SPECTROPHOTOMETRIC DETERMINATION OF TRACE URANIUM
IN PLUTONIUM NITRATE AND OXIDE WITH
2-(2-PYRIDYLAZO)-5-DIETHYLAMINOPHENOL

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ABSTRACT

A spectrophotometric method for the determination of trace uranium in plutonium was developed and evaluated. Uranium was separated from plutonium in a 4M HCl-2M $\text{NH}_2\text{OH}\cdot\text{HCl}$ matrix with Aliquat-336. The uranium in the organic was determined by spectrophotometry using 2-(2-pyridylazo)-5-diethylaminophenol (PADAP). The parameters for color development were evaluated. The effect of Pu on the U determination was examined for both Aliquat-336 and trioctylphosphine oxide extractions. Three methods for preparing and dissolving PuO_2 samples for the analysis were studied and the effect of HCl, HF, and organic-to-aqueous ratio on the extraction determined. The spectrophotometric analysis of U in PuO_2 was compared with X-ray emission analysis of the same material. The average spectrophotometric result on U in PuO_2 was $100.4 \pm 8.4\%$ compared with $108.3 \pm 2.5\%$ for X-ray emission. Uranium analyses for an FFTF PuO_2 standard were bias 20% high for both techniques but had precisions of less than $\pm 5\%$. Of the 33 ions tested, only palladium seriously interfered. Eight milliequivalents of HNO_3 can be tolerated by the Aliquat-336 uranium extraction. When no uranium extraction is necessary, a direct spectrophotometric method for measuring U levels between 1 and 10 μg was examined. The spectrophotometric determination of U with PADAP offers a sensitive and selective method for analyzing U in many nuclear materials.

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INTRODUCTION

Uranium analyses are needed in the nuclear reprocessing industry in order to control the separation of uranium from plutonium, evaluate the quality of the final product, and ensure that the integrity of the environment is maintained. The determination of trace U has been accomplished in the past^[1] using fluorescence, spectrophotometric, and X-ray emission techniques. Fluorescent methods offer the advantage of high sensitivity but are subject to poor precision and numerous interferences. X-Ray methods are more selective but lack the desired sensitivity for many problems.

Florence, Johnson, and Farrar^[2] have described the application of 2-(2-pyridylazo)-5-diethylaminophenol (PADAP) to the determination of trace U in water and ores.^[3] Steele, Cook, and Geregthy^[4] and Pakalns^[5] have also examined the application of PADAP to the determination of U in ores. These studies indicated that PADAP gives improved sensitivity and selectivity over other spectrophotometric reagents and heterocyclic azo dyestuffs used for U(VI) analyses.

Our interest in the PADAP uranium analysis originated with an effort to improve the sensitivity and reliability of an earlier X-ray method^[6] to analyze trace U in Fast Flux Test Facility (FFTF) PuO₂. In addition to this work, the applicability of the PADAP method to environmental uranium analyses and analyses of trace uranium in Hanford waste tanks stimulated this investigation.

SUMMARY

A spectrophotometric method for the determination of uranium in plutonium nitrate and oxide was investigated. The procedure is based on the analysis of the colored uranium complex which is formed with 2-(2-pyridylazo)-5-diethylaminophenol (PADAP) in a buffered alcohol-water matrix. The extraction of uranium from Pu with the high-molecular weight quaternary amine, Aliquat-336^R (General Mills Company), coupled with fluoride washes of the extracted uranium and the addition of complexing agents to the color-developing reaction makes the method highly selective. The method has a molar absorptivity of 5.3×10^4 liters mole⁻¹-cm⁻¹. The extraction method has a lower detection limit of 20 µg of U or about 100 parts of uranium per million parts of Pu (ppm) for a 200-mg Pu sample. When no U extraction was required, a direct method was capable of measuring 1 µg of U in 10 ml of H₂O or 1×10^{-4} g/liter U.

The optimum conditions for color development were investigated and several differences with references found. The most stable color was found to form in an alcohol-water mixtures using 1.5 g/liter PADAP. For the direct spectrophotometric method the color was fully developed in 30 minutes and indefinitely stable. However for the extracted uranium method, the color required 1.5 to 2.0 hours for full development and the linearity was limited to less than 200 µg of uranium. Recent literature indicates that changes in the concentration of the complexing agents and the order of adding the reagents may shorten the time and improve linearity.

Initial attempts to separate uranium from plutonium using trioctylphosphine oxide (TOPO) resulted in the

extraction of sizable quantities of Pu which were thought to be causing high results. Attempts to remove Pu from the TOPO with fluoride washes failed and other tests on PuO_2 indicated that the separation method was inadequate for plutonium analyses. However the feasibility of using the TOPO extraction for U separation from Hanford's nuclear waste was established; which, when coupled with the spectrophotometric analysis of U, provides a needed method.

An alternate method for separating U from Pu using Aliquat-336 in a 4M HCl-2M $\text{NH}_2\text{OH}\cdot\text{HCl}$ matrix was successfully applied to $\text{Pu}(\text{NO}_3)_4$ and PuO_2 analyses. Fluoride washes reduced the Pu concentration in the organic to less than 20 $\mu\text{g/ml}$ without affecting the U result. Results on $\text{Pu}(\text{NO}_3)_4$ analyses with fluoride washes were still bias about 10% high at the 300-mg Pu level. Since this bias was about the same for Aliquat-336 without the wash and TOPO extractions, plutonium may not be the sole cause of the high recoveries. A test in which small amounts of Pu(III) and Pu(IV) were added directly to the spectrophotometric procedure indicated that Pu(IV) at the 25 μg level would give an absorbance equivalent to 3 μg of U. Plutonium(III) did not affect the procedure. Other potential causes of the high results such as incorrect blank corrections, differences between the calibration procedure and the actual sample matrix could not be eliminated without purifying the plutonium available and preparing uranium in plutonium standards.

The method was applied to the analysis of uranium in PuO_2 following a study of the effect of the dissolution procedure using HCl and HF. In this work extracted uranium was measured using the PADAP spectrophotometric method and an X-ray emission analysis; X-ray data indicated that variations in HCl concentration and the presence of HF from the

dissolution procedure could cause errors in the analysis. The ratio of the organic-to-aqueous volume was found to have no effect on the extraction of U.

Plutonium dioxide dissolutions in which evaporation and aluminum were used to reduce the effect of HCl and HF indicated that significant differences existed between methods of dissolution. A procedure in which PuO_2 was dissolved in HCl and HF, then evaporated to dryness and $\text{Al}(\text{Cl}_3)_3$ added to remove residual fluoride, was chosen since it would give the most reproducible sample matrix. In a comparison of the X-ray and PADAP analyses the X-ray spike recoveries were $108.3 \pm 2.5\%$ versus $100.4 \pm 8.4\%$ for the colorimetric technique. The results for the FFTF standard were $118.7 \pm 3.1\%$ for X-ray and $122.1 \pm 2.2\%$ for spectrophotometric analyses.

The 20% bias in the results for the FFTF standards are difficult to explain in light of earlier PuO_2 work. Potential causes may be found from interfering ions or differences in calibration and sample matrices.

An X-ray calibration made from spiking pure PuO_2 with known amounts of U gave an average percent recovery of 110.6 for the FFTF standard. This indicates that the bias is not totally due to calibration differences. Since X-ray and spectrophotometric analyses are subject to different interferences, interfering ions are probably not the cause of the high result. There is also a possibility that the FFTF standard was in error but this was not evaluated.

Thirty-three potential interfering ions were studied at the 1000- μg level compared with the 100- μg level of uranium. Palladium caused significantly high results even at the 100- μg level. Most ions caused errors of less than 5%. Up to eight milliequivalents of HNO_3 were added to the procedure without causing a significant error.

In addition to the uranium in plutonium work, a direct U method was tested in order to evaluate potential applications of the spectrophotometric method for analysis of environmental and Hanford waste samples. Problems in analyzing U below 10 μg were encountered due to a shifting baseline caused by the spectral overlap between the excess PADAP reagent and the colored U-PADAP complex. Attempts to extract the colored U-PADAP complex into 12 organics revealed that carbon tetrachloride was effective in removing the excess PADAP and leaving the pink uranium complex in the ethanol matrix. Calibrations using the CCl_4 wash and a lower concentration of PADAP resulted in a 30-fold improvement in the precision of the slope and intercept. Application of this technique using 5-cm absorption cells indicated that 0.25 μg of U could be measured with a $\pm 25\%$ accuracy. However, 1 μg of U represents a more reasonable measurement limit. Recent availability of a purer, more sensitive reagent, 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol (Br-PADAP), should improve the lower limits of measurement for uranium. Because of the selectivity and sensitivity for the spectrophotometric determination of U with these reagents, the methods represent excellent alternatives for other techniques used for uranium analyses of nuclear materials.

EXPERIMENTAL

REAGENTS

Complexing Solution

Add 50.0 g of (1,2 cyclohexylenedinitrilo)tetraacetic acid (CDTA), 5.0 g of sodium fluoride (NaF), and 130 g of sulfosalicylic acid to 500 ml of deionized H_2O . Neutralize to a pH of 8.5 with NaOH and dilute to 1.0 liter with

deionized H_2O . Store in a dark bottle. Replace reagent when standard recoveries are low for low-level (10-50 μg) U.

Triethanolamine Buffer (TEA)

Add 149 g (132.5 ml) of TEA to 800 ml of deionized H_2O . Neutralize to pH 8.5 with HCl and dilute to 1.0 liter with deionized H_2O . Store in a dark bottle. Replace when standard recoveries are poor or if algae is observed in the buffer.

Trioctylphosphine Oxide - 0.1M TOPO

Dissolve 2.86774 g of TOPO in 100 ml cyclohexane.

2-(2-Pyridylazo)-5-Diethylaminophenol - Zinc Chloride Complex - 1.53 g/liter PADAP, Eastman Kodak No. 11265

Dissolve 0.15 g of PADAP in 100 ml of ethanol by stirring for 1 to 2 hr. The reagent was very dark-purple and cloudy, making it difficult to judge the rate of dissolution; therefore a long stirring time was used. After stirring, the solution was filtered to remove solids. The solution was filtered through a Whatman No. 42 filter into a dark bottle. The reagent was used as-received without further purification. A new calibration was normally required for each new batch of PADAP.

