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Controlled-Potential Coulometric and Potentiometric Titrations of Uranium and Plutonium in Ceramic-Type Materials

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CONTROLLED-POTENTIAL COULOMETRIC AND POTENTIOMETRIC TITRATIONS OF URANIUM AND PLUTONIUM IN CERAMIC-TYPE MATERIALS

by

Glenn R. Waterbury, Gilbert B. Nelson, Karl S. Bergstresser,

and Charles F. Metz

ABSTRACT

Accurate and precise measurements of the plutonium and uranium contents of mixed oxide, mixed carbide, and mixed nitride materials are now possible by methods developed for this purpose or by previously existing methods. Chemical separation of the elements before analysis is not necessary. Under optimum conditions for repeated analyses of $(U_xPu_y)O_2$, $(U_xPu_y)C$, and solutions containing high-purity uranium and plutonium, the relative standard deviation and the bias range from 0.03 to 0.14%. For analysis of sintered uranium-plutonium nitrides, the relative standard deviations did not exceed 0.3%. The effects of certain impurities and techniques for eliminating carbonaceous decomposition products were investigated.

INTRODUCTION

The importance in current reactor programs of ceramic-type fuels containing uranium and plutonium prompted an investigation of methods for determining these two metals. Several reliable methods exist for assaying plutonium or uranium individually,[1-3] but few are applicable to analysis of materials containing both elements unless chemical separations are employed. To minimize analysis time we wished to avoid, if possible, preliminary separation of uranium and plutonium. A literature survey indicated that controlled-potential coulometric titrations[1-5] and potentiometric titrations,[1-4, 6, 7] after some modifications, were usable for these measurements without a prior chemical separation. Amperometric titration[8, 9] should also be applicable to the measurement of plutonium without interference from uranium. The titration reaction in the amperometric method is the reduction of plutonium(VI) with iron(II) as in the potentiometric titration.[6] This investigation, however, was limited to controlled-potential coulometric and potentiometric methods.

Assays of ceramic-type materials are complicated by the diversity of their chemical compositions.[4] The atom ratios of uranium to plutonium and of metal to nonmetal often vary in these materials which may contain oxygen, carbon, nitrogen, or some combination of these elements as the nonmetals. In some potential reactor fuels, limited amounts of nonfissionable metals such as iron or chromium are present along with uranium, plutonium, or thorium. Other ceramic fuel materials may contain significant amounts of impurities introduced inadvertently. Such variations were considered during development or modification of the analytical methods. Most of our work, however, dealt with analysis of uranium-plutonium solutions and uranium-plutonium oxides and carbides that contain about three or four times as much uranium as plutonium. Each of the selected methods was applied successfully to analysis of uranium-plutonium oxides, carbides, and nitrides of various compositions.

CAUTION

Because of the toxicity of plutonium, extreme care must be exercised in its handling. Plutonium and plutonium-containing materials must be handled in laboratories designed to adequately protect the analyst. The analyst must take every precaution to avoid inhaling or ingesting plutonium. All work with solid plutonium must be done in a glovebox. Dissolved plutonium solutions may be handled in a fume hood or glovebox with the gloves removed.

DISSOLUTION OF SAMPLES

Most of the carbide ceramic materials investigated contained uranium and plutonium in the ratio of 4:1. Such samples dissolved in a reasonable time in hot, concentrated nitric acid. This method of dissolution caused the formation of some relatively stable organic products which, at times, interfered in the electrometric titrations. Therefore, a prolonged treatment with boiling perchloric acid was added to the dissolution procedure.

If the uranium-plutonium carbide material also contained free carbon, it was advantageous to ignite these samples in a platinum crucible at approximately 700°C for several hours. Unannealed material occasionally disintegrated very rapidly during the first stage of heating, apparently because of internal strains, and a covered container was necessary. The oxide residue was dissolved in concentrated nitric acid if the proportion of uranium was relatively high. Addition of a small amount of hydrofluoric acid to the nitric acid accelerated dissolution. Ignition of all carbides to oxides prior to dissolution was preferred to prolonged boiling with perchloric acid.

Nitric-perchloric acid dissolution was not suitable for all refractory reactor-fuel materials. If the ratio of uranium to plutonium was small, or if plutonium was the only major metallic constituent, the dissolution began with addition of hydrochloric acid. This reagent also was used in dissolving some nitride samples. Many high-fired oxide products did not respond to any treatment limited to the temperature obtained from boiling acids. Dissolution of these materials required either the ammonium-hydrogen sulfate fusion procedure, described by Milner,[4] or the sealed-tube dissolution method.[10] Uranium oxide-20% plutonium oxide that had been ignited at 1550°C to form a solid solution dissolved almost completely in hot 15$\underline{M}$ nitric acid during a 2-h treatment, but material of the same composition that had been ignited at 925°C was less soluble.[11] In each case, the residue was dissolved by fuming once or twice with hydrofluoric-nitric-sulfuric acids.

Addition of sulfuric acid was avoided in sample dissolution if any of the dissolved material was taken as an aliquot for potentiometric determination of plutonium[6] because this type of analysis required a sulfate-free solution. It was desirable, however, to dissolve samples in the presence of sulfuric acid if only coulometric measurements followed dissolution. Addition of sulfuric acid restricted most of the oxidation of plutonium to Pu(IV) and thereby avoided the expenditure of time required for coulometric reduction of Pu(VI) to Pu(IV). For coulometric analyses, 200-mg samples were dissolved in several milliliters of concentrated nitric acid and 0.5 ml of concentrated sulfuric acid. After dissolution and removal of organic traces with perchloric acid, the residue of salt and sulfuric acid was dissolved in 15 ml of water. This mixture was transferred and diluted to volume with 0.5$\underline{M}$ sulfuric acid in a 50-ml volumetric flask.

POTENTIOMETRIC METHOD: PLUTONIUM

A potentiometric method for measuring plutonium was selected because of its precision and freedom from interference by uranium and iron. Although various potentiometric methods are available, most require chemical separation of the uranium and plutonium before analysis. The method used here does not require this separation. In this method,[6] a sample containing at least 200 mg of plutonium was fumed strongly with perchloric acid to oxidize the plutonium to the (VI) oxidation state. The plutonium(VI) was reduced to plutonium(IV), or a mixture of plutonium(III) and (IV), by addition of a slight excess of iron(II) solution, and the excess iron(II) and any plutonium(III) were titrated potentiometrically with standardized cerium(IV) sulfate. A platinum-saturated calomel electrode system was used to indicate the endpoint at a potential of + 780 mV.

APPARATUS

Analytical balances, two, 0.01- and 0.1-mg sensitivities.

Fuming apparatus. A multiple-unit electric hot plate with four infrared heat lamps mounted above it. Fumes were swept directly into an exhaust duct that was washed with water from fine spray nozzles.

Gloveboxes. Stainless steel gloveboxes with safety glass windows were used for handling solid samples and plutonium-238 solutions, and similar enclosures with the gloves removed were used for handling other solutions.

Potentiometer, with platinum-saturated calomel electrodes. A Beckman Instruments, Inc., Model G pH meter or its equivalent has been found satisfactory.

Stirrer, magnetic, with plastic-covered stirring bars.

Weight burets, Friedman and LaMer, 60-ml.

REAGENTS

Cerium(IV) sulfate, standard solution (0.05M). Dissolve about 26 g of cerium(IV) bisulfate, $Ce(HSO_4)_4$, in 500 ml of 2M sulfuric acid, filter through a fine sintered-glass filter into a 1-liter bottle, and dilute to volume with water. Mix thoroughly and let stand overnight.

