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ELECTRONIC SPECTRA OF PLUTONIUM IONS IN NITRIC
ACID AND IN LITHIUM NITRATE SOLUTIONS

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CONTENTS

SUMMARY

The absorption spectra of plutonium ions in nitric acid have been described. There is a characteristic change in the absorption spectra of PuV in lithium nitrate solutions. In 2 M-lithium nitrate a new peak at 969 nm and high absorption at 1200 nm are noticed. A decrease in the absorption by about 20% and the appearance of a new shoulder at 1120 nm in 6 M-lithium nitrate are found. There is no change in the spectrum in 4 M-lithium nitrate.

The absorption spectra of plutonium ions in the spectral range 200 - 400 nm are interesting. All plutonium ions have an intense band in the region 250 - 260 nm as well as a less intense and rather diffuse band at 320- 330 nm

In lithium nitrate solutions the sharp band at 250-260 nm has disappeared. This suggests that this band is very sensitive to the environmental field. The band is probably produced by $5f^{q} \longrightarrow 5f^{q-1} 6d$ transition as well as electron transfer.

It is believed that the spectrum of PuV at pH 6.5 represents the hydrolysis product $PuO_2(OH)$.

INTRODUCTION

Plutonium is an artificially produced heavy metal of atomic number 94. It is discovered by Seaborg et al (1) when uranium oxide was bombarded with deutrons in a cyclotron. Since then, much information concerning its chemical properties, production on a larger scale and modification of aqueous and pyro-metallurgical separation process has been obtained. The most important and feasible separation technique, so far is solvent extraction.

The aqueous chemistry of plutonium is complex due in part to the multiplicity of oxidation states and equilibria existing between them. In a situation rare in chemistry, plutonium possesses four oxidation states in aqueous solution. Pu^{3+}, Pu^{4+}, PuO_2^{+}, and PuO_2^{2+} can exist simultaneously in solution in finite concentrations. PuIII is stable but easily oxidised to PuIV. In fuel reprocessing PuIV is of great importance due to its stability in concentrated acid and its tendency to form nitrate complexes. PuV is unstable and very difficult to work with. PuVI is stable but undergoes self-reduction to PuV by its own alpha radiation especially at low acidity. Heptavalent plutonium (2) has been prepared by the action of ozone on P(VI) in alkaline solution. It is very similar to Pu(II) but less stable. The solution chemistry of plutonium is further complicated by the tendency of PuIV and PuV to disproportionate, hydrolysis of PuIV at low pH to give polymeric species, existence of various complexes and self-reduction of plutonium ions by alpha radiation.

The present report deals with the spectra of plutonium in lithium nitrate solutions to show the feasability of formation of Pu(V) nitrato-complexes where no data are available yet on such complexes.

EXPERIMENTAL

Handling of Plutonium

The transuranium elements, in general, pose a significant radiological and toxicological hazard if absorbed into the body. Plutonium is a very toxic material and extreme precautions are essential. The maximum body burden of Pu 239 is 0.044 μCi (Gram/Curie=16.2). Plutonium, if ingested or inhaled, concentrates predominantly in the bone, causing serious damage.

To prevent any bodily contact with plutonium most of the work has been conducted in a glove box of Harwell Type MKII. The box was maintained at a negative pressure of 2" water gauge by a centrifugal air extractor. Air is drawn from the box through a "Vokes" filter, to prevent alpha activity reaching the main ventilation duct. Regular checks were made on the neoprene gauntlets and any perished or punctured ones were replaced.

Waste disposal was treated as follows. Solid waste and tissues were stored temporarily in waxed cartons and the accumulated liquid waste absorbed onto vermuculite contained in a glass bottle. All Waste was disposed of from time to time out of the box via the waste disposal port into a PVC bag by a standard technique.

