

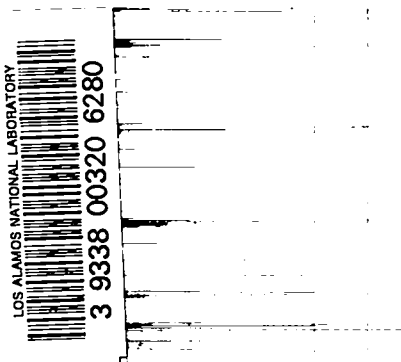
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Investigation of Two Methods
for Measuring Free Acid
in Plutonium Solutions



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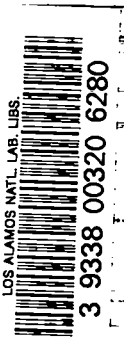
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CONTENTS

| | <u>Page</u> |
|---|-------------|
| Abstract | 3 |
| Introduction | 3 |
| Apparatus and Reagents | 4 |
| Recommended Procedures | 4 |
| Iodate Method | 4 |
| Citrate Method | 5 |
| Experimental | 5 |
| Determination of Free Acid in Plutonium(IV) Solutions . . | 5 |
| Effect of Plutonium(III) | 5 |
| Effect of Plutonium and Free Acid Concentrations | 6 |
| Determination of Free Acid in Thorium(IV) Solutions . . . | 6 |
| Determination of Free Acid in Cerium Solutions | 7 |
| Determination of Free Acid in Ceric Ammonium Nitrate Solutions | 7 |
| Conclusions | 8 |
| Acknowledgment | 8 |
| References | 8 |

INVESTIGATION OF TWO METHODS FOR MEASURING
FREE ACID IN PLUTONIUM SOLUTIONS

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ABSTRACT

The reliabilities of two methods for measuring free acid in plutonium solutions were determined by applying each to the analysis of plutonium, thorium, and cerium solutions having known free acid concentration. In the iodate method, the hydrolyzable ion was precipitated with iodate and separated by filtration, and the free acid in the filtrate was titrated with standard base. In the citrate method, the hydrolyzable ion was complexed with citrate during the titration of the free acid with standard base. Between 99 and 100% of the free acid in plutonium(IV) solutions was measured using the iodate method, and high results, 106 to 109%, were obtained using the citrate method. Neither was reliable for determining free acid in plutonium(III) solutions; the iodate method gave low results (94 to 96%), and the citrate method gave high results (108 to 109%).

INTRODUCTION

Low results for free acid in plutonium(IV) nitrate solutions were reported⁽⁵⁾ by the iodate method,⁽⁶⁾ in which the plutonium was precipitated as the iodate and removed by filtration prior to titration of the free acid. The bias was presumed to be caused by precipitation of some acid iodate.⁽⁵⁾ Complexing of the plutonium with citrate during the titration of the free acid was recommended even though this method was reported to have a small positive bias. The iodate method was recommended recently⁽⁷⁾ for measuring free acid in plutonium(IV) nitrate solutions that also contained uranium. Considerable speculation has developed over which of these methods gives the more reliable results. The present investigation clarifies the

status of each method.

Perhaps the greatest difficulty in testing measurements of free acid lies in the preparation of solutions having known free acid concentrations. In the present work, the plutonium(III) solutions were prepared by dissolving high purity plutonium metal in standardized hydrochloric acid solutions while trapping any evolved acid. Plutonium(IV) solutions were prepared either by dissolving plutonium oxide in hydrochloric acid without loss of acid by the sealed-tube method,⁽³⁾ or by dissolving plutonium hexachloride in hydrochloric acid of known molarity. Thorium(IV) solutions also were analyzed because this monovalent ion can not cause changes in free acid due to changes in oxidation state. The applicability of the method to

measurement of free acid in cerium solutions also was determined.

APPARATUS AND REAGENTS

Apparatus:

Magnetic mixer, electrically driven, equipped with magnetic stirring bars.

Meter, pH, Beckman Zeromatic II, or equivalent instrument, equipped with glass and saturated calomel electrodes.

