

SOME ASPECTS OF THE CHEMISTRY OF
PLUTONIUM V

by

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Abstract

The stability of PuV in about 0.5 M-ammonium nitrate and 6 M-lithium nitrate has been investigated at pH 3.5. The rate of PuV disappearance depends on the second power of PuV concentration and the first order of the total plutonium concentration. The main product of PuV disappearance is PuIV. The favourable formation of PuIV is explained by the auto-reduction of PuV and the high pH value. Also it was found that as NO_3^- increases the rate of disappearance of PuV increases. This is due to the formation of reducing species, NO_2^- , by the action of alpha bombardment of NO_3^- .

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 m μ and high absorption at 1200 m μ are noticed. A decrease in the absorption by about 20% and the appearance of a new shoulder at 1120 m μ in 6 M-lithium nitrate were 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 m μ are interesting. All plutonium ions have an intense band in the region 250 - 260 m μ as well as a less intense and rather diffuse band at 320 - 330 m μ .

In lithium nitrate solutions the sharp band at 250 - 260 m μ 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.

The presence of more than one nitrate complex of PuV in lithium nitrate has been confirmed by ion exchange results. There is adsorption of PuV in 4 and 6 M- lithium nitrate onto De-Acidite FF while no adsorption at all occur in 2 M-lithium nitrate. The identity of the complex species held on the resin was checked by conducting an elution experiment. The spectrum of the elutriant gave concrete evidence that the only ionic species adsorbed is PuV.

Further, PuV in 5 M-thiocyanate and 1.69 M-sulphate was adsorbed onto De-Acidite FF. This indicates that PuV exists as anionic complexes in both solutions. The composition of these complexes is not known.

It is believed that the spectrum of PuV at pH 6.5 represents the hydrolysis product $\text{PuO}_2(\text{OH})$.

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CHAPTER I
INTRODUCTION

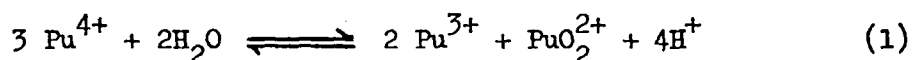
Plutonium is an artificially produced heavy metal of atomic number 94. It was discovered by Seaborg et al (1) when uranium oxide was bombarded with deuterons in a cyclotron. Since then, much information concerning its chemical properties, production on a larger scale and modifications of aqueous and 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 five oxidation states in aqueous solution. Pu^{3+} , Pu^{4+} , PuO_2^+ and PuO_2^{2+} can exist simultaneously in solution in finite concentrations. Pu III is stable but easily oxidised to Pu IV. Pu IV is of great importance in fuel reprocessing due to its stability in concentrated acid and its tendency to form nitrate complexes. Pu V is unstable and very difficult to work with. Pu VI is stable but undergoes self reduction to Pu V and Pu IV by its own alpha radiation especially at low acidity. Recently, heptavalent plutonium (2) was prepared by the action of ozone on Pu VI in alkaline solution. It is very similar to Np VII, but less stable. The solution chemistry of plutonium is further complicated by the tendency of Pu IV and Pu V to disproportionate, hydrolysis of Pu IV at low pH to give polymeric

species, existence of various complexes and self reduction of plutonium ion by alpha radiation.

Disproportionation

The rate of disproportionation of Pu IV and Pu V depends on acidity, concentration of plutonium, presence of complexing anions and temperature. In low acidity (3), 0.5M HCl and at 25°C, Pu IV disproportionates according to the following reaction.

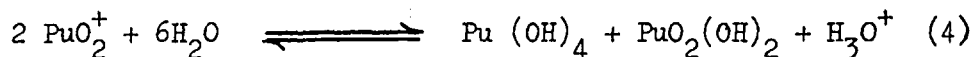
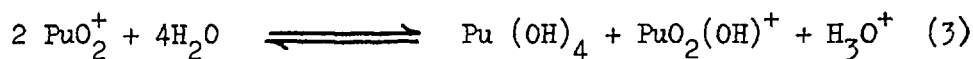
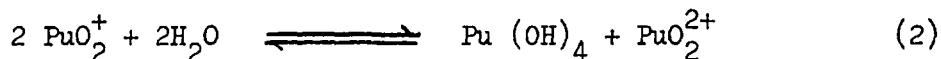


The equilibrium constant of reaction (1) is inversely proportional to the fourth power of hydrogen ion concentration.

The same mechanism is valid in 0.3 and 0.4 M nitric acid. In 0.1 and 0.2 M nitric acid, Artyukhin et al (4), suggested the presence of Pu V beside Pu III and Pu VI in Pu IV disproportionation. This seems reasonable since Pu V is stable at low acidities, but disproportionates if the acidity increases. The equilibrium constant of Pu IV in nitric acid is found experimentally to be inversely proportional to the hydrogen ion concentration raised to 5.3 power.

Artyukhin et al (4) are probably in error because of the various ionic strengths of nitric acid at which the measurements were conducted. Also no considerations for the effect of alpha reduction, hydrolysis and complex formation in nitric were taken into account. Consequently it can be concluded that the rate of Pu IV disproportionation in strong acid is negligible because of its dependence upon the fourth power of hydrogen ion concentration and complex formation.

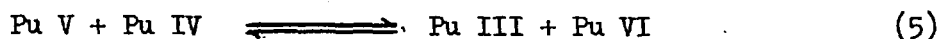
Pu V is unstable at low and high pH, but stable to considerable extent at pH 3.5. At pH above 3 the disproportionation takes place with increase in hydrogen ion concentration and precipitation of Pu IV (5). The mechanism is represented as follows:



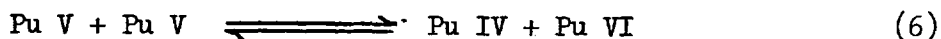
Reaction 3 occurs at pH around 4 whilst reaction 4 is predominant at pH 5 or greater.

The disproportionation of Pu V is faster than Pu IV. The mechanism of Pu V disproportionation was first studied by Connick et al (6) in 0.5 M - HCl and at room temperature. The solution was initially a mixture of Pu III, Pu V, and Pu VI. The percentage of Pu V was 45%.

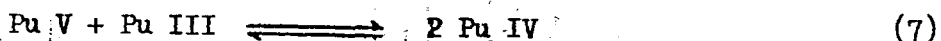
The appearance of Pu III and Pu VI at the start of the disproportionation was explained by the following fast reaction



Pu IV was initially produced by the reaction:

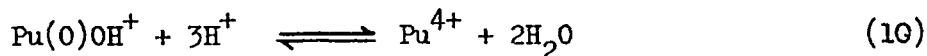
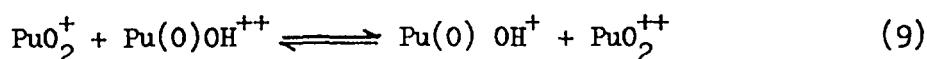
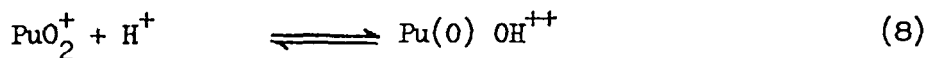


When Pu V concentration reach a low limit, Pu IV starts to increase while Pu III decreases. These observations were explained by the second slow reaction.



The disproportionation of pure Pu V, i.e. the mechanism of the reaction Pu V - Pu V was studied by Rabideau (7) in 1 M-HClO₄.

The first power dependence of the rate constant on the hydrogen ion concentration of the slow reaction 6 is consistent with the following mechanism



As soon as Pu IV is formed by reaction 10 it will react rapidly according to reaction 5. This mechanism is more logic and acceptable.

The rate of Pu V disproportionation is very dependent on temperature. By raising the temperature from 10 to 35°C the rate increased nearly 12 fold.

The first power dependence of the rate constant on the hydrogen ion concentration was also observed in dilute nitric acid (4). The mechanism of Pu V - Pu V disproportionation was therefore assumed to be similar to that in perchloric acid. This solution contained initially about 5% Pu VI (the total concentration of plutonium is not known).

At the start of the disproportionation, in 0.2 and 0.3 M nitric acid, the concentration of Pu III is higher than Pu IV in a similar fashion to that observed in 0.5 M HCl by Connick et al (6). When the concentration of Pu V has decreased to about 35% Pu IV starts to increase and Pu III decrease. The increase of Pu III at the beginning of the disproportionation was explained by autocatalytic growth although this does not agree with Connick et al who explained it by reaction 5.

As soon as the concentration of Pu V and Pu III reaches

a maximum reaction 7 is predominant.

In 0.1 M nitric acid, Pu III is always higher than Pu IV. It is reasonable to say that reaction 5 is more likely to occur.

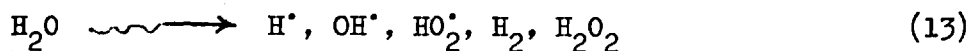
A systematic study of the disproportionation of Pu V in oxalate solutions was described recently by Mazumdar et al (8). The effect of the solution parameters such as pH, oxalate concentration and Pu V concentration on the stability of Pu V were established as a function of the percentage of Pu VI formed during disproportionation. Pu IV was calculated by the difference between the total plutonium and the sum of Pu VI and Pu V. No Pu III was observed. Increasing the oxalate concentration from 0.01 M to 0.03 M increased the amount of Pu VI by 25%. This result is expected since in presence of complexing agent, the stability of pentavalent ion decreases, while the tetra - and hexavalent increase. Pu V was found to be more stable at pH 5.0 than 3.5. There appears to be little doubt if their results are correct because in the present work it was observed that Pu V is less stable at higher pH values. Furthermore, they have not noticed the effect of alpha-radiolysis during the course of the investigation, although it is very likely that at concentration of 4.46 mg/ml the effect of alpha-radiation would be significant. Pu V is stable in the pH range 2 - 5 and at room temperature (5). Gel'man (9) defined the exact stability range of Pu V in nitric acid. At pH 3.5 - 4.5 and concentration $\leq$ 2.5 g/l Pu V is stable but at higher concentration of plutonium the effect of alpha irradiation is significant. Gel'man's conclusions seem to be more relevant to the present work.

In contrast to this behaviour Np V is very stable and disproportionates only at high acidities (7 - 8 M) due to the formation of Np IV complexes (10). Np V is stable to disproportionation because the oxidation reduction potential of the couple Np V/Np VI is more negative than the couple Np IV/Np V.

Am V disproportionates in strong acid, but reduces fairly rapidly under the influence of its own alpha radiation at low acidities (11).

Self-reduction

The aqueous chemistry of plutonium is in some respect related to its radioactivity. The half life of Pu 239 is 24,360 years, which is still short enough so that its radiation can induce changes in the mean oxidation states of plutonium ions. The radiolysis of water by γ irradiation is well known to produce free radicals and molecular products as follows:



G - value of free radicals are highest for γ and X-ray irradiation, while the molecular products are highest for alpha-particle irradiation. In the presence of nitrate ions the situation is much more complicated (12). The irradiation of NO_3^- by alpha-particles produces a variety of products such as nitrogen oxides (NO , NO_2 , N_2O_4) and nitrous acid. The species which play an important role in the chemistry of plutonium nitrate solution are hydrogen peroxide and nitrous acid. Both of them can reduce plutonium to Pu IV or Pu III in acid solutions. The effect of alpha-irradiation on the stability of Pu V has been observed by

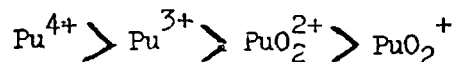
Gel'man and Zaitseva (9). They prepared solutions varied in Pu V concentration from 5 to 0.5 g/l and pH from 2 - 6. It was noticed that in solution with an initial pH of 4 - 6, the pH decreased to 3.5 while in solutions with initial pH 3 the pH was increased to 3.5. They attributed the changes of pH to self reduction and oxidation of Pu V by interaction with water radiolysis products.

In the case of Pu VI, a much greater volume of information exists about the effect of alpha-irradiation, although some of it is qualitative in nature (13). The rate of self reduction of Pu VI in nitric acid was found to increase as the nitrate concentration increased and hydrogen ion concentration decreased. The former was explained as due to the formation of more stable Pu IV complexes. The latter can be explained in terms of the reduction reaction involving H_2O_2 . Reduction of Pu VI to Pu IV by H_2O_2 (radiolysis product of H_2O) produces H^+ , therefore, an increase in H^+ concentration in solution would effect the equilibrium and suppress the reduction process.

Complex Chemistry

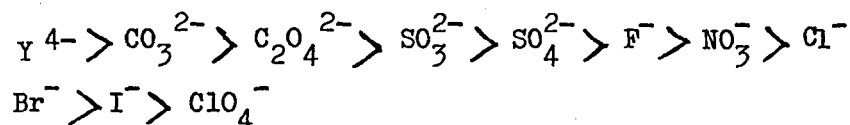
The tendencies of the actinides to form complexes with co-ordinating groups have been widely used for separation and determination of these elements. The methods are based upon the different ability of these elements towards complex formation. As the ionic size decreases with increasing atomic number, the complex power increases in the order $\text{Np} < \text{Pu} < \text{Am}$. The tendency of the ions of a given element to form complexes depends on the structure,

dimension and charge of the cation and the co-ordinating species. The small, highly charged ions such as Pu^{4+} show the greatest degree of hydration, hydrolysis and complex formation. The values of the ionic potential ϕ ($\phi = \frac{Z}{r}$ where Z is the charge and r is the radius of the ion) have been reported (14). Accordingly the order of decreasing complex forming ability is



The order differs from that for hydrolysis and tendency to form oxalate complexes in the relative position of Pu^{3+} and PuO_2^{2+} .

The relative complexing power for anions can be arranged as follows:



Where $\text{Y} = \text{EDTA}$

i.e. the weaker the acid from which the anion is derived the stronger is the complexing properties.

Among the most frequently used methods for studying the complex formation are ion exchange and spectrophotometry.

The effect of ligand concentration on ion exchange equilibria has been exploited to determine the stability constant assuming the identity of the complex is known. The spectrophotometric method is also very useful if only one complex is formed and considerable change in the spectrum occurs. However, spectrophotometry alone cannot be used as clear cut evidence to indicate the formation of new species. Often the spectrum of the complexed ion resembles that of the hydrated ion. Thus the use of other

techniques such as ion exchange or electromigration measurements together with spectrophotometry is very essential. The importance of ion exchange and spectrophotometry will be very clear from the following survey of the various plutonium ions complexes.

The spectra of Pu III has been studied in 1 - 5 M nitric acid (15). The changes of the spectra have indicated the formation of Pu III nitrate complexes. Investigation in more concentrated acid was hampered because of the oxidation of Pu III to Pu IV. The distribution coefficient of Pu III between tertiary amines and aqueous nitric acid was found to be higher at low acidity and high nitrate concentration (16) indicating the formation of Pu III complex.

Marcus et al (17-19) studied the ion exchange behaviour of trivalent actinide and lanthanide ion in lithium nitrate solutions. The large distribution coefficient obtained in 10 M LiNO_3 echos the same trends observed in amine extraction. The composition of Pu III anionic complexes is not exactly known, but it is very likely to be similar to the lanthanide nitrate complexes, i.e. $\text{M}(\text{NO}_3)_5^{2-}$.

Pu IV exhibits the greatest tendency to form complexes in accordance with its ionic potential. The existence of plutonium hexanitate species, $\text{Pu}(\text{NO}_3)_6^{2-}$ has been established by spectrophotometric (20), solvent extraction (21), ion exchange (22) and electro-migration studies (23).

Ryan (22), who studied the spectra of Pu IV in 5 - 10M nitric acid solution and Pu IV loaded on Dowex 1, X - 1 concludes that the only species on the resin is $\text{Pu}(\text{NO}_3)_6^{2-}$.