Preparation of Plutonium Solutions:

Preparation of Pu (IV):

The original plutonium stock solution available contained 200 mg. The acidity was adjusted to 7.5 M-nitric acid, and all plutonium loaded onto an anion exchange column (1.0x10 cm). This step was to exclude Am-241 which forms from beta decay of Pu 241 (Plutonium adsorbed on the resin as $Pu(NO_3)_6^{2-}$

while Am 241 passes through). The exchange column

was washed twice with 5 ml of 7.5 M- nitric acid to remove any unadsorbed ions. Elution of plutonium held on the resin was made with 20 ml of 1M nitric acid. The effluent was collected in a 50 ml tube and reduced to the trivalent state by the addition of a few crystals of hydroxylamine hydrochloride and stirred for a short while.

After thirty minutes the change of the solution colour to deep blue indicated the reduction to the trivalent state. Plutonium was then precipitated by adding concentrated ammonia solution, stirring and centrifuging. The supernate was transferred into another tube from which sample was withhrawn for alpha counting. Whenever the concentration of plutonium in the supernate was found less than 7 μg/ml it was disposed of into a special bottle. The precipitate

(Pu(OH)$_3$ and Pu(OH)$_4$ was dissolved in one ml. of concentrated nitric acid, heated at 80°C for one hour and left to cool. The solution was centrifuged and the clear spinach green solution was transferred to a clean tube. The last step provides pure Pu IV in concentrated nitic which can be diluted to the required acidity and used in subsequent preparations. Dilution was made with dilute nitric acid (not less than 0.3M) to avoid fromation of colloidal Pu IV.

Preparation of Pu V

The acidity of Pu IV stock solution was adjusted to 0.5M and oxidised to Pu VI by heating at 80°C for seven hours After cooling, the spectrum was recorded to check the purity of Pu VI and the pH adjusted to 3.5 by adding ammonia solution.

Pu V was obtained by the quantitative reduction of Pu VI with potassium iodide. The titration was carried out in a 50 ml tube which contained Pu VI solution at pH 3.5, a platinum electrode immersed in Pu VI solution and platinum wire stirrer. Pctassium iodide was added stepwise from a 2 ml. burette subdivided into 0.02 ml. divisions. The end point of the titration was determined by following the potential change on a Beckman pH meter. After each addition of potassium iodide the solution was allowed to stand for a

short while until the potential reading was constant. Near the end point a change of 70 millivolt was noticed, at this stage no more potassium iodide was added.

The solution was extracted with several portions of carbon tetrachloride to remove iodine. After the iodine was completely extracted, the pH of the Pu V solution was checked and the spectrum recorded.

Care was taken not to exceed the end point of titration and to ensure complete extraction of the iodine to avoid any interference in the spectral measurements.

Preparation of Pu III, Pu V and Pu VI Nitrate Complexes

Pu V was investigated at various molarities of lithium nitrate. The use of lithium nitrate was preferred rather than any other salt for two reasons. Firstly, lithium nitrate has nearly the same activity coefficient as nitric acid. Secondly the dehydrating effect of lithium ion is higher than any other univalent cations, which may cause partial stripping of the hydration sheath of the metal ion, and thereby enhance the formation of the complex.

An appropriate volume of PuV was transferred into a standard flask and made up to the mark with concentrated lithium nitrate solution so that the final molarity after mixing would be 2,4 or 6 M - lithium nitrate. For instance, to prepare Pu V in 6M - lithium nitrate, 2 ml. of Pu V was transferred to 10 ml. flask and the volume made up with 7.5 M - lithium nitrate. In all preparations, the pH of PuV and , the added salt solutions were at 3,5 prior to mixing. The flask was well shaken and the spectrum recorded. Samples were also taken for analysis. Pu III and Pu VI solutions in lithium nitrate were similarly prepared.

Spectra Measurements

Absorption spectra of plutonium solutions were performed at room temperature, $20 \pm 2\,^{\circ}C$, using a Unicam SP 700 A recording spectrophotometer, The spectrophotometer was operated throughout at scan speed 4, damping 2 chart speed 90 inches per hour and resolution 3.

The positioning of the spectrophotometer was planned so as to keep the housing cell compartment very near to the entrance of the fume hood. A specially designed perspex tunnel was fitted on the top of the housing cell to avoid contamination of the laboratory atmosphere and the body of the spectrophotometer (See Plate 1) .

