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COULOMETRIC DETERMINATION OF PLUTONIUM IN SOLUTIONS OF DISSOLVED REACTOR FUEL ELEMENTS

By

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COULOMETRIC DETERMINATION OF PLUTONIUM  
IN SOLUTIONS OF DISSOLVED REACTOR FUEL ELEMENTS

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January, 1970

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## ABSTRACT

Controlled potential coulometry has been applied to the determination of plutonium in the complex, highly-radioactive mixture of uranium, plutonium, neptunium, and fission products which results from the dissolution of reactor fuel elements in nitric acid. It was found that a separation of plutonium from fission products was necessary prior to the titration because of the poisoning effect of zirconium on the working electrode and the significant concentrations of fission product elements with oxidation potentials close to that of the Pu(III)/Pu(IV) couple. A strongly-basic anion exchange resin containing pyridinium exchange groups was used in small (9 cm x 0.5 cm) columns for the separations. The separation procedure gave better than 99 percent recovery of plutonium and resulted in the elimination of significant concentrations of interfering ions. The measured radiation of the sample was also reduced from an average of 3 roentgens/hr to about 150 milliroentgens/hr. Coulometric analysis of 7 plutonium samples resulted in a relative standard deviation of  $\pm 1.1$  percent at the 95 percent confidence interval.

COULOMETRIC DETERMINATION OF PLUTONIUM  
IN SOLUTIONS OF DISSOLVED REACTOR FUEL ELEMENTS

INTRODUCTION

Nitric acid solutions of spent reactor fuel elements (dissolver solutions) must be analyzed for plutonium content before entering separation process streams in the Purex Plant. Present methods of analysis are alpha counting (coupled with alpha energy analysis) and isotopic dilution. Because of the uncertainty in the many factors that are involved in calculating a plutonium value from alpha counting, the accuracy of this method is relatively poor. Isotopic dilution followed by mass spectrometric analysis of plutonium offers reasonable accuracy, but requires lengthy and expensive determinations.

Controlled potential coulometry was chosen as the method to be developed for determining the plutonium concentration of dissolver solutions because of its speed, accuracy, and ability to measure specific ions in the presence of others. This report summarizes the analytical data obtained from the determination of plutonium in synthetic and actual plant dissolver solutions using the coulometric method. The specific procedure which was developed for these solutions is also described.

SUMMARY

Controlled potential coulometry has been applied to the determination of plutonium in synthetic and plant dissolver solutions. It was found that a separation of plutonium from fission products and iron was necessary because of their interference with the titration. An anion exchange procedure was developed which eliminated significant quantities of

interfering species and which gave quantitative plutonium recovery. After the anion exchange procedure was performed on plant dissolver solutions, the measured radiation of the plutonium samples was low enough ( $\sim 150$  milliroentgens/hr at the sample surface) so that the coulometric titrations could be performed in an unshielded hood. Titration of plutonium separated from seven plant samples resulted in a plutonium recovery of 101 percent and a relative standard deviation of  $\pm 1.1$  percent.

## EXPERIMENTAL

### EQUIPMENT

A controlled potential coulometer system Model 3 (M-T Electronics Company) which consisted of a potentiostat and an integrator module was used for all titrations. A Darcy 440 digital multimeter was connected to the integrator for use as the readout device. The instrument was electrically calibrated by substituting a precision resistor (100 ohms,  $\pm 0.005$  percent tolerance) and a 1.4 volt mercury battery for the electrolysis cell. Measurements of time with a Type S-1 (The Standard Electric Time Company) electric timer versus current gave calibration values (in faradays/volt) which were reproducible to within  $\pm 0.05$  percent.

The cell used for the titrations, shown in Figure 1, is similar to that described by Scott and Peekema.<sup>(1)</sup> The three cell compartments are separated by porous, unfired Vycor disks about one-half millimeter thick. The disks were soaked in  $1M$   $HNO_3$  electrolyte for several hours before use. These salt bridges provided very little electrical resistance, and leakage of electrolyte between compartments was not detectable. Helium gas (99.995 percent purity) was used to stir and deaerate the electrolysis solution.