Pu V is expected to have the least tendency to form complexes. But this ion does in fact form complexes to a greater extent than was supposed merely on the basis of spectrophotometry (5). For example, the spectra of Pu V in 10 M-ammonium nitrate and in 8 M ammonium chloride was found to be identical with that of a perchlorate solution and so the spectra have been interpreted to indicate the absence of Pu V complex. Such a conclusion is in fact incorrect.

There are quantitative data about the stability of pentavalent actinides Pa, Np and Pu complexes (24). Pu V in oxalate solution and pH 3 - 5 forms two complexes, $\text{PuO}_2(\text{C}_2\text{O}_4)^-$ and $\text{PuO}_2(\text{C}_2\text{O}_4)_2^{3-}$ with stability constants 2.4×10^7 and 3.3×10^4 respectively (14). The distribution of Pu V between 0.05 M ammonium chloride and cation exchange resin KU - 2 was studied in the pH range 3 - 5 and then repeated in the presence of 0.001 M disodium salt of EDTA. It was found that the distribution of Pu V between solution and ion exchange in presence of EDTA depends very strongly on pH value. At pH 5 and above practically the whole Pu V is in the form of complex $\text{PuO}_2\text{Y}^{3-}$. Below pH 4 there is no complex formation at all. The stability constant was found to be 1.5×10^{10} .

From potentiometric studies, Kabanova (25), has concluded the existence of EDTA complex at a molar ratio of Pu V: EDTA of 1:2.

The only Pu V complex in chloride solution is PuO_2Cl with association constant 0.69 (26).

There is much more data available in the literature (14) about the complexes of NpV which is an analogue of Pu V. This is probably due to the stability of NpV and hence it is easy to work with.

NpV forms complexes with a number of organic anions, e.g. tartarate, citrate, trihydroxyglutarate, salicylate, 2,3-dihydroxyphthalate, acetate, EDTA and 1-nitroso - 2 - naphthol. It is of interest to note that the stability constant of $\text{NpO}_2 \text{Y}^{3-}$ is close to that of $\text{PuO}_2 \text{Y}^{3-}$.

Ion exchange behaviour of NpV in 4M HCl indicates the presence of an anionic complex.

Am V is much more difficult oxidation state to study, due to its readiness to disproportionate and the high specific activity of Am. There is only qualitative evidence for the formation of chloride complex by Am V in hydrochloric acid (27).

This present work investigates the stability of Pu V in nitrate solution, and substantially the identification and establishment of the possible nitrate complexes of Pu V in the pH range 3.5 -5.

CHAPTER II EXPERIMENTAL

2.1 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 μ Ci (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.

The layout of the box was arranged so as to minimise undue cross-contamination. All work was carried out in four two inch deep enamel trays lined with tissues. Most of the preparations of solutions and analysis were done in the two trays at the side farthest from the access port. The other two trays in the second half of the box were used for keeping clean equipment and glassware. All micropipettes and planchettes were kept in special containers to prevent their contamination.

The other equipment in the box included a ministirrer,

centrifuge, infra red lamp, microcombined pH probe and platinum electrode.

The connection of the electrodes to a Beckman pH meter outside the box was via a lead through a co-axial connector across the wall of the box.

Waste disposal was treated as follows. Solid waste and tissues were stored temporarily in waxed cartons and the accumulated liquid waste absorbed on to vermiculite 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.

2.2 Preparation of Plutonium Solutions

2.2.1 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. This step was to exclude Am 241 which forms from beta decay of Pu 241 (Plutonium adsorbed on the resin as $\text{Pu}(\text{NO}_3)_6^{2-}$ while Am 241 passes through). The ion exchange column was washed twice with 5 ml of 7.5 M - nitric acid to remove any unabsorbed 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 withdrawn for alpha counting. Whenever the concentration of plutonium in the supernate was found less than $7 \mu\text{g/ml}$ it was disposed of into a special bottle. The precipitate $(\text{Pu}(\text{OH})_3 \text{ and } \text{Pu}(\text{OH})_4)$ was dissolved in one ml. of concentrated nitric acid, heated at 80° 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 nitric acid 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 formation of colloidal Pu IV.

2.2.2 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. Potassium 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.

2.2.3 Establishment of the Specific Activity of Plutonium by Spectrophotometric Analysis

A sample of about 1 ml. of Pu IV in 8 M-nitric acid was transferred to 10 ml. flask and the volume made up with 20% hydroxylamine hydrochloric in 0.2 M-nitric acid. The flask was shaken and allowed to stand for one hour. The experiment was planned so that the concentration of Pu III would be around 4 mg/ml.

The spectrum of Pu III was recorded in one cm. silica cell to check the absence of all other valence states of plutonium. The optical density at 603 mu was used to calculate the specific activity of plutonium. By using the value of $E = 36.7$ at 603 mu (31)

the specific activity of plutonium would be 2.9×10^6 alpha / sec / mg. This value deviates by only 3% from that calculated from the mass analysis data, i.e. 2.815×10^6 alpha / sec / mg. (Appendix 1). The discrepancy can be ascribed to counting error (2%), optical density reading (0.5%) and different instrumental calibration. The value of 2.9×10^6 alpha / sec / mg is used in all calculations. The method of calculation of the specific activity is shown in Appendix 4.

2.3 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 Pu V 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 6 M - 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 Pu V 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.

2.4 Preparation of Pu V in Lithium Sulphate

Two ml. of Pu V in about 0.5 M - NH_4NO_3 was made up to 5 ml. with 2.65 M - lithium sulphate at pH 4.4. The solution was shaken and sample was taken for alpha-analysis.

2.5 Preparation of Pu V in Ammonium Thiocyanate

An accurate volume of Pu V, 400 $\mu\text{l.}$ in 0.5 M - NH_4NO_3 and of known concentration was added to 2 ml. of 6 M - ammonium thiocyanate at pH 4.2. The solution was stirred and used in subsequent equilibration experiments.

2.6 Spectra Measurements

Absorption spectra of plutonium solutions were performed at room temperature, $20 \pm 2^\circ\text{C}$, 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 mμ 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 carbon tetrachloride; iodide, exceeding the end point of the titration; acetone from cleaning the cells, and

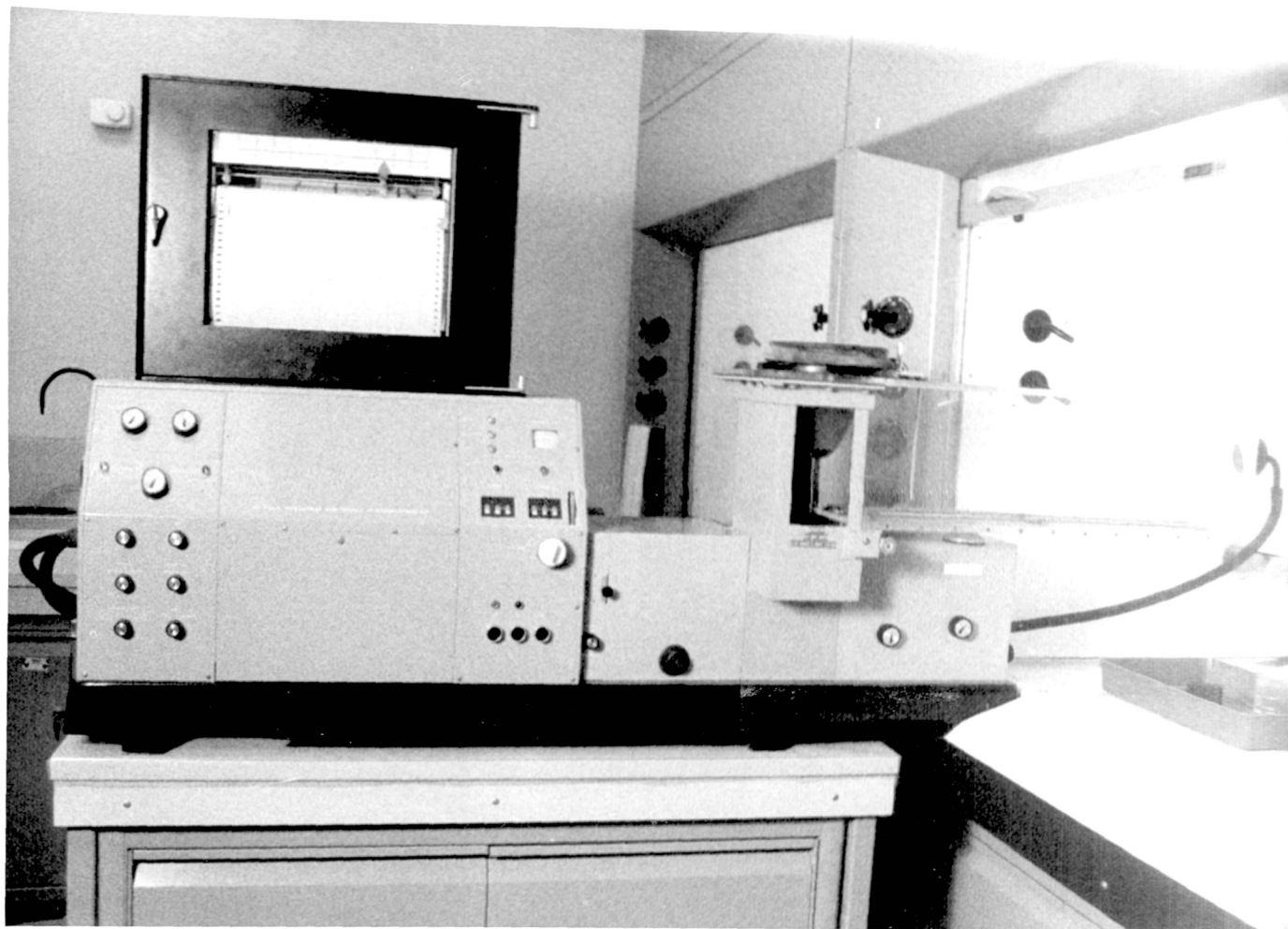


PLATE 1.

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 (See Appendix 5).

2.7 Disproportionation of Pu V

No systematic study has been attempted to investigate the stability of Pu V in nitrate solution. Three experiments were performed in conjunction with the equilibration of Pu V on ion exchange. The first solution containing 33×10^{-3} M Pu V, 0.5 M - ammonium nitrate at pH 3.5.. The second one was 8×10^{-3} M Pu V in 6 M - lithium nitrate and pH 3.5. The last solution was prepared in a different way, 4.2 g. of lithium nitrate dissolved in Pu V solution at pH 3.5 so that the final volume was 10 ml. This represents Pu V in 6 M - lithium nitrate.

Samples of each of these solutions of about 3 ml. were transferred into one cm. silica cells. The spectra were recorded daily for a period over a month. Whenever the solution was found turbid (due to self-reduction and hydrolysis) and affecting the

reproductibility of the spectra it had to be transferred back to the glove box and centrifuged. The spectrophotometric cell was then washed several times with 7.0 M - nitric acid, water and acetone to remove the stains on the surface of the cell. After the solution had been well centrifuged, the clear solution was transferred to the clean cell and recording of the spectra was resumed. Estimation of the different valence states of plutonium were made by measuring the optical density at 603,570 and 950 mμ corresponding to Pu III, Pu V and Pu VI respectively (Appendix 5). Pu IV concentration was calculated from the difference between the total plutonium and the sum of Pu V, Pu III and Pu VI.

2.8 Determination of Capacity of De-Acidite FF.

The resin was purified before capacity determination by repeated cycling with water, methanol, and nitric acid. The capacity was determined by the Fisher-Kunin (28) method which was modified to take account of possible hydrolysis of the strong base group.

An accurate weight of resin dried in air for 24 hours at 60°C in the nitrate form was placed in 5 x 1 cm. ion exchange column ^{was converted to the chloride form by using 4% HCl} and washed with water. The resin was treated with methanol to remove interstitial hydrochloric acid.

Dilute ammonia was passed through the column (100 ml/g). The excess hydroxide on the resin was washed with water until the effluent was neutral to methyl orange indicator. The elutriant and

washings were collected in 250 ml. flask (A) and the volume was made up to the mark with water. The concentration of chloride ion was determined by Volhard's method and hence the weak base capacity was calculated.

The strong base capacity was measured by treating the resin with 4% sodium sulphate (100 ml/g). The effluent and washings were collected in 250 ml. flask (B), and the chloride ion estimated.

The hydroxide ion concentration in flask (B), as a result of the hydrolysis of strong base which had occurred when the resin was treated with dilute ammonia solution, was measured by titration with 0.1 M hydrochloric acid to methyl orange end point. The correction to the weak base capacity was then made. Details of the calculations are given in Appendix 3.

2.9 Equilibration with De-Acidite FF.

Identification of Pu V nitrate complex in 6 M - lithium nitrate was first established on an ion exchange column. An ion exchange column, 5 x 1 cm. containing about 1 g. of De-Acidite FF in the nitrate form was treated with 6 M - lithium nitrate solution at pH 3.5. 6 ml. of Pu V in 6 M - lithium nitrate at the same pH was passed through the column at a very low flow rate. The column was then washed with 4 ml. of 6 M - lithium nitrate pH 3.5 to remove unadsorbed Pu V. The effluent and washings were collected for analysis. The amount of Pu V adsorbed on the resin was calculated by the difference between the concentration of Pu V before

and after contact with the resin.

An estimate of the exact composition of the complex was made possible by conducting a series of batch equilibration experiments. Before any equilibration could commence, it was necessary to standardise the techniques employed to reduce the number of the variables. It was decided to equilibrate 6 ml. of aqueous phase and 10 mg. of the resin unless otherwise stated elsewhere. Equilibration was performed in 50 ml. tubes and solutions stirred at the same speed for all samples by a ministirrer controlled from outside the box. The resin to be used was weighed in the dry nitrate form and equilibrated with 6 M - lithium nitrate at 3.5 prior to mixing with Pu V in 6 M - lithium nitrate.

The rate of Pu V uptake by the resin was followed by withdrawing samples at selected time intervals after the solution was centrifuged. The amount of Pu V adsorbed on the resin was calculated by difference from the change of the solution concentration before and after equilibration, with correction for the amount of plutonium removed by sampling. At the time the equilibration was being conducted, the spectrum of a sample of the same solution was run. It is important to correct for the amount of Pu V which has disproportionated or reduced during the equilibration experiment.

Pu V nitrate complex has a dark pink colour on the resin. If the colour of the resin after equilibration with Pu V was not pink, say, green the species adsorbed was definitely not Pu V but mostly Pu IV and the run was excluded.

2.10 Elution of Plutonium Nitrate Complex

After the equilibration experiment had finished the mixture was centrifuged and the aqueous phase transferred to a different flask. The resin was washed twice with 5 ml. of 6 M - lithium nitrate at pH 3.5, centrifuged and washings transferred to 50 ml. tube, taking care ^{not} to transfer any of the resin beads with the washings.

Elution of the resin was conducted by adding 15 ml. of 0.2 M - ammonia nitrate at pH 3.5 and stirring the mixture overnight. The mixture was centrifuged and the eluent transferred to a clean tube. A sample of the eluent was taken for spectrophotometric analysis and another for alpha-counting.

2.11 Analysis

Plutonium concentration was estimated by direct alpha-counting. Suitable aliquots of plutonium solutions were withdrawn by micropipette and the volume made up accurately to 10 ml. Further aliquots were taken in duplicate and transferred to polished, stainless steel, one inch counting discs. The micropipette washed out with dilute nitric acid and added to the same counting tray which was then evaporated under an I.R. lamp to dryness. When cool, it was transferred into a special container which had been put into the posting tunnel from the outside. The planchettes were taken out from the outside and placed in the fume cupboard where they were heated to redness for one minute in Bunsen flame. The last step

was important to reduce the thickness of the film and hence the counting error due to self absorption of alpha particles.