Standardize against alkaline arsenite solution, or sodium oxalate whose use is described here. Dry National Bureau of Standards (NBS) Standard Reference Material (SRM) No. 40g, sodium oxalate, $Na_2C_2O_4$, for 2 h at 105°C and cool in a desiccator. Weigh approximately 500 mg of the dried salt to the nearest 0.01 mg, and transfer quantitatively to a weighed, 100-ml flask. Dissolve the salt in about 50 ml of water, mix thoroughly by swirling, and weigh the flask and solution. Transfer six weighed aliquots of this solution, each containing 80 to 100 mg of sodium oxalate, into separate beakers. Dilute each to about 25 ml, heat to 75 to 80°C and titrate at that temperature with the cerium(IV) sulfate solution. Follow the titration using a potentiometer with platinum-saturated calomel electrodes; the endpoint is at about -850 mV, but varies somewhat. Add the cerium(IV) sulfate solution from a calibrated buret, and approach the endpoint cautiously. Take the total volume at which the largest potential change per increment of titrant is obtained as the endpoint. Calculate the normality of the solution as follows.

$$\text{Cerium(IV) Sulfate Normality} = \left[\frac{\text{mg of } Na_2C_2O_4 \text{ in aliquot}}{(67.000)(\text{ml of } Ce(HSO_4)_4 \text{ solution})}\right] . \quad (1)$$

Hydrochloric acid, 12M, specific gravity 1.18.

Hydrochloric acid, 6M.

Hydrofluoric acid (1M). Dilute 1 volume of 36% hydrofluoric acid (HF) with 35 volumes of water.

Iron(II) sulfate, standard solution (0.5 to 0.7M). Dissolve 200 g of iron(II) ammonium sulfate $[FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O]$ in 250 ml of 2M sulfuric acid and dilute to 1 liter with water. Bubble nitrogen through the solution for at least 4 h to remove oxygen, and store the solution in a glass-stoppered bottle. Standardize daily or immediately before use against NBS SRM No. 136b, potassium dichromate, $K_2Cr_2O_7$; or NBS SRM No. 949b, plutonium metal.

If $K_2Cr_2O_7$ is the standard, dry the salt at 120°C, cool it in a desiccator, and accurately weigh at least 2 g into a weighed flask. Dissolve the salt in 50 to 100 ml of water, mix the solution thoroughly, reweigh the flask, and transfer weighed aliquots of the solution containing about 200 mg of $K_2Cr_2O_7$ to 250-ml tall-form beakers. Insert the platinum-calomel electrodes of the potentiometer, stir the solution mechanically, and slowly add iron(II) sulfate solution from a weight buret. Watch the meter fluctuations which warn of near approach to the endpoint, and stop the addition when a large potential change shows the first presence of excess iron (II). Reweigh the buret. Titrate the excess iron (II) sulfate solution with cerium(IV) sulfate solution added from a microburet. Take the endpoint in this titration as the volume at which the potential change per unit increment of titrant added is the greatest. Add the milliequivalents (meq) of cerium (IV) sulfate solution to the meq of $K_2Cr_2O_7$ used and divide by the grams of iron(II) sulfate solution to obtain meq per gram of solution. Multiply this quotient by one-half of the atomic weight of the plutonium in the sample to obtain milligrams of plutonium per gram of iron(II) sulfate solution.

Fe(II) solution, meq/g

$$= \left[\frac{(\text{ml of Ce(HSO}_4)_4\text{ solution})\ (N) + (\text{mg of } K_2Cr_2O_7 \text{ in aliquot}/49.032)}{\text{g of Fe(II) solution}}\right] . \tag{2}$$

Mg of Pu/g of Fe(II) solution

$$= (\text{Fe(II) solution, meq/g})(A_p/2), \tag{3}$$

where A_p is the appropriate atomic weight of the plutonium as determined by isotopic analysis. Note that the equivalent weight of $K_2Cr_2O_7$ is one-sixth of its molecular weight (294.21/6), and the equivalent weight of plutonium is one-half of its atomic weight in this determination.

For standardization against plutonium metal, use two issue units of SRM No. 949b (about 1 g). Break open each sealed ampoule, dissolve the metal in approximately 10 ml of 6M hydrochloric acid, and wash out the ampoule with this same acid. Add the washings to the solution. Record the weights of plutonium metal given on the ampoule label, and thoroughly mix the solution by swirling it. A high-purity plutonium metal having a reliable impurity analysis may also be used for this purpose. Weigh at least 2 g of the clean metal to + 0.01 mg, dissolve it in 10 ml of 6M hydrochloric acid, and thoroughly mix the solution by swirling it. Weigh aliquots of the solution containing at least 200 mg of plutonium, and analyze each as described under Analysis of Sample. From the titration results and the known concentrations of the cerium(IV) sulfate and the plutonium solutions, calculate the concentration of the iron(II) sulfate solution for each aliquot as follows.

Mg of Pu/g of Fe(II) solution

$$= \left[\frac{(\text{mg Pu}) + (\text{ml Ce(HSO}_4)_4\text{ solution})\ (M)\ (A_p/2)}{\text{g of Fe(II) solution}}\right], \tag{4}$$

where A_p is the appropriate atomic weight of plutonium.

Nitric acid, 15.6M, specific gravity 1.42.

Nitric acid, (1:3). Dilute 1 volume of 15.6M nitric acid with 3 volumes of water.

Perchloric acid, (70%) reagent grade.

Plutonium metal, high-purity, NBS SRM No. 949b.

Potassium dichromate, NBS SRM No. 136b.

Sulfuric acid, 2M. Dilute 1 volume of sulfuric acid (H_2SO_4), specific gravity 1.84, with 8 volumes of water.

Sulfuric acid, 0.5M. Dilute 1 volume of 2M H_2SO_4 with 3 volumes of water.

Sulfuric acid, (1:1). Dilute 1 volume of H_2SO_4, specific gravity 1.84, with 1 volume of water.

Sulfuric acid, 18M, specific gravity 1.84.

SAMPLING

Take a 4- to 5-g sample, if available, to provide adequate material for repeated determinations of total uranium plus plutonium, precise determination of plutonium, and the coulometric titrations. For a single determination of plutonium only, the sample must contain at least 200 mg of plutonium. Carefully inspect the sample and remove any foreign material such as lint. Weigh the sample accurately and dissolve it as described below.

DISSOLUTION OF SAMPLE

Uranium-Plutonium Dioxides. Dissolve uranium-plutonium dioxides in hot 15.6M nitric acid containing a trace of hydrofluoric acid. Avoid using sulfuric acid because it interferes.

Uranium-Plutonium Carbides. Ignite uranium-plutonium carbide samples that contain more uranium than plutonium in covered platinum crucibles at 900°C overnight in air. Dissolve the mixed oxide product in hot 15.6M nitric acid containing a trace of hydrofluoric acid. Avoid using sulfuric acid.

Uranium-Plutonium Nitrides. Dissolve uranium-plutonium nitrides in hydrochloric acid, add nitric acid, and evaporate the solution to incipient dryness. Repeat the evaporation with nitric acid to convert the solution quantitatively to nitrate. Avoid use of sulfuric acid.

For other types of samples, use appropriate acids or fusions described elsewhere,[1-4, 8] or use the sealed-tube method.[10]

ANALYSIS OF SAMPLE

1. Transfer the prepared solution to a weight buret, and accurately weigh out three aliquots containing at least 200 mg of plutonium into 250-ml tall-form beakers with Fisher Scientific Company Speedyvap or ribbed watch-glass covers.

