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## IV. THORIUM

### A. Determination of Impurities in Thorium Metal

Aluminum . . . . . . . . . . . . . . . . . . . . IV-A-1
Carbon . . . . . . . . . . . . . . . . . . . . . IV-A-4
Fluorine . . . . . . . . . . . . . . . . . . . . IV-A-9
Iron . . . . . . . . . . . . . . . . . . . . . . IV-A-13
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Nickel . . . . . . . . . . . . . . . . . . . . . IV-A-20
Nitrogen . . . . . . . . . . . . . . . . . . . . IV-A-22
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Titanium . . . . . . . . . . . . . . . . . . . . IV-A-27
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## Determination of Aluminum in Thorium Metal

Ames Procedure

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## I. Apparatus

- A. Beckman, Model DU Quartz Spectrophotometer.
- B. Matched 1-cm. Corex cuvettes.
- C. Beckman, Model G, pH meter.
- D. Burrell shaker.
- E. Squibb type Separatory Funnels, 250-ml., equipped with teflon stopcock plugs.
- F. Glass stoppered Erlenmeyer Flasks, 25-ml.

## II. Reagents

### A. Standard Aluminum Solution

A stock solution of aluminum sulfate was prepared by dissolving 7.0654 g. of very pure aluminum metal in 75 ml. of reagent-grade sulfuric acid and diluting to one liter. A standard solution was prepared by diluting 28.31 ml. of the stock solution to one liter.

### B. 1,10-Phenanthroline Solution

A 0.1 per cent solution was prepared by dissolving reagent-grade 1,10-phenanthroline monohydrate in distilled water.

### C. Hydroxylammonium Chloride Solution

A 10 per cent solution was prepared by dissolving reagent-grade hydroxylammonium chloride in distilled water.

### D. Concentrated Acetate Solution

An acetic acid-ammonium acetate buffer solution was prepared by dissolving 600 g. of ammonium acetate and 600 ml. of glacial acetic acid in enough distilled water

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to make 2 liters of solution. This solution was then purified by three extractions with 100-ml. portions of a 1 per cent solution of 8-quinolinol in chloroform, followed by washing with 100-ml. portions of chloroform until all 8-quinolinol had been removed from the aqueous layer.

E. 8-Quinolinol Solution

A 1 per cent solution of 8-quinolinol in chloroform was prepared by dissolving 10 g. of reagent-grade 8-quinolinol in one liter of reagent-grade chloroform.

F. Fluosilicic Acid Solution

One ml. of a 30 per cent solution of fluosilicic acid was diluted to 2 liters.

G. Alkaline Cyanide Solution

A cyanide wash solution was prepared by dissolving 40 g. of ammonium nitrate, 20 g. of potassium cyanide and 10 ml. of concentrated ammonium hydroxide solution in enough distilled water to make one liter.

III. Procedure

Weigh 4 g. of thorium metal into a 100-ml. beaker and dissolve by warming with 50 ml. of 1:1 nitric acid and 2 ml. of the dilute fluosilicic acid solution. Evaporate the excess nitric acid and dilute to volume in a 100-ml. volumetric flask. Take a 25 ml. aliquot and add to it 1 ml. of the hydroxylammonium chloride solution and 20 ml. of the 1,10-phenanthroline solution. After allowing a few minutes for the complete formation of tris(1,10-phenanthroline)iron(II) ion add 100 ml. of concentrated acetate solution. Adjust the pH to 4.80. Prepare a blank containing all reagents in the same concentration and at the same pH. Transfer to a 250-ml. separatory funnel and add exactly 20 ml. of the 1 per cent solution of 8-quinolinol in chloroform to each. Shake once and release the pressure and then shake for three minutes. Allow the phases to settle for a few minutes. Transfer the lower layer (chloroform-8-quinolinol extract) to a 250-ml. separatory funnel containing 25 ml. of the concentrated acetate solution, 20 ml. of the 1,10-phenanthroline solution, 1 ml. of the hydroxylammonium chloride solution and 50 ml. of water. Extract again. To remove zinc, copper, cobalt and nickel interferences transfer the chloroform-8-quinolinol extract from the second extraction to another separatory funnel containing 100 ml. of the alkaline cyanide solution. Extract as before, drain the chloroform-8-quinolinol layer into a 25-ml. glass stoppered Erlenmeyer flask containing 1-2 g. of anhydrous sodium sulfate. Shake well and allow to stand, unexposed to sunlight, for 15 minutes in insure dryness of the chloroform before measuring the absorbancy of the tris(8-quinolinolo)aluminum(III) at 385 mμ.

A calibration curve is obtained by preparing a series of solutions containing varying known amounts of aluminum from 10 to 120 μg. These solutions are treated as was the aliquot above. The plot of absorbancy against μg Al/20 ml. of chloroform-8-quinolinol solution conforms to Beer's law over the concentration range of 0-120 μg of Al per 20 ml. of chloroform-8-quinolinol solution.

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## Determination of Carbon in Thorium Metal - Combustion Method

Ames Procedure

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### I. Apparatus

A. Fisher Induction Carbon Apparatus

B. Preheater consisting of a resistance furnace capable of maintaining 800°C containing a silica tube which is packed with copper oxide.

C. Nesbitt absorption bulb containing Caroxite or Ascarite.

D. Wiley mill for reducing thorium metal to the optimum particle size.

E. Oxygen cylinder, regulator, and flow meter.

### II. Theoretical Background

A. Theory of Induction Heating

The Fisher Induction Carbon Apparatus is commercially available from the Fisher Scientific Company. This instrument relies on induction heating to combust the sample. Induction heating occurs when a metallic sample is placed in an electromagnetic field. The phenomena may arise from one or both of two sources. The phenomena are hysteresis and eddy currents. Hysteresis is defined as a lagging in the values of magnetization due to changing magnetizing force, while eddy currents are defined as an induced electric current circulating wholly within the mass of metal. A magnetic substance is initially heated by hysteresis while a nonmagnetic substance is heated entirely by eddy currents.