Uranium Standard

Several uranium standards near 1.000 g/liter U were used in this study. Some were made from dilutions of standard uranium nitrate solutions. Others were prepared by dissolving high-purity U_3O_8 from the National Bureau of Standards in HNO_3 .

Plutonium Nitrate Standard - 282 g/liter Pu in 3M HNO₃

Hydroxylamine Hydrochloride in HCl - 2M NH₂OH·HCl-4M HCl

Dissolve 139.0 g of reagent-grade NH₂OH·HCl into 320 ml of concentrated HCl and dilute to 1.0 liter with deionized H₂O.

Aluminum Chloride Solution - 1.0M AlCl₃-4.0M HCl

Dissolve 48.31 g of AlCl₃·6H₂O in 4.0M HCl and dilute to 200 ml with 4M HCl. The 4M HCl is necessary to maintain constant acid conditions for the extraction and to prevent hydrolysis of heavy ions when AlCl₃ is added.

Aliquat-336 (General Mills Company) - 30% in xylene

Dilute 300 ml of Aliquat-336 to 1.0 liter with xylene. Aliquat-336 was in chloride-form and used without further purification. Aliquat-336 is a mixed trioctyl and tridecyl methyl ammonium chloride.

APPARATUS

Glass Vials: 35-ml, 19-cm tall, 2.5-cm in diameter.

Stirrer: High-speed stirrer capable of forming complete emulsions with 1 ml of organic and 20 ml aqueous phases.

Heating Block: Aluminum heating block capable of heating several vials to 70° C.

Flasks: 25-ml volumetric.

Spectrophotometer: Cary 118 C ratio recording spectrophotometer with digital readout.

Absorption Cells: 1- and 5-cm silica cells.

GENERAL PROCEDURE

Direct Analysis (No Extraction)

Pipet the sample containing less than 0.25 milliequivalents (meq) of acid into a 25-ml volumetric flask containing 9 ml of deionized H_2O and rinse. Add 2.0 ml of complexing solution, 2.0 ml of TEA buffer, and 9.0 ml of ethanol--swirling the flask to mix after each addition. Add exactly 2.0 ml of 1.5 g/liter PADAP, swirl and dilute to volume with deionized H_2O . Allow the solution to stand 30 minutes and then measure its absorbance against a reagent blank at 565 nm.

PuO_2 Uranium Procedure (Extraction)

Dissolve 200 mg of PuO_2 in 5 ml of concentrated HCl and 100 μ l of concentrated HF. Heat to boiling until completely dissolved. Evaporate the solution to near-dryness but do not bake. Add 18 ml of 2M $NH_2OH \cdot HCl$ -4M HCl solution to reduce Pu(IV) to Pu(III) and to dissolve the residue. Add 2 ml of 1M $AlCl_3$ -4M HCl to complex residual fluoride. Heat at 70° C for 30 minutes to insure reduction of Pu. Allow the solution to cool and pipet 2 ml of Aliquat-336 (30%) into the vial. Stir for 5 min to an emulsion, allow the phases to separate, and transfer to a 2-dram vial containing 5.0 ml of 2.0M $NH_2OH \cdot HCl$ -4M HCl and 50 mg of NaF. Stir for 3 min, allow phases to separate, and transfer the organic to another 2-dram vial containing the same reagents and stir for another 5 min. Allow the phases to separate, and transfer 1 ml of the organic to a clean 25-ml volumetric flask. Add 2.0 ml of complexing solution, 2.0 ml of TEA buffer, 15 ml of ethanol, 2.0 ml of 1.5 g/liter PADAP and bring to volume with deionized H_2O . Swirl the flask after each addition to mix, and thoroughly stir the final solution.

Allow the solution to stand 1.5 hr and measure its absorbance at 565 nm versus a reagent blank.

RESULTS AND DISCUSSION

EVALUATION OF COLOR DEVELOPMENT PARAMETERS

Florence, Johnson, and Farrar^[2] found that the maximum sensitivity for the uranyl PADAP complex was obtained between pH's of 7.8 and 8.7 in a 35 to 40% acetone-water mixture. The practical molar absorptivity under these conditions was 6.59×10^4 liter mole⁻¹ cm⁻¹.

When it was attempted to develop the color in the acetone-water mixture the final solutions became cloudy. Since this condition could not be tolerated on a routine procedure, a 44% ethanol-water matrix was used to develop the color. These solutions were stable and no cloudiness was observed; however a loss in the sensitivity occurred as shown in Figure 1. The nonlinearity in Figure 1 was caused by an insufficient amount of PADAP. When the concentration of the PADAP was increased from 0.5 g/liter to 1.5 g/liter the system was linear over the range of 10 μ g to 125 μ g uranium (Figure 2). The additional PADAP was probably required because of the impure nature of the reagent as indicated by the large amount of undissolved solids in the final PADAP solution. The practical molar absorptivity for the uranyl-PADAP complex in the ethanol-water system was 5.3×10^4 liter mole⁻¹ cm⁻¹. Cook and Gereghty^[4] indicated that it was important to add the complexing solution before adding the buffer since the Al interference was greater at high pH values. This order of additions was adopted since there was a possibility of forming hydroxides which may not redissolve if the buffer were added first. Also for

FIGURE 1
COMPARISON OF ABSORBANCE OF U-PADAP COMPLEX IN ACETONE AND ETHANOL

FIGURE 2
CALIBRATION IN ETHANOL MATRIX WITH 1.59/LITER PADAP

high-acid samples if may be necessary to neutralize the excess acid with NaOH since 2 ml of the buffer can tolerate only 0.25 meq of acid. In this case the complexing solution is needed to prevent localized precipitation while neutralizing. The addition of H₂O (9 ml) to the flask prior to adding the other reagents did not affect the procedure.

The time required for full-color development in the direct (no extraction) uranium analysis was 30 min--the same as that found by Florence, Johnson, and Farrar.^[2] This color remained stable for over two hours. Several differences were found for the extracted uranium. First it was found necessary to increase the amount of alcohol from 11 to 17 ml in order to form a homogeneous solution. Less alcohol resulted in the separation of the organic extractant; more alcohol resulted in precipitation of the complexing agents. The extracted uranium required between 1.5 and 2 hours for full-color development and the response was linear only up to 200 µg U or an absorbance of 0.6 to 0.7. Therefore only absorbances <0.7 were used for extracted uranium data in order to utilize a linear system.

Closer examination of more recent references^[3,4,7,8] indicate some changes in the procedure that may alleviate these problems. In these studies the concentration of the complexing solution has been reduced by a factor of four and the solution is allowed to stand 10 minutes after adding the PADAP and buffer in that order and before diluting to final volume. The reduced concentration of complexant would prevent the precipitation of the complexing agent that occurred in our earlier test, and improve linearity. The lower complex ion concentration and the reaction of U with PADAP before dilution may improve the reaction kinetics and reduce the color development times. Unfortunately these

parameters were not evaluated in this study.

Calibrations were necessary whenever a new batch of PADAP was used. Occasionally low recoveries were obtained at low U concentrations. These results are believed to be due to degradation of the TEA buffer and complexing solutions. These reagents should be replaced whenever standard recoveries become poor.

EVALUATION OF TOPO AS AN EXTRACTANT FOR URANIUM FROM PLUTONIUM

Since TOPO extractions^[3] were compatible with the spectrophotometric method and since TOPO had been used for the separation of U from Pu for X-ray determinations^[6,9] it was decided to investigate this approach for analyzing trace U in Pu. The procedure was calibrated by adding U standards directly to the 4M HCl-2M NH₂OH·HCl matrix and extracting with 2 ml of TOPO in cyclohexane and proceeding as described earlier. No Pu, HF, or heating were used in the calibration. In order to determine the effect of plutonium on the procedure, a 108.9 µg uranium spike was added to varying quantities of a 282 g/liter Pu(NO₃)₄ solution in the extraction matrix. The results of this test are shown in Table I. Percent recoveries are based on two different values for the U in the Pu(NO₃)₄ standard. The 38 µg/ml value was determined by a single analysis of a 141 mg Pu aliquot without a spike. The 26.5 µg/ml U value was determined by a standard additions test in which 70.5-mg aliquots of Pu(NO₃)₄ were spiked with increasing amounts of uranium as shown in Table II.

The X intercept for the least squares line of these data is the amount of U in 70.5 mg of Pu and is equivalent to 26.6 ± 10 µg U per ml of Pu(NO₃)₄, or 282 mg of Pu. Even

TABLE I
EFFECT OF Pu ON THE DETERMINATION OF U WITH
PADAP AFTER EXTRACTION WITH TOPO

<u>mg Pu</u>	<u>% U Recovery Direct Blank Measurement</u>	<u>% U Recovery Standard Additions Blank Measurement</u>
Blank		
(141.0) no U	38 µg/ml	26.5 µg/ml
28.2	104.4	105.5
56.4	104.0	106.1
141.0	106.0	112.0
282.0	109.5	120.0

TABLE II
STANDARDS ADDITION TESTS ON $\text{Pu}(\text{NO}_3)_4$
WITH TOPO AND PADAP

<u>mg Pu</u>	<u>µg U</u>	<u>Absorbance (A)</u>
70.5	0	0.0185
70.5	27.2	0.0894
70.5	54.4	0.1764
70.5	108.9	0.3490
70.5	217.8	0.6418

though the precision on this value was poor, it was essentially the same value found earlier^[2] by X-ray analysis. Therefore the higher recoveries were considered more valid.

A test to determine the effect of a fluoride wash on the method was carried out in which the extracted U was washed with 5 ml of 4M HCl-2M $\text{NH}_2\text{OH}\cdot\text{HCl}$ containing varying amounts of NaF and then analyzed spectrophotometrically. The results of these tests are outlined in Table III.

When a 141-mg sample Pu was analyzed using a 50-mg NaF wash, a 117% recovery was obtained--indicating that the fluoride wash was not effective in removing the extracted Pu or lowering the recovery.