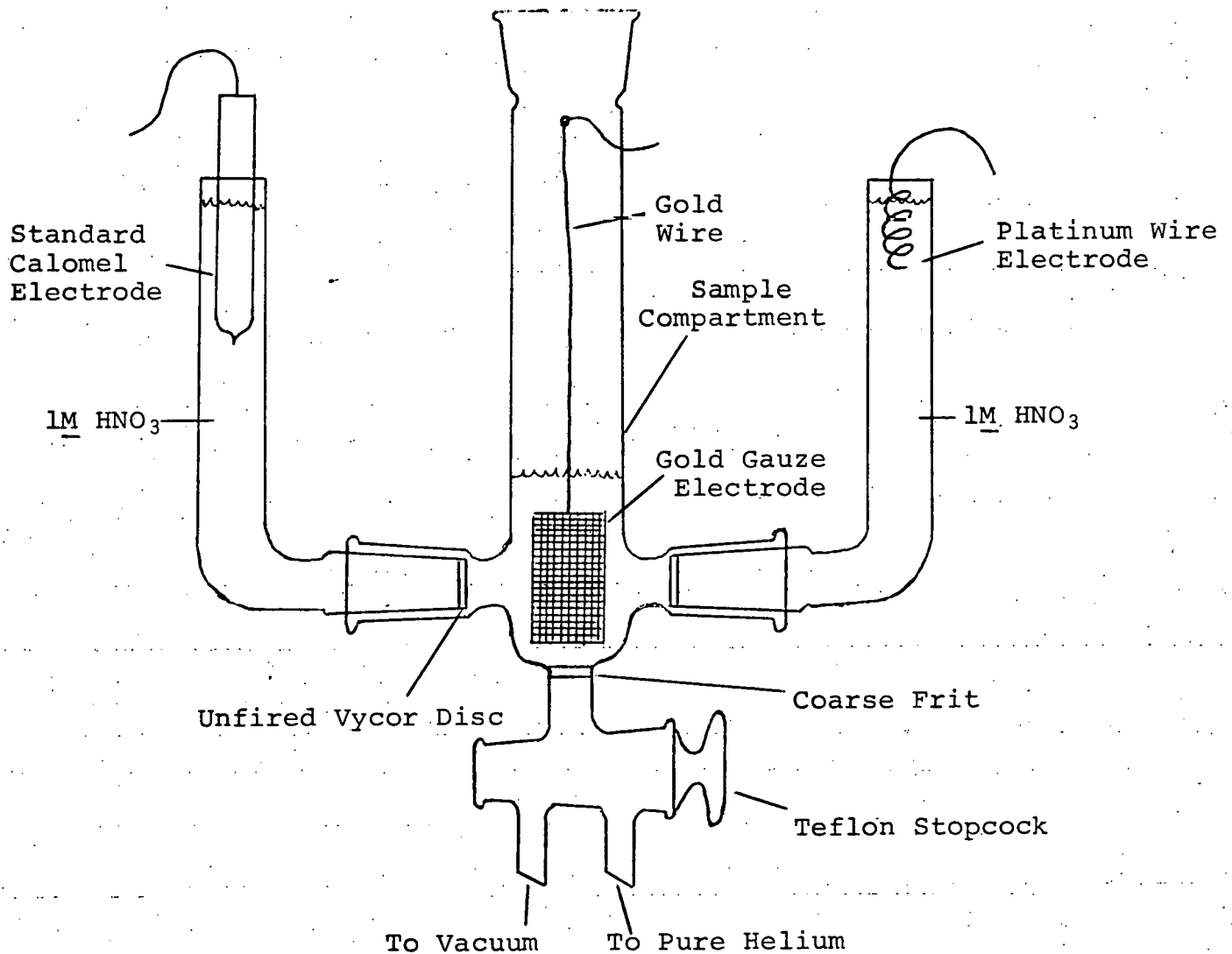


FIGURE 1  
ELECTROLYSIS CELL

Notes

- a. The unfired Vycor discs are attached to the glass joints with sealing wax.
- b. The 1M HNO<sub>3</sub> electrolyte in the side arms is changed weekly.
- c. A ground glass joint filled with glass wool may be attached to the sample compartment in order to prevent plutonium contamination.

