

光溶液化学反応過程の基礎研究

(平成4年度東工大-動燃共同研究報告書)

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動力炉・核燃料開発事業団

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光溶液化学反応過程の基礎研究

(平成4年度東工大―動燃共同研究報告書)¹⁾

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要旨

本報告は、平成4年度に東京工業大学 原子炉工学研究所の富安研究室と動燃事業団 先端技術開発室とで光化学研究関連について行った共同研究の成果報告書である。

今年度の研究は、Np(V)とU(V)の不均化反応における光励起効果および硝酸と亜硝酸のアクチノイド元素との反応における光照射効果を調べた。

その結果、Np(V)がNp(IV)とNp(VI)へ不均化反応する光励起効果は明確には確認できなかったが、Np(VI)への光照射効果は確認された。U(V)の不均化反応はこの原子価の存在寿命が短いため確認することができなかった。しかし、U(IV)からU(VI)への光照射効果は顕著であった。

また、硝酸溶液中での硝酸および亜硝酸によるアクチノイド元素の光励起反応効果は明確に判別できなかった。しかし、光照射効果は明確に確認された。

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- 1) 本報告は、東京工業大学と動力炉・核燃料開発事業団との契約により実施した業務の成果である。 契約番号：044F005
 - 2) 動燃事業団 核燃料技術開発部 先端技術開発室
 - 3) 東京工業大学 原子炉工学研究所

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1。共同研究实施担当

1. 共同研究実施担当

研究項目	主担当および担当者
(1) Np(V)の不均化反応における光励起効果	動燃事業団 先端技術開発室 和田幸男
(2) U(V)の不均化反応における光励起効果	東京工業大学 原子炉工学研究所 富安博
(3) 硝酸および亜硝酸とアクチノイド元素 の光励起効果	動燃事業団および東京工業大学

2。研究目的および成果概要

2. 研究目的および成果概要

2-1 Np(V)の不均化反応における光励起効果

(1) 目的:

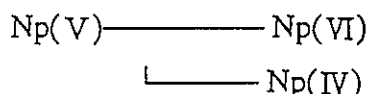
Np-237は約2X106年の半減期を有し、しかも使用済核燃料物質中の主要なアクチノイド元素のひとつである。そのため、Npを回収し再び核燃料としてU, Puと共に燃焼させる研究がなされている。しかし、Npは再処理工程の硝酸溶液中では、原子価IV, V, VI の状態をとり、しかもそれぞれが異なる溶媒抽出性を有する。そのため、化学試薬のみでそれらの原子価を特定の価数に調整することは難しい。

そこで、光量子効果を利用した原子価調整の可能性を評価する。特に本年度は不均化反応を起こすNp(V)の光化学反応挙動を実験的に調べる。

(2) 成果概要

Npの硝酸溶液にNp(V)の最大吸収波長である980nmの半導体レーザー光を照射し、その不均化反応挙動を調べた。その結果、

- ① 980nmの半導体レーザー光(10mW)の照射では、



の不均化反応は検出できなかった。これは、980nm光のエネルギー吸収では回転、振動励起準位のための量子効果で、酸化還元反応が生じる電子遷移励起のエネルギーレベルへの励起は生じなかったためと思われる。

- ② Np(IV)→Np(V)→Np(VI)の水銀ランプ光照射による光酸化反応が可能であることが、原理実証された。
- ③ ②の場合、400nm以上の光照射のみでは反応は進まず、硝酸光励起イオン種(*NO₃-)が光酸化反応に大きく寄与していることが証明された。

以上のことにより、Pu, Npの相互分離 (Pu(IV, VI) and Np(V))および共抽出(Pu(IV, VI) and Np(VI))に必要な原子価条件に、光化学調整が可能と判断される。

2-2 U(V)の不均化反応における光励起効果

(1) 目的：

Uの原子価はIV、V、VIの原子価を取り得るが各々の溶媒抽出性は溶媒側に抽出される性質を有する。U(IV)は酸化還元電位が低く、PuのPu(III)への還元剤として使用される。

U(V)は硝酸溶液中では不均化反応しU(IV)とU(VI)になるが、この反応の光照射一励起効果を調べ、分離または共抽出に係わる調整の可能性を検討する。

(2) 成果概要：

硝酸溶液中でのU(V)は不安定であり、光照射によるその不均化反応を今年度調べるとはできなかった。この測定には、高速分解スペクトロメータが必要でそのためのシステムの構築必要であった。

