THE EFFECT OF RADIATION ON THE VALENCE STATE OF PLUTONIUM IN NITRIC ACID SOLUTIONS

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We investigated the effect of x-radiation on the valence state of plutonium in nitric acid solutions from 0.3 to 2.0 M and also in 0.3 M nitric acid solutions containing varying concentrations of $UO_2(NO_3)_2$ and $K_2Cr_2O_7$. The effect of radiation on nitric acid solutions, not containing $UO_2(NO_3)_2$, causes only oxidation of plutonium and the oxidation yield decreases with an increase in the concentration of NO_3^- ions and acidity of the solution. We put forward the hypothesis that the oxidation is effected by OH radicals. Under certain conditions the reduction of plutonium was observed in the presence of $UO_2(NO_3)_2$. Apparently, it is not effected by atomic hydrogen but by UO_2^+ ions. Potassium dichromate causes an acceleration in radiation oxidation of plutonium but under the given conditions it does not retard its reduction.

The effect of radiation on the valence state of plutonium in solution is hardly mentioned in the literature. The few reports on this problem refer to the effect of the α-radiation of plutonium itself and are observations of a casual nature [1, 2].

We systematically investigated changes in the valence state of plutonium in nitric acid solutions when treated with external radiation.

Besides pure nitric acid solutions, we investigated solutions containing also uranyl nitrate and potassium dichromate, which have the capacity of increasing the reduction or the oxidation of plutonium during irradiation.

Experimental Procedure

Radiation. As the radiation source we used a sealed x-ray tube, operating at 50 kv and 200 ma with the beam directed vertically upward. A cylindrical glass cell with a thin membrane was used in the work [3]. All investigations were carried out with constant mixing of the solution in an atmosphere of nitrogen. The temperature of the solution being irradiated was controlled by a thermocouple and in separate experiments it fluctuated from 20 to 25° C. The apparatus was shut off for short periods when samples were taken for analysis.

Dosimetry. The dose strength in the solutions was determined by the ferrous sulfate dosimetric method, considering 15.6 Fe^{++} ions oxidized per 100 ev of absorbed energy [4]. We took into consideration the relation of the soft x-radiation absorption to the thickness of the solution being irradiated and the difference in the energy absorption of the dosimetric solution and that of the systems being investigated. The dose strength in our experiments was from $5 \cdot 10^{16}$ to $9 \cdot 10^{16}$ ev/cm^3·sec.

Analysis. In solution plutonium may have four valence states: Pu^{+3}, Pu^{+4}, PuO_2^+, and PuO_2^{++}. We did not aim at the identification of all the valence states of plutonium but limited ourselves to separating them into two forms: oxidized and reduced, considering the sum of $PuO_2^+ + PuO_2^{++}$ as the oxidized form and the sum of $Pu^{+3} + Pu^{+4}$ as the reduced form.

The two forms were separated by isolating Pu^{+3} and Pu^{+4} by precipitating the double sulfate of potassium and lanthanum from a solution saturated with potassium sulfate [5]. The amount of plutonium in the precipitate and in the solution was determined by the α-activity.

Reagents. All the salts used were specially purified to remove foreign materials and, before the experiment, recrystallized three times from doubly distilled water.

The working solutions of plutonium were prepared from a starting solution containing a mixture of oxidized and reduced plutonium with a total concentration of 2 g/liter of plutonium in 0.5 N HNO_3. The oxidized plutonium solutions were prepared by heating the starting solution on a boiling water bath. The reduced plutonium was prepared by passing hydrogen through the starting solution in the presence of platinized platinum. This method had been used previously only for the reduction of Pu^{+4} in hydrochloric acid solutions [6].

Results

We examine below the oxidation and reduction processes of plutonium in solutions containing nitric acid, sodium nitrate, uranyl nitrate and potassium dichromate in various concentrations and combinations.