STANDARD SOLUTIONS

Standard plutonium nitrate solutions containing 1M HNO<sub>3</sub> were prepared from a standardized stock solution. These standard solutions were used to verify the electrical calibration of the instrument and determine the accuracy and precision of the coulometric titrations.

The synthetic dissolver solution contained the following elements in 0.46M HNO<sub>3</sub>:

<u>Element</u>	<u>Concentration</u> <u>g/liter</u>
U	>400
Pu	0.224
Np	0.0019
Rb	0.0042
Sr	0.0111
Y	0.0057
Zr	0.0404
Nb	0.0093
Mo	0.0330
Ru	0.0180
Rh	0.0045
Pd	0.0039
Cd	0.00018
Sn	0.00020
Sb	0.00013
Te	0.0049
Cs	0.0268
La	0.0629
Ce	0.0279
Se	0.00056

## PROCEDURE

Hydroxylamine hydrochloride solution was added to an accurately-measured sample (3 or 4 ml) of dissolver solution in order to reduce all the plutonium to the (III) valence state. A small amount of ferric nitrate solution was added to catalyze the reduction, and the solution was heated for 20 min at about 90 C. The nitric acid concentration was adjusted to 3M and the solution was cooled to room temperature. A sodium nitrite solution was then slowly added in order to oxidize the plutonium to the (IV) valence state. The nitric acid concentration was adjusted to 7.0M and the resulting solution was added to a column (9 cm x 0.5 cm) of 50 to 100 mesh Bio-Rex 9 (Bio-Rad Laboratories) anion exchange resin which had previously been converted to the nitrate form and stored in 7.0M HNO<sub>3</sub>. The column was washed several times with 7.0M HNO<sub>3</sub> and the plutonium was then eluted with 0.5M HNO<sub>3</sub>. The eluate was then transferred to the electrolysis cell while purging the cell with helium. One drop of saturated sulfamic acid solution was added to the cell in order to destroy any nitrite present. The plutonium sample was pre-oxidized to (IV) valence at +0.860 volt [versus standard calomel electrode (SCE)] until the cell current reached 5  $\mu$ a. The sample was then reduced to (III) valence at +0.500 volts (versus SCE) until the cell current reached 5  $\mu$ a. The electrolysis procedure was also applied to a blank solution containing a volume of 1M HNO<sub>3</sub> equivalent to the sample solution plus one drop of saturated sulfamic acid solution. The value obtained from the reduction of the blank was subtracted from the value obtained from reduction of the sample.

## DISCUSSION

The determination of plutonium in dissolver solution presents several problems which this study has attempted to solve.

They are as follows:

