.467	2.50	.177	5.50	.0221
0.02	.986	1.12	.460	2.55	.171	5.60	.0206
0.04	.973	1.14	.454	2.60	.165	5.70	.0192
0.06	.959	1.16	.447	2.65	.159	5.80	.0180
0.08	.946	1.18	.441	2.70	.154	5.90	.0167
0.10	.933	1.20	.435	2.75	.149	6.00	.0156
0.12	.920	1.22	.429	2.80	.144	6.10	.0146
0.14	.908	1.24	.423	2.85	.139	6.20	.0136
0.16	.895	1.26	.418	2.90	.134	6.30	.0127
0.18	.883	1.28	.412	2.95	.129	6.40	.0118
0.20	.871	1.30	.406	3.00	.125	6.50	.0111
0.22	.859	1.32	.401	3.05	.121	6.60	.0103
0.24	.847	1.34	.395	3.10	.117	6.70	.0096
0.26	.835	1.36	.390	3.15	.113	6.80	.0090
0.28	.824	1.38	.384	3.20	.109	6.90	.0084
0.30	.812	1.40	.379	3.25	.105	7.00	.0078
0.32	.801	1.42	.374	3.30	.102	7.10	.0073
0.34	.790	1.44	.369	3.35	.0981	7.20	.0068
0.36	.779	1.46	.364	3.40	.0947	7.30	.0063
0.38	.768	1.48	.358	3.45	.0915	7.40	.0059
0.40	.758	1.50	.354	3.50	.0884	7.50	.0055
0.42	.747	1.52	.349	3.55	.0853	7.60	.0052
0.44	.737	1.54	.344	3.60	.0825	7.70	.0048
0.46	.727	1.56	.339	3.65	.0797	7.80	.0045
0.48	.717	1.58	.334	3.70	.0769	7.90	.0042
0.50	.707	1.60	.330	3.75	.0743	7.00	.0039
0.52	.697	1.62	.325	3.80	.0718	8.10	.0036
0.54	.688	1.64	.321	3.85	.0693	8.20	.0034
0.56	.678	1.66	.316	3.90	.0670	8.30	.0032
0.58	.669	1.68	.312	3.95	.0647	8.40	.0030
0.60	.660	1.70	.308	4.00	.0625	8.50	.0028
0.62	.651	1.72	.304	4.05	.0604	8.60	.0026
0.64	.642	1.74	.299	4.10	.0583	8.70	.0024
0.66	.633	1.76	.295	4.15	.0563	8.80	.0022
0.68	.624	1.78	.291	4.20	.0544	8.90	.0021
0.70	.616	1.80	.287	4.25	.0525	9.00	.0020
0.72	.607	1.82	.283	4.30	.0507	9.10	.0018
0.74	.599	1.84	.279	4.35	.0490	9.20	.0017
0.76	.590	1.86	.275	4.40	.0474	9.30	.0016
0.78	.582	1.88	.272	4.45	.0457	9.40	.0015
0.80	.574	1.90	.268	4.50	.0442	9.50	.0014
0.82	.566	1.92	.264	4.55	.0427	9.60	.0013
0.84	.559	1.94	.261	4.60	.0413	9.70	.0012
0.86	.551	1.96	.257	4.65	.0398	9.80	.0011
0.88	.543	1.98	.253	4.70	.0385	9.90	.0010
0.90	.535	2.00	.250	4.75	.0372	10.00	.0010
0.92	.529	2.05	.241	4.80	.0359		
0.94	.521	2.10	.233	4.85	.0347		
0.96	.514	2.15	.225	4.90	.0335		
0.98	.507	2.20	.218	4.95	.0324		
1.00	.500	2.25	.210	5.00	.0313		
1.02	.493	2.30	.203	5.10	.0292		
1.04	.486	2.35	.196	5.20	.0272		
1.06	.480	2.40	.189	5.30	.0254		
1.08	.473	2.45	.183	5.40	.0237		

GAMMA ACTIVITY - ION CHAMBER METHOD

Method No. 27

I. PRINCIPLE

Gamma rays are highly penetrating electromagnetic radiation, analogous in properties to x-rays. They are not charged and therefore are not detectable as such by counting devices. The electrons ejected from matter by the passage of gamma rays cause ionization which is then detected by the use, in this method, of an ionization chamber filled with gas under pressure.

II. STATUS

This method is applicable to liquid or solid samples. Aliquots of liquid samples are pipetted into a center thimble of an ion chamber filled with argon gas at approximately 30 atmospheres pressure. The ionization current is measured by determining the potential drop across a known high resistor by means of a Vibrating Reed Electrometer. The measurements may be recorded on a Brown Strip Recorder.

The principles and limitations of the ion chamber method of gamma activity measurement, as well as the development, calibration and use of the 100% geometry Ion Chamber are discussed in the references.

References:

1. Jones, J. W., and Overman, R. T., "The Use and Calibration of a 100% Geometry Ion Chamber", MonC-399, (March 20, 1948).
2. Rodden, C. J., Analytical Chemistry of the Manhattan Project, Ch. 28, McGraw-Hill, New York (1950).
3. Glasstone, S., Sourcebook on Atomic Energy, Ch. VI, Van Nostrand, New York (1950).

III. REAGENTS AND APPARATUS

A. Reagents

1. Radium Solution Standards, 0.2 to 100 μ g Ra. Supplied in ampoules by the National Bureau of Standards, Washington, D. C.

B. Apparatus

1. Ion Chamber, high pressure gamma, 100% geometry type. See Apx. 1 and 2 and Ref. 1, pgs. 6-8. Also see drawings:

D-3172 A	Assembly Drawing
D-3173, -4, -5	Detail Drawings
D-2799	Make-up of Assembly (Shielding and Housing)
E-3793	Special Cables and Fittings

in files of the ORNL Instrument Division.

2. Vibrating Reed Electrometer, Model 30, A.E.C. Contract No. AT-40-1Gen-724, available from Applied Physics Corp., 30 West Green St., Pasadena, Calif. See Apx. 2 and the manufacturer's "Instruction Manual for Vibrating Reed Electrometer Model 30, Serial No. 204".

3. Potentiometer, voltage range of 0.1 to 1.0 v., supplied by the Rubicon Co., Philadelphia, Pa., Cat. No. 2731. Operating instruction are attached to the instrument.

4. Test Tubes, Pyrex glass, 21 inch length x 1.5 inch i.d.

IV. PROCEDURE

A brief description of the instrument controls follows as an introduction to the procedure for measuring gamma activity by the Ion Chamber method.

The controls which are used to carry out measurements on the ion chamber are the scale selector, voltmeter range control, potentiometer decade and slide wire, and the chamber grounding switch.

The scale selector or grid leak selector is located on the face of the vacuum container which is situated beneath the ion chamber. The selection of grid leak is determined by the intensity of the sample to be measured and the

method of measurement. The scales in order of decreasing intensities are 10^8 , 10^9 , 10^{10} , and 10^{11} for the null point reading and 10^{12} and "open" for drift measurements.

The voltmeter range control is located on the right hand side of the Rubicon potentiometer. The settings are 10 mv, 100 mv, and 1000 mv¹ when the scale selector is set at 100 mv. The potentiometer should be checked occasionally against a standard cell in the potentiometer.

The ion chamber when not in use is kept grounded, and is ungrounded only during a measurement. The switch is of the toggle type and is located near the front on the left hand side of the chamber mount.

The potentiometer decade and slide wire are part of the standard potentiometer box. The decade switch has settings from 0.1 volts to 1.1 volt in steps of 0.1 volt. The 1.1 volt position is not to be used as this may lead to inaccurate readings. The slide wire permits reading to be made from 0.0000 volts to 0.1200 volts and can be added to the decade reading. The slide wire can be used to shift the Rubicon potentiometer indicator to any convenient portion of the scale or to zero. Both the slide wire and the Brown indicator cover the same range.

A. Null Point Procedure

1. Check the instruments in the following manner.

(a) Turn the switch which connects the Ion Chamber to the Vibrating Reed Electrometer to the "ON" position.

(b) Check the background readings on all resistor scales of the Chamber. These resistors are indicated by the approximate resistance in ohms as 10^8 , 10^9 , 10^{10} , 10^{11} , 10^{12} and "open". The 10^{12} and "open" settings are for rate of drift measurements and are capacitances, while the other scales are for null point readings.

$C =$ sample aliquot, ml

Then:

Gamma activity at 100% geometry, mv/ml $= \frac{A - B}{C}$

B. Rate of Drift Procedure

Rate of drift measurements are in general made on samples of low intensity (0.1 rd Co or less) by use of the "open" scale; however measurements up to several rutherford equivalents of cobalt can be made using the 10^2 scale.

1. Check the instruments, take an aliquot of the sample and place it in the Ion Chamber, as described in Part A above.

2. For samples of weak activity proceed as follows.

(a) Set the scale selector on "open", the voltage range control on 1000 mv and the timer to zero. (The decade resistance setting does not affect the drift readings.)

(b) Unground the Ion Chamber. The indicator will drift across the scale. When it reaches 100 mv turn on the timer, and when it reaches 800 mv stop the timer. Ground the Ion Chamber with the toggle switch. Record the drift time in seconds. Do not use a drift time less than 15 seconds since it will have no significance.

3. For samples of more intense activity; use the 10^{12} scale as follows:

(a) Set the decade resistance and slide wire to zero, the scale selector on 10^{12} and the voltmeter range control on 1000 mv.

(b) Make the measurement in the same manner as for the "open" scale.

Calculations

Let: $A =$ rate of drift for sample, scale divisions/sec

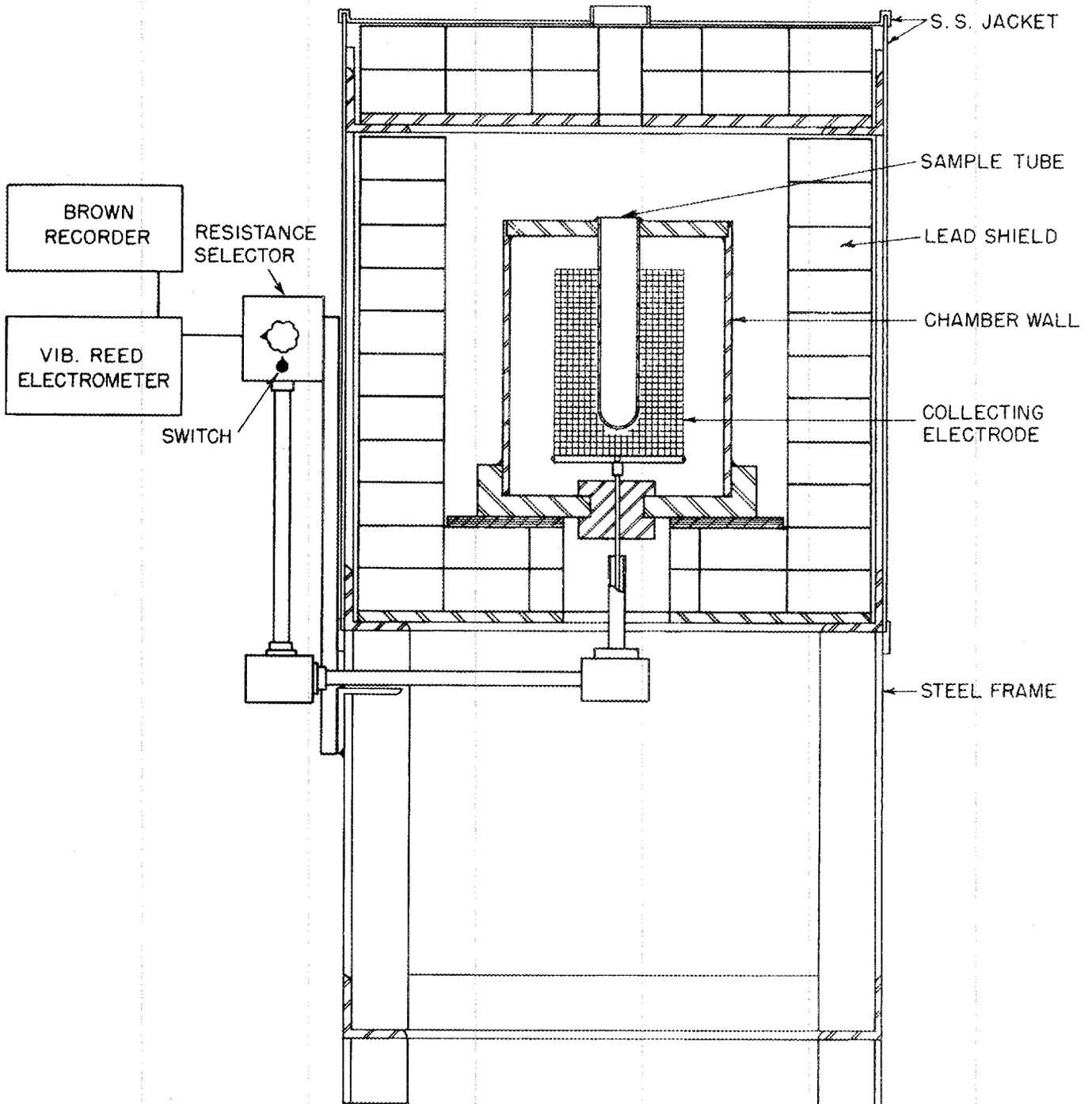
$B =$ background rate of drift, scale division/sec