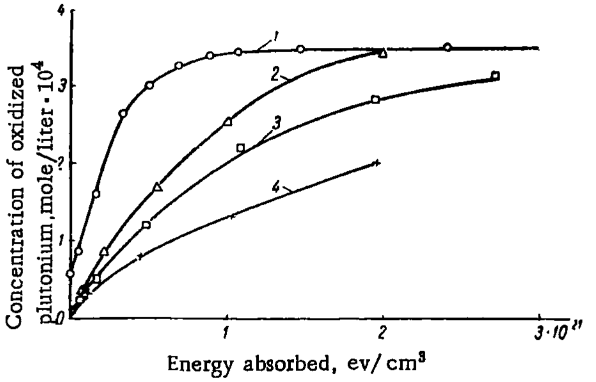

Fig. 1. Plutonium oxidation under the effect of x-radiation. The total plutonium concentration was $3.4 \cdot 10^{-4}$ mole/liter. 1) 0.3 N HNO_3; 2) 0.35 M $NaNO_3$ in 0.3 N HNO_3; 3) 0.88 M $NaNO_3$ in 0.3 N HNO_3; 4) 1.76 M $NaNO_3$ in 0.3 N HNO_3.

Solutions of HNO_3 and $NaNO_3$. When nitric acid solutions of reduced plutonium were treated with x-radiation, the latter was oxidized. The character and the rate of the process depended both on the NO_3^- ion concentration and on the acidity. Figure 1 gives plutonium oxidation curves in solutions of 0.3 N HNO_3 containing varying concentrations of $NaNO_3$. The curves show that the rate of increase in the concentration of oxidized plutonium in all the solutions investigated decreased with the absorption of energy. The initial oxidation yield decreased with an increase in the $NaNO_3$ concentration. Plutonium behaved similiarly when solutions of it in pure nitric acid were subjected to x-radiation, the only difference being that nitric acid depressed the oxidation yield of plutonium more efficiently than sodium nitrate.

Figure 2 gives the values of the oxidation yields of plutonium, determined from the tangent of the initial parts of the corresponding curves.

In solutions with equal NO_3^- ion contents but with different H^+ ion concentrations the initial oxidation yield of plutonium is lower, the greater the acidity of the solution. This conclusion was confirmed by results from direct experiments with solutions of variable H^+ ion concentrations and constant NO_3^- ion concentration (Fig. 3).

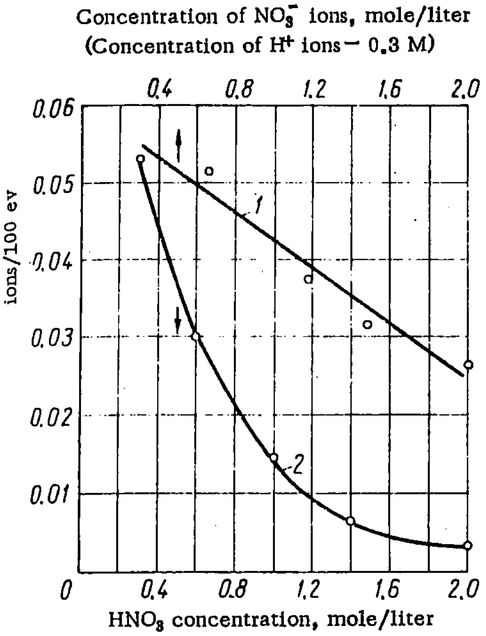

Fig. 2. The relation of the oxidation yield of plutonium 1) to $NaNO_3$ concentration; 2) to HNO_3 concentration.

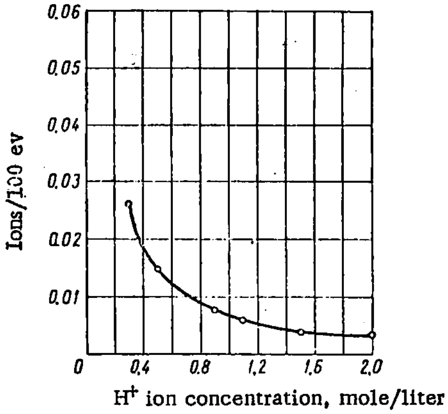

Fig. 3. The relation of the oxidation yield of plutonium to acidity. NO_3^- ion concentration – 2.0 M.

Solutions of $UO_2(NO_3)_2$ in 0.3N HNO_3. The behavior of plutonium in nitric acid solutions containing $UO_2(NO_3)_2$ was very closely related to the concentration of the latter.

