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UNITED STATES ATOMIC ENERGY COMMISSION

MANUAL OF SPECIAL MATERIALS ANALYTICAL LABORATORY PROCEDURES

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James H. Patterson

Authors:
J. H. Patterson
H. B. Evans
C. M. Stevens
A. L. Harkness
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V. R. Wiederkehr
R. J. Ferretti

March 1955

Argonne National Laboratory
Lemont, Illinois

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ARGONNE NATIONAL LABORATORY
P. O. Box 299
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PROCEDURE 1: TITRIMETRIC DETERMINATION OF URANIUM WITH THE JONES REDUCTOR

I. INTRODUCTION

A. Abstract

Uranium in sulfuric acid solution is reduced by amalgamated zinc to a mixture of U(IV) and U(III). The U(III) is air oxidized to U(IV), and the uranium titrated with potassium permanganate or ceric sulfate.

B. Principles

The most stable oxidation state of uranium in aqueous solution is U(VI). Strong reducing agents, however, will completely reduce U(VI) to U(IV), U(III), or to a mixture of the two. U(III) is readily oxidized to U(IV) by air, but the latter oxidation state is stable in aqueous solutions at room temperature for several hours. U(IV), in turn, can be quantitatively reoxidized to U(VI).

The method to be described utilizes the reactions given above. Uranium (VI) in sulfuric acid solution is reduced by amalgamated zinc to a mixture of U(III) and U(IV). Following conversion of the U(III) to U(IV) by air, the uranium is reoxidized with standard potassium permanganate or ceric sulfate.[1] Since the reaction between uranium (IV) and cerium (IV) is too slow at room temperature to permit accurate detection of the end point, excess ceric sulfate is added and a back titration with standard ferrous sulfate employed. The zinc used as reducing agent is amalgamated to decrease hydrogen evolution and the associated loss of zinc.

The reactions which occur in the determination may be represented by the following equations:

Reduction:

1. $2UO_2SO_4 + 4H_2SO_4 + 3Zn \rightarrow U_2(SO_4)_3 + 3ZnSO_4 + 4H_2O$

2. $UO_2SO_4 + 2H_2SO_4 + Zn \rightarrow U(SO_4)_2 + ZnSO_4 + 2H_2O$

---

[1] Quadrivalent cerium exists in sulfuric acid solution in the form of anions, $Ce(SO_4)_3^{-2}$ or $Ce(SO_4)_4^{-4}$, so that this oxidizing agent is more properly named sulfato-ceric acid. However, the name ceric sulfate is in general use and will also be employed here.

Aeration:

3. $2H_2SO_4 + 2U_2(SO_4)_3 + O_2 \rightarrow 4U(SO_4)_2 + 2H_2O$

Titration:

4. $5U(SO_4)_2 + 2KMnO_4 + 2H_2O \rightarrow 5UO_2SO_4 + 2KHSO_4 + 2MnSO_4 + H_2SO_4$,

or

5. $U(SO_4)_2 + 2Ce(SO_4)_2(\text{excess}) + 2H_2O \rightarrow UO_2SO_4 + Ce_2(SO_4)_3 + 2H_2SO_4$,

and

6. $2Ce(SO_4)_2 + 2FeSO_4 \rightarrow Fe_2(SO_4)_3 + Ce_2(SO_4)_3$

C. Interferences

There are a considerable number of ions and organic compounds that are reduced by zinc in acid media to states that will consume the oxidizing agent. Some ions will plate out as metals on the zinc and interfere with its reducing action. The most common interferences, in addition to organic matter, are nitrate, iron, nickel, copper, and chromium ions. A complete list of the interfering elements and the type of interference is given in Table I.(1,2)

Those elements which are reduced to the metal may be removed by treatment with granulated zinc before reduction in the Jones reductor. Solutions containing nickel can be reduced in a reductor containing a 10% amalgam without inactivating the zinc since increasing the mercury concentration decreases the reducing ability of the amalgam.(3) Elements that consume the oxidizing agent must be removed prior to the reduction step unless the amount of interference is known. The procedure to be used in purifying uranium will depend on the type of interference and the type of solution. If the uranium can be obtained in a nitrate solution, solvent extraction offers a convenient and rapid purification from practically all cationic interferences. If hydrogen sulfide is used to make any separations, polythionic compounds are produced which will consume the oxidizing agent. These must be destroyed as described below. Nitrate and fluoride ion can be removed by fuming with sulfuric acid several times. The treatment necessary for the removal of organic matter varies with the stability of the material to oxidation. In some cases the addition of potassium permanganate solution to the dilute sulfuric acid solution of the sample until a permanent pink color is obtained is sufficient. Polythionic compounds can also be destroyed in this way. Complete destruction of more resistant organic compounds can be obtained by careful heating with nitric and perchloric acids or by heating with excess potassium permanganate and concentrated sulfuric acid. Perchloric acid solutions may be

Table I

Element	Type of Interference
Antimony	Reduced chiefly to metal; partially reduced to poisonous SbH_3 gas which consumes oxidizing agent.
Arsenic	Reduced to poisonous AsH_3 gas which consumes oxidizing agent.
Bismuth	Reduced to metal.
Cadmium	Reduced to metal.
Carbon	Certain organic compounds will consume oxidizing agent.
Chromium	Reduced to Cr(II); consumes oxidizing agent.
Cobalt	Reduced to metal.
Niobium	Reduced to indefinite valences; consumes oxidizing agent.
Copper	Reduced to metal.
Europium	Reduced to Eu(II); consumes oxidizing agent.
Fluorine	Hydrofluoric acid causes high results.
Germanium	Reduced to metal.
Gold	Reduced to metal.
Indium	Reduced to metal.
Iridium	Reduced to metal.
Iron	Reduced to Fe(II); consumes oxidizing agent.
Lead	Reduced to metal.
Mercury	Reduced to metal.
Molybdenum	Reduced to Mo(III); consumes oxidizing agent.
Nickel	Reduced to metal.
Nitrogen	Nitrates and nitrites are reduced to hydroxylamine which consumes oxidizing agent.
Osmium	Reduced to indefinite valences; consumes oxidizing agent.
Paladium	Reduced to metal.
Platinum	Reduced to metal.
Polonium	Reduced to metal.
Rhenium	Reduced to indefinite valences; consumes oxidizing agent.
Rhodium	Reduced to metal.
Ruthenium	Reduced to indefinite valences; consumes oxidizing agent.
Selenium	Reduced to metal.
Silver	Reduced to metal.
Sulfur	Polythionic compounds consume oxidizing agent.
Tellurium	Reduced to metal.
Thallium	Reduced to metal.
Tin	Reduced to metal.
Titanium	Reduced to Ti(III); consumes oxidizing agent.
Vanadium	Reduced to V(II); consumes oxidizing agent.
Wolfram	Reduced to indefinite valences; consumes oxidizing agent.

passed through the reductor. However, sulfuric acid must be present during the titration with ceric sulfate and may be added before or after the reduction.

II. APPARATUS

The reduction is carried out in the conventional type of Jones reductor,(1,3) using an amalgamated zinc column 25 cm long and 2 cm in diameter. Provision is made for drawing air through the reduced uranium solution into the receiving flask with the aid of an aspirator.

The amalgamated zinc is prepared by washing 20-30 mesh zinc with 1N HCl for one minute and shaking it with sufficient 0.25M mercuric nitrate or chloride solution to give an amalgam containing 0.5 - 1% mercury. The zinc amalgam is washed with distilled water by decantation and transferred to the reductor column, tamping the amalgam in place periodically to prevent the formation of air spaces. The zinc must be kept covered with water when not in use to prevent the formation of basic salts which may clog the reductor.

All titrations are carried out with weight burets. Since the burets are weighed only to the nearest milligram, the time necessary to perform and record a titration is not much longer than with volumetric burets, and increased accuracy is obtained.

III. REAGENTS

Zinc, reagent grade, 20-30 mesh
Ceric sulfate, reagent, approximately 0.05N in 2N sulfuric acid (prepared from ceric hydrogen sulfate)
Ferrous ammonium sulfate, reagent, approximately 0.025N in 2N sulfuric acid
Potassium permanganate, reagent, approximately 0.05N
Ferrous orthophenanthroline indicator (ferroin), 0.025M
Osmic acid, C.P., 0.01M in 0.1M sulfuric acid
Arsenious oxide, Bureau of Standards primary standard, 99.99%
Sodium oxalate, Bureau of Standards primary standard, 99.96%
Uranium oxide, U_3O_8, MS-ST, 99.95%
Hydrogen peroxide, reagent, 30%
Sulfuric acid, reagent, concentrated
Sulfuric acid, reagent, 5%
Sulfuric acid, reagent 6N
Hydrochloric acid, reagent, concentrated
Nitric acid, agent, concentrated
Nitric acid, reagent 8N
Nitric acid, reagent, 8N - hydrofluoric acid, reagent, 0.01N (mixture)
Perchloric acid, reagent, concentrated
Sodium hydroxide, reagent, 2N

Standardization of potassium permanganate: Sodium oxalate (0.15-0.2 g), dried at 105°C., is dissolved in 250 ml of 5% sulfuric acid. The sulfuric acid is boiled 10-15 minutes and cooled to 27 ± 3°C. before use to destroy any hydrogen peroxide formed during dilution. Approximately 90% of the required amount of permanganate is added at the rate of 25-35 ml per minute while stirring slowly. After the pink color has disappeared, the solution is heated to 55-60°C., and the titration completed at that temperature by adding permanganate slowly until the pink color persists for thirty seconds. To determine the amount of permanganate required to color the solution visibly, a blank is titrated at 55-60°C. using the same amount of sulfuric acid solution as was used for the sodium oxalate.

Standardization of ceric sulfate: Approximately 0.15 g of arsenious oxide, dried at 105°C., is dissolved in 15 ml of 2<u>N</u> sodium hydroxide, warming slightly if necessary. When the sample is completely dissolved, the solution is cooled to room temperature, and 25 ml of 6<u>N</u> sulfuric acid, 60 ml of water, 0.15 ml of 0.01<u>M</u> osmic acid, and 0.05 ml of ferroin indicator are added. Osmic acid catalyzes the slow reaction between cerium(IV) and arsenious acid. Ceric sulfate is added until an excess, as shown by a color change of the indicator from pink to pale blue, of 2/3 ml is present. The excess is titrated with ferrous sulfate until the color of the solution again becomes pink. The blank is negligible. The concentration of the ferrous sulfate solution is determined by titrating 20-25 ml of ceric sulfate solution in sulfuric acid of the same concentration as used in the standardization. The same amount of indicator is used. The results of the standardization of the potassium permanganate and ceric sulfate solutions and the analytical method itself are frequently checked with MS-ST standard uranium oxide. The uranium oxide is analyzed in a manner identical with that used for unknown uranium samples.

IV. PREPARATION OF SAMPLE

A. Uranium Dioxide and U_3O_8

1. Dry the sample to constant weight (± 0.1 mg) over silica gel or magnesium perchlorate in a desiccator.

2. Treat a 0.3-0.4 g sample with 5 ml of concentrated sulfuric acid and 0.5 ml of 30% hydrogen peroxide.

3. Heat the mixture gradually until sulfur trioxide fumes appear and continue fuming for fifteen minutes. At this point the sample should be completely in solution and all the hydrogen peroxide destroyed. Hydrogen peroxide itself introduces no error in the analysis since it is completely reduced to water in the reductor.

4. If the sample is not completely in solution, add an additional 0.5 ml of hydrogen peroxide and repeat Step 3.

5. Interfering elements, if present, must be removed before continuing.

NOTE: Uranium oxides may also be dissolved in nitric acid, sulfuric acid alone, or perchloric acid. Since the use of the first two acids is time-consuming (nitric acid must be removed by fuming and the rate of solution in sulfuric acid alone is slow) and since there are explosive hazards connected with the use of perchloric acid, the procedure described above is preferred.

B. Uranium Metal

1. Dissolve a sample weighing 0.2-0.3 g in 10-20 ml of 8N nitric acid, warming if necessary.

2. After solution is complete, add 5 ml of concentrated sulfuric acid and evaporate to sulfur trioxide fumes three or four times. Wash the watch glass and sides of the beaker with water after each fuming.

3. Interfering elements, if present, must be removed before reduction.

C. Thorium-Uranium Alloys

1. Dissolve a sample containing 0.2-0.3 g of uranium in 50-100 ml of 8N nitric acid containing 0.01N hydrofluoric acid as a catalyst.

2. After the sample is completely dissolved, add 5 ml of 72% perchloric acid and evaporate the solution to perchloric acid fumes three or four times, washing down the watch glass and sides of the beaker with water after each fuming.

3. Interfering elements, if present, must be removed before reduction.

D. Zirconium-Uranium Alloys

1. Treat a sample containing 0.2-0.3 g of uranium with approximately 100 ml of aqua regia and 5 ml of concentrated sulfuric acid.

2. Allow the reaction to proceed at room temperature, and when the initial reaction subsides, heat until reaction ceases.

3. If the sample is not reduced to a fine black powder, add more aqua regia and repeat Step 2.

4. Evaporate to sulfur trioxide fumes and continue fuming until the sample is completely dissolved.

5. Fume two more times as described under B-2 above.

6. If prolonged fuming is required to dissolve the sample, cool and replace the sulfuric acid lost by evaporation periodically.

7. Interfering elements, if present, must be removed before reduction.

NOTE: The rate of reaction varies with the composition of the alloy. Since the uranium reacts more rapidly than the zirconium, those alloys high in uranium are easier to dissolve. The black residue remaining after the reaction with aqua regia is principally zirconium, and is almost completely in solution after several minutes of fuming with sulfuric acid. (See Procedure 11 for additional comments.)

E. Uranium Salts Containing Anions of Volatile Acids (Nitrate, Fluoride, Etc.)

1. Dissolve a sample containing 0.2 to 0.3 g of uranium in 5 ml of concentrated sulfuric acid (and water if necessary).

2. If the salt contains ions that interfere in the analysis (e.g., nitrate, fluoride), fume three times as described in B-2. Fluoride ion is particularly difficult to remove completely, and strong fuming is necessary.

3. Other interfering elements, if present, must be removed before proceeding.

V. PROCEDURE

A. Reduction

1. If the reductor is freshly prepared or has been standing idle for some time, pass through it 200 ml of 5% sulfuric acid followed by 50 ml of water. Catch the liquid in a 500 ml Erlenmeyer flask and titrate as described under B or C below.

2. Calculate this blank as indicated under Section VI. Repeat Step 1, if necessary, until a blank of 0.15 g or less of oxidizing agent is obtained.

3. Prepare a solution of the sample as described above free from interferences in 5 ml of concentrated sulfuric acid. Add 95 ml of water, and cool to 20-25°C. Dilute solutions containing thorium in perchloric acid with 90 ml of water, then add 5 ml of concentrated sulfuric acid and cool.

4. Pass the following solutions through the reductor at the rate of about 50 ml per minute in the order listed and collect them in a 500 ml Erlenmeyer flask: 50 ml of 5% sulfuric acid, the uranium solution, 50 ml of 5% sulfuric acid, and 100 ml of water. Rinse the beaker that contained the uranium solution several times with portions of the second sulfuric acid wash solution. Do not allow the level of the solution to fall below the amalgam surface since low results may be obtained if air enters the reductor.

5. Bubble clean air through the solution for 5 minutes.

6. Wash the aerator tube with water and titrate by one of the methods given below.

B. Titration with Potassium Permanganate

1. Add 0.15 ml of ferroin indicator to the reduced solution.

2. Add potassium permanganate solution from a weight buret until one drop changes the color of the solution from pink to yellowish-green.

3. Run a blank on the entire procedure at least once each day.

C. Titration with Ceric Sulfate

1. Add 0.15 ml of ferroin indicator to the reduced solution.

2. Add sufficient ceric sulfate solution to provide an excess of approximately 2 g over that required to change the color of the solution from pink to yellowish-green.

3. Titrate the excess ceric sulfate with ferrous sulfate solution until the pink color of the indicator reappears.

4. Run a blank on the entire procedure at least once each day. The amount of ceric sulfate added to the blank should be approximately the same amount of excess used in the determination.

5. Determine the concentration ratio of ceric sulfate to ferrous sulfate daily by titrating 25 g of ceric sulfate solution with the ferrous sulfate solution using 0.15 ml of ferroin as the indicator. The titration should be carried out in a solution of the same sulfuric and hydrochloric acid concentrations as are present in the uranium solutions when titrated.