Microburet, 5-ml volume, having 0.02-ml graduations.

Miscellaneous equipment. Normal laboratory equipment, including beakers, filter paper, funnels, pipets, and volumetric flasks.

Reagents:

Ceric ammonium nitrate, G. F. Smith Chemical Co., Columbus, Ohio.

Ceric sulfate, anhydrous, Fisher Scientific Co., Pittsburgh, Pa.

Cerous nitrate, hydrated, G. F. Smith Chemical Co., Columbus, Ohio.

Dicesium plutonium hexachloride, prepared as described by Miner, De Grazio, and Byrne.⁽⁴⁾ This salt reportedly has the stoichiometric composition and stability suitable for a primary standard.

Hydrochloric acid, reagent grade, 12M.

Hydrochloric acid, reagent grade, ~ 6M. Dilute 500 ml of 12M hydrochloric acid to 1 liter with water, mix well, and titrate with standardized 0.3 to 0.4M sodium hydroxide solution.

Nitric acid, reagent grade, 15M.

Nitric acid, reagent grade, ~ 1M. Dilute 67 ml of 15M nitric acid to 1 liter with water, mix well, and titrate with standardized 0.3 to 0.4M sodium hydroxide solution.

Plutonium metal. The total of the concentrations of the detected impurities was less than 100 ppm in the metal used.

Potassium iodate, 0.3M. Dissolve 128.4 g of the salt in 2 liters of water and adjust the pH to 4.3 by adding dilute nitric acid.

Sodium citrate, 10% solution. Dissolve 50 g of the salt in 500 ml of water. Adjust the pH to between 8.0 and 9.0. The pH of each of the sodium citrate solutions used was 8.3.

Sodium hydroxide, 0.3 to 0.4M. Prepare, standardize, and store this solution as described by Kolthoff and Sandell.⁽¹⁾

Sulfuric acid, reagent grade, 18M.

Sulfuric acid, reagent grade, ~ 1M. Dilute 56 ml of 18M sulfuric acid to 1 liter with water, mix well, and titrate with standardized 0.3 to 0.4M sodium hydroxide solution.

Thorium dioxide, reagent grade.

RECOMMENDED PROCEDURES

Caution: Health safety rules for the handling of plutonium must be rigidly followed, and adequate protection for the operator must be ensured by the use of suitable dry boxes and protective clothing.

Iodate Method

1. Pipet 50 ml of 0.3M potassium iodate solution into a 100-ml beaker and add, while stirring, an aliquot of the sample solution containing not greater than 50 mg of plutonium.
2. Filter the mixture through Whatman No. 42 filter paper and collect the filtrate in a 200-ml beaker.
3. Wash the precipitate with two 25-ml portions of 0.3M potassium iodate solution, and combine the washings with the original filtrate.
4. Wash the precipitate from the filter paper into a beaker with a small stream of water. Dissolve the precipitate and any residual solids adhering to the filter paper in 12M hydrochloric acid, and transfer the solution to a residue bottle.
5. Place a magnetic stirring bar in the beaker containing the filtrate, place the beaker on the magnetic mixer, lower the glass and saturated calomel electrodes into the solution, and start the magnetic mixer.
6. Titrate the free acid in the solution by adding the standardized sodium hydroxide solution from a 5-ml buret and plot the titration curve (pH versus ml of base).
7. Determine the end point of the titration from the mid point of the inflection, and read the amount of sodium hydroxide consumed in titrating the free acid.
8. Pipet 100 ml of the 0.3M potassium iodate solu-

tion into a 200-ml beaker and perform Steps 5 through 7 to determine a blank for the titration.

9. Subtract the titration blank from the ml of sodium hydroxide obtained in Step 8 and multiply the difference by the normality of the sodium hydroxide solution to calculate the free acid in the sample solution aliquot added.