Then:

Gamma Activity, scale divisions/sec $= A - B$

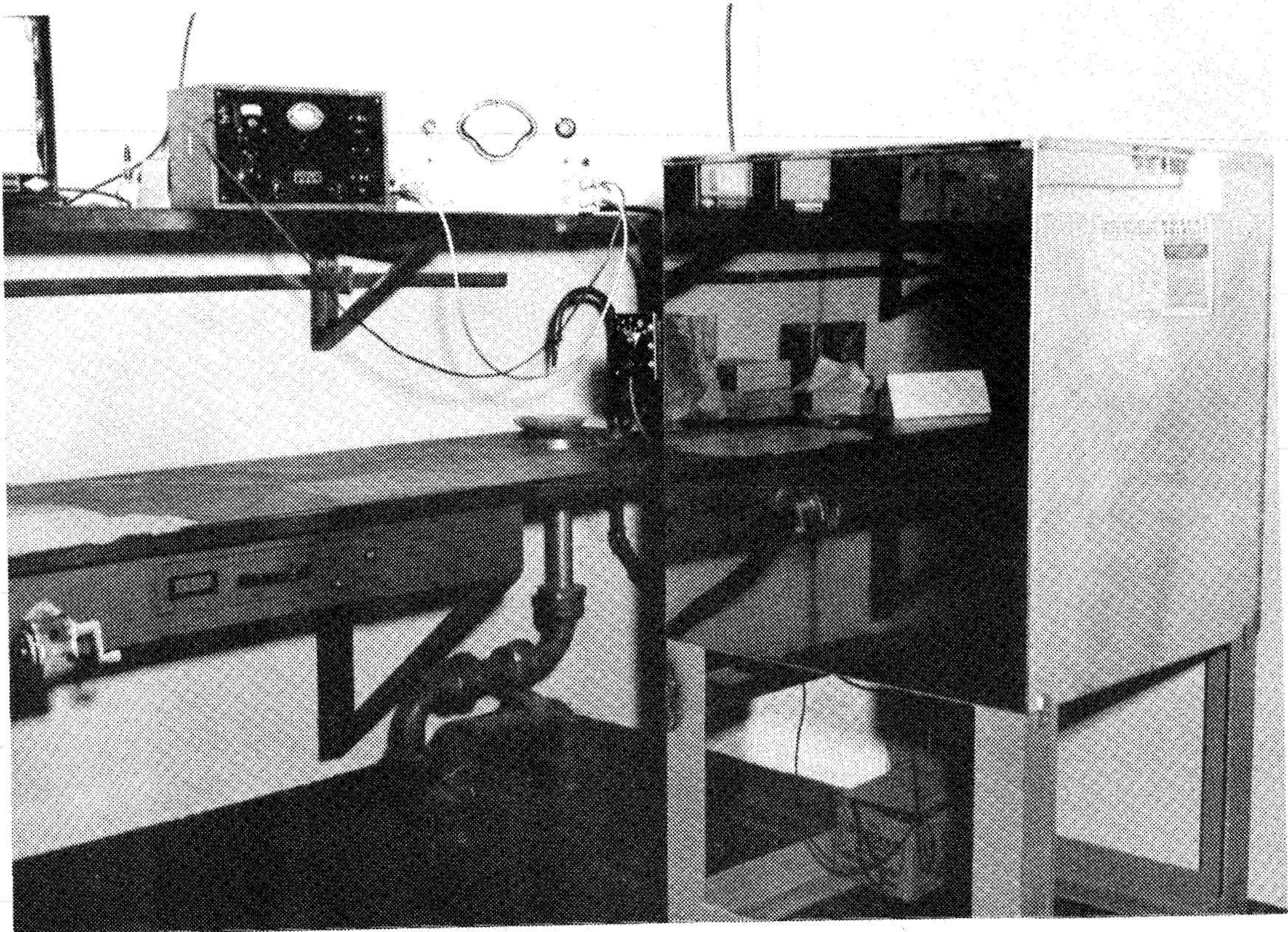
27-APX.1
6-1-51

NOT CLASSIFIED
DWG. 10078



HIGH PRESSURE GAMMA CHAMBER
(SCHEMATIC)

NOT CLASSIFIED
PHOTO 7857



ASSEMBLY FOR MEASURING GAMMA ACTIVITY

27-APPX. 2
6-1-51

GROSS BETA ACTIVITY

Method No. 28

I. PRINCIPLE

Gross beta activity is determined by counting with a thin-window Geiger-Müller counter at a fixed geometry of approximately 10 per cent.

II. STATUS

The methods and techniques of radiochemical activity analysis are discussed in detail in Method No. 26 of this manual⁽¹⁾. The principle and design of the Geiger-Müller counter are described in reference 2.

References:

1. "Methods and Techniques of Radiochemical Activity Analysis", Method No. 26, this manual.
2. Glasstone, S., Sourcebook on Atomic Energy, p. 136, Van Nostrand, New York (1950).

II. REAGENTS AND APPARATUS

A. Reagents

1. Cerous Nitrate, saturated solution of $Ce(NO_3)_3 \cdot 6H_2O$.
2. Sodium Hydroxide Solution, 10% NaOH. Prepare by dissolving 10 g NaOH, analytical reagent grade, and diluting to 100 ml with distilled water.
3. Ruthenium Carrier. Prepare by dissolving 28 g of commercial ruthenium chloride (mixture of hydrated di- and tetra-chlorides) and diluting to 1 liter with distilled water. Standardize as follows:

Pipet 5 ml of carrier into a 250 ml Erlenmeyer flask and add 25 ml of water and 2 ml HCl. Add 0.4 g of powdered Mg in small portions, swirling after each addition. Add a few drops of aerosol solution, and boil gently until the Ru is well coagulated and the supernate is clear and colorless. (More Mg may be necessary to complete reduction.) Add 10 ml of HCl and boil two minute

Filter quantitatively in a tared sintered glass crucible^(a) and wash three times each with hot water, alcohol and ether. Dessicate as described in preparation of crucible. Express standardization as mg. of Ru/ml.

B. Apparatus

1. Geiger-Müller Counter, Scaler and Recorder, Model Q-762, available from Nuclear Instrument and Chemical Corp., 223-W. Erie Street, Chicago 10, Ill.
2. Infra-red Lamp.
3. Watch Glass, 25 mm diameter.
4. Cardboard Mounting Card, illustrated in Apx. 1 of Method No. 26.
5. Cellophane Film.

III. PROCEDURE

1. Pipet suitable aliquots^(b) (1 ml maximum volume; 500 to 9000 cts/min), as designated on the analysis card, in duplicate onto 25 mm watch glasses.
2. If the samples do not have a solid concentration of ~ 20 mg in the specified aliquot, make the following additions in the order listed: 2 drops of ruthenium carrier, 2 drops of saturated $\text{Ce}(\text{NO}_3)_3$ solution, and 2 drops of 10% NaOH solution.
3. Evaporate the samples to dryness under an infra-red lamp.
(Evaporate organic solutions under a light of low intensity until all the solvent is removed. Increase the intensity for the final evaporation step.)
4. Mount the watch glass on a cardboard mounting card according to the instructions given in Reference 1.
5. Insert the sample into the second shelf of the chamber (geometry ~ 10%) and count for four minutes.
6. On the data sheet record the number of registered counts and the number of scaler lights.

Calculations

- Let:
- A = measured beta count of sample aliquot, cts/min.
 - B = coincidence correction, cts/min. Obtain from Table 1 (or Tables 2 and 3 if counts are run for other than 4 minutes). B may also be calculated from the equation:

$$B = (\text{observed counts})^2 \times 5 \times 10^{-6}$$
 - C = background correction, cts/min.
 - D = correction to standard, cts/min. = $\frac{\text{accepted count value for std.}}{\text{observed count value for std.}}$
 - E = volume factor for converting sample aliquot to ml.

Then:

Gross Beta Activity at 10% geometry^(c), cts/min/ml =
 $(A + B - C) D \times E$

Notes

(a) Prepare the sintered glass crucible as follows: Wash crucible thoroughly with water, alcohol and ether. Place in a vacuum desiccator (containing no desiccant) and apply vacuum for two minutes. Admit air, then evacuate again for two minutes. Weigh and repeat desiccation until a weight constant to 0.2 mg is obtained.

(b) The aliquots selected for analysis should not contain more than 20 mg of solids after evaporation.

(c) The results are usually reported without attempt to correct for geometry factors, counter efficiency, etc.

Table 1

COUNTS PER MINUTE
CORRECTED FOR COINCIDENCE LOSS (0.5%/1000)
SCALE/OF/64; 4-MIN. COUNTS
(Divide residual count by 4 and add)

Scaler Rdg. 0	1	2	3	4	5	6	7	8	9	
0	0	16	32	48	64	80	96	112	128	144
1	160	176	192	208	224	240	256	272	288	304
2	321	337	353	369	385	401	417	433	449	465
3	481	497	513	529	545	562	578	594	610	626
4	642	658	674	690	706	723	739	755	771	787
5	803	819	835	852	868	884	900	916	932	948
6	965	981	997	1013	1029	1045	1062	1078	1094	1110
7	1126	1142	1159	1175	1191	1207	1223	1240	1256	1272
8	1288	1304	1321	1337	1353	1369	1385	1402	1418	1434
9	1450	1467	1483	1499	1515	1532	1548	1564	1580	1597
10	1613	1629	1645	1662	1678	1694	1710	1727	1743	1759
11	1775	1792	1808	1824	1841	1857	1873	1890	1906	1922
12	1938	1955	1971	1987	2004	2020	2036	2053	2069	2085
13	2102	2118	2134	2151	2167	2183	2200	2216	2232	2248
14	2265	2281	2297	2314	2330	2347	2363	2380	2396	2413
15	2429	2445	2462	2478	2494	2511	2527	2543	2560	2576
16	2593	2609	2626	2642	2658	2675	2691	2707	2724	2740
17	2757	2773	2790	2806	2823	2839	2855	2872	2888	2905
18	2921	2938	2954	2971	2987	3004	3020	3037	3053	3070
19	3086	3103	3119	3136	3152	3169	3185	3202	3218	3235
20	3251	3267	3284	3300	3317	3333	3350	3366	3383	3400
21	3416	3433	3450	3466	3483	3499	3516	3532	3549	3565
22	3582	3598	3615	3632	3648	3665	3681	3698	3714	3731
23	3747	3764	3780	3797	3814	3830	3847	3864	3880	3897
24	3914	3930	3947	3964	3980	3997	4013	4030	4047	4064
25	4080	4097	4113	4130	4146	4163	4180	4196	4213	4230
26	4246	4263	4280	4296	4313	4330	4346	4363	4380	4396
27	4413	4430	4447	4463	4480	4497	4514	4530	4547	4563
28	4580	4597	4614	4630	4647	4664	4681	4698	4714	4731
29	4748	4765	4782	4798	4815	4832	4849	4866	4882	4899
30	4915	4932	4949	4965	4982	4999	5016	5033	5049	5066
31	5083	5100	5117	5133	5150	5167	5184	5201	5217	5234
32	5251	5268	5285	5301	5318	5335	5352	5369	5385	5402
33	5419	5436	5453	5469	5486	5503	5520	5537	5553	5570
34	5587	5604	5621	5638	5655	5672	5689	5706	5723	5740
35	5757	5774	5791	5808	5825	5841	5858	5875	5892	5909
36	5926	5943	5960	5977	5994	6011	6027	6044	6061	6078
37	6095	6112	6129	6146	6163	6180	6197	6214	6231	6248
38	6265	6282	6299	6316	6333	6350	6367	6384	6400	6417
39	6434	6451	6468	6485	6502	6519	6536	6553	6570	6587
40	6604	6621	6638	6655	6672	6689	6706	6723	6740	6757
41	6775	6792	6809	6826	6843	6860	6877	6894	6911	6928
42	6945	6963	6980	6997	7014	7031	7048	7065	7083	7100
43	7117	7134	7151	7169	7186	7203	7220	7237	7254	7271
44	7288	7305	7322	7340	7357	7374	7391	7408	7425	7442
45	7459	7476	7493	7511	7528	7545	7562	7579	7597	7614