2. Evaporate the aliquots to near-dryness using heat lamps and low heat from a hot plate. Allow the beakers to cool, and wash down their walls with a little water and 5 to 10 ml of 70% perchloric acid. (If organic material exists in the solution, use 6M nitric acid instead of water to wash down the beaker walls.)

3. Evaporate the solutions to strong fumes of perchloric acid, allow the beakers to cool, add small amounts of water and perchloric acid, and evaporate the solutions again until the final volume is 2 to 3 ml. (Do not evaporate to dryness, or low results will be obtained. If the beakers do approach dryness, add nitric acid and a small amount of 1M hydrofluoric acid and heat. When solution is complete, start again at Step 2.)

4. Remove the beaker from the hot plate, immediately cool it rapidly to below 100°C by placing it on a cool metal surface, and then immediately dilute the solution with about 50 ml of water.

5. Insert the potentiometer electrodes in the solution, stir, and add 10 ml of H_2SO_4 (1:1). Weigh the buret containing the iron(II) sulfate solution, then add the reagent until the potentiometer shows a large potential change. Keep the excess iron(II) solution minimal. Reweigh the buret.

6. Add cerium(IV) sulfate solution from a microburet until a large potential change indicates the endpoint. Titration to a predetermined potential (about -780 mV) or to the maximum potential change per increment of cerium(IV) sulfate solution added are satisfactory methods of determining the endpoint.

7. (a) Calculate the grams of iron(II) sulfate solution equivalent to the volume of cerium(IV) sulfate added in the back titration as follows.

Equivalent g of Fe(II) solution

$$= \left[\frac{(\text{ml of Ce(HSO}_4)_4\text{ solution) } (\underline{M})}{\text{meq/g of Fe(II) solution}}\right] . \qquad (5)$$

(b) Subtract this calculated weight of iron(II) sulfate solution from the grams added in the titration to obtain the net weight of iron(II) solution used.

(c) Calculate the plutonium concentrations as follows.

$$\%\ \text{Pu} = \left[\frac{(\text{net g of Fe(II) solution}) (\text{mg of Pu/g of Fe(II) solution}) (100)}{\text{mg of sample in aliquot}}\right] . \qquad (6)$$

POTENTIOMETRIC METHOD: URANIUM

A method[7] for titrating uranium in the absence of plutonium was adapted to the determination of total uranium and plutonium. A solution containing about 250 mg total uranium and plutonium in 3M hydrochloric acid-3M sulfuric acid was passed through a lead reductor to reduce the uranium to its (IV) oxidation state and the plutonium to its (III) oxidation state. The effluent solution was collected in a receiver beaker containing about 80% of the calculated quantity of standardized cerium(IV) solution to oxidize the reduced ions. Iron(III) solution was added to oxidize the remaining uranium(IV), and the iron(II) formed and the plutonium(III) were titrated potentiometrically with standardized cerium(IV) solution. Platinum-saturated calomel electrodes were used to indicate the endpoint at a potential of + 800 to + 850 mV. From this measurement of the total uranium and plutonium, and the results obtained separately for plutonium, the amount of uranium was calculated.

APPARATUS

The analytical balances, fuming apparatus, potentiometer, stirrer, and weight burets described under Potentiometric Method: Plutonium, Apparatus, are used in this method also. Additional apparatus includes the following.

Analytical balance, 2-kg capacity, 1-mg sensitivity.

Lead reductor, borosilicate glass, heavy-walled, having a 5-cm-high, approximately 4.5-cm-diam reservoir on top; a 20-cm-long, 2.5-cm-diam column; and a 3-mm-bore Teflon stopcock with a 12-cm-long, 10-mm-diam tip. A small glass wool plug retains the reagent grade granular lead that fills the column to a depth of 15 cm. The column is filled with 0.1M hydrochloric acid when not in use. Occasional high and erratic reagent blanks in the potentiometric titration of uranium usually were reduced by washing the reductor with 12M hydrochloric acid, followed by 0.8M hydrochloric acid and copious amounts of water. Otherwise, the granular lead was replaced and the washing operation was repeated. The lead in the reductor was covered with 0.1M hydrochloric acid when not in use. Reagent blanks were determined prior to each set of analyses to detect deterioration of the reductor.

REAGENTS

The 0.05M cerium(IV) sulfate standard, hydrochloric acid (1.18 specific gravity), 1M hydrofluoric acid, and 0.5M sulfuric acid described under Potentiometric Method: Plutonium, Reagents, are used in this method also. Other reagents needed are as follows.

Ferroin indicator, 0.025M solution. Dissolve 0.98 g of ferrous ammonium sulfate $[Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O]$ and 1.487 g of 1,10 phenanthroline in 100 ml of water.

Hydrochloric acid, distilled from borosilicate glassware, 6M.

Hydrochloric acid, 0.8M. Dilute 83 ml of 6M hydrochloric acid to 500 ml with water.

Iron(III) sulfate, 0.5M, dissolve 482 g of ferric ammonium sulfate, $[Fe(NH_4)(SO_4)_2 \cdot 12H_2O]$, in 0.5 M sulfuric acid. Add about 0.5 g of ammonium peroxydisulfate, $[(NH_4)_2S_2O_8]$, to the solution, heat to boiling, cool, and dilute to 2 liters with 0.5 M sulfuric acid.

Lead, granular, analytical reagent.

Nitric acid, 15.6M analytical reagent.

Osmium catalyst solution, 0.05M. Dissolve 0.5 g of osmic acid in 40 ml of 0.5M sodium hydroxide.

Sodium hydroxide, 0.5M. Dissolve 2 g of NaOH in 100 ml of distilled water.

Sulfuric acid, 9M. Redistill reagent-grade acid from fused-silica ware, and dilute distillate 1:1 with distilled water.

Uranium standard solution. Dissolve NBS SRM No. 950a, U_3O_8, or high-purity uranium metal that has been polished to remove surface contamination, in nitric or nitric and hydrofluoric acids. Add a few milliliters of 9M sulfuric acid and fume the solution to dryness. Dissolve the residue in 0.5M sulfuric acid, and weigh solution. Take weighed aliquots containing 250 mg of uranium for analysis.

SAMPLING AND DISSOLUTION

Take a 4- to 5-g sample, if available, to provide adequate material for repeated determinations of total uranium plus plutonium, for precise determination of plutonium, and for the coulometric titrations. For a single determination of uranium plus plutonium, the sample must contain between 200 and 250 mg of uranium. Carefully inspect the sample and remove any foreign material such as lint. Weigh the sample to the nearest 0.1 mg and dissolve it as described under Potentiometric Method: Plutonium, Dissolution of Sample.

ANALYSIS OF SAMPLE

1. Wash the lead reductor with 100 ml of 12M hydrochloric acid, 200 ml of 0.8M hydrochloric acid, and 400 ml of distilled water, in that order, at no time allowing the lead to come in contact with air.

2. Place a 400-ml beaker containing about 50 ml of distilled water under the lead reductor with the reductor delivery tip about 3 mm from the bottom of the beaker. Pass a blank solution, containing 25 ml of distilled water, 30 ml of 6M hydrochloric acid, and 20 ml of 9M sulfuric acid, through the lead reductor at a flow rate of 5 ml/min.

3. Wash the column with three 100-ml portions of 0.8$\underline{M}$ hydrochloric acid, allowing each wash to drain to the top of the lead before adding the next. Drain the last 200 ml of wash solution at a fast flow rate.

4. Fill a weight buret with standardized cerium(IV) sulfate solution and weigh to the nearest 0.1 mg. Insert the platinum-saturated calomel electrode tips into the solution.

