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SPECTROPHOTOMETRIC DETERMINATION OF PLUTONIUM III, IV, AND VI IN NITRIC ACID SOLUTIONS

Paul G. Hagan and Frend J. Miner

Abstract. A method is reported for the quantitative spectrophotometric determination of plutonium (III), (IV), and (VI) existing separately or in mixed oxidation states in nitric acid. The nitric acid concentration varied from 1 to 4 molar for Pu(III), and 1 to 10 molar for Pu(IV) and (VI).

Molar absorptivity values are given for the major absorption peaks with an evaluation of their spectral reproducibility. With these molar absorptivity data and the mathematical approach of Ochsenfeld and Schmieder[1] a method is presented for a calculation to determine the molar concentration of each oxidation state.

SUMMARY

A method was developed for the quantitative spectrophotometric determination of Pu(III), (IV), and (VI), existing separately or in mixed oxidation states in nitric acid media. The nitric acid concentration varied from 1 to 4 molar for Pu(III), and 1 to 10 molar for Pu(IV) and (VI). The spectra of the separate valent states in varying concentrations of nitric acid were prepared, and a study of the anomalies of the major absorption peaks of plutonium was made. Molar absorptivity values were calculated from these absorption peaks and evaluated for their analytical reproducibility.

INTRODUCTION

Plutonium possesses four oxidation states in aqueous solutions: (III), (IV), (V), and (VI). Because of only slight differences in oxidation – reduction potentials, these oxidation states can exist simultaneously in solution. In nitric acid, however, Pu(V) is not present in detectable concentrations, and Pu(III) is only present at acid concentrations of less than five molar.

Spectrophotometric studies of aqueous plutonium systems have been quite extensive. The initial spectrophotometric work, which demonstrated the utility of spectra in plutonium oxidation state analysis, was done by Hindman and Kraus in the early 1940's.[2] Subsequently, Myers[3] and Colvin[4] investigated the absorption spectra of plutonium in nitric acid solutions. They determined molar absorptivity values for Pu(III), (IV), and (VI), and showed how the spectra depended on nitric acid concentration. Colvin developed a series of formulas to calculate the concentration of particular oxidation states from absorbance measurements. Later, Ochsenfeld and Schmieder[1] improved the data by using a spectrophotometer with better resolution.

The objective of this work was to establish a method to quantitatively determine the concentration of a plutonium valence species in nitric acid solutions containing mixed plutonium valencies. To obtain this objective, a spectrophotometer with good resolving characteristics was used to analyze plutonium solutions of high valence spectral purity. Molar absorptivity data for the major peaks of the various valencies were determined in nitric acid up to 4M for Pu(III), and to 10M for Pu(IV) and (VI). These data were then used to obtain equations which permit the rapid calculation of the concentration of an individual valence state in a solution of mixed valencies. Determinates, solved by the computer, were used to obtain the equations.

EXPERIMENTAL

Four different concentrations of plutonium in nitric acid solutions were prepared for each of the three plutonium valence states.

Pu(III) from 0.024M or 5.7 g/l
to 0.0027M or 0.6 g/l

Pu (IV) from 0.013M or 3.1 g/l
to 0.001M or 0.3 g/l

Pu (VI) from 0.0019M or 0.46 g/l
to 0.0002M or 0.005 g/l

Plutonium Solution

These plutonium solutions were prepared by cutting plutonium metal of high purity to a desired weight

followed by dissolution in 5 ml of 6M $HClO_4$ in a volumetric flask. The resulting solutions were primarily Pu(III).

Pu(III) Preparation

To prevent oxidation, hydroxylamine hydrocholoride was added (the spectra appeared unaffected by the addition of this reductant). Measured quantities of concentrated HNO_3 was then added to obtain the desired HNO_3 concentrations and the volumetrics were brought to volume with 0.5M $HClO_4$. Because of the oxidizing properties of HNO_3, trivalent plutonium can only be studied in solutions up to 5M HNO_3, and over 4M the spectral purity of Pu(III) is questionable.

Pu(IV) Preparation

To the volumetrics used for the tetravalent solutions, concentrated HNO_3 was added to adjust the HNO_3 molarity and to oxidize the solutions to the Pu(IV) state. The volumetrics were made to volume with dilute $HClO_4$ and checked for Pu(IV) spectral purity by the absence of Pu(III) and Pu(VI).

Pu(VI) Preparation

A stock solution of hexavalent plutonium was prepared by fuming the excess of perchloric acid used in dissolving the plutonium metal. The solutions were checked spectrophotometrically and found to contain no detectable Pu(III) or Pu(IV). Aliquots were then mixed in volumetric flasks with varying amounts of 10M HNO_3 to yield the desired nitric acid concentrations.

Equipment

A Cary Model 14 continuous recording spectrophotometer was used for recording the spectra. Solutions were scanned, using 1 cm cells, from 1300 to 700 nm in the near infrared region (NIR) and from 700 to 300 nm in the visible region. A scanning speed of 0.5 nm/sec was used for optimum instrumental resolution.

The temperature of the solution in the absorption cell rose from ambient (~24°C) to ~32°C during the scanning of the NIR region. The temperature then dropped to ambient during the subsequent scanning of the visible region.