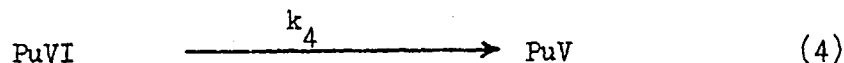
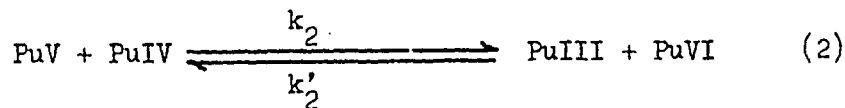
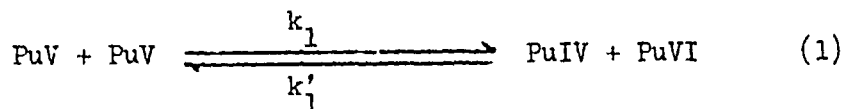
A drawer type scintillation counter was used in conjunction with an IDL 1700 Scaler unit. The EHT was kept at 1400 V and discriminator at 30 V throughout the work.

Regular checks were made of the background and the efficiency of the counter. Plutonium concentration was calculated by comparison with counting rates obtained under similar geometrical condition from a standard source.

CHAPTER 3RESULTS AND DISCUSSIONDisproportionation of Plutonium V

The behaviour of Pu V in 0.5 M-ammonium nitrate at pH 3.5 shows very interesting features totally different from any previous published work (4, 6, 8). Fig. 1 shows results for the disproportionation of Pu V at total concentration of 9.05 mg/ml. over a period of a month. Pu V disappears rapidly at first, then the rate decreases until it reaches equilibrium. The rate of Pu V disappearance is 0.29×10^{-3} M/L. hr. measured after 8.5 hours from the start of disproportionation. The predominant species is Pu IV which hydrolyses at pH 3.5. Pu VI has not been detected during the first three days and only about 3% of Pu III was formed. To account for these observations, the disappearance of Pu V cannot be explained in terms only of disproportionation, auto-reduction is also indicated. The alpha product energy released by 9.05 mg/ml. of plutonium is of the order 8.0×10^{15} ev/min. This is sufficient to produce 2.4×10^{14} reducing species (H_2O_2 and NO_2^-) per minute, assuming $G = 3$.

Therefore, to develop a kinetic equation representing both disproportionation and auto-reduction processes the following reactions are of interest:



The rate of PuV disappearance is

$$\begin{aligned} & - \frac{d\text{PuV}}{dt} \\ &= k_1(\text{PuV})^2 + k_2(\text{PuV})(\text{PuIV}) + k_3(\text{PuV}) - k'_1(\text{PuIV})(\text{PuVI}) \\ & \quad - k'_2(\text{PuIII})(\text{PuVI}) - k_4(\text{PuVI}) \end{aligned} \quad (5)$$

Similarly the rate of PuIV formation is

$$+ \frac{d\text{PuIV}}{dt} = k_1(\text{PuV})^2 + k'_2(\text{PuIII})(\text{PuVI}) + k_3(\text{PuV}) \quad (6)$$

Adding equations 5 and 6, the reaction rates are given by:

$$\begin{aligned} - \frac{d\text{PuV}}{dt} + \frac{d\text{PuIV}}{dt} &= 2k_1(\text{PuV})^2 + k_2(\text{PuIV})(\text{PuV}) \\ & \quad + 2k_3(\text{PuV}) - k_4(\text{PuVI}) \\ & \quad - k'_1(\text{PuIV})(\text{PuVI}) \end{aligned} \quad (7)$$

At pH 3 and higher the contribution of the reverse reaction k'_1 would be very small owing to the formation of PuIV

hydrolysis products and can be neglected.

k_3 and k_4 depend on the total concentration of plutonium Pu_T and represent the rate of autoreduction. Thus equation 7 becomes:

$$\begin{aligned} -\frac{dPuV}{dt} + \frac{dPuIV}{dt} &= 2k_1(PuV)^2 + k_2(PuV)(PuIV) + 2k_3Pu_T - k_4Pu_T \\ &= 2k_1(PuV)^2 + k_2(PuV)(PuIV) + Pu_T(2k_3 - k_4) \end{aligned} \quad (9)$$

Reaction 2 does in fact exist and accounts for the appearance of Pu III, but its rate is very small in comparison with reaction 1 at pH 3.5 because of the formation of Pu IV hydroxide.

Then equation 9 in an approximate representation takes the form:

$$-\frac{dPuV}{dt} + \frac{dPuIV}{dt} \simeq 2k_1(PuV)^2 + Pu_T(2k_3 - k_4) \quad (10)$$

For convenience the term $Pu_T(2k_3 - k_4)$ will be replaced by $\propto$.

Therefore:

$$-\frac{dPuV}{dt} + \frac{dPuIV}{dt} \simeq 2k_1(PuV)^2 + \propto \quad (11)$$

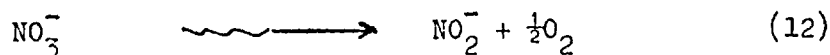
Equation 11 is very important. It includes two terms, one is dependent on the second order of Pu V concentration and the other on the first power of the total plutonium concentration. The former represents the disproportionation of Pu V and the latter represents the rate of self reduction.

Assuming the value of k_3 and k_4 in HClO_4 is $6.25 \times 10^{-4} \text{ hr}^{-1}$ (7) the value of k_1 can be calculated from equation 10 as follows. From Fig. 1 the values of $-d\text{PuV}/dt$, $d\text{PuIV}/dt$ and (PuV) after 8.5 hours are $0.29 \times 10^{-3} \text{ M/L hr}$, $0.21 \times 10^{-3} \text{ M/L hr}$ and 33.2 M/L .

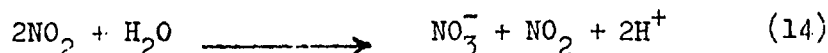
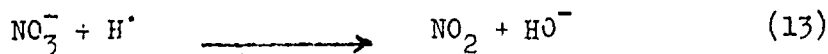
By substituting for the above values in equation 10. Therefore k_1 is equal to 0.22 L/M hr . This is in agreement with the results shown in Fig. 1 which indicate the slow rate of disproportionation at pH 3.5. The main reason for the disappearance of PuV is the autoreduction to PuIV.

At lower concentration of PuV, 1.9 mg/ml . and in 6 M-LiNO_3 , PuV is fairly stable as shown in Fig. 2. The rate of PuV disappearance after 8.5 hours is $0.009 \times 10^{-3} \text{ M/L hr}$. As the concentration of PuV decreases the rate of disproportionation decreases. The immediate appearance of PuVI indicates the effect of nitrate concentration on the rate of disproportionation. As would be expected in 6 M-LiNO_3 the equilibrium of reaction 1 will be shifted to the right hand side due to the formation of PuVI nitrate complexes and PuIV hydrolysis at pH 3.5.

Moreover, as the nitrate concentration increases, there is higher possibility for NO_2^- to exist as a result of alpha irradiation. The formation of NO_2^- can proceed by direct or indirect mechanism as follows:



or



The indirect mechanism, i.e. using nitrate ion as a scavenger for the hydrogen atom (one of the radiolysis products of water) and the direct action of alpha particles are very likely to occur in higher nitrate concentration.

It was noticed that the pH has changed from 3.5 to 2.0 at the end of the experiment. This may indicate the occurrence of reaction 14.

When solid LiNO_3 was dissolved in PuV solution so that the final concentration was 6.57 mg/ml. Pu in 6 M- LiNO_3 the rate of disappearance of PuV as shown in Fig. 3 is 3.6×10^{-3} M/L hr. This high rate is, possibly, due to the immediate change of pH value to, say, 6 or 7 upon dissolving solid LiNO_3 in PuV solution. This, of course, favours the formation of hydrolysis products of plutonium ions in addition to the effect of alpha irradiation in high nitrate concentration.

PuV solutions having concentrations around 1.9 mg/ml. and excess of iodide were found to be stable over a long period of time. After a few days the PuV solution in the stoppered spectrophotometric cell turned a deep yellowish colour. When the solution was stirred with carbon tetrachloride the yellow colour disappeared from the aqueous phase and transferred to carbon

tetrachloride phase indicating the formation of molecular iodine. The aqueous solution was centrifuged and the spectrum indicated the purity of PuV and the absence of all other states.

The same phenomenon happened for solutions of PuV in 6 M-LiNO₃, except for the appearance of Pu(OH)₄ after a few days.

These observations simply reveal the simultaneous reduction of PuVI (which may be formed by the disproportionation of PuV) back to PuV. Thus it can be concluded that PuV is stable towards disproportionation at pH 3.5. The important factor which affects the stability of PuV is the self-reduction.

FIGURE 1. DISPROPORTIONATION OF Pu(V) IN ABOUT
0.5 M-AMMONIUM NITRATE
pH = 3.5

$Pu_T = 37.85 \text{ mM}$

PERCENTAGE OF PLUTONIUM IONS

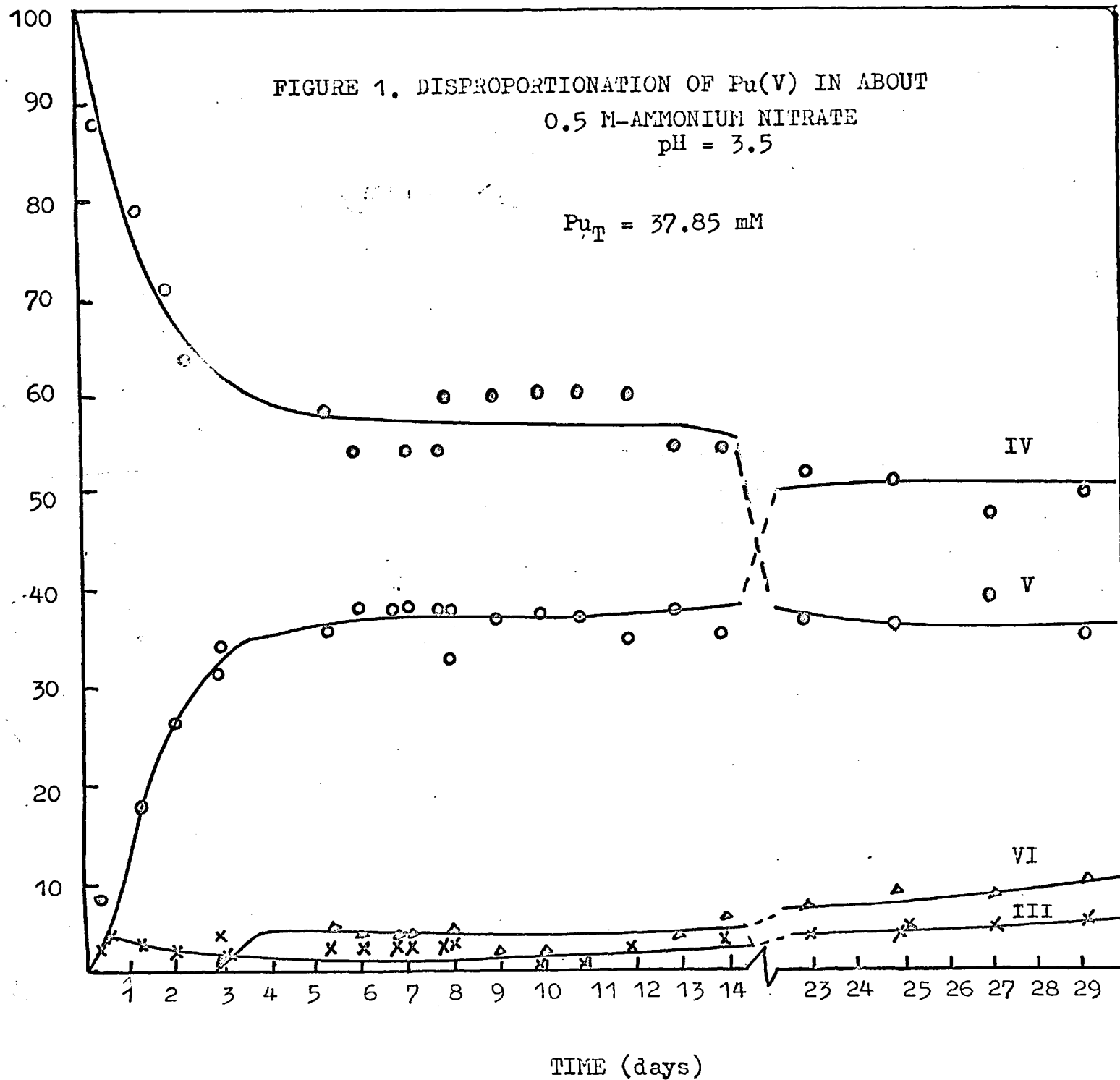
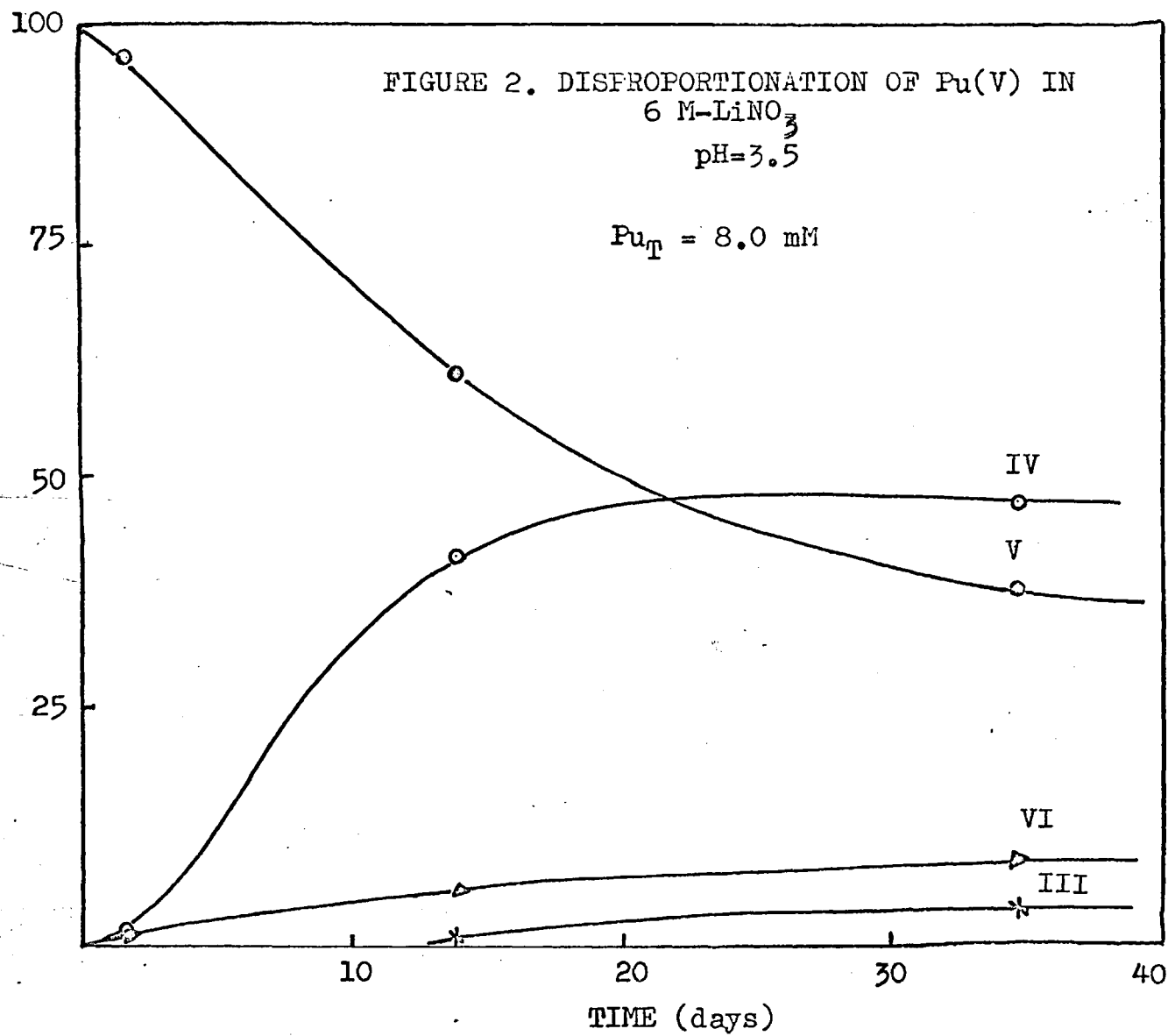