Scaler Rdg.	0	1	2	3	4	5	6	7	8	9
46	7631	7648	7665	7683	7700	7717	7734	7752	7769	7786
47	7803	7820	7837	7855	7872	7889	7906	7923	7941	7958
48	7975	7992	8009	8027	8044	8061	8078	8096	8113	8130
49	8147	8165	8182	8199	8217	8234	8251	8269	8286	8303
50	8320	8337	8354	8372	8389	8406	8423	8441	8458	8475
51	8493	8510	8527	8545	8562	8579	8597	8614	8631	8649
52	8666	8683	8701	8718	8736	8753	8770	8788	8805	8822
53	8839	8856	8874	8891	8909	8926	8943	8961	8978	8996
54	9013	9031	9048	9065	9083	9100	9117	9135	9152	9170
55	9187	9204	9222	9239	9257	9274	9291	9309	9326	9344
56	9361	9379	9397	9414	9432	9449	9466	9484	9501	9519
57	9536	9553	9571	9588	9606	9623	9640	9658	9675	9693
58	9710	9728	9745	9763	9780	9798	9816	9833	9850	9868
59	9885	9903	9920	9938	9955	9973	9991	10008	10026	10043
60	10061	10078	10096	10113	10131	10148	10166	10183	10201	10218
61	10236	10254	10271	10289	10306	10324	10342	10359	10377	10394
62	10412	10430	10447	10465	10482	10500	10518	10535	10553	10570
63	10588	10606	10623	10641	10659	10677	10694	10712	10730	10747
64	10765	10783	10800	10818	10836	10854	10871	10889	10907	10924
65	10942	10960	10977	10995	11013	11031	11048	11066	11084	11101
66	11119	11137	11154	11172	11190	11208	11225	11243	11261	11278
67	11296	11314	11331	11349	11367	11385	11402	11420	11438	11455
68	11473	11491	11508	11526	11544	11562	11579	11597	11615	11633
69	11650	11668	11686	11704	11721	11739	11757	11775	11793	11811
70	11828	11846	11864	11882	11899	11917	11935	11953	11971	11989
71	12006	12024	12042	12060	12077	12095	12113	12131	12149	12167
72	12184	12202	12220	12238	12255	12273	12291	12309	12327	12345
73	12362	12380	12398	12416	12434	12452	12470	12488	12506	12524
74	12541	12559	12577	12595	12613	12631	12649	12667	12685	12703
75	12720	12738	12756	12774	12792	12810	12828	12846	12864	12882
76	12900	12918	12936	12954	12972	12990	13008	13026	13044	13062
77	13080	13098	13116	13134	13152	13170	13188	13206	13224	13242
78	13260	13278	13296	13314	13332	13350	13368	13386	13404	13422
79	13440	13458	13476	13494	13512	13530	13548	13566	13584	13602
80	13620	13638	13656	13674	13692	13710	13728	13746	13764	13782
81	13800	13818	13836	13854	13873	13891	13909	13927	13945	13963
82	13982	14000	14018	14036	14054	14073	14091	14109	14127	14145
83	14163	14182	14200	14218	14236	14254	14273	14291	14309	14327
84	14345	14363	14382	14400	14418	14436	14455	14473	14491	14509
85	14527	14545	14563	14581	14599	14617	14636	14654	14672	14690
86	14708	14726	14744	14763	14781	14799	14817	14835	14853	14871
87	14890	14908	14926	14944	14962	14981	14999	15017	15036	15054
88	15072	15090	15109	15127	15145	15164	15182	15200	15219	15237
89	15255	15273	15292	15310	15328	15347	15365	15383	15402	15420
90	15438	15456	15475	15493	15511	15530	15548	15566	15585	15603
91	15621	15639	15658	15676	15694	15713	15731	15749	15768	15786
92	15804	15822	15841	15859	15877	15896	15914	15932	15951	15969
93	15987	16005	16024	16042	16060	16079	16097	16115	16134	16152
94	16171	16189	16208	16226	16245	16263	16282	16300	16319	16337
95	16356	16374	16393	16411	16430	16448	16467	16485	16504	16522
96	16541	16559	16578	16596	16615	16633	16652	16670	16689	16707
97	16726	16744	16763	16781	16800	16818	16837	16855	16874	16892
98	16911	16929	16948	16966	16985	17003	17022	17040	17059	17077
99	17096	17114	17133	17151	17170	17188	17207	17225	17244	17262

Table 2
CONVERSION TABLE FOR SCALER READINGS TO COUNTS/MIN.
(Count/min. values to be divided by counting time)
Scale of 64

Scaler Rdg:	0	1	2	3	4	5	6	7	8	9
0	0000	00064	00128	00192	00256	00320	00384	00448	00512	00576
1	00640	00704	00768	00832	00896	00960	01024	01088	01152	01216
2	01280	01344	01408	01472	01536	01600	01664	01728	01792	01856
3	01920	01984	02048	02112	02176	02240	02304	02368	02432	02496
4	02560	02624	02688	02752	02816	02880	02944	03008	03072	03136
5	03200	03264	03328	03392	03456	03520	03584	03648	03712	03776
6	03840	03904	03968	04032	04096	04160	04224	04288	04352	04416
7	04480	04544	04608	04672	04736	04800	04864	04928	04992	05056
8	05120	05184	05248	05312	05376	05440	05504	05568	05632	05696
9	05760	05824	05888	05952	06016	06080	06144	06208	06272	06336
10	06400	06464	06528	06592	06656	06720	06784	06848	06912	06976
11	07040	07104	07168	07232	07296	07360	07424	07488	07552	07616
12	07680	07744	07808	07872	07936	08000	08064	08128	08192	08256
13	08320	08384	08448	08512	08576	08640	08704	08768	08832	08896
14	08960	09024	09088	09152	09216	09280	09344	09408	09472	09536
15	09600	09664	09728	09792	09856	09920	09984	10048	10112	10176
16	10240	10304	10368	10432	10496	10560	10624	10688	10752	10816
17	10880	10944	11008	11072	11136	11200	11264	11328	11392	11456
18	11520	11584	11648	11712	11776	11840	11904	11968	12032	12096
19	12160	12224	12288	12352	12416	12480	12544	12608	12672	12736
20	12800	12864	12928	12992	13056	13120	13184	13248	13312	13376
21	13440	13504	13568	13632	13696	13760	13824	13888	13952	14016
22	14080	14144	14208	14272	14336	14400	14464	14528	14592	14656
23	14720	14784	14848	14912	14976	15040	15104	15168	15232	15296
24	15360	15424	15488	15552	15616	15680	15744	15808	15872	15936
25	16000	16064	16128	16192	16256	16320	16384	16448	16512	16576
26	16640	16704	16768	16832	16896	16960	17024	17088	17152	17216
27	17280	17344	17408	17472	17536	17600	17664	17728	17792	17856
28	17920	17984	18048	18112	18176	18240	18304	18368	18432	18496
29	18560	18624	18688	18752	18816	18880	18944	19008	19072	19136
30	19200	19264	19328	19392	19456	19520	19584	19648	19712	19776
31	19840	19904	19968	20032	20096	20160	20224	20288	20352	20416
32	20480	20544	20608	20672	20736	20800	20864	20928	20992	21056
33	21120	21184	21248	21312	21376	21440	21504	21568	21632	21696
34	21760	21824	21888	21952	22016	22080	22144	22208	22272	22336
35	22400	22464	22528	22592	22656	22720	22784	22848	22912	22976
36	23040	23104	23168	23232	23296	23360	23424	23488	23552	23616
37	23680	23744	23808	23872	23936	24000	24064	24128	24192	24256
38	24320	24384	24448	24512	24576	24640	24704	24768	24832	24896
39	24960	25024	25088	25152	25216	25280	25344	25408	25472	25536
40	25600	25664	25728	25792	25856	25920	25984	26048	26112	26176
41	26240	26304	26368	26432	26496	26560	26624	26688	26752	26816
42	26880	26944	27008	27072	27136	27200	27264	27328	27392	27456
43	27520	27584	27648	27712	27776	27840	27904	27968	28032	28096
44	28160	28224	28288	28352	28416	28480	28544	28608	28672	28736
45	28800	28864	28928	28992	29056	29120	29184	29248	29312	29376
46	29440	29504	29568	29632	29696	29760	29824	29888	29952	30016
47	30080	30144	30208	30272	30336	30400	30464	30528	30592	30656
48	30720	30784	30848	30912	30976	31040	31104	31168	31232	31296
49	31360	31424	31488	31552	31616	31680	31744	31808	31872	31936

Table 3

COINCIDENCE CORRECTIONS FOR G-M COUNTERS
(Based on Coincidence Loss of 0.5% per 1000 Cts/Min.)
(Corrections To Be Added To Cts/Min.)

Counts/Minute	Correction	Counts/Minute	Correction	Counts/Minute	Correction
0-316	0	3900	76	7800	304
317-547	1	4000	80	7900	312
548-707	2	4100	84	8000	320
708-836	3	4200	88	8100	328
837-948	4	4300	92	8200	336
949-1048	5	4400	97	8300	344
1049-1140	6	4500	101	8400	353
1141-1224	7	4600	106	8500	361
1225-1303	8	4700	110	8600	370
1304-1378	9	4800	115	8700	378
1379-1449	10	4900	120	8800	387
1450-1516	11	5000	125	8900	396
1517-1581	12	5100	130	9000	405
1582-1643	13	5200	135	9100	414
1644-1702	14	5300	140	9200	423
1703-1760	15	5400	146	9300	432
1761-1816	16	5500	151	9400	442
1817-1870	17	5600	157	9500	451
1871-1923	18	5700	162	9600	461
1924-1974	19	5800	168	9700	470
2000	20	5900	174	9800	480
2100	22	6000	180	9900	490
2200	24	6100	186	10000	500
2300	26	6200	192	11000	605
2400	29	6300	198	12000	720
2500	31	6400	205	13000	845
2600	34	6500	211	14000	980
2700	36	6600	218	15000	1125
2800	39	6700	224	16000	1280
2900	42	6800	231	17000	1445
3000	45	6900	238	18000	1620
3100	48	7000	245	19000	1805
3200	51	7100	252	20000	2000
3300	54	7200	259	21000	2205
3400	58	7300	266	22000	2420
3500	61	7400	274	23000	2645
3600	65	7500	281	24000	2880
3700	68	7600	289	25000	3125
3800	72	7700	296		

CERIUM - BETA COUNT METHOD

Method No.29

I. PRINCIPLE

Cerium, together with other rare earths, is removed from the bulk of fission activities and other elements by precipitation with HF in acid solution. The rare earth fluoride precipitate is dissolved in boric and nitric acids and oxidized in the cold with bromate. Insoluble ceric iodate is precipitated, taking down all the Ce and a few per cent of the other rare earth activities. The Ce is purified by reprecipitation and Zr and UX removed on a $Zr(IO_3)_4$ scavenger-precipitate while the Ce is held in the trivalent state. Hydroxide precipitations are used to remove alkaline earth activities and the Ce is converted to the oxalate for weighing and counting.

II. STATUS

More detailed discussions of the chemistry of the cerium separation procedure and of radiochemical activity analysis are given in the references. The principle and design of the Geiger-Müller counter are described.

References:

1. "Methods and Techniques of Radiochemical Activity Analysis", Method No. 26, this manual.
2. Glasstone, S., Sourcebook on Atomic Energy, p. 136, Van Nostrand, New York (1950).
3. Hume, D. N., Ballou, N. E., and Glendenin, L. E., "A Manual of Radiochemical Determinations of Fission Product Activities", CN-2815 (June 30, 1945).
4. Flagg, J. F., Rider, B. F., and Andrus, W. S., "Methods of Chemical Analysis for Separation Process Research Unit. Part II, Radiochemical Methods", KAPL-348 (July 7, 1950).

III. REAGENTS AND APPARATUS

A. Reagents

1. Ammonium Hydroxide, 15 M NH_4OH (conc.), analytical reagent grade.
2. Boric Acid, sat. H_3BO_3 . Prepare by adding 56 g H_3BO_3 to 1 liter of distilled water.
3. Cerium Carrier. Prepare by dissolving 31 g $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and diluting to 1 liter with distilled water.

Standardize in triplicate by adding 5 ml of the carrier and 20 ml of water to a beaker. Heat to boiling and add with stirring 15 ml saturated oxalic acid. Cool in an ice bath for ten minutes (clock). Filter in a tared crucible^(a) and desiccate as described in preparation of the crucible. Express the standardization in mg of $\text{Ce}_2(\text{C}_2\text{O}_4)_2/\text{ml}$.

4. Hydrochloric Acid, (conc.) 12 M and 6 M. Prepare 6 M by diluting 500 ml conc. to 1 liter with distilled water.
5. Hydrofluoric Acid, conc., 27 M.
6. Iodic Acid, 0.035 M HIO_3 . Prepare by dissolving 61.5 g HIO_3 and diluting to 1 liter with distilled water.
7. Lanthanum Holdback Carrier. Prepare by dissolving 31 g $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and diluting to 1 liter with distilled water.
8. Nitric Acid, conc. (16 M) and 6 M. Prepare 6 M by diluting 384 ml conc. HNO_3 to 1 liter with distilled water.
9. Oxalic Acid, saturated. Prepare by adding 110 g $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ to 1 liter of distilled water.
10. Sodium Bromate, 1 M NaBrO_3 . Prepare by dissolving 151 g NaBrO_3 and diluting to 1 liter with distilled water.
11. Sodium Hydroxide, 19 M NaOH . Prepare by dissolving 1 lb of NaOH in 454 ml H_2O . Filter through asbestos and store in a plastic or waxed-glass bottle.