RESULTS AND DISCUSSION

Plutonium(III)

Although trivalent plutonium does not have a tendency to form strong complexes in solution, a slight spectral change is evidenced as the nitrate ion is increased (see Fig. 1). The trivalent plutonium nitrate complex is presumed to be the Pu^{3+} ion associated with either one, two, or three nitrate ions: $Pu(NO_3)^{2+}$, $Pu(NO_3)_2^{+}$, or $Pu(NO_3)_3$. Association quotients for these three complexes have been assigned by Shevchenko, et al.,[5] from solvent extractions studies. Spectrophotometrically, these complexes cannot presently be differentiated.

Quantitative molar absorptivity values were calculated using the absorbance values of the principal peaks and selected troughs at constant wavelengths. These values, calculated at various nitric acid concentrations, show the effect of nitrate complex formation. Pu(III) molar absorptivity values are listed in Table 1. Calculations were made at two major peaks (560 and 600 nm) using two troughs (585 and 610 nm) and the baseline (450 nm) where any Pu(IV) absorbance would be minimal. Also listed are values at 476 nm, the principal Pu(IV) peak, which were used to check the spectral purity of Pu(III) with reference to Pu(IV).

The evaluation shows that the molar absorptivity value obtained using the 560 nm peak and 640 nm trough is the most reproducible. The value obtained using the 600 nm peak with the 640 nm trough is about as reproducible; however, when either of these two peaks is evaluated with the 585 nm trough or baseline, the average relative standard deviation increases considerably.

Plutonium(IV)

Tetravalent plutonium easily combines with nitrate ions forming complexes from $Pu(NO_3)^{3+}$ to $Pu(NO_3)_6^{2-}$. The lower acidities of HNO_3 (1 to 4M) favor the mono-, di-, and trinitrato complexes, whereas the higher acidities promote increasing formation of $Pu(NO_3)_6^{2-}$.

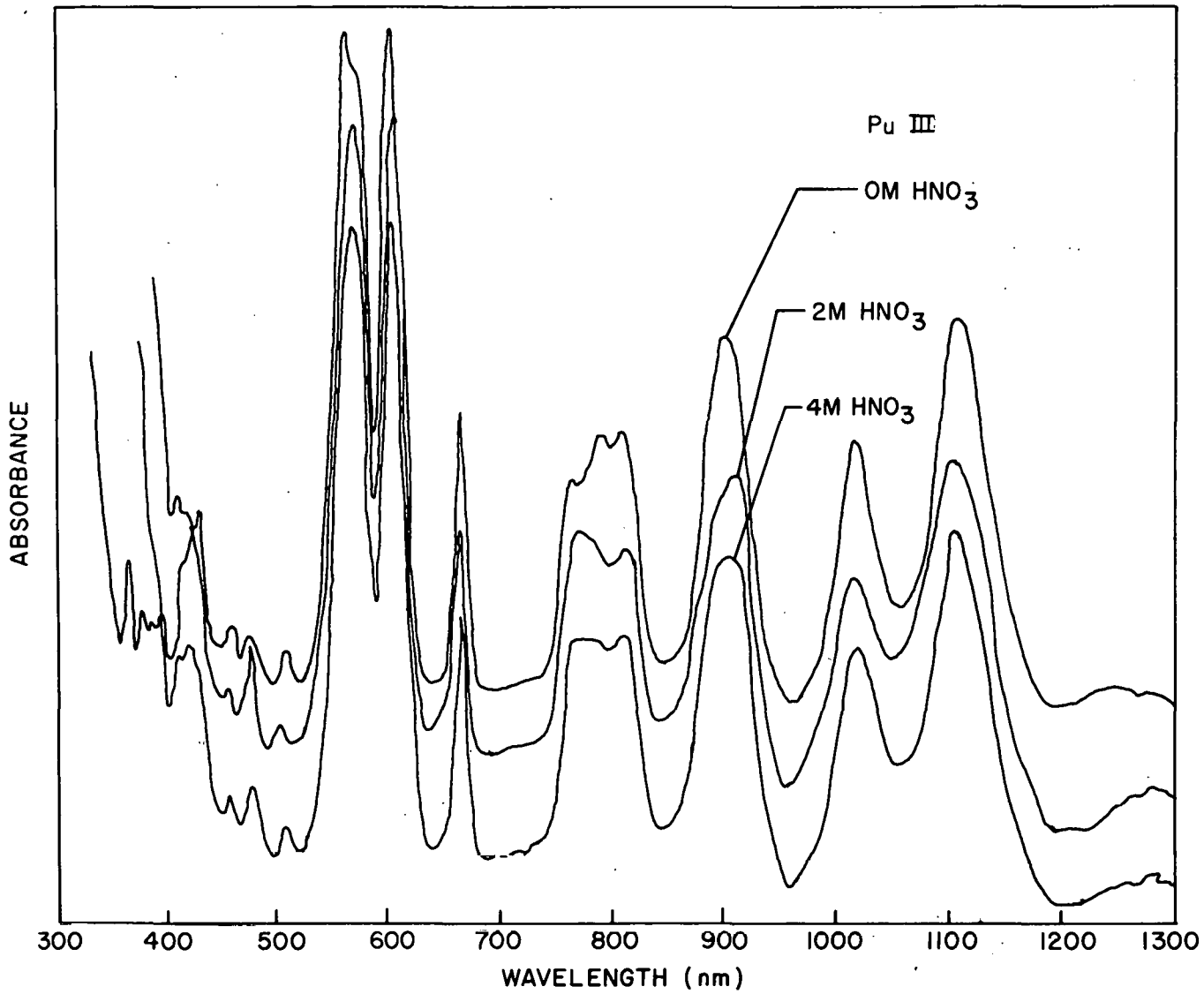


Figure 1. Absorption Spectra of Plutonium III in OM, 2M, and 4M HNO_3.

