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**MEASUREMENT OF ACIDITY AND DENSITY
OF PLUTONIUM SOLUTIONS**

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BARNWELL NUCLEAR FUEL PLANT

Barnwell, South Carolina

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MEASUREMENTS OF ACIDITY AND DENSITY OF

PLUTONIUM SOLUTIONS

By

K. J. Hofstetter, D. L. Bowers and R. P. Kemmerlin

1.0 INTRODUCTION

Several techniques have been suggested to determine the quantity of plutonium in solution form stored in process tanks in a reprocessing plant. One simple technique would involve the measurement of the solution density at a given temperature and the acid concentration followed by computation of the plutonium concentration. To estimate the concentration accurately, correlations of acidity, density at various temperatures with plutonium content are required. Scientists at Lawrence Livermore Laboratory (LLL), developing these correlations, requested acid, density and plutonium concentration data from Allied-General Nuclear Services (AGNS) on a contract basis.

Many properties of plutonium nitrate solutions have been measured in our laboratory for various projects. One such project, sponsored by Division of Safeguards and Security, Department of Energy, is to develop and test an on-line isotopic and total plutonium concentration monitor. Plutonium nitrate solutions were prepared for this project and characterized for isotopic content by mass spectrometry and total plutonium concentration by controlled potential coulometry. A number of these solutions were set aside for density and acid analyses for this project.

2.0 EXPERIMENTAL

2.1 Solution Preparation

All the plutonium nitrate solutions were prepared from one primary stock solution. The stock solution was prepared by dissolving PuO_2 in 10N nitric acid with the addition of a few drops of hydrofluoric acid. The make-up value for the initial concentration of this solution was approximately 500 grams plutonium per liter. Solutions at other acid and plutonium concentrations were prepared by dilution of the stock solution with nitric acid of the appropriate molarity to achieve the required final acid and plutonium concentration. The acidity of the stock solution was determined to be 5.9N.

The plutonium used in this study was typical light water reactor grade material having isotopic composition given in Table I. The plutonium is aged material containing equilibrium quantities of ^{241}Am . No attempt was made to correct the bulk solution density for americium content.

A few milligrams of solid NaNO_2 were added to each solution after preparation to minimize gas formation. Gases are produced in plutonium solutions by two mechanisms. One mechanism involves the chemical reduction of Pu(VI) to produce oxygen gas. The other mechanism involves the radiolysis of the solution to produce hydrogen and oxygen gas. It has been observed that the addition of nitric acid to plutonium nitrate solutions, followed by concentration by evaporation will produce significant quantities of Pu(VI) as PuO_2^{++} . This PuO_2^{++} species undergoes reduction to Pu(IV) in aqueous nitrate solution to produce oxygen gas at a constant reaction rate.⁽¹⁾ When a freshly prepared plutonium sample was placed in the densimeter, a stable reading could not be obtained due to gas formation in the solution tube. We have found that a few crystals of NaNO_2 added to these freshly prepared solutions greatly accelerates this reduction reaction to stabilize the Pu(IV) species. The amount of gas formed by the radiolytic decomposition of the solution did not present a problem in measuring the density of the solutions except at the highest plutonium concentration.

2.2 Density Measurements

A remote head for the DMA-10 Anton Parr densimeter was placed in a glove box and thermostatic lines installed from a Lauda RC-20 constant temperature circulating bath located in a hood outside the box. These lines went through existing penetrations (reagent feedthrough lines) and were covered with Amorflex to minimize heat loss and permit constant temperature control. A contact thermistor was placed on the densimeter head and an immersion thermistor placed in the constant temperature bath reservoir. Both thermistors were calibrated with an NBS certified thermometer over the temperature region of interest (25-60°C). The thermistor probes were connected to a Digitek Model 5810 digital thermometer. The temperature stability of the system was better than 0.02°C during a single experiment. The maximum difference in temperature between the remote head and the constant temperature bath was 2°C at 60°C.