TABLE III
EFFECT OF FLUORIDE WASH ON THE
EXTRACTION OF U WITH TOPO

<u>mg NaF</u>	<u>% Recovery U</u>
10	103.9
25	102.7
50	100.5
100	97.7

At the same time these studies were being made an X-ray procedure^[8] for U was being tested on PuO₂. In these tests the samples were dissolved in HCl-HF, boiled to dryness, dissolved in the extraction matrix, and extracted into 1 ml of TOPO rather than the 2 ml used for the spectrophotometric method. A 250-μl aliquot of these extractions was analyzed spectrophotometrically to determine potential problems for applications to PuO₂. The average percent recovery for three 54.5-μg U spikes was 146.1% and 132.5% for three 217.8-μg spikes. Based on these results the TOPO separation of U from Pu appeared to be inadequate for spectrophotometric analyses and therefore a different extractant, Aliquat-336, was investigated. The TOPO extraction and fluoride wash data may be applied to other uranium analyses where Pu is not the major component. Trioctylphosphine oxide extractions of U from HNO₃ are more specific than TOPO or Aliquat-336 extractions from HCl and may prove to be very valuable in separating and concentrating U from Hanford waste tanks before analysis with PADAP.

EVALUATION OF ALIQUAT-336 AS AN EXTRACTANT FOR URANIUM FROM PLUTONIUM

The application of high molecular weight amines to the separation of actinides has been described previously.^[10-12] The extraction of numerous ions in Aliquat-336 from

chloride solutions has been described by Seeley and Crouse.^[13] These data indicated that the quaternary amine, Aliquat-336, would have high extraction coefficients for U(VI) but low extraction coefficients for Pu(III) and Pu(IV) from chloride systems. Aliquat-336 was used in its chloride-form as received from the manufacturer and without further purification diluted to 30% in xylene. The calibrations were carried out in the same manner as those with TOPO. The results were linear over a slightly larger concentration range than TOPO. When a second extraction was made to check the completeness of the extraction no uranium was found, indicating that the extraction was quantitative.

A test to determine the effect of Pu on the Aliquat-336 separation and PADAP spectrophotometric determination was carried out by spiking a constant amount of U (100 µg) into varying amounts of Pu(NO₃)₄. Table IV shows the results of these tests.

TABLE IV
EFFECT OF Pu ON THE DETERMINATION OF U WITH PADAP
AFTER EXTRACTION WITH ALIQUAT-336 (NO FLUORIDE WASH)

<u>mg Pu</u>	<u>U % Recovery</u>	<u>U % Recovery</u>	<u>µg Pu</u>
	<u>26.5 µg/ml U Blank</u>	<u>39.4 µg/ml U Blank</u>	<u>ml Aliquat-336</u>
27	99.5	98.3	20
70.5	103.8	101.8	40
141.0	110.7	104.8	80
211.5	118.0	109.1	160
282.0	124.2	112.4	300

In these studies a fraction of the organic was analyzed for Pu by alpha counting. Two blank values were used for comparing the results. The 26.5 µg/ml U value is based on the standard additions data for TOPO in Table II. The 39.4 µg/ml U blank result is based on a standard additions test conducted with Aliquat-336 on 141 mg of Pu(NO₃)₄ as outlined in Table V.

TABLE V
STANDARD ADDITIONS DETERMINATION OF U BLANK IN
 $\text{Pu}(\text{NO}_3)_4$ WITH ALIQUAT-336

<u>mg Pu</u>	<u>$\mu\text{g U}$</u>	<u>A</u>	<u>$\mu\text{g Pu}$</u> <u>ml Aliquat-336</u>
141	10.9	0.0898	1.7
141	27.2	0.1224	2.0
141	54.4	0.2012	2.1
141	108.9	0.3557	2.5
141	217.7	0.6510	2.9

A least squares analysis of the data gave an X intercept of $39.4 \pm 3.0 \mu\text{g/ml}$ for the U blank in the $\text{Pu}(\text{NO}_3)_4$. This value is more accurate than earlier assays. The low concentration of Pu in the Aliquat-336 was the result of fluoride washes described later.

Obviously the determination of the blank U value is significant in evaluating the method, and leaves uncertainty in the results. Comparison of TOPO with Aliquat-336 data does not show significant differences ($>10\%$); however based on earlier work^[6] the amount of plutonium extracted appears to be less in the Aliquat-336 and therefore it was studied further.

Since preliminary tests revealed that a fluoride wash of the Aliquat-336 could reduce the Pu content from 160 $\mu\text{g Pu/ml}$ to 60 $\mu\text{g Pu/ml}$ the effect of fluoride on the procedure was studied in greater detail. This parameter was investigated by washing uranium extracted in Aliquat-336 twice with 3 ml of 4M HCl-2M $\text{NH}_2\text{OH}\cdot\text{HCl}$ containing varying amounts of NaF. The results of this test are shown in Table VI.

These data show that the extracted uranium is unaffected by two washes containing 50 mg of NaF. Because of the limited solubility of NaF, a 5-ml volume of 4M HCl-2M $\text{NH}_2\text{OH}\cdot\text{HCl}$ was chosen for later experiments. Cloudiness

TABLE VI
EFFECTS OF FLUORIDE WASH ON THE EXTRACTION
OF URANIUM WITH ALIQUAT-336

<u>mg NaF</u>	<u>U, % Recovery</u>
10	97.15
25	94.58
50	99.27
100	75.21

observed in the washes did not affect the results.

In order to evaluate the two fluoride washes, 141- and 282-mg Pu samples of $\text{Pu}(\text{NO}_3)_4$ were spiked with 54.4 μg of U and analyzed. After correcting for a blank background of 39.4 μg U/ml $\text{Pu}(\text{NO}_3)_4$, the percent recoveries were 104.5 and 142.9, respectively. When the organic was analyzed for Pu by α counting, the Pu concentration in the 141-mg sample was 0.9 μg Pu/ml organic and 20 μg Pu/ml of organic for the 282-mg Pu sample. When another 282-mg sample of Pu was analyzed with a 108.9 μg U spike a 111.1% recovery was obtained and only 6 μg Pu/ml found in the organic.

In order to determine the extent of the interference that may be expected from small quantities of Pu, microgram-quantities of Pu(IV) and Pu(III) were pipeted without extraction directly into the spectrophotometric method. The results of this test are shown in Table VII.

TABLE VII
EFFECT OF SMALL AMOUNTS OF Pu(III) AND Pu(IV) ON
THE SPECTROPHOTOMETRIC DETERMINATION OF URANIUM

<u>μg Pu</u>	<u>Equivalent μg of U Pu(IV)</u>	<u>Equivalent μg of U Pu(III)</u>
5	3.01	Negative
10	Negative	Negative
25	2.97	Negative
50	3.85	Negative
100	5.62	Negative

In these studies only small absorbance changes were noticed. When the absorbance change was above zero a uranium equivalent was calculated. Plutonium(IV) gave an absorbance equivalent to about 5.6 $\mu\text{g U}$ at the 100 $\mu\text{g Pu}$ level. Since most of our extractions contained less than 20 μg of Pu, the error of analyzing 50 μg of U in Pu would be about 6% and only 3% for 100 $\mu\text{g U}$ levels. This may help to explain part of the high percent recoveries. The plutonium spectra were similar but broader than those of the U. Other factors such as errors in the blank analysis, interferences from other ions, and the effect of Pu(VI) could also account for some of the high results. All of these factors become more critical as the uranium concentration decreases. Florence^[2] suggested the addition of mercaptoacetic acid to the direct spectrophotometric method to reduce Pu(IV) to Pu(III). This technique was not evaluated in this study but is recommended for further work to minimize potential high results from Pu(IV).

The effect of Pu on the method was reevaluated using the new procedure with fluoride washes, and the results are described in Table VIII. A 108.9 μg uranium standard analyzed at the same time gave only a 93.2% recovery. A closer examination showed the calibration had shifted because of degrading reagents. Therefore a corrected percent recovery has been included in Table VIII.

TABLE VIII

EFFECT OF PLUTONIUM ON THE DETERMINATION OF URANIUM
WITH ALIQUAT-336 EXTRACTION AND FLUORIDE WASHES

<u>mg Pu</u>	<u>U % Recovery</u> <u>39.4 $\mu\text{g/ml}$ Blank</u>	<u>Corrected</u> <u>% Recovery</u>	<u>$\mu\text{g Pu}$</u> <u>ml</u>
28.2	84.9	91.1	0.4
70.5	86.5	92.8	0.6
141.0	97.0	104.0	4.0
282.0	105.3	112.9	13.0

In comparing results with those of the unwashed Aliquat-336 (Table IV) and the TOPO extractions (Table I) there are no significant improvements in the high recoveries. However the Pu concentration has been reduced from greater than 200 $\mu\text{g/ml}$ of Aliquat-336 to 13 $\mu\text{g/ml}$ for the 282 mg plutonium sample size. Many factors could be causing the high results with increasing sample sizes. Based on these three extraction systems it would not appear to be due to Pu. Since multiple extraction data indicates that greater than 95% of the uranium is extracted with one contact, the high results should not be due to an increase in the U extraction efficiency when adding $\text{Pu}(\text{NO}_3)_4$. An error in the blank value or other ion interferences from impurities in the $\text{Pu}(\text{NO}_3)_4$ would cause increasingly high results with increasing sample size. Later examination of interfering ions shows that the method is highly selective, therefore large errors in high-purity plutonium products would not be expected. Even though the relationship between high results and increasing sample sizes cannot be completely explained, the method is applicable to the determination of U in plutonium nitrate at the 300-ppm level providing errors of $\pm 10\%$ can be tolerated. In order to evaluate the method further it was tested on high-purity PuO_2 since the uranium blank would be lower in this material and therefore have less influence on the results.

Since the Aliquat-336 extraction provides superior decontamination of U from Pu its applicability to the X-ray determination of uranium in PuO_2 was evaluated at the same time as the spectrophotometric method. X-Ray analyses do not require a 1- to 2-hour waiting period and were used to evaluate some of the parameters for the extraction. Because the factors and interferences affecting the X-ray analyses are different from those influencing the spectrophotometric

method, the two techniques are complementary. The procedures used for the X-ray analyses were essentially the same as those used in ARH-2835^[6] except the Aliquat-336 separation was employed in place of the TOPO. In order to improve the measurement limits the extractions for X-ray analyses were made into 1 ml of Aliquat-336 instead of the 2 ml used for spectrophotometric work. X-Ray procedures are outlined in Appendix E.