12. Hydrogen Peroxide, 30% H_2O_2 , analytical reagent grade.
13. Sulfurous Acid Solution, 6% H_2SO_3 . Prepare by diluting 60 ml to 1 liter with distilled water.
14. Zirconium Holdback Carrier. Prepare by dissolving 29 g $ZrO(NO_3)_2 \cdot 2H_2O$ and diluting to 1 liter with distilled water. Add a little HNO_3 to effect complete solution.

B. Apparatus

1. Clinical Centrifuge.
2. Centrifuge Cones, 50 ml capacity.
3. Lusteroid Tubes, 50 ml capacity.
4. Ice Bath.
5. Filtering Apparatus, suction type.
6. Geiger-Müller Counter, Scaler and Recorder, Model Q-762, available from Nuclear Instrument and Chemical Corp., 223-W. Erie Street, Chicago 10, Illinois.

IV. PROCEDURE

1. (a) For aqueous samples which do not contain Al:

Pipet sample and 2 ml Ce carrier, 2 ml each La holdback carrier and Zr holdback carrier into a lusteroid tube. Swirl. Make 2 M in HNO_3 and swirl. Add 2 ml conc. HF and swirl. Centrifuge and discard supernatant. Add about 10 ml water; slurry precipitate by stirring; transfer contents to 50 ml glass tube. Centrifuge and discard supernatant.

- (b) If the samples contain appreciable aluminum:

Place sample in a glass centrifuge tube. Add 1 ml 6 M HCl and 2 ml Ce carrier and swirl. Add sufficient 19 M NaOH to redissolve the $Al(OH)_3$ initially precipitated. Centrifuge and wash precipitate in 10 ml water. Centrifuge and discard wash. Dissolve the precipitate in 3 ml 6 M HNO_3 , and

transfer to a lusteroid tube. Add 2 ml each of La and Zr holdback carriers, and proceed as in 1 (a).

(c) If the samples are submitted in a hexone medium:

Place sample in a glass centrifuge tube. Add 1 ml 6 M HCl and 2 ml Ce carrier. Swirl. Heat to drive off hexone. Transfer to a lusteroid tube and add 2 ml La holdback and 2 ml Zr holdback. Proceed as in 1 (a).

2. To precipitate, add about 1 ml saturated H_3BO_3 . Stir well. Add 8 ml conc. HNO_3 . Stir to dissolve; a drop or two more of H_3BO_3 may be necessary. With stirring add 0.5 ml 1 M $NaBrO_3$ or 0.1 to 0.2 g $KBrO_3$. Wait about one minute. (The color should be deep red-orange). Place tubes in ice bath, add 20 ml 0.35 M HIO_3 and stir. Digest 1 to 2 minutes. Centrifuge and discard supernatant. Wash precipitate by stirring well in about 20 ml water. Centrifuge and discard supernatant.

3. To yellow ceric iodate precipitate, add 2 drops conc. HCl, and 2 drops 30% H_2O_2 . Stir well. Add about 8 ml conc. HNO_3 . Stir to dissolve. Treat with 2 ml of 1 M $NaBrO_3$ or 0.5 g $KBrO_3$. Add 20 ml 0.35 M HIO_3 and stir. Record the time of precipitation. Digest about five minutes. Centrifuge and discard supernatant. Wash precipitate by stirring well in about 20 ml water. Centrifuge and discard supernatant.

4. To yellow Ce iodate precipitate, add 1 drop conc. HCl and 3 drops 30% H_2O_2 . Stir well. Add about 8 ml conc. HNO_3 . Stir to dissolve. Add 1 ml Zr holdback carrier; swirl; should a slight precipitate come out, add about 2 more drops each of conc. H_2O_2 and HCl to dissolve the precipitate. Add 20 ml 0.35 M HIO_3 . Stir well and digest five minutes. Centrifuge and transfer solution to new tube, discarding the whitish solid.

5. Place tube in ice-bath. Precipitate the Ce as $Ce(OH)_3$ by stirring and cautiously adding an excess of 19 M NaOH; about 8 ml; add minimum amount more if a reddish color persists. Centrifuge and discard supernatant. Wash the

tube walls and precipitate with about 10 ml water. Centrifuge and discard supernate wash. Add 2 ml 6 N HCl to the precipitate; swirl to dissolve; dilute to a 10 ml volume by slowly adding water. Add about 1 ml 6% H₂SO₃ and swirl. (Red color should appear and disappear; solution should become decolorized).

6. Precipitate the Ce by adding dropwise and with stirring conc. NH₄OH; add a drop or two in excess. Centrifuge. Discard supernate.

7. Wash the precipitate twice with 10 ml portions of water.

8. Dissolve the Ce(OH)₃ in about 2 ml 6 N HCl. Add about 15 ml water. Heat to boiling, and add with stirring about 15 ml saturated oxalic acid. Continue to stir until precipitate appears, and for a short while thereafter. Cool tube and place in ice-bath for ten minutes digestion. During the digestion, tare papers.

9. Centrifuge and discard supernate. Swirl in 5 - 10 ml water and filter with suction on a moistened tared paper. Wash three times with hot water, three times with alcohol, and three times with ether. Dry one minute.

10. Weigh as cerium oxalate. Mount. Count no sooner than two hours after the time recorded in Step 3 (two hours allows for seventeen minutes Pr¹⁴⁴ to come into equilibrium with its Ce¹⁴⁴ parent).

Calculations:

Let: A = measured beta count of sample aliquot, cts/min.

B = coincidence correction, cts/min. Obtain from Method 28, Apx. 1 (or Apx. 2 and 3 if counts are run for other than four minutes). B may also be calculated from the equation:

$$B = (\text{observed count})^2 \times 5 \times 10^{-6}$$

C = background correction, cts/min.

D = correction to standard, cts/min =

$$\frac{\text{accepted count value for standard}}{\text{observed count value for standard}}$$

[REDACTED]

E = yield, decimal per cent.

F = volume factor for converting sample aliquot to ml.

Then:

Cerium in Sample, measured at 10% geometry, cts/min/ml = $\frac{(A+B-C)}{E} \times F$

Notes:

(a) Prepare the sintered glass crucible as follows. Wash it thoroughly with water, alcohol and ether. Place it in a vacuum desiccator (containing no desiccant) and apply vacuum for two minutes. Admit air, then evacuate again for two minutes. Weigh and repeat desiccation until a weight constant to 0.2 mg is obtained.

[REDACTED]

NIOBIUM - BETA COUNT METHOD

Method No. 30

I. PRINCIPLE

Niobium is separated as the hydrous oxide from fission product activities and other elements. The hydrous oxide is ignited at 800° C, weighed and counted for beta activity.

II. STATUS

More detailed discussions of the chemistry of the niobium separation and of radiochemical activity analysis are given in the references. The principle and design of the Geiger-Müller counter are described.

References:

1. "Methods and Techniques of Radiochemical Activity Analysis" Method No. 26, this manual.
2. Glasstone, S., Sourcebook on Atomic Energy, p. 136, Van Nostrand, New York (1950).
3. Hume, D. N., Ballou, N. E., and Glendenin, L. E., "A Manual of Radiochemical Determinations of Fission Product Activities", CN-2815 (June 30, 1945).
4. Flagg, J. F., Rider, B. F., and Andrus, W. S., "Methods of Chemical Analyses for Separation Process Research Unit. Part II, Radiochemical Methods", KAPL-348 (July 7, 1950).

III. REAGENTS AND APPARATUS

A. Reagents

1. Ammonium Hydroxide Solution, conc. 15 M NH_4OH , analytical reagent grade.
2. Barium Nitrate Solution, 50 mg $\text{Ba}(\text{NO}_3)_2$ /ml. Prepare by dissolving 50 g $\text{Ba}(\text{NO}_3)_2$, analytical reagent grade, and diluting to 1 liter with distilled water.

3. Hydrochloric Acid, 6 M HCl, Prepare by diluting 500 ml conc. (12 M) to 1 liter with distilled water.
4. Hydrofluoric Acid, conc., 27 M HF (48%).
5. Nitric Acid, conc. (16 M) and 6 M. Prepare 6 M from conc. by diluting 384 ml to 1 liter with distilled water.
6. Niobium Carrier. Prepare by dissolving 26 g potassium hexaniobate ("columbate"), $K_2Nb_6O_{19} \cdot 16 H_2O$, in 200 ml water. Heat almost to boiling, then add 15 ml conc. HNO_3 slowly with stirring. Continue heating and stirring for approximately three minutes, then centrifuge and wash three times with 50 ml portions of hot 2% NH_4NO_3 solution. Add 200 ml of saturated oxalic acid, heat and stir until Nb_2O_5 dissolves. Cool and dilute to one liter. If the solution is cloudy, filter.
Standardize in triplicate by pipeting 5 ml of the carrier into a beaker, add 30 ml 6 M HNO_3 and 1 g $KBrO_3$ and heat to boiling. Boil gently with stirring for about five minutes. Cool and add conc. NH_4OH to a pH of 8 to 10 (about 15 ml). Filter quantitatively on No. 42 paper and wash with hot water. Transfer to a previously ignited and tared crucible, "smoke off" paper and ignite to about $800^\circ C$ for twenty minutes. Weigh and calculate as mg of Nb_2O_5/ml .
7. Niobium Wash No. 1. Prepare by dissolving 96 g NH_4NO_3 , adding 38 ml conc. HNO_3 and diluting to 1 liter with distilled water.
8. Niobium Wash No. 2. Prepare by dissolving 53 g NH_4NO_3 , adding 89 ml conc. HNO_3 and diluting to 1 liter with distilled water.
9. Oxalic Acid Solution, saturated. Prepare by adding 110 g $H_2C_2O_4 \cdot 2H_2O$ to 1 liter of distilled water.
10. Phenolphthalein Indicator Solution, 0.01% in 70% C_2H_5OH . Prepare by dissolving 1 g of indicator in 1 liter of the $C_2H_5OH - H_2O$ solvent.
11. Potassium Bromate, solid $KBrO_3$.
12. Zirconium Holdback Carrier. Prepare by dissolving 29 g $ZrO(NO_3)_2 \cdot 2H_2O$

in 1 liter of distilled water. Add a little HNO_3 to effect complete solution.

B. Apparatus

1. Geiger-Müller Counter, Scaler and Recorder, Model Q-762, available from Nuclear Instrument and Chemical Corp., 223-W. Erie St., Chicago 10, Illinois.
2. Centrifuge, clinical.
3. Centrifuge Tubes, 50 ml capacity.
4. Lusteroid Tubes, 50 ml capacity.
5. Electric Muffle, set at 800°C .
6. Filter Paper, Whatman No. 42.

IV. PROCEDURE

1. (a) If the samples are submitted in an aqueous medium:

To a 50 ml glass centrifuge tube add: 1 ml Zr holdback carrier, aliquot of sample (not over 10 ml), conc. HNO_3 (volume equal to sample volume), 1 ml 6 M HCl, 1 ml saturated oxalic acid, and 2 ml Nb carrier. Swirl. Heat solution nearly to boiling and add 0.5 g KBrO_3 in small portions, boiling for a few seconds after each addition. Digest five minutes; centrifuge and discard supernatant. Wash the Nb_2O_5 precipitate by stirring into it up to 10 ml of Nb Wash No. 1. Heat mixture nearly to boiling; transfer to lusteroid tube; centrifuge and discard supernatant.

- (b) If the samples are submitted in a hexone medium:

Add sample aliquot, 1 ml 6 M HCl, 2 ml saturated oxalic acid, and 2 ml Nb carrier. Stir well. Heat to near boiling to volatilize hexone. Cool and add 4 ml conc. HNO_3 . Make the KBrO_3 addition and continue as in 1 (a).

2. Dissolve the Nb_2O_5 in 1 ml conc. HF. Add 2 ml 6 M HNO_3 , 1 ml Zr holdback, 5 ml water, swirl. Add dropwise 1 ml $\text{Ba}(\text{NO}_3)_2$ solution (50 mg/ml) stir for one minute. Centrifuge, discard the precipitate, decanting the supernatant into a lusteroid tube. To the solution add 1 ml Zr carrier, swirl, centrifuge, and discard

the precipitate.

3. Decant the supernatant into a lusteroid tube, add with subsequent swirling a drop of phenolphthalein indicator, then conc. NH_4OH to pH 8 to 10 (phenolphthalein will turn pink). Centrifuge and discard the supernatant. Losing no time, wash the Nb_2O_5 precipitate by stirring up in 10 ml of Nb Wash No. 2. Centrifuge and discard the supernatant wash. Repeat the washing. Use the wash solution to transfer the precipitate to a glass centrifuge tube. Heat nearly to boiling and centrifuge, discarding the supernatant wash. To the precipitate add 0.5 ml 6 M HNO_3 and proceed immediately to Step 4.

4. Dissolve the precipitate of Nb_2O_5 by heating with 2 ml saturated oxalic acid. To the dissolved precipitate, add 3 ml water and 5 ml conc. HNO_3 and heat nearly to boiling. Add 0.5 g of KBrO_3 in small portions, boiling a few seconds after each addition, and digest five minutes. Centrifuge and discard supernatant. Wash the Nb_2O_5 with Wash No. 1. Heat nearly to boiling and filter on No. 42 filter paper. If the first portion of the filtrate is not clear, return it to the filter.