2-3 硝酸および亜硝酸とアクチノイド元素の光励起効果

(1) 目的：

再処理工程の工程液はすべてが硝酸溶液として流れている。そのため、硝酸およびその分解生成物の亜硝酸とアクチノイド元素との反応を把握することは、これらの元素の分離および共抽出に係わる原子価調整のために重要である。

特に今年度は、硝酸の光分解生成物の亜硝酸濃度と光照射強度及び硝酸濃度との関連、および亜硝酸存在下または亜硝酸がない状態でのアクチノイド元素の光酸化反応を調べる。

(2) 成果概要：

- ① 硝酸の光分解、亜硝酸生成は硝酸濃度には比例せず、0.1M HNO₃のときが最も亜硝酸生成濃度が高かった。硝酸濃度が1M→3Mと高くなるにしたがってその濃度は低くなった。
- ② 亜硝酸によるPuの光酸化反応は亜硝酸濃度による変化は確認できなかったが、硝酸濃度の増加に従いその反応速度は増加した。このことから、Puの光酸化反応は亜硝酸によるものではなく、光励起硝酸、*NO₃⁻、によるものと判断された。
- ③ Np(V)→Np(VI)の光酸化反応が確認され、その反応速度は硝酸濃度、光照射強度に比例した。このことから、この反応も亜硝酸によるものではなく、光励起硝酸、*NO₃⁻、によるものと判断された。