Density standards were prepared and characterized by our Standards Laboratory. These control samples were made from bismuth nitrate solutions (maximum density 1.4 g/ml) and uranium nitrate solutions (maximum density 1.7 g/ml). These controls were run at 25°, 35°, 45°, and 60°C using the remote densimeter apparatus along with water and air to insure that the cells were clean. The results of the analyses of the controls indicate that the densities are accurate to $\pm 0.04\%$ relative standard deviation (one sigma). Control samples were run daily to verify instrument operation during the experiments to determine plutonium solution density.

TABLE I
Isotopic Composition of Plutonium Used in This Study

<u>Isotope</u>	<u>Weight Percent</u>
Pu-238	0.455
Pu-239	70.320
Pu-240	22.156
Pu-241	4.50
Pu-242	2.56
Am-241	0.80

Approximately five hundred microliters of solution were required to make a density measurement. Replicate density analyses of the plutonium nitrate solutions were performed at each temperature to better than 0.03% precision (one sigma relative standard deviation).

Due to the high specific alpha activity, radiolysis of the 500 g/% plutonium solutions presented some problems in obtaining a stable reading at 60°C with the densimeter. The uranium density control (1.7 g/ml) was used to determine the time required for the sample to reach equilibrium temperature. The density reading for the plutonium solutions was taken at the same sample equilibrium time.

2.3 Acid Determination

The determination of the free acid concentration in the plutonium nitrate solutions was accomplished using an oxalate-complex titration method. A copy of the method from our Analytical Chemistry Methods Manual is attached in Appendix 1. An Orion 801-A pH meter was used to follow the progress of the titration and determine the endpoint. A standard combination pH electrode was used. A microburet was used to deliver a titrant. All manipulations were carried out in a glove box.

Acid controls were prepared and characterized by the Standards Laboratory. These control samples were of two different types. One type contained nitric acid of known normality. The other type was uranyl nitrate solutions with nitric acid added to simulate acid solutions containing hydrolyzable metal ions. These samples were analyzed using the experimental setup in the glove box. The results of the analyses of these control samples indicate that the acid concentrations could be measured within 0.7% relative standard deviation (one sigma) of the reference value. Two hundred microliters of samples were required to perform an analyses using micro techniques. The precision of the technique based on the analyses of replicate samples was 0.5% relative standard deviation.

2.4 Concentration Measurements

The solutions were analyzed for total plutonium content by controlled potential coulometry. The detailed procedure is attached in Appendix 2. A PAR-Model 380 Controlled Potential Digital Coulometer System was used in this study. The concentrations were determined in grams plutonium per gram solution and converted to grams per liter using the density at 25°C. Plutonium standards were prepared from SRM-946e plutonium metal obtained from the National Bureau of Standards.

A weighed quantity (200-500 mg) of the plutonium nitrate solution was converted to the sulfate form by the addition of sulfuric acid followed by evaporation to near dryness. The residue was dissolved in fresh sulfuric acid, the solution evaporated, and the entire process repeated.

A minimum of two "sufonations" on each plutonium nitrate solution were prepared. Each resulting plutonium sulfate solution was analyzed a minimum of two times using the coulometer. Reagent blanks and secondary standards were run daily during the experiments to determine the plutonium concentrations. Analyses of the NBS standards demonstrated that the plutonium concentration determinations could be determined to within 0.2% of the reference value. The precision on replicate analyses of the same sulfonated sample was better than 0.1% relative standard deviation.

3.0 RESULTS

The solutions were analyzed for acidity and total plutonium concentration at ambient temperature while the density was determined at 25°C, 35°C, 45°C, and 60°C. The results are summarized and given in Table II. It was requested that data be supplied on the following solutions:

<u>Pu, g/l</u>	<u>H⁺, N</u>	<u>Temperature of Density Measurement, °C</u>			
50	3	25	35	45	60
250	1.5	25	35	45	60
250	3	25	35	45	60
250	4.5	25	35	45	60
500	3	25	35	45	60

While the analyzed solutions are not exactly the requested conditions, it was decided that time would not be spent making up new solutions specifically for this project. Analyses were performed on existing solutions with minor acid adjustments.