TABLE I. Relative Molar Absorptivity Values of Plutonium III as a Function of HNO_3 Concentration.

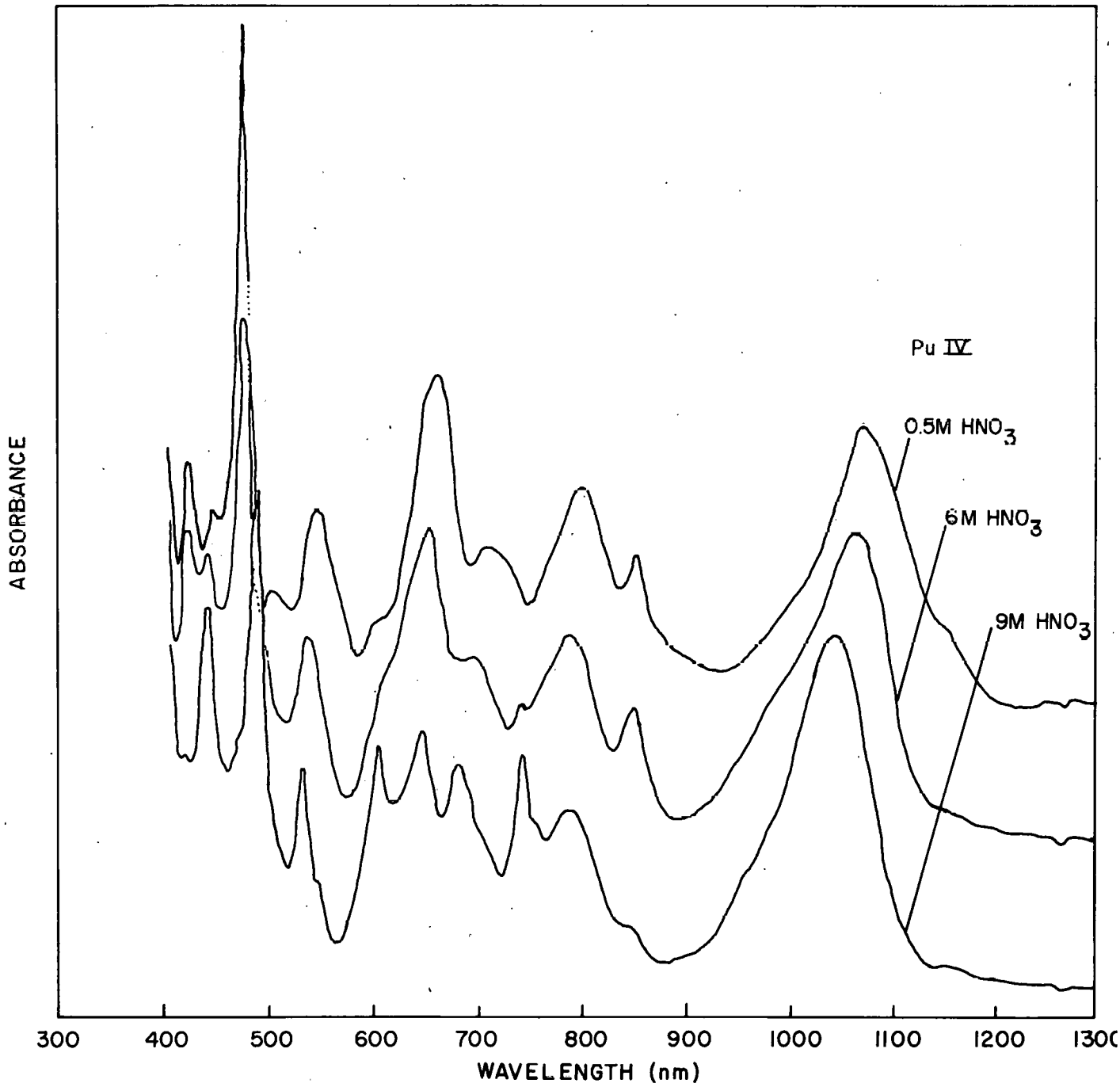
HNO_3, M	A 560 – 585 nm $\bar{\epsilon}$	±SD	A 560 – 640 nm $\bar{\epsilon}$	±SD	A 600 – 585 nm $\bar{\epsilon}$	±SD	A 600 – 640 nm $\bar{\epsilon}$	±SD	A 560 – Baseline nm $\bar{\epsilon}$	±SD	A 600 – Baseline nm $\bar{\epsilon}$	±SD	A 476 – 515 nm $\bar{\epsilon}$	±SD	A 476 – Baseline nm $\bar{\epsilon}$	±SD
0	22.4	0.2	36.7	0.2	21.3	0.1	35.7	0.2	40.3	1.3	39.2	1.2	2.3	0.1	6.1	0.5
1	20.9	0.5	36.5	0.2	20.9	0.9	36.5	0.6	40.5	1.7	40.4	1.4	2.6	0.3	6.7	2.1
2	19.2	0.8	35.6	0.7	19.9	1.2	36.3	0.9	37.3	2.1	38.0	1.6	2.4	0.2	4.3	2.4
3	17.7	1.0	34.8	0.6	19.9	1.1	37.5	1.2	37.4	0.9	39.0	1.8	2.8	0.8	5.5	1.3
4	16.4	*	30.9	*	19.0	*	33.5	*	35.1	*	38.2	*	2.6	*		
Average RSD (%)		3.4		1.4		4.1		2.0		3.9		3.8		13.8		29.8

* Values not included because of dubious spectral purity.