Before any spectral measurements were made it was essential to match the cells and check the accuracy of the wavelength scale by standard procedures. One and four cm. silica cells were used after being cleaned with acid, water, acetone and then dried with soft tissue, The cell was filled with plutonium solution inside the box and transferred to the cell

carriage lying in the transfer tunnel after being stoppered tightly. The transfer tunnel is an airtight, cylindrical chamber, some 14" long and 12" diameter. It has two doors, one opening to the interior of the box, and the other to the laboratory. To ensure that no direct mixing between the interior of the box and the laboratory, one door only must be opened at a time while the other is closed. The cell carriage was then taken out of the tunnel to the nearby fume cupboard and consequently to the cell housing of the spectrophotometer.

The blank solution was made to match the sample solution except for the absence of plutonium. Spectra were run from 200 to 1200 nm unless otherwise stated.

The handling of up to 20 mg. of Pu 239 in a well ventilated fume cupboard instead of a glove box is acceptable provided that rigorous working precautions such as wearing of surgical rubber gloves and regular monitoring of the laboratory are considered.

When UV spectra were recorded, care was taken to avoid any interference from the following impurities. The presence of iodine, not completely extracted by carhon tetrachloride; iodide, exceeding the end point of the titration; acetone from cleaning the cells, and finally, nitrate, at a higher or lower concentration in the reference cell. All these impurities can cause misleading results in the position and intensity of the absorption bands.

The visible and near infra-red absorption spectra are used for the estimation of each oxidation state in the present work. It is necessary to take several absorbance readings at selected wavelengths. Using the absorbances and molar extinction coefficient (E) for each oxidation state at each wavelength, a set of three equations can be formulated and solved for the concentrations of each oxidation state.

RESULTS AND DISCUSSION

Absorption Spectra of Plutonium Ions

The absorption spectra of the various oxidation states in 0.5+ 0.1 M nitric acid (except for Pu (V) in 0.5 M ammonium nitrate and pH 3.5) are summarized in Fig 1 and Table 1. In Fig 1 the complexity of plutonium ions spectra is obvious. Each valence state has numerous characteristic narrow and intense absorption bands in the visible and near infra red region. These spectra are similar to those of the lanthanide ions. It was recognised (3) that the absorption spectra in both lanthanide and actinide ions are caused by similar internal transitions within the 4f and 5f shells (forbidden transition). The transition probability of the actinide ions is ten times higher than those of the lanthanides. Also the absorption bands of the actinide ions are less sharp than their analogues of the lanthanides. These are due to less shielding of 5f electrons which increases their susceptibility to disturbances by environmental fields.

The blue solution of Pu III has two principal bands at 560 and 603 nm, a sharp peak at 655, broad bands at 76)-810 and 900 nm.

Pu IV in dilute nitric acid is yellowish green in colour. The spectrum of Pu IV has characteristic sharp bands at 405, 420, 476, 500 and 655 nm. Further diffuse bands at 540, 710 790 and 850 nm. The molar extinction coefficient for these bands are given in Table 1 .Variation of nitric acid concentration causes shifting of the absorption peak at 476 nm with a variations in the extinction coefficient (4). This is, of course, due to complex formation. Thus the peak at 476 nm can only be used for analytical purposes after a calibration graph is drawn at the required acidity.

Pu V has a reddish pink colour at concentrations higher than 2 mg/ml. When the concentration is less than 2 mg/ml the solution appears colourless unless exposed to artificial light. The spectrum of Pu V found here is very similar to that reported by Connick et al (5) in 0.5 M hydrochloric acid except for a slightly higher absorption near 400 nm The solution is possibly contaminated with trace impurities of ferric iron or Pu IV whose absorption increases rapidly below 450 nm.Pu V has absorption bands at 450, 484, 516, 552, 566, 655, 766, 840, 885 and 995 nm.