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B. Description of Apparatus

The Fisher Induction Carbon Apparatus produces an alternating electric field whose frequency is 18 megacycles causing metallic samples to heat to about 3000°C in about 20 seconds. The apparatus contains a drying towers which ~~is~~ are filled with manganese dioxide and magnesium perchlorate to remove sulfur containing gases and water from the exhaust gas prior to the absorption of the carbon dioxide in the Nesbitt absorption bulb. The Fisher apparatus also contains a flow meter and a platinum oxidizer to convert any carbon monoxide to the dioxide. The oxygen flow is started and stopped automatically by means of a solenoid-operated valve which is controlled by the timer on the instrument. Experimental data indicate that the two minute cycle for which the instrument was designed was insufficient to obtain complete combustion of the thorium metal. Therefore, the instrument was modified by placing an interval timer in the timer circuit of the Fisher instrument⊙. This modification enables the combustion and sweeping cycles to be varied over wide ranges. The timer on the apparatus is not in operation while the auxiliary timer is operating.

## III. Procedure

A. Sample Preparation

Samples of production thorium metal which are presented for carbon analysis are in the form of millings which are free from cutting oil. Therefore, preliminary cleaning is

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unnecessary. The particle size of thorium metal should be minus 20 mesh for optimum combustion when induction heating is used. This particle size is obtained by passing the thorium millings through a Wiley mill which contains a protective nitrogen atmosphere.

Experimental data indicate that zirconia is the most feasible bedding material. The zirconia is preignited at 1100°C for 15 to 30 minutes in a Glowbar tube furnace which contains an atmosphere of oxygen to remove any residual carbon. The zirconia is ground in a porcelain mortar until all of the particles will pass through a 100 mesh screen. This material is used for bedding material.

B. Blank Determination

A sample of thorium metal is ignited in the apparatus to saturate the system with carbon dioxide. The blank determination is made using the boat, bedding material, and the ceramic sleave and running for 8 minutes. The Nesbitt bulb was weighed before and after the cycle. The weight change should be less than 0.2 milligram. If the weight change is greater than this amount but is consistent, the blank may be used as a factor.

C. Determination

A sample weighing 2.73 grams is placed in the boat (Fisher catalog 10-464-30) which contains a layer of zirconia bedding material in which has been placed a groove to accommodate the sample and then placed in the ceramic

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sleave (Fisher catalog number [illegible]-5) and [illegible] in the reaction chamber with the positioning tool which is supplied with the instrument. This will position the sample in the center of the induction coil and the sleave will protect the quartz tube from any spattering as the metal sample burns. The apparatus should be allowed to warm up for ten minutes before analyzing the first sample. The starter button is pushed in and held until the red light glows. The timer will automatically start the sample heating and the oxygen will begin to flow after 20 seconds as the solenoid is activated by the timer. The auxiliary timer is set for two minutes and set to operate after 30 seconds. The timer on the apparatus is not operating while the auxiliary timer is operating. When the timer on the panel of the instrument has reached 100 seconds the power to the induction coil is shut off and the apparatus is allowed to sweep. When the apparatus has reached 110 seconds the auxiliary timer is set in operation for four minutes and the oxygen is shut off when the timer on the apparatus reaches 120 seconds. This procedure provides a 20 second preheating period, a total of 200 seconds for combustion and a 260 second sweeping period. The Nesbitt bulb is disconnected and weighed. The difference between the tare and gross weight corresponds to the amount of carbon dioxide absorbed by Ascarite or Caroxite.

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## IV. Calculations

$$\% \text{ Carbon} = \frac{(\text{Wt. of bulb after} - \text{Wt. of bulb before} - \text{blank}) \times 12.0 \times 100}{\text{Weight of sample} \times 44.0}$$

$$\text{ppm Carbon} = \frac{(\text{Wt. of bulb after-Wt. of bulb before-blank}) \times 12.0 \times 1{,}000}{\text{Weight of sample} \times 44.0}$$

## V. Reactions

$$\text{Th} + O_2 \rightarrow \text{ThO}_2$$

$$x\,\text{Th} + y\,\text{C} + (x + y)O_2 \rightarrow x\text{ThO}_2 + y\,\text{CO}_2$$

$$\text{CO}_2 + 2\,\text{NaOH} \rightarrow \text{Na}_2\text{CO}_3 + \text{H}_2\text{O}$$

$$6\,\text{H}_2\text{O} + \text{Mg(ClO}_4)_2 \longrightarrow \text{Mg(ClO}_4)_2 \cdot 6\,\text{H}_2\text{O}$$

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## The Determination of Fluorine in Thorium Metal

### Ames Procedure

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I. Apparatus

A. The apparatus used is that described by J. C. Warf and W. D. Cline (1).

B. Five ml. micro-burets.

C. Nessler tubes, 50 ml. tall-form, type K with a fused bottom.

II. Reagents

A. Indicator Solution

A 0.01 per cent aqueous solution of sodium alizarin sulfonate, $C_6H_4COC_6H\text{-}1,2\text{-}(OH)_2\text{-}3\text{-}SO_3NaCO$, is prepared by dissolving 0.1000 g. of sodium alizarin sulfonate in 1 liter of distilled water.

B. Hydrochloric Acid, HCl

A 0.05 N hydrochloric acid solution is prepared by diluting a previously standardized more concentrated solution with the appropriate amount of redistilled water.