In solutions with $UO_2(NO_3)_2$ concentrations not greater than 0.3 M the plutonium was oxidized due to the radiation. The initial oxidation yield fell from 0.052 ions/100 ev for pure acid to 0 in a 0.3 M solution of $UO_2(NO_3)_2$, in which the ratio of the oxidized and reduced forms of plutonium remained unchanged during the irradiation process. We observed plutonium reduction at $UO_2(NO_3)_2$ concentrations higher than 0.3 M. The reduction yield increased with an increase in the $UO_2(NO_3)_2$ concentration from 0 to 0.17 ion/100 ev at 0.88 M $UO_2(NO_3)_2$.

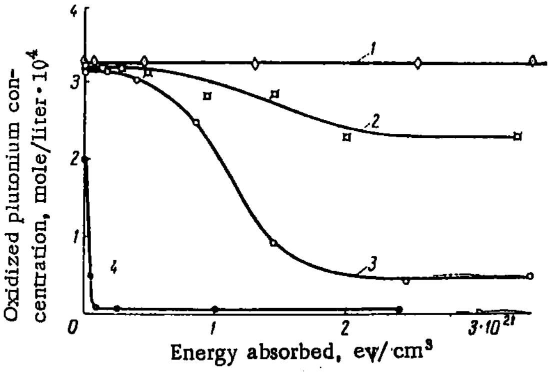

Fig. 4. The effect of x-radiation on the valence state of plutonium in 0.3 N HNO_3 solutions containing $UO_2(NO_3)_2$ in concentrations of: 1) 0.3 M; 2) 0.45 M; 3) 0.6 M; 4) 0.88 M.

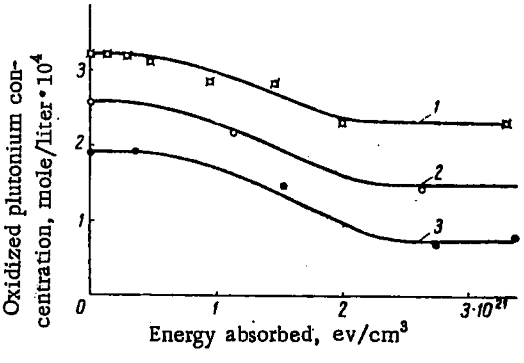

Fig. 5. The effect of radiation on the valence state of plutonium in solutions of 0.3 N HNO_3 and 0.45 M $UO_2(NO_3)_2$ at various initial concentrations of oxidized plutonium. 1) $3.3 \cdot 10^{-4}$ M; 2) $2.6 \cdot 10^{-4}$ M; 3) $1.8 \cdot 10^{-4}$ M.

The plutonium reduction curves are given in Fig. 4. The initial solutions contained plutonium wholly in the oxidized form.

The curves for solutions of intermediate $UO_2(NO_3)_2$ concentrations were of a complicated character. At concentrations of 0.45 and 0.6 M, reduction of plutonium was observed only after the absorption of a definite energy dose and did not proceed to the end but to a definite stationary state. The reduction of plutonium began earlier and proceeded in higher yield the higher the $UO_2(NO_3)_2$ concentration. In a solution of 0.45 M $UO_2(NO_3)_2$ plutonium was reduced at approximately $5 \cdot 10^{20}$ ev/cm^3, and the reduction yield, calculated from the tangent at the inflection point of the curve, equals approximately 0.002 ion/100 ev, and at a 0.6 M concentration the reduction began after the absorption of approximately $2 \cdot 10^{20}$ ev/cm^3 and proceeded with a yield of 0.02 ion/100 ev.

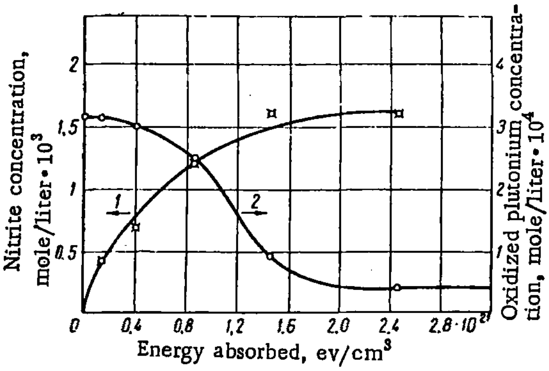

Fig. 6. The relation of the concentration of nitrite formed (1) and oxidized plutonium (2) to the radiation dose in a 0.3 N HNO_3 and 0.6 M $UO_2(NO_3)_2$ solution. The total plutonium concentration was $3.2 \cdot 10^{-4}$ mole/liter.