Before analyzing PuO_2 the effect of the dissolution procedure with concentrated HCl-HF on the extraction needed to be determined. The dissolution procedure would increase the HCl concentration for the extraction and introduce HF into the matrix. The final concentration of these components cannot be predicted since the solutions are boiled and sometimes additional reagents added. Therefore an X-ray study was made on uranium extracted from the normal 4M HCl -2M $\text{NH}_2\text{OH}\cdot\text{HCl}$ matrix with varying amounts of HF added. These results are shown in Table IX. Compared with a control standard with no fluoride, the results are definitely higher with fluoride present.

TABLE IX
EFFECT OF HF CONCENTRATION ON THE EXTRACTION OF
URANIUM WITH ALIQUAT-336

<u>millimoles</u>	<u>Net counts per second (c/s) U</u>
0	132.87
0.25	150.18
0.50	184.14
0.75	160.44
1.00	161.66
1.50	143.84
3.00	151.52

However the extent of enhancement was difficult to estimate due to counting errors at the 50 μg U level. The

effect of the fluoride would be further influenced by any plutonium present, and therefore was not studied in great detail.

The effect of concentrated HCl was studied by adding varying quantities of HCl to the extraction matrix and measuring the changes in the uranium X-ray intensities in 1-ml Aliquat-336 extractions. These data are outlined in Table X.

TABLE X
EFFECT OF HCl CONCENTRATION ON THE EXTRACTION
OF URANIUM WITH ALIQUAT-336

<u>Final HCl Concentration</u>	
<u>M</u>	<u>Net c/s Uranium</u>
1	130.37
2	129.00
4	173.24
6	144.33
8	150.00

Even though the 50 μ g uranium spike was too small for an accurate examination of the data, the results definitely indicate that varying amounts of HCl could cause greater than normal variations in the results. In both these latter studies the wash steps were eliminated.

The organic-to-aqueous ratio was another variable that could result from the dissolution of PuO_2 . The organic-to-aqueous ratio was varied over a range of 0.03 to 0.2, analyzed by X-ray and the results described in Table XI.

TABLE XI
EFFECT OF THE ORGANIC-TO-AQUEOUS RATIO ON THE
EXTRACTION OF URANIUM WITH ALIQUAT-336

Volume 4M HCl-2M NH ₂ OH·HCl ml	Organic-to-Aqueous Volume Ratio	Net c/s Uranium
5	0.2	314.35
10	0.1	320.12
15	0.07	347.63
20	0.05	343.40
25	0.04	330.09
30	0.03	321.41

The volume of Aliquat-336 was held constant at 1 ml and the uranium spike increased to 100 μ g. The variations in the data are within the precision of the method; the organic-to-aqueous ratio is expected to have little influence on the results. This also means that the Aliquat-336 extraction should be effective in concentrating U from large volumes.

The HCl and HF studies indicated that if the concentration of these ions were not controlled, then variations in the results would occur. However no serious loss of sensitivity occurred by varying the HCl and HF concentrations. In order to verify these data and determine the effect of Pu on the dissolutions parameters, three different approaches to the sample preparation were evaluated. In Method 1 a sample of PuO₂ was spiked with 100 μ g of U and then dissolved in 5 ml of concentrated HCl and 100 μ l of concentrated HF. The solution was evaporated to dryness and redissolved in 20-ml 4M HCl-2.0M NH₂OH·HCl. Two milliliters of 1M AlCl₃ were added to the solution and the uranium extracted into 1 ml of Aliquat-336. Method 2 was the same except the solution was not evaporated to dryness and no AlCl₃ was added. In Method 3 the procedure was identical to Method 2 except this time AlCl₃ was included. Method 1

should produce the most consistent extraction matrix since most of the excess HCl and HF are removed by evaporation or complexation. Method 2 should be the least controllable but considerably faster since the evaporation is not used. Method 3 should indicate if Al by itself could reduce the positive effects of fluoride on the extraction. The extracted U was analyzed by both X-ray and spectrophotometric methods. The X-ray results should be the most reliable since the extraction was made into 1 ml of Aliquat-336 according to the X-ray calibrations. Spectrophotometric results were based on 150- μ l aliquots from the 1-ml extraction and were calculated using two standards run by the same procedure. Because of this and the relatively low absorbance reading, the spectrophotometric method is less accurate. The results of this work are shown in Table XII.

Looking at the part per million (μ g U per gram of PuO_2) data the results increase going from Method 1 to Method 3. This trend might be expected from earlier HCl-HF studies; however the higher results of Method 3 over Method 2 are more difficult to explain. These data definitely indicate that the sample preparation method affects the final results. Method 1 using evaporation and AlCl_3 treatment was chosen since it was felt that it would be the most reproducible and consistent with the calibrations being used. If the sealed tube^[14] dissolution technique were utilized or if the uranium calibration were made by spiking high-purity PuO_2 , then the dissolution conditions could probably be controlled adequately to use the shorter Methods 2 and 3. The net micrograms of U were calculated using a blank of 4.13 μ g U per 200 mg PuO_2 . This value was determined by standard addition tests using both X-ray and spectrophotometric techniques and by direct spectrophotometric analyses. Blank results range from 0.41 μ g U to 7.14 μ g U. The

TABLE XII
EFFECT OF DISSOLUTION PROCEDURE ON THE
EXTRACTION OF URANIUM INTO ALIQUAT-336

<u>Dissolution Method</u>	<u>PuO₂ mg</u>	<u>X-Ray Results</u>				
		<u>Net c/s U</u>	<u>Total μg U</u>	<u>Net μg U</u>	<u>% Spike Recovery</u>	<u>μg U g PuO₂</u>
1	234.8	238.52	115.97	110.2	109.2	493.91
2	204.1	226.91	110.95	106.7	105.8	543.61
3	201.2	237.44	115.50	111.3	110.3	574.07
	Average			109.4	108.4	537.20
<u>Spectrophotometric Results</u>						
		<u>A^a</u>	<u>Total μg U</u>	<u>Net μg U</u>	<u>% Spike Recovery</u>	<u>μg U g PuO₂</u>
1	234.8	0.0857	109.38	104.5	103.6	465.84
2	204.1	0.0856	109.28	105.1	104.2	535.42
3	201.2	0.0582 ^b	123.75	119.6	118.6	615.05
	Average			109.7	108.8	538.77

^aAbsorbence.

^bOnly 100 μl of organic were used in the analysis.

4.13 μg U value is an average of two standard addition tests and one direct measurement. Even though these results were considered to be the best available from the data, an error of ± 50% in the blank value is possible. Again the ability to establish an accurate blank made low-level U analyses difficult to evaluate. This uncertainty has only a small effect on the accuracy of 100-μg spikes but could introduce 10 to 20% errors at the 25 μg U level which is equivalent to 100 ppm U for a 200-mg PuO₂ sample. A comparison of X-ray and spectrophotometric results for the three methods shows excellent correlation under the experimental conditions with the maximum difference being about 7%. The high percent recoveries of the spike may be due to the differences

between the calibration and the sample procedure that results from the dissolution.

For a further comparison of the X-ray and spectrophotometric methods, six different PuO_2 samples were analyzed. The oxides were prepared by Method 1 (Appendix A). In three of the samples (1 to 3) the uranium was extracted into 1 ml of Aliquat-336 and 500 μl analyzed by X-ray as normal and 150 μl analyzed for U by the PADAP spectrophotometric method. The spectrophotometric results were based on two calibration points analyzed in the same manner as the samples using 1-ml extractions and 150- μl portions for color analysis. In the other three tests (4 to 6) the U was extracted into 2 ml of Aliquat-336 and analyzed as normal by spectrophotometry. A 500- μl portion of the 2-ml extraction was mounted for X-ray U analysis and the results calculated from the regular (1-ml) calibration using a correction factor of 2 for the dilution effect. The results of these analyses are shown in Table XIII.

Standards 1 and 2 were analyzed using a 1-ml extraction. The spectrophotometric results on Standards 1 and 2 were calculated by the normal calibration curve using 2-ml extractions and 1 ml of the organic for color development. These recoveries indicated that this calibration was not valid for 150- μl portions of 1-ml extractions. Therefore a two-point calibration based on these standards was used to calculate the data on Tests 1, 2, and 3. The X-ray results on Standards 3 and 4 indicate the correction factor of 2 used to correct for differences in calibration and analyses was valid. Agreement between the two methods was excellent except at very low U levels (Tests 1 and 4). This was caused by large errors resulting from low count rates on the X-ray and small absorbances on the spectrophotometer.

TABLE XIII
RESULTS OF COMPARISON BETWEEN X-RAY AND
SPECTROPHOTOMETRIC ANALYSIS OF U IN SIX
DIFFERENT SAMPLES OF PuO₂

Standard or Test Number	U Spike μg	Net c/s U	A	X-Ray μg U	Spec ^a μg U	X-Ray, % Recovery	Spec ^a % Recovery	% Range Average
Standard 1	54.43	111.08	0.0272	-	-	84.7	67.8	
Standard 2	272.15	838.29	0.2598	-	-	101.7	117.2	
Standard 3	54.43	53.06	0.1501	-	-	101.4	102.5	
Standard 4	108.86	129.43	0.3235	-	-	95.5	109.2	
Test 1	-	22.86	0.0091	17.94	37.44	-	-	70.4
Test 2	54.43	238.41	0.0614	86.81	86.39	-	-	0.5
Test 3	272.15	1345.03	0.4161	440.36	418.40	-	-	5.1
Test 4	-	1.32	0.0834	22.12	31.51	-	-	35.0
Test 5	54.43	59.43	0.1783	59.27	66.02	-	-	10.8
Test 6	108.86	153.53	0.3539	119.38	129.87	-	-	10.2

^aSpectrophotometric.

Standard data showed that the X-ray results may be biased low at low U concentrations. Extracted plutonium would make the colorimetric results biased high.