C. Redistilled Water

D. Thorium Nitrate, $Th(NO_3)_4$

A stock solution and a standard solution of thorium nitrate are prepared in the following manner.

1. Stock Solution

A stock thorium nitrate solution is prepared by dissolving 5.52 g. of thorium nitrate tetrahydrate, $Th(NO_3)_4 \cdot 4H_2O$, in enough water to make 1 liter of solution.

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2. Standard Solution

A standard thorium nitrate solution (0.0004 N) is prepared by diluting 10 ml. of the stock solution to 1 liter.

E. Sodium Fluoride, NaF

A stock solution and a standard solution of sodium fluoride are prepared in the following manner.

1. Stock Solution

A stock sodium fluoride solution, containing 1000 micrograms of fluorine per ml., is prepared by dissolving 2.211 g. of reagent grade sodium fluoride in enough water to make 1 liter of solution.

2. Standard Solution

A standard sodium fluoride solution, containing 10 micrograms of fluoride per ml., is prepared by diluting 10 ml. of the stock solution to 1 liter. These solutions should be stored in wax or rubber bottles.

## III. Procedure

A. The pyrohydrolysis furnaces are heated to 700-800°C and steam is passed through the apparatus at a rate of 0.5 g. per minute. This rate corresponds to a setting of 80 volts on the variable transformer which regulates the temperature of the water heater. The tip of the condenser should not dip beneath the surface of water in the silver dish receiver. A sample of thorium metal, containing from 0.5 to 40 micrograms of fluorine, (usually about

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2 g.) is weighed into a platinum foil boat and inserted in the platinum reaction tube of the pyrohydrolysis apparatus. A steam rate of 0.5 g. per minute is maintained until the vigorous evolution of hydrogen has subsided and it is then increased to 5 g. per minute and maintained at this rate until a total of 35 ml. of distillate has been collected. This rate corresponds to a setting of 120 volts on the variable transformer. The distillate is transferred to a 50 ml. Nessler tube, 2.0 ml. of 0.05 N hydrochloric acid and 1.0 ml. of the indicator solution are added and the solution diluted to the mark with redistilled water. This solution is titrated with 0.0004 N thorium nitrate to a pink end-point. A reference solution is prepared by adding 40 ml. of redistilled water, 1.0 ml. of the indicator solution, and 2.0 ml. of 0.05 N hydrochloric acid to a 50 ml. Nessler tube and diluting to the mark with redistilled water. A volume of 0.0004 N thorium nitrate equal to that required by the sample is added to the reference solution. The reference solution is now titrated with the standard sodium fluoride solution until the color matches that of the end-point of the sample. The amount of sodium fluoride added is a measure of the quantity of fluorine in the sample.

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IV. Calculations

A. $\% \; F = \frac{(\text{Ml. std. NaF})\,(0.001)}{\text{Wt. sample (grams)}}$

B. $\text{p.p.m.} \; F = \frac{(\text{Ml. std. NaF})\,(10)}{\text{Wt. sample (grams)}}$

V. Reactions

A. $Th + 2H_2O \longrightarrow ThO_2 + 2H_2$

B. $ThF_4 + 2H_2O \longrightarrow ThO_2 + 4HF$

C. Indicator (pink) + HF ⟶ Indicator (colorless).

D. $4HF + Th(NO_3)_4 \longrightarrow ThF_4 + 4HNO_3$

VI. References

A. Apparatus

1. Warf, J. C., and W. D. Cline, CC-2723 (June 30, 1945).

B. Procedure

1. Tevebaugh, R. D., and W. D. Cline, "The Analysis of Certain Metals for Trace Quantities of Fluorine", Collected Paper.

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## The Determination of Iron in Thorium Metal

Ames Procedure

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I. Apparatus

A. Coleman spectrophotometer with one and five cm. cuvettes.

II. Reagents

A. Hydrochloric Acid, $HCl$

Reagent grade, 12 molar.

B. Nitric Acid, $HNO_3$

Reagent grade, 16 molar.

C. Fluosilic Acid, $H_2SiF_6$

Add 2 drops of 48 per cent fluosilicic acid to 50 ml. water, place in a dropper bottle and mix by shaking.

D. Hydroxylammonium Chloride, $NH_3OHCl$

Prepare a 10 per cent aqueous solution by dissolving 10 grams reagent-grade crystalline hydroxylammonium chloride in water and diluting to 100 ml.

E. 1,10-Phenanthroline, $C_{12}H_8N_2$

Prepare a 0.1 per cent aqueous solution by dissolving 0.55 g. 1,10-phenanthroline monohydrate in 500 ml. distilled water. The rate of dissolution may be accelerated by warming the solution by immersion in hot water.

F. Ammonium Tartrate, $(NH_4)_2\ C_4H_4O_6$

Prepare a 25 per cent solution by dissolving 250 g. of reagent grade diammonium tartrate in distilled water and diluting to a liter.

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G. Ammonium Hydroxide, $NH_4OH$

Prepare a 1:1 solution by adding concentrated reagent grade ammonium hydroxide to an equal volume of distilled water.

H. Standard Iron Solution

Prepare an iron solution containing 100 µg. Fe/ml. by dissolving 100 mg. pure iron wire in dilute sulfuric acid and diluting to a liter with distilled water. This solution is stable indefinitely if it is acidic; to prepare the calibration curve, dilute a 100 ml. aliquot of this stock solution to a liter to prepare a standard solution containing 10 µg. Fe/ml.