The degree of plutonium reduction increased with an increase in the $UO_2(NO_3)_2$ concentration. However, the ratio of oxidized and reduced forms in the stationary state could be different even at the same $UO_2(NO_3)_2$ concentration, if the starting concentrations of the oxidized form were different. This may be seen from Fig. 5, using as an example solutions with a 0.45 M content of $UO_2(NO_3)_2$. In the initial solution all the plutonium was in the oxidized form.

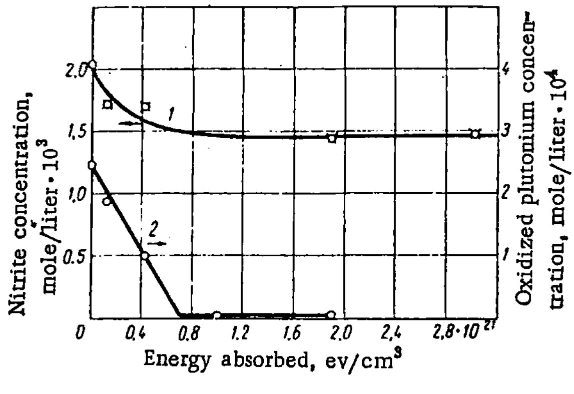

Fig. 7. The relation of nitrite (1) and oxidized plutonium (2) concentrations to radiation dose in a solution of 0.3 N HNO_3, 0.6 M $UO_2(NO_3)_2$ and $2.1 \cdot 10^{-3}$ M $NaNO_3$. The total plutonium concentration was $2.5 \cdot 10^{-4}$ mole/liter.

Besides determining the valence forms of plutonium, the irradiated solutions were analyzed for nitrite content, which was formed due to the radiation. It was interesting to compare the nitrite accumulation with the behavior of the plutonium in the same solutions. Figure 6 gives the corresponding curves for a solution containing 0.6 M $UO_2(NO_3)_2$. Noticeable reduction of oxidized plutonium started only after the accumulation of a certain nitrite concentration in the solution (approximately $5 \cdot 10^{-4}$ mole/liter) and proceeded only to a constant value for the nitrite concentration.

The relation between plutonium reduction and the change in nitrite concentration under the effect of radiation was observed also in the case when, before irradiation, nitrite was introduced into the solution at a concentration higher than its stationary value in this system (Fig. 7).

Solutions of $UO_2(NO_3)_2$ and $K_2Cr_2O_7$ in 0.3 N HNO_3. As is known, potassium dichromate is capable of oxidizing reduced plutonium to a hexavalent state. This nonradiation effect was taken into account when calculating the initial yield of the radiation oxidation of plutonium.

On introducing $K_2Cr_2O_7$ into the solutions investigated above, in all cases plutonium oxidation and potassium dichromate reduction was observed from the beginning of the irradiation. However, if oxidation occurred without potassium dichromate, its yield rose.

When the $UO_2(NO_3)_2$ concentration was not greater than 0.3 M, the plutonium, oxidized at the start of the irradiation, remained in an oxidized state up to a dose of $4.2 \cdot 10^{21}$ ev/cm^3. The reduction of plutonium was observed in solutions with higher uranyl nitrate concentrations and energy absorptions greater than a dose of $1.2 \cdot 10^{21}$ ev/cm^3.

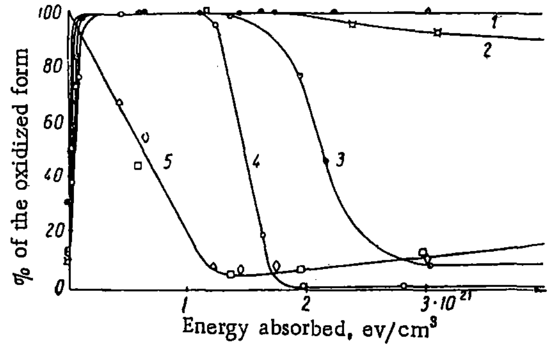

Fig. 8. The effect of radiation on the valence state of plutonium in solutions of 0.3 N HNO_3 and 0.1 N $K_2Cr_2O_7$, containing $UO_2(NO_3)_2$. 1) 0.3 M; 2) 0.45 M; 3) 0.6 M; 4) 0.88 M; 5) disappearance curve for $K_2Cr_2O_7$: ○) 0.3 M $UO_2(NO_3)_2$; △) 0.6 M; □) 0.88 M.