VI. CALCULATIONS

The "weight normality," n_p, as equivalents/gram solution, of the potassium permanganate is given by:

$$n_p = \frac{0.9996\ G_o}{E_o x\ (W_p - b_p)} \quad ,$$

where G_o = weight of sodium oxalate, 99.96% pure,
E_o = equivalent weight of sodium oxalate (67.01),
W_p = weight of potassium permanganate solution,
and b_p = weight of potassium permanganate solution required for blank.

The weight normality, n_c, of the ceric sulfate is given by,

$$n_c = \frac{0.9999\ G_A}{E_A\ x\ (W_c - W_F A)} \quad ,$$

where G_A = weight of arsenious oxide, 99.99% pure,
E_A = equivalent weight of arsenious oxide (49.455),
W_c = weight of ceric sulfate,
W_F = weight of ferrous sulfate solution,
and A = weight of ceric sulfate solution equivalent to one gram of ferrous sulfate solution.

The uranium equivalent of the standard solution, C, is given by:

$$C = nE_u$$

where E_u = equivalent weight of uranium, one-half the atomic weight,
and n = equivalents/gram of the oxidizing agent.

The atomic weight of uranium will vary with the isotopic composition and must be known to calculate the uranium content. The atomic weight of naturally occurring uranium is 238.07, and this figure is used for the standard MS-ST U_3O_8. The atomic weight of uranium containing other than the normal isotopic composition is given by:

$$\text{atomic weight} = \frac{100}{\frac{\text{Weight \% } U^{234}}{234.06} + \frac{\text{Weight \% } U^{235}}{235.07} + \frac{\text{Weight \% } U^{238}}{238.07}}$$

The percentage of uranium is given by:

$$\%U(\text{by } KMnO_4) = \frac{(W_P - b_P)\, C \times 100}{G_S}$$

where G_s = weight of the unknown sample taken,

and $$\%U(\text{by ceric sulfate}) = \frac{(W_C - W_F A - b_C)\, C \times 100}{G_S} ,$$

where b_C = the calculated amount of ceric sulfate required for the blank, the remaining symbols have been previously defined.

The ceric sulfate blank is calculated from:

$$b_C = W_C - W_F A \quad ,$$

where the weights of the reagents, W_C and W_F, refer to those used in determining the blank.

VII. DISCUSSION

The accuracy and precision of the method may be inferred from the results of analyses of MS-ST standard uranium oxide. The results of thirty-four analyses of this oxide with potassium permanganage and ten with ceric-ferrous sulfate are given in Table II. The σ given is the standard deviation of a single measurement. To find the standard deviation of the mean, divide σ by the square root of the number of results. The slight bias toward high results with the permanganate titration, as shown by the average, 100.07%, is within experimental error. However, considerable inconsistency was observed in the results. Occasionally values several per cent high were obtained. The reasons for these very high results are not completely understood, but they can be discarded on a statistical basis.

The ceric-ferrous titration is considered more reliable although experience with it is more limited. The accuracy is good, and the precision, as measured by the standard deviation, is considerably better than the permanganate method.

Table II

	No. of Results	Av. % U Found	Standard Deviation, σ	Limit of Error in 95% Confidence Belt, 2 σ
Permanganate	34	100.07	± 0.22	±0.44
Ceric-Ferrous	10	99.99	± 0.12	±0.24

VIII. REFERENCES

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3. "Manual of Analytical Methods for the Determination of Uranium and Thorium in Their Ores," pp 1-10, Government Printing Office, Washington, D. C., (1950).

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PROCEDURE 2: THE TITRIMETRIC DETERMINATION OF URANIUM WITH THE LEAD REDUCTOR

I. INTRODUCTION

A. Abstract

Uranium(VI) in hydrochloric acid-sulfuric acid solution is reduced by metallic lead to U(IV) and reoxidized with standard ceric sulfate solution. The excess ceric sulfate is then titrated with standard ferrous sulfate solution.

B. Principles

Uranium(VI) in hydrochloric acid-sulfuric acid solution is reduced by metallic lead to U(IV) and reoxidized with standard ceric sulfate solution. The excess ceric sulfate is then titrated with standard ferrous sulfate solution. The back titration is necessary because the reaction between cerium(IV) and uranium(IV) is too slow at room temperature to permit accurate detection of the end point.

The reactions which occur in the determination may be represented by the following reactions:

Reduction

1. $UO_2SO_4 + 2H_2SO_4 + PB \rightarrow U(SO_4)_2 + PbSO_4 + 2H_2O$

Titration

2. $U(SO_4)_2 + 2Ce(SO_4)_2(\text{excess}) + 2H_2O \rightarrow UO_2SO_4 + Ce_2(SO_4)_3 + 2H_2SO_4$

3. $2Ce(SO_4)_2 + 2FeSO_4 \rightarrow Fe_2(SO_4)_3 + Ce_2(SO_4)_3$

The method is similar to the conventional one using the Jones reductor, but has several important advantages. No uranium(III) is formed, eliminating the aeration step necessary when zinc is used as the reducing agent. The lead reductor is easily prepared, no amalgamation being necessary since the reaction between lead and non-oxidizing acids is slow. Some of the elements that interfere with the use of zinc have no effect on the lead reductor. The interferences are discussed more fully in C below.

The application of the lead reductor to the determination of uranium is described by Cooke, Hazel, and McNabb.(1) They point out that when sulfuric acid solutions are used, the solutions must also be at least 2.5N in hydrochloric acid to prevent the formation of lead sulfate. The lead sulfate adheres to the lead and decreases its reducing efficiency.

C. Interferences

There are two general types of interferences in the method. Certain ions and organic compounds will be reduced by lead to states that consume the oxidizing agent, or they are originally in a state that will consume the oxidizing agent and remain unaffected by the reductor. Some ions will plate out on the lead as metals and interfere with its reducing action. The former type of interference will yield high results, while the latter type will, in time, depending on the amount present, inactivate the reductor and give low results. The most common interferences are organic matter, nitrate ion, and iron. A complete study of the interfering elements is not available and has not been made. However, it is possible to determine which elements should interfere from the electrode potentials of the reactions involved. A complete list of the interfering elements and the type of interference determined in this way is given in Table I. In some cases it is not certain what course a particular reaction will take under the conditions of the method, and this uncertainty is noted in the table.

Those elements which are reduced to the metal may be removed by treatment with granulated zinc or lead before reduction in the lead reductor. Elements that consume the oxidizing agent must be removed prior to the reduction step unless the amount of interference is known. The procedure to be used in purifying will depend on the type of interference and the type of solution. If the uranium can be obtained in a nitrate solution, solvent extraction offers a convenient and rapid purification from practically all interferences. If hydrogen sulfide is used to make any separations, polythionic compounds are produced which are stable toward lead and which will subsequently be titrated. They must be destroyed as described below. Nitrate and fluoride ions and hydrogen peroxide can be removed by fuming with sulfuric acid. The treatment necessary to render organic matter harmless varies with the stability of the material to oxidation. In some cases the addition of potassium permanganate to the dilute acid solution of the sample until a permanent pink color is obtained is sufficient. Polythionic compounds can also be destroyed in this way. Complete destruction of more resistant organic compounds can be accomplished by careful heating with nitric and perchloric acids, or by heating with excess potassium permanganate and

Table I

Element	Type of Interference
Antimony	Reduced chiefly to metal
Arsenic	Reduced chiefly to metal
Bismuth	Reduced to metal
Carbon	Certain organic matter will consume the oxidizing agent
Niobium	Reduced partially to Nb(III); consumes the oxidizing agent
Copper	Reduced to metal
Fluorine	Fluoride causes high results
Germanium	Probably does not interfere
Gold	Reduced to metal
Hydrogen	Hydrogen peroxide is incompletely reduced in the reductor and consumes the oxidizing agent
Iridium	Reduced to metal
Iron	Reduced to Fe(II); consumes the oxidizing agent
Mercury	Reduced to metal
Molybdenum	Reduced to Mo(III); consumes the oxidizing agent
Nitrogen	Nitrates and nitrites consume the oxidizing agent
Osmium	Reduced to indefinite valences; consumes the oxidizing agents
Palladium	Reduced to metal
Platinum	Reduced to metal
Polonium	Reduced to metal
Rhenium	Reduced to indefinite valences; consumes the oxidizing agent
Rhodium	Reduced to metal
Ruthenium	Reduced to indefinite valences; consumes the oxidizing agent
Selenium	Reduced to metal
Silver	Reduced to metal
Sulfur	Polythionic compounds consume oxidizing agent and are not reduced by lead
Tellurium	Reduced to metal
Tin	May interfere by oxidation of Sn(II) by oxidizing agent; may be partially reduced to metal
Titanium	Reduced to Ti(III); consumes oxidizing agent
Vanadium	Reduced to V(III); consumes oxidizing agent
Wolfram	Reduced to indefinite valences; consumes oxidizing agent

concentrated sulfuric acid. Perchloric acid solutions may be passed through the reductor, but sulfuric acid must be present during the titration and may be added before or after reduction.

II. APPARATUS

A column of lead 25 cm long and 2 cm is diameter is used and provision is made for drawing the solution through the column by means of an aspirator and collecting it in a 500 ml Erlenmeyer flask. Before a reductor is used for the first time, it is washed with 2-3N hydrochloric acid until the lead appears bright. When not is use, the reductor is filled with 3N hydrochloric acid containing 0.1% iron(III). Unless this iron is present, the first determination each day is a few tenths per cent low.(1) Before use each day, the reductor is washed with 200 ml of 0.8N hydrochloric acid.

All titrations are made with weight burets, the weighings being made to the nearest milligram.

III. REAGENTS-STANDARDIZATION

Lead, reagent grade, granulated
Ceric sulfate, reagent, approximately 0.05N in 2N sulfuric acid (prepared from ceric hydrogen sulfate)
Ferrous ammonium sulfate, reagent, approximately 0.025N in 2N sulfuric acid
Ferrous orthophenanthroline indicator (ferroin), 0.025M
Osmic acid, C.P., 0.01M in 0.1M sulfuric acid
Arsenious oxide, Bureau of Standards primary standard, 99.99%
Uranium oxide, U_3O_8, MS-ST, 99.95%
Hydrogen peroxide, reagent, 30%
Sulfuric acid, reagent, concentrated
Sulfuric acid, reagent, 6N
Hydrochloric acid, reagent, concentrated
Hydrochloric acid, reagent, 6N
Hydrochloric acid, reagent 3N containing 0.1% iron as ferric chloride
Hydrochloric acid, reagent, 0.8N
Nitric acid, reagent, concentrated
Nitric acid, reagent, 8N
Nitric acid, reagent, 8N - hydrofluoric acid, reagent, 0.01N (mixture)
Perchloric acid, reagent, 72%
Sodium hydroxide, reagent, 2N

The ceric sulfate is standardized by titration against arsenious acid. Approximately 0.15 g of arsenious oxide, dried at 105°C., is dissolved in 15 ml of 2N sodium hydroxide, warming slightly if necessary. When the sample is completely dissolved, the solution is cooled to room temperature, and 25 ml of 6N sulfuric acid, 60 ml of water, 0.15 ml of 0.01M osmic acid, and 0.05 ml of ferroin indicator are added. Osmic acid catalyzes the slow reaction between cerium(IV) and arsenious acid. Ceric sulfate is added until the color of the solution changes from pink to pale blue. An excess of 2-3 ml of ceric sulfate is then added and the excess titrated with ferrous sulfate until the color of the solution again becomes pink. The blank is negligible. The concentration of the ferrous sulfate solution is determined by titrating 20-25 ml of ceric sulfate solution in sulfuric acid of the same concentration as used in the standardization. The same amount of indicator is used.

The results of this standardization, as well as of the analytical method itself, are frequently checked with MS-ST standard U_3O_8. This U_3O_8 is analyzed in a manner identical with that used for the unknown uranium samples.

IV. PREPARATION OF SAMPLE

A. Aluminum-Uranium Alloys

1. Treat a sample containing 0.2-0.3 g of uranium with 50-100 ml of 6N hydrochloric acid.
2. After the first vigorous reaction has ceased add 1 ml 30% hydrogen peroxide and warm until all the sample is in solution.
3. Add 5-10 ml concentrated sulfuric acid and evaporate until there has been copious evolution of sulfur trioxide fumes for fifteen minutes.
4. Interfering elements, if present, must be removed before reduction (see I-C).

B. Other Uranium Samples

For the preparation of other uranium samples see Procedure 1, Section IV.

V. PROCEDURE

A. Reduction

1. Dilute the solution of uranium in 10 ml of concentrated sulfuric acid to 50 ml by adding 25 ml of 6N hydrochloric acid and 15 ml of water and cool to 20-25°C.

Solutions of thorium and uranium in perchloric acid are diluted in the same way.

2. If the reductor has been stored under a hydrochloric acid-ferric ion solution, wash the reductor by passing through it, with the aid of an aspirator, 200 ml of 0.8N hydrochloric acid in 25 ml portions.

3. Pass the cooled uranium solution through the reductor at the rate of approximately 25 ml per minute.

4. Wash the reductor with 150 ml of 0.8N hydrochloric acid added in 15-25 ml portions, rinsing the beaker that contained the uranium solution several times with portions of the wash solution. Leave the reductor full of wash solution between samples.

5. Collect the solution and washings in a 500-ml Erlenmeyer flask.

B. Titration

1. Add 50 ml of water to the reduced solution in the Erlenmeyer flask. Also add 10 ml of concentrated sulfuric acid to solutions containing thorium and uranium.

2. Add 0.15 ml of ferroin solution.

3. Add sufficient ceric sulfate solution solution to provide an excess of approximately 2 ml over that required to change the color of the solution from pink to yellowish-green.

4. Titrate the excess ceric sulfate with ferrous sulfate solution until the pink color of the indicator reappears.

5. Run a blank on the entire method at least once each day. The amount of ceric sulfate added to the blank should be approximately the same as the amount of excess used in the determination.

6. Determine the concentration ratio of ceric sulfate to ferrous sulfate daily by titrating 25 g of the ceric sulfate solution with ferrous sulfate solution using 0.15 ml of ferroin solution as the indicator. The titration should be carried out in a solution of the same sulfuric and hydrochloric acid concentrations as are present in the uranium solution when titrated.

VI. CALCULATIONS

The "weight normality," n, in equivalents/gram of solution, of the ceric sulfate is given by:

$$n = \frac{0.9999\,G}{E(W_C - W_F A)} \quad ,$$

where G = weight of arsenious oxide, 99.99% pure,

E = equivalent weight of arsenious oxide (49.455),

W_C = weight of ceric sulfate solution used,

W_F = weight of ferrous sulfate solution used,

and A = weight of ceric sulfate solution equivalent to one gram of ferrous sulfate solution.

The uranium equivalent, C, in grams of uranium per gram of ceric sulfate solution is given by:

$$C = nE_u \quad ,$$

where E_u = equivalent weight of uranium, one half of the atomic weight.

The atomic weight of uranium will vary with its isotopic composition. The atomic weight of naturally occurring uranium is 238.07 and this value is used for MS-ST U_3O_8. The atomic weight of uranium containing other than the normal isotopic composition is given by:

$$\text{Atomic Weight} = \frac{100}{\frac{\text{Weight \% } U^{234}}{234.06} + \frac{\text{Weight \% } U^{235}}{235.07} + \frac{\text{Weight \% } U^{238}}{238.07}}$$

The percentage of uranium is given by:

$$\%U = \frac{(W_C - W_F A - b)\, C \times 100}{G_s} \quad ,$$

where b = calculated amount of ceric sulfate required for the blank,

and G_s = weight of unknown sample.

The remaining symbols have been previously defined.

The blank is calculated from:

$$b = W_c - W_F A \quad ,$$

where the weights of reagents, W_c and W_F, refer to those used in determining the blank.

VII. DISCUSSION

Since unknown samples are usually run in duplicate, the accuracy and precision of the method can best be inferred from results of analyses of MS-ST uranium oxide. Seventeen results gave an average per cent uranium found of 100.01% and a standard deviation of a single measurement, σ, of 0.08%. The "95% confidence limit," $\pm\ 2\ \sigma$, is then ± 0.16%. This accuracy and precision is approximately the same as that obtained with the Jones reductor using the same titrating reagents. The lead reductor, however, is considerably easier to prepare and use and is preferred from that point of view.