## III. Procedure

### A. Dissolution of Sample

Weigh out 3-5 g. samples of the metal turnings on a triple beam balance, place in 250 ml. beakers and cover with a watch glass. Cautiously add 100 ml. concentrated hydrochloric acid; when the evolution of gas has decreased, add 25 ml. concentrated nitric acid and heat the solution to boiling on the hot plate. The black slurry will change to brown and slowly dissolve giving a yellowish solution with a small amount of white crystalline residue. This last residue may be dissolved by adding a few drops of dilute fluosilicic acid and digesting the solution. If the sample contains large amounts of oxide, it may be necessary to repeat the digestion, adding more nitric

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and fluosilicic acids. When the sample has been dissolved, evaporate the solution to about 10 ml. volume, transfer to a 100 ml. volumetric flask and dilute to volume with distilled water.

B. Development of Color and Estimation of Iron

Transfer an aliquot of the sample solution containing approximately one gram of thorium to a 100 ml. volumetric flask. To the flask add in this order with shaking:

(1) 1 ml. 10 per cent hydroxylammonium chloride.
(2) 10 ml. 0.1 per cent 1,10-phenanthroline.
(3) 25 ml. 25 per cent ammonium tartrate.

Dilute to about 75 ml. and add dilute ammonium hydroxide with shaking until the white flocculent precipitate dissolves; the pH of the solution is now approximately 5 as shown by Hydrion paper and is ideal for color development. Dilute the solution to the mark with distilled water, allow it to stand at room temperature for one hour or more (overnight standing is not harmful) and determine the transmittancy of the solution in the Coleman spectrophotometer at a wavelength of 515 mμ against distilled water as a blank. Record the cell thickness, transmittancy and volumes of flasks and pipettes used.

C. Preparation of Calibration Curve

To 100 ml. volumetric flasks add 2, 4, 6, 8, 10, 15, 20, 30 and 40 ml. aliquots of the standard iron solution containing 10 μg. Fe/ml. To each flask add in this order with shaking

(1) 1 ml. 10 per cent hydroxylammonium chloride.
(2) 10 ml. 0.1 per cent 1,10-phenanthroline.
(3) 25 ml. 25 per cent ammonium tartrate.

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Dilute the solutions to about 75 ml. and adjust the pH to 5.0 ± 0.5 with dilute ammonium hydroxide as shown by Hydrion paper. Dilute the solutions to volume and allow them to stand for one hour or more before determining the transmittancies at 515 mμ with both the one and the five cm. curvettes in the Coleman spectrophotometer. Plot per cent transmittancy vs. micrograms Fe/ml. solution on semilogarithumic graph paper such as that supplied by the Coleman Company; the points should fall on a straight line. This curve is used to determine the concentration of iron which corresponds to the transmittancy of an unknown solution.

## IV. Calculations

A. $$\text{ppm Fe} = \frac{(\mu\text{g. Fe/ml.})\ (\text{flask volume})\ (\text{dilution factor})}{\text{wt. sample in grams}}$$

## V. Reactions

A. $Th + 4\ HCl \longrightarrow ThCl_4 + 2\ H_2$

B. $Fe + 2\ HCl \longrightarrow FeCl_2 + H_2$

C. $3\ FeCl_2 + HNO_3 + 3\ HCl \longrightarrow 3\ FeCl_3 + NO + 2\ H_2O$

D. $4\ FeCl_3 + 2\ NH_3OHCl \longrightarrow 4\ FeCl_2 + N_2O + 6\ HCl + H_2O$

E. $FeCl_2 + 3\ C_{12}H_8N_2 \longrightarrow Fe(C_{12}H_8N_2)_3\ Cl_2$

## VI. References

A. Fortune, W. B. and M. G. Mellon, Ind. Eng. Chem., Anal. Ed., 10, 60-64 (1938).

B. Ericson, R. P. and E J. Formfeld, CC-2933, (September 10, 1945).

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## The Determination of Manganese in Thorium Metal

Ames Procedure

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### I. Apparatus

A. Coleman Universal Spectrophotometer, Model 11.

B. One-, two-, four- and five-cm. cuvettes.

### II. Reagents

A. Potassium Meta Periodate, $KIO_4$

Reagent grade.

B. Electrolytic Manganese, Mn

Obtained from Electro Manganese Corporation, Knoxville, Tennessee. 99.9+ per cent Mn.

C. Nitric Acid, $HNO_3$

Reagent grade.

D. Fluosilicic Acid, $H_2SiF_6$

A 1:100 aqueous solution of fluosilicic acid is prepared by adding 1 ml. of concentrated (48%) reagent grade acid to 100 ml. of water.

E. Manganous Nitrate, $Mn(NO_3)_2$

A stock solution and a standard solution of manganese are prepared in the following manner:

1. Stock Solution

A stock manganese solution, containing 0.1 mg. manganese per ml., is prepared by dissolving 100 mg. of electrolytic manganese in 20 ml. of 1:10 nitric acid and diluting the resulting solution to 1000 ml.

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2. Standard Solution

A standard manganese solution, containing 0.01 mg. manganese per ml., is prepared by diluting 100 ml. of the stock solution to 1000 ml.

III. Procedure

A. Calibration Curve

Solutions containing 0, 0.01, 0.02, 0.03, 0.04, 0.05, 0.08, and 0.1 mg. manganese per 50 ml. are prepared by placing 0, 1, 2, 3, 4, 5, 8, and 10 ml. of the standard manganese solution in a series of eight 100 ml. beakers. Fifteen ml. of 2:1 nitric acid is added to each of the beakers and the solutions heated to boiling. About 0.5 g. of potassium meta periodate is added to each beaker and the solutions boiled for 5-10 minutes. After cooling the solutions are transferred to 50 ml. volumetric flasks, diluted to the calibration mark and mixed thoroughly. These solutions are, one at a time, placed in a 5-cm. cuvette and their per cent transmittancy, 100 T or 100 I/Io, determined at 522 mμ with the spectrophotometer. These per cent transmittancies are plotted as logarithmic ordinates against the concentrations of manganese in mg. per 50 ml. or as ordinates on a semilogarithmic graph paper such as Keuffel and Esser No. 358-51. This curve is used to determine the concentration of manganese which corresponds to the per cent transmittancy of an unknown sample.