The reduction curves (Fig. 8) are very similar to the curves obtained without potassium dichromate. A dose equal to $1.2 \cdot 10^{21}$ ev/cm^3 corresponded to almost complete disappearance of hexavalent chromium (Curve 5), whose concentration was determined polarographically with a 1 N KOH background. The reduction yield for hexavalent chromium did not depend on the uranyl nitrate concentration. It is interesting to note that under the effect of radiation the hexavalent chromium concentration passed through a minimum after which it increased slowly.

On increasing the HNO_3 concentration from 0.3 to 1.5 N, after the absorption of a certain amount of energy, we observed the reduction of oxidized plutonium; however, as Curves 1 and 2 in Fig. 9 show, it began long before the complete disappearance of potassium dichromate. A similar phenomenon was observed on simultaneously increasing the $K_2Cr_2O_7$ concentration to 0.3 N and only the initial plutonium reduction was displaced.

Solutions with high HNO_3 and $K_2Cr_2O_7$ concentrations were irradiated by an electron beam with 0.8 Mev energy at a dose strength of approximately $5 \cdot 10^{17}$ ev/cm^3 • sec. The oxidized plutonium concentration was determined in these experiments by extraction with ethyl ether in the presence of ammonium nitrate.

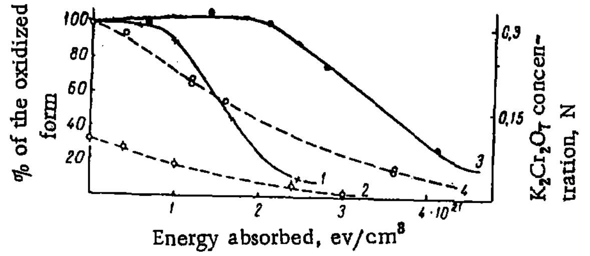

Fig. 9. The effect of radiation on the valence state of plutonium. 1) 1.5 N HNO_3, 0.1 N $K_2Cr_2O_7$ and 0.8 M $UO_2(NO_3)_2$; 3) 1.5 N HNO_3, 0.3 N $K_2Cr_2O_7$ and 0.8 M $UO_2(NO_3)_2$; reduction of $K_2Cr_2O_7$: 2) in solution 1; 4) in solution 3.

DISCUSSION

Some conclusions may be drawn from the results examined on the mechanism of the effect of x-radiation on the valence state of plutonium in nitric acid solutions. The direct effect of radiation on plutonium ions and the effect of its own α-radiation may be disregarded at low plutonium contents. All changes in the valence state of plutonium should be considered as the result of a reaction of plutonium ions with the radiolysis products of the medium, which were formed under the effect of external radiation.

Of the series of oxidation-reduction conversions of plutonium ions from Pu^{+3} to PuO_2^{++}, occurring due to radiation, the conversions Pu^{+3} - Pu^{+4} and PuO_2^{+} - PuO_2^{++} proceed most readily, as they only consist of the transfer of one electron. In contrast to this, the conversion at the Pu^{+4}-PuO_2^{+} stage or the reverse is more difficult as it requires the breaking or formation of the chemical bond of the oxygen-plutonium ion; the conversion can occur only under the effect of strong oxidants or reducing agents.

In the radiolysis of aqueous solutions of HNO_3 and $NaNO_3$, in which oxidation of plutonium ions was observed, in the absence of oxygen, various products were formed: H, OH, H_2, H_2O_2, HNO_2 and nitrogen oxides. Molecular hydrogen does not react with plutonium in the absence of platinum. Hydrogen peroxide and nitrous acid, as is known, are incapable of oxidizing tetravalent plutonium to the hexavalent state, as they reduce the latter and this reduction proceeds with disproportionation [7, 8], which takes place very slowly (days). These reactions cannot be used to explain the processes occurring under the effect of x-radiation for short periods of time (of the order of tenths of a minute). For the same reason the stable nitrogen oxides: NO, NO_2 and N_2O_4, formed in the solutions, are not taken into consideration.