VIII. REFERENCES

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PROCEDURE 3: THE GRAVIMETRIC PEROXIDE METHOD FOR THE DETERMINATION OF URANIUM

I. INTRODUCTION

A. Abstract

Uranium is precipitated with hydrogen peroxide from an acetic acid-nitric acid solution at pH 2-2.5. This precipitate is filtered and ignited to uranous uranate and weighed as such. The method was adapted from reports RL 4.7.600(1) and M-4282.(2)

B. Precautions and Interferences

The precipitation of uranium with peroxide is quantitative for analytical purposes under certain conditions. The solubility of uranium peroxide causes low results if the concentration is too low.(3) Therefore, the solution should have a volume of one hundred milliliters or less after precipitation. The usable pH range is reported to be 0.5-3.5 .(4,5) Best results were obtained at pH 2-2.5 . The blue-to-violet color change of methyl violet occurs in this region. Below pH 1.5 low results were obtained. Excess of hydrogen peroxide greater than thirty per cent is reported to have no effect on the precipitation.(3) The huge excess used in the present procedure (1500%) allows for loss of hydrogen peroxide on standing overnight. Vanadium, zirconium, hafnium, and thorium interfere by co-precipitation.(6) Iron in large concentrations interferes by catalytically destroying the hydrogen peroxide.(7,8,9,10) With small amounts of iron, lactic, acetic, and malonic acids have been reported to prevent this.(10,11,12,13,14,15) Acetic acid has been found satisfactory in this respect. Malonic acid caused low results.

Ammonium, potassium, and alkaline earths retard precipitation.(6) This has been overcome by allowing the precipitate to stand overnight before filtration. After this time precipitation is complete. If these ions are not present, the precipitation is complete in about thirty minutes. Sulfate, chloride, and fluoride cause incomplete precipitation.(16,17,18,19) Fluoride may be complexed with aluminum.(20) Rare earths,(21) magnesium,(22) aluminum,(20) nickel,(23) titanium,(24,25) and sodium(26) do not interfere.

II. REAGENTS

Nitric acid solution (1 to 1). Mix equal parts of concentrated nitric acid and water.

Nitric acid, concentrated

Acetic acid, glacial

Methyl violet, 0.1% in alcohol. Dissolve 0.1 g methyl violet in 127 ml ethyl alcohol.

Ammonium hydroxide (1 to 1). Mix equal parts of concentrated ammonium hydroxide and water.

Hydrogen peroxide, 30%

Filter pulp suspension. Macerate ten 11-cm circles of Whatman #42 by shaking them with 50 ml concentrated hydrochloric acid in a 500 ml Erlenmeyer flask. Dilute to 400 ml with water and filter. Wash the pulp with water until the washings are neutral. Suspend the pulp in 500 ml of water.

Wash solution, 3% ammonium nitrate-hydrogen peroxide. Dissolve 30 g ammonium nitrate in 900 ml water and mix with 100 ml 30% hydrogen peroxide.

III. PREPARATION OF SAMPLE

A. Uranium Metal and Oxide

1. Weigh sufficient sample to contain between 300 and 1000 mg uranium.

2. Transfer the sample to a 400 ml beaker.

3. Wet the sample with water.

4. Add 20 ml nitric acid (1 to 1).

5. Cover the beaker with a watch glass and heat on hot plate at low heat for thirty minutes.

B. Oxide-Polystyrene Mixtures

1. Heat a platinum crucible at 800°C. in a muffle furnace for thirty minutes.

2. Cool in a desiccator and weigh.

3. Repeat steps 1 and 2 until the weight remains constant to ± 0.1 mg between successive weighings.

4. Weigh a sample of approximately 0.5 g into the platinum crucible and heat slowly to 200-300°C. in a muffle furnace.

5. Maintain this temperature until the volatile material has been removed.

6. Raise the temperature slowly to 800°C. and repeat steps 1 and 2 until constant weight is again obtained.

7. Add 3 ml concentrated nitric acid to the ash in the crucibles, and warm until the oxide is in solution.

8. Dilute to 20 ml and filter on Whatman #42 paper, washing the crucible and filter paper thoroughly with 1N nitric acid.

9. Composite as many samples as needed to give 0.3-1 g uranium, if this is permissible.

IV. PROCEDURE

1. Evaporate the solution nearly to dryness at medium heat.

2. Wash cover and sides with 50 ml water.

3. Repeat steps 1 and 2.

4. Add 5 ml glacial acetic acid and 3 drops of methyl violet or enough to give a strong color to the solution.

5. If the solution is blue or yellow, add ammonium hydroxide (1 to 1) until solution just begins to turn from blue to violet.

6. If the solution is violet add nitric acid (1 to 1) until it begins to turn blue.

7. Add 20 ml 30% hydrogen peroxide with stirring.

8. Add 25 ml filter pulp suspension.

9. Allow the mixture to stand overnight.

10. Filter through a #42 Whatman filter paper.

11. Wash with 3% hydrogen peroxide-ammonium nitrate solution.

12. Ignite at 800°C. to constant weight.

13. Cool in a desiccator.

14. Weigh as U_3O_8.

V. CALCULATIONS

$$\frac{\text{Weight ash}}{\text{Weight sample taken}} \times 100 = \text{per cent ash in the sample}$$

$$\frac{\text{Weight } U_3O_8 \times 100}{\text{Weight sample}} = \text{per cent } U_3O_8$$

VI. DISCUSSION OF RESULTS: ACCURACY

The error in milligrams seems to be independent of sample size, as would be expected if the main source of error is the solubility of the precipitate. The standard deviation for thirteen samples of MS-ST U_3O_8 analyzed by the recommended procedure was ± 0.30 mg, or $2\sigma = \pm 0.59$ mg. Samples larger than 0.3 g have values of 2σ less than 0.2%.

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PROCEDURE 4: GRAVIMETRIC DETERMINATION OF URANIUM IN ESSENTIALLY PURE OXIDES

I. INTRODUCTION

The application of this method has been limited to material containing only spectroscopic amounts of impurities. The method consists of igniting the sample to U_3O_8 at 800°C. and subtracting from the ignited weight the amount of impurities determined in parts per million by emission spectroscopy. The method has been applied to uranium dioxide and mixtures of uranium dioxide and U_3O_8.

II. PROCEDURE

1. Dry the sample to constant weight (± 0.1 mg) over magnesium perchlorate or silica gel in a desiccator. This serves to remove the small amount of loosely bound water which may be present.

2. Heat a platinum crucible at 800°C. in a muffle furnace for thirty minutes.

3. Cool in a desiccator and weigh.

4. Repeat steps 2 and 3 until the weight remains constant to ± 0.1 mg between successive weighings.

5. Place a weighed sample, at least 0.2 g, in the platinum crucible and repeat steps 2 and 3 until constant weight is again obtained.

III. CALCULATIONS

The percentage of each of the elements determined spectroscopically is converted to percentage as ignited oxygen compounds in equilibrium with air at 800°C. and subtracted from the ignited weight of U_3O_8.

If the concentration of an element is below the limit of detectability of the spectrograph, the amount of this element present is assumed to be one-half of this lower limit. Since the limit of detectability is very low, the error involved in this assumption is, for all practical purposes, negligible.

The per cent uranium is then calculated from:

$$\% \, U = \frac{(A - B) \frac{3U}{U_3O_8} \times 100}{\text{Sample Weight}} \quad ,$$

where A is the weight of the impure ignited U_3O_8
and B is the calculated ignited weight of the impurities.

The atomic weight of uranium used in calculating the gravimetric factor varies with the isotopic composition. The atomic weight of uranium containing other than the normal isotopic composition is calculated from the formula:

$$\text{Average Atomic Weight} = \frac{100}{\frac{\text{Weight \% U}^{234}}{234.06} + \frac{\text{Weight \% U}^{235}}{235.07} + \frac{\text{Weight \% U}^{238}}{238.07}}$$

The atomic weight of naturally occurring uranium is 238.07.

IV. DISCUSSION

The effect of the large error in the spectroscopic analysis on the final result is minimized since the method has only been applied to samples containing no more than 0.1 per cent impurities. The error in the spectroscopic analysis is estimated to be ± 100 per cent. If the sample contains 0.1 per cent impurities, the magnitude of this error, as it affects the final uranium concentration, is ± 0.1 per cent. If the error in a single weighing is ± 0.0001 g, the error in determining the weight of ignited U_3O_8, which depends on two weighings, is ± 0.00014 g. This error is independent of sample size. Using a 0.3 g sample, this error amounts to ± 0.05 per cent. Combination of these two errors gives a total error of ± 0.11 per cent. Since the operations involved in an analysis are simple and few in number, good precision can be obtained. Triplicate analyses of the same sample have given a maximum spread of 0.05 relative per cent. There are two important indeterminate errors: (1) change in weight of the platinum crucibles on heating, which has been found to be negligible with crucibles that have been used for some time, and (2) the presence of impurities undetected by the spectrograph. The latter error is not considered important since the results of chemical and gravimetric analyses on identical samples have agreed within experimental error.

PROCEDURE 5: SPECTROPHOTOMETRIC DETERMINATION OF URANIUM WITH THIOCYANATE

I. INTRODUCTION

A. Abstract

Uranium is determined spectrophotometrically as a thiocyanate complex in an aqueous acetone medium at 375 millimicrons. The most important interferences are lead, cobalt, molybdenum and thorium.

B. Principles

This method has been adequately described in an AECD report(1) and will therefore be only briefly outlined here.

The absorbances of the uranium thiocyanate complex is measured at 375 millimicrons to avoid interference from fluorescence and absorption of other ions at lower wave lengths. The strong interference of ferric ion, along with that of cupric and mercuric ions, is removed by reduction with stannous chloride. Lead and thorium interfere by precipitation as sulfates, while cobalt and molybdenum have strongly absorbing complexes at 375 millimicrons. A high concentration of acetone is used to suppress the ionization of acids whose anions compete with the thiocyanate in complexing the uranium. The samples are fumed with sulfuric acid to obtain reproducible conditions. Too much sulfate will cause the solution to separate into two layers. The ammonium thiocyanate solution must be freshly prepared or erratic results will be observed. Uranium may be separated from interfering elements by extraction with ether from a nitric acid solution. Sulfuric acid interferes very strongly with this extraction. For more precise results the "differential colorimetric" method may be used.(2)

II. APPARATUS

Spectrophotometer, Beckman Model DU, with tungsten source.

Absorption cells, glass-stoppered to prevent evaporation of acetone.

III. REAGENTS

Hydrochloric acid, 6N, reagent grade
Ammonium thiocyanate, saturated solution in acetone (3.25-3.50M)
Hydrogen peroxide, 30%

Stannous chloride solution, 10% aqueous solution. Dissolve ten grams of reagent in 10 ml concentrated hydrochloric acid, dilute to 100 ml and filter through #42 Whatman paper.

Nitric acid, 8N, reagent grade

Hydrofluoric acid, 1N

Uranium standard solutions, prepared from MS-ST U_3O_8 dissolved in nitric acid.

Sulfuric acid, concentrated, reagent grade

Aluminum nitrate, reagent grade

Diethyl ether, reagent grade

IV. PREPARATION OF SAMPLES

A. Aluminum-Uranium Alloys

1. Treat a sample containing about 1 mg of uranium with 5-25 ml of 6N hydrochloric acid.

2. After the first vigorous reaction has ceased, add 0.1 ml 30% hydrogen peroxide, and warm until all the sample is in solution.

B. Thorium Alloys

1. Dissolve the sample in 5-25 ml of 8N nitric acid that is 0.01N in hydrofluoric acid.

2. Extract uranium from this solution as described in section C.

C. Samples Containing Interfering Elements

1. Add sufficient aluminum nitrate and nitric acid to make the solution 1.8N and 0.75N in these chemicals, respectively. (If large quantities of fluoride are present more aluminum nitrate should be added to complex this ion.)

2. Extract 3 times with two volumes of ether for each volume of solution.

3. Add an equal volume of water to the ether extracts and evaporate the ether.

V. PROCEDURE

1. Transfer solution to a small flask and add 1 ml of concentrated hydrochloric acid and 0.5 ml of concentrated sulfuric acid.

2. Heat to dense white fumes of sulfur trioxide.

3. Cool, dilute with a few ml of water and transfer to a 25 ml volumetric flask.

4. Add 20 drops of 10% stannous chloride and 15 ml of the saturated acetone solution of ammonium thiocyanate, mixing well after each addition.

5. Dilute to 25 ml with distilled water and mix thoroughly.

6. Measure the absorbance at 375 millimicrons against a blank prepared the same way as the samples, using glass-stoppered cells.

7. Determine the concentration from absorbance vs. uranium concentration curves obtained from standard solutions of MS-ST U_3O_8.

VI. CALCULATION

$$\frac{C \times 100}{W} = \%\ U$$

C = concentration in terms of grams of uranium per 25 ml.

W = weight of the sample in grams.

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PROCEDURE 6: THE SPECTROPHOTOMETRIC DETERMINATION OF URANIUM WITH POTASSIUM FERROCYANIDE

I. INTRODUCTION

A. Abstract

This method depends on the metastable complex formed between uranyl and ferrocyanide ions in the pH range of 3-6. The absorbance is read at 480 millimicrons at a slit width of 0.02 millimeter. There are other methods for uranium included in this manual that should be used where accuracy and precision are desired. This method is fast and readily adapted to the quantitative determination of uranium in solutions where there are no interfering ions. In this laboratory the method is used principally as an aid in the selection of proper aliquots for other methods and also in many other operations where an accuracy of 2-4 per cent is sufficient.

B. Precautions and Principles

The development of the color is dependent upon the pH, concentration of potassium ferrocyanide(1,2,3) and time allowed for development. The adjustment of the acidity is probably the most critical and can be controlled with a formate buffer.(1) Tartrate, citrate, acetate, carbonate and in some instances sulfate interfere with color production by their negative effect. The optimum pH is in the range 3-6 and is easily adjusted by the use of the internal indicator p-nitrophenol. Colored ions interfere but may be minimized in most instances by utilizing a similar blank; many ions, such as aluminum, cuprous, ferric, nickel, etc., form precipitates while others interfere through their complexing action on uranium, such as the anions already referred to as well as sulfate and fluoride. This method is used for nitric acid solutions of uranium. Solvent extraction techniques using ammonium nitrate as the salting agent may also be utilized in eliminating many interferences. Fluoride may be eliminated by the use of boric acid or fuming, while the interference from elements of variable valence can often be minimized by reduction.(4) The working range is 0.5-2.0 mg uranium per fifty milliliters. The absorbance is read at 480 millimicron within fifteen minutes after adding the ferrocyanide.

II. REAGENTS

Nitric acid, 8M
Ammonium hydroxide, concentrated, reagent grade
Paranitrophenol, 1% aqueous solution
Potassium ferrocyanide, 10% aqueous solution

III. PROCEDURE

1. Transfer a dilute nitric acid solution of sample containing 0.5-1.5 mg uranium to 50 ml volumetric flask. Dilute to approximately 25 ml with water.

2. Add 2 drops of p-nitrophenol and mix well. Add ammonium hydroxide until the appearance of a permanent yellow color. Then add 8M nitric acid dropwise until the yellow color disappears.

3. Dilute to 40 ml with water and add 3 ml of a 10% solution of potassium ferrocyanide. Dilute to mark and mix well.

4. After fifteen minutes read at 480 millimicron with a 0.02-millimeter slit width. Refer to reference chart for uranium concentration.

IV. CALCULATION

$$\frac{\text{Weight of uranium found x volume factor}}{\text{Weight of sample}} \times 100 = \%\ \text{U}$$

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PROCEDURE 7: THE FLUOROPHOTOMETRIC DETERMINATION OF URANIUM

I. INTRODUCTION

The analyses of SF materials for trace amounts of uranium by the fluorophotometric method are done by the Industrial Hygiene and Safety Division.

A. Abstract

This method of uranium determination offers advantages in respect to sensitivity, range, specificity, and freedom from interferences possessed by few other analytical methods for any element.

The usual range of the method is from about 10 to 0.0001 micrograms of uranium, work below 0.001 microgram requiring great care in avoiding contamination. Usually analyses are run in duplicate; for routine work the standard error of the mean of the pair is below 10% except when near the sensitivity limit or when unusually large amounts of interfering substances are present. No element besides uranium has been shown to produce detectable fluorescence under the conditions recommended in this paper. A number of elements interfere by quenching fluorescence, but no element has been found to cause noticeable quenching in amounts much below 1 microgram, and milligram amounts of many substances can be tolerated.

