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ORNL PROCEDURES FOR CONTROLLED-POTENTIAL COULOMETRIC
TITRATION OF PLUTONIUM

W. D. Shults

ABSTRACT

This report presents six procedures, in stepwise form, that can be used for the determination of plutonium in several forms by controlled-potential coulometric titration.

NOTICE

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This report presents six analytical procedures that have been used at ORNL for the determination of various plutonium species by controlled-potential coulometric titration. These procedures are presented here in stepwise form in order to fulfill two objectives: first, to have them all available in one report for ready reference, and, second, to have them written in a form that will be of utmost usefulness to those who are already familiar with this technique and its application to the determination of plutonium. No discussion of the developmental work that has gone into these procedures is presented, nor is there discussion of the methods themselves. That information is contained in a general article that is being submitted for publication in Talanta. The general article also contains information about equipment, interferences, precision, accuracy, and principles of the methods.

Procedure I, the most frequently used, is designed for the determination of total plutonium in solutions that contain Pu(III) and(or) Pu(IV) with no more than 50 μg of Pu(VI) and in which the iron content is less than 2% of the plutonium present. It is used also to determine "ionic" plutonium in the presence of the polymeric species by using a supporting electrolyte solution of 0.25 M HClO_4 (Procedure V, A).

Procedure II is applicable for the determination of total plutonium when the sample contains sulfate or greater amounts of Pu(VI) than 50 μg . The procedure can also be used to determine Pu(VI) if "holding" oxidants are absent, as noted in the procedure. Titration in H_2SO_4 is useful as well for the determination of total plutonium after depolymerization (Procedure V, B) or after anion exchange separation (Procedure VI, B).

Procedure III is useful for the determination of total plutonium in samples that contain large amounts of iron. Procedure III-A is applied if the sample does not contain sulfate; Procedure III-B if the sample contains sulfate.

Procedure IV has been used for the oxidation-state analysis of "pure" solutions that contain Pu(III), Pu(IV), and(or) Pu(VI). Such samples have been encountered infrequently during the course of spectrophotometric studies of the various plutonium species. In Procedure V, the determination of "ionic" and "polymeric" plutonium has been requested only during the course of studies of these species at ORNL.

The final procedure, VI, is designed for analysis of dissolver solutions or samples that contain small amounts of plutonium in which cases a separation or concentration step is a desirable prelude to coulometric titration.

PROCEDURES

Procedure I. Determination of Total Plutonium (Ionic)

A. Sample Preparation

1. If the sample contains reducing impurities, add 3 to 5 drops of concentrated HNO_3 and evaporate the test portion in the cell to near dryness. Alternatively, small amounts of reducing agents can be destroyed by adding 0.1 M $\text{Ce}(\text{NO}_3)_4$ solution dropwise until the yellow color of Ce(IV) persists.

2. If the sample is likely to contain small amounts of Pu(VI), add 2 drops of 1% $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ solution to the test portion in the cell and warm it until the blue color of Pu(III) is evident. Then, destroy the excess N_2H_4 by adding 0.1 M $\text{Ce}(\text{NO}_3)_4$ solution dropwise until the yellow color of Ce(IV) persists.

B. Titration

1. To the test portion in the cell (preferably containing ~5 mg of Pu) that has been freed of interfering materials, add 10 to 15 ml of 1 M HClO_4 and 5 drops of saturated $\text{NH}_2\text{SO}_3\text{H}$ solution.

2. Reduce at +0.535 volt vs S.C.E. until the current decreases to 30 μa . (If the presence of iron is likely, reduce at +0.555 volt).

3. Zero the integrator.

4. Oxidize at +0.895 volt vs S.C.E. until the current decreases to 30 μa .

5. Read and record the read-out voltage, Q.

6. mg Pu titrated = Q x coulometric Pu factor (n = 1).