Plutonium oxidation under the effect of radiation may be explained by a reaction involving OH radicals, by the scheme

$$Pu^{+4} + OH + H_2O \rightarrow PuO_2^{+} + 3H^{+}, \qquad (1)$$

as it is known that the OH radical is a strong oxidant in an acidic medium. Its normal potential for reduction to H_2O equals 2.8 v [9]. It is also possible that oxidation also occurs with the participation of unstable higher nitrogen oxides.

The radiation-chemical oxidation yield of plutonium was very low. The highest yield, obtained in 0.3 N HNO_3, was equal to approximately 0.05 ion/100 ev. The decrease in the initial yield with an increase in the NO_3^- ion concentration was, apparently, due to the capacity of reduced plutonium to form complexes with the nitrate ion [10-12]. The low reactivity of such a complex was confirmed with nonradiation experiments. It is known, for example, that the thermal oxidation of plutonium with nitric acid was considerably slowed down at high nitric acid or uranyl nitrate concentrations [13]. We observed a similar phenomenon in the nonradiation oxidation of plutonium with potassium dichromate. In this reaction the oxidation was retarded much more strongly by nitric acid than by nitrate salts at equal NO_3^- ion concentrations. The results of the radiation-chemical oxidation of plutonium are also related to this phenomenon. It was suppressed more effectively by nitric acid than by sodium nitrate.

The absence of reduction in these solutions could be explained by a possible reaction with atomic hydrogen

$$PuO_2^+ + H + 3H^+ \rightarrow Pu^{+4} + 2H_2O \tag{2}$$

being fully suppressed by the reaction

$$NO_3^- + H \rightarrow NO_2 + OH^- \tag{3}$$

with the existing ratio of plutonium ion and NO_3^- concentrations. As the experimental data given show, plutonium reduction in nitric acid solutions becomes possible if the solution contains $UO_2(NO_3)_2$.

Miller et al. [14] established that under the effect of ionizing radiation, pentavalent uranium formed in solutions of uranyl salts. The normal oxidation-reduction potential of the UO_2^{++}/UO_2^+ pair is equal to 0.05 v [15], i.e., close to that of hydrogen. On this basis the following scheme for plutonium reduction under the effect of UO_2^+ ions may be proposed:

$$PuO_2^+ + UO_2^+ + 4H^+ \rightarrow Pu^{+4} + UO_2^{++} + 2H_2O. \tag{4}$$

Due to the commensurable concentration of uranyl and nitrate ions the H radicals were distributed between them. With this, the reduction rate of the NO_3^- ion by the UO_2^+ ion was considerably less than its reduction by atomic hydrogen and as a result UO_2^+ accumulated to a concentration that was sufficient for plutonium reduction.

The changes observed in the valence state of plutonium in solutions containing $UO_2(NO_3)_2$ may be explained by the simultaneous occurrence, from the very beginning of irradiation, of two opposed processes – oxidation and reduction–with oxidation predominating up to 0.3 M $UO_2(NO_3)_2$ and reduction predominating after 0.6 M. At the start of irradiation the oxidation and reduction rates were equal in the range of $UO_2(NO_3)_2$ concentrations from 0.3 to 0.6 M. The start of plutonium reduction only after the absorption of a definite energy dose showed that it was possible only after certain radiation-chemical reactions in the system. Direct experiments, whose results are given graphically in Figs. 6 and 7, showed that plutonium reduction in suitable solutions was due to the presence of sufficient nitrous acid in them, formed due to radiation or introduced into the starting solution. However, its role in this process remains unclear. It is possible that it slows down plutonium oxidation as it is an acceptor of OH radicals.

Turning to solutions containing $K_2Cr_2O_7$, we may note that plutonium oxidation was observed in them at any $UO_2(NO_3)_2$ concentrations at the start of irradiation. The increase in yield due to $K_2Cr_2O_7$ may be caused by the oxidation of pentavalent uranium that was formed by $Cr_2O_7^{--}$ ions. After the reduction of all the potassium dichromate in solutions of 0.3 M HNO_3 and 0.1 N $K_2Cr_2O_7$ with varying $UO_2(NO_3)_2$ concentrations, the character of the changes in the valence state of plutonium was, in general, the same as in solutions not containing $K_2Cr_2O_7$.

Plutonium reduction in the presence of $K_2Cr_2O_7$, observed in solutions with 1.5 N HNO_3, apparently should be attributed to increased complex formation by the reduced plutonium at this acidity. This hypothesis requires additional experimental data for substantiation.

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