FIGURE 2. DISPROPORTIONATION OF Pu(V) IN
6 M-LiNO₃
pH=3.5

Pu_T = 8.0 mM

PERCENTAGE OF PLUTONIUM IONS



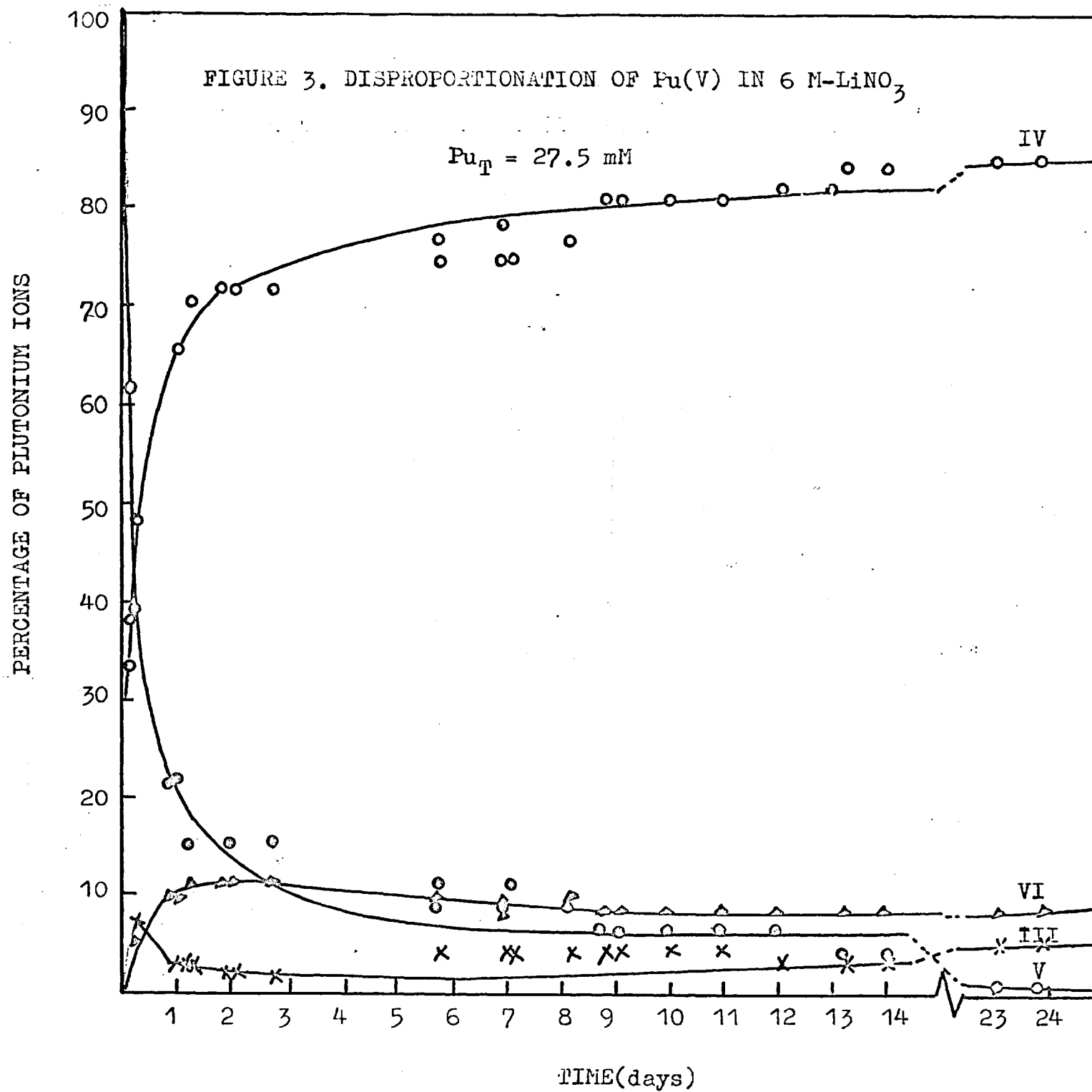


TABLE 1

DISPROPORTIONATION OF Pu(V) IN ABOUT 0.5 M-AMMONIUM NITRATE pH = 3.5,

$$t = 20_{-}^{+} 2^{\circ}\text{C}$$

TIME (days)	C _{III}	C _{IV} *	C _V	C _{VI}
0.00	-	-	37.8	-
0.25	1.11	3.48	33.2	-
0.29	1.42	3.16	33.2	-
1.29	1.18	6.85	29.8	-
2.00	0.91	9.96	26.9	-
2.29	1.68	11.95	24.2	-
3.00	0.65	13.00	23.5	0.59
5.29	1.06	12.60	22.2	2.04
5.33	1.06	14.50	22.2	2.04
6.00	1.05	14.45	20.6	1.67
6.75	1.05	14.45	20.6	1.67
7.08	1.05	14.45	20.6	1.67
7.79	1.05	14.45	20.6	1.67
7.91(a)	0.58	11.25	24.0	1.90
7.96	0.57	14.50	22.7	1.15
7.98	0.46	12.50	23.2	0.69
8.92	0.16	14.1	22.8	0.69
9.00	0.16	14.10	22.8	0.69
9.96	0.16	14.10	22.8	0.69
10.83	0.16	14.1	22.8	0.69

TIME (days)	C _{III}	C _{IV} *	C _V	C _{VI}
11.92	1.01	13.3	22.8	0.69
12.92	1.38	14.4	20.6	1.43
13.92	1.37	13.5	20.6	2.29
22.92	1.40	19.7	14.0	2.75
24.79	1.38	19.2	13.9	3.25
26.79	1.38	17.8	14.9	3.16
29.00	1.88	18.8	13.4	3.78

TABLE 2

DISPROPORTIONATION OF Pu(V) IN 6.0 M-LITHIUM NITRATE pH = 3.5,

$$t = 20_{-}^{+} 2^{\circ}\text{C}$$

TIME (days)	C _{III}	C _{IV} *	C _V	C _{VI}
0.00	-	-	8.0	-
1.70(a)	-	0.17	7.7	0.13
13.79(a)	0.10	3.40	5.0	0.49
34.63(a)	0.32	3.84	3.1	0.74

TABLE 3

DISPROPORTIONATION OF Pu(V) IN 6 M-LITHIUM NITRATE, $t = 20 \pm 2^\circ\text{C}$

TIME (days)	C _{III}	C _{IV} *	C _V	C _{VI}
0.00	-	-	2.75	-
0.04	0.21	10.5	16.70	0.04
0.17	2.02	13.2	10.80	1.48
0.92	0.76	18.0	6.00	2.72
1.00	0.76	18.0	6.00	2.72
1.21	0.80	19.3	4.25	3.14
1.79	0.46	19.6	4.28	3.16
2.00	0.46	19.6	4.28	3.16
2.71	0.46	19.6	4.28	3.16
3.75	1.20	21.0	2.50	2.76
5.79	1.18	20.4	3.18	2.69
6.92	1.18	20.4	3.18	2.69
6.96	1.23	21.5	2.52	2.26
7.08	1.18	20.4	3.18	2.69
8.18	1.24	21.0	2.50	2.76
8.81(a)	1.24	22.1	1.82	2.31
8.89	1.24	22.1	1.82	2.31
9.08	1.24	22.1	1.82	2.31
9.96	1.24	22.1	1.82	2.31
10.96	1.24	22.1	1.82	2.31
11.96	0.89	22.4	1.83	2.34
12.00	0.89	22.4	1.83	2.34
13.21	0.92	23.0	1.15	2.38
14.00	0.92	23.0	1.05	2.38
23.08	1.55	23.2	0.24	2.43
23.87	1.55	23.2	0.24	2.43

*C_{IV} was worked out by difference between the total plutonium and the sum of PuIII, PuVI and PuV. All concentrations are expressed in mM/L.

(a) Solution was centrifuged.

CHAPTER 4RESULTS AND DISCUSSION4.1 Absorption Spectra of Plutonium Ions

As a preliminary to the investigation of the stability and complex formation of Pu V, details of the absorption spectra of Pu III, Pu IV, Pu V and Pu VI were necessary under the various conditions that would prevail in the experimental work. 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. 4. These spectra were taken with a Unicam SP 500 spectrophotometer which was available at that time.

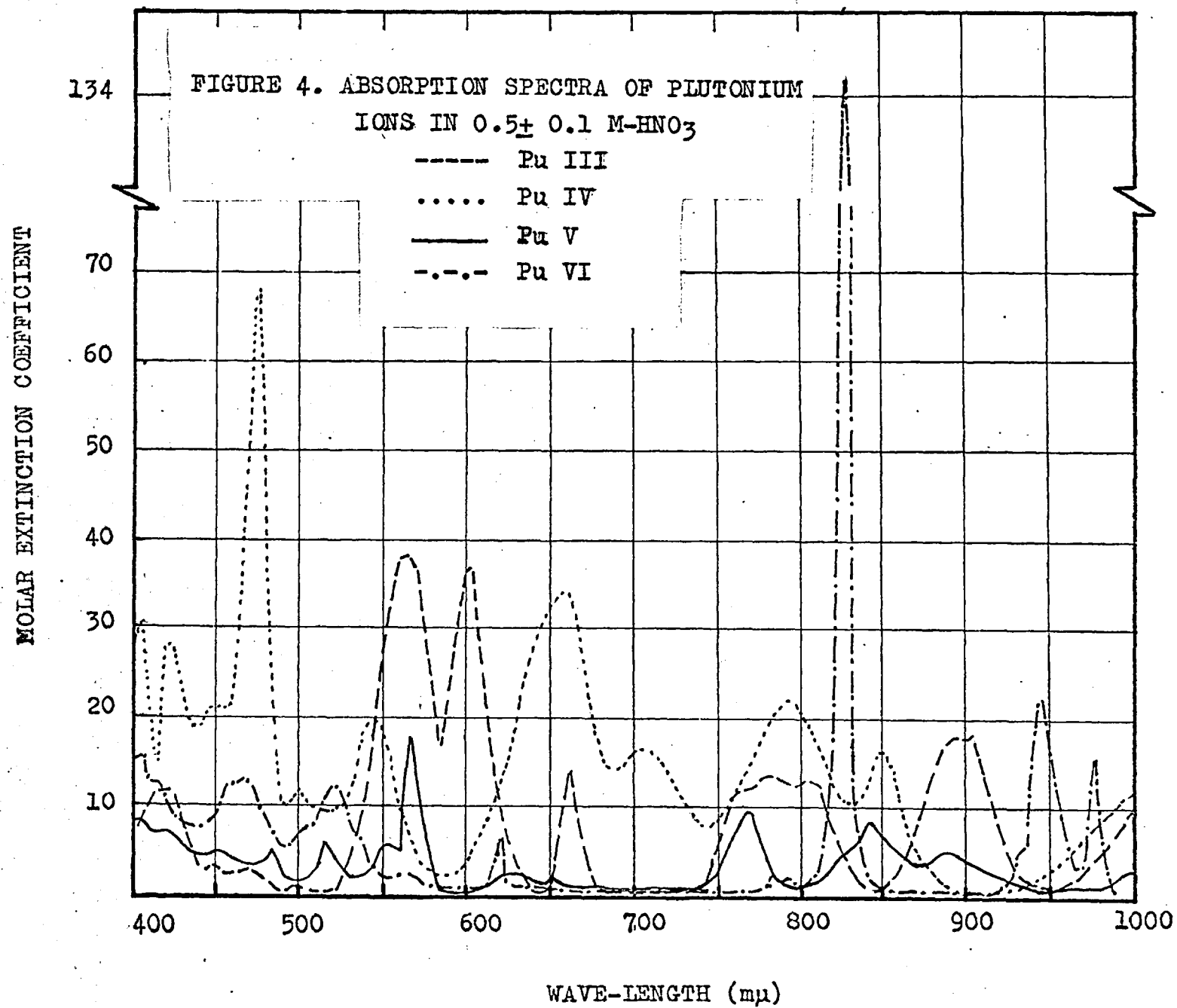
In Fig 4 can be seen the complexity of plutonium ions spectra. Each valence state has numerous, characteristic narrow and intense absorption bands in the visible and near infra red region. These spectra are similar to those of the lanthanide ions. It was recognised (29) that the absorption spectra in 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.

TABLE 4. MOLAR EXTINCTION COEFFICIENTS OF VARIOUS PLUTONIUM
IONS IN 0.5 M-HNO₃

Wavelength mμ	Pu III	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-NH₄NO₃ and pH 3.5.



The blue solution of Pu III has two principal bands at 560 and 603 m μ , a sharp peak at 655, broad bands at 760 - 810 and 900 m μ .

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 m μ . Further diffuse bands at 540, 710, 790 and 850 m μ . The molar extinction coefficient for these bands are given in table 4.

Variation of nitric acid concentration causes shifting of the absorption peak at 476 m μ and variations in the extinction coefficient (20). This is, of course, due to complex formation. Thus the peak at 476 m μ 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 concentration 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 (32) in 0.5 M-hydrochloric acid except for a slightly higher absorption near 400 m μ . The solution is, possibly, contaminated with trace impurities of ferric iron or Pu IV whose absorption increases rapidly below 450 m μ . Pu V has absorption bands at 450, 484, 516, 552, 566, 655, 766, 840, 885 and 995 m μ . There is an error in the location of the absorption bands especially in the near infra red region of about 5 m μ . This is mainly due to an inaccuracy in the wavelength calibration of the SP500. 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 presence 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. Pu VI has several absorption bands at 456, 470, 520, 560, 770, 785, 830, 945 and 975 m μ . The intense band of plutonyl ion in the 825 m μ 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 against concentration of Pu VI at a fixed slit width before using this peak for analytical purposes.

The values of the molar extinction coefficients of Pu III, Pu IV and Pu VI ions in Fig. 4 confirms the results obtained by Hall (33) and refute the higher values by Myers (30).

4.2 Absorption Spectra of Plutonium Ions in Lithium Nitrate Solutions

Fig 5 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 μ with a value of $E = 7$, and a shift of the 1008 μ peak to 1012 μ . Also the intense band at 1135 μ has been shifted to 1142 μ together with high absorption at 1240 - 1350 μ .

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 5.

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 (5) 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.