An attempt was made to fit our data to the equation developed by R. A. daRozza⁽²⁾ using the values of the six parameters determined in their study. Our data showed large deviations at the medium concentrations (approaching 2% lower than predicted). The data daRozza used in developing the six parameter fit (Table 4 of Reference 2) were plotted as deviations of the experimental density from the calculated density as a function of density. The percent deviations are shown in Figure 1. It can be seen that the spread in the data at 1.1 g/ml, for example, is $\pm 1.2\%$. This indicated that the primary source data had questionable precision.

We began to investigate the source of the data used by daRozza. The data supplied by AGNS for his fitting study was taken from J. L. Swanson⁽³⁾, a report prepared for AGNS under contract with Battelle Northwest Laboratories. These data contain estimates of the plutonium and acid concentrations. The densities reported are $\pm 10\%$ measurements determined by a hydrometer. The two French reports⁽⁴⁾ contain data of low precision, namely concentration $\pm 1\%$, acidity $\pm 5\%$, and density $\pm 2\%$.

A least squares fitting program was developed to fit the twenty pieces of experimental data obtained in this study to the six parameter equation proposed

TABLE II

Results of Acid, Density, Concentration
Study for Plutonium Nitrate Solutions

Plutonium Concentration (g/l)	Acid Concentration (N)	Density g/ml at			
		25°C	35°C	45°C	60°C
51.06 (.04)*	2.95 (.02)*	1.1708	1.1649	1.1585	1.1481
230.80 (.41)	1.47 (.01)	1.4076	1.4004	1.3921	1.3789
235.07 (.49)	3.07 (.02)	1.4500	1.4400	1.4323	1.4171
249.45 (.45)	4.27 (.03)	1.4987	1.4888	1.4791	1.4609
477.09 (.38)	2.87 (.02)	1.8070	1.7952	1.7816	1.7632

* Numbers in parentheses are one sigma errors based on replicate measurements (e.g., 51.06 $\pm$ 0.04 g/l).

by daRoza. A comparison of the AGNS parameters and the LLL parameters is shown in Table III along with the relative contribution of each term for a 250 g/l solution of 3N acidity at 35°C. It can be seen that the square of the plutonium concentration term has a small contribution to the overall solution density. The standard error of estimate (using the formalism of daRoza) for our data fit by the computed equation is 0.0191. The maximum deviation of any data point from the computed value is 0.18%. These deviations are shown in Figure 2 for the equation determined in this study by the least squares technique.

Other equations were tested by the least squares technique. It was found that the density could be computed to within 1% of the experimental value using the equation:

$$D = 1 + 0.0477[H^+] - 4.25 \times 10^{-3}[H^+]^2 + 1.477 \times 10^{-3}[Pu] - \frac{T-25}{1000}$$

If the initial constant (unity) and the final temperature coefficient (1/1000) were allowed to float as parameters, densities could be computed to better than 0.5% deviation when compared to the experimental densities. The significance of pursuing correlations using more complex equations with such few data points is questionable. It would appear that more data (a minimum of 100 points for a 5 parameter equation) are required to develop an accurate algorithm for deducing plutonium concentrations from acid, density and temperature measurements.

4.0 REFERENCES

- (1) D. T. Crawley, APH-1093, July 1969.
- (2) R. A. daRoza, MC 77-116, March 10, 1977 (Livermore Report).
- (3) J. L. Swanson and J. H. Gray, "Properties of Concentrated Plutonium Nitrate Solutions", paper presented at American Nuclear Society Meeting, Savannah, Georgia, March, 1978.
- (4) Jean Georges Bruna, et.al., "Results Obtained with Homogeneous Critical Experiments on Pu-239, U-235, and U-233", Report CEA-R-2814, Saclay, France, October, 1965.
- (5) Francis Barbry, et.al., "Theoretical and Experimental Research into the Heterogeneous Poisoning of Fissile-Matter Solutions by Tubes or Rings of Borosilicate Glass", Report CEA-R-3931, Saclay, France, December, 1969.