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B. Analysis of a Sample

Five g. samples of thorium are weighed into 150 ml. beakers and treated with 25 ml. of concentrated nitric acid. Five to 10 drops of fluosilicic acid are added to each sample to facilitate solution. The samples are warmed until solution is complete and then 5 ml. of concentrated nitric acid is added to each beaker and enough water to bring the volume of each solution up to 25-35 ml. About 0.5 g. of potassium meta periodate is added to each sample and the solutions boiled for 5-10 minutes. After cooling the solutions are transferred to 50 ml. volumetric flasks, diluted to the calibration mark and mixed thoroughly. These solutions are now compared with a reagent blank prepared as above.

## IV. Calculations

A. $$\% \text{ Mn} = \frac{(\text{mg. Mn/50 ml.})\ (1/10)}{\text{Wt. sample (grams)}}$$

B. $$\text{ppm Mn} = \frac{(\text{mg. Mn/50 ml.})\ (1000)}{\text{Wt. sample (grams)}}$$

## V. Reactions

A. $$\text{Th} + 8\text{HNO}_3 \xrightarrow{(\text{H}_2\text{SiF}_6)} \text{Th(NO}_3)_4 + 4\text{NO}_2 + 4\text{H}_2\text{O}$$

B. $$\text{Mn} + 4\text{HNO}_3 \longrightarrow \text{Mn(NO}_3)_2 + 2\text{NO}_2 + 2\text{H}_2\text{O}$$

C. $$2\text{Mn(NO}_3)_2 + 5\text{KIO}_4 + 3\text{H}_2\text{O} \longrightarrow 2\text{HMnO}_4 + 5\text{KIO}_3 + 4\text{HNO}_3$$

## VI. References

A. Procedure

1. Willard, H. H., and L. H. Greathouse, J. Am. Chem. Soc., 39, 2366, 2377 (1917).

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# Determination of Nickel in Thorium Metal

## Ames Procedure

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## I. Apparatus

A. Beckman Model DU Spectrophotometer.

B. Matched Corex Cells.

## II. Reagents

A. Citric Acid, $C_6H_8O_7$.

Prepare a 50 per cent aqueous solution.

B. Ammonium Hydroxide, $NH_4OH$.

Concentrated reagent grade.

C. Saturated Bromine Water.

D. Nitric Acid, $HNO_3$.

Concentrated reagent grade.

E. Saturated Aqueous Solution of 1,2-Cycloheptanedionedioxime.

## III. Procedure

### A. Dissolution of Sample

Dissolve a 4 g. sample of thorium metal in concentrated nitric acid containing a trace of fluosilicic acid. If any chloride is present it is necessary to evaporate the solution of fumes with perchloric acid* as chloride ion interferes with the determination. Aliquots of the sample solution containing 0.4 g. of thorium are transferred to a 100-ml. volumetric flasks.

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* Analyst must obtain the group leader's permission before using this reagent.

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B. Color Development.

To the sample solution the following additions are made:

(1) 10 ml. of 50 per cent citric acid solution.

(2) 15 ml. of concentrated ammonium hydroxide and allow to cool to room temperature.

(3) 10 ml. of saturated bromine water and immediately** add 10 ml. 1,2-cycloheptanedionedioxime. Dilute to mark and measure the absorbancy <u>vs</u>. a reagent blank 35 ± 10 minutes after the addition of the 1,2-cycloheptanedionedioxime.

C. Absorbancy Measurement.

The absorbancies are measured using the Beckman model DU Spectrophotometer at 443 mμ with a slit width of 0.03 mm. Matched Corex cells should be used. For best accuracy the matching should be performed for each series of measurements.

## IV. Calculations

For each series of determinations it is necessary to prepare a standard curve from solutions containing known amounts of nickel. Known quantities of nickel are added to the thorium solutions and the absorbancies are plotted versus the concentration of nickel. Because of the delicate techniques involved, each analyst should prepare a separate calibration curve.

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** It is extremely important that the 1,2-cycloheptanedionedioxime solution be added as quickly and reproducibly as possible and without delay after adding the bromine water if accurate, reproducible results are to be obtained.

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# The Determination of Nitrogen in Thorium Metal

## Ames Procedure

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## I. Apparatus

A. The apparatus used is that described by T. S. Ma and G. Zuazaga (1).

## II. Reagents

A. Sodium Hydroxide, NaOH.

A 35 per cent solution is prepared by dissolving 35 g. of reagent grade sodium hydroxide in 65 ml. of water.