In order to make a better comparison of the two methods and gather sufficient data for an estimate of the precision and accuracy, eight additional tests were made on a single PuO_2 material. The first four tests (4 through 7) were optimized for X-ray analysis by extracting the U into 1 ml. Again 150 μl of the organic were analyzed spectrophotometrically using two standards for calibration. Tests 8 through 11 were optimized for the PADAP method by extracting into 2 ml. For comparison purposes, Tests 4 through 11 have been summarized in Table XIV along with the results from the three dissolution tests (1 through 3) described earlier. Percent recoveries were corrected for the 4.13 μg U per 200 mg PuO_2 .

The X-ray and spectrophotometric results compare to within 10%: however the X-ray results are biased high and have a better precision. The superior X-ray precision could have resulted because six of the tests were optimized for X-ray versus three for the PADAP. In addition, variations in the 2-ml extractions for X-ray analysis are less severe than the modifications for spectrophotometric (spec) analyses of 1-ml extractions. If the high and low recoveries for the PADAP analyses are omitted, the precision for spike recoveries is $99.6 \pm 3.3\%$. Part of the bias in the X-ray and spec results may have been caused by a shift in the spectrophotometer calibration curve--particularly at U concentrations below 75 μg . Recalibration of the method following this study showed a curvature at low U calibration points caused by degrading reagents. Other areas that may have caused the bias are (1) differences in U standards used for X-ray and spec calibrations and (2) differences in the

TABLE XIV
SUMMARY OF X-RAY AND SPECTROPHOTOMETRIC URANIUM RESULTS ON PuO₂

Test No.	μg U Spike	ml Extracted	mg PuO ₂	X-Ray Results			Spectrophotometric Results			Range Δ μg X-Ray-Spec	Average μg U	% Range Over Average
				Net c/s	μg U	% Recovery	Absorbance	μg U	% Recovery			
1	100.8	1	234.8	238.52	115.97	110.2	0.0857	109.38	103.7	+6.59	112.7	5.8
2	100.8	1	204.1	226.91	110.95	105.8	0.0856	109.28	104.1	+1.67	110.1	1.5
3	100.8	1	201.2	237.44	115.50	110.5	0.0582	123.75	118.6	-8.25	119.6	6.9
4	0	1	200.8	0	0	-	0.0005	26.0	-	-	-	-
5	50.4	1	210.4	103.10	57.75	105.9	0.0305	55.3	101.1	+2.44	56.5	4.3
6	100.8	1	206.3	227.06	111.30	106.1	0.0792	102.8	97.7	+8.50	107.1	7.9
7	201.6	1	235.3	496.46	227.70	110.5	0.1787	199.9	96.7	+27.80	213.8	13.0
8	0	2	198.3	0	0	-	0.0078	4.02	-	-	-	-
9	50.4	2	203.1	35.31	57.4	105.6	0.1300	48.46	87.8	+8.94	52.9	16.9
10	100.8	2	200.7	106.61	116.8	111.8	0.2773	102.02	97.1	+14.78	109.4	13.5
11	201.6	2	200.9	232.84	221.8	108.0	0.5443	199.11	96.7	+22.69	210.5	10.8
Average				$\bar{x} = 108.3 \pm 2.5\%$			$\bar{x} = 100.4 \pm 8.4\%$					

calculation and analytical procedures used for calibrations and PuO_2 sample analyses. However considering these differences, a 10% disagreement in the methods does not seem unreasonable and the accuracy and precision for both methods are acceptable for analysis of Fast Flux Test Facility (FFTF) PuO_2 materials.

Before attempting to analyze the FFTF PuO_2 standard for trace U, an effort was made to remove any potential sources for bias between the methods. Both instruments were recalibrated using a standard prepared from the National Bureau of Standards (NBS) U_3O_8 . The addition of AlCl_3 was included in the calibration procedure to compensate for any increase in the extraction coefficient caused by a higher salt strength or chloride activity.

Six 200-mg portions of the FFTF PuO_2 standard were analyzed for U by the X-ray and PADAP methods following dissolution and extraction of U into Aliquat-336 as described earlier. The samples were analyzed in two groups--three with 1-ml extractions and three with 2-ml extractions. All extraction aliquots were analyzed for U by X-ray and spectrophotometry as described in the last Section. The results of these analyses are described in Table XV. In evaluating the data, Test 3 is omitted since it is an obvious flyer. The best X-ray results are those in Tests 1 and 2 and the best spectrophotometric results are Tests 4, 5, and 6. Except for Tests 3 and 6 the methods agreed within 10%. For some unexplained reason the X-ray data on Tests 4, 5, and 6 gave unusually high results. Tests 7, 8, and 9 were run later by X-ray using the 1-ml extraction method.

If we look at the results from what should be the most accurate of the X-ray data we obtain an average value of 439.2 μg U per gram PuO_2 or $118.7 \pm 3.1\%$ recovery. The

TABLE XV
SUMMARY OF X-RAY AND SPECTROPHOTOMETRIC RESULTS FOR FFTF STANDARD

Test No.	Weight PuO ₂	c/s U	Absorbance	μg U X-Ray	μg U Spec	μg U/g PuO ₂ X-Ray	μg U/g PuO ₂ Spec	% Recovery X-Ray	% Recovery Spec	% Range Average
1	0.1999	173.20	0.0531	87.25 ^a	85.18	436.5	426.1	118.0 ^a	115.2	2.4
2	0.2022	172.47	0.0509	86.95 ^a	82.89	430.0	409.9	116.2 ^a	110.8	4.8
3	0.1989	103.03	0.0179	58.54 ^a	48.57	294.3	244.2	79.5	66.0	18.6
4	0.2040	63.22	0.2690	42.25	91.75 ^a	414.2	449.8	111.9	121.6 ^a	8.3
5	0.1980	75.84	0.2572	47.41	88.03 ^a	478.9	444.6	129.4	120.2 ^a	7.4
6	0.2205	101.59	0.3001	57.95	101.55 ^a	525.6	460.5	142.1	124.5 ^a	13.2
7	0.2016	182.96	-	-	-	430.6	-	116.4	-	-
8	0.2001	194.99	-	-	-	458.6	-	123.9	-	-
9	0.1947	180.24	-	-	-	440.2	-	118.9	-	-

Precision and accuracy of data optimized for X-ray analysis (Tests 1, 2, 7, 8, and 9) $\bar{x}$ = 439.2 μg U/g PuO₂ or 118.7 ± 3.1% recovery.

Precision and accuracy of all X-ray data (except Test 3) $\bar{x}$ = 451.8 μg U/g PuO₂ or 122.1 ± 9.7% recovery.

Precision and accuracy of data optimized for spectrophotometric analysis (Tests 4, 5, and 6) $\bar{x}$ = 451.6 μg U/g PuO₂ or 122.1 ± 2.2% recovery.

Precision and accuracy for all spectrophotometric data (except Test 3) $\bar{x}$ = 438.2 μg U/g PuO₂ or 118.5 ± 5.4% recovery.

^aThese analyses should be the best since they were performed using the same procedure as the calibrations.

optimized PADAP data had an average uranium value of 451.6 $\mu\text{g U/g PuO}_2$ or $122.1 \pm 22\%$ recovery. This time the spec results are biased higher than the X-ray results by 3.4% and both methods are biased 20% high compared with the standard value. Based on earlier work this high bias cannot be explained since in most of those studies the average spike results were only about 10% high.

There are several possible causes for the bias but most would not cause such a large difference. The possibility that the uranium standard made from NBS U_3O_8 was incorrect was checked by comparing its analysis with three other U standard solutions. All the standards agreed to within 2%. Interfering ions are not a probable cause for the high recoveries since the X-ray and spec methods are subject to different interferences. A qualitative X-ray scan of the extracted U did not show any large amounts of other metallic ions. High results would also occur if the addition of Pu caused a significant increase in the extraction efficiency or if a more extractable U species formed during the dissolution process. However based on multiple extraction tests that indicated greater than 95% U extracted with one Aliquat-336 contact, a 20% high result would not be likely. An X-ray calibration was made by spiking 200 mg of high-purity PuO_2 with known amounts of U and carrying the oxide through the dissolution and extraction procedures. The average percent recovery for the FFTF standards using this calibration was 110.6.

Since X-ray tests on the PuO_2 (Table XIV) did not show any U present, no blank correction was made. If there is U present in the PuO_2 as indicated in spec results, then failure to compensate for the U blank in the PuO_2 would cause results to decrease from 1 to 10% over the calibration range

assuming the U blank value was 4.13 μg U/200 mg PuO_2 . Therefore the decrease in the results may not be totally due to a more valid calibration. There is also a possibility that the value of the FFTF standard is incorrect. The method^[15] used to characterize this material requires ion exchange separations and boil-downs which would be subject to U losses. For verification, considerably more work would be necessary including preparation of some high-purity plutonium materials for making low-level U standards. Even though there is some question concerning the accuracy of the analysis, normally due to high results, the precision of the X-ray and PADAP methods were excellent. Both techniques should be applicable to the analysis of trace U in plutonium materials.

INTERFERING ION STUDY

Florence, Johnson, and Farrar^[2,3] carried out extensive interference studies on a direct uranium analysis and a TOPO extraction of uranium using PADAP. In order to study the effect of interfering ions on the Aliquat-336 extraction and PADAP spectrophotometric determination of U, 1000 μg of the ion being investigated was added to 100 μg of U and then carried through the normal procedure. This level of interference is 10 to 100 times higher than what would be expected in high-purity Pu materials. The results of these studies are shown in Table XVI.