5. With a stirring rod, fold the top portion of the filter paper down, putting the sample and paper into a compact form. Transfer by the aid of a stirring rod to a crucible, burn off the filter paper on the entrance of a muffle furnace, and heat at 800°C for twenty minutes.

6. Tare a watch glass without paper. Remove crucible from muffle and cool in a desiccator. Transfer contents to watch glass by means of a spatula. Weigh. Mount in the manner of a gross beta determination and count.

Calculations:

Let: A = measured beta count of sample aliquot, cts/min.

B = coincidence correction, cts/min. Obtain from Method 2§, Apx. 1 (or Apx. 2 and 3 if counts are run for other than four minutes). B may also be calculated from the equation:

$$B = (\text{observed count})^2 \times 5 \times 10^{-6}$$

[REDACTED]

C = background correction, cts/min.

D = correction to standard, cts/min =
$$\frac{\text{accepted count value for standard}}{\text{observed count value for standard}}$$

E = yield, decimal per cent.

F = volume factor for converting sample aliquot to ml.

Then:

Niobium in sample, measured at 10% geometry, cts/min/ml =

$$\frac{(A + B - C) D}{E} \times F$$

[REDACTED]

RUTHENIUM - BETA COUNT METHOD

Method No. 31

I. PRINCIPLE

Ruthenium is separated cleanly from other fission products, except element 43, by distillation as RuO_4 from HClO_4 . The RuO_4 is mounted and determined by beta counting.

II. STATUS

In the distillation carrier is added to prevent volatilization of I, and NaBiO_3 is included to oxidize it to non-volatile IO_3^- or IO_4^- . The presence of phosphates avoids the volatilization of small amounts of Mo. The RuO_4 is caught in NaOH solution and Ru is precipitated in the basic solution as a mixture of Ru_2O_3 and RuO_2 by reduction with ethanol. Element 43, which is also volatilized by HClO_4 , is not affected by the ethanol treatment and remains in solution. In the analysis of process solutions, 43 activity is not determined because the longest-lived 43 isotope so far detected in fission is the six hour daughter of 67 hour Mo. The ruthenium oxide precipitate is dissolved in HCl , and Ru is precipitated in a weighable form by reduction with powdered Mg metal. The chemical yield is 90% or better. Discussions of radiochemical activity analysis and of the principle and design of the Geiger-Muller counter are given in the references.

References:

1. "Methods and Techniques of Radiochemical Activity Analysis", Method No. 26 this manual.
2. Glasstone, S., Sourcebook on Atomic Energy p. 136, Van Nostrand, New York (1950).
3. Hume, D. N., Ballou, N. E., and Glendenin, L. E., "A Manual of Radiochemical Determinations of Fission Product Activities", CN-2815 (June 30, 1945).

4. Flagg, J. F., Rider, B. F., and Andrus, W. S., "Methods of Chemical Analyses for Separation Process Research Unit. Part II, Radiochemical Methods", KAPL-348 (July 7, 1950).

5. Kuney, J. H., "Perchloric Acid, Friend or Foe", Chem. and Engr. News, 25 1658 (1947).

III. REAGENTS AND APPARATUS

A. Reagents

1. Aerosol, O.T., 0.1% Solution. Prepare by adding 0.1 g to 100 ml distilled water.
2. Diethyl Ether, $(C_2H_5)_2O$, anhydrous, analytical reagent grade.
3. Ethyl Alcohol, 95% C_2H_5OH .
4. Hydrochloric Acid, conc. (12 M) and 6 M. Prepare the 6 M by diluting 500 ml conc. to 1 liter with distilled water.
5. Iodine Holdback Carrier. Prepare by dissolving 13 g KI and a few mg $NaHCO_3$ and diluting to 1 liter with distilled water.
6. Magnesium Metal, powdered, analytical reagent grade.
7. Methyl Red Indicator Solution, 0.2% in 60% Ethanol. Prepare by dissolving 1 g methyl red in 300 ml C_2H_5OH and diluting to 500 ml with H_2O .
8. Perchloric Acid, 70% $HClO_4$, analytical reagent grade.
9. Phosphoric Acid, 85% H_3PO_4 , analytical reagent grade.
10. Ruthenium Carrier. Prepare by dissolving 28 g $RuCl_3 - RuCl_4$ mixture and diluting to liter with distilled water.

Standardize in triplicate by pipetting 5 ml of carrier into a 250 ml Erlenmeyer flask and adding 25 ml water and 2 ml conc. HCl. Add 0.4 g powdered Mg in small portions, swirling after each addition. Add a few drops of 0.1% Aerosol - O.T. solution and boil gently until the Ru is well coagulated and the supernatant is clear and colorless. More Mg may be necessary to complete reduction. Add 10 ml

[REDACTED]

of conc. HCl and boil two minutes. Filter quantitatively in a tared sintered glass crucible^(a) and wash three times each with hot water, alcohol and ether. desiccate as described in the preparation of the crucible. Express the standardization as mg Ru/ml.

11. Sodium Bismuthate, NaBiO_3 , solid, analytical reagent grade.
12. Sodium Hydroxide Solution, 6 M NaOH. Prepare by dissolving 240.06 g NaOH, analytical reagent grade, and diluting to 1 liter with distilled water.

B. Apparatus

1. Geiger-Müller Counter, Scaler and Recorder, Model Q-762, available from Nuclear Instrument and Chemical Corp., 223- W. Erie Street, Chicago 10, Ill.
2. Centrifuge, Clinical.
3. Centrifuge Tubes, 50 ml capacity.
4. Ruthenium Still, as shown in Apx. 4.
5. Fisher Filtrator.
6. Hirsch Funnel.
7. Hot plate, electric.

IV. PROCEDURE

CAUTION: This procedure requires the use of perchloric acid, a reagent presenting an explosion hazard. Before proceeding, become thoroughly familiar with the possible hazard and the method of safely handling the reagent⁽⁵⁾. It is most important to avoid the formation of the anhydrous acid. The dehydrating agents, sulfuric acid and phosphorous pentoxide, can convert H_3PO_4 to the anhydrous acid. Contact with organic material or porous materials should be avoided. The distillation should be carried out in a fireproof hood of special construction.

1. (a) If the samples are submitted in an aqueous medium:

To each of the two distillation flasks (free of straw or other organic material) add: sample aliquot (no more than 5 ml), 2 ml Ru carrier,

[REDACTED]

0.5 g NaBiO_3 , 1 ml 85% H_3PO_4 , 1 ml iodine holdback carrier, and 10 ml 70% HClO_4 .

(b) If the samples are submitted in a hexone medium:

Pipet sample aliquot into distillation flask and add 1 to 2 ml of ethanol. ~~Swirl~~ and add 2 ml Ru carrier. Let stand five minutes. Place distillation flask on hot plate with temperature control set at "low" and volatilize off organic mixture, evaporating almost to dryness. Remove the flask, cool, and add 1 ml of iodine holdback, 0.5 g NaBiO_3 , 1 ml 85% H_3PO_4 , and 10 ml 70% HClO_4 .

2. In a hood space free of paper or other organic material, set up a Ru still (Apx. 4). Use asbestos-center wire gauze under flask. Insert the delivery tube into 12 ml of 6 M NaOH contained in a centrifuge tube in an ice bath. Adjust the air influx to the system to give 1 to 2 bubbles per second. Heat the flask gently at first; then distill rapidly. During this last operation, set the burner directly under the flask and move back from the hood; watch to see that bumping does not occur. (A yellow oil should come over.) Rinse the delivery tube by continuing to heat until 1 to 2 ml of HClO_4 distills over. (This happens 1 to 2 minutes after HClO_4 fumes appear in the distillation flask.)

3. Add 3 ml of 95% ethanol to the distillate, swirl or stir to mix, dry tube bottom, and heat just to boiling by swirling over free flame. Ruthenium oxide will precipitate. Cool tube, centrifuge, and note if the supernatant is colored. If it is not colored (indicating complete precipitation), discard the supernatant and proceed to Step 5.

4. Pour the colored supernatant into a marked centrifuge tube. Neutralize the solution with concentrated HCl (use methyl red indicator). Add 1 ml 6 M NaOH. Make an ethanol precipitation as in Step 3. Centrifuge and discard supernatant. Use

10 ml of water to wash the precipitate into the marked tube that contains the first precipitate.

5. In 10 ml of water, stir so as to suspend the precipitate, add 1 ml 6 M NaOH, heat just to boiling, centrifuge, and discard supernatant.

6. To the precipitate add 2 ml of 6 M HCl, heat just to boiling to dissolve, and add 10 ml water. Add 0.2 g powdered Mg metal in small portions shaking after each addition. Add a few drops of 0.1% Aerosol O.T. to minimize frothing and boil gently until Ru is well precipitated. Continue boiling for two minutes.

7. Cool tubes slightly; place in water bath, slowly wash down the tube walls with 5 ml concentrated HCl to remove excess Mg, wipe tube and then boil until the Ru coagulates. Centrifuge and discard supernatant. Swirl precipitate in water. Filter with suction on a moistened tared paper supported on a Hirsch funnel in a filtrator. Wash three times with hot water, three times with alcohol, and three times with ether. Dry one minute, mount, and count.

Calculations:

Let: A = measured beta count of sample aliquot, cts/min.
B = coincidence correction, cts/min. Obtain from Method 28, Apx. 1 (or Apx. 2 and 3 if counts are run for other than four minutes). B may also be calculated from the equation:

$$B = (\text{observed count})^2 \times 5 \times 10^{-6}$$

C = background correction, cts/min.

D = correction to standard, cts/min. = $\frac{\text{accepted count value for standard}}{\text{observed count value for standard}}$

E = yield, decimal per cent

F = volume factor for converting sample aliquot to ml

Then:

Ruthenium in sample, determined at 10% geometry, cts/min/ml =

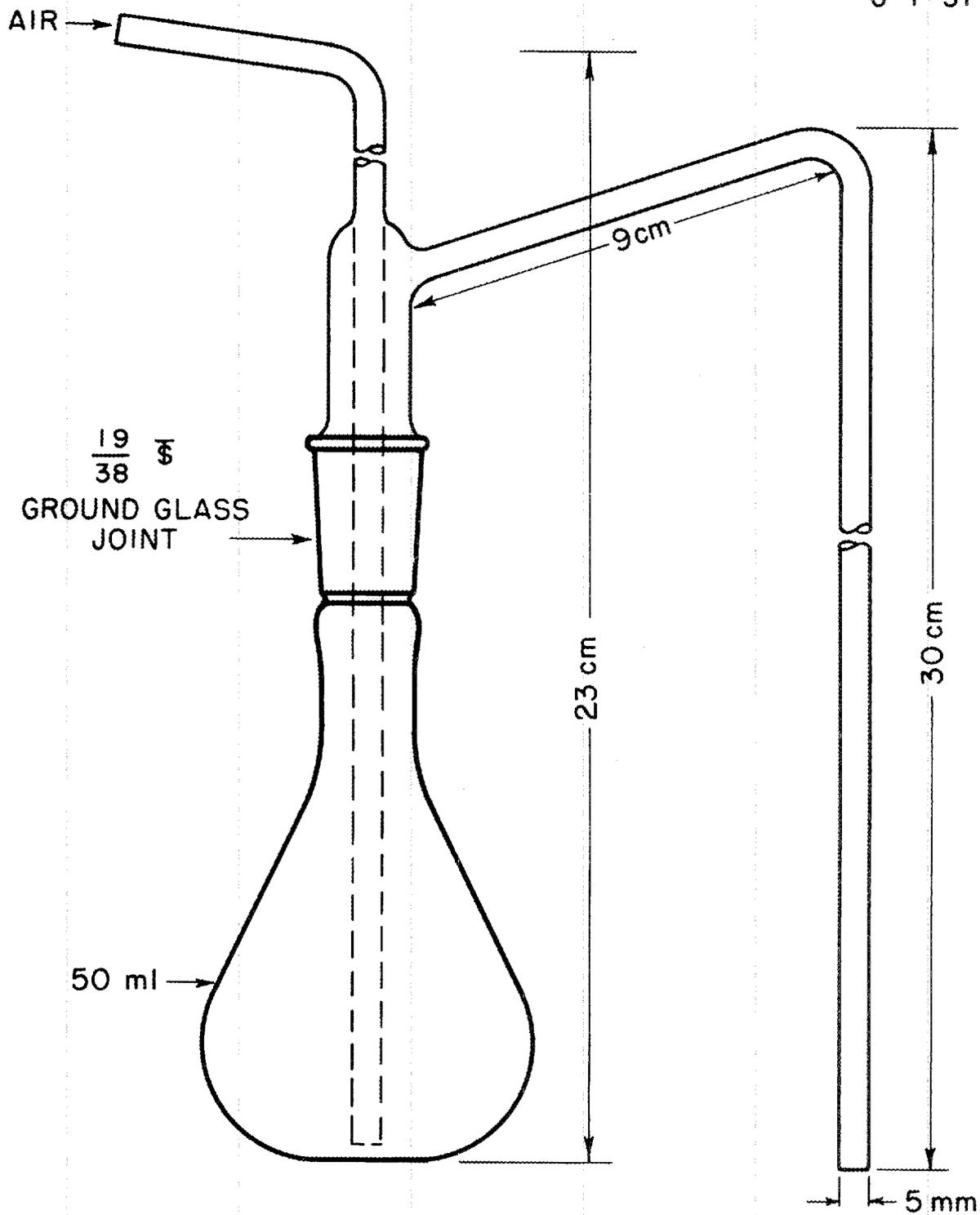
$$\frac{(A + B - C) D}{E} \times F.$$

Notes:

(a) Prepare the sintered glass crucible as follows. Wash it thoroughly with water, alcohol and ether. Place it in a vacuum desiccator (containing no desiccant) and apply vacuum for two minutes. Admit air, then evacuate again for two minutes. Weigh and repeat desiccation until a weight constant to 0.2 mg is obtained.