Citrate Method

1. Add 30 ml of 10% sodium citrate solution to a 100-ml beaker, and set the beaker on the magnetic mixer.
2. Place a magnetic stirring bar in the beaker, lower the glass and saturated calomel electrodes into the solution, turn on the magnetic mixer, and measure the pH of the solution.
3. Add an aliquot of the sample solution containing not greater than 25 mg of plutonium.
4. Titrate the free acid in the solution by adding the standardized sodium hydroxide solution from a 5-ml buret to the stirred solution until the pH is equal to the pH determined in Step 2.
5. Calculate the free acid concentration from the normality and volume of the standard sodium hydroxide solution used and the volume of the sample solution aliquot.

EXPERIMENTAL

Determination of Free Acid in Plutonium(IV) Solutions.

Plutonium(IV) solutions having known acidities were prepared by dissolving either plutonium dioxide or dicesium plutonium hexachloride in hydrochloric acid. In the first method, high purity plutonium metal was oxidized in air at 600° C, and the plutonium oxide was dissolved in a known quantity of standard hydrochloric acid by the sealed-tube method.⁽³⁾ Four plutonium solutions were prepared in this manner. To determine the amount of acid lost during the tube sealing and opening operations, a volume of the standard hydrochloric acid solution equal to that used in dissolving the plutonium oxide was taken through the entire sealed-tube method and then titrated. Duplicate determinations on four solutions showed that less than 0.5 milliequivalent, out of a total of 84 milliequivalents of acid, was lost during the dissolution process.

The 300° C temperature and the 3,000 to 4,000 lb/in.² pressure for 12 hr in the sealed-tube method may have caused rapid disproportionation

of plutonium(IV). As four hydrogen ions form for each plutonyl ion produced, it was necessary to determine the quantity of plutonium(VI) or (III) in the solutions in order to calculate the free acid concentration. According to Smith,⁽⁶⁾ a double break in the titration curve for the iodate method is evidence of plutonium(VI); the titration curves obtained showed that significant concentrations of plutonium(VI) were not present. Spectrophotometric measurements of the plutonium(VI) adsorption peak at 833 m μ , and potentiometric titrations with iron(II) solutions, indicated that a maximum of 3% of the plutonium was in the (VI) oxidation state. The maximum increase in the free acid, therefore, would be 0.5 milliequivalent or about 1% of the total. It is probable that the increase in free acid was much smaller.

In the second method for preparing plutonium (IV) solutions, accurately weighed amounts of dried dicesium plutonium hexachloride were dissolved at room temperature in known amounts of standardized hydrochloric acid. As the dissolution of the plutonium salt neither contributed nor consumed acid, the free acid concentration was equal to the molarity of the standardized hydrochloric acid.

Duplicate aliquots of each of the plutonium solutions were analyzed by each of the two methods. The results (Table I) obtained by the iodate method were approximately equal to the calculated amounts of free acid, but the results obtained by the citrate method were between 8 and 9% high. Increasing the quantity of sodium citrate 20-fold, as was done for solutions 3 and 4, was not beneficial.

Effect of Plutonium(III)

A solution containing plutonium(III) and having a known acidity was prepared by dissolving 1 g of plutonium metal in standard hydrochloric acid solution while the evolved acid fumes were caught in a water trap. The dissolved plutonium and the contents of the water trap were combined and diluted to 100 ml with water. The free acid was calculated by subtracting the acid required to form the plutonium trichloride from the total quantity of acid added. Aliquots were analyzed for free acid by each of the two methods. The results obtained