5. Add 2 ml of 0.5$\underline{M}$ iron(III) sulfate to the reagent blank solution, immediately start stirring, and titrate with the cerium(IV) sulfate. (Only 1 or 2 drops of the titrant are required to increase the potential of + 850 mV which is taken as the indication of the endpoint.)

6. Reweigh the weight buret, and wash the lead reductor with 400 ml of distilled water to remove lead sulfate after each reduction.

7. If more than 50 mg of ceric sulfate solution is required for the blank titration, repeat Steps 1 through 6 until the blank is reduced to the normal level.

8. Weigh to the nearest 0.1 mg three aliquots, each containing about 250 mg of uranium from the prepared solution of the ceramic material, and three from the uranium standard solution. Place each aliquot in a 100-ml beaker, add 5 ml of 9$\underline{M}$ sulfuric acid, and fume the solutions to dryness on the hot plate under infrared heat lamps.

9. Dissolve each residue in 25 ml of distilled water, and add 30 ml of 6$\underline{M}$ hydrochloric acid and 20 ml of 9$\underline{M}$ sulfuric acid.

10. From the preweighed weight buret containing standardized cerium(IV) sulfate solution, weigh out an aliquot containing approximately 80% of the cerium(IV) needed for titration of the sample, and place the aliquot in a 400-ml beaker.

11. Place the beaker under the reductor column so that the tip is under the cerium(IV) solution surface to prevent air oxidation of the reduced uranium(IV) and plutonium(III).

12. Pass the sample solution through the lead reductor at a flow rate of 5 ml/min, and wash the reductor with three 100-ml portions of 0.8$\underline{M}$ hydrochloric acid.

13. Add 2 ml of 0.5$\underline{M}$ iron(III) sulfate solution, start the magnetic stirrer, insert the electrodes, and continue the titration by carefully adding cerium(IV) sulfate solution from the weight buret until a potential of + 850 mV is attained. Reweigh the buret.

14. Repeat Steps 10 through 13 for each of the six solutions. Calculate the uranium recovery factor, U_{RF}, from the titrations of the uranium standard solutions in the following manner.

$$U_{RF} = \frac{(W_s - W_b)(M)\ (A_{su})}{(U\ \text{taken, mg})\ (2)}\ , \qquad (7)$$

in which

W_s = weight of cerium(IV) sulfate solution for sample, g.

W_b = weight of cerium(IV) sulfate solution for blank, g.

M = meq/g of cerium(IV) sulfate solution.

A_{su} = at. wt of the standard uranium.

15. Calculate the percentage of uranium in the sample as follows.

$$U,\ \% = \frac{\left[(W_s - W_b)M - (1\%\ \text{Pu})(\text{mg of sample})/100\ A_p\right]\ (A_u/2)(100)}{(\text{mg of sample})(U_{RF})}\ , \qquad (8)$$

in which

A_p = at. wt of sample plutonium.

A_u = at. wt of sample uranium.

% Pu is from an independent plutonium assay.

CONTROLLED-POTENTIAL COULOMETRIC METHODS

Controlled-potential coulometric titrations were made initially with an Oak Ridge National Laboratory (ORNL) Model Q-2005 coulometer[12] and later with a transistorized instrument described by Harrar and Behrin.[13] Operating conditions for titrating plutonium were similar to those suggested by Shults.[5] An aliquot containing 6 to 10 mg of plutonium in 10 ml of 1$\underline{N}$ sulfuric acid was analyzed using a cell with a platinum working electrode. The plutonium was reduced to the (III) oxidation state at a potential of + 310 mV relative to a saturated calomel electrode. Completion of this reduction was shown by a decrease in cell current to an almost steady 30 μA. The plutonium(III) was oxidized to plutonium(IV) at + 670 mV until completion of the reaction was again shown by a decrease in cell current to 30 μA. The quantity of plutonium was obtained from the coulombs required for the oxidation. The read-out voltage was measured on a differential voltmeter. On the transistorized instrument, the readout was calibrated directly in milligrams of plutonium.

The method described by Thomason[14] was applied to the measurement of uranium. An aliquot containing 3 to 4 mg of uranium in a volume of 7 ml of 1<u>N</u> sulfuric acid was transferred to a cell having 7 ml of mercury as the working electrode. The cell was swept with argon for 5 min, and a preliminary reduction of reducible ions other than uranium was made at a potential of + 85 mV relative to a saturated calomel electrode. Completion of this preliminary reduction was shown by a decrease in cell current to 50 μA. The uranium(VI) was then reduced to uranium(IV) at a potential of -325 mV relative to the saturated calomel electrode until the cell current again fell to 50 μA. The read-out voltage was then measured on a differential voltmeter. Electrical calibration was used for the plutonium titration, but chemical calibration was preferred for the uranium measurements.

APPARATUS

Battery, Mercury. Burgess Battery/Gould, Inc., mercury activator, 1.35-V or equivalent.

Cells, coulometric titration. The success of all controlled-potential coulometric methods is strongly dependent upon the design of the titrating cells which is, therefore, of the utmost importance. The cells consist of a titration beaker, cover, stirrer, electrodes, and inert gas tube. The 42-mm-o.d., 40-mm-high beaker is fabricated by cutting off the top of a 50-ml borosilicate, low-form beaker and fire-polishing the edge. The cells for titrating plutonium and uranium are similar except in the position of the electrodes (Figs. 1 and 2) and the type of working electrode (Figs. 1, 2, and 3). The tight-fitting Teflon cover (Figs. 1 and 2) has a circular groove for secure retention of a 0.125-in.-wall, 1.687-in.-o.d., Du Pont Viton O-ring. A small laboratory jack forces the titration beaker up against the O-ring, making an air-tight seal.

The stirrer is made from 5.1- to 5.2-mm glass rod by forming a 1.5-cm-diam, 2- to 3-mm-thick disk on the end. The disk is slightly irregular or fluted to improve stirring action. The rod is rotated by an 1800-rpm synchronous motor at the mercury-aqueous interface. Magnetic stirring, which simplifies cell design, also is satisfactory. A 13-mm-long, 8-mm-diam stirring bar is adequate for the uranium titration cell, and a 24-mm-long, 10-mm-diam bar is used in the plutonium titration cell. The flow through the gas tube is approximately 300 cc/min of oxygen-free argon saturated with water vapor.

The counter electrode is a spiral about 1 in. long and 3/16 in. in diameter made from a 6-in. length of No. 18 platinum wire. The spiral is inserted into 0.5<u>M</u> sulfuric acid solution contained in an unfired Corning Glass Works Vycor tube, 45 mm long. The Vycor tube is held about 2 mm above the mercury working electrode by the Teflon cover.

The reference electrode is a micro saturated-calomel electrode similar to a Beckman Instruments, Inc., No. 39270 electrode. It is inserted into 0.5<u>M</u> sulfuric acid solution in an unfired Vycor tube as described above.

The working electrode in the plutonium titration cell (Figs. 1 and 3) is made from a 2.25- by 3.25-in. piece of 45-mesh platinum gauze and a 6-in. length of 0.035-in.-diam platinum wire. The gauze is folded in fourths lengthwise to form the

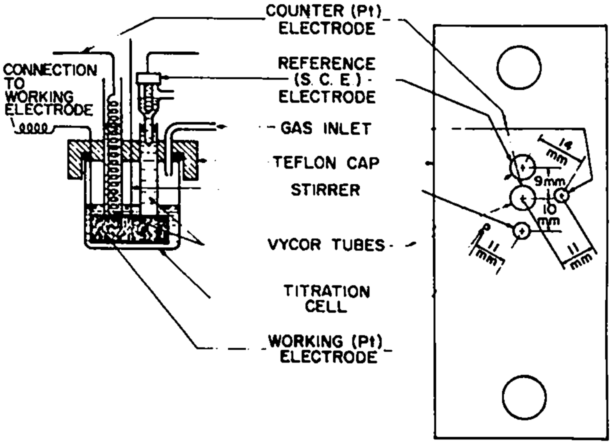

Fig. 1. Plutonium titrating cell and cover.