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RUTHENIUM STILL

ZIRCONIUM - BETA COUNT METHOD

Method No. 32

I. PRINCIPLE

Zirconium is determined after separation from other fission elements and interfering substances by precipitation as insoluble barium fluozirconate. The precipitate is mounted and the beta count determined.

II. STATUS

The original sample is treated with HF and scavenged with LaF_3 to remove UX, rare earths and much of the Ba and Sr before precipitation of Zr. The fluozirconate precipitate is easily dissolved in HNO_3 or HCl containing H_3BO_3 . The latter serves to remove F^- as stable BF_4^- . After two reprecipitations and removal of excess Ba as sulfate, the Zr is converted to cupferrate for ignition to ZrO_2 and weighing. The chemical yield is 60 to 70 per cent.

The classical separation of Zr as the phosphate is unreliable as complete interchange is not obtained. The oxalate method is not applicable in the presence of BiPO_4 without lengthy preliminary treatment of the sample, and the interchange between carrier and tracer may be incomplete.

References:

1. "Methods and Techniques of Radiochemical Activity Analysis", Method No. this manual.
2. Glasstone, S., Sourcebook on Atomic Energy, p. 136, Van Nostrand, New York (1950).
3. Hume, D. N., Ballou, N. E., and Glendenin, L. E., "A Manual of Radiochemical Determinations of Fission Product Activities", CN-2815 (June 30, 1945).
4. Flagg, J. F., Rider, B. F., and Andrus, W. S., "Methods of Chemical Analysis for Separation Process Research Unit. Part II, Radiochemical Methods", KAPL-348 (July 7, 1950).

III. REAGENTS AND APPARATUSA. Reagents

1. Barium Nitrate Solution, 50 mg $\text{Ba}(\text{NO}_3)_2/\text{ml}$. Prepare by dissolving

50 g $\text{Ba}(\text{NO}_3)_2$, analytical reagent grade, and diluting to 1 liter with distilled water.

2. Boric Acid Solution, saturated H_3BO_3 . Add 56 g H_3BO_3 to 1 liter of distilled water.
3. Cupferron Solution, 6%. Dissolve 6 g cupferron and 0.1 g $(\text{NH}_4)_2\text{CO}_3$ and dilute to 100 ml with distilled water.
4. Hydrochloric Acid, conc. (12 M) and 1 M. Prepare 1 M by diluting 86 ml conc. to 1 liter with distilled water.
5. Hydrofluoric Acid, conc., 27 M.
6. Lanthanum Holdback Carrier. Prepare by dissolving 31 g $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ in 1 liter of distilled water.
7. Nitric Acid, conc. (16 M) and 6 M. Prepare 6 M by diluting 384 ml conc. to 1 liter with distilled water.
8. Sodium Hydroxide Solution, 19 M. Prepare by dissolving one pound of NaOH in 454 ml distilled water. Filter through asbestos and store in a plastic or wax-glass bottle.
9. Sulfuric Acid, conc.
10. Zirconium Carrier. Prepare by dissolving 29 g $\text{ZrO}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ and diluting to 1 liter with distilled water.

Standardize by adding 5 ml of carrier to a beaker, dilute to 25 to 30 ml, add 6 ml conc. HCl and cool in ice to approximately 10°C . Add with stirring a slight excess of 6% cupferron, and filter quantitatively on No. 42 paper. Wash with cold 2 M HCl containing a little cupferron. Transfer to a previously ignited and tared crucible, "smoke off" the paper and ignite at 800°C for twenty minutes. Weigh and calculate as mg ZrO_2/ml .

B. Apparatus

1. Geiger-Muller Counter, Scaler and Recorder, Model Q-762, available from Nuclear Instrument and Chemical Corp., 223-W Erie Street, Chicago 10, Illinois.
2. Electric Muffle, set at 600°C .

3. Clinical Centrifuge.
4. Centrifuge Tubes, 50 ml capacity.
5. Lusteroid Tubes, 50 ml capacity.
6. Polythene Stirrer.
7. Whatman Filter Paper, No. 40.

IV. PROCEDURE

1. (a) For aqueous samples which do not contain aluminum:

Add 1 to 4 ml sample to a lusteroid tube, dilute to 4 ml, make 4 to 5 M in HNO_3 . Add 2 ml conc. HF, and 2 ml of Zr carrier^(a).

- (b) If the solution contains appreciable aluminum:

Place the sample in a glass centrifuge tube and add 2 ml Zr carrier^(a), 1 ml conc. HCl, swirl. Precipitate Zr by addition of sufficient 19 M NaOH to redissolve $\text{Al}(\text{OH})_3$ initially formed. Centrifuge. Dissolve the precipitate in 4 ml 6 N HNO_3 , and transfer to a lusteroid tube. Add 2 ml conc. HF.

- (c) If the samples are submitted in a hexone medium:

Place sample, 3 ml conc. HCl and 2 ml Zr carrier^(a) in a glass centrifuge tube. Stir well and heat to volatilize the hexone. Transfer the aqueous phase to a lusteroid tube. Add 2 ml conc. HF.

2. Add 1 ml La holdback carrier, mix well by stirring with a polythene stirrer and centrifuge briefly. Add a second 1 ml portion La holdback carrier to the supernatant. Swirl in a gentle manner so as not to disturb the first precipitate, and centrifuge the new precipitate down on top of the first. Decant the supernatant into a new lusteroid tube, and discard the precipitate.

3. To the solution, add 1 ml $\text{Ba}(\text{NO}_3)_2$ reagent (50 mg/ml), mix by swirling or stirring, digest one minute. Centrifuge and discard the supernatant.

4. To the precipitate, add 2 ml of saturated H_3BO_3 and stir to suspend all of the precipitate. Add 1 ml conc. HNO_3 , stir, then add 5 ml of water, and stir

until precipitate is completely dissolved.

5. Add 1 ml conc. HF and repeat Steps 3 and 4.

6. Add 1 ml conc. HF and repeat Step 3.

7. To the precipitate add 2 ml saturated H_3BO_3 and stir to suspend all of the precipitate. Add 3 ml conc. HCl, stir, add 5 ml water, and stir to dissolve. Remove stirrer. Add a drop of conc. H_2SO_4 , swirl and centrifuge. Transfer the supernatant to a clean glass tube. Discard the precipitate.

8. Dilute the solution to 20 ml. Set the tube in an ice bath to bring the solution to ice temperature. Fill a glass tube about two-thirds full with 1 M HCl, add a few drops of cupferron, and place this also in the ice bath. (This solution is used to wash the zirconium cupferron precipitate.) While the solutions are being cooled, set up funnels fitted with No. 40 filter paper.

9. Precipitate the cooled sample solution with 2 ml of 6% cupferron solution. Working reasonably fast from this stage on, centrifuge and discard the supernatant. Stir up the precipitate in cold 1 M HCl and filter the suspended precipitate through the funnels that have been set up.

10. With a stirring rod, fold the top portion of the filter paper down, putting the sample and paper into a compact form. With the aid of a stirring rod transfer the filter paper to a crucible, burn off the filter paper on the edge of a muffle furnace, and heat at $600^{\circ}C$ for twenty minutes.

11. Tare a watch glass without paper. Remove the crucible from the muffle furnace and cool. Transfer contents to watch glass by means of a spatula, and weigh. Mount glass and contents in the manner for a gross count.

Calculations

Let: A = measured beta count of sample aliquot, cts/min.

B = coincidence correction, cts/min. Obtain from Method 28, Apx. 1 (or Apx. 2 and 3 if counts are run for other than four minutes). B may also be calculated from the equation:

[REDACTED]

$$B = (\text{observed count})^2 \times 5 \times 10^{-6}$$

C = background correction, cts/min.

D = correction to standard, cts/min. =
$$\frac{\text{accepted count value for standard}}{\text{observed count value for standard}}$$

E = yield, decimal per cent.

F = volume factor for converting sample aliquot to ml.

Then:

Zirconium in sample measured, at 10% geometry, cts/min/ml =

$$\frac{(A + B + C) D}{E} \times F.$$

Notes:

- (a) Make the interval between sample addition and carrier addition as short as possible.

[REDACTED]

fluoride, phosphate and oxalate, the latter markedly inhibiting the chelation of zirconium with TTA⁽¹⁾. The method has been found accurate to within -1% and to have a precision better than 3%. The developmental work on the method is discussed in detail in references 1 thru 4.

References:

1. Runion, T. C., "Chelate Process for Isolating Zirconium", ORNL-105 (Aug. 9, 1948).
2. Chemistry Division Quarterly Report for Period Ending June 30, 1949, p. 228, ORNL-286 (Sept., 1949).
3. Chemistry Division Quarterly Report for Period Dec., 1948 to Feb., 1949., p. 117, ORNL-336 (May 4, 1949).
4. Brennan, M. E. and Flagg, J. F., "The Determination of Radio-zirconium by TTA". KAPL-332 (April 19, 1950).
5. Hume, D. N., Ballou, N. E. and Glendenin, L. E., "A Manual of Radiochemical Determinations of Fission Product Activities", CN-2815 (June 30, 1945)
6. Flagg, J. F., Rider, B. F., and Andrus, W. S., "Methods of Chemical Analyses for Separation Process Research Unit. Part II. Radiochemical Methods", KAPL-348 (July 7, 1950).

III. REAGENTS AND APPARATUS

A. Reagents

1. Hydroxylamine Hydrochloride, $\text{NH}_2\text{OH}\cdot\text{HCl}$, solid.
2. Nitric Acid, conc. HNO_3 .
3. Thenoyltrifluoroacetone (TTA) Solution in Xylene, 0.5 M TTA. Prepare by dissolving 111.0 g TTA, (supplied by Dow Chemical Corp., Midland, Mich.) in 1 liter of xylene, analytical reagent grade.

B. Apparatus

1. Geiger-Müller Counter, Model Q-762, available from Nuclear Instrument and Chemical Corp., 223 W. Erie St., Chicago 10, Ill.

2. Watch Glass, 1 inch diameter.
3. Steel Washer, to support 1 inch watch glass.
4. Hot Plate, electric.
5. Centrifuge Tube, 15 ml capacity.
6. Flask, glass-stoppered Erlenmeyer, 25 ml capacity.

IV. PROCEDURE

1. Place an appropriate aliquot of the sample (not over 4 ml) in a 25 ml glass-stoppered Erlenmeyer flask. Dilute to 5 ml with distilled water and sufficient conc. HNO_3 to make the solution 2 M.
2. Add 0.1 g $\text{NH}_2\text{OH}\cdot\text{HCl}$.
3. Add 2.0 ml of 0.5 M TTA in xylene. Shake for 10 minutes.
4. Transfer the solution to a centrifuge tube and centrifuge three minutes. Remove the aqueous phase with a transfer pipet.
5. Transfer a suitable aliquot^(a) of the organic phase to a watch glass preheated on a large washer on a hot plate^(b) (see Fig. 1).

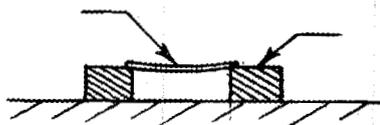


Fig. 1

6. Mount and count according to the procedure described in Method No. 26.

Calculation

- Let:
- A = measured beta count of sample aliquot, cts/min.
 - B = coincidence correction, cts/min. Obtain from Method 28, Apx. 1 (or Apx. 2 and 3 if counts are run for other than 4 minutes). B may also be calculated from the equation:
- $$B = (\text{observed count})^2 \times 5 \times 10^{-6}.$$

C = background correction, cts/min

D = correction to standard, cts/min =
$$\frac{\text{accepted count value for standard}}{\text{observed count value for standard}}$$

E = yield, decimal per cent

F = volume factor for converting sample aliquot to ml.

Then:

Zirconium in sample at 10% geometry, cts/min/ml =

$$\frac{(A + B - C) D}{E} \times F$$

Notes:

(a) Do not transfer more than 0.5 ml at a time. If it is necessary to transfer all of the organic phase, rinse the flask with approximately 1 ml xylene. Add the wash to the tube, centrifuge, then transfer to the watch glass.