Some ions were observed to extract by visual inspection or by X-ray emission analysis. However not all ions were tested for extractability and the extent of extraction was not established. Tantalum and tungsten precipitated before extracting and caused low results. Palladium extracted and formed a purple complex with PADAP, causing high percent

TABLE XVI
INTERFERING ION STUDY

<u>Ion</u>	<u>% Recovery</u>	<u>Comment</u>
Fe ⁺³	103.2	Extracted
Cu ⁺²	94.7	Extracted
Zn ⁺²	105.1	Extracted
Cd ⁺²	100.8	None extracted
Si ⁺⁴	103.8	None extracted
Pb ⁺²	96.8	
Th ⁺⁴	100.5	
Al ⁺³	99.6	
Sr ⁺²	97.4	
Mn ⁺²	95.0	
Cr ⁺⁶	98.9	
Ga ⁺³	103.8	
As ⁺³	98.6	
Ta ⁺⁵	95.6	Precipitated
W ⁺⁶	98.0	Precipitated
Sb ⁺⁵	103.2	
Zr ⁺⁴	97.7	
Ag ⁺¹	94.4	
Mo ⁺⁶	103.8	
Nd ⁺³	101.4	
Sn ⁺⁴	95.3	
Pd ⁺² (1000 µg)	-	Absorbance too high - purple color
Pd ⁺² (100 µg)	132.2	
Au ⁺³	140.2	Extracted (unfiltered)
Au ⁺³	94.8	Extracted (filtered)
Bi ⁺⁵	105.2	Extracted
SO ₄ ⁻²	103.6	
PO ₄ ⁻³	103.6	
EDTA	103.0	
Ti ⁺⁴	100.5	None extracted
Citrate	103.6	
V ⁺⁵	108.4	None extracted
Ge ⁺⁴	103.6	Extracted
Ru ⁺⁴	125.9	Extracted (unfiltered)
Ru ⁺⁴	98.9	Extracted (filtered)
Rh ⁺³	106.8	Extracted

recoveries. The Pd spectrum and its effect on the determination of U are shown in Figure 3. A shoulder at 610 nanometers (nm) indicates the presence of Pd; however at Pd concentrations less than 100 μg this shoulder could be suppressed by the U spectrum. Palladium could represent a serious interference and its presence in the sample should be closely examined before applying this procedure. If Pd were present the TOPO extraction of U from nitric acid could be more specific and useful, providing the amount of Pu extracted were not too large. There is also a possibility that the Pd could be prevented from extracting by using complexing agents such as ethylenediaminetetraacetic acid (EDTA) and citrate. The Pd-PADAP complex has a molar absorptivity of about $3 \times 10^3 \text{ liter mole}^{-1} \text{ cm}^{-1}$. Both gold and ruthenium extracted and formed very finely suspended precipitates in the color-developing matrix that made the final solution opaque. These cloudy solutions gave higher than normal absorbances. This condition was corrected by filtering the solutions before making the absorbance measurement. Rhodium and vanadium caused slightly high results but they are not normally present at these concentrations. With the exception of Pd, the method was subject to only small interferences from other ions that are present at concentrations 10 times higher than U.

Cook and Gereghty^[4] found that the fluoride in the complexing solution caused precipitation with calcium and magnesium in the direct U method and therefore it was left out of their procedure. Their data indicated that careful attention should be given to the interference caused by the total cation content and not necessarily a single cation. This problem was not evaluated for Pu products since the total cation content other than Pu is normally low; however

FIGURE 3
PALLADIUM INTERFERENCE ON URANIUM SPECTRA

in applying the procedure to other problems, this possibility deserves consideration.

When applying the method to $\text{Pu}(\text{NO}_3)_4$ solutions there is a possibility that varying amounts of HNO_3 could affect the procedure. In order to evaluate this parameter varying amounts of HNO_3 were added to 100 μg of U in the 4M HCl -2M $\text{NH}_2\text{OH}\cdot\text{HCl}$ extraction matrix and the procedure performed as normal. The results of this study are shown in Table XVII. Increasing amounts of HNO_3 cause slightly higher results. However a control standard analyzed at the same time had a 104.3% recovery, indicating the effect may be less than that shown in Table XVII. The Aliquat-336 extraction method for U should be applicable to samples with a wide range of HNO_3 concentrations.

TABLE XVII
EFFECT OF NITRIC ACID ON THE
DETERMINATION OF URANIUM

millequivalent <u>HNO_3</u>	<u>U</u> <u>% Recovery</u>
1	105.2
2	106.2
4	108.4
8	108.4

EVALUATION OF A DIRECT LOW-LEVEL URANIUM ANALYSIS WITH PADAP

Since many environmental and waste tank samples may not require a separation prior to the determination of U with PADAP but probably would require higher sensitivity than the present method, several studies were made in an attempt to lower the analytical detection limit. In the initial studies attempts were made to exploit the scale expansion and digital readout capabilities of the Cary 118

Spectrophotometer (Varian Instrument Division). Attempts to measure the absorbance in 5-cm cells were also investigated.

In the analysis of U concentrations below 10 μg , the absorbance of the baseline starting at 600 nm was changing with each sample and calibration point. Because of the small absorbance differences between the U-PADAP complex and the PADAP blank, significant errors resulted in the final absorbance reading. Corrections to the absorbance of the peak were made by subtracting the absorbance of the baseline at 600 nm. This resulted in better linearity of the calibration data but large variations still existed in the absorbance readings.

The shifting baseline is believed to be the result of small variations in the concentration of the PADAP reagent in the final solution. Since the PADAP and uranium-PADAP spectra overlap, the variations in the PADAP concentration for the blank and sample will cause shifts in the baseline and errors in the small absorbance measurement associated with low U levels. This spectra overlap is illustrated in Figure 4. The problem was enhanced by the need for 1.5 g/liter PADAP solution in place of the recommended 0.5 g/liter PADAP. Purification of the PADAP reagent would probably aid in lowering the effect of the blank.

In order to reduce the effect of the overlapping spectra and the high absorbance from PADAP, the concentration of the PADAP was lowered to 0.5 g/liter. Tests using varying amounts of 0.2 g/liter PADAP indicated that over 3 ml would be necessary in order to reach the maximum absorbance for 20 μg of U. Two milliliters of 0.5 g/liter PADAP were used for less than 20 μg of U to minimize the volume and to insure an excess of reagent was present.

Another possible way of reducing the effect of the

A' SPECTRUM OF U-Br-PADAP COMPLEX
VS Br-PADAP REAGENT BLANK

B' SPECTRUM OF Br-PADAP
REAGENT BLANK VS AIR

C' SPECTRUM OF U-Br-PADAP
COMPLEX VS AIR
 $A' = C' - B'$

A SPECTRUM OF U-PADAP COMPLEX
VS PADAP REAGENT BLANK

B SPECTRUM OF PADAP REAGENT
BLANK VS AIR

C SPECTRUM OF U-PADAP COMPLEX
VS AIR
 $A = C - B$

NOTE: 20 μ g U WAS USED FOR ALL SPECTRA
ORIGINAL PADAP CONCENTRATION = 1.59/L
ORIGINAL Br-PADAP CONCENTRATION = 0.59/L

FIGURE 4

COMPARISON OF SPECTRA FOR PADAP AND
Br-PADAP AND THEIR U COMPLEXES

PADAP reagent would be to extract the red U-PADAP complex away from the highly colored dye. Portions of a sample in which the color had already been formed were contacted with various organics to extract the complex. The results of these contacts are summarized in Table XVIII.

TABLE XVIII
EFFECT OF WASHING U-PADAP SOLUTION
WITH VARIOUS ORGANICS

<u>Organic</u>	<u>Comment</u>
Xylene	Extracted yellow color
Chloroform	Extracted yellow color and some pink with a small volume change
Carbon tetrachloride	Extracted yellow color
Hexone	Extracted yellow color with large volume change
Butylacetate	Extracted yellow color with large volume change
Toluene	Extracts yellow color
Cyclohexane	Extracts yellow color
Butanol	Soluble
Iso-amyl alcohol	Large volume change
Cyclohexone	Very soluble
Hexanol	Volume change and extracted some yellow color

None of the reagents effectively extracted the red U-PADAP complex. However spectra of the yellow organic phases revealed that several of the organics were separating the unreacted PADAP. The alcohol used to develop the color was soluble in many of the organics, causing large volume changes. Carbon tetrachloride (CCl_4) effectively removed the free PADAP from the aqueous-alcohol phase without large volume changes. It was also convenient since it was heavier than the aqueous phase and did not have to be removed.

In order to evaluate the effect of the CCl_4 wash on the procedure, two calibrations were prepared over the range 1 to 10 $\mu\text{g u}$. One portion of the solution was not washed and a second 5-ml portion was washed with 5 ml of CCl_4 before measuring the absorbance at 565 nm. The results of these calibrations are illustrated in Figure 5 and the least squares evaluation of the data is shown in Table XIX.

TABLE XIX
LEAST SQUARES DATA OF LOW-LEVEL U CALIBRATIONS

<u>Least Squares</u>	<u>CCl_4 Washed</u>	<u>CCl_4 Not Washed</u>
Slope	0.0041 $\pm$ 0.00006	0.0064 $\pm$ 0.00025
Intercept	+0.00047 $\pm$ 0.00042	-0.00463 $\pm$ 0.00169

A 30-fold improvement in the precision of the slope and intercept resulted when the solution was washed with CCl_4 . The intercept was 10 times smaller in the CCl_4 -washed calibration and the slope decreased by about 1.5. The CCl_4 curve shows greater linearity and an intercept closer to 0. Since these studies showed that CCl_4 washes should improve low-level U analyses, an attempt was made to apply the technique to absorption measurements using 5-cm cells. Two 10-ml CCl_4 washes were needed to remove all of the excess PADAP. The calibration indicated that it should be possible to detect 0.25 μg of U. However the problem of a varying baseline still existed at these levels and absorbances corrected for the baseline gave improved calibrations. Attempts to reproduce the data indicated that variances of $\pm 25\%$ might be expected at the 0.25- μg U level. The absorbance for this concentration of U in 5-cm cells was only 0.0020; therefore the large errors could have resulted from variations in the cleanliness and degree of matching in the absorption cells, temperature fluctuations, or in the chemical preparation of the samples. The practical limit

FIGURE 5
COMPARISON OF U CALIBRATIONS WITH AND WITHOUT CCl₄ WASH

for the measurement of U with PADAP using the Cary 118 is about 1 μg or 1×10^{-4} g/liter U for a 10-ml H_2O sample. If lower limits are to be reached a concentration technique or more sensitive reagent must be used.