TABLE III

A Comparison of AGNS Determined Parameters
With LLL Determined Parameters for Acid
Density, Temperature, Concentration Study

<u>Parameter*</u>	<u>LLL</u>	<u>AGNS</u>
C1	0.99708	0.99708
P1	1.81668×10^{-3}	1.65625×10^{-3}
P2	2.6374×10^{-2}	3.2959×10^{-2}
P3	-3.158×10^{-4}	-5.9915×10^{-4}
P4	7.74×10^{-6}	-4.8706×10^{-6}
P5	-2.323×10^{-6}	-1.4217×10^{-6}
P6	-6.312×10^{-7}	-3.418×10^{-8}

<u>Term</u>	<u>LLL % Contribution</u>	<u>AGNS % Contribution</u>
C1	68	70
P1 · [Pu]	31	29
P2 · [H ⁺]	5.4	7.0
P3 · T	0.75	1.5
P4 · [Pu] · [H ⁺]	0.40	0.26
P5 · [Pu] · T	1.4	0.88
P6 · [Pu] ²	2.7	0.15

* Formalism adopted from Reference 2.

Figure 1. A comparison of the calculated density versus experimental density in terms of percent deviation using the data and equations in Reference 2.

Figure 2. A comparison of the calculated versus experimental densities determined in this study using the six parameter equation proposed by daRoz.

DETERMINATION OF THE ACIDITY OF AQUEOUS SOLUTIONS
CONTAINING HYDROLYZABLE METAL IONS USING OXALATE COMPLEXATION1. Scope

- 1.1 This method is applicable to the determination of acidity of aqueous solutions containing hydrolyzable metal ions. The method is suitable for samples containing uranium, plutonium, and fission products in nitric acid solutions. The titration range is approximately 0.3 to 2.5 meq of acid.

2. Summary

- 2.1 Hydrolyzable metal ions of uranium, plutonium, and fission products are complexed with oxalate and the acidity is determined by direct titration with sodium hydroxide (1,2). Complexing is affected by the addition of a large (tenfold) excess of oxalate.

3. Interferences

- 3.1 The determination of acidity using oxalate complexation is quite complicated and requires a careful consideration of several equilibria. Oxalic acid is a dibasic acid which ionizes to give the monovalent binoxalate, and bivalent oxalate ions according to the reversible equations (1) and (2), respectively. Equation (3) is the desired predominant reaction, but it is accompanied by reactions (4), (5), and (6). Equation (5) shows the consumption of hydrogen ion accompanying the formation of the metal binoxalate complex. Reactions causing a negative bias are observed, especially at moderate acidities where monovalent binoxalate ions are stable and predominant.

Equation (6), particularly troublesome at high pH, shows the hydrolysis of the metal ion and the release of acid. In the recommended procedure, the pH of the oxalate complexing solution is controlled at a value where the release of acid via reaction (6) is offset by the consumption of acid via reactions (4) and (5).

- 3.2 The oxalate ratio must be controlled to guarantee reliable results. Significant differences have been noted with changes in the sample to oxalate ratio.

4. Apparatus

- 4.1 pH Meter - Orion 701 or equivalent.
- 4.2 Beakers - Assorted sizes.
- 4.3 Buret
- 4.4 pH Electrode
- 4.5 Pipets - Macro and micro, assorted sizes.
- 4.6 Reference electrode
- 4.7 Magnetic stirrer - With plastic-coated stirring bars.

5. Reagents

- 5.1 Purity of reagents - Unless otherwise stated, reagent grade chemicals shall be used.
- 5.2 Purity of water - Unless otherwise indicated, all references to water shall be understood to mean distilled water.
- 5.3 Nitric acid - (HNO_3) - 2.0N - standard.
- 5.4 Potassium oxalate - (K_2Ox) - 0.45M - Prepare by dissolving 82.9 g of $\text{K}_2\text{Ox} \cdot \text{H}_2\text{O}$ in approximately 900 mls water. Adjust pH between 5.50 and 5.60 by adding NaOH or HNO_3 . Dilute to 1 liter with water.
- 5.5 Sodium hydroxide - (NaOH) - standard.