TABLE 5

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

Wavelength mμ	Molar Extinction Coefficients in			
	0.5M-NH ₄ NO 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	11.2	11.3	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:

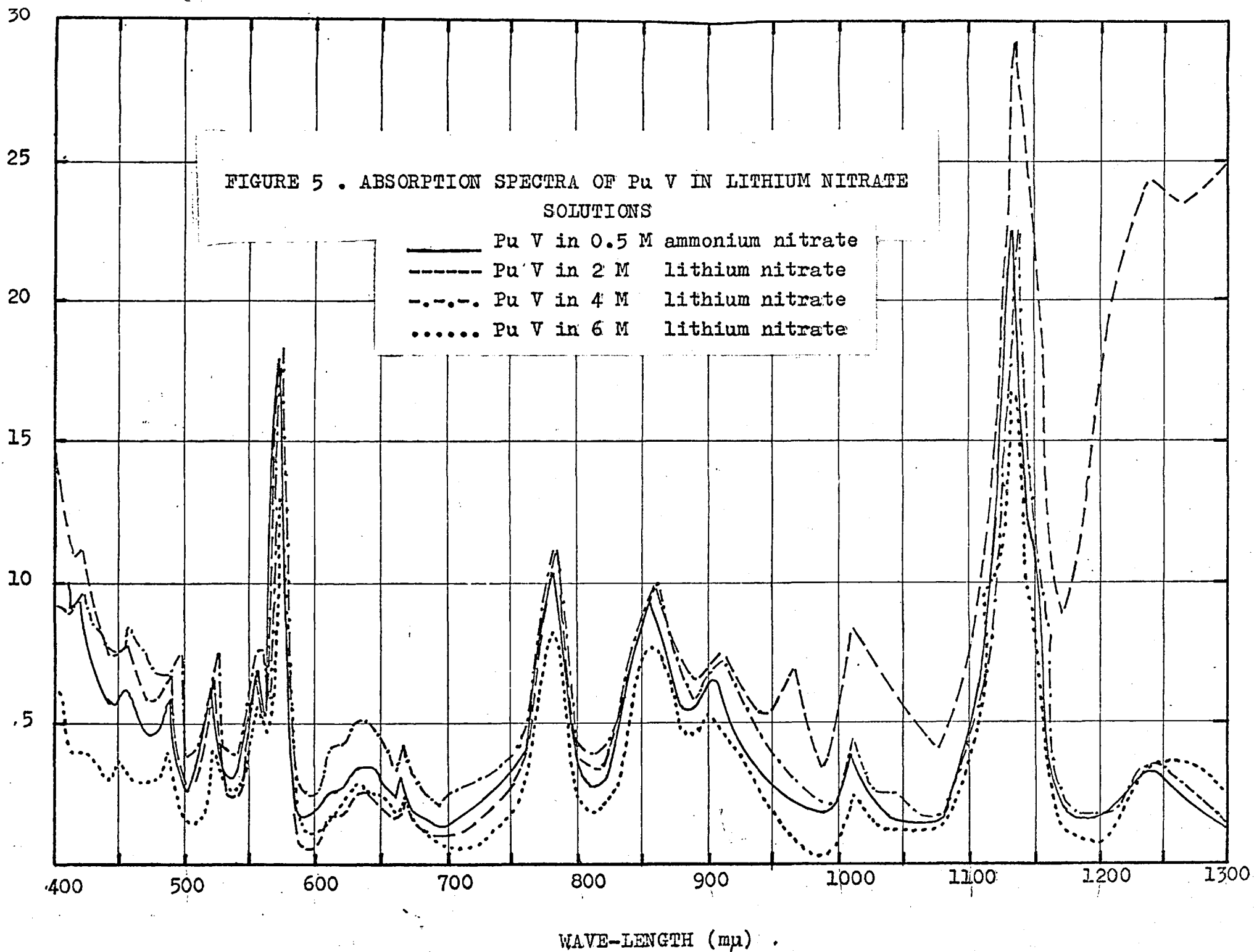
*These peaks shifted to higher wavelengths in lithium nitrate solutions by 3-4 mμ.

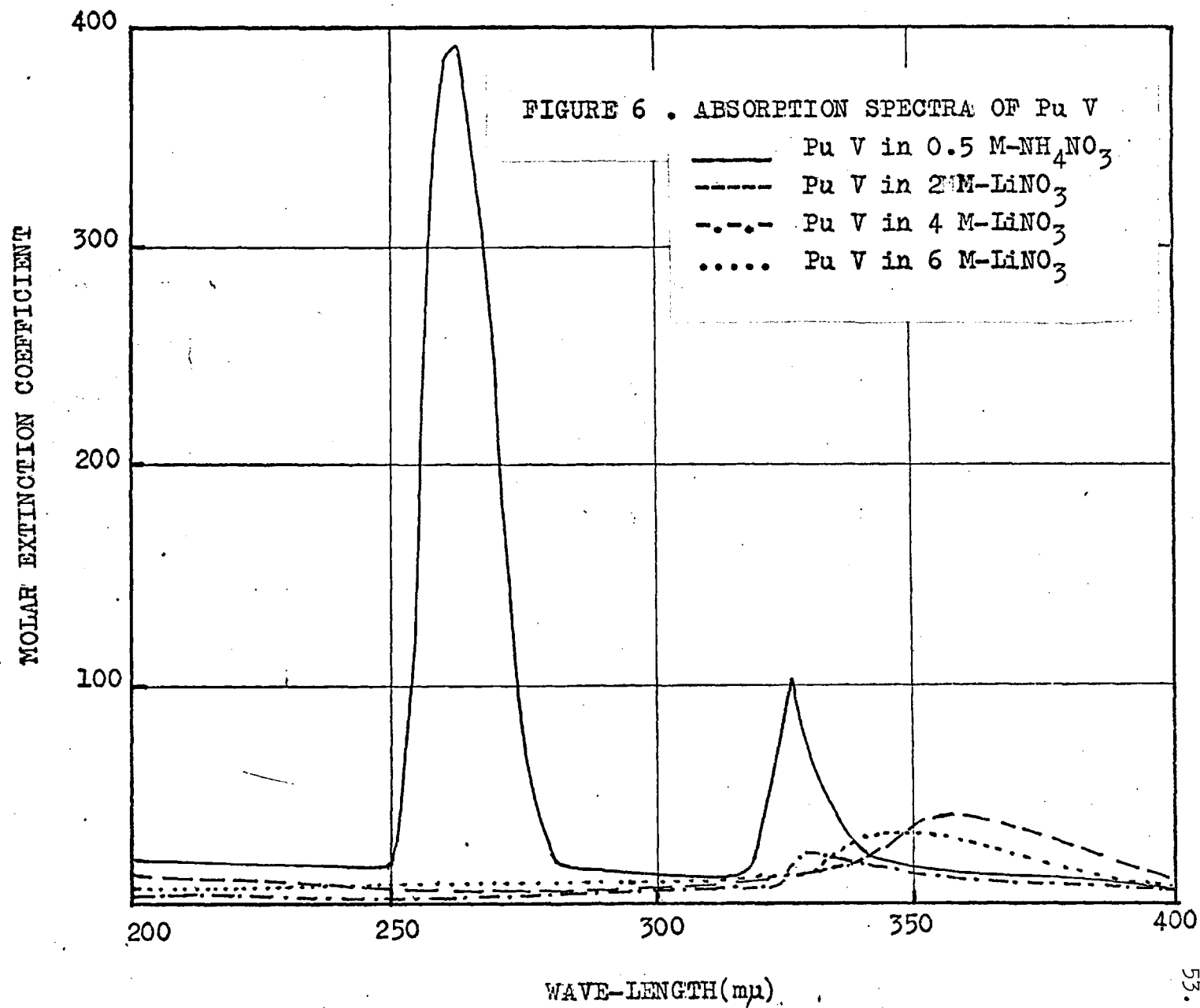
(a) This is a new peak in 2M-LiNO₃.

- (b) This peak shifted to 1012 μ in 2 M-LiNO₃ and to 1010 μ in 4 and 6 M-LiNO₃.
- (c) This peak shifted to 1142 μ in 2 M-LiNO₃ with side shoulder at 1154 μ and to 1140, 1138 μ in 4 and 6 M-LiNO₃ respectively.
- (d) This is a new side shoulder in 6 M-LiNO₃.
- (e) This is a very broad and intense band in 2 M-LiNO₃.

The absorption continues high up to 1330 μ then decreases steadily up to 1500 μ .

MOLAR EXTINCTION COEFFICIENT





PuV in 0.5 M-ammonium nitrate has two sharp bands at 262 and 326 μ with values of molar extinction coefficient of 390 and 102 respectively. The intense absorption band at 262 μ has disappeared completely when the spectrum of PuV was measured in 2, 4 and 6 M-lithium nitrate. The other band at 326 μ has been shifted to higher wavelengths and becomes broad and less intense. A shift of the band at 326 μ to 355, 330 and 345 μ 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 (34). Cohen's results show no characteristic peaks for PuV in ultra violet only two humps at about 260 to 240 μ . It appears that the reported spectrum of PuV in perchlorate is not correct, possibly, because of the presence of some impurities which absorb to a great extent near 200 μ .

The change of the spectrum of PuV in 2 M-LiNO₃ especially above 950 μ 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-LiNO₃ can be ascribed to the formation of new anionic species of PuV. This is confirmed by the ion exchange experiments mentioned in Section 4.5.

Furthermore, the absorption of PuV in 0.5 M-ammonium nitrate and in lithium nitrate give 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 6, the sharp peak at 262 mμ has disappeared. If the environmental perturbations do affect the internal transition in 5f orbitals as was shown above then 6d orbitals should be more liable to such effects.

It has previously been reported by several workers (29, 36, 37) that the absorption in the ultra violet by the actinide ions is caused by the allowed Laporte transition i.e. $5f^q \longrightarrow 5f^{q-1}6d$. Also quoted from reference (37) 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 mμ moved out of the observable range.

There is also a change in the intensity and location of the peak at 326 mμ. This diffuse band is of low intensity and produced by the electron transfer from the ligand to the PuV ion,

i.e. $\pi \longrightarrow 5f$ (37). A shift of the 326 m μ band to higher wavelengths 355, 330 and 345 m μ 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 7 and table 6. All plutonium ions have sharp and intense absorption bands over the region 250 to 260 m μ and diffuse and less intense bands at 325 - 330 m μ .

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

It has been reported by Seaborg (3) that the orbital energy difference of 5f and 6d 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 m μ . PuIII has absorption band at 252 m μ with value of molar extinction coefficient 353 (29). It is of interest to note that the ultra violet spectrum of PuIII reported by Stewart contradicts 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 m μ because the energy difference between 5f and 6d for atomic number Z=94 is roughly constant. The difference in the number of electrons in the 5f shell will probably affect the transition probability of 5f to 6d.

MOLAR EXTINCTION COEFFICIENT

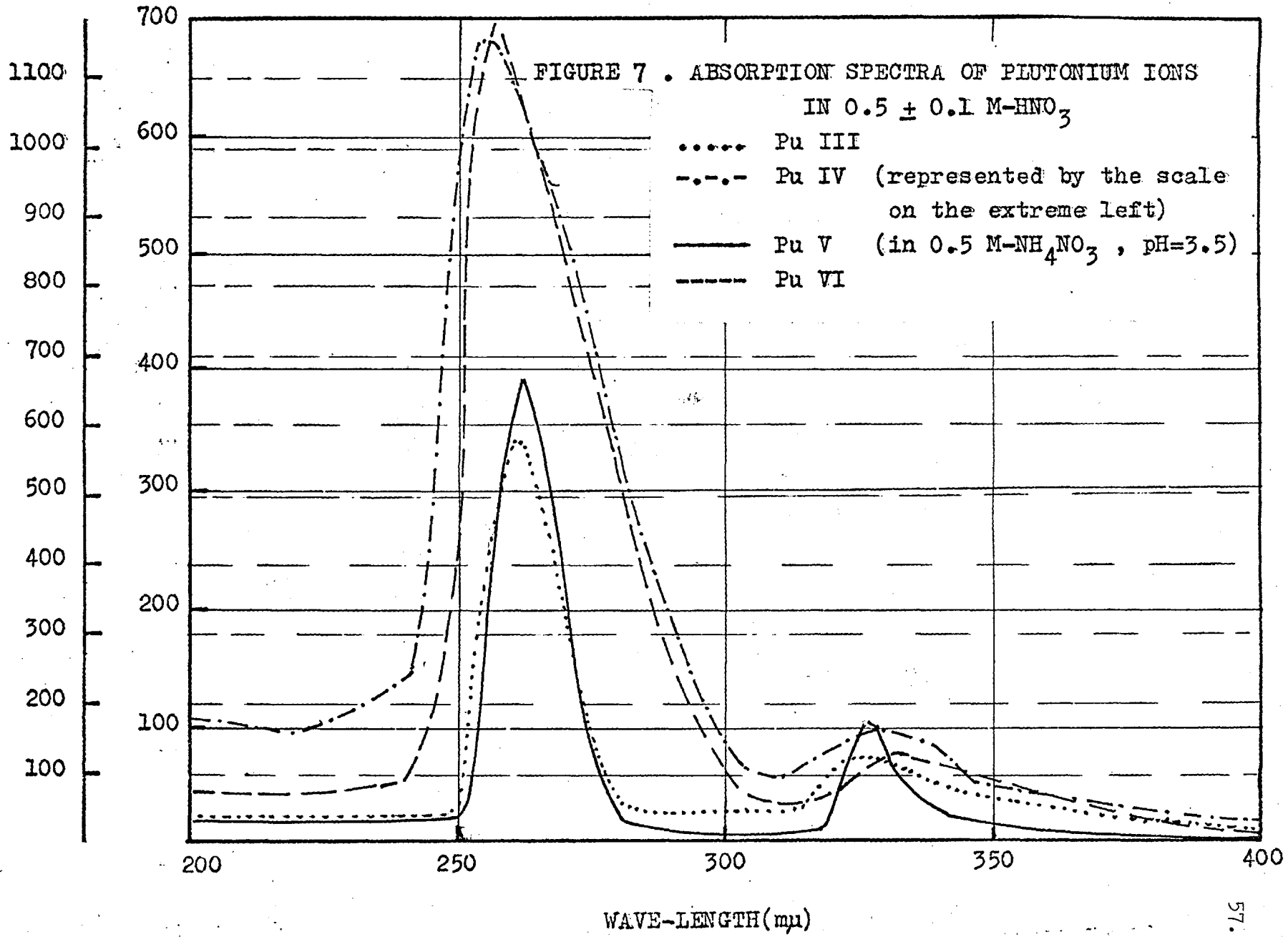


TABLE 6

MOLAR EXTINCTION COEFFICIENTS OF VARIOUS PLUTONIUM IONS IN

0.5 M-HNO₃

Plutonium ions	λ m μ	E	λ m μ	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-NH₄NO₃ and pH 3.5.

4.3 Absorption Spectra of PuIII and PuVI in 6 M-Lithium

Nitrate

Spectrophotometric studies of PuVI in nitric acid (38) show that above 4 M nitric acid there is a decrease in the values of molar extinction coefficient at 830 mμ and an increase of the band at 812 mμ. It was concluded that the appearance of a new peak at 812 mμ indicates the formation of $\text{PuO}_2(\text{NO}_3)_3^-$ complex. Vdenvenko et al (34) gave evidence by spectrophotometric method of mono, di and trinitrato complexes of PuVI in acetone. The appearance of a shoulder at 820 mμ in Fig 8 may represent the start of $\text{PuO}_2(\text{NO}_3)_3^-$ formation. The spectrum has also high absorption in the region 400 - 500 mμ.

PuIII in 6 M-lithium nitrate has high absorption below 500 mμ. There is a shift in the position of the principal bands at 565 and 603 mμ to 570 and 605 mμ with increase in values of molar extinction coefficient from 36.7 to 43.0. The band at 905 mμ has shifted to 920 mμ with a higher value of molar extinction coefficient equal to 23.6. The appearance of a new peak at 780 mμ indicates the splitting of the broad band at 790 - 820 mμ as was observed earlier by Hindman (15).