Table I
Determination of Free Acid in Plutonium(IV) Solutions

| Pu(IV) Solutions | Method Used | Calculated Total Free Acid, mequiv | Free Acid Found ^(c) | |
|---|--------------------------------|---------------------------------------|--------------------------------|-----|
| | | | mequiv | % |
| 1 (from PuO ₂) | Iodate ppt | 67.6 | 67.3 | 100 |
| | Citrate complex ^(a) | 67.6 | 73.6 | 109 |
| 2 (from PuO ₂) | Iodate ppt | 67.8 | 67.0 | 99 |
| | Citrate complex ^(a) | 67.8 | 74.2 | 109 |
| 3 (from PuO ₂) | Iodate ppt | 68.3 | 67.8 | 99 |
| | Citrate complex ^(b) | 68.3 | 73.7 | 108 |
| 4 (from PuO ₂) | Iodate ppt | 68.4 | 68.2 | 100 |
| | Citrate complex ^(b) | 68.4 | 74.7 | 109 |
| 5 (from Cs ₂ PuCl ₆) | Iodate ppt | 2.56 | 2.56 | 100 |
| | Citrate complex ^(b) | 2.56 | 2.71 | 106 |

(a) A 5-fold excess of sodium citrate was added to the plutonium solution.

(b) A 100-fold excess of sodium citrate was added to the plutonium solution.

(c) Average values of duplicate determinations.

by the iodate-precipitation method for two individually prepared solutions were low, 94 and 96%, and the results obtained by the citrate-complexing method were 8 to 9% high.

The low results from the iodate-precipitation method probably were caused by partial oxidation of the plutonium(III) by iodic acid. This was shown by a change of the plutonium iodate precipitate from green to brown. According to Latimer,⁽²⁾ iodate in acid solution is an oxidizing agent that causes six hydrogen ions to be neutralized for each iodate ion reduced. This reaction would reduce the free acid in the plutonium solution accordingly. The quantity of plutonium(III) oxidized in this manner was unknown, and calculation of the remaining free acid in the solution was not possible. It was concluded that plutonium(III) adversely affected the iodate-precipitation method.

Oxidation of some plutonium(III) also occurred in the citrate solutions, as evidenced by a change of the solution color from blue to brown. The free acid values were between 8 and 9% high, however, as they were for the plutonium(IV) solutions.

Effect of Plutonium and Free Acid Concentrations

Analyses were made of three sets of solutions having different plutonium and free acid concentrations to determine their effects on each method. Each set consisted of two solutions. The two solutions in the first set had equal plutonium concentrations but different acid concentrations, the second set had different plutonium concentrations but equal acid concentrations, and the third set had different plutonium and acid concentrations. These solutions were prepared by dissolving weighed portions of dried dicesium plutonium hexachloride in known amounts of hydrochloric acid. As shown in Table II, the difference between results obtained by the two methods was independent of acid concentration but varied directly with the plutonium concentration.

Determination of Free Acid in Thorium(IV) Solutions.

In another test of the methods, thorium(IV) solutions prepared by dissolving thorium dioxide using the sealed-tube method were analyzed. The free acid in the thorium solution was determined by each of the two titration methods. The values

Table II
Determination of Free Acid in Solutions Having Different Plutonium
and Acid Concentrations

| Set and Solution Numbers | Pu Added, mg | Acid Added, (a) mequiv | Iodate Method | | Citrate Method | |
|-----------------------------|--------------------|------------------------------|------------------------------|-----------------|------------------------------|-----------------|
| | | | Acid Found, (b) mequiv | Bias, mequiv | Acid Found, (b) mequiv | Bias, mequiv |
| 1, A | 22.4 | 2.56 | 2.56 | 0 | 2.71 | + 0.15 |
| 1, B | 22.4 | 5.12 | 5.10 | - 0.02 | 5.25 | + 0.13 |
| 2, A | 5.0 | 3.66 | 3.67 | + 0.01 | 3.70 | + 0.04 |
| 2, B | 24.3 | 3.66 | 3.66 | 0 | 3.83 | + 0.17 |
| 3, A | 7.5 | 0.85 | 0.86 | + 0.01 | 0.90 | + 0.05 |
| 3, B | 22.4 | 2.56 | 2.56 | 0 | 2.71 | + 0.15 |

(a) Assuming the Cs_2PuCl_6 salt did not contain free acid.