There is an error in the location of the absorption bands
expecially in the near infra red region of about 5nm. This
is mainly due to inaccuracy in the wavelength calibration of
the spectrophotometer.   It can be observed that Pu V has
relatively low absorption in comparison with Pu III, Pu IV
and Pu VI.   Thus Pu V peaks can be easily masked especially
in the pressence of even low concentrations of Pu III.

Pu VI has a straw yellowish colour in weak solutions
but at a concentration of about 6 mg/ml it is orange.   PuVI
has   several absorption bands at 456, 470, 520, 560, 770,
785, 830, 945 and 975 nm.   The intense band of plutonyl ion
in the 825 nm region has a very narrow bandwidth, and does not
obey Beer-Lambert's law.   The extinction coefficient of this
peak varies with plutonium concentration and the instrument
slit width.   Therefore, it is essential to plot a calibration
graph, i.e. optical density aginst concentration of Pu VI at a
fixed slit width before using this peak for analytical
purposes.

The values of the molar extinction coefficients of PuIII
Pu. IV and   Pu VI ions in Fig (1) confirms the results
obtained by Hall (6) and refute the higher values by
Myers (7).

Absorption Spectra of Plutonium Ions in Lithium Nitrate Solutions:

Fig 2 illustrates the absorption spectra of PuV in lithium nitrate solutions. In 2 M-lithium nitrate there is a change of the spectrum especially in the near infrared. A shift in the position of all absorption bands by about 0.3 - 0.5% and slightly higher values of molar extinction coefficients are shown in Table 5 . The most interesting of all is the appearance of a new peak at 969 nm with a value of E = 7, and a shift of the 1008 nm peak to 1012 nm. Also the intense band at 1135 nm has been shifted to 1142 nm together with high absorption at 1240-1350 nm.

In 4 M-lithium nitrate the spectrum of PuV is similar to that in 0.5 M-ammonium nitrate except for the slight shift of the absorption bands and the higher values of molar extinction coefficient in Table 2 . In 6 M-lithium nitrate there is a decrease in the absorption of all bands by about 20% and also a shift to higher wavelengths by about 0.3 - 0.5%.

Gevantman (4) claimed that there was no change in the spectra of PuV in 8 M-ammonium chloride and 10 M-ammonium nitrate, Probably he did not notice the change in the spectra because of the low optical density of PuV peaks especially at a lower concentration of PuV.

PuV in 0.5 M-ammonium nitrate has two sharp bands at 262 and 326 nm with values of molar extinction coefficient of 390 and 102 respectively. The intense absorption band at 262 nm has disappeared completely when the spectrum of PuV was measured in 2,4 and 6 M-lithium nitrate. The other band at 326nm has been shifted to higher wavelengths and becomes broad and less intense. A shift of the band at 326 nm to 355, 330 and 345 nm with values of molar extinction coefficient 41,23 and 34 at 2, 4 and 6 M-lithium nitrate respectively is noticed.

The ultra violet absorption spectra of plutonium ions in perchlorate solution have been reported earlier by Cohen(8) . Cohen's results show no characteristic peaks for PuV in ultra violet only two humps at about 260 to 240 nm .

The change of the spectrum of PuV in 2 M-LiNO$_3$ especially above 950 nm is due to unexplained effect on the transitions.

When the molarity of lithium nitrate was increased to
4 the new bands and the high absorption in the near infra
red region disappeared. This suggests that there must be a
change in the ionic species as the molarity of lithium nitrate
increased from 2 to 4.

The variations of values of E of PuV in 4 and 6 M-LiNO$_3$
can be ascribed to the formation of new anionic species of
PuV. Furthermore the absorption of PuV in 0.5 M-ammonium
nitrate and in lithium nitrate gives further confirmation
of the presence of new species of PuV. In all cases studied,
i.e. PuV in 2, 4 and 6 M-lithium nitrate, Fig 3, the sharp
peak at 252 nm has disappeared. If the environmental
perturbations do affect the internal transition in 5f orb-
itals as was shown above then 6d orbitals should be more
liable to such effects.