Because of the strong tendency for Pu(IV) to form complexes, the tetravalent nitrato spectra experiences considerable peak shifting and transformation (see Fig. 2). The principal peak at 476 nm shifts to a longer wavelength and decreases in molar absorptivity values as the nitrate concentration increases. Also, significant new peaks are introduced at 443-, 608-, and 743 nm.

Major absorption peaks at 476-, 660-, and 1075 nm with troughs at 495-, 690-, and 1200 nm, respectively, were used to calculate the molar absorptivity values of Pu(IV). A calculation was also made at the 476 nm peak using a baseline set to zero at 450nm. The molar absorptivity at the 476 nm peak at various acid concentrations was calculated using both a constant wavelength and a

Figure 2. Absorption Spectra of Plutonium IV in 0.5M, 6M, and 9M HNO_3.



maximum peak height. Both methods have certain drawbacks. Using a constant wavelength, the complexing of the NO_3^- ions shifts the peak absorbance. Using measurements at maximum peak heights, the observed peak shift, >15 nm, makes the calculation of mixed valancies slightly inaccurate unless corrections are made for the contribution from absorbance of Pu(III) and Pu(VI) at the changed wavelengths.

Relative molar absorptivity values for Pu(IV) are given in Table II. The relative standard deviations show the peak in the NIR region at 1075 nm to be the most reproducible with changing HNO_3 concentrations. The values in the visible region associated with the maximum 476 nm peak (including shift) and 660 peak have about the same precision.

Plutonium(VI)

The intense Pu(VI) peak at 831 nm in the NIR region (see Figure 3) was used to quantitatively determine the amount of hexavalent plutonium present. In recent years, instrument refinements have increased peak resolution in the NIR region; accordingly, the reported molar absorptivity values of the 831 nm peak have increased. At the same time, the questionable ability of the 831 nm peak to follow Beer's law has been resolved as reported by Costanzo and Biggers.[6]

The analytical approach for mixed valency solutions required the instrument to be set in an automatic scan function. The temperature in the absorption cell rose ~8°C during the NIR region scan of the solutions. Therefore, consistency of the scanning procedures is important because the absorbancy of the 831 nm peak has a large negative temperature coefficient, decreasing as the temperature increases.

An increase in nitric acid concentration also causes a decrease in the absorbance of the 831 peak. A plot of absorptivity values with respect to HNO_3 concentration is shown in Figure 4. This decrease is attributed to the formation of the various nitrato complexes. Hindman[2] has reported three nitrate complexes presumed to be $PuO_2(NO_3)^+$, $PuO_2(NO_3)_2$, and $PuO_2(NO_3)_3^-$. Thus, as the nitric acid concentration is increased to 4M, the decrease in absorption of the 831 nm peak is attributed to the formation of the mono- and dinitrato complexes (this presently can only be substantiated by spectral change). Near 4M nitric acid, a new peak appears at 815 nm and is attributed to the trinitrato plutonyl complex. As the nitric acid molarity is increased above 4M, the absorbance of the 815 nm peak increases while the 831 peak continues to decrease. The absorbance for these two peaks reaches the same value between 9 and 10M nitric acid. In higher nitric acid concentrations, the trinatrato species becomes predominant.

The relative molar absorptivity values for Pu(VI) are given in Table III. These values are calculated using peaks at 831 nm and 815 nm with a trough at 850 nm.

TABLE II. Relative Molar Absorptivity Values of Plutonium IV as a Function of HNO_3 Concentration.

HNO_3, M	A 475 – 495 nm $\bar{\epsilon}$	±SD	A ~476* – 495 nm $\bar{\epsilon}$	±SD	A ~476* – Baseline nm $\bar{\epsilon}$	±SD	A 660 – 690 nm $\bar{\epsilon}$	±SD	A 1075 – 1200 nm $\bar{\epsilon}$	±SD
1	61.5	3.3	68.1	1.3	77.2	3.0	19.3	0.7	28.7	2.2
2	62.8	3.3	70.1	1.1	82.0	5.4	19.6	0.4	28.9	0.9
3	56.8	4.8	66.7	2.3	78.5	3.5	18.9	1.3	29.8	0.5
4	53.8	1.2	60.5	1.0	73.1	0.4	18.6	0.5	30.5	0.2
5	42.0	1.6	51.2	0.3	64.4	1.7	17.0	0.2	30.8	0.2
6	28.3	1.3	35.1	0.9	55.1	1.0	13.1	0.6	29.6	0.2
7	11.6	2.8	18.3	1.4	44.2	1.4	8.0	0.5	27.1	0.2
8			10.8	0.5	45.7	1.3	2.7	0.2	24.2	0.4
9			12.0	1.2	59.7	8.5			22.7	1.7
10			11.8	1.2	56.8	3.3			22.0	1.2
Average RSD(%)		7.7		4.4		4.7		4.3		3.0

* Peak shifts from 476 to 491. Readings taken at maximum peak height.
** This peak was evaluated but not used because of interference from Plutonium III.