(b) Average values of duplicate determinations.

shown by the iodate method were equal to the calculated amount of free acid, and the results shown by the citrate method were 9% high. As thorium exists only in the (IV) oxidation state in solution, the problem of disproportionation was avoided, and there was no reason to question the calculated quantity of free acid in the solution. Although these data are valid only for thorium solutions, the chemical similarity of thorium(IV) and plutonium (IV) cause doubt concerning the applicability of the citrate method to measurement of free acid in plutonium solutions also. This doubt is substantiated somewhat by the fact that the results obtained using the citrate method are 9% high for both the plutonium and thorium solutions.

Determination of Free Acid in Cerium Solutions

The methods were tested further by applying

them to the determination of free acid in solutions containing cerium(III) and (IV). The solutions were prepared by dissolving anhydrous ceric sulfate and hydrated cerous nitrate in standardized sulfuric and nitric acid, respectively. The salts were considered not to contain free acid in calculating the acidity of these solutions. Titration of each solution by each method showed, Table III, that either method determined free acid reliably in cerium(III) solutions, but both methods gave high results for cerium(IV) solutions.

Determination of Free Acid in Ceric Ammonium Nitrate Solutions

Because ceric ammonium nitrate is a pure reagent with several applications to analytical methods, the effect of the ammonium ion in this salt on the free-acid titration was investigated

Table III
Determination of Free Acid in Cerium(IV) and Cerium(III)
Solutions

| Method Used | Cerium Added, Oxidation State, mg | Acid Added, mequiv | Acid Found | |
|-----------------|--------------------------------------|-----------------------|------------|-----|
| | | | mequiv | % |
| Iodate ppt | (III), 25 | 2.51 | 2.51 | 100 |
| Citrate complex | (III), 25 | 2.51 | 2.52 | 100 |
| Iodate ppt | (IV), 19 | 4.31 | 4.34 | 101 |
| Citrate complex | (IV), 19 | 4.31 | 4.55 | 106 |

Table IV
Effect of Ammonium Ion on Determination of Free
Acid in Cerium Solutions

| Method Used | Cerium Added, Oxidation State, mg | Acid Added, mequiv | Acid Found | |
|-----------------|--------------------------------------|-----------------------|------------|-----|
| | | | mequiv | % |
| Iodate ppt | (IV), 25 | 2.51 | 2.59 | 103 |
| Citrate complex | (IV), 25 | 2.51 | 2.69 | 107 |
| Iodate ppt | (III), 12; (IV), 12 | 2.51 | 2.55 | 102 |
| Citrate complex | (III), 12; (IV), 12 | 2.51 | 2.61 | 104 |

using a solution prepared by dissolving the salt in standardized nitric acid. Titrations of free acid in this solution, and also in mixtures of this solution with the cerous nitrate solution (Table IV), had suppressed or poor end points, and the results were high, as expected. Hydrolysis of metal ions in the solutions could cause these effects, but spectrophotometric analysis for cerium showed that less than 400 μg of the original 25 mg of cerium remained after the iodate precipitation. The total of the concentrations of 41 impurity elements found by spectrographic analysis of the ceric ammonium nitrate was less than 0.36%. It seemed unlikely that there were enough cerium or impurity elements in the iodate filtrate to cause the high results.

The effect of ammonium ion alone was determined by titrating the free acid in a nitric acid solution containing ammonium nitrate. A buffering effect beginning just below pH 7 and continuing through pH 8 was observed. This buffering resulted in a poor end point and high results. In the presence of a buffering agent, such as ammonia, the iodate method is less affected by ammonium ion because the end point is at pH 7, as compared to 8.3 for the citrate method. Ammonium ion interferes significantly in either method for measuring free acid, however.

CONCLUSIONS

A probable explanation for the high results shown by the citrate complexing method is partial hydrolysis of the metal ions present. It also is possible that dissolved carbon dioxide plays a role at the upper pH range of the titration in the citrate method. In any event, the iodate precipitation

method seems to be reliable for determining free acid in solutions containing plutonium(IV), thorium(IV), or cerium(III). Evidence was not obtained to show that significant amounts of acid coprecipitated with plutonium iodate. Ammonium ion causes high results from either method.

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