B. Boric Acid - Mixed Indicator Solution.

Dissolve 20 g. reagent grade crystalline boric acid, $H_3BO_4$, in about 800 ml. redistilled water and add one of the following indication solutions:

1. Indicator as recommended by Ma and Zuazaga; dissolve 100 mg. bromcresol green (tetra-bromo-m-cresolsulfonphthalein), $C_6H_4SO_2OC(C_6H\text{-}3,5\text{-}Br_2\text{-}2\text{-}CH_3\text{-}4OH)_2$, and 20 mg. methyl red (p-dimethylaminoazolbenzene-o-carboxylic acid), $4\text{-}(CH_3)_2NC_6H_4N{:}NC_6H_4\text{-}2\text{-}COOH$, in 95 per cent ethyl alcohol and dilute to 100 ml. with ethyl alcohol. Pipette 10 ml. of this stock indicator solution into the boric acid solution.
2. Indicator as used prior to 1950 at Ames Laboratory; dissolve 80 mg. bromcresol green and 110 mg. methyl red in ethyl alcohol, and dilute to 100 ml. with ethyl alcohol. Pipette 10 ml. of this stock indicator solution into the boric acid solution.
3. Indicator as used after this date at Ames Laboratory; pipette 10 ml. "methyl purple" indicator solution as

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purchased from Fleischer Chemical Company, Benjamin Franklin Station, Washington 4, D.C. into the boric acid solution.

Dilute the boric acid-mixed indicator solution to a liter and mix the solution well. Pipette 10 ml. of this solution into the receiving flask of the distillation apparatus. Dilute, with redistilled water, to the same volume as a distillate titration and titrate with 0.01 N hydrochloric acid to a neutral gray end point. If an appreciable volume of HCl is required, adjust the stock mixed indicator-boric acid solution with 0.01 N hydrochloric acid so that less than 0.1-0.2 ml. HCl is required to titrate a "blank" of this type to the end point.

C. Hydrochloric Acid, HCl.

A 0.01 N hydrochloric acid solution is prepared and standardized by a conventional procedure.

III. Procedure

A. The thorium metal which is to be analyzed is cleaned by placing it in dilute (8 N) nitric acid, adding a small amount (6 mg.) of sodium fluosilicate and warming the mixture until the surface of the thorium metal is bright. The thorium metal is then removed from the nitric acid, washed with water and dried. A 5 g. sample of the thorium is CAUTIOUSLY dissolved in 50 ml. of dilute ( 6 N) hydrochloric acid containing a small amount (6 mg.) of sodium fluosilicate. It may be necessary to warm the mixture to effect complete solution. The solution is quantitatively transferred to a 100 ml. volumetric flask, diluted to volume and 20 ml. aliquot is pipetted into the Kjeldahl apparatus. Twenty ml. of the boric acid-mixed indicator solution is divided between the 125 ml. Erlenmeyer receiving flask and the vapor trap. Fifty ml. of the sodium hydroxide solution is added to the thorium chloride solution and the alkaline solution steam distilled. Fifty ml. of condensate is collected in the boric acid-mixed indicator solution. The

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receiving flask is lowered, the top of the condenser is washed of with distilled water and the ammonia is titrated with 0.01 N hydrochloric acid using a micro buret. The end-point is observed as a change from green through violet to a faint pink. A reagent blank should be run by the above procedure.

## IV. Calculations

A. $$\% \text{ N} = \frac{[\text{Ml. (sample)} - \text{Ml. (blank)}]\ \text{N(HCl)}\quad 1.4008}{\text{Wt. sample (grams)}}$$

B. $$\text{ppm N} = \frac{[\text{Ml. (sample)} - \text{Ml. (blank)}]\ \text{N(HCl)}\quad 14{,}000}{\text{Wt. sample (grams)}}$$

## V. Reactions

A. $Th + 4HCl \longrightarrow ThCl_4 + 2H_2$

B. $Th_3N_4 + 16\ HCl \longrightarrow 3ThCl_4 + 4NH_4Cl$

C. $ThCl_4 + 4NaOH \longrightarrow Th(OH)_4 + 4NaCl$

D. $NH_4Cl + NaOH \longrightarrow NaCl + H_2O + NH_3$

E. $2NH_3 + 4H_3BO_3 \longrightarrow (NH_4)_2\ B_4O_7 + 5H_2O$

F. $(NH_4)_2B_4O_7 + 2HCl + 5H_2O \longrightarrow 2NH_4Cl + 4H_3BO_3$

## VI. References

### A. Apparatus

1. Ma, T. S., and G. Zuazaga, Ind. Eng. Chem., Anal, Ed., 14, 280-282 (1942).

### B. Procedure

1. Fisher, R. W., and L. Smith, CC-726 (June 15, 1943).
2. Fornefeld, E., CC-2710 (April 10, 1945).

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# Determination of Oxygen in Thorium Metal

## Ames Procedure

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## I. Reagents

A. Hydrochloric Acid, HCl.

A 1:1 solution is prepared by diluting concentrated reagent-grade hydrochloric acid with an equal volume of distilled water.

B. Nitric Acid, $HNO_3$.

Concentrated reagent grade.

C. *Perchloric Acid, $HClO_4$.

70 - 72 Per cent reagent grade.

## II. Procedure

The thorium metal samples should be in the form of large pieces as oxygen would be picked up in the turning operations. The pieces should be treated with dilute nitric acid containing a small amount of fluosilicic acid to remove any oxide which had formed on the surface of the metal. The metal is removed from the acid, washed with water, and dried. Samples weighing from 2-5 grams are convenient size for handling. The sample is weighed and transferred to a 250 ml. beaker and treated with 8 ml. of the 1:1 hydrochloric acid, 2 ml. of concentrated nitric acid, and 10 ml. of 70-72 per cent perchloric acid. The beakers are covered with watch glasses and allowed to stand until the vigorous evolution of hydrogen has ceased. The beakers

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*Analyst must obtain the group leader's permission before using this reagent.

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are transferred to the hot plate and evaporated to copious fumes of perchloric acid for 10 minutes. The beakers are removed from the hot plate and allowed to cool to room temperature. Any material adhering to the watch glasses is washed into the corresponding beakers and the solution is diluted to about 50 ml. A small amount of white crystalline precipitate remains which is assumed to be the combined oxygen as thorium dioxide. The solutions are filtered using S & S Blue Ribbon filter paper into 400 ml. beakers. Each of the precipitates is washed well with ten 20-ml. portions of water.** The residues are dried and ignited to constant weight in platinum crucibles in a muffle furnace at 1100°C. The perchloric acid insoluble thus obtained is taken as a measure of the combined oxygen in the thorium metal.