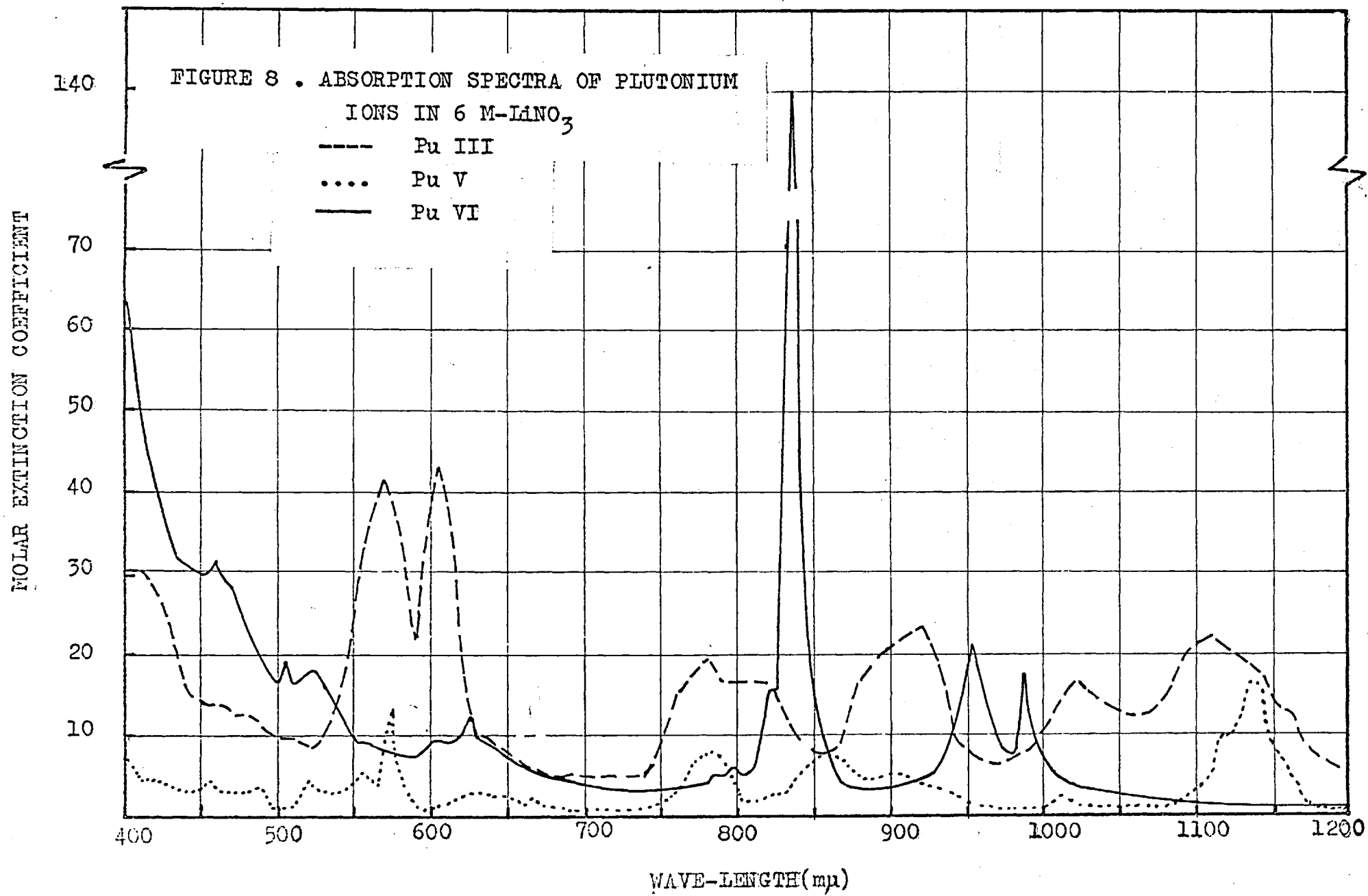
The disappearance of the absorption bands of PuIII and PuVI in the region 250 - 260 mμ, Fig 9, echos the same trends observed in the case of PuV.

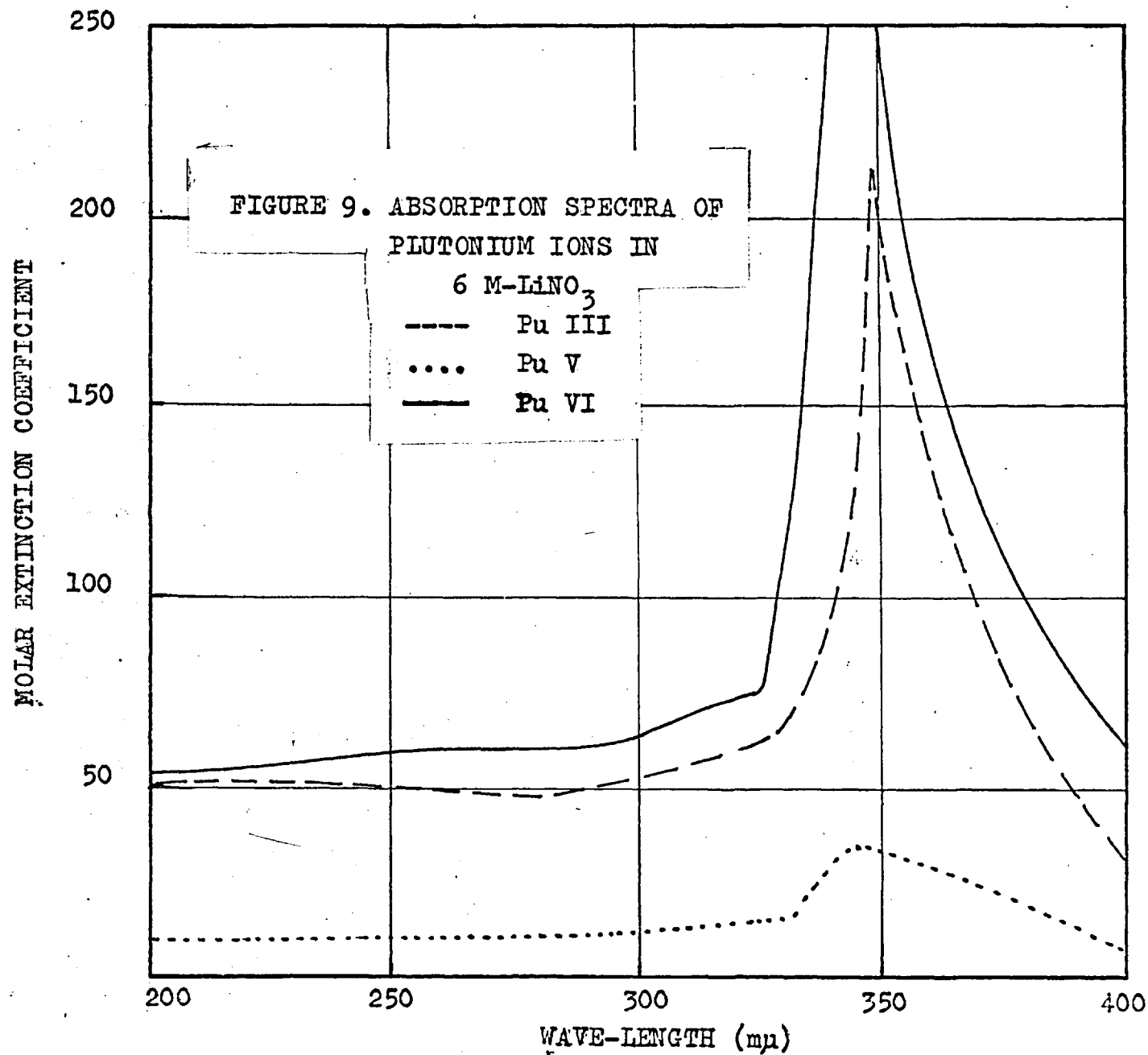
TABLE 7

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

Wavelength mμ	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	5.5	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

61
5





4.4 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 (40) found that Pu V starts to hydrolyse at pH 8 - 9. This does not agree with the Russian workers Gel'man and Zaitseva (9) who found that Pu V hydrolyses at pH 6.8. 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 10, has high absorption below 500 mu, peaks at 520, 555, 570, 640, 775 mu. There is an intense and sharp band at 845 mu. The peak at 1000 mu became broad and intense. There is no change in the position of the band at 1125 mu. These observations do not agree at all with Gevantman (5) 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 $\text{PuO}_2(\text{OH})$.

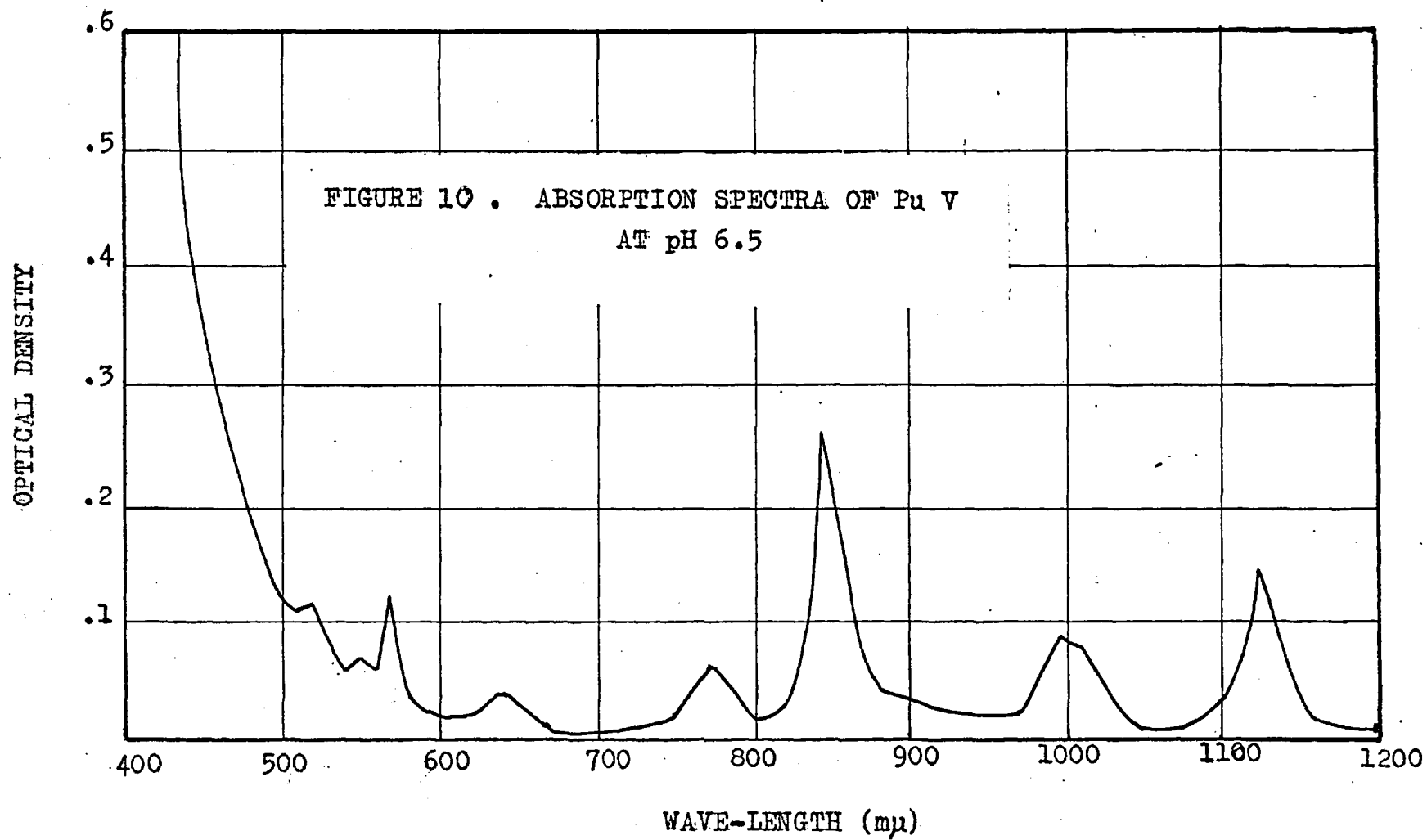
The hydrolytic behaviour of Pu VI has been investigated spectrophotometrically in much greater detail by Kraus and

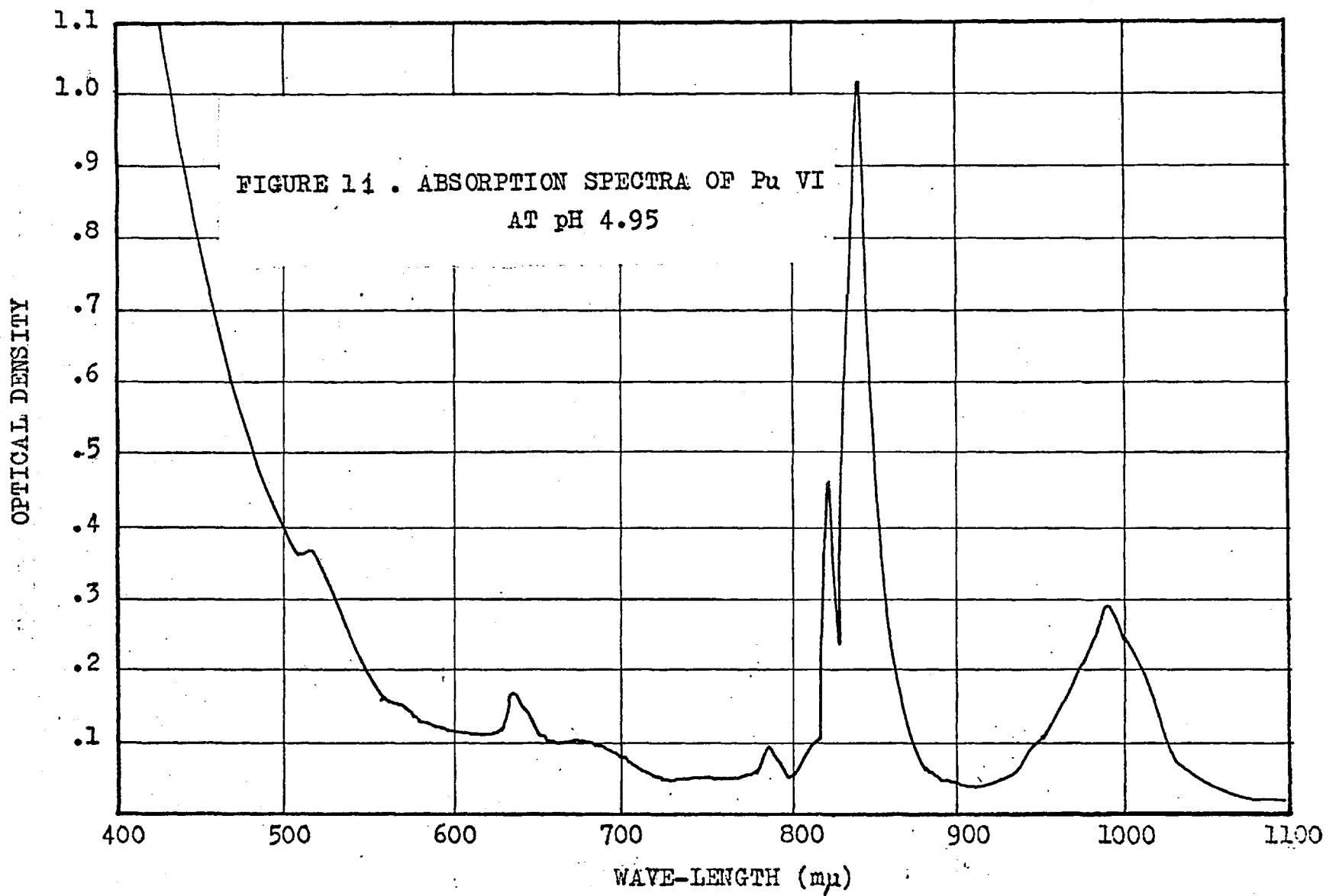
Moore (41). The regular change of the spectra at pH above 4 indicated the formation of several hydrolysis products.

At pH 4.95, Fig. 11, the absorption is continuous and higher below 600 mu except for the appearance of little peak at 518 mu and shift of the subsidiary peak at 625 to 635 mu. The two peaks at 778 and 794 mu have disappeared and instead a new one appears at 788 mu. The intensity of the 830 mu peak has decreased and shifted to 826 mu with a hump at 815 mu. There is an intense and sharp peak at 845 mu. The two peaks at 952 and 985 mu have combined into one broad band at 990 mu. The shape of the band at 990 mu is similar to that reported by Moore and Kraus at pH 6.4 except for its location at 1000 mu. The identity of the various hydrolysis products has been reported as a function of pH by Milyukova et al (42). Accordingly the hydrolytic species of Pu VI at pH 5 is $(\text{PuO}_2)_2(\text{OH})_3^+$.