6. Safety

- 6.1 Wear rubber gloves when handling strong acid samples. Pipet the sample aliquot into the water, rather than the water into the acid -- as the heat of reaction can cause the acid to spatter. Wash any areas of the skin or eyes contacted by acids or bases with copious amounts of water.

7. Calibration

- 7.1 Select a bench standard with a matrix similar to that of the sample being analyzed and determine the acidity according to the procedure in Section 8.
- 7.2 If the results are within the limits set by the Quality Control Laboratory, proceed with sample analysis.

8. Procedure

- 8.1 Wash the pH meter electrodes with distilled water and dry them with absorbent tissue paper.
- 8.2 Standardize the pH meter against a pH 7.00 buffer solution, then wash the electrodes with water and wipe with tissue paper.
- 8.3 Pipet 50 ml of the 0.45M K_2Ox reagent, preadjusted to pH 5.55, into a 100-ml beaker containing a stirring bar.
- 8.4 Lower the pH electrodes into the solution and stir the solution for about 3 minutes.
- 8.5 The pH must be in the range of 5.50 to 5.60; if not, adjust by adding NaOH or HNO_3 as required.
- 8.6 Pipet 500 μ l of sample into the oxalate solution, stir, then observe the pH. If the pH is below 5.3, continue. If the pH is above 5.3, discard the solution and pipet a larger aliquot. Sample aliquots up to 10 ml may be taken with no adverse effect if the aliquot does not contain more than 3.0 meq of hydrolyzable metal ion.
- 8.7 Titrate with 0.100N NaOH to the pH selected in step 8.5.
- 8.8 Record the data and calculate the results as shown in the calculations section.

9. Calculations

- 9.1 Determine the volume of NaOH used for the titration from the buret reading.

Calculate the sample acidity as follows:

$$N = \frac{A \times B}{V}$$

where:

N = normality of sample,

A = normality of NaOH,

B = volume of NaOH in ml, and

V = volume of sample aliquot in ml.

9.2 Typical Calculation

$$A = 0.100N$$

$$B = 6.80 \text{ ml}$$

$$V = 0.50 \text{ ml}$$

$$N = \frac{A \times B}{V}$$

$$N = \frac{(0.100N)(6.80 \text{ ml})}{0.50 \text{ ml}}$$

$$N = 1.360N$$

References

- (1) Idaho Nuclear Corporation Analytical Chemistry Manual, Acidity-Vol-1, November 1968.
- (2) G. L. Booman, M. C. Elliot, et al, Anal. Chem. 30, (1958), 284.

DETERMINATION OF PLUTONIUM BY
CONTROLLED-POTENTIAL COULOMETRY

1. Scope

- 1.1 This method is applicable to the determination of the plutonium content of relatively pure aqueous solutions of plutonium nitrate. Optimum precision is obtained when sample aliquots containing approximately 5 mg of plutonium are used. The estimated precision for a single measurement by this method is 0.15% relative standard deviation.

2. Summary

- 2.1 The basic principle of coulometric analysis is contained in Faraday's Law which states that the weight of a substance oxidized or reduced at an electrode is proportional to the coulombs of electricity passed through the electrode. By measuring the number of coulombs required to quantitatively oxidize or reduce a substance from one valence state to another, the number of equivalents of the substance present can be determined. Those substances which have redox potentials near that of the substance being determined constitute interferences. In controlled-potential coulometry, the potential of the working electrode is controlled at the desired potential and the number of possible interferences is thus greatly reduced. Detailed discussions on this method can be found in References (1) through (6).
- 2.2 Sulfuric acid is used as the supporting electrolyte in this method because Pu(VI) can be electrolytically reduced to Pu(III) quantitatively in the medium. It is only partially reduced in solutions of other mineral acids. The plutonium is first reduced to Pu(III) at +0.310 volts versus a saturated calomel electrode (SCE). The Pu(III) is then oxidized to Pu(IV) at +0.670 volts versus a SCE. The quantity of plutonium present is calculated from the number of coulombs required for the oxidation according to the following equation:

$$W = \frac{MQ}{nF}$$

where:

- W = weight of plutonium electrolyzed in g,
- M = gram-molecular weight of plutonium (must be adjusted for isotopic variations),
- Q = number of coulombs required by the electrolysis,
- n = number of electrons involved in the electrode reaction, and
- F = Faraday constant in coulombs/equivalent.