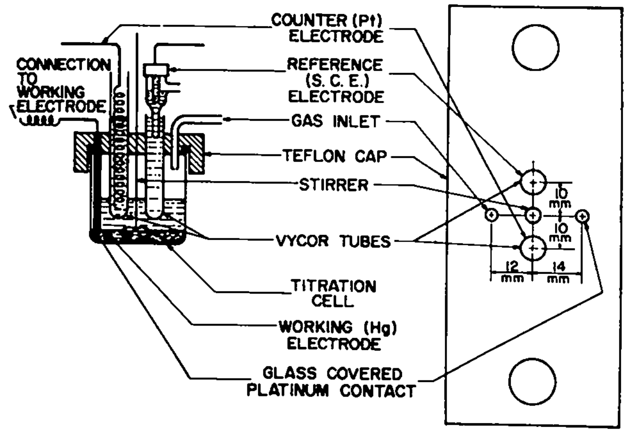

Fig. 2. Uranium titrating cell and cover.

body of the electrode, four layers 0.5 in. wide and 3.25 in. long. The folded gauze is bent around a 1.5-in.-diam mandrel, and a 3.25-in. length of the platinum wire is spot-welded along the top inner edge for reinforcement. A 2.75-in. length of the wire is spot-welded to one end of the folded gauze and to the reinforcing wire to form the upright support and electrical contact. The electrode is stored in 7.8M nitric acid when not in use.

The working electrode of the uranium titration cell is 7 ml of triple-distilled mercury. The mercury is replaced daily or whenever a film or scum is visible on the surface. Electrical contact is made through a platinum wire sheathed in a 4-mm glass tube.

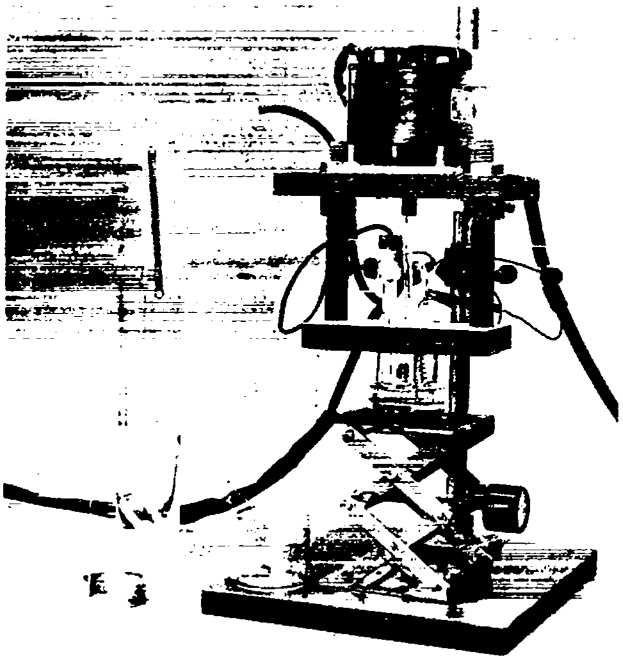

Fig. 3. Controlled-potential coulometric titrating cell and electrodes.

Controlled-potential coulometer. The all-solid-state instrument for controlled-potential electrolysis and coulometry consists of two plug-in modules, a potentiostat and integrator, which are interconnected by wiring in the main frame of the coulometer chassis. The original design was developed by the Lawrence Radiation Laboratory, Livermore, California.[13] The instrument is marketed by the M-T Electronics Company, 536 Lewelling Blvd., San Leandro, California 94579. Other instruments of equal competence may be used. In the initial work, an ORNL Q-2005 Coulometer[12] was used.

Differential voltmeter (DVM). John Fluke Manufacturing Company, Inc., Model 881A or equivalent.

Resistor, Precision. 150-Ω. Calibrated to 0.01 Ω.

Stopwatch, capable of measuring to 0.2 sec.

REAGENTS

Argon, high purity.

Hydrofluoric acid, 28M, reagent grade, 47%.

Mercury, triple-distilled.

Nitric acid, 15.6M, reagent grade.

Nitric acid, 7.8M. Dilute one volume of 15.6M nitric acid with one volume of distilled water.

Plutonium standard solution, prepared by dissolving NBS SRM No. 949b, plutonium metal, or equivalent in hydrochloric acid. After dissolution, 6M sulfuric acid is added and the hydrochloric acid is evaporated from the solution. The solution is then adjusted to a final acidity of 1M, and weighed aliquots containing 5 to 10 mg of plutonium are taken for analysis.

Sulfuric acid, 18M, reagent grade.

Sulfuric acid, 6M and 1M. Prepared by adding 167 or 27.8 ml of 18M sulfuric acid to 800 ml of water and diluting to 1 liter.

Uranium standard solutions, prepared by dissolving NBS SRM No. 950a, uranium oxide or equivalent, or high-purity metal that has been polished to remove surface contamination, in nitric acid. After dissolution, 6M sulfuric acid is added and the nitric acid is evaporated from the solution. The solution is diluted with 1M sulfuric acid, and weighed aliquots containing 3 to 5 mg of uranium are taken for analysis.

Uranium-Plutonium standard solutions, prepared by aliquoting portions of the above standard solutions into a flask and diluting to volume with 1M sulfuric acid.

CALIBRATION OF THE COULOMETER

1. General

Calibration of the all-solid-state coulometer[13] is described here. Either electrical or chemical calibration is satisfactory for plutonium titration, but chemical calibration is recommended for uranium titration. A positive bias as large as 0.1% may occur if electrical calibration is used in the uranium measurements. Although electrical calibration has been found satisfactory for measurement of plutonium with the equipment described here, chemical calibrations are recommended at first and at regular intervals thereafter.

1a. Under all normal conditions, leave the power switch for the potentiostat and integrator modules and the DVM turned on. Have the DVM connected to the integrator readout (front panel) at all times unless otherwise instructed in the section on Electrical Calibration.

1b. Leave the front panel controls set as follows except when other instructions are given under Checkout Procedure, Electrical Calibration, or Chemical Calibration.

Potentiostat Module

Load res. : 27
Range : 1 A
Operating switch : standby
Control pot. : 0
Current limiter : off

Integrator Module

Readout : -
Operating switch : zero

Differential Voltmeter

Range : 1
Null : TVM

1c. Leave the three electrodes disconnected at the drybox terminal of the three-wire cable, except when preparing for chemical calibration. Insert appropriate stabilizing network.

2. Checkout Procedure

2a. Potentiostat Voltage Offset Check. Set the panel controls as follows.

Potentiostat Module

Load res. : 27
Range : 100 μA
Operating switch : standby
Control pot. : 0
Current limiter : off

Integrator Module

Readout : -
Operating switch : zero

Differential Voltmeter

Range : 1
Null : TVM

Turn the operating switch to "check." The meter reading should be less than 1 mV (full scale on the 100-μA range). (If necessary, adjust voltage offset trims of P85AU or P2A amplifiers until reading is less than 1 mV).

2b. Potential Control Check. Set the panel controls as follows.