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.





4.5 Equilibration of Pu V with De-Acidite FF.

Preliminary ion exchange experiments were performed to test the possibility of the presence of Pu V anionic complexes in 6 M-lithium nitrate. It was discovered that 2.82mg of Pu V in 6 M-lithium nitrate adsorbed on an anion exchange column. This result was encouraging and it was decided to obtain more quantitative data on the behaviour of Pu V in different molarities of lithium nitrate.

A study of the equilibration of Pu V with anion exchange resins requires an understanding of the aqueous chemistry of plutonium particularly of the formation and stability of the oxidation states in solution and their hydrolysis reactions. Some of the runs were disposed of because of the uncertainty of the identity of the complex species on the resin and sometimes due to difficulty in producing essentially pure plutonium V at the start of an experiment.

The equilibration data are represented in tables 8 and 9.

The likely reaction of PuO_2^+ forms an anion and goes onto the resin is:



and perhaps that other anions might be formed.

At constant temperature, pressure and concentration of lithium nitrate the position of the equilibrium is controlled by the concentration of each species in solution. As the concentration

of plutonium increases the equilibrium tends to shift to the right hand side.

The equilibrium results are expressed in terms of the fraction C/C_0 , where C is the effective capacity and C_0 is the theoretical capacity of a divalent ion.

It should also be noticed that the mixing time of the resin with Pu V in 6 M-lithium nitrate does not exceed 24 hours in table 8. This precaution was taken to avoid any unnecessary error due to disproportionation or self-reduction of Pu V at longer times.

The ion exchange data in table 8 reveal that in 2 M lithium nitrate no adsorption of Pu V occurs. This implies that Pu V species exists either as uncomplexed ions or neutral species. In 6 M-lithium nitrate the amount of Pu V adsorbed on the resin indicates the existence of divalent anionic species. The amount of Pu V adsorbed never exceeded that of the divalent ion, i.e. 478 mg/g dry resin. It is of interest to note that the plutonyl ion PuO_2^{++} forms trinitrato complex in nitric acid concentration above 4 M (38).

In intermediate molarities, 4.5 M-lithium nitrate, there is an adsorption of 126 mg Pu V/g dry resin. This shows that Pu V exists in the anionic form but whether it is uni or divalent anion is difficult to say merely on the basis of ion exchange results.

In table 8 the mixing of the resin and Pu V solutions were carried out for different periods of time. As will be seen

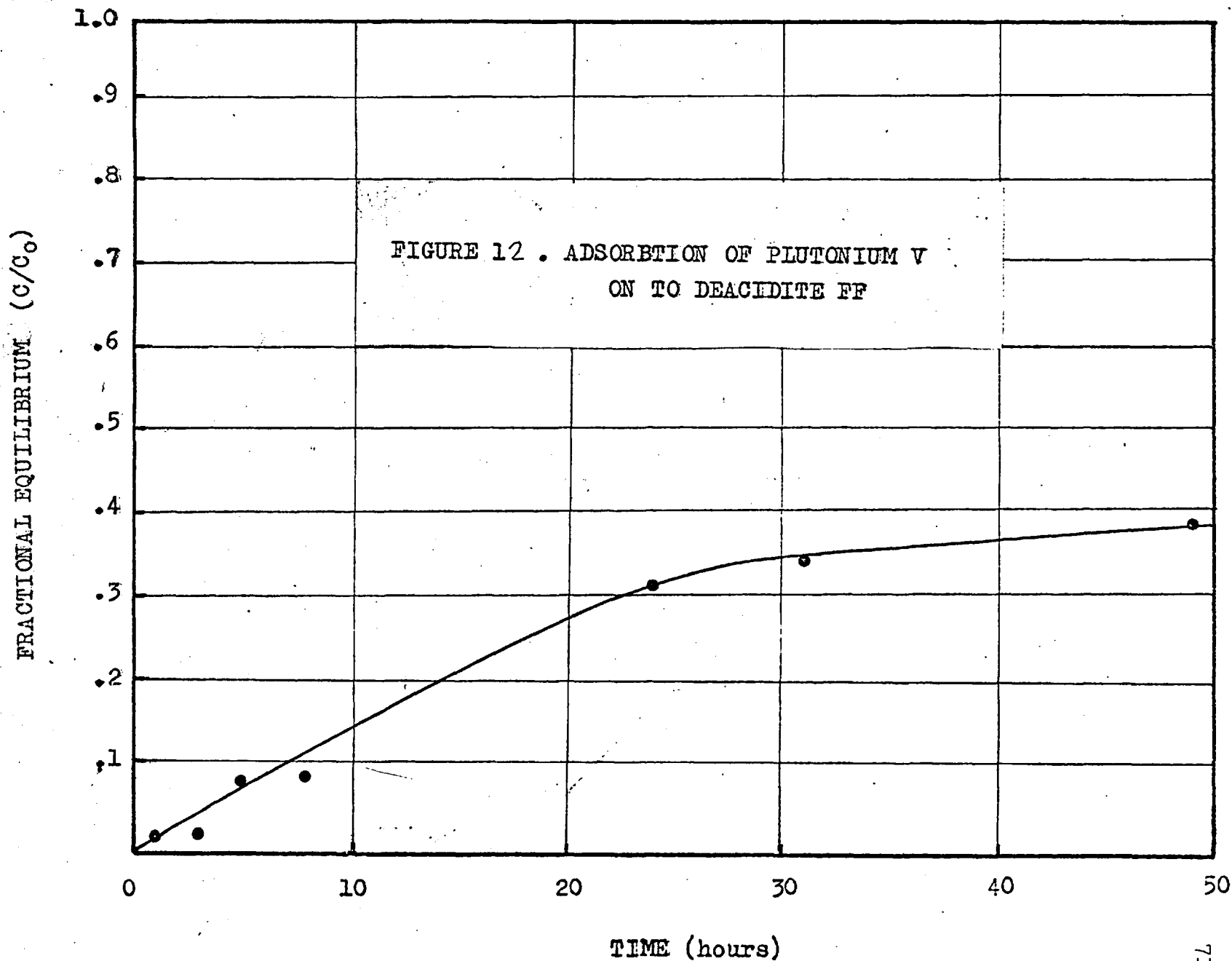
later the rate of Pu V uptake is slow and variation of the mixing time between 14 and 24 hours does not affect the uptake dramatically.

The rate of Pu V uptake is shown in Fig. 12 and table 9. The optimum stirring time to reach equilibrium is about 30 hours. This is considered slow in comparison with Pu IV hexanitrate complex in nitric acid.

To account for the slow rate of adsorption the size of Pu V complex, pore size of the resin and other factors must be considered.

A very rough estimate of the size of $\text{PuO}_2(\text{NO}_3)_3^{2-}$ can be made on the assumption that Pu V complex has a planar geometry, the size of PuO_2^+ is $0.87 \text{ \AA}$ and the bond distance of N — O is $1.21 \text{ \AA}$ (43). On the basis of these data the complex ion has a diameter of about $11 \text{ \AA}$. This does not include the hydration shell around the complex ion.

The pore size of the gel type resin is around $20 \text{ \AA}$ (44). The porosity and pore structure of such resin depends on the electrolyte concentration, solvent and exchangeable ions. The most relevant factor to this discussion is the electrolyte concentration. When the concentration of the electrolyte increases the swelling of the resin decreases, i.e. the resin shrinks. This, of course, affects the pore structure of the resin and it becomes less than the actual size of a fully swollen bead. In 6 M-lithium nitrate the pore structure of 8% crosslinkage De-Acidite FF is definitely less than in dilute aqueous solution. Since the ion exchange reaction is a diffusion of the ions into the resin matrix,



the size of the complex and pore structure of the resin play an important role in the kinetic of adsorption.

The second factor is related to self reduction and hydrolysis of Pu IV. It is observed that Pu IV separated as a fine powder and so will be expected to precipitate on the resin bead blocking its pores.

Thus the environmental conditions affect the rate of adsorption. The adsorption data has been corrected for the self reduction of Pu V by spectrophotometric measurement. The reproducibility of these results are within $\pm 7\%$.

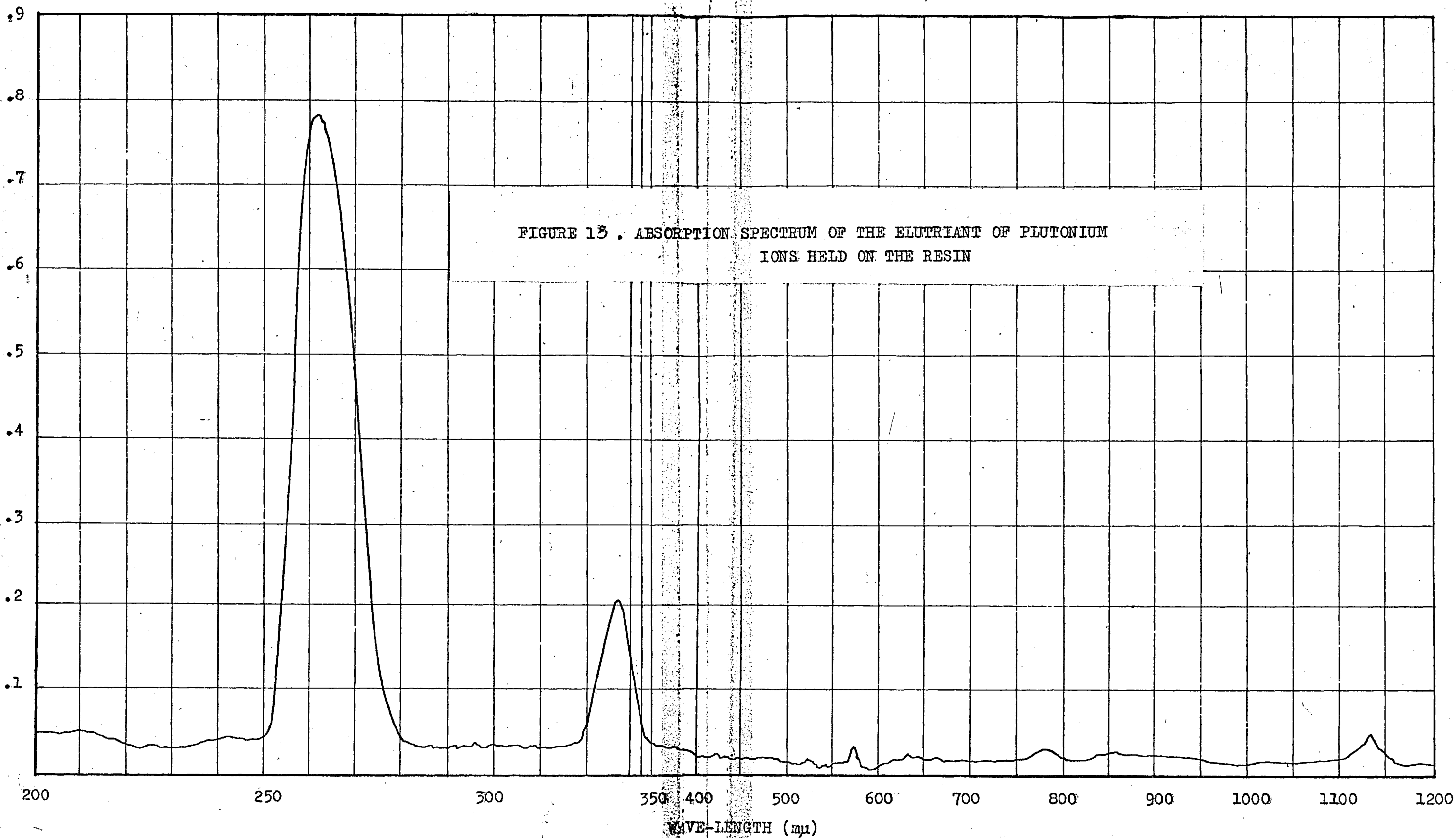
Variation of pH between 3-5 has no significant effect on the behaviour of Pu V adsorption. This is because H^+ does not take part, in contrast to EDTA complex, in the complex formation.

As further evidence that the Pu V complex had actually undergone exchange onto the resin an elution experiment was performed. After stirring the resin overnight with 15 ml. of 0.2 M ammonium nitrate (pH 3.5) it was possible to elute about 25% of the adsorbed species. The spectrum of the elutriant is shown in Fig. 11. Clearly, there is no trace of Pu VI, Pu IV or Pu III which have much higher adsorption in the visible and near infra red region. There are small peaks at 570, 775 and 1135 $m\mu$ of Pu V. This gives evidence that the species adsorbed on the resin is only Pu V. The UV spectrum has already been discussed in a previous section.

The data in table 10 confirms the existence of

OPTICAL DENSITY

FIGURE 13 . ABSORPTION SPECTRUM OF THE ELUTRIANT OF PLUTONIUM
IONS HELD ON THE RESIN



thiocyanate and sulphate anionic complexes of Pu V in 5 and 1.59 M ammonium thiocyanate and lithium sulphate respectively. The discussion can not be extended further to elucidate the composition of these species. Probably Pu V forms anionic complex of SO_4^{2-} or HSO_4^- in a similar manner to its analogue Pu VI (13).

There is no data in the literature available on the thiocyanato complexes of Pu VI.

TABLE 8. ADSORPTION OF Pu V ONTO DE-ACIDITE FF X 8 (100-200)

$$t = 20 \pm 1^\circ\text{C}$$

MIXING TIME hours	pH	LiNO_3 M	mg/ml Aqueous	mg/g dry resin	C/C_0
24	3.8	2.0	1.15	nil	-
24	5.0	4.5	0.458	126	0.26
24	5.0	6.25	0.077	1.15	0.0024
19	3.5	6.0	0.84	168.8	0.35
14.5	3.5	6.0	1.147	242	0.507

TABLE 9. RATE OF Pu V UPTAKE ONTO DE-ACIDITE FF@ X 8 (100-200)

$$t = 20 \pm 1^{\circ}\text{C}$$

MIXING TIME (hours)	mg/ml Aqueous	mg/g dry resin	mg/g dry resin (2% correction)	c/c _o
1	1.74	10.2	10.1	0.021
3	1.72	12.3	12.3	0.025
5	1.52	40.8	40.6	0.085
8	1.49	44.3	44.0	0.092
24	0.66	159.6	156.5	0.33
31	0.56	174.5	169.2	0.35
49	0.37	199.9	191.9	0.40

@ 44.7 mg resin was equilibrated with 6 ml. of Pu V in 6 M-lithium nitrate.

TABLE 10. ADSORPTION OF Pu V ONTO DE-ACIDITE FF X 8 (100-200)

$$t = 20 \pm 1^{\circ}\text{C}$$

MIXING TIME (hours)	pH	NH ₄ SCN M	mg/ml Aqueous	mg/g dry resin
18.0	4.2	5.0	0.0083	0.349
		Li ₂ SO ₄ M		
14.0	5.7	1.59	0.154	3.14

CHAPTER 5CONCLUSIONS

The present work illustrates the behaviour of Pu V in concentrated nitrate solutions which has not been described in the literature.

Pu V seems to be fairly stable at pH 3.5. The alpha radiolysis products affect the stability of Pu V to a greater extent than disproportionation does. By increasing the NO_3^- concentration the rate of disappearance of Pu V increases due to the formation of the more stable nitrate complexes of Pu VI as well as the formation of the radiolysis products such as NO_2^- . The stability of Pu V is very sensitive to pH value. At pH greater than 4 the stability of Pu V decreases to a considerable extent.

Pu V is most stable at concentration of about 1 mg/ml and pH 3.5 for a period of a week without any significant disproportionation or self-reduction. This is enough time to perform an equilibration experiment satisfactory.