3. Interferences

- 3.1 Interference is caused by ions which are electrically active at the oxidation-reduction potentials used or by species that prevent 100% current efficiency (e.g., oxidants, reductants, organics). Since there is less than 50 mV difference in the formal potentials of Fe(II)-Fe(III) and Pu(III)-Pu(IV) when sulfuric acid is used as the supporting electrolyte, iron is an interference in this method. If iron is present, the procedure developed by Stokely (3) can be used to eliminate the interference.
- 3.2 Polymerized plutonium is not electrolyzed, and unless the plutonium is known to be in the ionic state, the sample must be depolymerized by treatment with hydrofluoric acid and heating.
- 3.3 Oxygen interferes by oxidizing Pu(III) to Pu(IV) and must be eliminated by sparging with argon.
- 3.4 Free fluoride cannot be tolerated even in trace amounts; subsequently, samples or standards containing fluoride must be evaporated to copious fumes of H_2SO_4 to remove all fluoride.

4. Apparatus

- 4.1 Controlled-Potential Coulometer - The coulometer used should be a solid state instrument capable of controlling the cell potential to ± 1 mV. The coulometer should include a high precision electronic integrator capable of integrating cell currents from 30 μA to 100 mA with a precision of $\pm 0.02\%$.

- 4.2 Digital voltmeter - 10-volt range, 5-digit readout, 0.01% accuracy.
- 4.3 Cell assembly - The success of controlled-potential coulometric methods is strongly dependent upon the design of the titrating cell. The cell dimensions, electrode area and spacing, and stirring rate are important parameters in a design which will minimize the time required for titration. Cell assemblies of various satisfactory designs are described in the literature (2,4). The following components are required:
- 4.3.1 Cell - The cell is fabricated from borosilicate glass, normally 42 mm od, threaded to match like threads in the Teflon cap. Dimensions and electrode spacing are given in Reference (4).
- 4.3.2 Counter electrode and salt bridge tube - The counter electrode is a coiled length of 0.020-inch diameter platinum wire. The spiral is inserted into an unfired vycor tube filled with 0.5M H_2SO_4 .
- 4.3.3 Reference electrode and salt bridge tube - The reference electrode is a micro-saturated calomel electrode (SCE). The salt bridge is an asbestos-fiber-tipped tube filled with 0.5M H_2SO_4 .
- 4.3.4 Working electrode - The working electrode is fabricated from 45 mesh platinum gauze. Details may be obtained from Reference (4). The electrode is stored in 8M HNO_3 when not in use.
- 4.3.5 Stirrer - Either a paddle-type stirrer driven at 1800 rpm by a synchronous motor, or a magnetically driven stirring bar is adequate. Magnetic stirring slightly simplifies the arrangement of the cell cap.
- 4.4 Inert gas inlet tube - A glass tube, approximately 5 mm od, is inserted in the cell so that its tip is about 1 cm above the surface of the electrolyte solution. The gas flow is adjusted so that the surface of the solution is depressed almost 1/4 inch. The gas usually used is oxygen-free argon. An inert gas blanket is required for titrations in sulfuric acid.