It has previously been reported by several workers
(3,9,10) that the absorption in the ultra violet by the
actinide ions is caused by the allowed laporte transition i.e.
$5f^q$ --- $5f^{q-1}$ 6d. Also quoted from reference (10) by Jorgensen
"the perturbations from the ligands for a partly filled shell
seem to increase in the order"

4f $<$ 5f $<$ 3d $<$ 4d $<$ 5d

Thus the ligand field perturbations may be so strong or
presumably the band at 262 nm moved out of the observable
range.

There is also a change in the intensity and location
of the peak at 326 nm. This diffused band is of low inten-
sity and produced by the electron transfer from the ligand
to the PuV ion. i.e π^{λ} ---→ 5f (10). A shift of the 326 nm
band to higher wavelengths 355, 330 and 345 nm with values
of E equal to 41, 23 and 34 at 2, 4 and 6 M-lithium nitrate
respectively indicates the influence of nitrate ion.

The ultra violet spectra of PuIII, PuIV and PuVI are
summarized in Fig 4 and Table 3. All plutonium ions
have sharp and intense absorption bands over the region
250 to 260 nm and diffuse and less intense bands at 325 -
330 nm.

As a matter of fact the absorption below 250 nm is
uncertain because nitrate ion absorbs strongly at that region.

It has been reported by Seaborg (11) that the orbital
energy difference of 5f and 6f progressively increases as
the atomic number increases. Stewart has confirmed Seaborg's
assumption by recording the spectra of the trivalent ions
U,Np,Pu and Am in the spectral range 200 to 400 nm. PuIII has
absorption band at 252 nm with value of molar extinction
coefficient 353 (3). It is of interest to note that the
ultra violet spectrum of PuIII reported by Stewart contra-
dicts the results of Cohen, but it is in agreement with this
present work.

It seems quite possible that all plutonium ions absorb
in the same spectral range 250-260 nm because the energy
difference between 5f and 6d for atomic number $Z=94$ is rou-
ghly constant. The difference in the number of electrons in
the 5f shell will probably affect the transition probability
of 5f to 6d.

Absorption Spectra of PuIII and PuVI in 6 M-lithium Nitrate:

Spectrophotometric studies of PuVI in nitric acid(12)
show that above 4 M nitric acid there is a decrease in the
values of molar extinction coefficient at 830 nm and an
increase of the band at 812 nm. It was concluded that the
appearance of a new peak at 812 nm indicates the formation
of $PuO_2(NO_3)$-complex. Vdenvenko et al (13) gave evidence
by spectrophotometric method of mono, di and trinitrato
complexes of PuVI in acetone. The appearance of a shoulder
at 820 nm in Fig 5 may represent the start of $PuO_2(NO_3)_3^-$
formation. The spectrum has also high absorption in the
region 400 - 500 nm.

PuIII in 6 M-lithium nitrate has high absorption below
500 nm. There is a shift in the position of the principal
bands at 565 and 603 nm to 570 and 605 nm with increase in
values of molar extinction coefficient from 36.7 to 43.0.
The band at 905nm has shifted to 920 nm with a higher value
of molar extinction coefficient equal to 23.6. The appear-
ance of a new peak at 790nm indicates the splitting of
the broad band at 790-820 nm as was observed earlier by
Hindman (4).

The disappearance of the absorption bands of PuIII and PuVI in the region 250-270 nm Fig 6 echos the same trends observed in the case of PuV •

Absorption Spectra of Pu V and Pu VI at High pH:

The hydrolytic behaviour of Pu V has not been studied extensively due to its disproportionation at high pH Kraus and Dam (14) found that Pu V starts to hydrolyse at pH 8-9 • This does not agree with the Russian workers Gel'man and Zaitseva (15) who found that Pu V hydrolyses at pH 8. The discrepancy between the two workers is probably due to conducting the measurements at different Pu V concentration.