Procedure II. Determination of Total Plutonium (Ionic) in H_2SO_4 Medium

1. Pipet the sample test portion (~5 mg Pu) into cell.

2. Dilute to 10-15 ml with 0.5 M H_2SO_4 .

3. De-gas 10 minutes with He.

4. Reduce at +0.310 volt vs S.C.E. until current decreases to 30 μa .

5. Zero integrator.
6. Oxidize at +0.670 volt vs S.C.E. until current decreases to 30 μ a.
7. Read and record read-out voltage, Q, volt.
8. mg Pu titrated = Q x coulometric Pu factor (n = 1)
= volt x $\frac{\text{mg Pu/volt}}{1}$ = mg Pu.

Note: If a measure of Pu(VI) content is desired, take read-out voltages of both reduction and oxidation steps and calculate Pu(VI) as follows:

$$(Q_{\text{red}} - Q_{\text{ox}}) \times \text{coulometric Pu factor (n = 2)} = \text{volt} \times \frac{\text{mg Pu/volt}}{2}$$

Procedure III. Determination of Total Pu by Secondary Coulometric Titration

A. Preparation of Pu(VI) with HClO₄

1. Pipet the sample test portion (~5 mg Pu) into the titration cell.
2. Add 1 ml conc. HClO₄, 2 drops conc. HNO₃, and 0.5 ml of a solution that contains ~5 mg Fe/ml as FeCl₃.
3. Evaporate to fumes under an infrared lamp.
4. Transfer to a hot plate and continue fuming for 10 to 15 minutes.
5. Cool, place the cell in position under a He atmosphere, and then dilute to 15 ml with 0.5 M H₂SO₄.

B. Preparation of Pu(VI) with AgO

1. Pipet the sample test portion (~5 mg Pu) into the titration cell.
2. Add 0.5 ml conc. H₂SO₄ and 0.5 ml of a solution that contains ~5 mg Fe/ml as FeCl₃.
3. Evaporate to fumes.
4. Cool, dilute to ~10 ml with water.
5. Add solid AgO in small portions until a small amount of the black solid remains on the bottom of the cell.
6. Warm to 85 °C until the solution clears and all solid material dissolves.
7. Place the cell in position under a helium atmosphere and dilute to 15 ml with water.

C. Titration of Oxidized Test Portion

1. De)gas the solution 10 min. with He. Titrate under He cover.
2. Reduce at +0.270 volt until an excess of 10 to 20 μeq of Fe(II) has been generated. (See Note)
3. Stop the reduction and record the read-out voltage, Q_{red} , volt.
4. Zero the integrator.
5. Oxidize at +0.670 volt until the current decreases to 50 μa .
6. Record the read-out voltage, Q_{ox} , volt.
7. mg Pu(VI) titrated = $(Q_{\text{red}} - Q_{\text{ox}})$ x coulometric Pu factor ($n = 2$)
$$= \text{volt} \times \frac{\text{mg Pu/volt}}{2}$$

Note: When the ORNL Model Q-2005 coulometric titrator is used on the X5 sensitivity range, the reduction is allowed to proceed until the read-out voltage in volts equals 0.2 times the milligrams of plutonium expected in the test portion.

Procedure IV. Oxidation-State Analysis of Samples that Contain Pu(III), Pu(IV), and(or) Pu(VI)

A. Determination of Iron Titer

1. Pipet an aliquot of standard FeCl_3 solution into the cell 1 mg Fe(III) .
2. Dilute to 15 ml with 10% HClO_4 .
3. Oxidize at +0.895 volt until the current decreases to 30 μa . Read and record the read-out voltage, $Q_{\text{ox},1}^{\text{Fe}}$, volt.
4. Reduce at +0.285 volt until the current decreases to 30 μa . Read and record the read-out voltage, $Q_{\text{red},1}^{\text{Fe}}$, volt.
5. Oxidize at +0.895 volt until the current decreases to 30 μa . Read and record the read-out voltage, $Q_{\text{ox},2}^{\text{Fe}}$, volt.