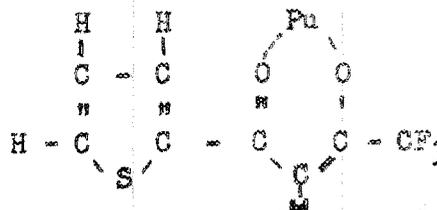
(b) The temperature of the hot plate must be regulated to give rapid evaporation of xylene without boiling.

PLUTONIUM - TTA-XYLENE EXTRACTION AND ALPHA COUNT

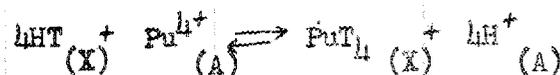
Method No. 34

I. PRINCIPLE

Plutonium (IV) forms a chelate complex with thenoyltrifluoroacetone (TTA). Both the chelating agent and the metal chelate have a negligible solubility in the aqueous phase and can be extracted with an organic solvent such as xylene. The chelate species extracted into the xylene is a neutral molecule consisting of a plutonium atom bonded to four TTA ions. Presumably each TTA ion is attached by two oxygens in the following manner:



The extraction of the plutonium into the xylene-TTA solution from the aqueous solution containing a non-complexing anion may be represented simply by the equation(1):



in which:

- HT = TTA, acid enol form
- X = xylene phase
- A = aqueous phase

II. STATUS

The method was developed by Moore and Hudgens⁽¹⁾ who have made a thorough report of this study. Since many ions form chelate compounds with TTA they are separated from one another by taking advantage of the high acid dependence of the extraction of the chelate compounds into non-polar solvents. The procedure described achieves a clean separation of plutonium from cesium, columbium, ruthenium, cerium, rare earths, uranium and aluminum.

The plutonium content of the organic phase is determined by alpha counting.

References:

1. Moore, F. L. and Hudgens, J. E., Jr., "A Solvent Extraction Method for Plutonium Analysis", ORNL-153 (Sept. 2, 1948).
2. Runion, T. C., "Chelate Process for Isolating Zirconium", ORNL-105 (Aug. 9, 1948).
3. Hume, D. N., Ballou, N. E. and Glendenin, L. E., "A Manual of Radiochemical Determinations of Fission Product Activities", CN-2815 (June 30, 1945)
4. Flagg, J. F., Rider, B. F. and Andrus, W. S., "Methods of Chemical Analyses for Separation Process Research Unit. Part II. Radiochemical Method", KAPL-348 (July 7, 1950).

III. REAGENTS AND APPARATUS

A. Reagents

1. Aluminum Nitrate, 2 M $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$. Prepare by dissolving 375.14 g in distilled water and diluting to 1 liter.
2. Hydroxylamine Hydrochloride, 1 M $\text{NH}_2\text{OH} \cdot \text{HCl}$. Prepare by dissolving 69.5 g $\text{NH}_2\text{OH} \cdot \text{HCl}$, analytical reagent grade, and dilute to 1 liter with distilled water.
3. Hydrofluoric Acid, 4 M HF. Prepare by diluting 29.6 ml of reagent grade (48%) hydrofluoric acid to 200 ml with distilled water. Store in a hard rubber bottle.

4. Nitric Acid, 2 M and 8 M HNO_3 . Prepare 8 M by diluting 100 ml of reagent grade concentrated HNO_3 to 200 ml. Prepare 2 M by dilution of the 8 M.

5. Sodium Nitrite, 1 M and 2 M NaNO_2 . Prepare 2 M by dissolving 138 g NaNO_2 , reagent grade and diluting to 1 liter with water. Prepare the 1 M by dilution of the 2 M.

6. Thenoyltrifluoroacetone (TTA) Solution in Xylene, 0.5 M TTA. Prepare by dissolving 111.0 g TTA (supplied by Dow Chemical Corp., Midland, Mich.) and diluting to 1 liter with xylene.

B. Apparatus

1. Proportional Alpha Counter, Methane, Model 117 available from Nuclear Instrument and Chemical Corp., 223 W. Erie St., Chicago 10, Ill., see Apx. 1.
2. Stainless Steel Plates, 2 inch discs.
3. Hot plate, electric.
4. Centrifuge, clinical.
5. Erlenmeyer Flask, glass-stoppered, 125 ml capacity.
6. Centrifuge Cones, 15 ml capacity.
7. Burner, Meeker type.
8. Shaker, Burrell "Wrist-action" type is recommended.

IV. PROCEDURE

A. In the Absence of Ferrous Sulfamate (HNO_3 Method)

1. Pipet the appropriate aliquot (5,000 to 10,000 cts/min) of the sample into a glass-stoppered 25 ml Erlenmeyer flask. Rinse the pipet three times with H_2O and add washings to sample volume.
2. Add 2 ml of conc. HNO_3 .
3. Evaporate to near dryness on a hot plate.
4. Repeat Steps 2 and 3.
5. Pipet 2 ml of 2 M HNO_3 into the flask. Swirl.

6. Add 20 drops of 1 M $\text{NH}_2\text{OH} \cdot \text{HCl}$, swirl, and warm for five minutes at 80°C .
7. Remove from the hot plate and add 20 drops of 1 M NaNO_2 , swirl and let stand for five minutes.
8. Test for completeness of oxidation by adding NaNO_2 dropwise until the effervescing ceases.
9. Pipet 4 ml of TTA-xylene solution into the flask and seal with scotch tape.
10. Agitate for ten minutes.
11. Transfer both phases to a 15 ml centrifuge cone and centrifuge for five minutes.
12. Pipet 500 λ aliquots from the organic phase onto stainless steel plates.
13. Dry plates on a hot plate^(a) and flame each plate after it is dry with a Meeker burner.
14. Count for α activity for four minutes at 52% geometry.

B. In the Presence of Ferrous Sulfamate (HF Method)

1. Pipet 100 λ of the sample into a glass-stoppered 25 ml Erlenmeyer flask. (Do not rinse the pipet with H_2O .)
2. Wash the pipet with 100 λ of 8 M HNO_3 and add washings to sample.
3. Wash the pipet twice with 100 λ portions of 4 M HF. Add to sample and swirl.
4. Let the solution stand for ten minutes.
5. Add 2 ml of 2 M $\text{Al}(\text{NO}_3)_3$ and swirl.
6. Let stand for five minutes.
7. Add 0.6 ml of 8 M HNO_3 and 1.0 ml of 1 M $\text{NH}_2\text{OH} \cdot \text{HCl}$. Swirl.
8. Warm for five minutes at 80°C .
9. Add 2 ml of 2 M sodium nitrite and swirl.

10. Extract with 4 ml of TTA-xylene solution for ten minutes. (Seal the stopper in the flask with scotch tape.)
11. Transfer to a 15 ml centrifuge cone and centrifuge for five minutes.
12. Pipet appropriate aliquots from the organic phase onto stainless steel plates.
13. Dry on a hot plate^(a) and flame each plate after it is dry with a Meeker burner.
14. Count for α activity for four minutes at 52% geometry.

Calculations

Let: A = total number of counts = (No. of registered counts x scale factor) + No. residual counts

B = total counts/minute = $\frac{A}{t}$

C = background, counts/min.

D = correction factor for converting sample aliquot to ml.

Then:

Plutonium in sample at 52% geometry, cts/min/ml = (B - C) x D.

Notes:

(a) Rings, the centers of which are filled with asbestos, are placed on the hot plate and used as supports for the plates.

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PROPORTIONAL ALPHA COUNTER

34,35-APX.1
6-1-51

[REDACTED]

PLUTONIUM - LANTHANUM FLUORIDE AND ALPHA COUNT METHOD

Method No. 35

I. PRINCIPLE

Plutonium is reduced to the (III) and (IV) valence states by hydroxylamine hydrochloride. It is then carried from solution on a lanthanum fluoride precipitate. The lanthanum fluoride is then mounted on a stainless steel plate and the plutonium alpha particles counted in standard equipment.

II. STATUS

The various factors which affect this analysis have been investigated and are discussed in the references. They are summarized in Reference 1.

References:

1. Clifford, A. F. and Koshland, D. E., Jr., "Development of Radiochemical Analytical Procedures for Plutonium -(1) Synthetic Solutions", CN-2040 (Sept. 23, 1944).
2. Koshland, D. E., Jr., "Development of Radiochemical Analytical Procedures for Plutonium -(2) Recommendations for a Standard Procedure and Tests in Change Solutions," CN-2041 (Jan. 8, 1945).

III. REAGENTS AND APPARATUS

A. Reagents

1. Hydroxylamine Hydrochloride Solution, 10% $\text{NH}_2\text{OH}\cdot\text{HCl}$. Prepare by dissolving 10 g $\text{NH}_2\text{OH}\cdot\text{HCl}$ and diluting to 100 ml with distilled water.
 2. Lanthanum Nitrate Solution, 5 mg La/ml. Prepare by dissolving 15.5 g $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, analytical reagent grade, and diluting to 1 liter with distilled water.
 3. Nitric Acid, 1 N HNO_3 . Prepare by diluting 65.0 ml of 15.4 M (69%) HNO_3 to 1 liter with distilled water.
 4. Hydrofluoric Acid, conc. HF.
 5. Hydrochloric - hydrofluoric Acid Solution, 1 N HCl and 1 N HF.
- [REDACTED]

Prepare by diluting 86.0 ml of 11.6 M (36%) HCl and 37 ml of conc. (48%) HF to 1 liter with distilled water.

6. Nitric - hydrofluoric Acid Solution, 1 N HNO₃ and 1 N HF. Prepare by diluting 65.0 ml of 15.4 M (69%) HNO₃ and 37 ml of conc. (48%) HF to 1 liter with distilled water.

B. Apparatus

1. Proportional Alpha Counter, Methane, Model 117, see Method 34, Apx. 1. Nuclear Instrument and Chemical Corp., 223 W. Erie Street, Chicago 10, Ill.
2. Centrifuge, clinical.
3. Centrifuge Cones, 15 ml capacity
4. Infra-red Lamp
5. Micro-burner
6. Stainless Steel Plates, 2 inch diameter
7. Transfer pipets, micro, 200 λ capacity.

IV. PROCEDURE

1. Pipet a suitable aliquot (5000 to 10,000 cts/min.) into a glass centrifuge tube.
2. Dilute to 2 ml with H₂O.
3. Make the solution 2 N in HNO₃ (~ 8 drops conc. HNO₃).
4. Add 50 λ of La(NO₃)₃ solution (5 mg La/ml).
5. Add 4-6 drops of 10% NH₂OH·HCl solution.
6. Make the solution 2 N in HF (~ 8 drops conc. HF).
7. Stir the solution until homogeneous.
8. Digest for five minutes at room temperature without agitation.
9. Centrifuge five minutes at full speed in a clinical centrifuge.
10. Remove the supernatant by the standard method^(b).
11. Wash the precipitate with 0.5 ml of 1 N HCl - 1 N HF solution^(c).
(If BiPO₄ is in solution, digest this wash ten minutes at room temperature before centrifuging.)

12. Repeat steps (9) and (10).
13. Wash the precipitate with 0.5 ml of a 1 N HNO₃ - 1 N HF solution.
14. Repeat steps (9) and (10).
15. Transfer precipitate to a stainless steel disk using 25 λ of 1 N HNO₃ solution to slurry and transfer.
16. Wash the cone three times with 25 λ portions of 1 N HNO₃ solution. Centrifuge a few seconds after the last wash to carry down any liquid on the sides of the cone.
17. Transfer each of the cone washes to the stainless steel plate.
18. Dry under an infra-red lamp.
19. Flame the plate cautiously to a dull red heat. Do not use a Fisher burner for this. A micro Bunsen burner is the best.
20. Count the sample as usual (four minutes).

Calculations:

- Let:
- A = total number of counts = (No. of registered counts x scale factor) + No. residual counts.
 - B = total counts/minute = $\frac{A}{t}$
 - C = background, counts/min.
 - D = volume factor for converting sample aliquot to ml.

Then: Plutonium in sample, counted at 52% geometry, cts/min/ml = (B - C) x D.

Notes:

(a) This method affords a clean separation from uranium. Am, Cm and Np²³⁷ if present will also carry on the LaF₃ precipitate. If these elements are present, refer to ORNL-961 (Np²³⁷) and ORNL-286 (Am, Cm).

(b) A piece of capillary tubing which is connected to a vacuum line is inserted in the supernatant and the liquid volume is drawn off.

(c) For samples which contain a high concentration of uranium, omit the HF-HCl wash and wash three times with 1 ml portions of 1 N HNO₃-1 N HF solution

III. PHYSICAL METHODS

Methods Nos. 51-75

[REDACTED]

DENSITY OF RADIOACTIVE AQUEOUS SOLUTIONS -
FALLING DROP METHOD

Method No. 51

I. PRINCIPLE

The density of an aqueous solution is determined by measuring the time required for a drop of it to fall a fixed distance in an immiscible organic medium (reference liquid), the density being found by reference to a calibration curve. The falling time is related to the density by an expression derived from Stokes law⁽¹⁾. The reciprocal of the falling time in seconds when plotted versus density on coordinate graph paper gives a straight line.