B. Definition of Terms

Quenching is any process occurring within a fluorescent substance that decreases the observed intensity of fluorescence; a quencher is a chemical substance causing quenching. The two principal methods of treating quenching are by dilution (taking a smaller aliquot) and by "spiking" (addition of a known amount of uranium to determine the magnitude of quenching so that it can be corrected for mathematically). Quenching should be expected when (1) there is a large amount of residue in the dish after evaporation of the solution, (2) the flux is not white after fusion, (3) the bottom of the dish is strongly colored after removal of the disc, and (4) when the amount of fluorescence found falls on the non-linear portion of the calibration curve. Quenching can be detected with certainty by "spiking" or by making a dilution and finding whether fluorescence is proportional to concentration. When the general composition of the sample is known within rough limits, one can predict whether dilution or "spiking" will probably be necessary.

When there is reason to expect quenching, one should take as small an aliquot as uranium concentration permits without reaching the level where analysis becomes more difficult and less accurate. (Detection of 0.01 microgram per dish is routine; 0.001 microgram requires some precautions for best accuracy; at the 0.0001 microgram level great care is necessary to obtain a standard error as low as 20%.) When uranium concentration has been reduced as much as is expedient, and quenching is still found, it is necessary to "spike" the sample. The procedure is as follows. One takes 4 dishes of identical shape and pipets 1 microgram of uranium into each of two of these and evaporates to dryness. The unknown solution should be sufficiently diluted so that not more than 0.1 microgram of uranium is contained in the aliquot used. The two "unspiked" dishes are pipetted first, and then one of the "spiked" dishes. The pipet is washed and the remaining "spiked" dish is pipetted.

II. NECESSARY EQUIPMENT - Special Equipment needed includes the following:

1 photoelectric fluorophotometer
1 fusion material dispenser
1 special high temperature stove
A set of stock uranium solutions
100 special platinum dishes
A supply of fusion material (90% NaF - 10% Na_2CO_3 - called 10% mixture)
1 dozen micro pipets (assorted sizes)
1 micro pipet washer
1 pair didymium glasses
HNO_3 (concentrated)
HCl (concentrated)

III. DISH CLEANING

Dishes are cleaned by "tapping out" the disc of fused salt into the depressions of a spot test plate. The dishes are then boiled in concentrated hydrochloric acid for ten minutes, rinsed thoroughly with tap water and boiled in concentrated nitric acid for fifteen minutes. They are then rinsed thoroughly with tap water and finally with distilled water and dried under a heat lamp. They are then filled with about 0.25 microgram of 10% mixture, fused and read in the fluorophotometer. The more contaminated dishes are re-treated as many times as is necessary to obtain readings sufficiently low.

IV. PROCEDURE

Pipet two 0.1-ml aliquots of the unknown solution into the depressions of two clean platinum dishes. Then pipet two more 0.1-ml aliquots of the same unknown solution into the depressions of two clean platinum dishes containing a known amount of uranium. Evaporate to dryness under a heat lamp. If a large residue of readily volatilizable or decomposable material remains, the sample in the dish is heated in a flame. To the dry residue in the dish, approximately 0.25 microgram of the 10% mixture is added and fused in the flame of a gas stove. After cooling, the disc of fused salt is irradiated with light from the 365-millimicron mercury line, and the yellow-green fluorescence is measured by a photoelectric fluorophotometer. The amount of uranium present in the unknown is then calculated from the readings obtained.

V. CALCULATIONS

With "spiking," results are evaluated by the following equation:

$$\text{microgram U in aliquot} = (AS/D-A) - B/C$$

where $\underline{A}$ is the fluorescence reading for the "unspiked" sample, and $\underline{D}$ is the reading for the "spiked" sample. $\underline{B}$ is the average fluorescence reading of the unquenched blanks being run at the same time; $\underline{C}$ is the reading for 1 microgram of uranium under the fusion conditions employed and in the absence of quencher; and $\underline{S}$ is the number of micrograms of uranium in the "spike."

PROCEDURE 8: TITRIMETRIC DETERMINATION OF PLUTONIUM

I. INTRODUCTION

A. Abstract

Plutonium in sulfuric acid is reduced to the trivalent state with saturated zinc amalgam, and titrated with standard ceric sulfate to the tetravalent state.

B. Principles

This method was developed at Los Alamos(1) and has been changed only slightly for use here. Plutonium ions in sulfuric acid, which may be in the tetravalent or hexavalent state, are reduced quantitatively to the trivalent state by means of a saturated zinc amalgam under an atmosphere of carbon dioxide to prevent air oxidation. It is then reoxidized to the tetravalent state quantitatively with ceric sulfate using a potentiometric end-point. The oxidation-reduction reactions involved may be represented as follows:

$$2\ PuO_2SO_4 + 3\ Zn(Hg) + 4\ H_2SO_4 \rightarrow Pu_2(SO_4)_3 + 3\ ZnSO_4 + 4\ H_2O$$

$$2\ Pu(SO_4)_2 + Zn(Hg) \rightarrow Pu_2(SO_4)_3 + ZnSO_4$$

$$Pu_2(SO_4)_3 + 2\ Ce(SO_4)_2 \rightarrow 2\ Pu(SO_4)_2 + Ce_2(SO_4)_3$$

Titanium, vanadium, iron, tungsten, molybdenum, and uranium all interfere with this titration, giving high results, as they are reduced and titrated in the same way as the plutonium. They must either be removed or determined separately for correction of the apparent plutonium concentration. Most of the elements that interfere with the Jones reductor method for uranium will probably interfere with this titration too. See Procedure 1.

II. APPARATUS

Assorted micropipets, calibrated, of 10 to 500 microliter capacity.

Transfer pipets, about 1 to 10 ml capacity.

Weight burets, 0.5 to 3 ml capacity (see Fig. 1). The outside of the tip of the buret should be desicoted to prevent wetting. The tip should be such that there is no flow of the solution when the tip is not immersed, and a flow not greater than 2 mg of solution per second for the buret used at the end point.

Syringe controls to be used with pipets and burets.

Analytical balance

Platinum crucibles, 10 ml. capacity

Heat lamp

Variable transformer for heat lamp

Evaporation chamber, consisting of a 3" crystallizing dish covered with a slightly larger crystallizing dish. A glass tube attached to a vacuum line through a glass-wool trap passes through a hole in the top dish to the bottom of the chamber to draw air out of the chamber.

Titration vessels (see Fig.2) and a frame to hold them

pH meter, model G or H, Beckman, equipped with platinum and calomel electrodes with 40-inch leads

Variable speed stirring motor with glass stirrers

III. REAGENTS

Sulfuric acid, reagent grade, dilute
Ceric sulfate, about 0.05N in 1N sulfuric acid. This may be standardized by the method described in Procedure 2.
Saturated zinc amalgam. This may be prepared by mixing granulated zinc, reagent, with triple-distilled mercury, and allowing it to stand under a small amount of very dilute sulfuric acid.
Nitric acid, reagent
Hydrofluoric acid, about 0.1M

IV. HEALTH SAFETY PRECAUTIONS

Plutonium in all of its chemical forms is extremely poisonous because of its high specific activity and the physiology of its absorption by the body. Every precaution should be taken that no plutonium be ingested, inhaled, or injected into the blood stream, even in minute amounts. All operations using plutonium should be carried out in a drybox or a well-ventilated hood, preferably with a glove panel instead of an open hood face, and plutonium should be removed from these places only in tightly closed containers. Personnel working with the material should be protected with rubber gloves and disposable clothing and shoes or shoe covers. If it is necessary to work with plutonium without the protection of a hood or dry box, as in cleaning up a spill or decontaminating a hood or drybox, everyone present should also wear a respirator and disposable head covering. The air in the room where plutonium work is done should be monitored for alpha activity, and an alpha survey meter should be available to monitor hands, gloves, clothings, shoes, floors, and any other surface that might become contaminated.

V. PREPARATION OF SAMPLES

Plutonium metal and oxides are dissolved by warming with concentrated nitric acid about 0.005$\underline{M}$ in HF. The metal may also be dissolved in 6$\underline{N}$ HCl. Plutonium tetrafluoride dissolves readily when warmed with concentrated nitric acid.

VI. PROCEDURE

1. Pipet 3 samples of 5 to 20 mg of plutonium in nitric acid into 10-ml platinum crucibles.
2. Add to each about 0.2 ml of 6$\underline{N}$ sulfuric acid and dilute to at least 0.5 ml.
3. Place crucibles in evaporation chamber and adjust the vacuum line to pass a slow stream of air through the chamber.
4. Adjust the voltage of the heat lamp to obtain evaporation without boiling until copious sulfur trioxide fumes are evolved.
5. Cool the crucibles and wash down the sides with about 0.5 ml of water.
6. Repeat steps 3 to 5 twice to remove all traces of nitric acid.
7. With stopcock A open (see Fig. 2), add to the reservoir of the titration vessel 1 ml of dilute sulfuric acid and enough amalgam to bring the level to the carbon dioxide side-arm.
8. Raise the amalgam to about 0.5 cm in the titration cup by means of the syringe control and close stopcock A.
9. Transfer the plutonium solution with a transfer pipet and rinse the crucible with 2 ml of 1$\underline{N}$ sulfuric acid in three portions.
10. Raise the amalgam to about 1 cm in the cup, insert the carbon dioxide lead through the plastic cover to the cup, and stir for one hour at a moderate rate with the stirrer blade half immersed in the amalgam.
11. Lower the amalgam level just to the carbon dioxide side-arm and pass in carbon dioxide at a minimum rate to raise the solution out of the capillary into the cup.

12. Close stopcock B and adjust amalgam level so that the side-arm is closed and the capillary is filled with carbon dioxide. All of the solution but none of the amalgam must be in the cup at this time.

13. Remove the plastic cover, lower the electrodes into the solution, and titrate with standard ceric sulfate in a weight buret. The buret may be force-drained until a pH meter reading (on the millivolt scale) of 600 to 650 mv. The rest of the titration to the endpoint between 750 and 780 mv. is carried out by adding ceric sulfate in small portions by touching the tip of the buret to the surface of the solution.

14. After the titration is complete, transfer the solution to a waste bottle and rinse the cup and capillary several times with water. The titration vessel is stored with the cup filled with dilute sulfuric acid, 0.5 cm of dilute sulfuric acid over the amalgam in the reservoir, and the stopcocks closed.

VII. PRECAUTIONS

1. Since water is decomposed by high alpha activity, aliquote should be taken of samples received in solution within a few hours to prevent high results from the decrease in volume of the solution.

2. A reagent blank should be determined by carrying through the complete procedure without addition of plutonium. If the endpoint is unstable and the blank is higher than about 1 mg of standard ceric solution, the electrodes are not working properly, or there are interfering impurities in the reagents. The zinc and the mercury should be especially checked; and one or both should be replaced by reagent from a different batch.

3. The titration should be performed immediately after the reduction has been stopped to prevent error due to air oxidation of the plutonium.

4. The endpoint must be interpolated from steady potential readings. If the potential is rising, equilibrium has not as yet been reached. The endpoint is sometimes slow, especially below 20° C. If the potential is falling at the endpoint, examine the titration cup and capillary for amalgam in contact with the partially titrated solution. If this is the case, the results obtained are worthless.

5. Interfering elements in the samples must be removed or determined separately and an appropriate correction made in the plutonium analysis. Iron is the most common impurity. This may be determined by Procedure 16.

VIII. CALCULATION

$$\frac{100(\text{g Ce-IV soln} - \text{blank})\ N \times 0.239}{\text{sample wt.} \times \text{Pu aliquot}} - 4.28 \times \%\text{Fe} = \%\ \text{Pu}$$

N is defined as milliequivalents per gram of solution.

IX. REFERENCE

1. H. E. Boaz, P. Numerof, H. A. Potratz, and W. H. Throckmorton, MDDC-279, January 24, 1946.

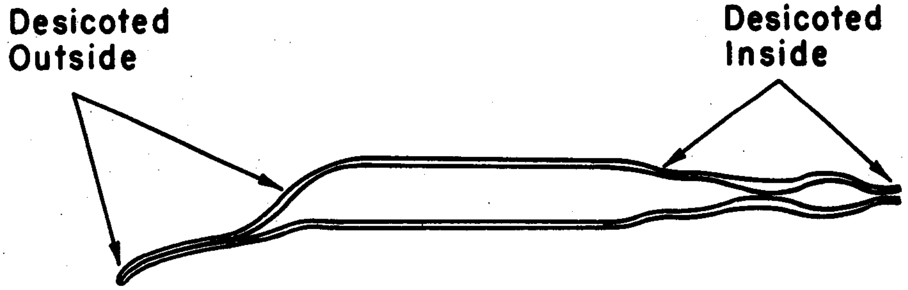

FIGURE I.
WEIGHT BURET
Scale: I"-I"

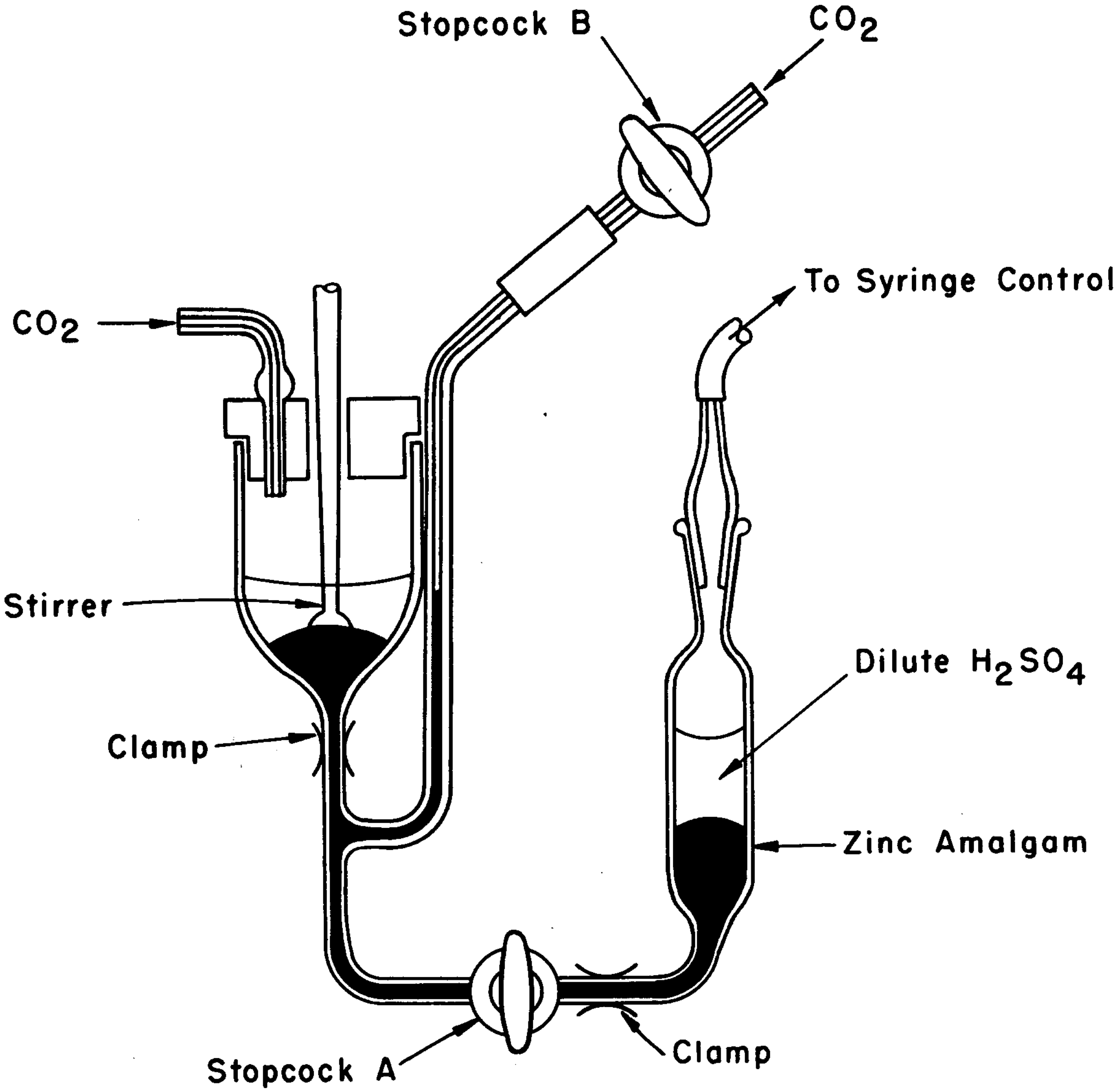

FIGURE 2
TITRATION VESSEL (DURING REDUCTION)

Scale: 1" - 1"

PROCEDURE 9: THE RADIOMETRIC DETERMINATION OF PLUTONIUM

I. INTRODUCTION

A. Abstract

The samples are dissolved in nitric acid, and plates are prepared by the normal evaporation technique preceded by lanthanum fluoride separation if necessary. They are counted with PC-1 and Nuclear Instrument Model 117 alpha counters and compared with a standard alpha source.