B. Titration of Sample

1. Pipet the same amount of standard FeCl_3 solution into the cell.
2. Pipet the sample test portion (5-10 mg Pu) into the cell.
3. Dilute to 15 ml with 10% HClO_4 .

4. Oxidize at +0.895 volt until the current decreases to 30 μ a. Read and record the read-out voltage, $Q_{ox,1}^{Pu}$, volt.

5. Reduce at +0.285 volt until the current decreases to 30 μ a. Read and record the read-out voltage, $Q_{red,1}^{Pu}$, volt.

6. Oxidize at +0.895 volt until the current decreases to 30 μ a. Read and record the read-out voltage, $Q_{ox,2}^{Pu}$, volt.

C. Calculation of Results

1. mg Pu(III) in test portion = $(Q_{ox,1}^{Pu} - Q_{ox,1}^{Fe}) \times$
coulometric Pu factor (n = 1) = volt x mg Pu/volt.

2. mg Pu(VI) in test portion =
 $(Q_{red,1}^{Pu} + Q_{red,1}^{Fe} - Q_{ox,2}^{Pu} - Q_{ox,2}^{Fe}) \times$ coulometric
Pu factor (n = 2) = volt x mg Pu/volt.
2

3. mg Pu(total) in test portion =
 $(Q_{ox,2}^{Pu} - Q_{ox,2}^{Fe}) \times$ coulometric Pu factor (n = 1) =
volt x mg Pu/volt.
1

4. mg Pu(IV) in test portion = mg Pu(total) -
mg Pu(III) - mg Pu(VI).

Procedure V. Determination of Ionic and Polymeric Plutonium

A. Ionic Plutonium

Total ionic plutonium is determined in the presence of polymer by titrating a test portion of the sample in 0.25 M HClO₄ by Procedure I-B.

B. Total Plutonium (Ionic and Polymeric)

1. Pipet sample test portion (5 mg Pu) into cell.
2. Add 0.5 ml conc. H₂SO₄ and 1-2 drops conc. HF.
3. Evaporate and fume 10 minutes on hot plate.
4. Cool, dilute to 15 ml with distilled water.
5. Titrate the sample by Procedure II, beginning with step 3.

C. Polymeric Plutonium

The difference between the results of the ionic and total plutonium analyses is a measure of the amount of polymer present.

Procedure VI: Anion Exchange Separation and Coulometric Titration of Plutonium

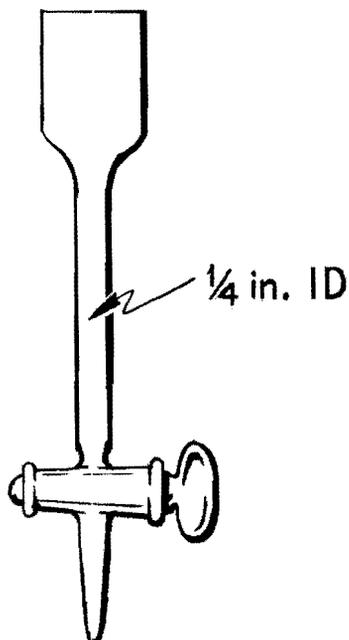
A. Separation

1. Place 3 g Dowex 1-X4 (50-100 mesh) in a resin column tube.
2. Wash the resin with 25 ml of 8 M HNO₃.
3. Pipet the sample test portion containing 1 mg Pu(IV) in 8 M HNO₃ onto the column and allow the liquid to flow through the column at the rate of about 3 drops/sec.
4. Wash with 25 ml 8 M HNO₃ and allow to drain dry.
5. Elute Pu(IV) from the column with small portions of 0.1 M HNO₃·0.01 M HF solution, collecting the effluent in the titration cell. Collect a total volume of 20 ml.

B. Titration

1. Add 0.5 ml conc. H₂SO₄ to the solution in the cell.
2. Evaporate and fume the solution 10 min. on hot plate.
3. Cool, dilute to 15 ml with distilled water.
4. Titrate Pu by Procedure II, beginning with step 3.

C. Diagram of Resin Column Tube



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