Figure 3. Absorption Spectra of Plutonium VI in 1M, 6M, and 9M HNO_3.

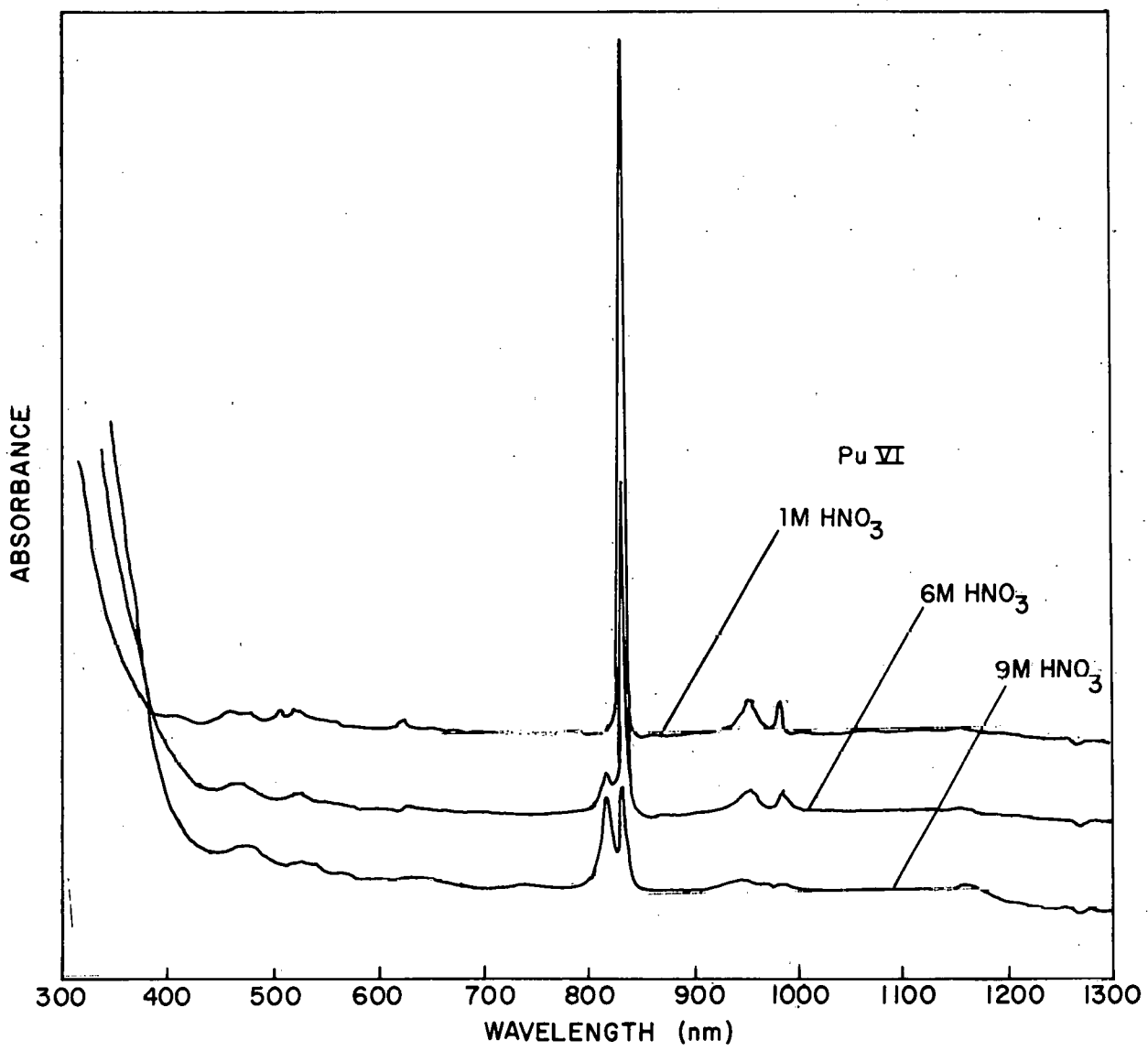


TABLE III. Relative Molar Absorptivity Values of Plutonium VI as a Function of HNO_3 Concentration.