The spectrum of Pu V at pH 6.5 , Fig 7 , has high absorption below 500 nm, peaks at 520, 555, 570, 640 775 nm There is an intense and sharp band at 845 nm. The peak at 1000 nm became broad and intense. There is no change in the position of the band at 1125 nm. These observations do not agree at all with Gevantman (4) who reported earlier that there is no change in the spectrum of Pu V up to pH 9. It was also noticed in the present work that Pu V forms grey precipitate at pH 6.5 which on reacidification dissolved back and gave pure Pu V solution. This is likely to be $PuO_2(OH)$ •

The hydrolytic behaviour of Pu VI has been investigated spectrophotometrically in much greater detail by Kraus and Moore (16) • The regular change of the spectra at pH above 4 indicated the formation of several hydrolysis products.

At pH 4.95,Fig 8 , the absorption is continuous and higher below 600 nm except for the appearance of little peak at 518 nm and shift of the subsidiary peak at 625 to 635nm. The two peaks at 778 and 794 nm have disappeared and instead a new one appears at 788 nm. The intensity of the 830 nm peak has decreased and shifted to 826 nm with a hump at 815 nm . There is an intense and sharp peak at 845 nm. The two peaks at 952 and 985 nm have combined into one broad band at 990 nm • The shape of the band at 990 nm is similar to that reported by Moore and Kraus at pH 6.4 except for • its location at 1000 nm. The identity of the various hydrolysis products has been reported as a function of pH by Milyukova et al (17). Accordingly the hydrolytic species of Pu VI at pH 5 is $(PuO_2)_2(OH)_3^+$.

Unfortunately, no analysis has been done on Pu V or Pu VI at pH 6.5 and 4.95 respectively to compare the intensity of all the absorption bands quantitatively with the published values.

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TABLE (1)

MOLAR EXTINCTION COEFFICIENTS OF VARIOUS PLUTONIUM IONS IN 0.5 M-HNO$_3$

Wavelength nm	PuIII	Pu IV	Pu V[@]	Pu VI
400	6.4	28.0	8.0	14.8
420	11.6	28.6	7.1	10.7
476	2.6	67.8	3.8	11.5
560	38.0	8.6	5.1	2.4
566	37.5	6.0	17.5	2.0
603	36.7	5.9	1.4	0.7
655	13.8	35.4	1.6	0.4
700	1.0	16.5	1.0	1.0
766	11.0	14.0	9.3	1.0
823	5.0	11.0	5.0	134.0
945	1.0	2.5	1.0	22.0
975	1.3	7.5	1.0	15.7

@ Pu V in 0.5 M-NH$_4$NO$_3$ and pH 3.5.

TABLE (2)

EFFECT OF NITRATE CONCENTRATION ON ABSORPTION
SPECTRA AND COEFFICENTS OF PLUTONIUM V

Wavelength nm	Molar Extinction Coefficients in			
	$0.5M-NH_4NO_3$	$2M-LiNO_3$	$4M-LiNO_3$	$6M-LiNO_3$
200	25.0	15.8	8.3	10.9
262	390.0	12.0	8.3	12.0
326	102.5	13.0	15.0	13.0
330	65.0	15.0	23.0	14.8
345	18.0	30.0	15.5	34.0
355	16.0	41.0	13.0	32.0
400*	10.0	14.7	9.2	7.4
520*	6.2	6.8	7.5	4.4
572*	17.4	17.9	18.3	13.5
630*	3.4	2.6	5.0	2.9
780*	10.3	10.3	11.2	8.2
855*	9.4	10.0	10.0	7.6
903	6.4	7.6	7.1	5.3
969(a)	2.0	7.1	2.0	1.0
1008(b)	4.2	8.5	4.4	2.4
1134(c)	22.2	29.0	22.5	16.9
1120(d)	11.3	12.4	10.0	10.2
1240(e)	3.2	24.0	3.3	3.5

NOTES

*These peaks shifted to higher wavelengths in lithium nitrate solutions by 3-4 nm .

(a) This is a new peak in $2M-LiNO_3$.

(b) This peak shifted to 1012 nm in 2 M-LiNO$_3$ and to 1010 nm in 4 and 6 M-LiNO$_3$.