5. Reagents

- 5.1 Purity of reagents - Unless otherwise stated, reagent grade chemicals shall be used.
- 5.2 Purity of water - Unless otherwise indicated, all references to water shall be understood to mean distilled water.
- 5.3 Argon - Oxygen-free.
- 5.4 Hydrochloric acid - (HCl) - 6M - Prepare by diluting 500 ml of concentrated HCl to 1 liter with water.
- 5.5 Hydrofluoric acid - (HF) 28M - Prepare by diluting 480 ml of concentrated HF to 1 liter with water.
- 5.6 Nitric acid - (HNO_3) - 8M - Prepare by diluting 500 ml of concentrated HNO_3 to 1 liter with water.
- 5.7 Plutonium standard solution - Dissolve the entire contents of one 0.5 g ampoule of NBS 949 plutonium metal in a minimum quantity of 6M HCl. Add 10 ml of 3M H_2SO_4 and evaporate to copious fumes of H_2SO_4 . Dilute with 0.5M H_2SO_4 to approximately 50 ml and weigh to ± 0.2 mg.
- 5.8 Sulfuric acid - (H_2SO_4) - 18M.
- 5.9 Sulfuric acid - (H_2SO_4) - 0.5M - Prepare by adding 28 ml of concentrated H_2SO_4 to water with constant stirring and diluting to 1 liter with water.

6. Safety

- 6.1 Because of the toxic nature of plutonium, extreme care must be exercised in its handling. Take every precaution to avoid inhaling or ingesting plutonium.

7. Calibration

- 7.1 The coulometer incorporates an electronic integrator circuit. This circuit develops an output voltage that is proportional to the quantity of electricity conducted during electrolysis. The relationship between coulombs of electricity and integrator readout voltage must be established by calibration.

- 7.2 Either chemical or electrical calibration can be used for the determination of plutonium. The chemical and electrical factors should be identical within a difference of 0.05%. If the factors are different, the reason for the discrepancy should be determined and proper corrections made before samples are analyzed.

7.2.1 Electrical Calibration

Check equipment as per manufacturer's instructions. Determine the electrical calibration factor (F = equivalents/volt of readout) from cell operation for oxidation and reduction cycles.

7.2.2 Chemical Calibration

- 7.2.2.1 Quantitatively transfer a weighed aliquot of the plutonium calibration solution containing 5 to 10 mg of plutonium into the cell with 0.5M H_2SO_4 .
- 7.2.2.2 Add a sufficient quantity of 0.5M H_2SO_4 to the cell to obtain the desired liquid level in the cell.
- 7.2.2.3 Screw the cell into the Teflon cap; connect the cable from the potentiostat to the electrodes.
- 7.2.2.4 Start the argon gas flow at a rate of 300 ml/minute. The argon flow purges air from the cell and prevents air oxidation of Pu(III).
- 7.2.2.5 Set the control potential to +0.310 volts versus the SCE. Plutonium is reduced to Pu(III). Iron impurity is reduced to Fe(II).
- 7.2.2.6 After 5 minutes of argon gas flow, turn the current on.
- 7.2.2.7 Turn off the current when it decreases to the background level. The current should decrease exponentially to the background level which is usually about 50 μA . Determine this value by a preliminary titration of a blank solution.

Complete reduction of plutonium to Pu(III) is indicated by the decrease in current to the background level.

- 7.2.2.8 Set the control potential to +0.670 volts. Pu(III) is oxidized only to Pu(IV) in the presence of sulfate which complexes and stabilizes tetravalent plutonium. Iron(II) impurity is oxidized to Fe(III).
- 7.2.2.9 Turn the current on at a maximum initial level of 30 mA.
- 7.2.2.10 Turn off the current when it decreases to the background level. Complete oxidation of Pu(III) to Pu(IV) is indicated by the decrease in current to the background level.
- 7.2.2.11 Record the readout voltage. This is proportional to the milliequivalents of Pu(III) oxidized to Pu(IV).
- 7.2.2.12 Repeat 7.2.2.1 through 7.2.2.11 using a blank solution.
- 7.2.2.13 Calculate the chemical calibration factor F_c as follows:

$$F_c = \frac{E_{Pu}}{R-B}$$

where:

F_c = equivalent/volt of readout,

E_{Pu} = equivalents of plutonium in aliquot of standard,

R = integrator readout voltage for plutonium titration, and

B = integrator readout voltage for blank titration.