## III. Calculations

$$\% \text{ Oxygen} = \frac{(\text{Wt. of perchloric acid insoluble})\ (0.12116)\ (100)}{\text{Wt. of sample (grams)}}$$

## IV. Reactions

A. $Th^{o} + 4\ HCl \rightarrow ThCl_4 + 2\ H_2$

B. $ThCl_4 + HClO_4 \rightarrow Th(ClO_4)_4 + 4\ HCl$

## V. Reference

A. Ayers, A. S., CC - 2403 (May 12, 1945)

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** Since it is very difficult to completely wash perchloric acid from the filter paper, it is necessary to cover the wet filter paper with ammonium oxalate crystals prior to the ignition to avoid a rapid deflagration.

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# Determination of Titanium in Thorium Metal

## Ames Procedure

9-1-52

## I. Apparatus

A. Coleman Universal Spectrophotometer, Model 11.

B. Cuvettes, 1 and 5-cm.

## II. Reagents

A. Nitric Acid, $HNO_3$.

Dilute concentrated nitric acid with an equal volume of distilled water.

B. Hydrogen peroxide, $H_2O_2$.

28-30 Per cent aqueous solution.

## III. Determination of Titanium

Dissolve a 5.00 g. sample of thorium metal in 1:1 nitric acid containing a small amount of fluosilicic acid to complete the solution. The solution is transferred to a 100-ml. volumetric flask and diluted to volume. A 20-ml. aliquot which represents a 1 g. sample is transferred to a 25-ml. volumetric flask. Six drops of the 28 per cent hydrogen peroxide are added to the solution which is mixed well by shaking and diluted to the mark. The complete color reaction develops immediately and titanium may be determined as low as 10 ppm by this reaction. The intensity of the color which develops will determine the particular absorption cell which is to be used: the more intense solutions require the 1-cm. cell while the more faint solution require the 5-cm. cell.

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The transmittancy is measured at 410 mμ using the Coleman Universal Spectrophotometer. The titanium content of the solution is obtained from the relation of the transmittancy to a previously prepared standard curve.

## IV. Preparation of Standard Titanium Curve

Prepare a standard titanium solution by dissolving 0.739 g. of reagent-grade potassium titanium oxalate, $K_2TiO(C_2O_4)_2 \cdot 2H_2O$, in 40-ml. of hot concentrated sulfuric acid. Dilute this solution to one liter and mix well. This produces a solution containing 10 μg of titanium per ml. Pipette 5-, 10-, 20-, 30- and 40-ml. aliquots of this solution into 100-ml. volumetric flasks. Add 4 ml. of concentrated sulfuric acid to each solution and dilute with distilled water to about 80 ml. Add 4 ml. of 28 per cent hydrogen peroxide solution to each flask, dilute to volume and mix well. Determine the transmittancies of these solutions in both the 1- and 5-cm. cuvettes in the Coleman Universal Spectrophotometer against water as a reference solution at 410 mμ. Plot the transmittancies versus the corresponding concentration on semi-logarithmic graph paper and construct a line through the points; a straight line should result in both cases.

## V. Calculations

$$\text{ppm of titanium} = \frac{(\mu\text{g. Ti/ml.})\ (25)\ (100/20)}{\text{Weight of sample}}$$

## VI. Reactions

$$Th + 4\ HNO_3 \rightarrow Th\ (NO_3)_4 + 2\ H_2$$

$$TiO(NO_3)_2 + H_2O_2 + H_2O \rightarrow H_4TiO_5 + 2\ HNO_3$$

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## Determination of Uranium in Thorium Metal

### Ames Procedure

9-1-52

I. Apparatus

- A. Beckman Spectrophotometer, Model DU, equipped with a hydrogen lamp for use in the ultraviolet.
- B. Matched 5-cm. cuvettes
- C. Steam bath.
- D. 100-ml. separatory funnels.

II. Reagents

A. Ammonium Thiocyanate, $NH_4SCN$.

Prepare an 8 molar solution by dissolving 608 g. of reagent-grade ammonium thiocyanate in enough distilled water to make 1000 ml. of solution. The solution is filtered through sintered glass filter (fine porosity) and the pH is adjusted to 7 with ammonium hydroxide.

B. Stannous Chloride Dihydrate, $SnCl_2 \cdot 2H_2O$.

Prepare a 10 per cent solution by dissolving 50 g. of reagent-grade stannous chloride dihydrate in 50 ml. of concentrated hydrochloric acid, filtering through a sintered glass filter (fine porosity) and diluting to 500 ml. with distilled water.

C. Hydrochloric Acid, HCl.

Prepare a 1 normal solution by diluting 86 ml. of concentrated reagent-grade hydrochloric acid to 1 liter with distilled water.

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D. Nitric Acid, $HNO_3$.

Prepare an 8 molar solution by diluting 520 ml. of concentrated reagent-grade nitric acid to 1 liter with distilled water.

E. Fluosilicic Acid, $H_2SiF_6$.

Prepare a dilute solution by diluting 1 drop of 30% reagent-grade fluosilicic acid with 30 ml. of distilled water.

F. Diethyl Ether, $C_4H_{10}O$.

Purified by distillation from a calcium oxide suspension.