(c) This peak shifted to 1142 nm in 2 M-LiNO$_3$ with side shoulder at 1154 nm and to 1140, 1138 nm in 4 and 6 M-LiNO$_3$ respectively.

(d) This is a new side shoulder in 6 M-LiNO$_3$.

(e) This is a very broad and intense band in 2 M-LiNO$_3$. The absorption continues high up to 1330 nm then decreases steadily up to 1500 nm.

TABLE (3)
MOLAR EXTINCTION COEFFICIENTS OF VARIOUS
PLUTONIUM IONS IN 0.5 M-HNO$_3$

Plutonium ions	λ,nm	E	λ,nm	E
PuIII	260	334.6	325	73.4
PuIV	254	1166.6	330	166.6
PuV[@]	262	390.0	326	102.5
PuVI	256	688.8	330	75.5

[@] In 0.5 M-NH$_4$NO$_3$ and pH 3.5.

TABLE (4)

MOLAR EXTINCTION COEFFICIENTS OF PLUTONIUM
IONS IN 6 M-LITHIUM NITRATE

Wavelength nm	PuIII	PuVI
200	50.0	54.5
300	52.7	63.6
340	211.1	very high
400	30.5	63.6
460	13.8	31.0
500	9.7	16.8
570	41.6	7.8
605	43.0	9.0
625	12.0	12.3
700	5.2	3.8
780	19.4	5.1
795	16.6	6.2
820	16.6	15.6
834	11.1	140.3
920	23.6	3.8
953	8.3	21.2
987	8.3	17.5
1020	16.6	3.8
1110	22.2	2.0

Plate 1

FIGURE 1. ABSORPTION SPECTRA OF PLUTONIUM IONS IN 0.5± 0.1 M-HNO₃

Pu III
Pu IV
Pu V
Pu VI

MOLAR EXTINCTION COEFFICIENT

WAVE-LENGTH (mμ)

FIGURE 2. ABSORPTION SPECTRA OF Pu V IN LITHIUM NITRATE SOLUTIONS

Pu V in 0.5 M ammonium nitrate
Pu V in 2 M lithium nitrate
Pu V in 4 M lithium nitrate
Pu V in 6 M lithium nitrate

MOLAR EXTINCTION COEFFICIENT

FIGURE 3 . ABSORPTION SPECTRA OF Pu V

Pu V in 0.5 M-NH$_4$NO$_3$
Pu V in 2 M-LiNO$_3$
Pu V in 4 M-LiNO$_3$
Pu V in 6 M-LiNO$_3$

WAVE-LENGTH (mμ)

FIGURE 4. ABSORPTION SPECTRA OF PLUTONIUM IONS IN 0.5 ± 0.1 M-HNO$_3$

- ∘ ∘ ∘ ∘ ∘   Pu III
- −∘−∘−   Pu IV (represented by the scale on the extreme left)
- ———   Pu V (in 0.5 M-NH$_4$NO$_3$, pH=3.5)
- ———   Pu VI

MOLAR EXTINCTION COEFFICIENT

WAVE-LENGTH(mμ)

FIGURE 5. ABSORPTION SPECTRA OF PLUTONIUM IONS IN 6 M-LiNO₃

- - - Pu III
···· Pu V
—— Pu VI

MOLAR EXTINCTION COEFFICIENT

WAVE-LENGTH (mμ)

- 25 -

FIGURE 2 · ABSORPTION SPECTRA OF
PLUTONIUM IONS IN
6 M-LiNO$_3$

—— Pu III
····· Pu V
—·— Pu VI

FIGURE 7 .   ABSORPTION SPECTRA OF Pu V
AT pH 6.5

OPTICAL DENSITY

WAVE-LENGTH (mμ)

.6
.5
.4
.3
.2
.1

400   500   600   700   800   900   1000   1100   1200

FIGURE 8 . ABSORPTION SPECTRA OF Pu VI
pE 4.95

OPTICAL DENSITY

WAVE-LENGTH (mμ)