B. Precautions

The procedure is subject to the usual errors of alpha counting - back scattering, resolution loss, self-absorption, geometry, and statistical errors. In addition, the isotopic content of the plutonium must be known. Back scattering and geometry corrections can be largely nullified by comparing the count with that of a known alpha source mounted on plates of the same material as those of the samples. Self-absorption is low unless the solution contains large amounts of nonvolatile material. In this case, some method of spreading the sample over the plates should be used,(1) or a lanthanum fluoride separation can be used. Resolution loss may be minimized by keeping the samples small enough that the counting rate is less than one hundred thousand per minute. If larger samples are used, the resolution loss of the particular instrument used is determined experimentally. Statistical errors are negligible if total counts of more than one hundred thousand are used. The isotope ratio of the plutonium is generally obtained by mass spectrometric measurement.

C. Interference

The presence of any other alpha-emitting material causes high results. Beta and gamma activity do not interfere. Large amounts of nonvolatile material causes increased self-absorption.

II. APPARATUS

The two alpha counters used are a Nuclear Measurements PC-1 and a Nuclear Instruments Model 117. In the latter, a Borkowski chamber was substituted for the one supplied. P-10 gas, 90% argon and 10% methane, was used for the chambers of both instruments. Polished stainless steel plates of slightly less than two inches diameter were used. For a standard, about one hundred thousand counts/min of plutonium were deposited electrolytically over a half-centimeter diameter circle on a polished stellite plate.(1) This was counted very accurately by Bentley with a low geometry counter. To determine resolution loss, several of the two-inch plates were cut in half. Equal counts of approximately fifty thousand c/m were deposited on two half-plates. On each of two other half-plates counts of approximately twice the size of either of the first two were deposited. Plates were made up in this way until a pair of plates was obtained that totaled five hundred thousand counts/min - the limit of the instruments used. Each member of a pair was counted separately, and then the two were counted together. The difference between the total of the two individual counts and the count of the two combined represented the amount of loss in doubling the size of the sample. Per cent loss was plotted against size of sample in counts per minute and the best straight line was determined by the least squares method.

TTA extractions are carried out in a small flask with a glass stirrer on a motor.

III. REAGENTS

Nitric acid, concentrated.
Hydrofluoric acid, concentrated (27M).
Hydroxylamine hydrochloride, 10%. Dissolve 10 g hydroxylamine hydrochloride in 90 ml water.
Lanthanum nitrate solution, 50 mg La/ml. Dissolve 15.6 g lanthanum nitrate hexahydrate in water and dilute to 100 ml.
Aluminum nitrate, 1.5M in 1M nitric acid. Dissolve 37.5 g $Al(NO_3)_3 \cdot 9H_2O$ in water. Add 6.4 ml concentrated nitric acid and dilute to 100 ml.
Sodium hydroxide, 10M. Dissolve 40 g sodium hydroxide in water and dilute to 100 ml.
Sodium hydroxide wash solution, 2M. Dissolve 8 g sodium hydroxide in water and dilute to 100 ml.
Nitric acid, 10M. Dilute 64 ml concentrated nitric acid to 100 ml.
Sodium nitrite, 6M. Dissolve 41.4 g sodium nitrite in water and dilute to 100 ml.
TTA, 0.5M in benzene. Dissolve 11.1 g thenoyltrifluoroacetone in benzene and dilute to 100 ml with this solvent.

IV. PREPARATION OF SAMPLES

A. Metal and Oxide

1. Weigh as small a sample as possible for the accuracy desired.

2. Transfer to a 150-ml beaker.

3. Add 5 ml nitric acid and 1 drop of hydrofluoric acid.
4. Place on low heat until metal or oxide has dissolved.

B. Fluoride

1. Weigh out a sample no larger than necessary to obtain the desired accuracy in weighing.
2. Transfer to a 150-ml beaker.
3. Add 5 ml HNO_3.
4. Place on low heat until the sample has dissolved.
5. Evaporate to dryness two or three times with nitric acid to eliminate hydrofluoric acid.

C. Lanthanum Fluoride-TTA Separation(2) (used only when sample contains large amounts of non-volatile solid residue)

1. Transfer to a 15-ml graduated lusteroid centrifuge tube.
2. Adjust acidity and volume of solution so that the sample is in 11 ml of 0.5 to 4.0N nitric acid.
3. Add 1 ml 10% hydroxylamine hydrochloride.
4. Stir well with a stainless steel stirring rod.
5. Add 400 λ of lanthanum nitrate solution.
6. Stir well and allow to stand 10 minutes.
7. Add 1.1 ml hydrofluoric acid.
8. Stir vigorously for 3-5 minutes.
9. Wash stirring rod into tube on removal, and allow mixture to stand 30 minutes.
10. Centrifuge and remove supernatant.
11. Wash pipet with water containing 2 drops of hydrofluoric acid.
12. Centrifuge and remove supernatant.

13. Dissolve in 1.5 ml aluminum nitrate-nitric acid solution.
14. Add 4 ml 10M sodium hydroxide, precipitating lanthanum hydroxide and plutonium hydroxide.
15. Wash stirring rod with 2M sodium hydroxide.
16. Centrifuge and remove supernatant.
17. Wash precipitate with 2M sodium hydroxide.
18. Centrifuge and remove supernatant.
19. Dissolve in 1 ml 10M nitric acid.
20. Dilute to 5 ml with water.
21. Add 500 λ 10% hydroxylamine hydrochloride.
22. Repeat steps 7-13.
23. Wash into extraction vessel with 500 λ water.
24. Add 100 λ 6M sodium nitrite.
25. Allow to stand 10 minutes.
26. Extract with 2 ml 0.5M TTA in benzene for one hour.
27. Scrub with 2 ml water for 5 minutes.
28. Backwash with 1.5 ml of 10M nitric acid for 10 minutes.
29. Repeat with 1 ml nitric acid solution, washing down sides of flask.
30. Combine backwashes to be used for plutonium assay.

V. PROCEDURE

1. Transfer solution from Section IV A, B, or C to a volumetric flask of capacity such that an aliquot of 10 to 100 λ contains 0.5 to 4 μg plutonium, and dilute to volume.
2. Transfer an aliquot containing 0.5 to 4 μg of plutonium to a polished stainless steel plate. Draw the solution into the micropipet just to the mark.

3. Wash the pipet with 10M nitric acid, depositing the washings on the plate.

4. Repeat with water.

5. Evaporate the solution on the plate under the heat lamp without bubbling.

6. Ignite to a dull red heat with a microburner.

7. Store the plate in a desiccator to exclude moisture.

8. Place the plate in the counting chamber and purge 1 minute with P-10 gas.

9. Count the sample for 10 minutes.

10. Count the alpha standard source under the same conditions.

VI. CALCULATIONS

$$\frac{(C \pm c)(L_s \pm l_s)(D \pm d) \times 100}{(L_c \pm l_c)(S \pm s)(W \pm w)(F \pm f)(A \pm a)} = P \pm p$$

where C = observed counts/min

L_c = correction for resolution loss in sample count = $\frac{100 - \%\ \text{loss}}{100}$

L_s = same for standard count

D = total disintegrations/minute of standard

S = standard count

A = aliquot of original sample counted

W = weight of original sample in milligrams

F = specific activity in disintegrations per minute per milligram of the plutonium of the isotopic ratio of the sample. Calculation for this: $\%Pu^{239} \times \text{sp. act.}^{239} + \%Pu^{240} \times \text{sp. act.}^{240} = F$. sp. act.^{239} and sp. act.^{240} are respectively 1.36×10^{8} d/mg x min and 5.02×10^{8} d/mg x min.

P = % Pu

The small letters are the corresponding 2 σ values for the quantities. "c" is taken as 2% of "C" to allow for self-absorption. "p" generally is about 5% of "P."

VII. REFERENCES

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2. R. G. Hart, PDB-39 (Oct. 24, 1951)

PROCEDURE 10: SPECTROPHOTOMETRIC DETERMINATION OF ZIRCONIUM

I. INTRODUCTION

A. Abstract

Zirconium is determined spectrophotometrically at 520 millimicrons as the alizarin sulfonate lake. The absorption obeys Beer's law between 0.1 and 0.4 mg Zr per 100 ml solution. Separation of uranium is unnecessary. A correction for uranium absorption is required if U/Zr is greater than 500. A standard error of about 1% was obtained using known samples.

B. Principles and Interferences

Sodium alizarin sulfonate forms a red lake with zirconium in a hydrochloric acid solution.(1) In the absence of nitric acid the formation of the complex is complete in one hour after the reagents are mixed, and is stable for the next four hours or longer, dependent on the concentration of zirconium. After one day most of the lake has precipitated. Nitric acid is reported to cause delay in color formation.(1) The absorbance is measured at 520 millimicrons with a Beckman DU spectrophotometer. The absorbance is proportional to the zirconium concentration up to 0.4 mg Zr per 100 ml. Above this concentration the absorbance tends to become constant even though the alizarin sulfonate is still greater than 50% in excess of the zirconium. The molar extinction coefficient of this complex ion at this wavelength is 6275. The uranium interference is 10 ppm of uranium concentration and is therefore negligible except in very high concentrations of the uranium. The reported interference of sulfate was tested at low concentrations of this ion, and it was found that 0.01N sulfate could be tolerated. This makes it possible to use sulfuric acid for dissolution of samples and removal of nitrate ion. In this procedure all the excess sulfuric acid is fumed away to keep the concentration of sulfate as low as possible. It has been found that barium and niobium interfere, but that a small amount of calcium does not. Phosphate is reported to interfere, as well as thorium in large amounts.(1) No interference is reported from Fe(III), Ni, V(V), Mo(VI), Cr(III), Mn(II), Al, Ce(IV), Mg, Be, chloride and perchlorate. Hydrolysis of the zirconium ions may cause low results unless the sample is boiled with 10% hydrochloric acid the same day it is analyzed.

II. REAGENTS

Nitric acid, concentrated
Hydrochloric acid, concentrated
Sulfuric acid, concentrated
Aqua regia. Mix one part of concentrated nitric acid with three parts of concentrated hydrochloric acid.
Hydrochloric acid, 10% of concentrated solution
Sodium alizarin sulfonate, 0.05% solution

III. PREPARATION OF SAMPLES

1. Weigh samples containing 0.1 to 0.4 mg Zr into 150-ml beakers.
2. Treat each sample with 20 ml aqua regia and cover the beaker until the vigorous reaction has ceased.
3. Add 1 ml concentrated sulfuric acid, evaporate to fumes, and continue fuming for 15 minutes. The samples should now be completely dissolved.
4. Wash down the sides and cover of the beaker and again evaporate to fumes.
5. Repeat step 4.
6. Evaporate all the sulfuric acid until the salts are dry.

IV. PROCEDURE

1. Cool the dry salts, add 10 ml 10% hydrochloric acid, and heat to boiling.
2. Cool, transfer to a 100-ml volumetric flask, and dilute to about 90 ml. Mix well.
3. Add 5 ml 0.05% sodium alizarin sulfonate solution and dilute to volume. Mix well.
4. After one hour, measure the absorbance at 520 millimicrons against a blank with the same concentration of hydrochloric acid and sodium alizarin sulfonate. The slit of the Beckman DU spectrophotometer is set at 0.02 mm and the blue photocell is used.
5. Determine the zirconium concentration corresponding to this absorbance from a standard curve obtained by carrying known zirconium solutions through the above procedure. The slope of this line was found to be 1.453 mg Zr/100 ml per absorbance unit.

V. ACCURACY AND PRECISION

Twenty-nine samples with known zirconium concentrations ranging from 0.03 to 0.48 mg/100 ml were analyzed by this method with a standard deviation of 6.6 micrograms per 100 ml. The seven samples in the optimum range of 0.2 to 0.4 mg Zr per 100 ml had a standard deviation of 1.8 micrograms per 100 ml. This is less than 1% of the zirconium concentrations of these samples. Forty-five known samples containing 0.075 to 0.45 mg Zr and 20 to 1000 mg U per 100 ml had a standard error of 7.9 micrograms per 100 ml.

VI. REFERENCE

1. Ruth Guenther and Richard H. Gale, KAPL-305, March 10, 1950.

PROCEDURE 11: GRAVIMETRIC DETERMINATION OF ZIRCONIUM IN THE NIOBIUM-URANIUM TERNARY ALLOY(1)

I. INTRODUCTION

This procedure(1) was originally designed for the determination of zirconium and niobium in the uranium ternary alloy. The method is time consuming and is not recommended for niobium. The colorimetric method for niobium (Procedure 13) is fast, accurate and readily adaptable to routine analysis without separation from other components.

A. Abstract

Zirconium and niobium are separated from uranium by a cupferron precipitation from a 10% sulfuric acid solution.(2,3) The separation of zirconium from niobium is effected by a carbonate fusion; the soluble niobium is in the filtrate. The zirconium precipitate is solubilized by a pyrosulfate fusion and precipitated with cupferron. The zirconium cupfurate is filtered, ignited and weighed as ZrO_2. If iron is present, the iron and zirconium oxides are dissolved and iron is determined colorimetrically. Necessary corrections are then made in the weighed oxides.

B. Precautions and Interferences

Several laboratories have reported explosions during the pickling, etching or dissolution of zirconium alloys. This laboratory has investigated the mechanism of these explosions as well as the preventive measures.(5) Our dissolutions are done in a closed hood usually with small quantities of turnings.

The cupferron method as presented will precipitate quantitatively iron, titanium, tantalum, zirconium, niobium, vanadium, quadrivalent uranium and probably hafnium. Among the interfering elements are lead, tin, silver, bismuth, rare earths, thorium and tungsten. Silica, phosphorus, the alkaline earths and alkali salts interfere only when excessive amounts are present.(4) It will be noted that some are of the hydrogen sulfide group, while others seldom will occur.

II. REAGENTS

Hydrofluoric acid, 48%
Nitric acid, concentrated, reagent grade
Hydrochloric acid, 1.0N, reagent grade
Sulfuric acid, concentrated, reagent grade

Potassium carbonate, 2% solution

Potassium carbonate, anhydrous

Potassium pyrosulfate

Ammonium oxalate

Phenolphthalein, 1% solution in ethyl alcohol

Filter pulp suspension. Macerate three filter tablets by shaking them with 50-100 ml of hydrochloric acid in a 500-ml Erlenmyer flask. Dilute to about 400 ml with water and filter. Wash the pulp with water until the washings are neutral. Suspend the pulp in 500 ml of water.

Cupferron solution, 6% aqueous solution. This solution should be freshly prepared. Its stability can be increased by adding 50 mg of acetphenetidine per 150 ml and keeping in a cool dark place. The reagent itself should be kept in a cool, dark place preferably under a bag of ammonium carbonate suspended from stopper of bottle.

III. PREPARATION OF SAMPLE

1. Weigh out alloy containing approximately 100 mg of zirconium into a platinum beaker containing 15 ml of water. Add an acid solution containing 15 ml of nitric acid and 2 ml hydrofluoric acid and cover. Heat at low heat until no more fumes of nitrogen dioxide are evolved.

2. Continue heating until completely dissolved. If UF_4 is present, add additional nitric acid.

3. Cool and add 40 ml of sulfuric acid. Evaporate to fumes of sulfur trioxide.

4. Cool, wash cover and sides with about 10 ml water and again evaporate to fuming. Continue strong fuming for 15 minutes.

IV. PROCEDURE

1. Cool and dilute with 30 ml of water. Transfer to a 600-ml beaker containing 2.0 g of ammonium oxalate dissolved in water. Dilute to 300 ml. Cool to 10°C in an ice bath and slowly add 25 ml of a cold 6% cupferron solution with constant stirring. Add 15 ml of paper pulp slurry and allow to settle.

2. Filter through #42 Whatman paper with the aid of suction and a filter cone. Wash with 1N hydrochloric acid. Dry and ignite precipitate at 1000°C for one hour. Check filtrate for completeness of precipitation. Note: At this point the precipitate contains zirconium, niobium and iron. Separation of zirconium and iron from niobium is effected in the next step by an alkaline fusion.

3. Mix 4.0 g of potassium carbonate with the oxides in the platinum crucible. Fuse for 15 minutes with occasional swirling of the liquid melt. Cool, wash cover and dissolve melt in 30-40 ml water. Heat to near boiling. Add 10 ml paper pulp and allow precipitate to settle. Filter through #42 Whatman paper and wash thoroughly with 2% potassium carbonate.