Johnson and Florence^[7] described the use of a more sensitive bromonated derivative of PADAP, 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol (Br-PADAP) for the determination of U. More recently Prall^[8] has used BrPADAP in an automated U method and Pakalns^[5] has applied it to U analyses of ores that have been dissolved in pressure dissolution bombs. In addition to improving sensitivity, the reagent can tolerate larger amounts of iron and is easier to prepare in a pure state. Recently this reagent has become available from the G. Frederick Smith Company. Figure 4 shows a comparison of the absorption spectra of PADAP and Br-PADAP using 20 μg of U. The absorbance of the PADAP blank at the 565 nm U peak is about 2.5 times greater than the Br-PADAP blank at the 480 nm U peak. In addition, the absorbance of the uranium Br-PADAP complex is 70% greater. These advantages and the fact that Br-PADAP is much easier to dissolve and requires no filtering makes it a superior reagent for low-level U analyses. The reagent can be substituted into the described procedures without any major modifications.

CONCLUSIONS

During the development of this procedure several significant observations were made which, although not thoroughly explored, should improve the methods. Therefore the author would like to recommend some changes in the procedures discussed in the text and described in detail in the Appendixes.

RECOMMENDATIONS

- Instead of the PADAP reagent, Br-PADAP should be used since it is now available and is more sensitive and convenient.
- Any further studies on Pu should be performed with highly purified $\text{Pu}(\text{NO}_3)_4$ or PuO_2 to minimize the effect of U in the blank. This may require multiple ion exchange separation of U from Pu and firing to the oxide under carefully controlled conditions. This material could then be spiked with known amounts of U and used, if necessary, for calibrations.
- The concentration of the complexing agents should be lowered according to Johnson and Farrar^[7] and the color developed with Br-PADAP before diluting in order to reduce color-development times.
- The potential of extracting the uranium Br-PADAP complex into an organic should be studied in greater detail.
- Mercaptoacetic acid should be used in the color-developing stage to insure that any Pu present is in the three valence state.

We hope in the future to explore the use of Br-PADAP in greater detail with subsequent application to environmental samples and characterization of Hanford's nuclear waste.

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APPENDIXES

APPENDIX A
PuO₂ DISSOLUTION AND PREPARATION PROCEDURE

Procedure	Comment
1. Accurately weigh 200 mg of PuO ₂ and quantitatively transfer to a 40-ml glass vial. For calibrations in PuO ₂ or spike data a known amount of U (25 to 400 µg) is also added at this point. Only pure PuO ₂ with negligible U can be used for calibrations.	Weight should be controlled at 200 ± 5 mg in order to obtain reproducible results.
2. Add 5 ml of concentrated HCl, cover with a watch glass, and heat to boiling.	
3. Add 2 drops of concentrated HF and boil until sample is completely dissolved.	a. Swirl every 5 min. b. Use additional HCl and HF only if the sample does not completely dissolve in 30 min.
4. Evaporate the solution to dryness to remove excess HF.	Do not overheat since this may cause splattering.
5. Add 18 ml of 2M NH ₂ OH·HCl-4M HCl and stir using a Teflon-coated or glass stir bar.	a. NH ₂ OH·HCl-HCl solution is added before the AlCl ₃ since a precipitate may form if reversed. b. NH ₂ OH·HCl is used to reduce Pu(IV) to Pu(III) and the 4M HCl is required for good extraction of the U.
6. Add 2 ml of 1M AlCl ₃ -4M HCl to the vial to complex the remaining fluoride.	a. The aluminum acts as a fluoride complexant and salting agent to increase U extraction. b. The volume of 2M NH ₂ OH·HCl-4M HCl is regulated so that the total volume is 20 ± 2 ml.

Procedure	Comment
7. Heat the solution to near boiling for 30 min in order to completely reduce Pu(IV) to Pu(III). After heating allow the solution to cool to room temperature.	a. Cover the vial with a watch glass to avoid excessive volume loss. Volume losses should be adjusted to 20 ml with 2M $\text{NH}_2\text{OH}\cdot\text{HCl}$ -4M HCl. b. The solution should be deep-blue characteristic of Pu(III). Green or yellow solutions may indicate incomplete reduction and will result in large amounts of Pu in the organic, causing high spectrophotometer and low X-ray results.
8. The sample is now ready for the extraction of uranium with Aliquat-336 as described in Step 3 of Appendix B. The solution may be transferred from the glove box into a clean vial for the remaining procedure using a 2-ml 2M $\text{NH}_2\text{OH}\cdot\text{HCl}$ -4M HCl wash.	

APPENDIX B

PROCEDURE FOR EXTRACTION OF URANIUM WITH ALIQUAT-336

1. For $\text{Pu}(\text{NO}_3)_4$ solutions or other samples requiring extractions due to interferences or high-acid conditions pipet the sample directly into 20 ml of 4 HCl -2 M $\text{NH}_2\text{OH}\cdot\text{HCl}$. Prepare two 2-dram vials containing 5 ml of 4 M HCl -2 M $\text{NH}_2\text{OH}\cdot\text{HCl}$ and 50 mg NaF and a Teflon-coated or glass stir bar.
 - a. Samples containing high concentration of acid >0.25 meq may be extracted to avoid neutralization and localized precipitation.
 - b. Samples low in Pu but high in Fe and other ions found in rocks or ores may be better analyzed by extraction with TOPO from 2 M HNO_3 .
 - c. When the extraction is used for concentrating U from large volumes, the HCl concentration should be adjusted to 4 to 6 M and sufficient $\text{NH}_2\text{OH}\cdot\text{HCl}$ added to reduce Fe and Pu present.
2. For samples high in Pu (>5 mg) heat in $\text{NH}_2\text{OH}\cdot\text{HCl}$ - HCl matrix for 30 min at 70°C and then allow to cool to room temperature to insure reduction of $\text{Pu}(\text{IV})$ to $\text{Pu}(\text{III})$.

If the method is being used to calibrate for U in PuO_3 , or if fluoride is present, add 2 ml of 1 M AlCl_3 before extracting.
3. Add exactly 2 ml of Aliquat-336 and stir to a good emulsion for 10 min.
 - a. For X-ray analysis, a 1-ml portion of Aliquat-336 is used.
 - b. Due to the small organic-to-aqueous volume ratio an excellent stirrer is required.
 - c. This extracts $\text{U}(\text{VI})$ and other ions that form stable chloride complexes and separates them from $\text{Pu}(\text{III})$, $\text{Am}(\text{III})$, rare earths, and other ions.
4. Centrifuge or allow the phases to separate and transfer as much of the organic as possible to one of the 2-dram vials containing 5 ml of 4 M HCl -2 M $\text{NH}_2\text{OH}\cdot\text{HCl}$ and 50 mg NaF and emulsify for 3 min.

This step uses fluoride to wash residual $\text{Pu}(\text{III})$ and $\text{Pu}(\text{IV})$ from the organic.

5. Repeat Step 4 after transferring the organic to the second 2-dram vial.
6. Centrifuge or allow the phases to thoroughly separate and transfer exactly 1 ml of the organic to a clean 25-ml volumetric flask and follow the spectrophotometric procedure described in Appendix C.

For X-ray analysis follow the procedure described in Appendix E.

APPENDIX C
SPECTROPHOTOMETRIC DETERMINATION OF
EXTRACTED URANIUM WITH PADAP

Note: This Appendix describes the spectrophotometric procedure used for studies described in this document. Since recent developments indicate the procedure could be improved, these proposed modifications have been included in the comment section and are noted by the prefix (M).

Procedure	Comment
1. To the 1 ml of extracted U in the 25-ml volumetric flask, add 2 ml of the complexing solution and swirl to mix.	M-1-a. The method may be improved for the determination of U in Pu by adding 1 ml of 10% mercaptoacetic to reduce any residual Pu(IV) to Pu(III) before complexing. M-1-b. A new complexing solution which is diluted 1:2 with H ₂ O may be substituted for the 2 ml of the more concentrated reagent. This may shorten color-development times and improve the linearity of the calibration. c. The complexing solution is used to remove interfering ion effects. This should be less for extracted U and therefore the concentration of this reagent can be reduced. d. The complexing solution is added before the buffer to prevent precipitation of hydrolyzable ions.
2. Add 2 ml of TEA buffer to the flask and swirl.	M-2-a. Florence and Farrar ^[3] added 2 ml of PADAP before the TEA buffer. Our test indicated no significant differences in this order of addition.

Procedure	Comment
	b. The 2 ml of buffer can tolerate 0.25 meq of H^+ . Larger amounts of acid require neutralization before developing the color.
	c. Observe buffer contents closely; if algae has formed replace the buffer.
3. Add 15 ml of ethanol and swirl.	M-3-a. Florence and Farrar ^[3] add 1 ml of buffer at this stage, mix thoroughly, and allow the solution to stand 10 min before diluting with 18 ml of ethanol. Because of the heterogeneous nature of the mixture we felt that the alcohol at this stage may improve the kinetics of removing the uranium from the organic so it can react with PADAP. However the dilution with alcohol may be one factor causing the long color development times in this complex equilibrium.
4. Add 2 ml of PADAP and swirl to mix and bring to volume with deionized H_2O . Add a Teflon-coated or glass stir bar and mix thoroughly; allow to stand 1.5 hr before reading the absorbance versus a reagent blank at 565 nm.	M-4-a. Br-PADAP should be used in place of PADAP, if possible, because of its improved purity, sensitivity, and selectivity. b. Solutions containing significant amounts of Au or Ru may require filtration before absorption measurement. c. The absorbances were measured in 1-cm silica cells. Cells must be carefully cleaned with H_2O and ethanol. Sometimes a precipitate forms on cleaning which requires a small amount of 50% ethanol-50% 3M HCl for removal before final rinses with H_2O and ethanol.

CALIBRATIONS

The method is calibrated by adding 25 to 200 μg of standard uranium to the extraction procedure in Appendix B and then carried through the spectrophotometric procedure in Appendix C. Uranium in PuO_2 calibrations were prepared without the use of PuO_2 and without the concentrated HCl and HF of the dissolution procedure. However the AlCl_3 is added after Step 2 of Appendix B. Some typical calibration data are shown in Table XX.