HNO_3, M	$A_{831\,nm} - A_{850\,nm}$ $\bar{\epsilon}$	±SD	RSD	$A_{815\,nm} - A_{850\,nm}$ $\bar{\epsilon}$	±SD	RSD
0	502.5	11.3	2.2			
1	469.6	11.9	2.5			
2	447.8	5.6	1.3			
3	426.3	9.8	2.3			
4	372.6	3.2	0.9			
5	318.9	6.0	1.9			
6	246.1	5.4	2.2	28.6	1.0	3.5
7	174.4	1.4	0.8	42.9	0.8	1.9
8	117.0	0.9	0.8	55.5	1.9	3.4
9	73.2	4.2	5.6	65.1	0.9	1.4
10	48.2	0.9	1.9	69.7	0.6	0.9
Average RSD(%)			2.0			2.2

Calculations for the Quantitative Determination of the Individual Valencies of Plutonium

The mathematical approach used by Ochsenfeld and Schmieder[1] is adaptable for calculating the concentration of all three plutonium valencies occurring simultaneously. The method first states that the absorbance of any principal peak is the product of the molar absorptivity value and the molarity of the individual valence species of plutonium. To this principal peak, minor additive values of absorbance are contributed by other valencies of plutonium present. This is given by the following equations:

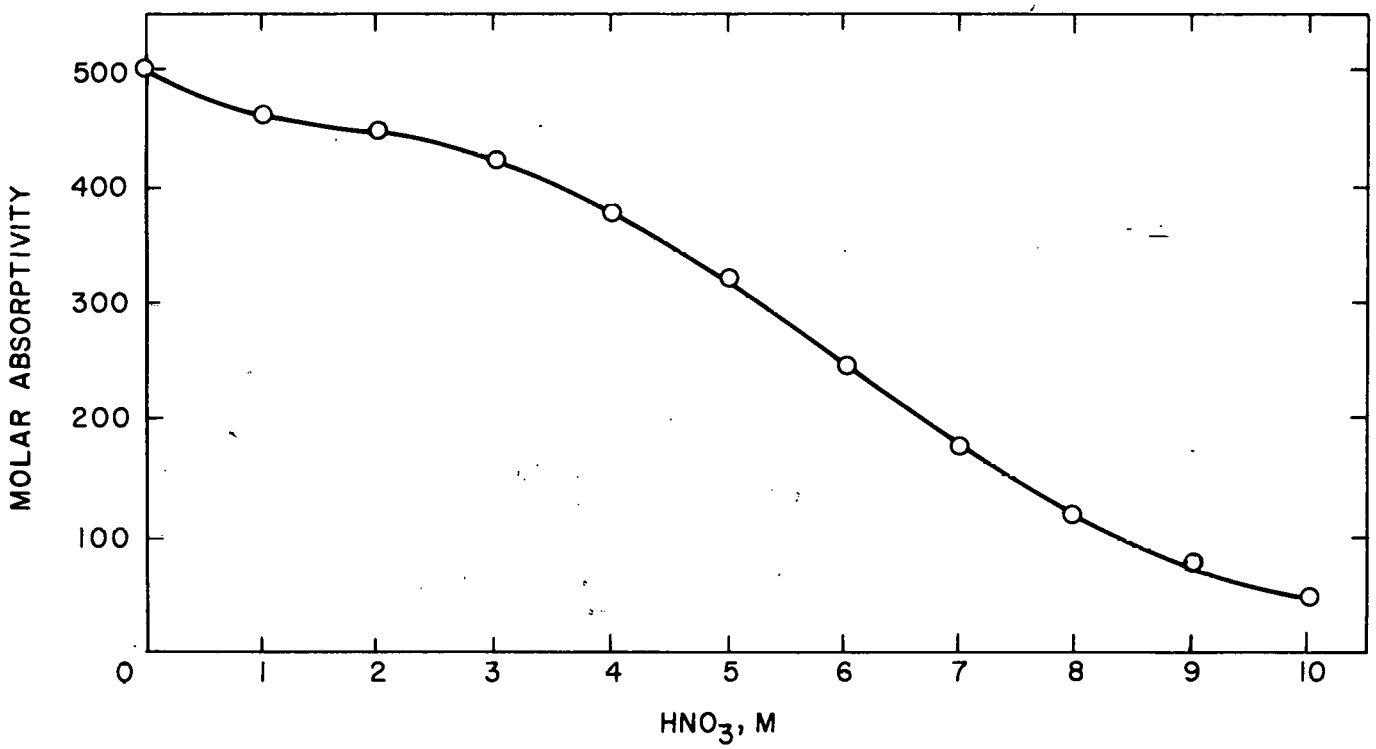
$$\Delta A_1 = \epsilon(III),_1 \cdot M(III) + \epsilon(IV),_1 \cdot M(IV) + \epsilon(VI),_1 \cdot M(VI)$$
$$\Delta A_2 = \epsilon(IV),_2 \circ M(IV) + \epsilon(III),_2 \cdot M(III) + \epsilon(VI),_2 \cdot M(VI)$$
$$\Delta A_3 = \epsilon(VI),_3 \circ M(VI) + \epsilon(III),_3 \cdot M(III) + \epsilon(IV),_3 \cdot M(IV)$$

Where: ΔA_1 is absorbance at 560 nm (peak) –640 nm (trough)
ΔA_2 is absorbance at 476 nm (peak) – 495 nm (trough)
ΔA_3 is absorbance at 831 nm (peak) – 850 nm (trough)

$\epsilon(III),_1$ is relative molar absorptivity value from Table IV where the Roman numeral indicates the oxidation state and the Arabic numeral the wavelength at which the absorbance was measured.

M(III) is molar concentration of Pu(III), etc.
The wavelengths used in the equations above were selected on the basis of having the best precision, as noted in Tables I, II and III, as well as minor interference from other oxidation states.

Figure 4. Molar Absorptivity Decrease of the 831 Peak of Plutonium VI as a Function of HNO_3 Concentration.