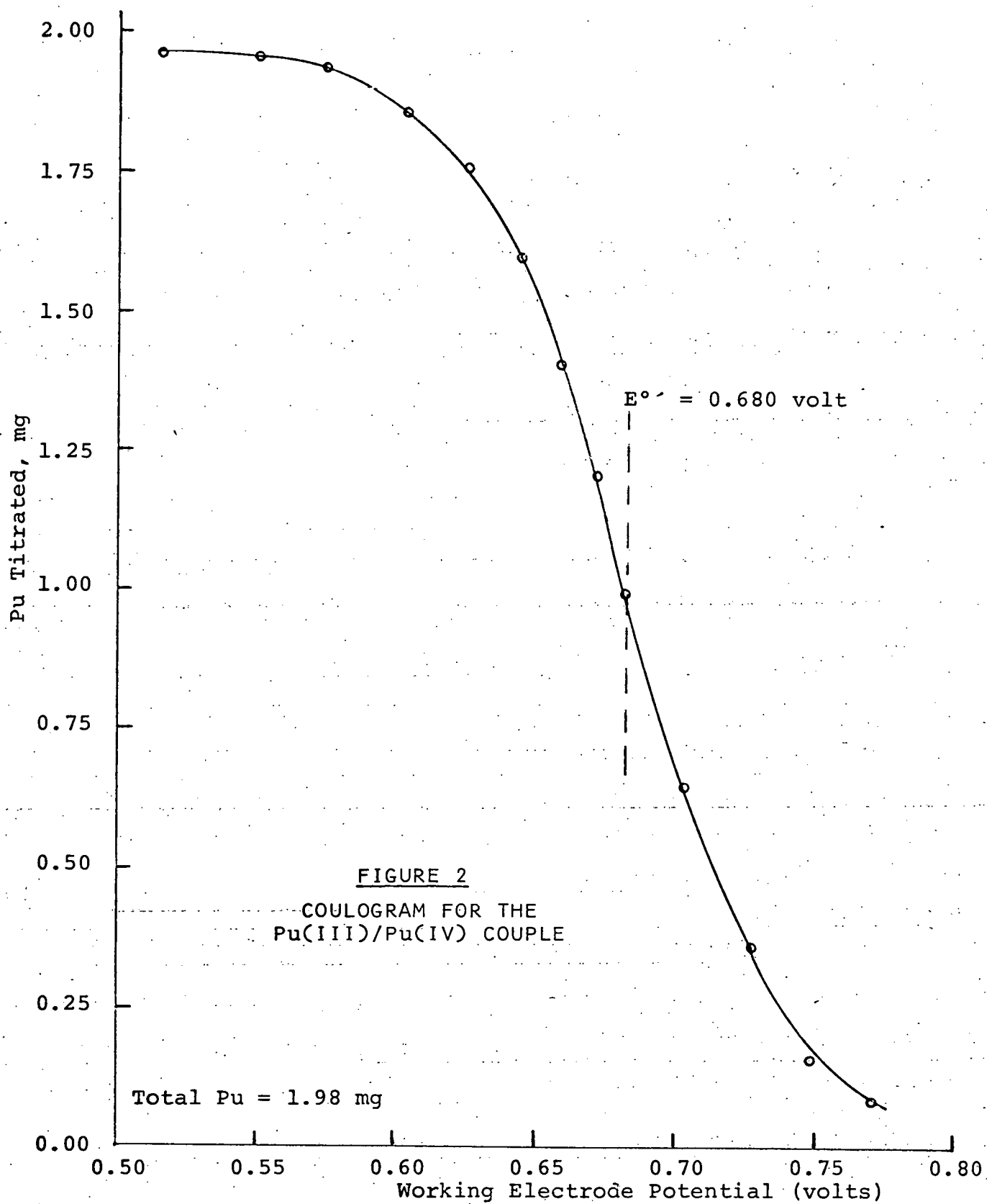
- The high radiation field associated with the solutions necessitates the use of remote manipulators when handling the solutions.
- In the complex mixture of uranium, plutonium, neptunium, and about 20 different fission product elements in significant quantities, some element is very likely to interfere with the plutonium measurement no matter what method is used.
- The low plutonium content (wt Pu/wt U < 0.001) requires that relatively large sample volumes be analyzed.

Controlled potential coulometry appeared to be well suited for this type of determination because the amount of plutonium required for accurate analysis is small (0.2 to 1.0 mg) and the method is not sensitive to nitrate, uranium, or the majority of other species present in dissolver solutions. Also, it has been shown<sup>(1)</sup> that Pu(III) can be oxidized and Pu(IV) reduced with 100 percent current efficiency at a platinum electrode. Therefore, Faraday's Law can be applied.