Potentiostat Module

Load res. : 27
Range : 1 A
Operating switch : standby
Control pot. : -1000 mV
Current limiter : off

Integrator Module

Readout : -
Operating switch : zero

Differential Voltmeter

Range : 10
Null : TVM

Turn the operating switch to "check." Cell current meter should indicate reduction current of 100 mA. Adjust the DVM to -1.000 and turn null to 0.01. Reading on the DVM should be -1.000 ± 0.002. If necessary, very carefully adjust the span at R2 on the rear panel of the potentiostat. Return null to "TVM" and operating switch to "standby." Then repeat the above test after changing control potentiometer to + 1000 mV.

2c. Integrator Bias Check. Set the panel controls as follows.

Potentiostat Module

Load res. : 27
Range : 1 A
Operating switch : standby
Control pot. : 0
Current limiter : off

Integrator Module

Readout : 1.0000
Operating switch : operate

Differential Voltmeter

Range : 1
Null : 0.0001

Use a shorting plug to connect the counter electrode jack to the reference electrode jack on the front panel.

Turn the operating switch to "hold" and determine the drift of the integrator for at least 1 min using the stopwatch. If necessary, very carefully adjust the bias by means of the potentiometer on the front panel of the integrator at the point marked BAL. The drift rate should be less than 10 μV/min and should not differ by more than 50 μV/min when the load resistor is changed among the three positions (0-27-270).

Return the operating switch to "standby" and remove the shorting plug from the jacks.

3. Electrical Calibration

3a. Set the panel controls as follows.

Potentiostat Module

Load res. : 27
Range : 10 mA
Operating switch : standby
Control pot. : 0
Current limiter : off

Integrator Module

Readout : 1.0000
Operating switch : zero

Differential Voltmeter

Range : 10
Null : TVM

3b. Connect the counter electrode to the positive battery terminal and the reference electrode to the negative terminal. Connect the precison 150-Ω resistor to the working electrode and the counter electrode. Remove the plug from the integrator readout and connect it across the precision 150-Ω resistor, with the "hot" (red) lead connected to the working side of the resistor.

3c. Turn the potentiostat operating switch to "operate" and measure the potential across the 150-Ω resistor by turning the null and adjusting knobs to give a zero meter reading. Turn the null back to "TVM," but do not change the potentiostat operating switch. Remove the two-prong plug from its connection with the 150-Ω resistor and reconnect it to the integrator readout.

3d. Using a stopwatch, determine the time required to change the potential reading of the integrator readout from 0.5000 to 20.5000 V. Start this operation by turning the integrator operating switch from "zero" to "operate." After the timing interval, return this operating switch to "zero" and again measure the potential across the 150-Ω resistor.

3e. The average value of the two potential determinations is used in the following calculations.

$$\text{Calibration value (cv), in coulombs/V,} = \frac{v \times t}{R \times \Delta V}, \tag{9}$$

in which

v = average potential across the 150-Ω resistor.
t = time, in sec, from 0.5 to 20.5 V.
R = exact value of 150-Ω resistor.
$\Delta V = 20.5 - 0.5 = 20$ V.

3f. Calculate the setting of the Dial-A-Vider readout, for direct readout in milligrams as follows.

$$\text{DS} = (\text{cv}) \times \text{electrochemical equivalent} \tag{10}$$

where DS = Dial-A-Vider setting for 1 mg = 1 V and electrochemical equivalent is given in milligrams per coulombs as follows.

(EE) electrochemical equivalent

$$= \frac{Aw}{\text{electron change} \times 96.493} , \qquad (11)$$

where Aw = atomic weight of the element analyzed, whether standard or sample uranium, or standard or sample plutonium. The atomic weight should be calculated from a mass spectrometric determination of the isotopic abundance.

3g. Calibration for oxidation is the same except that the battery terminals are reversed.

4. Chemical Calibration, Plutonium.

4a. Insert the proper stabilizing network[13] in rear panel. Rinse the cell and Vycor tubes with 0.5$\underline{M}$ sulfuric acid and quantitatively transfer 5 to 10 mg of plutonium into the titration beaker.

4b. Place the Teflon cover on the beaker and connect the cable from the potentiostat module to the three cell electrodes.

4c. Start the argon gas flowing through the cell and after 5 min set the panel controls as follows.

Potentiostat Module

Load res. : 27
Range : 100 mA
Operating switch : standby
Control pot. : + 310 mV
Current limiter : off

Integrator Module

Readout : DS = (cv) x (EE)
Operating switch : zero

Differential Voltmeter

Range : 10
Null : TVM

4d. Turn the potentiostat operating switch to "operate" and allow the coulometric reduction to continue until the current level has just decreased to a predetermined value (about 30 μA).

4e. Return the operating switch to "standby" and set the panel controls as follows.

Potentiostat Module

Load res. : 27
Range : 100 mA
Operating switch : standby
Control pot. : + 670 mV
Current limiter : on

Integrator Module

Readout : DS = (cv) x (EE)
Operating switch : operate

Differential Voltmeter

Range : 10
Null : TVM

4f. Turn the potentiostat operating switch to "operate" and allow the coulometric oxidation to continue, but restrict the initial current level to about 30 mA using the current limiter.

4g. Discontinue coulometric oxidation when the current has just decreased to 30 μA by changing the potentiostat operating switch to "hold." Switch the DVM null and adjusting knobs to give a zero meter reading and record the read-out voltage (mg of plutonium) from the DVM dial settings.

4h. Change these panel controls in the following order. Change the DVM null to "TVM," the integrator operating switch to "zero," and the potentiostat operating switch to "standby."

4i. Divide DVM reading by the milligrams of standard plutonium added to obtain the recovery factor.

$$\text{Recovery Factor} = \text{DVM reading/mg of Pu.} \qquad (12)$$

5. Chemical Calibration, Uranium

5a. Insert the proper stabilizing network[11] in the rear panel. Rinse the cell and Vycor tubes with 0.5$\underline{M}$ sulfuric acid, add 7 ml of triple-distilled mercury, and quantitatively transfer 3 to 5 mg of uranium into the titration beaker.

5b. Place the Teflon cover on the beaker and connect the cable from the potentiostat module to the three cell electrodes.

5c. Start the argon gas flowing through the cell and after 5 min set the panel controls as follows.

Potentiostat Module

Load res. : 27
Range : 100 mA
Operating switch : standby
Control Pot. : + 85 mV
Current limiter : off

Integrator Module

Readout : DS = (cv) x (EE)
Operating switch : zero

Differential Voltmeter

Range : 10
Null : TVM

5d. Turn the potentiostat operating switch to "operate" and allow the coulometric preliminary reduction to continue until the current level has just decreased to a predetermined value (about 50 μA). The level may be read more easily on the 1-mA range to minimize the effect of current oscillations.

5e. Return the operating switch to "standby" and set the panel controls as follows.

Potentiostat Module

Load res. : 27
Range : 100 mA
Operating switch : standby
Control pot. : -325 mV
Current Limiter : off

Integrator Module

Readout : DS = (cv) x (EE)
Operating switch : operate

Differential Voltmeter

Range : 10
Null : TVM

5f. Turn the potentiostat operating switch to "operate" and allow the coulometric reduction to continue until the current level has just decreased to a predetermined value (about 50 μA).

5g. Turn the potentiostat operating switch to "hold" and adjust the DVM null and adjusting knobs until the meter is at zero. Measure the read-out voltage (mg of uranium). Record the DVM reading.

5h. Change these panel controls in the following order. Change the DVM null to "TVM," the integrator operating switch to "zero," and the potentiostat operating switch to "standby."

5i. Divide the DVM reading by the milligrams of standard uranium added to obtain the recovery factor.