TABLE XX
SPECTROPHOTOMETRIC CALIBRATION

$\mu\text{g U}$	Absorbance	% Recovery
25.22	0.0575	99.5
35.31	0.0818	92.7
50.44	0.1398	101.2
75.66	0.2184	100.2
100.88	0.3030	101.6
151.32	0.4601	102.5
201.76	0.6074	98.3

$$\mu\text{g U} = (A - I)(1/S).$$

$$\mu\text{g U} = (A + 0.0221)(315.18896) \text{ and}$$

$$S = \text{least square slope} \left(\frac{A}{\mu\text{g U}} \right)$$

where

A = absorbance

I = least square intercept (-0.0221)

New calibrations were made with each new batch of PADAP or when other reagents appeared to be deteriorating and causing poor recoveries of low U concentrations. Calibrations incorporating PuO_2 or $\text{Pu}(\text{NO}_3)_4$ were not used because the purity of available materials was questionable. However if extremely pure plutonium compounds are available with negligible uranium, then calibrations should be made using these materials.

APPENDIX D

PROCEDURE FOR THE DIRECT SPECTROPHOTOMETRIC
DETERMINATION OF LOW-LEVEL URANIUM WITH PADAP

Procedure	Comment
1. Add 9.0 ml of deionized H ₂ O to a 25-ml volumetric flask.	<p>a. H₂O is used to rinse micro-pipets and keep complexing solution from precipitating.</p> <p>b. For large samples (>1-ml) omit H₂O.</p>
2. Pipet sample or standard into the flask and rinse pipet with H ₂ O.	<p>a. Uranium standards for calibration should cover the range of 10 to 100 µg of U.</p> <p>b. The amount of acid or base added in the sample or standard should be <0.25 meq. If >0.25 meq is added, neutralize after Step 3 with an equivalent amount of acid or base.</p> <p>c. Small amounts (<100 µl) of organic uranium solutions [tributylphosphate (TBP)-CCl₄] have also been analyzed by this method. Large amounts of organics may not be totally miscible and also may result in longer color development times or changes in sensitivity. If U concentrations in organics are high enough, they may be diluted in ethanol before analyzing.</p> <p>d. Large amounts of As(V), Cr(III), Cr(VI), Cu(II), Ni(II), Pu(IV), V(V), PO₄⁻³, SiO₃⁻², or small amounts of Pd may interfere.</p>
3. Pipet 2 ml of complexing solution into the flask and swirl.	If necessary, neutralize the sample with equivalent amounts of acid or base. Neutralization with base before adding the complexing solution may result in an irreversible hydrolysis of uranium which would

Procedure	Comment
	give low results. For this same reason the complexing solution should always be added before the buffer solution.
4. Pipet 2 ml of triethanolamine buffer into the flask and swirl.	The sample may also be neutralized after this step if desirable.
5. Add 9 ml of ethanol to the flask and swirl to mix.	Alcohol is added to prevent precipitation of PADAP.
6. Pipet 2 ml of 1.5 g/liter PADAP into the flask and swirl to mix.	a. The PADAP should be pipeted slowly and accurately since the excess PADAP spectrum overlaps the U-PADAP spectrum so that large variations in the excess PADAP could result in inaccurate analyses. b. Br-PADAP is recommended for higher sensitivity.
7. Dilute the flask to the mark with deionized H ₂ O, add a glass or Teflon-coated stir bar and stir on a magnetic stirrer for 2 to 3 min making sure a vortex is formed in the neck of the flask.	The solution should be clear with no solids present. The reagent blank should be yellow-brown in color and the uranium solutions orange-red depending on the concentration.
8. Let the solutions stand for 30 min to fully develop color. Then measure the absorbance of the solution versus a reagent blank at 565 nm.	a. The reagent blank is prepared by following the procedure as described, but omitting Step 2. b. If extremely low uraniums are being analyzed (<10 µg U), then there may be an advantage in washing a portion of the final solution with CCl ₄ to remove excess PADAP. For these levels of uranium a separate calibration using 0.5 g/liter PADAP in place of 1.5 g/liter PADAP and 5-cm absorption cells may be useful. c. Cells are normally washed with deionized H ₂ O followed with

Procedure	Comment
	ethanol and then dried by vacuum. A 50% ethanol-50% 3M HCl wash may be necessary if a film forms on the cells.

CALIBRATION

The spectrophotometer is normally calibrated by carrying the following aliquots of uranium: 10, 25, 50, 75, and 100 μg through the described procedure and measuring their absorbances versus a reagent blank at 565 nm in 1-cm silica absorption cells. The absorbance is plotted versus micrograms of uranium and a least squares equation of the line determined. Typical calibration data and curves are shown in Table XXI and Figure 6.

TABLE XXI
CALIBRATION DATA FOR DIRECT SPECTROPHOTOMETRIC METHOD

$\mu\text{g U}$	Absorbance	Slope (S)	$= 0.008758 \pm 7.5 \times 10^{-5}$
A 10.09	0.049	Intercept (I)	$= -0.042 \pm 4.6 \times 10^{-3}$
B 25.22	0.175		
C 50.44	0.398	1/Slope (S)	$= 114.18601 \frac{\mu\text{g}}{\text{A}}$
D 75.66	0.628	$\mu\text{g U}$	$= (A - I) (1/S)$
E 100.88	0.838	$\mu\text{g U}$	$= (A + 0.042) (114.18601)$

EXAMPLES OF TYPICAL CALIBRATION DATA AND SPECTRA

The data and spectra shown were generated with a Cary Model 118 Ratio Recording Spectrophotometer. The instrument was operated in a dual-beam mode with automatic slit adjustment and constant gain on the photomultiplier. The detector slit width at the peak was normally 0.1 mm when using the visible tungstenhalogen light source at normal intensity. Scans were made over the range 600 to 500 nm with a chart speed of 20 nm/inch and a scan speed of 0.5 nm/second.

FIGURE 6

SPECTRA FROM CALIBRATION OF DIRECT SPECTROPHOTOMETRIC
DETERMINATION OF U WITH PADAP

APPENDIX E
X-RAY OPERATING CONDITIONS AND PROCEDURES

A General Electric XRD-5 X-ray emission spectrometer with Model-700 detector and electronics was used for the uranium analyses described in this document.

X-RAY OPERATING CONDITIONS

X-Ray Tube:	Molybdenum target, G. E. Type EA-75.
Tube Voltage:	50 kilovolts (kV).
Tube Current:	40 milliamps (mA).
Diffraction Crystal:	LiF (200), $2d = 4.0267$.
Detector:	NaI(Tl) scintillation counter.
Collimation:	0.01 Sollier slits.
Sample Mask:	2.0-cm, circular, aluminum.
Count Time:	100 seconds.
Path Media:	Air.

GONIOMETER SETTINGS

Element	X-Ray Line	Analysis Angle	Background Angle
		2θ	2θ
U	$L\alpha-1$	26.14°	25.60°
Pu	$L\alpha-1$	24.90°	24.20°

X-RAY MOUNTING PROCEDURE

1. Place a 2 in.² piece of 1/4 mil Mylar on top of a properly cut Capplug that is ~12" below a heat lamp.
2. Place a filter paper pad on the Mylar and turn on the lamp. If the lamp is too close, the Mylar will melt. The pad is preheated to help prevent oversaturation with the organic.
3. Slowly pipet exactly 250 μ l of the organic phase on the pad. Do not flood the pad with solution. After the pad is dry (~10 minutes) pipet another 250- μ l aliquot of the organic on the pad and dry.

4. Place another 2" square of Mylar on top of the dry pad, being careful not to disturb the pad.
5. Make certain the pad is centered over the hole in the Capplug and sandwiched between the two Mylar squares before placing the trimmed curtain ring on the Capplug to hold the filter in place.
6. Survey the mount for Pu contamination by smearing with a Kimwipe[®] (Kimberly-Clark) dampened with alcohol or acetone since the alpha radiation from Pu will penetrate the Mylar.
7. In a clean work area with clean gloves wrap the mount in a 6" piece of Mylar. Place the Mylar over the mount and make it tight on the face by pulling the edges to the rear. Holding the excess tail in the left hand, twist the mount toward you until the excess forms a tight Mylar stem. Wrap an 0.5" piece of cellophane tape around the stem to hold it tight. Cut off any stem over 0.5" and seal the cut end with cellophane tape to prevent the Pu from escaping.
8. Survey the mount for alpha contamination. If it is smearable, clean both the mount and work area, and with clean gloves wrap a second 6" piece of Mylar around the mount as in Step 7. This second piece of Mylar should be added as an additional safeguard against contamination even if the mount is clean.
9. Under no circumstances should a mount that is smearable with radiation be analyzed. The special safety precautions discussed in ARH-2835 should be consulted for additional information.

NOTE: Mounts should be surveyed before and after placing in the X-ray.

Sample mask should be ground smooth to prevent possible tearing of Mylar.

Mounts should be stored in a hood for a limited time and carefully surveyed before removing to an uncontrolled area.

Mounts that are contaminated with plutonium must be labeled.

X-RAY CALIBRATION PROCEDURE AND CALCULATIONS .

The X-ray was calibrated with and without Pu in the system. One calibration was made by spiking PuO_2 with between 25 and 500 μg of a uranium standard and carrying these standards through the dissolution and extraction procedures in Appendixes A and B. Other calibrations were made without Pu present and without the use of the dissolution procedure steps. However the AlCl_3 was added as noted in Appendix B. A typical calibration of this type is shown in Table XXII.

TABLE XXII
TYPICAL X-RAY CALIBRATION FOR FFTF U ANALYSES.

<u>$\mu\text{g U}$</u>	<u>Net c/s U</u>	<u>% Recovery</u>
25.22	29.87	105.0
50.44	89.81	101.9
100.88	206.41	99.0
252.20	566.76	99.0
504.40	1182.44	100.3

$$\mu\text{g U} = (c/s - I)(1/S)$$

$$\mu\text{g U} = (c/s + 33.80)(0.41578)$$

where

c/s = net counts per second at
U peak

I = least squares intercept
(-33.80 c/s)

S = least squares slope
(2.4051 c/s/ $\mu\text{g U}$)

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