## III. Procedure

A. Preparation of Thorium Nitrate Solution.

Ten grams of clean thorium metal are weighed to the nearest hundreth of a gram and dissolved in 100 ml. of 8 M nitric acid to which 1 ml. of the dilute fluosilicic acid has been added. After all the metal has been dissolved, the solution is evaporated to about 10-15 ml. on a hot plate. It is removed to a steam bath and evaporated to dryness. The major portion of the residue being thorium nitrate tetrahydrate. The residue is dissolved in 15 ml. of water and filtered through sintered glass filter (medium porosity). The filter is washed with 5 ml. of water which is added to the 15 ml. of sample solution.

B. Extraction of the Uranium.

The thorium nitrate solution is placed in a 100-ml. separatory funnel which contains 25 ml. of redistilled diethyl ether. The mixture is shaken vigorously for 5

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minutes and the two phases placed in different beakers. The water phase ( the bottom layer) is returned to the original funnel and 25 additional ml. are added. After shaking again for 5 minutes the water layer is discarded and the two ether layers are combined. If the ether solutions are carefully transferred to a 150 ml. beaker any remaining water will remain behind. Twenty ml. of distilled water are added to the ether phase and the beaker is placed on a LOW TEMPERATURE hot plate. When all of the ether has evaporated, the liquid is shaken gently and allowed to evaporate to 5-10 ml. It must not be evaporated to dryness. The uranium content is ready to be determined.

C. Determination of Uranium by Thiocyanate Color.

The uranium solution is transferred to a 25-ml. volumetric flask and the pH adjusted to 0.7 ± 0.3. For the procedure as given above, 2 ml. of 1 N hydrochloric acid are satisfactory. Two ml. of a 10 per cent stannous chloride solution are added and the flask is shaken vigorously. The stannous tin removes the ferric iron which interferes with the uranium determination. Two ml. of the stannous chloride solution will compensate for 2 mg. of ferric iron. The flasks should be removed to a location which is convenient to the spectrophotometer and before the thiocyanate solution is added. The spectrophotometric data must be obtained 5 minutes ± 30 seconds after the thiocyanate is added. Ten ml. of 8 M ammonium thiocyanate are added and the solution diluted to 25.00 ml. with water immediately. The flasks are shaken well and readings are made against

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a reagent blank 5 minutes after the thiocyanate addition. A standard curve is used to calculate the micrograms of uranium present from the spectrophotometric data. The standard curve is prepared by using the procedure as given with known amounts of uranium added to a solution of pure thorium. The blanks are prepared at the same time as the unknown samples as the blanks deteriorate with time. A stable blank may be prepared with chromic chromium. About 0.15 mg./ml. is equal to a freshly prepared blank at 380 mμ. The chromic chromium solution should be checked against fresh blanks from time to time. Spectrophotometric data are taken at 380 mμ.

## IV. Calculations

A. The micrograms of uranium are obtained directly from the standard curve.

B. $\text{ppm of uranium} = \dfrac{\text{Micrograms of uranium}}{\text{Wt. of sample in grams}}$

## V. References

A. Extraction

1. Fontana, B. J., Plutonium Project Report, NNES, <u>17B</u>, Paper 3.7.
2. Separation of Uranium from Other Elements by the Ethyl Ether Extraction of a Nitrate Solution, Purdue Research Foundation.

B. Thiocyanate Method Nelson, C. M., and Hume, D. N., MON C-28 Spectrophotometric Determination of Microgram Amounts of Uranium by the Ammonium Thiocyanate Method.

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## Determination of Zinc in Thorium Metal

Ames Procedure

9-1-52

### I. Apparatus

A. Sargent Polarograph, Model XXI, with accessories.

B. Nitrogen cylinder for purging electrode chamber.

### II. Reagents

A. Ammonium Hydroxide, $NH_4OH$.
Concentrated reagent grade.

B. Gelatin, reagent grade.
Prepare a 0.5 per cent solution.

C. Hydrochloric Acid.
Reagent grade, 12 normal

D. Sodium fluosilicate, reagent grade.

E. Sulfosalicylic acid, Eastman (676) white label grade, 2 molar solution.

F. Thorium metal, recast, containing less than 10 ppm of zinc.

G. Zinc metal, 99.99 per cent pure, electrolytic grade.

### III. Determination of Zinc

A sample of thorium metal weighing ten grams or less (depending on the zinc content) is weighed into a 600-ml. beaker and is covered with water. Fifty ml. of concentrated hydrochloric acid are carefully added. After the vigorous reaction has ceased, about 1 mg. of sodium fluosilicate is added and the solution boiled until the black residue has dissolved. The

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solution is evaporated to 20 ml. and 25 ml. of 2 molar sulfosalicylic acid and 4 ml. of a 0.5 per cent gelatin solution are added. Twenty ml. of ammonium hydroxide are added and the solution is stirred until all of the precipitate has dissolved. The pH of the solution is adjusted to 8.5 ± 0.2 and the solution transferred to a 100-ml. volumetric flask. The solution is diluted to volume. About 10 ml. of the solution is placed in the polarographic cell and purged for 15 minutes with the nitrogen to remove any residual oxygen from the solution, and the polarogram is recorded. The instrument is best calibrated by the standard addition method. A known amount of zinc is added to another sample of the same size and the sample treated in the same manner as the unknown. The concentration of zinc added, divided by the difference in the diffusion currents of the two polarograms gives the factor by which the diffusion current of the unknown is multiplied to determine the unknown amount of zinc in the thorium metal. When sulfosalicylic acid was used to complex the thorium the zinc half wave potential occurred at - 1.05 volts versus the saturated calomel electrode.

## IV. Reference

Patterson, J. H. and Banks, C. V., Analytical Chemistry, <u>20</u>, 897, (1948).

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