In order to determine the appropriate potentials to be used for the electrolysis, a coulogram was obtained by measuring 1.98 mg of Pu(IV) into the cell and decreasing the potential stepwise from 0.77 to 0.45 volts (versus SCE). The electrolysis was allowed to come to equilibrium after each step and the readout (in mg of Pu) was observed. A plot of mg of Pu titrated versus applied potential is shown in Figure 2. The inflection point of the curve is at 0.680 volts and corresponds to  $E^{\circ}$  where

$$E = E^{\circ} + 0.059 \log \frac{[\text{Pu(IV)}]}{[\text{Pu(III)}]}$$

From this equation, a separation of 360 mV ( $E^{\circ} \pm 180$  mV) for



oxidation and reduction at the one milligram level would result in electrolysis of 99.8 percent of the plutonium.

It was found that both platinum gauze and gold gauze working electrodes could be used for the titrations. However, the use of gold gauze resulted in a much lower background current than that of the platinum gauze in the 1M HNO<sub>3</sub> medium (0.5  $\mu$ a compared with 20  $\mu$ a).

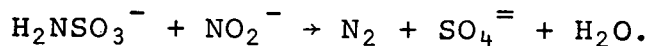
In order to determine the maximum possible accuracy and precision for the titrations, pure plutonium nitrate standard solutions were titrated coulometrically in 1M HNO<sub>3</sub> in the presence of a trace of sulfamic acid. For eight samples, the recovery was 100.09 percent with a relative standard deviation of +0.12 percent at the two milligram level.

At the beginning of this study, it was hoped that separation of plutonium from other dissolver solution components might not be necessary. Scott and Peekema<sup>(1)</sup> reported a relative error of +1.4 percent and a relative standard deviation of +0.5 percent for plutonium determinations with no previous separation of plutonium from other dissolver solution components. In the present work, however, coulometric titration of varying amounts of synthetic dissolver solution (in 1M HNO<sub>3</sub> plus a trace of sulfamic acid) repeatedly gave results which were high by 7 to 10 percent. Also, consecutive titrations of the same sample were not reproducible, but gave lower values with each titration. An even greater error would be expected from titrations of plant dissolver solutions since these solutions contain a significant amount of iron which has an oxidation potential near that of the Pu(III)/Pu(IV) couple [ $E^\circ = -0.9818$  volt]. Table I, page 9, lists some of the elements present in dissolver solution which might be expected to interfere.

TABLE I  
ELEMENTS WITH HALF-REACTION POTENTIALS NEAR THAT OF  
THE Pu(III)/Pu(IV) COUPLE

<u>Element</u>	<u>Half-Reaction</u>	<u>E°</u> <u>Volts</u>	<u>Mole Ratio</u> <u>Pu/Element</u>
Fe	$\text{Fe}^{2+} = \text{Fe}^{3+} + e^{-}$	-0.7701	Variable
Np	$\text{NpO}_2^{+} = \text{NpO}_2^{2+} + e^{-}$	-1.137	≈100
Ru	$\text{RuO}_4^{-} = \text{RuO}_4 + e^{-}$	-0.9	≈5
Pd	$\text{Pd} = \text{Pd}^{++} + 2e^{-}$	-0.987	≈25
N	$\text{NH}_4^{+} + 2\text{H}_2\text{O} = \text{HNO}_2 + 7\text{H}^{+} + 6e^{-}$	-0.86	Variable

Interference by nitrite can be eliminated by addition of sulfamic acid, the reaction being



The zirconium present in dissolver solutions seriously interferes with the coulometric titration by slowing the electrolysis and giving low results. According to Shults,<sup>(2)</sup> the interference is due to hydrolysis of  $\text{Zr}^{4+}$  at the working electrode surface which causes fouling of the electrode.