SAMPLING AND DISSOLUTION

Use a sample weighing between 4 and 5 g, if available, to provide adequate material for repeated coulometric titrations of uranium or plutonium, total uranium plus plutonium, and of plutonium alone. For repeated coulometric titrations of uranium and plutonium, approximately 200 mg of sample is adequate. Carefully inspect the sample and remove any foreign material such as lint. Weigh the sample accurately, and dissolve it as described under Potentiometric Method: Plutonium, Dissolution of Sample.

ANALYSIS OF SAMPLE

Plutonium

1. Perform Steps 4a through 4h under Chemical Calibration, Plutonium.

2. Determine the iron content (Fe, %) of the sample by a suitable spectrophotometric method.[15]

3. Calculate the quantity of plutonium in the sample aliquot titrated, as follows.

$$\text{Pu, \%} = \frac{\text{DVM reading x 100}}{\text{sample weight, mg x recovery factor}} - \frac{(\text{Fe, \%})\, A_p}{A_{Fe}}, \qquad (13)$$

in which

DVM reading = the DVM read-out voltage in mg of plutonium.
Recovery factor = factor determined in Steps 4a through 4i above.
A_p = at. wt of sample plutonium.
A_{Fe} = at. wt of iron.

Uranium

1. Perform Steps 5a through 5h under Chemical Calibration, Uranium.

2. Calculate the percentage of uranium as follows.

$$\text{U, \%} = \frac{\text{DVM reading x 100}}{\text{sample weight, mg x recovery factor}} \qquad (14)$$

in which

DVM reading = the DVM read-out voltage in mg of uranium.
Recovery factor = factor determined in steps 5a through 5i above.

RELIABILITIES

Prepared solutions containing known amounts of uranium and plutonium were analyzed to determine the reliabilities of the methods under ideal conditions. The starting solution contained accurately weighed quantities of uranium and plutonium metals, each having less than 200 ppm of known impurities. The ratio of the concentrations of uranium to plutonium was 5:1. Weighed aliquots of this stock solution were diluted to prepare solutions from which aliquots were taken for the titrations. All measurements of aliquots and solutions were by weight. The average uranium and plutonium recoveries from 11 or 12 determinations of each metal by each method (see Table III) showed that the methods were not significantly biased. Use of electrical calibration data would have caused a small positive bias of 0.1% in the measurement of uranium by controlled-potential coulometry, but chemical calibration eliminated this bias. Either adjustment of the current level at which the titration was terminated to some value other than 50 μA or application of a background current correction could have been used to eliminate the bias, but these methods were not investigated. The precisions of the methods were about equal; as shown in Table I, the relative standard deviations were 0.07 or 0.08% for both potentiometric titrations and for the coulometric measurement of uranium, and 0.04% for the coulometric titration of plutonium.

Further tests were made by measuring uranium and plutonium in six 5-g samples of mixed carbide in which the uranium to plutonium atom ratio was about 4 to 1. These samples were ignited at 700°C, and the oxides were dissolved in hot nitric and hydrofluoric acids. Weighed aliquots were taken from each solution for the potentiometric titrations of each metal. Additional weighed aliquots were diluted to known volumes to prepare solutions from which volume aliquots were taken for the coulometric titrations which required less sample. Three determinations of each metal were made by both methods, for a total of 12 determinations per sample, Table II. The results were compared by calculating the average ratios of the percent of metal obtained by coulometric titration to those obtained by potentiometric titration. These ratios show that the difference between the two methods for determining plutonium or uranium is less than 0.1%. As the true concentrations of uranium and plutonium in these samples were not known, the accuracy of the methods can be assessed more reliably from the data obtained for the prepared solutions as described previously.

The relative standard deviations were obtained by pooling the data for the six samples which consisted of 18 measurements of each metal by each method. The precisions for the coulometric titrations were about the same as those determined for the prepared solutions, but the relative standard deviations of the potentiometric methods were slightly lower.

The methods were also used to analyze four samples of $(U_{0.75}Pu_{0.25})O_2$. The samples were dissolved as described above, and three weighed aliquots were taken from each solution for the determinations of each metal by each method. The average values (Table III) showed that results for each metal differed by less than 0.2 relative %, and that the relative standard deviations ranged from 0.06 to 0.14%.

The potentiometric and coulometric methods were also used to measure uranium and plutonium in mixed oxides whose uranium to plutonium atom ratios ranged between 20:1 and 2:1. The methods were not compared by analyzing the same sample; the method used depended on the plutonium concentration. Samples containing less than 15% plutonium were analyzed for this element by controlled-potential coulometry; higher plutonium concentrations and all uranium concentrations were measured by potentiometric titration. In addition to these mixed oxides, a few nitride samples were analyzed by the coulometric methods. The relative standard deviations of repeated measurements for each element were no greater than 0.3%.

As part of the evaluation of the adequacy of methods of analysis for Liquid Metal Fast Breeder Reactor - Fast Flux Test Facility mixed uranium-plutonium oxide fuel, six laboratories (AI, B & W, GE, LASL, NUMEC, and PNL) each analyzed, by the controlled-potential coulometric method alone, five sintered mixed-oxide pellets selected at random from one lot of pellets.[16] Each pellet was dissolved separately, and four aliquots from each solution were analyzed. Iron was measured sepa-

TABLE I

RELIABILITIES FOR MEASURING URANIUM AND PLUTONIUM

(Analyses of prepared solutions)

Method	Uranium Determination Recovery, %	Uranium Determination Rel. Std. Dev., %	Plutonium Determination Recovery, %	Plutonium Determination Rel. Std. Dev., %
CP Coulometric	100.00[a]	0.08	100.00	0.04
Potentiometric	99.97	0.07	99.98	0.07

[a] Corrected for difference of 0.1% between electrical and chemical calibration.

TABLE II

RELIABILITIES FOR MEASURING URANIUM AND PLUTONIUM

(Analyses of $(U_{0.8}Pu_{0.2})C$)

Metal Determined	Coulometric %/Potentiometric % Average Ratio	Rel. Std. Dev.,[a] % Coulometric	Rel. Std. Dev.,[a] % Potentiometric
Uranium	1.0006[b]	0.10	0.04
Plutonium	1.0009	0.03	0.05

[a] Based upon 18 determinations of each metal by each method.

[b] Corrected for difference of 0.1% between electrical and chemical calibration.

TABLE III

RELIABILITIES FOR DETERMINING URANIUM AND PLUTONIUM

(Analyses of $(U_{0.75}Pu_{0.25})O_2$)

Method	Uranium Determination Found, %	Uranium Determination Rel. Std. Dev., %	Plutonium Determination Found, %	Plutonium Determination Rel. Std. Dev., %
CP Coulometric	66.25	0.14	22.06	0.13
Potentiometric	66.13	0.06	22.05	0.08

rately, and the results for plutonium were corrected. The data were statistically analyzed by an analysis of variance. The calculated averages, measured standard deviations, and between-pellet standard deviations for plutonium and uranium measurement (Tables IV and V) agreed well among five of the laboratories.[16] The average plutonium content of 22.016% determined by laboratory L and the average uranium content of 65.786% determined by laboratory O were lower at the 0.05 significance level than the averages of 22.117% for plutonium and 66.168% for uranium determined by the other five laboratories. The significantly different data were excluded in calculating the pooled average.

The measured standard deviations, which were the reproducibilities of the analytical method within pellets and within laboratories expressed as absolute standard deviation of a single determina-

TABLE IV

CP COULOMETRIC ASSAYS FOR PLUTONIUM[16]

(Analyses of $(U_{0.75}Pu_{0.25})O_2$)

Laboratory	Av Pu, %	Analytical Method Standard Deviation, %	Between-Pellet Standard Deviation, %
L	22.016	0.042	0.032
M	22.138	0.015	0.010
N	22.166	0.046	0.150
O	22.076	0.030	0.024
P	22.087	0.032	0.066
Q	22.116	0.040	0.080
Pooled Data[a]	22.117		

[a] Data from laboratory L were excluded because the 22.016% plutonium average was lower at the 0.05 significance level than the 22.117% average obtained by the other five laboratories.

