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TO R. E. Curtis DEPARTMENT

FROM W. H. Johnston by J. W. Reynard DEPARTMENT

IN RE:

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470.1 Plutonium

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Attached please find two copies of "A Chemical Method for Plutonium Assay". This method was developed by members of Group II-W. This manuscript was prepared upon the suggestion of Mr. T. R. Hogness.

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A Chemical Method for Plutonium Assay

Introduction

The chemical method for the assay of plutonium consists of an electrometric titration from the +3 to the +4 valence state. Plutonium in solution can readily be reduced to the +3 valence state and oxidized quantitatively to the +4 valence state by ordinary chemical reagents. Spectrophotometric measurements can be made to indicate the completeness of oxidation or reduction. The stability of the +4 valence state makes an oxidation-reduction method very practicable.

Apparatus

1. A titration vessel having 2 ml. capacity with a neck of 2 cm. length and I.D. of 0.5 cm. is used for this determination.

2. A micro manipulator is employed to manipulate the nitrogen stream stirring device.

3. A capillary buret with elongated tip is used for the titration.

4. The electrode assembly consists of one platinum wire sealed into the buret in contact with the ceric sulfate and another platinum wire immersed in the sample solution.

5. A Beckman pH meter is used as an e.m.f. recorder.

Reagents

1. Dilute sulfuric acid (6N) is prepared by diluting reagent grade concentrated sulfuric acid.

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2. Standard ceric sulfate solution is prepared by dissolving reagent grade $Ce(HSO_4)_4$ in 2N H_2SO_4, and standardizing against an iron solution prepared by dissolving pure iron wire in HCl. The normality of the ceric sulfate depends upon the plutonium concentration.

3. Dilute $TiCl_3$(4%) is prepared by boiling 20 ml. of 20% $TiCl_3$(C.P.) with 5 ml. conc. HCl for five minutes and diluting to 100 ml. with distilled H_2O.

Procedure

1. Principle

The plutonium nitrate solution, 2N in HNO_3, is diluted with H_2SO_4 and titrated electrometrically from the +3 to the +4 valence state. Titanous chloride serves as the reducing agent and ceric sulfate as the oxidizing agent. The e.m.f. is measured by a Beckman pH meter or other potentiometer.

2. Method

A. Measure 75 λ of the plutonium nitrate solution (approx. 10 γ/λ) into the titration vessel. Add a total of 250 λ of 8N H_2SO_4, using portions as a rinse for the pipette and vessel walls. (a)

B. Clamp the titration vessel in position and direct a sufficient stream of nitrogen toward the surface of the solution to stir it vigorously and to maintain an inert atmosphere in the titration vessel. (b)

C. Add approximately 40 λ of 4% $TiCl_3$ (a proportional amount of a stronger solution may be used). Allow the reduction to continue

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for five minutes and add an additional 40 λ of 4% $TiCl_3$, washing the vessel walls with 25 λ of 6N H_2SO_4. (c)

D. Insert the buret, filled with standard $Ce(SO_4)_2$ solution into the titration vessel at once. (d) Introduce the platinum wire electrode into the solution and connect the two electrodes to the e.m.f. recorder.

E. Record the initial e.m.f. reading and the initial buret reading. After each addition of $Ce(SO_4)_2$ allow equilibrium to be established before recording the e.m.f. Add the $Ce(SO_4)_2$ in 1 mm. portions until the first inflection is passed; then gradually increase the additions to as much as 2 cm. until the next inflection is imminent. Then gradually decrease the additions to 1 mm. until the second inflection is passed. Several larger additions of $Ce(SO_4)_2$ will then complete the titration. (e)

F. Prepare a graph, plotting cm. of $Ce(SO_4)_2$ as abscissae against m.v. as ordinates. The difference between the two inflections represents the amount of $Ce(SO_4)_2$ equivalent to the amount of the product present in the sample. The calculation of the product recovery is made as follows:

λ $Ce(SO_4)_2$ x N. of $Ce(SO_4)_2$ x equiv. wt. of product = % Product

Notes

(a) After addition of all reagents the sample solution must contain a molar ratio of H_2SO_4 to plutonium of approximately 275.

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(b) This is accomplished by attaching a small glass tubing which is connected to an oxygen-free nitrogen source to a micro manipulator and inserting it into the titration vessel.

(c) The $TiCl_3$ must be removed from the stock solution under an atmosphere of CO_2 furnished by adding small pellets of dry ice to the solution.

(d) After the second addition of $TiCl_3$ the burst electrode must be inserted immediately to avoid possible air oxidation of the excess $TiCl_3$ before the e.m.f. can be recorded. Care must be exercised at this point to completely immerse the tip of the buret in the solution and at the same time allow for freedom of manipulation of the stirring device.

(e) If the correct amount of $TiCl_3$ has been added, the initial e.m.f. reading should be 1250 ± 100 m.v. Two or three small additions of $Ce(SO_4)_2$ should be sufficient to oxidize the excess $TiCl_3$, changing the e.m.f. to approximately 900 m.v. The product half oxidation potential is estimated to be 750-800 m.v. Several minutes may be required for equilibrium to be established during the inflections. Before the final inflection it is advisable to rotate the titration vessel to remove any solution from the vessel walls.

Summary

The assay of plutonium consists of reduction with titanous chloride and oxidation from the +3 to the +4 valence state with ceric sulfate. Low concentrations of nitrate ion do not cause interference. With this method it is possible to obtain reproducible results with an accuracy of ± 0.5% in ranges of 0.5-1.5 mg. of plutonium.

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