II. STATUS

The organic liquids used in this method are tetrabromoethane, mineral oil and xylene. Mixtures of these liquids are prepared to give a slightly lower specific gravity than the aqueous solutions to be measured. The mixtures are placed in graduated cylinders which are kept in a constant temperature bath at $25 \pm 1^\circ \text{C}$. A measured drop of sample is forced from a micro pipet beneath the surface of the organic liquid using a remote control sampler. The buret is raised above the surface of the liquid and the drop falls. The time required for the drop to fall a fixed distance is measured. The density of the sample is then determined by calculating the reciprocal of the falling time in seconds on a standard density curve, prepared by using $\text{Al}(\text{NO}_3)_3$ solutions of known density, and reading the density directly.

This method has been thoroughly studied in a similar system⁽²⁾ and the sources of experimental error reported to be (1) temperature fluctuations of the thermostat (2) variations in the radius of the drop and (3) errors in timing the drop fall. The suitability of various solvents and the precision of the method are discussed in detail.

[REDACTED]

References:

1. Keston, A. S., Rittenberg, D. and Schoenheimer, R. J., "Exchange Reactions of Organic Compounds with D_2SO_4 ", J. Biol. Chem. 122, 229 (1937).
2. Frilette, V. J. and Hanle, J., "Gravimetry of Heavy Water. New Reference Liquids for the Falling-Drop Method and Precision Attainable," Anal. Chem., 19, 984 (1947).
3. Hemphill, H. L., Secret Notebook, CL-1764.
4. Thomason, P. F., Secret Notebook, CL-1554.
5. Snell, F. D. and Biffen, F. M., Commerical Methods of Analysis, p. 43, McGraw-Hill, New York (1944).

III. APPARATUS AND REAGENTS

A. Reagents

1. Mineral Oil. Determine the specific gravity at $25^{\circ}C$ by the pycnometer method⁽⁵⁾.
2. Xylene, C.P. Determine the specific gravity at $25^{\circ}C$ by the pycnometer method⁽⁵⁾.
3. Tetrabromoethane, C.P., supplied by Eastman Kodak Company. Determine the specific gravity at $25^{\circ}C$ by the pycnometer method⁽⁵⁾.
4. Density Standards. Prepare solutions of $Al(NO_3)_3 \cdot 9H_2O$ at 0.05 M intervals over the concentration range of 1.3 to 2.5 M. Determine the exact densities of the solutions using the pycnometer method⁽⁵⁾. It may be desirable to prepare standards at closer intervals.
5. Reference Liquid. Prepare the organic medium (reference liquid) thru which the test solution drops by mixing tetrabromoethane and xylene. Obtain an estimate of the density of the sample at $25^{\circ}C$ and prepare a series of suitable density standards in the range of ± 0.03 about the estimated sample density. Determine the specific gravity of the lightest density standard

at 25°C by the pycnometer method⁽⁵⁾. Prepare the reference liquid to have a specific gravity 0.99 of the specific gravity of the lightest standard, determining the composition of the reference liquid from the following equations:

$$X = \frac{D (C - B)}{A - B}$$

in which

A = specific gravity of tetrabromoethane at 25°C

B = specific gravity of xylene at 25°C

C = desired specific gravity of reference liquid

D = desired volume of reference liquid, ml

X = volume of tetrabromoethane, ml

D - X = volume of xylene, ml.

A drop of the lightest density standard should fall thru the medium in approximately 40 seconds and of the heaviest in about 15 seconds.

For accurate results, i.e. density measurements to ± 0.0003 g/ml, each reference liquid should be used over a range of ± 0.005 density units. Criteria for change in density of the medium are (1) decrease in volume resulting from volatilization and (2) coloration caused by the radioactivity of the sample. If these changes occur, check the specific gravity of the reference liquid.

B. Apparatus

1. Modified Greiner Micro Buret, capacity 0.1 ml, operated by remote control. Details of the apparatus design are given in the following drawings, on file in the ORNL Instrument Division:

E-8502 - General Assembly of Specific Gravity Hood

E-8520 - Sub-Assembly of Specific Gravity Pipettes

D-8512 - Sub-Assembly of Rotating Specific Gravity Table

D-8521 - Specific Gravity Pipettes

The following general alterations are to be made to a Greiner buret:

- (a) Seal a mercury reservoir into the buret as shown.
- (b) Cut the U-shaped glass capillary section near the middle of the U and insert a ball joint. This modification provides a removable buret tip.
- (c) Construct a number of spare replacable units to the exact specification of the removable sections.
- (d) To aid the precision of drop formation, prepare a Teflon jacket for each buret tip as follows. Drill out $\frac{1}{2}$ inch lengths of Teflon rod ($\sim 5/16$ inch o.d.) to an i.d. of $1/64$ inch. Heat the buret tip and piece of Teflon. Carefully slip the Teflon over the tip of the buret until a very small section of the buret tip shows. Grind down the glass tip with emery cloth until the glass tip is even with the Teflon. Polish off the outside edge of the Teflon tip to a curved surface.

2. Constant Temperature Water Bath, $25 \pm 1^\circ\text{C}$. Assemble from the following equipment:

- (a) battery jar, filled with distilled water.
- (b) heater, knife type.
- (c) thermostat, mercury--to-wire, and a relay.

3. Timer, automatic, calibrated in 0.1 second.

4. Graduated Cylinders, 100 ml capacity, for containing the reference liquid, therefore uniformity of distance between 20 and 80 ml marks is essential. Distance between 100 and 80 ml mark should be 3.8 ± 0.1 cm. Distance between 80 and 20 ml mark should be 11.3 ± 0.1 cm.

5. Pycnometer, 10 ml capacity, provided with thermometer. Suggested type, ASTM D-153.

IV. PROCEDURE

1. Place the shielded sample on the table adjacent to the remote sampler.
2. Turn the plunger of the buret in until the column of mercury is approximately $\frac{1}{2}$ inch from the tip of the buret.
3. Draw sample into the buret until the column of sample is approximately $\frac{1}{2}$ inch from the ball joint.

4. Remove sample and lower the tip of the pipet to just beneath the surface of the organic liquid (a).
5. Discharge 5 λ of sample (b).
6. Raise the buret very slowly until the tip breaks the surface of the organic liquid.
7. Time the drop as it falls between the 80 and 20 ml marks (11.3 cm.) on the graduated cylinder (c).
8. Record the falling time (d) in seconds.
9. Calculate the reciprocal of the falling time and read the density from a standard curve (e).

Notes

(a) The graduated cylinders of organic liquids are immersed in a constant temperature bath to insure reproducibility of temperature.

(b) The delivery of the sample must be done very carefully and slowly to prevent shaking of the drop from the tip of the buret before the correct volume is delivered.

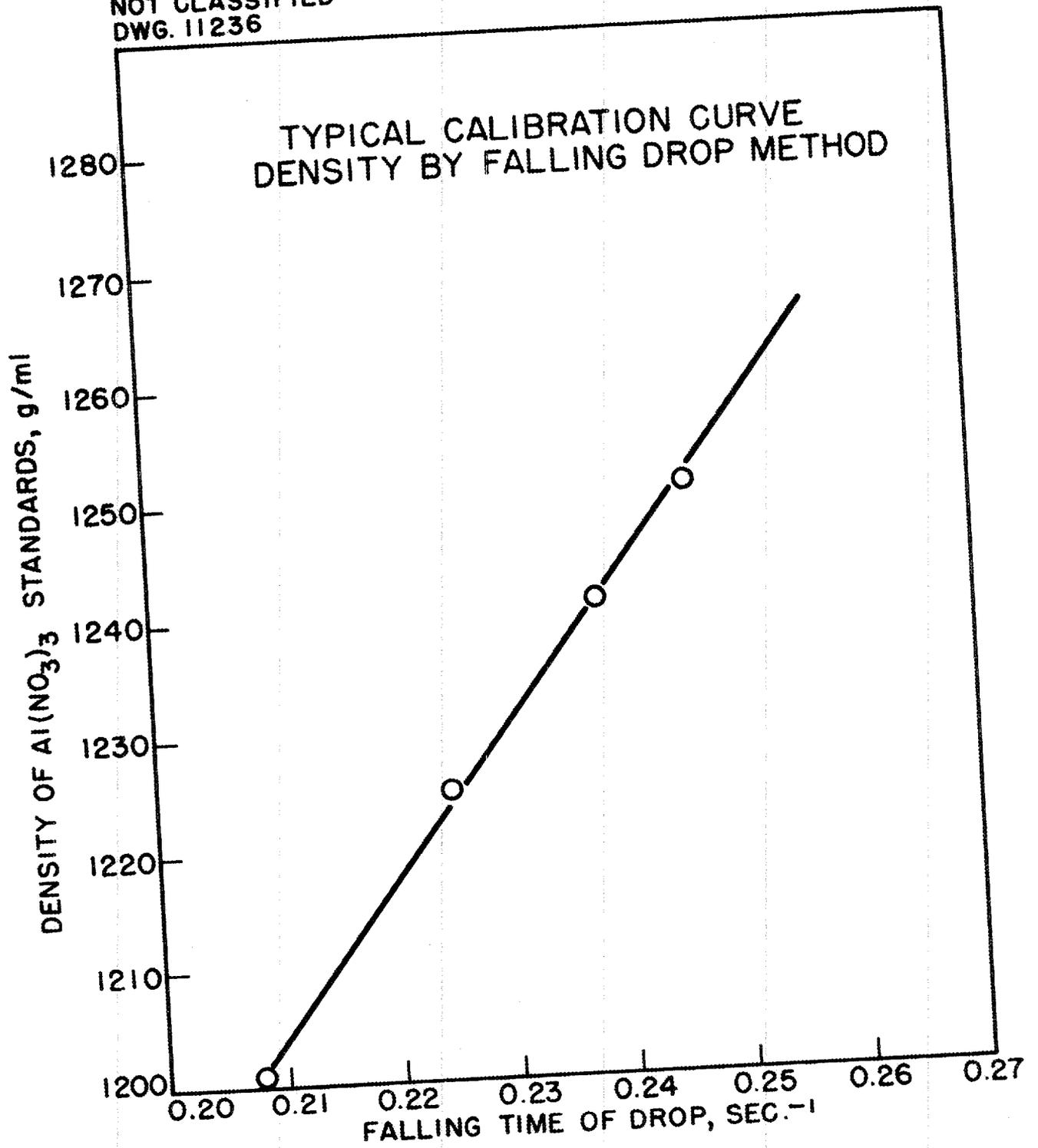
(c) The drop has attained a constant falling rate by the time it reaches the 80 ml (3.8 cm fall) mark.

(d) The density of the reference liquid should be close to that of the sample because the falling time should not be less than 7 seconds. Faster falling drops are difficult to time and also do not conform to Stokes law as they are not truly spherical.

(e) Prepare the standard density curve as follows. Determine the densities at 25°C of the density standards described in III-A. Determine the falling drop time for each standard according to the procedure. Calculate the reciprocals of the falling drop times and plot these values as abscissae versus the densities of the standards as ordinates, using rectangular coordinate graph paper. The resulting plot should be a straight line. A typical standard density calibration curve is shown in Apx. 1.

51-APX. 1
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SPECIFIC GRAVITY OF MAKE-UP SOLUTIONS

Method No. 52

I. PRINCIPLE

The specific gravity is obtained by comparing the weight of a solid object in air to the weight of the same object in the solution being analyzed. The specific gravity balance is calibrated to read specific gravity units directly.

II. STATUS

This method is to be used for non-radioactive make-up solutions only. It does not permit accuracy approaching that given by use of the specific-gravity bottle, but is desirable when a large number of samples are to be measured.

References:

1. Snell, F. D., and Biffen, F. M., Commercial Methods of Analysis p. 47, McGraw-Hill, New York (1944).
2. Brochure from E. Machlett and Son, 220 East 23rd Street, New York, N. Y., describing the Hohwald Improved Specific Gravity Chain Balance.

III. APPARATUS

1. Specific Gravity Chain Balance, Hohwald Improved, No. A4-012, supplied by E. Machlett and Son, 220 East 23rd Street, New York, N. Y. is suggested.
2. Forceps, of the type supplied with balance weights.

IV. PROCEDURE

1. Check the zero point of the balance. If adjustment is needed consult the supervisor.
2. Fill the cylinder of the balance to within 1/2 inch of the top with the liquid to be measured. The bulb should be totally submerged.
3. Check the plummet to be certain that it does not touch the sides of the cylinder.

4. Using a pair of forceps, move the rider weight along the balance beam until the approximate zero is obtained.

5. Balance to zero with the chainomatic scale.

6. Read the specific gravity to the fourth decimal place and record it along with the temperature of the solution in $^{\circ}\text{C}$ on the work sheet.

Example:—Suppose the roller weight is in the 1.2 notch on the beam, the 0 on the vernier between 0.045 and 0.046 on the chain post, and the seventh line on the vernier matches a line; the reading is then 1.2457 specific gravity.