Because of the interferences discussed above, it was necessary to effect a separation of plutonium from the interfering elements. Anion exchange was chosen as the separation method to be developed because of the ease of performing the separation remotely and the almost unique ability of plutonium(IV) anionic nitrate complex to absorb on anion resins in nitrate systems. Separation of plutonium(IV) by anion exchange from nitric acid solutions is a well known procedure<sup>(3)</sup> and is used as the final purification step for plutonium in the Purex process. Ryan<sup>(4)</sup> has given evidence that the plutonium species absorbed on the resin is  $\text{Pu}(\text{NO}_3)_6^{\equiv}$  and that the

absorption reaches a maximum at about  $7M$   $HNO_3$ . At lower  $HNO_3$  concentrations, the hexanitrate complex is destroyed and the Pu(IV) species becomes cationic and is desorbed from the resin.

Hanshuh<sup>(5)</sup> has used an anion exchange separation and subsequent coulometric titration of plutonium for the determination of plutonium in dissolver solutions. Several problems were encountered with elution of plutonium from the Dowex 1 x 4 (trade name, Dow Chemical Company) resin used in this study. First, large volumes of eluant were needed to give quantitative recovery. Second, organic material introduced into the eluate from the resin (probably because of degradation by strong  $HNO_3$ ) interferes seriously in the coulometric titration procedure.

In contrast to Dowex 1, Bio-Rex 9 resin is extremely resistant to strong oxidizing agents including hot, concentrated nitric acid. It contains strongly-basic pyridinium groups bonded to a polystyrene lattice. Because of its aromatic nature, it is also resistant to degradation by radiolysis.<sup>(6)</sup> The use of this resin for separation of plutonium prior to coulometric analysis does not seriously interfere with the titration. Also, the 10 milliliters of eluant needed to quantitatively elute the plutonium is not excessive. A noticeable increase in titration time occurs after 10 to 20 determinations, but the accuracy appears to be unaffected. The titration speed can be increased by cleaning the gold gauze electrode periodically by immersing it in chromic acid and then washing it thoroughly with distilled water.

The separation and coulometric titration procedures described in the EXPERIMENTAL section were performed on 4.00-ml samples of synthetic dissolver solution. The results are given in Table II, page 11.



TABLE II  
RESULTS OF Pu DETERMINATIONS  
IN SYNTHETIC DISSOLVER SOLUTIONS

<u>Sample No.</u>	<u>Pu Taken mg</u>	<u>Pu Found*</u> <u>mg</u>	<u>% Recovery</u>
1	0.896	0.906	101.1
2	0.896	0.898	100.2
3	0.896	0.890	99.3
4	0.896	0.892	99.6
5	0.896	0.894	99.8
6	0.896	0.897	100.1

\* Blank = 0.010 mg Pu.

The average recovery for this set of determinations is 100.0 percent and the relative standard deviation is  $\pm 0.63$  percent.

The plutonium separation procedure with real dissolver solution (3.00-ml samples) was carried out remotely in a shielded enclosure. After separation, the plutonium samples were colorless solutions with a measured radiation of about 150 milliroentgens per hour at the sample vial wall (compared with about 3 roentgens/hr before separation). The samples were then removed from the shielded enclosure and titrated coulometrically in a fume hood. The results of the titrations are given in Table III, page 12.

The average recovery for these determinations is 101.0 percent and the standard deviation is  $\pm 1.1$  percent. The bias between plutonium values obtained by alpha counting and coulometry is not surprising since the precision of the counting method is estimated to be relatively low ( $\pm 2.93$  percent). (7)

TABLE III  
RESULTS OF Pu DETERMINATIONS  
IN PLANT DISSOLVER SOLUTIONS

<u>Sample No.</u>	<u>Pu Concentration Calculated*†</u>	<u>Pu Concentration Experimental†</u>
1	1.00	1.004
2	1.00	1.001
3	1.00	0.997
4	1.00	1.016
5	1.00	1.005
6	1.00	1.021
7	1.00	1.025

\* Determined by an alpha counting procedure, the precision of which is +2.93 percent.

† Concentrations are in relative units.

#### ACKNOWLEDGMENTS

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