4. Dry and ignite the precipitate at 1000°C for one hour. Repeat the fusion as described in (3) above and combine filtrates.

5. The residue remaining after filtration of the carbonate melt is dried and ignited.

6. Cool and add a few drops of sulfuric acid. Add 3.0 grams of potassium pyrosulfate, cover and heat gently until a clear melt is obtained. Swirl crucible to assure intimate contact of melt with all contents of crucible.

7. Cool, wash cover and dissolve melt in 50-100 ml of water in a 600-ml beaker. Add 30 ml sulfuric acid and dilute to 300 ml. Cool to 10°C in an ice bath.

8. Add slowly 20 ml of 6% cupferron and 10 ml of paper pulp. Filter through #42 Whatman paper and wash thoroughly with a cold solution of 2.0N sulfuric acid containing 0.1% cupferron. Dry and ignite to constant weight at 1000°C for one hour. Cool and weigh as ZrO_2.

9. If the zirconium dioxide is not pure white, contamination is probably due to the oxide of iron (Fe_2O_3) and a correction should be made as follows.

10. Dissolve the contents of crucible by heating with 2 ml of 6N sulfuric acid and 3 ml hydrofluoric acid. (As an alternate method the contents may be dissolved by fusing with potassium pyrosulfate.) Evaporate to strong sulfur trioxide fumes. Cool, transfer to a 100 ml volumetric flask and make up to volume. Determine iron colorimetrically (see Procedure 16).

V. CALCULATIONS

$$\frac{\text{Weight of } ZrO_2 \times 0.7403}{\text{Weight of Sample}} \times 100 = \%\text{ Zirconium in alloy}$$

When iron impurities are present the corrected formula will be:

$$\frac{(\text{Total Weight of Oxides} - \text{Weight of } Fe_2O_3) \times 0.7403}{\text{Weight of Sample}} \times 100 = \%\text{ Zirconium}$$

VI. REFERENCES

1. R. F. Telford and R. Bane - To appear as an Argonne National Laboratory report.

2. W. W. Scott, "Standard Methods of Chemical Analysis."

3. W. F. Hillebrand and G. E. F. Lundell, "Applied Inorganic Analysis," John Wiley & Sons, Inc. (1929).

4. G. E. F. Lundell and H. B. Knowles, J. Am. Chem. Soc. 42, 1439 (1920).

5. R. P. Larsen, R. S. Shor, H. M. Feder and D. Stanley Flikkema, ANL-5135.

PROCEDURE 12: GRAVIMETRIC DETERMINATION OF ZIRCONIUM WITH PARACHLOROMANDELIC ACID

I. INTRODUCTION

A. Abstract

A gravimetric procedure has been devised which will quantitatively separate 20 to 200 milligrams of zirconium from up to 30 times as much uranium in one precipitation. Sulfuric acid interferes if it is more concentrated than 0.4 molar.

B. Principles and Interferences

Zirconium forms with p-chloromandelic acid a specific crystalline precipitate with a solubility lower than that of the mandelate precipitate. Determination of zirconium with this reagent was first proposed by Oesper and Klingenberg.(1) Klingenberg and Papucci have used it for the determination of zirconium in steel.(2) Neither of these papers include a systematic study of cation interferences. However, mandelic acid interferences were studied by Kumins and Hahn. Kumins(3) recommended this reagent for the determination of zirconium in the presence of titanium, iron, vanadium, aluminum, chromium, thorium, cerium, tin, barium, calcium, copper, bismuth, antimony, and cadmium. Hahn(4) showed that zirconium can be separated from cobalt, magnesium, manganese, mercury, nickel, uranium, and zinc with mandelic acid.

If at least 1 gram of the reagent is added in excess of the stoichiometric amount for the formation of the bis(parachoromandelate), sulfate up to 0.4M may be tolerated. Above this concentration low results are observed. The oxide from ignition of the precipitate is not always snow white. Sometimes brown or black specks have been observed. These have been identified spectrographically to be 0.05 to 0.1 mg of uranium oxide, probably from hydrolysis of uranium on the filter on washing with water.

II. APPARATUS

Constant temperature bath, with temperature control at 90°C ± 3°.

III. REAGENTS

Hydrochloric acid, concentrated, reagent grade
Nitric acid, concentrated, reagent grade
Sulfuric acid, concentrated, reagent grade
p-Chloromandelic acid, 0.159N solution (29 grams per liter). This reagent can be synthesized by the method of S. S. Jenkins(5).

IV. PREPARATION OF SAMPLES

Treat a sample containing 20 to 200 mg of zirconium by the method of Procedure 1, Section IV-D. It is not necessary to replace sulfuric acid lost by evaporation.

V. PROCEDURE

1. Evaporate the sulfuric acid solution to dryness.
2. Add 15 ml of concentrated hydrochloric acid.
3. Warm until the salts have dissolved completely.
4. Cool to room temperature and slowly add reagent - 28 ml for each 100 mg of Zr plus 34 ml in excess. Add water if necessary to bring volume to 100 ml. Stir well and let stand for 5 minutes.
5. Digest in a water bath at 90°C ± 3°C for 30 to 40 minutes.
6. Cool to 20°C and filter with Whatman #40 or 42 filter paper.
7. Wash 8 to 10 times with distilled water.
8. Dry, char slowly, and ignite at 960°C to 1000°C in a platinum crucible to constant weight.

VI. CALCULATIONS

$$\frac{0.74030 \text{ Weight of } ZrO_2}{\text{Weight of Sample}} = \% \text{ Zr}$$

VII. DISCUSSION OF THE RESULTS

The standard deviation of 12 known samples containing approximately 0.1 g Zr and 0 to 3 grams of uranium analyzed by the recommended procedure was 0.1 mg. This compares favorably with results using the cupferron method.

VIII. REFERENCES

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2. J. J. Klingenberg and R. Papucci, Anal. Chem. 24, 1862 (1952).
3. C. A. Kumins, Anal. Chem. 19, 376 (1947).
4. R. Hahn, Anal. Chem. 21, 1579 (1949).
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PROCEDURE 13: THE SPECTROPHOTOMETRIC DETERMINATION OF NIOBIUM IN URANIUM TERNARY ALLOYS

I. INTRODUCTION

This is a spectrophotometric method developed by the Special Materials Analytical Laboratory for the determination of niobium in uranium alloys. It has been used successfully in the presence of zirconium-uranium and tin-uranium ternary alloys. The method is rapid and simple and should be readily adaptable to routine analysis.

A. Abstract

The method is based on the formation of the peroxyniobic complex in concentrated sulfuric acid.(1,3) There is no evidence of a zirconium or tin peroxy complex that would interfere in the spectral range in which niobium has its maximum absorption. The color is developed in freshly fumed sulfuric acid with a sulfuric acid-hydrogen peroxide solution and the absorbance read at 362 mμ. A working range of 5.5-9.0 mg niobium per 50 ml was used with operation on the 0.1 scale of the Beckman Model DU Spectrophotometer. Conformity to Beers Law was observed over the range 2-200 ppm niobium when performed in 1-cm fused silica cells.

B. Precautions and Interferences

Bubble formation is often observed after the addition of hydrogen peroxide, during the mixing operation or in the cell. This is due to small amounts of impurities in the chemicals used or on the apparatus, which catalyze the decomposition of hydrogen peroxide. This effect is particularly hazardous if nitrates are not completely removed. It is recommended that the Giles type volumetric flask be used and that a carbonate solution as well as an adequate water supply be available for use in case of splattered droplets of the acid-peroxide solution. Transfer of the acid is done by means of a syringe and transfer pipet.

Precise control of the sulfuric acid concentration is necessary in both the samples and blank and is accomplished in a simple manner by a fuming technique. The equilibrium concentration of the peroxy complex(4) increases with increasing concentration of sulfuric acid and the absorption peak shifts toward the red. Fluorides, nitrates, chlorides, titanium, tantalum, molybdenum, rhenium and iron interfere.

The blank may be a hydrogen peroxide-sulfuric acid solution prepared in the same manner as the unknown or may contain an unperoxidized sample of the unknown containing the same concentration of ingredients as the sample to be analyzed. In this manner the uranium interference may be eliminated, otherwise a uranium correction curve must be made. The absorption peak will be found in the range 355-365 mμ for a sulfuric acid concentration of 87 to 100 percent, respectively. This peak may be used to advantage in regulating the acid concentration.

II. REAGENTS

Hydrogen peroxide-sulfuric acid solution. Transfer 4 ml of 30% hydrogen peroxide to a 100-ml volumetric flask. Slowly add to mark with mixing, a freshly fumed solution of sulfuric acid.

Sulfuric acid, concentrated, reagent grade

Hydrochloric acid, concentrated, reagent grade

Nitric acid, concentrated, reagent grade

Columbium oxide (niobium oxide), Hi Purity, from Fansteel Metallurgical Corporation.

Potassium pyrosulfate

Standard solution of niobium, made by solubilizing columbium oxide by a potassium pyrosulfate fusion. The melt is dissolved and adjusted to desired volume with concentrated sulfuric acid.

III. PREPARATION OF SAMPLE

1. Treat sample containing 5.5-9 mg of niobium with approximately 30 ml of aqua regia. Allow the reaction to proceed at room temperature. When the initial reaction subsides, apply moderate heat until reaction ceases.

2. Cool and add 15 ml of sulfuric acid and evaporate to sulfur trioxide fumes and continue fuming until sample is completely dissolved.

3. Cool, wash the under side of the cover glass and the sides of the container, and again evaporate to sulfur trioxide fumes. Continue heating for 15 minutes.

4. Cool, and again wash down sides of container. Add 10 ml of hydrochloric acid and evaporate to sulfur trioxide fumes. Continue strong fuming for 15 minutes.

5. If prolonged fuming is required to dissolve the sample, cool and replace the sulfuric acid lost by evaporation.

IV. PROCEDURE

1. Transfer the freshly fumed sample to a 50-ml volumetric flask. Wash container thoroughly with hot freshly fumed sulfuric acid.

2. Add 25 ml of freshly prepared hydrogen peroxide-sulfuric acid solution and mix well. Dilute to mark with freshly fumed sulfuric acid. Note: The mixing operation should be cautiously performed in a shielded area. Observe closely during the mixing to guard against any sudden pressure "build-ups" due to hydrogen peroxide decomposition.

3. Transfer aliquot of solution to a fused silica cell and read the absorbance on the spectrophotometer at 362 mμ with a 0.1-mm slit width.

4. The blank may be sulfuric acid-hydrogen peroxide or an unperoxidized sample of the same weight as the unknown. In either case the sulfuric acid concentration is controlled in a similar manner by the fuming technique.

V. CALCULATIONS

The niobium concentration of the solution may be found by referring to the standard or reference curve.

$$\frac{\text{mg Niobium Found}}{\text{Sample Weight}} \times 100 = \%\ \text{Niobium}$$

If an aliquot of sample is used for analysis, the above formula will include a volume factor.

The C/A(*) ratio may also be determined by taking known quantities of the niobium standard and treating in exactly the same way as the sample solution and measuring its absorbancy. It follows that:

$$C/A \times \text{Absorbance} = \text{Mg Niobium}$$

(*) C = Concentration or mg niobium per 50 ml solution.
A = Absorbance or optical density.

VI. REFERENCES

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PROCEDURE 14: IODOMETRIC DETERMINATION OF TIN IN NIOBIUM-URANIUM TERNARY ALLOYS

I. INTRODUCTION

A. Abstract

Tin and niobium are separated from uranium by precipitation of the sulfides from an acid solution. The sulfides are dissolved with ammonium sulfide and oxidized with nitric acid. The tin is reduced with sodium hypophosphite(1,2,3) and in turn titrated with a standard iodine solution. The reduction and subsequent oxidation are carried out in a carbon dioxide atmosphere.

B. Principles

Tin is separated from uranium and niobium by a sulfide precipitation. The stannic sulfide dissolves in ammonium sulfide to form ammonium thiostannate. The thiostannate and sulfide remaining after dissolution are oxidized to sulfate by nitric acid, and the metastannic acid is dissolved with sulfuric acid. Tin is reduced to the stannous state by hypophosphite in a hydrochloric acid solution and oxidized to stannic with a standard iodine solution.(5) The following reactions summarize the process.

(a) $SnCl_4 + 2H_2S = SnS_2 + 4\ HCl$

(b) $SnS_2 + (NH_4)_2S = (NH_4)_2SnS_3$

(c) $5(NH_4)_2SnS_3 + 40\ HNO_3 = H_{10}Sn_5O_{15} + 10\ NH_4HSO_4 + 5\ H_2SO_4 + 40\ NO + 5\ H_2O$

(d) $SnCl_4 + H_3PO_2 + H_2O = H_3PO_3 + SnCl_2 + 2\ HCl$

(e) $SnCl_2 + I_2 + 2\ HCl = SnCl_4 + 2\ HI$

C. Precautions and Interferences

The acid concentration during the sulfide precipitation may vary between 0.25-1.00N. This precipitation is also useful in separating the tin from iron, chromium, vanadium and tungsten as well as from uranium. It is recommended that the lowest acid concentration be used since the stannous form is more readily soluble in higher acid concentration. The fluoride ion must be completely destroyed, since stannic salts form complex ions with fluoride or oxalic acid which are not decomposed by hydrogen sulfide. In the decomposition of the sample and in subsequent operations with the stannic salt, care should be exercised to prevent volatilization of stannic chloride.(4) The concentration of solutions in covered beakers in the presence of sulfuric acid will minimize this volatilization. Caution must be exercised after the hypophosphite reduction to exclude air.

II. REAGENTS

Hydrofluoric acid, 48%, reagent grade
Sulfuric acid, concentrated reagent grade
Nitric acid, concentrated, reagent grade
Tartaric acid, 1.2M (0.2 g/ml)
Hydrogen sulphide (gas)
Ammonium sulfate, 2% aqueous solution, 0.1N in H_2SO_4
Ammonium sulfide, saturate 30 ml of a cold ammonium hydroxide solution with hydrogen sulfide. Then add 60 ml of 7.5M ammonium hydroxide.
Carbon dioxide, gas
Hydrochloric acid, 6M
Sodium hypophosphite
Mercuric cyanide, 1% aqueous solution
Potassium iodide, 4% aqueous solution
Citric acid, 50% aqueous solution
Starch solution, 1% aqueous solution
Sodium bicarbonate
Standard iodine solution, approximately 0.015N
Standard tin solution, approximately 1 mg per ml
Filter pulp suspension, refer to Procedure 11.

III. PREPARATION OF SAMPLE

1. Weigh out a quantity of alloy containing approximately 20 mg of tin into a platinum beaker containing 10 ml of water.

2. Add concentrated nitric acid slowly at the ratio of 10 ml acid per gram alloy. Heat at a low heat until the evolution of oxides of nitrogen ceases.

3. Wash the cover and sides of container with minimum quantity of water. Add 2-3 ml of hydrofluoric acid and heat gently until sample is completely dissolved.

4. Cool and add 10 ml concentrated sulfuric acid and evaporate to sulfur trioxide fumes. Continue fuming for 15 minutes.

5. Cool and repeat fuming procedure twice again. Add more sulfuric acid if necessary.

IV. PROCEDURE

1. To cool solution, add 20 ml water and heat moderately, if necessary, in order to get a clear solution. Transfer to an 800-ml beaker containing 10 ml of 1.2<u>M</u> tartaric acid. Dilute to 300 ml and saturate solution for 10 minutes with hydrogen sulfide.

2. Dilute solution to approximately 600 ml and again saturate with hydrogen sulfide for 10 minutes. Allow to stand 12 hours or more to facilitate filtering.

3. Add 10 ml of filter paper pulp suspension and filter through #40 Whatman filter paper. Wash three times with 2% acidulated ammonium sulfate solution.

4. Replace the beaker containing the filtrate with a 250-ml beaker. Dissolve the stannic sulfide with three 3-ml portions of ammonium sulfide solution. Wash with water after the addition of each aliquot of ammonium sulfide.

5. Cover the dissolved tin solution and evaporate to about 5 ml with moderate heat.

6. Cool, add 5 ml of nitric acid and 10 ml of sulfuric acid and take to fumes. If solution is not clear at this point it will be necessary to add more nitric acid and again fume. (See equation (C) in section I-B.)

7. After solution is clear, repeat sulfuric acid fuming, washing the cover and sides of container after each fuming period.