8. Procedure

- 8.1 Transfer a weighed aliquot containing 5 to 10 mg of plutonium into a 50-ml beaker or a 30-ml platinum dish. Weigh the aliquot to ± 0.2 mg.
- 8.2 Add 10 ml of $3M$ H_2SO_4 and 1-2 drops of concentrated HF . Evaporate to near dryness, or about 0.1 ml.
- 8.3 Rinse the plutonium titration cell and the outside of the vycor tubes containing the counter and reference electrode with $0.5M$ H_2SO_4 .
- 8.4 Quantitatively transfer the evaporated solution obtained in 8.2 with the aid of five 1-ml rinses of $0.5M$ H_2SO_4 to the cell. Add sufficient quantity of $0.5M$ H_2SO_4 to obtain the desired liquid level in the cell.
- 8.5 Screw the cell into the Teflon cap; connect the cable from the potentiostat to the electrodes.
- 8.6 Start the argon gas flow at a rate of 300 ml/minute.
- 8.7 Set the control potential at +0.310 volts versus SCE. At this potential plutonium is quantitatively reduced to $Pu(III)$. Iron impurity is reduced to $Fe(II)$.
- 8.8 After 5 minutes of argon flow, turn the current on.
- 8.9 Turn current off when it decreases to the background level. The current should decrease exponentially to the background level which is usually about 50 μA . Determine this value by preliminary titration or by titration of a blank solution. Complete reduction of plutonium to $Pu(III)$ is indicated by the decrease in current to the background level.
- 8.10 Set the control potential to +0.670 volts. At this potential, $Pu(III)$ is oxidized to $Pu(IV)$ in the presence of sulfate which complexes and stabilizes tetra-valent plutonium. Iron(II) impurity is oxidized to $Fe(III)$.
- 8.11 Turn the current on at a maximum initial level of 30 mA.

- 8.12 Turn off the current when it decreases to the background level. Complete oxidation of Pu(III) to Pu(IV) is indicated by the decrease in current to the background level. Record the readout voltage.
- 8.13 Repeat 8.1 through 8.12 without the plutonium sample. Record the readout voltage as B (blank).

9. Calculations

- 9.1 Calculate plutonium content of the sample as follows:

$$\text{Pu} = \frac{(R - B)F_c W_e}{S} \times 100$$

where:

Pu = plutonium content of sample in weight percent,

R = integrator readout for plutonium titration,

B = blank voltage readout,

F_c = chemical calibration factor in eq/V,

W_e = equivalent weight of plutonium (varies with isotopic enrichment) in g/eq, and

S = sample weight in g.

9.2 Typical Calculation

9.2.1 Calibration Factor

$$R = 1.200 \text{ V}$$

$$B = 0.010 \text{ V}$$

$$E_{\text{Pu}} = \frac{0.005 \text{ g of Pu in Standard Aliquot}}{239.09 \text{ eq wt of Pu Std}}$$

$$E_{\text{Pu}} = 2.091 \times 10^{-5} \text{ eq}$$

$$F_c = \frac{E_{\text{Pu}}}{R - B}$$

$$F_c = \frac{2.091 \times 10^{-5} \text{ eq}}{1.200 \text{ V} - 0.010 \text{ V}}$$

$$F_c = 1.758 \times 10^{-5} \text{ eq/V}$$

9.2.2 Plutonium Weight Percent

$$R = 1.100 \text{ V}$$

$$B = 0.010 \text{ V}$$

$$W_e = 239.09 \text{ g/eq}$$

$$S = 0.5000 \text{ g}$$

$$Pu = \frac{(R - B)F_c W_e}{S} \times 100$$

$$Pu = \frac{(1.100 \text{ V} - 0.010 \text{ V}) (1.758 \times 10^{-5} \text{ eq/V}) (239.09 \text{ g/eq})}{0.5000 \text{ g}} \times 100$$

$$Pu = 0.9163 \text{ weight percent}$$

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