The spectra of Pu V in concentrated nitrate solutions have revealed and replaced the old ideas about the inability of Pu V to form complexes with nitrate in similar manner to Pu VI. The much more pronounced changes of Pu V spectra (visible and near infra red) in concentrated lithium nitrate solutions indicate some of the following facts. The first is that Pu V spectra in 2 and 6 M- LiNO_3 possess a new characteristic features with different values of molar extinction coefficients, shift of the absorption peaks to

higher wavelengths and appearance of new peaks.

Secondly, no significant change of the spectrum occurs at intermediate molarities of LiNO_3 i.e. 4 M- LiNO_3 .

The conclusion which can be drawn from these observations are the presence of different species of Pu V at various molarities of lithium nitrate.

The nature of these complexes have been successfully demonstrated for the first time by ion exchange techniques. In 4 M and 6 M- LiNO_3 , Pu V exists as anionic complexes while in 2 M- LiNO_3 it is neutral or a cation. The amount of Pu V adsorbed on the resin in 6 M- LiNO_3 indicates that it is a divalent ion, i.e. $\text{PuO}_2(\text{NO}_3)_3^{2-}$. In 2 M- LiNO_3 it may be $\text{PuO}_2(\text{NO}_3)$ or PuO_2^+ . This work still needs more investigations.

The elution of the adsorbed species on the resin leaves no doubt and confirms the existence of Pu V anionic complex.

The discovery of the ultra violet spectra was accidental and no previous planning was made in conjunction with studying Pu V complexes. Although it seems difficult to explain why all plutonium ions have absorption bands at nearly the same wavelength and also the disappearance of the 262 mμ band in lithium nitrate solutions. But, nevertheless, it represents a new field of investigations. It is unfortunate that the time did not allow for more work to be done. Therefore the conclusion is not explicit with respect to the nature of the transition in the ultra violet region. But it can be easily concluded that plutonium ions have very high absorption below 240 mμ and less intense and diffuse bands

at 230 to 250 μ . It has also been demonstrated that the intense band below 240 μ is very sensitive to the environmental perturbations.

Finally the spectrum of Pu V at pH 6.5 may be explained by the formation of the hydrolysis product of Pu V, i.e. $\text{PuO}_2(\text{OH})$.

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APPENDIX 1CALCULATION OF THE PLUTONIUM SPECIFIC ACTIVITY

The plutonium used has the following mass analysis:

Pu 238	30 mCi/Ci Pu 239
Pu 239	91.4% w/w.
Pu 240	8.0% w/w.
Pu 241	0.6% w/w.

ISOTOPE OF PLUTONIUM

Isotopes	Mode of Disintegration	Half-life, years
Pu 238	alpha (5.495, 5.452, 5.352)	89.59
Pu 239	alpha (5.147, 5.134, 5.096)	24360
Pu 240	alpha (5.159, 5.115, 5.014)	6580
Pu 241	beta (99%) (0.0205)	13.0

The rate of disintegration of a given radioactive species is given by:

$$-\frac{dN}{dt} = \lambda N/M$$

where

N is Avogadro's number

λ is the decay constant

M is the Atomic weight

Accordingly, the specific activities of plutonium isotopes will be

$$\text{Pu 238} \quad 3.6 \times 10^{13} \text{ d min}^{-1} \text{ g}^{-1}$$

$$\text{Pu 239} \quad 1.3 \times 10^{11} \text{ d min}^{-1} \text{ g}^{-1}$$

$$\text{Pu 240} \quad 5.0 \times 10^{11} \text{ d min}^{-1} \text{ g}^{-1}$$

$$\text{The weight of Pu 238/30 mCi} = \frac{2.22 \times 10^{12}}{3.6 \times 10^{13}} \times 30 \times 10^{-3}$$

$$= 1.85 \times 10^{-3} \text{ g}$$

$$\text{w/w\% of Pu 238} = \frac{1.85 \times 10^{-3}}{16.28} \times 100 = 0.01138\% \text{ w/w}$$

The total specific activity of the sample S_T is the weighted sum of the individual specific activities

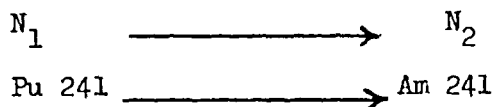
$$S_T = S_{238} W_{238} + S_{239} W_{239} + S_{240} W_{240}$$

Pu 241 is a beta emitter and can be neglected.

$$\text{Therefore } S_T = 1.113 \times 10^{-4} \times 3.6 \times 10^{13} + 0.914 \times 1.365 \times 10^{11} \\ + 0.08 \times 10^{11}$$

$$= 1.689 \times 10^{11} \text{ d min}^{-1} \text{ g}^{-1}$$

$$= 2.815 \times 10^6 \text{ d sec}^{-1} \text{ mg}^{-1}$$

APPENDIX 2GROWTH OF Am 241 FROM Pu 241

The general law governing radioactive decay and growth is

$$N_2 = \frac{\lambda_1}{\lambda_2 - \lambda_1} N_1^0 (e^{-\lambda_1 t} - e^{-\lambda_2 t}) + N_2^0 e^{-\lambda_2 t} \quad (1)$$

The last term can be omitted, assuming there is no Am 241 present initially.

$$N_2 = \frac{\lambda_1}{\lambda_2 - \lambda_1} N_1^0 (e^{-\lambda_1 t} - e^{-\lambda_2 t}) \quad (2)$$

$$\lambda_1 = 0.0533 \text{ yr}^{-1}$$

$$\lambda_2 = 0.001513 \text{ yr}^{-1}$$

The stock solution of plutonium contains 0.6 w/w Pu 241.

Thus the initial number of atoms of Pu 241 i.e. N_1^0

will be

$$6 \times 10^{-4} \times \frac{6 \times 10^{23}}{241} = 1.493 \times 10^{18}$$

By substituting for the above values in equation 2

Therefore N_2 is equal to 7.75×10^{16} atoms or 31.15 μg Am 241.

Similarly the growth of Am 241 at any time can be calculated and is represented in Fig 14.

After 3.5 years the growth of Am 241 is 1 μg / 1 mg Pu.

This will introduce an error of about 5.5% higher than the correct activity of Pu 239 since Am 241 has specific activity 53 times higher than Pu 239.

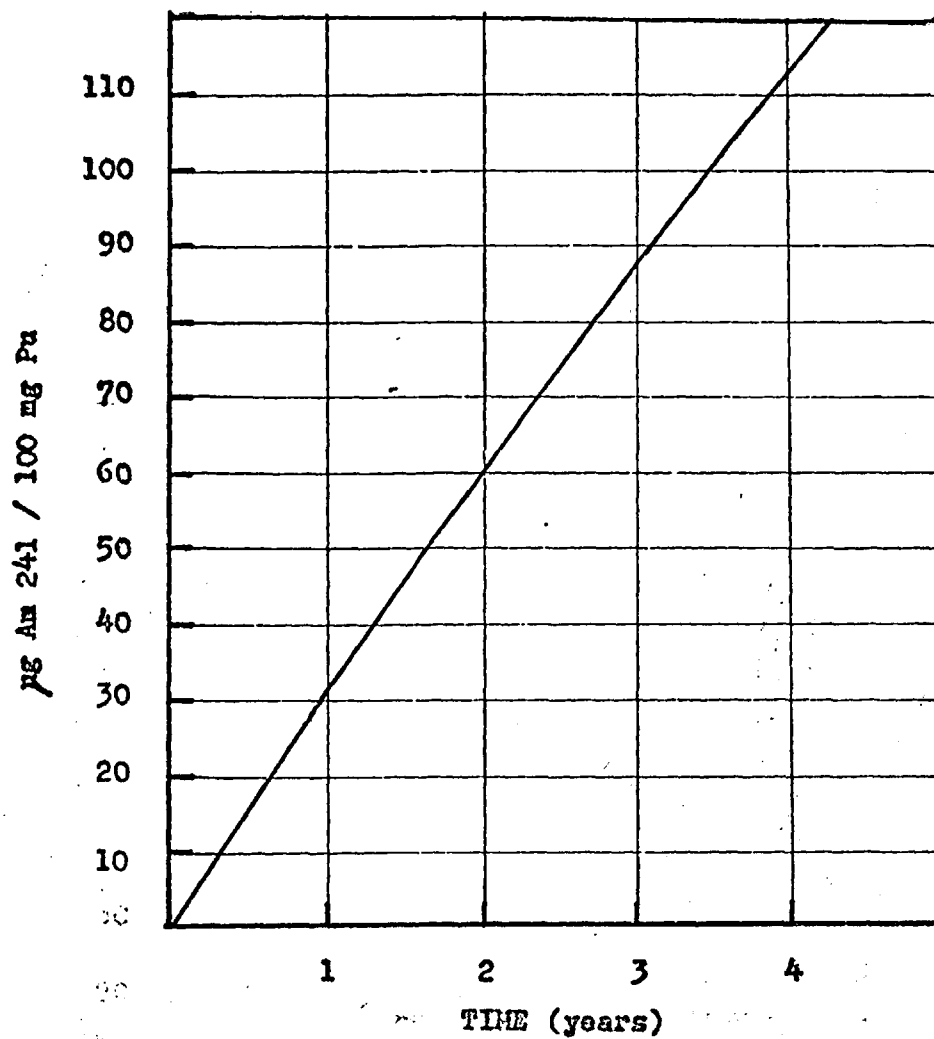
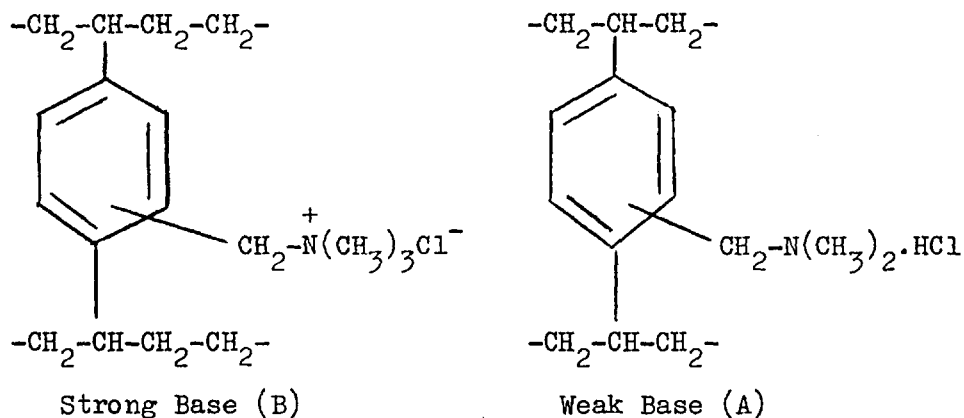


FIG. 14..GROWTH OF Am 241 FROM Pu 241

APPENDIX 3ESTIMATION OF ANION EXCHANGE CAPACITY

The resin which was used in the present work is De-Acidite FF X8 (100 - 200). It has strong and weak base functional groups as shown below:



The following procedure was used to determine both weak and strong base capacity.

Weight of the dry resin (chloride form) = 2.1935 g.

Determination of weak base capacity:

25 ml of solution (A) + 25 ml of 0.1M-HNO₃ + 10 ml of 0.1 N-AgNO₃ + 2 ml nitrobenzene + few drops of ferric salt indicator was titrated against 0.096 M-NH₄SCN.

Volume of thiocyanate consumed = 9.85 ml.

$$\begin{aligned}
 \text{Weak base capacity} &= \frac{10 \left[(\text{ml} \times N)_{\text{AgNO}_3} - (\text{ml} \times N)_{\text{SCN}^-} \right]}{\text{weight of dry resin}} \\
 &= \frac{10 \left[(10 \times 0.1) - (9.85 \times 0.096) \right]}{2.1935} \\
 &= 0.228 \text{ meq/g.}
 \end{aligned}$$

Determination of strong base capacity:

25 ml. of solution (B) was titrated as mentioned above against thiocyanate.

Volume of thiocyanate consumed = 1.8 ml.

$$\begin{aligned}\text{Strong base capacity} &= \frac{10 \left[(10 \times 0.1) - (1.8 \times 0.096) \right]}{2.1935} \\ &= 3.75 \text{ meq/g.}\end{aligned}$$

Correction for hydrolysis of the strong base:

25 ml of solution (B) was titrated against 0.08 M-HCl

Volume of HCl taken = 0.6 ml.

$$\begin{aligned}\text{Number of meq due to hydrolysis} &= \frac{0.6 \times 0.08 \times 10}{2.1935} \\ &= 0.219 \text{ meq/g.}\end{aligned}$$

The real weak base capacity = $0.228 - 0.219 = 0.009$ meq/g.

The real strong base capacity = $3.78 + 0.219 = 3.999$ meq/g.

The total anion exchange capacity = $3.999 + 0.009 = 4.008$ meq/g.

APPENDIX 4CALCULATION OF PLUTONIUM SPECIFIC ACTIVITY BY SPECTROPHOTOMETRY

The spectrum of Pu III in 1 M-HNO₃ was recorded in 1 cm cell in the spectral region 400 - 1200 mμ to check the absence of Pu IV, Pu V and Pu VI.

The optical density at 603 mμ is 0.54. The concentration of plutonium was calculated from the following formula:

$$\text{O.D.} = E C L$$

where

O.D. = Optical density of solution.

C = Concentration of plutonium in moles /litre.

E = Molar extinction coefficient.

L = Optical path length in cm.

The absorbance of Pu III at 603 mμ obeys Beer's law.

The published value of the molar extinction coefficient at 603 mμ is 36.7.

Therefore

$$C = \frac{0.54}{36.7} = 1.47 \times 10^{-2} \text{ M} = 3.52 \text{ mg/ml}$$

Consequently the specific activity of plutonium can be calculated as follows:

$$\text{Specific Activity} = \frac{C/\text{sec.}}{\text{Aliquot (ml)}} \times \frac{1}{\text{Counter efficiency}} \times \frac{1}{\text{Conc. (mg/ml)}} \times$$

$$\frac{1}{\text{Dilution factor}} = \frac{89.66}{25 \times 10^{-3}} \times \frac{10^2}{34.79} \times \frac{1}{3.52} \times$$

$$\frac{10}{10 \times 10^{-3}} = 2.93 \times 10^6 \text{ alpha/sec/mg.}$$

SPECTROPHOTOMETRIC ANALYSIS OF VARIOUS OXIDATION STATES OFPLUTONIUM

The spectrum of Pu V in 0.5 M-ammonium nitrate and at pH 3.5 was analysed for various oxidation states of plutonium at three selected wavelengths 570, 603, and 950 mμ corresponding to Pu V, Pu III and Pu VI respectively. The concentration of plutonium IV at pH 3.5 was calculated by the difference between the total plutonium concentration and the sum of Pu III, Pu V and Pu VI.

The following equations are used assuming that the absorbances are additive at each wavelength.

At 570 mμ

$$\text{O.D.} = 35 C_{\text{III}} + 17.5 C_{\text{V}} + 2.0 C_{\text{VI}} \quad 1$$

At 603 mμ

$$\text{O.D.} = 36.5 C_{\text{III}} + 1.4 C_{\text{V}} + 1.0 C_{\text{VI}} \quad 2$$

At 950 mμ

$$\text{O.D.} = 1.3 C_{\text{III}} + 2.0 C_{\text{V}} + 22.5 C_{\text{VI}} \quad 3$$

In 6 M-LiNO₃ the following equations are used

At 570 mμ

$$\text{O.D.} = 41.6 C_{\text{III}} + 13.2 C_{\text{V}} + 7.8 C_{\text{VI}} \quad 4$$

At 603 mμ

$$\text{O.D.} = 43 C_{\text{III}} + 6.2 C_{\text{V}} + 9.1 C_{\text{VI}} \quad 5$$

At 953 mμ

$$\text{O.D.} = 8.3 C_{\text{III}} + 3.7 C_{\text{V}} + 21.1 C_{\text{VI}} \quad 6$$

All values of molar extinction coefficient are taken from the experimental results.

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