8. Repeat (7) above. Note: It is necessary to completely eliminate nitrate before proceeding with the reduction step.

9. Transfer the solution containing the tin to a 500 ml Erlenmeyer flask with one-half its volume of concentrated hydrochloric acid. Add 80 ml of 6M hydrochloric acid using whatever part necessary for washing the original container, then add 4.0 grams sodium hypophosphite.

10. Place 10 ml of 6M hydrochloric acid into a small beaker and add 1 ml of the mercuric cyanide solution and 0.5 gram sodium hypophosphite. Boil for 1 minute and add to tin solution in Erlenmeyer flask.

11. Stopper immediately with a three-hole stopper through which passes: (1) an inlet tube for carbon dioxide gas that extends nearly to the bottom of flask, (2) a 60-ml pear shaped funnel with the stem extending about an inch below the stopper, (3) a glass tube extending about two inches below the stopper, the top of which is fitted with a Bunsen valve.(6) Note: The rubber tubing connecting the inlet tube for gas with the supply tank should be long enough to enable one to maneuver and perform the various operations that follow with a continuous flow of carbon dioxide.

12. Sweep out the flask with carbon dioxide for about 5-10 minutes. Remove the Bunsen valve and bring solution to a quick boil. Remove high heat, then continue to boil gently for 15 minutes in a carbon dioxide atmosphere.

13. Remove from heat, replace Bunsen valve immediately and cool under running water. Finally cool in an ice bath to about 10-15°C.

14. While the above tin solution is cooling, make up a diluting solution containing 10 ml of 4% potassium iodide, 20 ml of 50% citric acid, 250 ml of water and 5 ml of 1% starch solution. Cool to about 10-15°C. Add cautiously 3 grams of sodium bicarbonate with moderate stirring.

15. Remove the Bunsen valve and the short piece of glass tubing. Add the diluting solution immediately to the funnel, then to contents of the flask, being careful that no air is admitted.

16. Insert buret tip into hole vacated by Bunsen valve and titrate with a standard iodine solution to a permanent blue tint with a continued carbon dioxide flow.

V. CALCULATIONS

The iodine solution is standardized against a standard tin solution. The iodine standardization is expressed in terms of mg of tin per ml of solution.

VI. REFERENCES

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PROCEDURE 15: THE DETERMINATION OF SILICON IN URANIUM-SILICON ALLOYS

I. INTRODUCTION

A. Abstract

This is a gravimetric method for silicon based upon its isolation during the initial stages of the analyses by dehydration with sulfuric acid to silicon dioxide. Silicon is determined in this mixture of oxides by difference after volatilization with hydrofluoric and sulfuric acids.

B. Principle

The decomposition of low silicon alloys is easily accomplished with nitric acid. It may be necessary in the case of high silicon alloys to resort to an alkali carbonate fusion for solution.(1) After solution of sample the silica is isolated by dehydration with either sulfuric or perchloric acid. Complete recovery of silica requires a second dehydration,(2) since there is approximately 0.1% loss due to solubility or other factors. The residue obtained upon dehydration contains a mixture of oxides and may contain aluminum, titanium, tantalum, niobium, iron, calcium, barium, sodium or lead depending upon the acid used for dehydration. The amount of pure silica is determined by difference upon treatment of these oxides with hydrofluoric and sulfuric acids. The over-all reaction may be represented thus:

$$SiO_2 . x\ H_2O = SiO_2 + H_2O$$

$$SiO_2 + 4\ HF = SiF_4 \uparrow + 2\ H_2O$$

C. Precautions and Interferences

It is advisable to have a spectrochemical analysis on samples of unknown origin before proceeding with the silicon analysis. In many cases it is necessary to remove interfering elements.(3) For complete silicon recovery it is necessary to make a second dehydration.(2,4) Direct heating of moist silica and paper to a red heat must be avoided as silicon carbide is formed under such conditions.(5) The precipitate obtained upon dehydration is treated with a little sulfuric acid before the first ignition to convert interfering elements to sulfates. The precipitate is then silica and sulfates and after volatilization the impurities remain in the same form.(6,7) The oxides are ignited at 1150-1200°C; however, in the case of phosphorus, tantalum or tungsten impurities the second ignition should not be as vigorous as the first. In most cases it is desirable to run a blank.

II. REAGENTS

Sulfuric acid, concentrated, reagent grade
Hydrofluoric acid, 48%
Nitric acid, concentrated, reagent grade
Sulfuric acid, 1M
Sulfuric acid, 9M

III. PREPARATION OF SAMPLE

1. Weigh 3 grams of sample containing more than 0.5 per cent silicon or 5 grams of sample containing less than 0.5 per cent silicon into a 250-ml pyrex beaker. Add 20 ml water.

2. Slowly add 25 ml of hydrochloric acid. Heat moderately until the reaction is complete.

3. Add 5 ml of nitric acid and continue to heat until the solution is clear and uranium has been oxidized. Swirl beaker gently to observe any undissolved particles of alloy.

IV. PROCEDURE

1. Add 20 ml sulfuric acid, cover container and evaporate to strong fuming. Continue fuming for thirty minutes. Do not allow contents of beaker to become solid or incomplete separation of silica may result. Note: Perchloric acid is preferred in most instances over sulfuric acid on the ground that the silica obtained is purer and the salts formed are usually wholly and quickly dissolved. Precautions must be taken that the perchloric acid is not heated with organic matter in recovery operations.

2. Cool and carefully add 50 ml of water. Then add 125 ml of hot boiling water at one time. Heat for 5-10 minutes but do not boil.

3. Add 10 ml filter paper pulp and filter immediately. Use ashless, highly retentive, faster filtering paper. Wash several times with 1.0N H_2SO_4 and finally with hot water. Note: For complete recovery a second dehydration is necessary. In many cases the recovery of silicon during the second dehydration amounts to approximately 0.1% of the total. To make a second dehydration, use the combined filtrate plus washings from part 3 above and repeat parts 1-3 inclusive.

4. Transfer paper* and contents to a tared platinum crucible and add 4-5 drops of 9M sulfuric acid.

5. Dry and char in a drying oven at 150°C. Remove from oven and ignite partially covered crucible with a low flame for 10 minutes and gradually ignite to full flame of burner for 5 minutes. A draft around crucible may be avoided during ignition by sinking it about two-thirds of the way through an asbestos shield.

6. Transfer to a muffle furnace and ignite at 1150°-1200°C for thirty minutes. Repeat until constant weight is obtained. Keep crucible well covered during desiccation and weighing.

7. Add 3-4 drops 9M sulfuric acid and 5 ml of 48% hydrofluoric acid. Evaporate with moderate heat to dryness. Finally ignite at 900°C to constant weight and weigh. Note: One treatment is usually sufficient to remove all the silica. The sulfuric acid is used to convert the contaminating substances to non-decomposable sulfates since this was the form in which they existed with the impure oxide of silica. Titanium will volatilize as a fluoride and many of the base salts would decompose if not converted. The ignition temperature here may also be 1150-1200°C in the absence of phosphates, tantalum or tungsten.

V. CALCULATIONS

$$\frac{(\text{Weight of Impure SiO}_2 - \text{Weight After Volatilization})}{\text{Weight of Sample}} \times 0.4672 \times 100 = \%\ \text{Si}$$

VI. REFERENCES

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PROCEDURE 16: THE SPECTROPHOTOMETRIC DETERMINATION OF IRON IN THE PRESENCE OF URANIUM WITH 1,10-PHENANTHROLINE

I. INTRODUCTION

A. Abstract

This is a sensitive method for the determination of iron based on the formation of an orange-red complex, $[(C_{12}H_8N_2)_3Fe]^{++}$ between 1,10-phenanthroline(1,2,3) and ferrous iron. It is not necessary to make a uranium separation and the method can be adapted to other colored ions.(4) The acidity is adjusted by approaching the ammonium diuranate precipitation point by the slow addition of ammonium hydroxide. The precipitate formed is subsequently dissolved in the minimum quantity of hydrochloric acid. As an alternate method, a citrate buffer may be used to adjust the acidity to a pH range of 2.5-5.0. Readings are made at 510 millimicrons with a slit width of 0.02 millimeter. The color produced is stable and is not dependent on the pH of the solution over the pH range 2-9.

B. Precautions and Principles

An excellent article giving the interferences will be found in the discussion of Fortune and Mellon(1) and therefore the interferences will not be detailed in this procedure. Briefly, the following ions interfere to varying degrees. Bismuth and silver give precipitates and should be completely absent. Cadmium, mercury and zinc also give precipitates; however, when present in small amounts the interference from these ions can be eliminated by using an excess of 1,10-phenanthroline. Molybdenum, nickel, tungsten, aluminum, beryllium and tin also interfere, but control of pH will in some instances prevent their interference. The major interference from anions was experienced with cyanide, phosphate, dichromate, thiosulfate and nitrite. Methods are suggested for eliminating many of these interferences.(1,5,6,7)

The pH can be adjusted with ammonium hydroxide or hydrochloric acid. However, the use of citrate(7) buffers the solution with greater ease in the pH range 2.5-5.0. It is important when using the citrate buffer to add the latter after the addition of the 1,10-phenanthroline and hydroxylamine hydrochloride. The iron method is sensitive and has been used in this laboratory in the range of 5-300 micrograms per 50 ml (0.1-6 ppm). Six milliliters of a 0.1% aqueous solution of the reagent are required to produce the maximum color with 5.0 ppm of iron. Hydroxylamine hydrochloride has been found to be the most satisfactory reductant and one-tenth milliliter is required to reduce 50 micrograms of iron completely from the ferric to the ferrous state. The absorbance of the complex formed was measured on the Beckman Model DU Spectrophotometer at 510 millimicrons with a 0.02 millimeter slit width. The color reaction conforms to Beer's law over the entire range studied and is stable over a period of months. The interference from uranium is negligible when the sample is compared to a blank containing the same uranium concentration.

II. REAGENTS

Ammonium hydroxide, 6M
1,10-Phenanthroline, 0.1% aqueous solution. It may be necessary to heat solution to 80°C to completely dissolve this reagent.
Hydroxylamine hydrochloride, 10% aqueous solution
Standard iron solution, prepared from electrolytic iron.
Electrolytic iron
Hydrochloric acid, concentrated, reagent grade

NOTE: All water used in solution make-up as well as the reagents should be iron free.

III. PREPARATION OF SAMPLE

This method has been used for the most part to determine iron impurities, and small amounts of any of the mineral acids used in the various dissolution procedures do not interfere. In most cases iron impurities have been neglected inasmuch as the quantity generally found is so much smaller than the inherent errors of the methods used in determination of the alloy composition.

IV. PROCEDURE

1. Add sample containing from 20-200 micrograms of iron to a 50-ml volumetric flask. Add 1 ml of a 10% solution of hydroxylamine hydrochloride and 10 ml of 0.1% 1,10-phenanthroline solution and shake well.

2. Adjust pH by the slow addition of 6M ammonium hydroxide until the precipitation point is reached; then add hydrochloric acid dropwise with swirling until the precipitate dissolves.

3. Wash sides of container with iron-free water from a wash bottle and heat on water bath for 10 minutes. Observe contents of flask for complete solution. Cool and adjust to 50 ml.

4. Read absorbance at 510 millimicrons with a slit width of 0.02 millimeters. Refer to reference curve for iron concentration.

5. A reagent blank may be run and compared with water.

V. CALCULATIONS

$$\frac{\text{Weight of Iron Found x Volume Factor}}{\text{Weight of Sample}} \times 100 = \%\ \text{Fe}$$

In case of impure reagents the following correction should be made:

$$\frac{\text{(Wt. of Iron Found-Wt. of Iron in Reagents) x Volume Factor}}{\text{Weight of Sample}} \times 100 = \%\ \text{Fe}$$

VI. REFERENCES

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PROCEDURE 17: THE SPECTROCHEMICAL ANALYSIS OF HEAVY ELEMENTS

All spectrographic analyses of materials are carried out by the Analytical Group of the Chemistry Division. The procedure used for the determination of impurities in uranium oxide involves the carrier distillation method. Since this has been described by Scribner and Mullin(1) and also by Nachtrieb,(2) attention will be given here only to certain important details.

All samples are determined as the oxide. Uranium metal is converted to the oxide by igniting with a Meeker blast burner for forty-five minutes. Solutions are taken to dryness and ignited for two hours in a similar manner. Twenty-five milligrams of uranium oxide are ground with an agate mortar and pestle with two and one-half milligrams of pure gallium oxide. The sample is placed in the 5/32" diameter by 1/4" deep crater of a pedestal type graphite electrode. The sample is burned in the direct current arc with a 4-mm electrode gap at 12 amp with an exposure time of 5-40 seconds. The Bausch and Lomb spectrograph is used to record the spectrum, photographically. For the ultra-violet, SA #1 plates are used; I-N plates for the red. Plates are developed in D-19 developer under carefully controlled conditions of temperature and agitation. After drying the plates, the sample spectra are compared, visually, with the spectra of previously prepared standards. The standards are prepared by grinding known amounts of impurities with pure uranium oxide. These are exposed in the same manner as the samples to provide a standard plate for comparison. The lower limits for the various elements are given in Table I. The average deviation for the visual comparison precedure is ± 20% with a maximum deviation of a factor of 2.

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Table I

LOWER LIMITS FOR URANIUM OXIDE STANDARDS
(M.L. 79 and M.L. 80)

Element	Lower Limit
Fe	2 PPM*
B	0.1 PPM
Si	10 PPM*
P	20 PPM
Mn	0.2 PPM
Sb	2 PPM
Pb	1 PPM
Sn	5 PPM*
As	10 PPM
Mg	0.5 PPM
Be	0.5 PPM
Cr	1 PPM
Ag	1 PPM
Zn	20 PPM
Ni	5 PPM
Co	5 PPM
Al	5 PPM
Ca	20 PPM
Na	1 PPM
Li	1 PPM
K	20 PPM
Bi	2 PPM
Ti	50 PPM
Mo	20 PPM
Cu	1 PPM
Cd	Not investigated

* Sensitivity limited by residual impurities in electrodes or carrier material.

PROCEDURE 18: ISOTOPIC DETERMINATION BY THE MASS SPECTROMETER

I. INTRODUCTION

A mass spectrometer using a surface ionization type source(1, 2) is used in determining the isotopic composition of uranium and plutonium. The method is sensitive and contaminating activities at other masses do not interfere as they might with counting methods. The efficient source allows the use of very small samples. The method is absolute and there is not the memory effect of gas instruments, so the entire composition range can be covered with a single instrument. The sample preparation is simple and the time required for an analysis is relatively small.

A large number of variations in the arrangement and design of the instrument and the electronic controls are possible. For this reason the details of this report are restricted to operations of general application.

II. DESCRIPTION OF THE APPARATUS(3)

The mass spectrometer used for this work is a 60° sector type, built on a twelve-inch radius of curvature. The positive ions are emitted directly from a heated filament by surface ionization and accelerated through a potential of up to 10,000 volts. The ion beam is separated into its isotopic components by a magnetic field. The magnetic field is adjusted so that one particular mass is brought to focus on a slit in the collector end. The mass which is focused on the slit is a function of the accelerating potential and the magnetic field strength. By continuously changing the magnet current, the different isotopes are made to pass, one after another over the slit. The ions passing through the slit strike a collector and cause an electric current to flow. The voltage developed by this current passing through a high resistance is amplified and applied to the leads of a recording potentiometer. The deflection of the potentiometer is directly proportional to the number of ions striking the collector which, in turn, is directly proportional to the number of atoms of that isotopic mass in the sample on the filament.

III. PREPARATION OF SAMPLES

A. Pure Uranium Samples

1. Pure uranium samples in the form of metal turnings or chips or uranium oxide are dissolved in concentrated nitric acid. This solution is then diluted to a concentration of about 5 mg of metal per cc. A drop or two of dilute ammonia aids in giving a uniform deposit on the filament.

2. A large bulk of uranium metal can be sampled by placing a drop of concentrated nitric acid or aqua regia on the surface. This drop is picked up, after reacting with the metal, with a micropipet and the spot on the metal washed with water a number of times.

B. Uranium Alloys

Uranium which is in the form of an alloy must first be separated from the other elements before a satisfactory load can be made. This can be accomplished by an ether extraction method, outlined as follows:

1. Dissolve sample, calculated to contain about 10 mg of uranium, in nitric acid. If sample proves difficult to dissolve, transfer to a plastic test tube and add several drops of hydrofluoric acid. Make certain that there is some excess of HNO_3.
2. Add a small quantity of $Al(NO_3)_3$ crystals as a salting-out agent and to complex the excess fluorine when hydrofluoric acid has been used.
3. Add 25-50 cc of ethyl ether and shake for a few minutes.
4. Decant the ether into another vessel, being careful not to take any of the aqueous layer.
5. Add a small amount of distilled water and evaporate the ether.
6. Add a few drops of ammonia and dilute to a concentration of about 5 mg of uranium per cc.