TABLE V

CP COULOMETRIC ASSAYS FOR URANIUM[16]

(Analyses of $(U_{0.75}Pu_{0.25})O_2$)

Laboratory	Av U, %	Analytical Method Standard Deviation, %	Between-Pellet Standard Deviation, %
L	66.190	0.338	0.036
M	66.251	0.116	b
N	66.125	0.115	0.254
O	65.786	0.277	b
P	66.198	0.120	0.091
Q	66.078	0.166	b
Average[a]	66.168		

[a] Data from laboratory O were excluded because the 65.786% average was lower at the 0.05 significance level than the 66.168% average determined by the other five laboratories.

[b] Not statistically estimable.

tion, ranged between 0.015 and 0.046% for plutonium and between 0.115 and 0.338% for uranium. These standard deviations indicate the precisions to be expected in fuel-samples analyses. The data indicated that the controlled-potential coulometric method was reliable and that good standards were available. The between-pellet standard deviations indicated the magnitude of the errors to be expected in sampling a single lot of sintered pellets, and emphasized the well-known fact that great care must be exercised in obtaining a representative sample.

INTERFERENCES

A tungsten or carbon stinger was used in the arc-melting process during preparation of mixed carbides, and, therefore, the effects of tungsten and free carbon on the methods were investigated. Solutions containing known amounts of uranium and plutonium and tungsten concentrations ranging from 500 to 2000 ppm relative to the total metals were analyzed for uranium and plutonium by both methods. At the 2000-ppm concentration level, tungsten caused a positive bias of 0.1% in the potentiometric titration of uranium, but it did not interfere in the other measurements. For tungsten concentrations not greater than 1000 ppm, the interference was negligible.

Samples containing significant quantities of free carbon dissolved with great difficulty in acids, and the coulometric or potentiometric titrations of the solutions, even when they appeared free of contamination, did not proceed normally. It was concluded that traces of carbonaceous materials caused the abnormalities in the measurements. Igniting samples of this type to the oxides before dissolution eliminated the interference.

Iron, in concentrations greater than 100 ppm, interfered in the potentiometric titration of uranium and the coulometric titration of plutonium. Corrections could be applied if the iron concentration were known. Elements that were reduced by lead and oxidized by ceric sulfate also interfered in the potentiometric titration of uranium.

Additional information about impurities that interfere in the potentiometric titration methods is available in the original papers.[6,7]

The effects of two intensely radioactive alpha-particle emitters, plutonium-238 and americium-241, and of one beta emitter, plutonium-241, on the controlled-potential coulometric titration of plutonium were determined. Known amounts of each isotope were added individually to weighed aliquots of a solution prepared from plutonium metal containing predominantly plutonium-239, and the resultant solutions were analyzed according to the recommended method for total plutonium. The results, Table VI, show that interference with the method becomes evident when the plutonium-238 content is increased to approximately 6% or the americium-241 content is increased to approximately 20%. Interference at these concentrations is small, and any lower content of either isotope should be tolerated. Concentrations of plutonium-241 as high as 32% did not affect the method.

CONCLUSIONS

This investigation shows that precise and accurate determinations of uranium and plutonium in ceramic reactor-fuel materials can be made, without chemical separation of the metals, by either potentiometric or controlled-potential coulometric methods. Analytical results from the two methods are very similar in reliability. Under optimum conditions, both the deviation from known metal content and the precision of measurements range from 0.04 to 0.1 relative %. This level of reliability will not be attained under all conditions, particularly if trace impurities, such as iron, tungsten, or carbonaceous material, are not separated from the sample before titration or if corrections are not applied. The precisions to be expected for coulometric titrations of sintered mixed-oxide fuel pellets are 0.14 relative % for measuring plutonium and 0.27 relative % for measuring uranium.

Selection of one method for a specific analytical problem may depend upon some of the characteristics of the methods observed during this investigation. Sample size for coulometric titration is approximately 1/20 of that used in the potentiometric method, and this may be advantageous under certain circumstances. Determinations of either element by coulometry are usually more rapid. A direct chemical calibration of the coulometric instruments must be made with uranium materials of known purity, but electrical calibration has been used satisfactorily for titrations of plutonium with the equipment described here. The chemical calibrations at regular intervals are recommended for plutonium also. The coulometric measurements of uranium and plutonium in samples containing these metals are independent of each other, but potentiometric determinations of uranium in two-metal samples depends upon a titration correction based on the plutonium measurement. In general, coulometric methods may be preferred because of their speed, small sample size, and direct and independent measurement of uranium and plutonium. The coulometric methods, therefore, were well tested with highly satisfactory results.

ACKNOWLEDGMENTS

The authors acknowledge the assistance of Walter W. Wilson, who performed some of the controlled-potential coulometric titrations, and of Gary Tietjen, LASL Group C-5, who performed some of the statistical analyses. The high-purity plutonium and uranium metals were obtained from W. J. Maraman of Group CMB-11 and M. C.

TABLE VI

EFFECTS OF PLUTONIUM-238, PLUTONIUM-241 AND AMERICIUM-241 ON THE CONTROLLED-POTENTIAL COULOMETRIC TITRATION OF PLUTONIUM

Isotope Added	Quantity Added		Pu[b] Taken, mg	Total Pu Found, mg	Recovery	
	mg	%[a]			%	Av %
Pu-238[c]	0.3661	2.3	12.2200	12.5829	99.97	
	0.3661	2.4	12.0289	12.3950	100.00	
	0.3661	2.3	12.1666	12.5368	100.03	100.00
	0.5229	3.5	11.4666	12.0000	100.09	
	0.5229	3.5	11.4277	11.9432	99.94	
	0.5229	3.4	11.5190	12.0443	100.02	100.02
	1.0458	6.2	12.2728	13.3986	100.60	
	1.0458	6.2	12.4349	13.5595	100.58	
	1.0458	6.3	12.2464	13.3115	100.15	
	1.0458	6.1	12.5894	13.6687	100.25	100.40
Pu-241[d]	10.648	32	-	10.6496	100.02	
	10.648	32	-	10.6534	100.05	
	10.648	32	-	10.6256	99.80	
	10.648	32	-	10.6619	100.13	
	10.648	32	-	10.6603	100.12	100.02
Am-241	1.072	10.4	10.3319	10.3409	100.09	
	1.072	10.4	10.2880	10.2792	99.91	
	1.072	10.4	10.3002	10.3083	100.08	
	1.072	10.3	10.4211	10.4290	100.08	100.04
	2.144	19.8	10.8222	10.8276	100.05	
	2.144	21.8	9.7967	9.8285	100.32	
	2.144	20.6	10.3856	10.3935	100.08	
	2.144	20.5	10.4675	10.4675	100.15	
	2.144	20.3	10.5142	10.5723	100.55	
	2.144	20.5	10.3949	10.4413	100.45	100.27

[a] Weight percent of isotope in total quantity of plutonium.

[b] Plutonium having an atomic weight of 239.11.

[c] Plutonium containing 80 wt % plutonium-238.

[d] Plutonium containing 32 wt % plutonium-241.

Tinkle of Group CMB-8, respectively. The uranium-plutonium carbide and nitride materials were obtained from J. A. Leary and M. W. Shupe of Group CMB-11, which is under the supervision of W. J. Maraman.

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KT/cg: 300 (75)