Since molar absorptivity values change with nitric acid concentration, a new series of equations are required for each acid concentration of interest.

The preceding series of equations are applicable in solutions of nitric acid to 3M. Exceeding this acid concentration, Pu(III) is not stable and will oxidize to Pu(IV). The principal peaks are then attributed to the valencies of Pu(IV) and (VI) which, for the quantitative calculation, results in two equations with two unknowns:

$$\Delta A_2 = \epsilon(IV)_2 \cdot M(IV) + \epsilon(VI)_2 \cdot M(VI)$$
$$\Delta A_3 = \epsilon(VI)_3 \cdot M(VI) + \epsilon(IV)_3 \cdot M(IV)$$

A new peak appears for Pu(VI) at 6M HNO_3 and is measured at 815 nm (peak) minus 850 nm (trough). In the above notation this would be ΔA_4, $\epsilon(VI)_4$ and $\epsilon(IV)_4$ which would be substituted for ΔA_3, $\epsilon(VI)_3$ and $\epsilon(IV)_3$, respectively. The absorbance ΔA_1 is measured at 815 nm (peak) minus 850 (trough).

All the above mentioned equations can be made more useful for calculating the concentration of the individual valence states by substituting values of molar absorptivity from Table IV and the solving for M (III), (IV), and (VI) by determinants. The resulting equations for each acid concentration are summarized in Table V.

An example of a calculation for a typical plutonium solution is as follows:

A solution of mixed valencies is spectrophotometrically scanned from 1300 to 300 nm. The absorbance from the spectrum is recorded as follows:

ΔA_1 (560 peak – 640 trough) = – 0.130
ΔA_2 (476 peak – 495 trough) = + 0.753
ΔA_3 (831 peak – 850 trough) = + 0.217

The solution is 1.0 M HNO_3; therefore, the equation from Table V for 1.0 M HNO_3 is applied.

Pu(III), M = 0.0271 ΔA_1 + 0.00599 ΔA_2 – 0.000173 ΔA_3
Pu(IV), M = 0.0145 ΔA_2 – 0.000858 ΔA_1 – 0.000138 ΔA_3
Pu(VI), M = 0.00213 ΔA_3 – 0.000226 ΔA_1 + 0.0000685 ΔA_2

Substituting the ΔA values and solving for Pu(III), (IV), and (VI):

(0.0271)(0.130) + (0.00599)(0.753) – (0.000173)(0.217) = 0.00095M or 0.23 g/l Pu(III)

(0.0145)(0.753) – (0.000858)(–0.130) – (0.000138)(0.217) = 0.011M or 2.63 g/l Pu(IV)

(0.00213)(0.217) – (0.000226)(–0.130) + (0.0000685)(0.753) = 0.00054M or 0.13 g/l Pu(VI)

Total plutonium present = 2.99 g/l

Absolute molar absorptivity values are dependent on the resolution of the spectrophotometer used to measure the absorbance. For maximum accuracy, molar absorptivity values should be determined using the spectrophotometer that will be used for subsequent analyses and the values in Table V recalculated.

TABLE IV. Relative Molar Absorptivity Values for Plutonium III, IV, and VI as a Function of HNO_3 Concentration.

	A 560 – 640 nm			A* ~476 – 495 nm			A** ~831 – 850 nm			A 815 – 850 nm	
HNO_3,M	PuIII $\bar{\epsilon}III_1$	PuIV $\bar{\epsilon}IV_1$	PuVI $\bar{\epsilon}VI_1$	PuIV $\bar{\epsilon}IV_2$	PuIII $\bar{\epsilon}III_2$	PuVI $\bar{\epsilon}VI_2$	PuVI $\bar{\epsilon}VI_3$	PuIII $\bar{\epsilon}III_3$	PuIV $\bar{\epsilon}IV_3$	PuVI $\bar{\epsilon}VI_4$	PuIV $\bar{\epsilon}IV_4$
1	36.5	–15.1	2	68.1	2.2	4.6	469.6	3.8	–3.8		
2	35.6	–17.6	2	70.1	2.1	4.9	447.8	2.8	–5.3		
3	34.8	–18.4	2	66.7	2.5	5.3	426.3	3.1	–6.6		
4	30.9	–19.4	2	60.5		5.4	372.6		–6.0		
5				51.2		6.3	318.9		–5.2		
6				35.1		6.9	246.1		–4.0	28.6	2.3
7				18.3		7.4	174.4		–1.7	42.9	4.0
8				10.8		7.9	117.0		–0.4	55.5	5.5
9				12.0		8.8	73.2		2.1	65.1	7.1
10				11.8		8.4	48.2		3.0	69.7	7.7

*Peak shifts from 476 to 491. Readings taken at maximum peak height.
** Peak shifts from 831 to 830. Readings taken at maximum peak height.

Note: All trough subtractions made at constant wavelengths.

TABLE V. Equations for Calculating Plutonium Concentrations.