C. Plutonium Samples

Plutonium samples are submitted as a dry nitrate. The total amount of plutonium must be between about 1 and 100 micrograms.

IV. LOADING SAMPLES

A filament is made in a jig by spot welding a short length (about 15 mm) of 0.030" x 0.001" tantalum ribbon to the wire leads of two Kovar seals. The ribbon is bent in two places so that the leads are parallel to each other and about 8 mm apart. The Kovars are mounted in a filament support. The filament support is attached to a slit plate, identical to the one in the instrument source, and the filament position is adjusted so that the flat 0.030" x 8 mm portion of the ribbon lies approximately in the center of the slit and the top surface of the filament is just below the surface of the plate.

A pipet with a capacity of about 10 microliters is made by drawing a piece of 6-mm pyrex tubing down to a fine capillary and calibrated by comparison with a standard 10-microliter pipet. These pipets will then deliver 50 micrograms of uranium in a solution containing 5 mg of uranium per cc. They are used only once to prevent contamination. The standard load on the filament for plutonium is 20 micrograms, since the surface ionization of plutonium is about 2.5 times more efficient than uranium.

The filament and support are mounted under a heat lamp in a Type HD hood, the distance from the lamp is not extremely critical but about one inch is satisfactory. A 0-6 volt AC Variac controlled power supply is connected across the filament and the voltage adjusted until the current through the filament is about 1.5 amp. Only a Type HD hood equipped with a glove panel can be used when loading plutonium.

A 10-microliter portion of the sample is taken in a pipet and applied dropwise to the heated filament. Each drop is allowed to dry before the next is added. Under ideal conditions, the sample will remain in the center portion of the filament. After evaporating to dryness at 1.5 amp the current is increased to 2-2.5 amp and the sample changes to an orange uranium oxide.

V. RUNNING THE INSTRUMENT

The vacuum system of the mass spectrometer is vented with dry helium through a needle valve in the source section. This must be done slowly to prevent mercury vapor from the hot pumps from being swept into other sections of the instrument. The source assembly is removed. The filament support is located on the high voltage plate by two dowels and held in position with two screws.

When plutonium samples are to be analyzed, the source section of the mass spectrometer is encased in a special draft hood which is connected to a properly filtered exhaust system. No part of the instrument which might possibly become contaminated is touched except with rubber gloves.

After the source section has been replaced, the pumps are started and allowed to pump until the pressure in the analyzer section is less than about 6×10^{-7} mm Hg and the source about 2×10^{-6} mm Hg.

The electronic supplies are turned on and the accelerating voltage and magnetic field adjusted to the desired mass range.

The filament voltage is increased in about 5-volt steps on the primary of the Variac until the filament current is about 2.5 amp; then increase by 2-volt steps. Normal operating current is 2.8-3.0 amp. A sample is usually used up soon after the current reaches above 3 amp. After each increase, a scan is made over the mass range under observation.

Sometimes the first peaks to be recorded will have pointed tops and broad tapering zeros on each side and the intensity will drop rapidly with time. These are ions formed by a tertiary process. As the filament current is increased, direct surface ionization of the sample will result. These ions will have square-shaped peaks with flat tops and relatively sharp cut-offs at the sides. At this point, the drawing-out and focussing potentials are adjusted for maximum intensity.

The filament current is increased to such a value that the deflection produced by the rarest isotope is capable of being read with the desired accuracy. The deflection of the larger peaks can be reduced by factors of 2, 5, 10, 20, 50, 100, or 200 with the amplifier sensitivity control.

Ten to twenty scans of the complete spectrum should be made for a good analysis. As many as possible should be made without changing the filament voltage and at as high an intensity as possible. The intensities are usually quite steady with only a slight increase or decrease with time.

VI. CALCULATIONS

Allowance is made for a drift in intensity by assuming that these changes are linear. A straight line is drawn on the chart between successive peaks of one of the isotopes and interpolation is used as the basis for analysis. The deflection of each of the other peaks is determined by subtracting the zero level recording from the reading at the top of the peak. The deflection of the reference peak is determined by subtracting the zero level reading from the reading of the straight line at a point directly above the peak. A minimum of 10-12 sets of readings are taken for each isotope present. Each reading must be multiplied by the corresponding amplifier sensitivity factor and the calibration correction, if any, for the sensitivity scale on which it was recorded. These corrections are determined by accurate voltages applied in the negative feedback loop of the amplifier using a precision potentiometer such as the Leeds and Northrup, Type K.

The ratio of each isotope peak to the reference peak is taken and the ten or more such values are averaged.

A small correction for secondary electrons must be made to the ratios. The need for this correction arises from the fact that secondary electrons resulting from ions hitting the collector are not suppressed but are drawn away in order to augument the ion signal. About two electrons are emitted from the collector for each ion which strikes it, the exact number varying directly with the velocity of the ion or, as all of the energies are the same, inversely as the square root of the mass of the ion. Under normal conditions of operation, about two-thirds of the total signal is due to these secondary electrons. Each ratio is corrected then by the equation:

$$R_1 \text{ (correct)} = \left[\frac{R_1}{3} + \frac{2R_1}{3}\sqrt{\frac{m_1}{m_0}}\right] = R\left[1/3 + \frac{2}{3}\sqrt{\frac{m_1}{m_0}}\right]$$

where R_1 is the ratio previously calculated of $\frac{m_1}{m_0}$

m_1 is the mass of the ions under observation, and
m_0 is the mass of the reference ion.

The corrected ratios are summed (note that the ratio for the reference peak is always unity) and normalized to 100.00. These figures are the mole percentage composition of the samples.

Conversion to weight percentages is made in the usual way by multiplying each mole percentage by the corresponding atomic weight and normalizing the sum to 100.00%.

VII. ERRORS

The main source of error is due to the variation of emission of ions from the filament. Since the isotopes are measured at different times it is necessary to determine ratios by interpolation. By taking the average of a sufficient number of these values (about ten) this source of error is minimized. The average deviation of these individual ratios from the mean is a measure of the precision or reproducibility of this type of analysis. On the basis of the analysis of normal uranium and other samples of known isotopic composition the results obtained by this method are within 1% of the true absolute isotopic composition. The precision error described above is therefore taken to be the absolute error or accuracy of the measurement if it is greater than 1% of the ratio. However, if the precision is less than 1% and since there is no basis for knowing how absolute this method is below 1%, the error in such a measurement is reported as 1%. In most analyses the precision error is less than 1%.

VIII. MODIFICATIONS

A. Vacuum Lock Source(4)

If a vacuum lock is incorporated in the source section, and the samples introduced into the instrument by this means, the pumping time required to reach operating vacuums can be reduced from about 2-3 hours to 15-20 minutes.

B. Multiple Filament Source(5)

With the multiple filament source, atoms which are vaporized without ionization strike another filament maintained at about 2500°C where they are ionized. This gives much more efficient ionization and allows the use of smaller samples. A second advantage of this source is that metal ions predominate rather than oxide ions. This removes the necessity of correcting for O^{17} and O^{18} when analyzing a sample containing a small amount of one isotope in the presence of a large peak, one or two mass units lower.

C. Electron Multipliers

The signal resulting from the ion beam can be enhanced by a large factor (10^3 to 10^6) by the use of an electron multiplier.

D. Ratio Recording(6)

A grid with a transmission of about 50% can be placed before the slit in the collector section. The ions striking this grid give a signal which can be used as a monitor of the ion emission over a limited mass range from the filament. This signal is a more accurate reference for obtaining ratios than the values obtained by interpolating between successive peaks of one of the isotopes.

IX. REFERENCES

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2. M. G. Inghram & R. J. Hayden, "A Handbook on Mass Spectrometry," National Academy of Sciences, National Research Council publication 311.

3. C. M. Stevens & M. G. Inghram, Ap. 1954, 12 p Contract W-31-109-eng. 38 (ANL-5251).

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5. M. G. Inghram & Wm. A. Chupka, Rev. Sci. Inst. 24, 518, (1953).

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PROCEDURE 19: BALANCE TESTING PROCEDURE

There are several analytical balances in use by the Special Materials Division. The maximum capacity of these balances ranges from 200 grams to 4-1/2 kilograms. The sensitivity, which is a measure of a noticeable deflection of the beam from equilibrium due to a change in weight, varies with the style and purpose of the balance. The range of sensitivity for the 200-gram capacity balances is 0.025 mg to 0.1 mg. The 4-1/2 kilogram balances have a sensitivity of 1 mg. There is an additional balance, called a metrogram balance, within the Division which has a range from a few milligrams to ten kilograms.

These balances are used for various purposes. First, the analytical balances of 0.025-mg sensitivity are set aside to be used as a standard. Second, the balances having a sensitivity of 0.05 mg to 0.1 mg are used in normal analytical procedures. Third, there are three Gramatic balances used in general for routine weighings where accuracy and precision give way to speed. Fourth, the large two kilogram and 4-1/2 kilogram balances have multiple purposes; as an example, it may be used for its large capacity, mainly, or a combination of its capacity along with its good sensitivity.

The analytical balances are inspected, cleaned, adjusted, performance tested, and the beam and chain or other weight-carrying devices calibrated at four-month intervals.

The procedure used in the report is as follows: a general performance check is run and then compared to the performance of an earlier date. The balance is then taken apart and, piece by piece, laid out and cleaned. As the cleaning progresses (as given in the report sheet) an inspection of each part is made. The balance is then reassembled and adjustments made according to the procedure used in the testing of the balance performance.

The calibration of the beam and chain, or other weight device used, is made against a Class "S" set of weights certified by the Bureau of Standards. These weights are, in turn, once a year calibrated against a Class "M" set of weights certified by the Bureau of Standards.

The analytical weights used for the balances are calibrated by the method of substitution using the Class "S" certified (by the Bureau of Standards) weights.

The Outline Followed in the Report on the Condition of an Analytical Balance

Description of Balance

A. Manufacturer
B. Model
C. Serial
D. Type
E. Style
F. Capacity
G. ANL Number
H. Other

Maintenance Procedure

A. Cleaning and Inspection
    1. Materials Used:

        a. Soft hair brush
        b. Chamois skin
        c. CCl_4

    2. Case
    3. Rider mechanism
    4. Pan arrestment
    5. Damper arrestment
    6. Beam arrestment
    7. Beam table
    8. Beam
    9. Stirrups
    10. Pans
    11. Mechanism for applying weights
    12. Weights
    13. Knife edges
    14. Knife plates

B. Assembly and Adjustments

    1. Inspection

        a. Base plate
        b. Beam arrestment
        c. Beam table
        d. Rider mechanism
        e. Pan arrestment
        f. Beam
        g. Knife edges

- h. Knife plates
- i. Chain
- j. Mechanism for applying weights
- k. Weights attached to balance proper
- l. Damper device

2. Assembly

    - a. Beam
    - b. Stirrups
    - c. Pans
    - d. Rider
    - e. Chain or other weight device
    - f. Damper device

3. Adjustment and replacement of parts

    - a. Beam arrestment
    - b. Beam table position
    - c. Stirrup position
    - d. The knife-to-plate distance in the arrest position
    - e. The rider mechanism
    - f. The chain mechanism and chain or other device used in lieu of the chain weight method
    - g. The pan arrestment

C. Investigation of the Balance Performance and Comparison to the Tolerance Specifications Given by the Manufacturer and/or the Bureau of Standards

1. Sensitivity

    - a. Period of oscillation
    - b. No load
    - c. Full load
    - d. The plane or planes formed by the three knife edges

2. Arm length ratio
3. End load effect

D. Calibration of the Weight Devices Attached to Balance

1. Beam weight device
2. Chain weight device
3. Other weight device

E. Remarks

1. Cleaning
2. Inspection, assembly, and adjustment of parts
3. Investigation of the balance performance and comparison to the tolerance specifications
4. Calibration of the weight devices

F. Recommendations

1. Further adjustments by manufacturer
2. Balance may be used with limitations
3. Balance may be used to the specifications given by the manufacturer

G. Summary

ANALYTICAL BALANCE INSPECTION AND ADJUSTMENT REPORT

Balance Description

Custodian__________
Location __________
Manufacturer __________
Model __________
Serial Number__________
Type__________
Style__________
Capacity__________
ANL Number__________
Other__________

A. Cleaning and Inspection:
1. Beam__________
2. Beam Arrest__________
3. Beam Support __________
4. Knife Edge__________
5. Knife Plates__________
6. Knife-to-Plate Distance__________
7. Stirrup Position__________
8. Rider__________
9. Rider Rod__________
10. Rider Carriage__________
11. Pan__________
12. Pan Arrest__________
13. Damper__________
14. Weights__________
15. Mechanism for Applying Weights__________
16. Other__________

B. Assembly and Adjustment:
1. Beam__________
2. Beam Arrest__________
3. Beam Support__________
4. Knife Edge __________
5. Knife Plates__________
6. Knife-to-Plate Distance __________
7. Stirrup Position__________
8. Rider__________
9. Rider Rod__________
10. Rider Carriage__________
11. Pan__________
12. Pan Arrest__________
13. Damper__________
14. Weights__________
15. Mechanism for Applying Weights__________
16. Other__________

C. Performance:
1. Sensitivity
   a. Period of Oscillation__________
   b. No Load__________
   c. Full Load__________
   d. Knife Line__________
2. Arm Length Ratio__________
3. End Load Effect__________

D. Calibration:
1. Beam__________
2. Chain__________

E. Remarks:__________

F. Recommendations: __________

SPECIAL MATERIALS ANALYTICAL LABORATORY
SIGNATURE__________
DATE__________

PROCEDURE 20: ANALYTICAL WEIGHT CALIBRATION

The analytical weights are calibrated either by the method of substitution or the method of transposition.(1) The latter method is used only for special cases. The weights are calibrated against a standard set of Class "S" weights certified by the Bureau of Standards. This Class "S" set of weights is, in turn, calibrated against a Class "M" set of weights certified by the Bureau of Standards. The Class "M" weights are our primary standards, while the Class "S" set is considered only as a secondary standard.

When either method of calibration is used, balance defects such as arm length and end load effects are either cancelled out or compensated for by calculations.

Calibration of weights using the substitution method of weighing proceeds by either of two steps. First, the weights to be calibrated are compared to a standard weight of like denomination. Second, the weight taken from the set of unknowns is compared to a standard and all other weights to be calibrated are in turn related to this weight. The method used in the department is of the first step.

A tare weight is placed on the left pan which is of the order of denomination of the mass to be determined (W_0) or object weight. The tare weight is counterbalanced by W_0 and a rest point obtained, r_1. The W_0 is replaced by a standard weight, W_S, and a rest point, r_2, recorded. The sensitivity (S) of the balance is determined under the particular load conditions. The sensitivity (S) has the dimensions of divisions/mg. The weight, W_0, is calculated by the equation:

$$W_0 = W_S - \frac{r_1 - r_2}{S}$$

The following relationships are easily interpreted from the equation,

$$r_1 = r_2 \text{ then } \frac{r_1 - r_2}{S} = 0;\ W_0 = W_S$$

$$r_1 > r_2 \text{ then } \frac{r_1 - r_2}{S} \text{ is } > 0;\ W_0 < W_S$$

$$r_1 < r_2 \text{ then } \frac{r_1 - r_2}{S} \text{ is } < 0;\ W_0 > W_S$$

Calibration of weights using the transposition method of weighing is valuable because the precision obtainable is twice as great as in weighing by substitution. The calibration is carried out by placing the object weight,

W_0, on the left pan, and the standard weight, W_S, on the right pan. The rest point is obtained with the weights in this position (r_1). The weights are reversed in position, that is, W_S is placed on the left pan and W_0 on the right pan, and the rest point obtained is r_2.

The sensitivity (S) is determined for the particular load conditions. The following equation may be derived:

$$W_0 = W_S - \frac{r_2 - r_1}{2S}$$

The following relationships may then be interpreted from the equation:

$$r_1 = r_2 \text{ then } \frac{r_2 - r_1}{2S} = 0;\ W_0 = W_S$$

$$r_1 > r_2 \text{ then } \frac{r_2 - r_1}{2S} < 0;\ W_0 > W_S$$

$$r_1 < r_2 \text{ then } \frac{r_2 - r_1}{2S} > 0;\ W_0 < W_S$$

REFERENCE

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