HNO_3,M				
1	Pu(III),M =	$0.0271\ \Delta A_1$	$+0.00599\ \Delta A_2$	$-0.000173\ \Delta A_3$
	Pu(IV),M =	$0.0145\ \Delta A_2$	$-0.000858\ \Delta A_1$	$-0.000138\ \Delta A_3$
	Pu(VI),M =	$0.00213\ \Delta A_3$	$-0.000226\ \Delta A_1$	$+0.0000685\ \Delta A_2$
2	Pu(III),M =	$0.0277\ \Delta A_1$	$+0.00694\ \Delta A_2$	$-0.000199\ \Delta A_3$
	Pu(IV),M =	$0.0140\ \Delta A_2$	$-0.000816\ \Delta A_1$	$-0.000150\ \Delta A_3$
	Pu(VI),M =	$0.00223\ \Delta A_3$	$-0.000183\ \Delta A_1$	$+0.000123\ \Delta A_2$
3	Pu(III),M =	$0.0282\ \Delta A_1$	$+0.00776\ \Delta A_2$	$-0.000228\ \Delta A_3$
	Pu(IV),M =	$0.0147\ \Delta A_2$	$-0.00104\ \Delta A_1$	$-0.000177\ \Delta A_3$
	Pu(VI),M =	$0.00234\ \Delta A_3$	$-0.000221\ \Delta A_1$	$+0.000170\ \Delta A_2$
4	Pu(IV),M =	$0.0165\ \Delta A_2$	$-0.000239\ \Delta A_3$	
	Pu(VI),M =	$0.00268\ \Delta A_3$	$+0.000266\ \Delta A_2$	
5	Pu(IV),M =	$0.0195\ \Delta A_2$	$-0.000385\ \Delta A_3$	
	Pu(VI),M =	$0.00313\ \Delta A_3$	$+0.000318\ \Delta A_2$	
6	Pu(IV),M =	$0.0284\ \Delta A_2$	$-0.000796\ \Delta A_3$	
	Pu(VI),M =	$0.00405\ \Delta A_3$	$+0.000462\ \Delta A_2$	
6*	Pu(IV),M =	$0.0289\ \Delta A_2$	$-0.00698\ \Delta A_4$	
	Pu(VI),M =	$0.0355\ \Delta A_4$	$-0.00233\ \Delta A_2$	
7	Pu(IV),M =	$0.0544\ \Delta A_2$	$-0.00231\ \Delta A_3$	
	Pu(VI),M =	$0.00571\ \Delta A_3$	$+0.000531\ \Delta A_2$	
7*	Pu(IV),M =	$0.0568\ \Delta A_2$	$-0.00980\ \Delta A_4$	
	Pu(VI),M =	$0.0242\ \Delta A_4$	$-0.00529\ \Delta A_2$	
8	Pu(IV),M =	$0.0924\ \Delta A_2$	$-0.00624\ \Delta A_3$	
	Pu(VI),M =	$0.00853\ \Delta A_3$	$+0.000316\ \Delta A_2$	
8*	Pu(IV),M =	$0.0998\ \Delta A_2$	$-0.0142\ \Delta A_4$	
	Pu(VI),M =	$0.0194\ \Delta A_4$	$-0.00989\ \Delta A_2$	
9	Pu(IV),M =	$0.0851\ \Delta A_2$	$-0.0102\ \Delta A_3$	
	Pu(VI),M =	$0.0140\ \Delta A_3$	$-0.00244\ \Delta A_2$	
9*	Pu(IV),M =	$0.0906\ \Delta A_2$	$-0.0122\ \Delta A_4$	
	Pu(VI),M =	$0.0167\ \Delta A_4$	$-0.00988\ \Delta A_2$	
10	Pu(IV),M =	$0.0887\ \Delta A_2$	$-0.0155\ \Delta A_3$	
	Pu(VI),M =	$0.0217\ \Delta A_3$	$-0.00552\ \Delta A_2$	
10*	Pu(IV),M =	$0.0920\ \Delta A_2$	$-0.0111\ \Delta A_4$	
	Pu(VI),M =	$0.0156\ \Delta A_4$	$-0.0102\ \Delta A_2$	

* ΔA_4 Calculation from 815 nm peak for Pu (VI)

Reproducibility

The precision of the method is measured by the relative standard deviation (RSD) of the relative molar absorptivity values (Tables I, II, and III). The precision varies with the valencies with an RSD of 1.36% for Pu(III), 2.0% for Pu(VI) and 4.4% for Pu(IV).

The accuracy of the method could vary with the ratio of valencies and acid concentrations. A nominal measure of the accuracy was obtained by dissolving weighed metal samples and oxidizing aliquots of these solutions. Then known volumes of these solutions were combined and the resulting mixture analyzed for the concentration of the various valencies. The experimental concentrations of the individual valencies were added and the sum compared with the total plutonium known to be in the solution.

The data from these analyses is given in Table VI.

Table VI. Analytical Accuracy.

Sample No.	HNO_3, M	Experimental Plutonium Concentration (g/l) Pu (III)	Pu (IV)	Pu (VI)	Pu, Total	Total Known Pu Conc. g/l	*% Diff.
1	1	0.23	2.63	0.13	2.99	2.86	4.55
2	1	0.70	1.69	<0.003	2.39	2.50	−4.40
3	2	0.04	2.51	<0.003	2.55	2.50	2.00
4	5	0	1.01	0.17	1.18	1.24	−4.39
5	5	0	20.7	< .03	20.7	21.1	−1.90
6	8	0	2.14	0.44	2.58	2.47	4.45

$$* \%\ \text{Diff} = \left(\frac{\text{known-experimental}}{\text{known}} \right) 100$$

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