3。研究成果

3-1 Np(V)の不均化反応における光励起効果

- ① 硝酸溶液中のNp各原子価の吸光スペクトルデータ

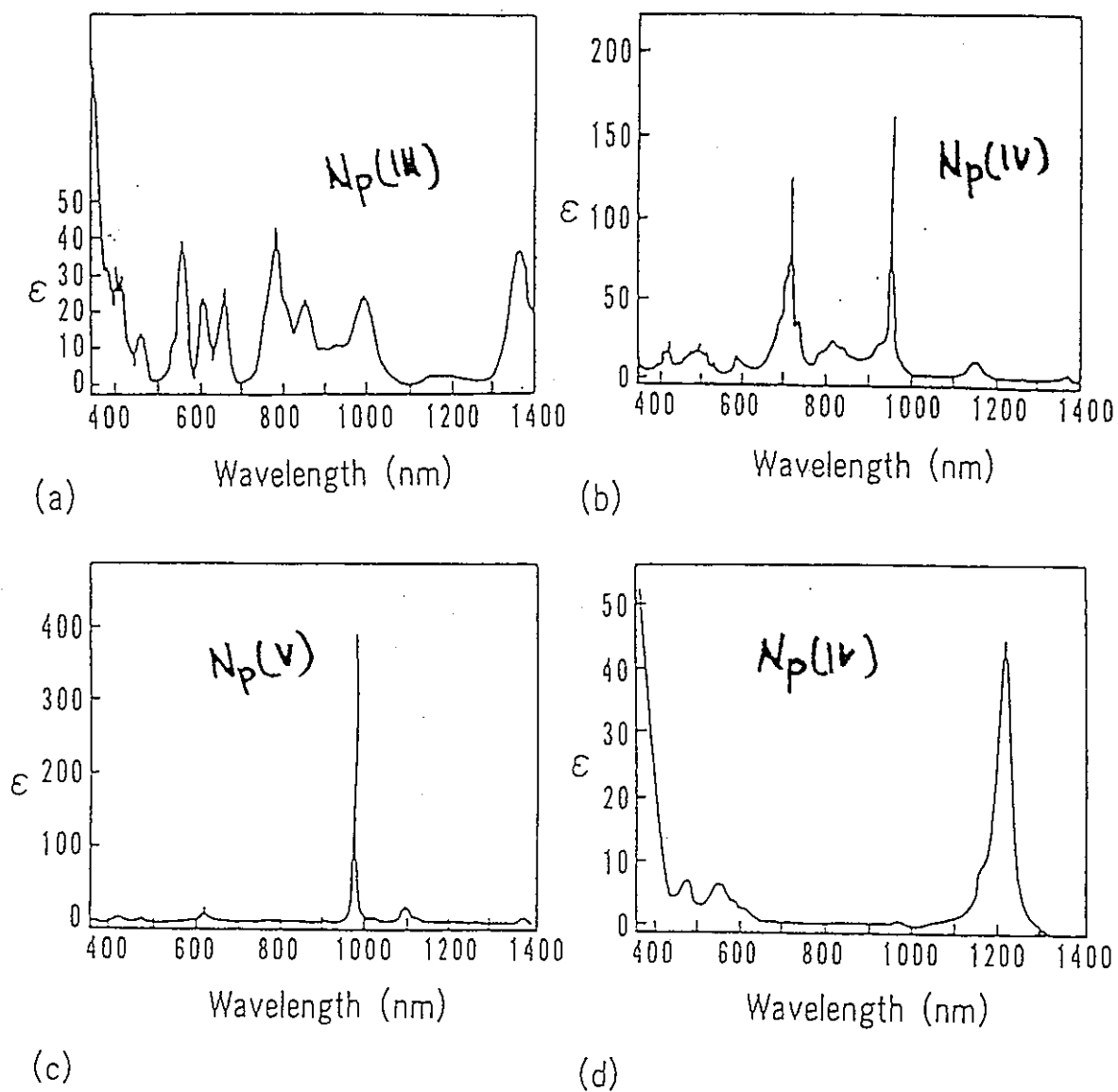
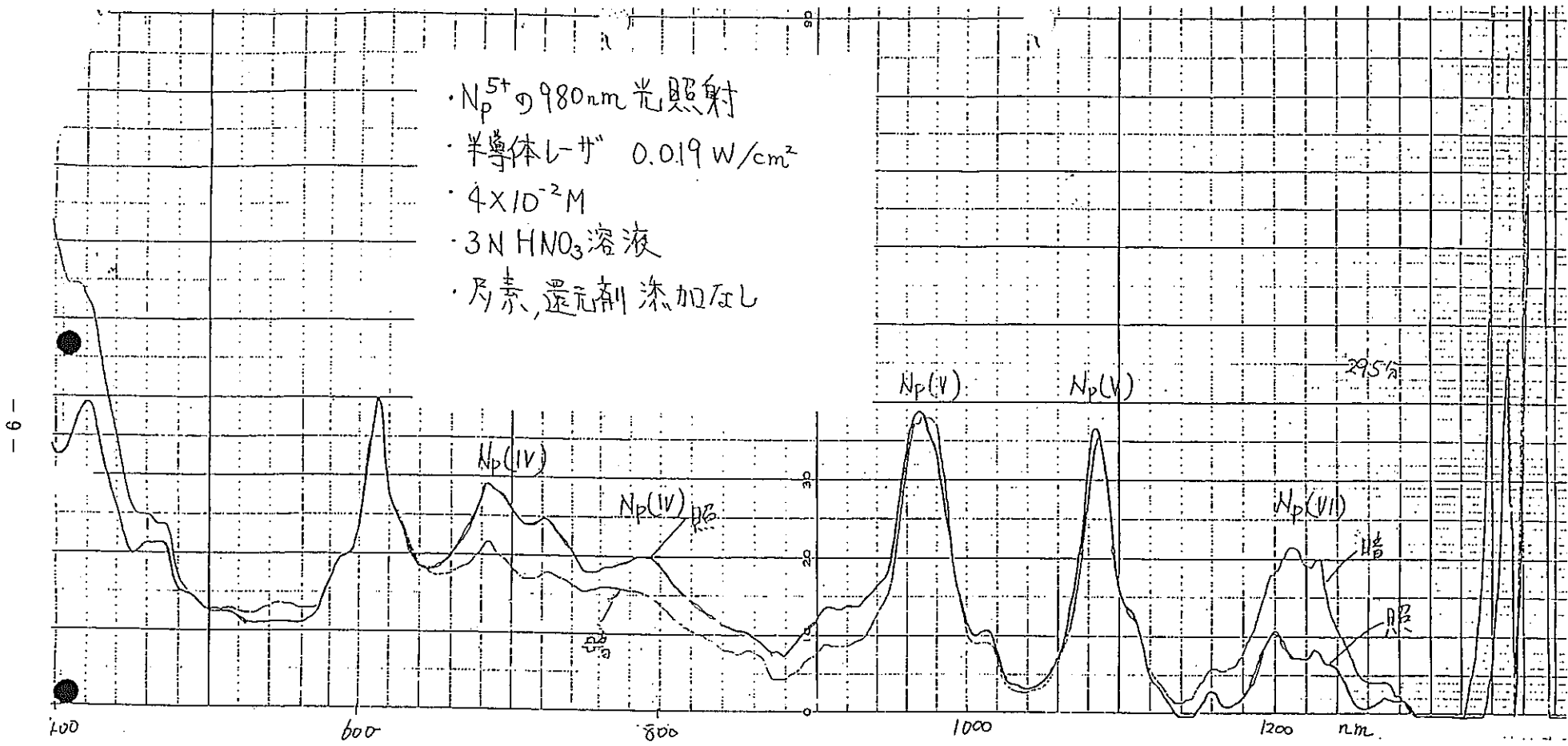
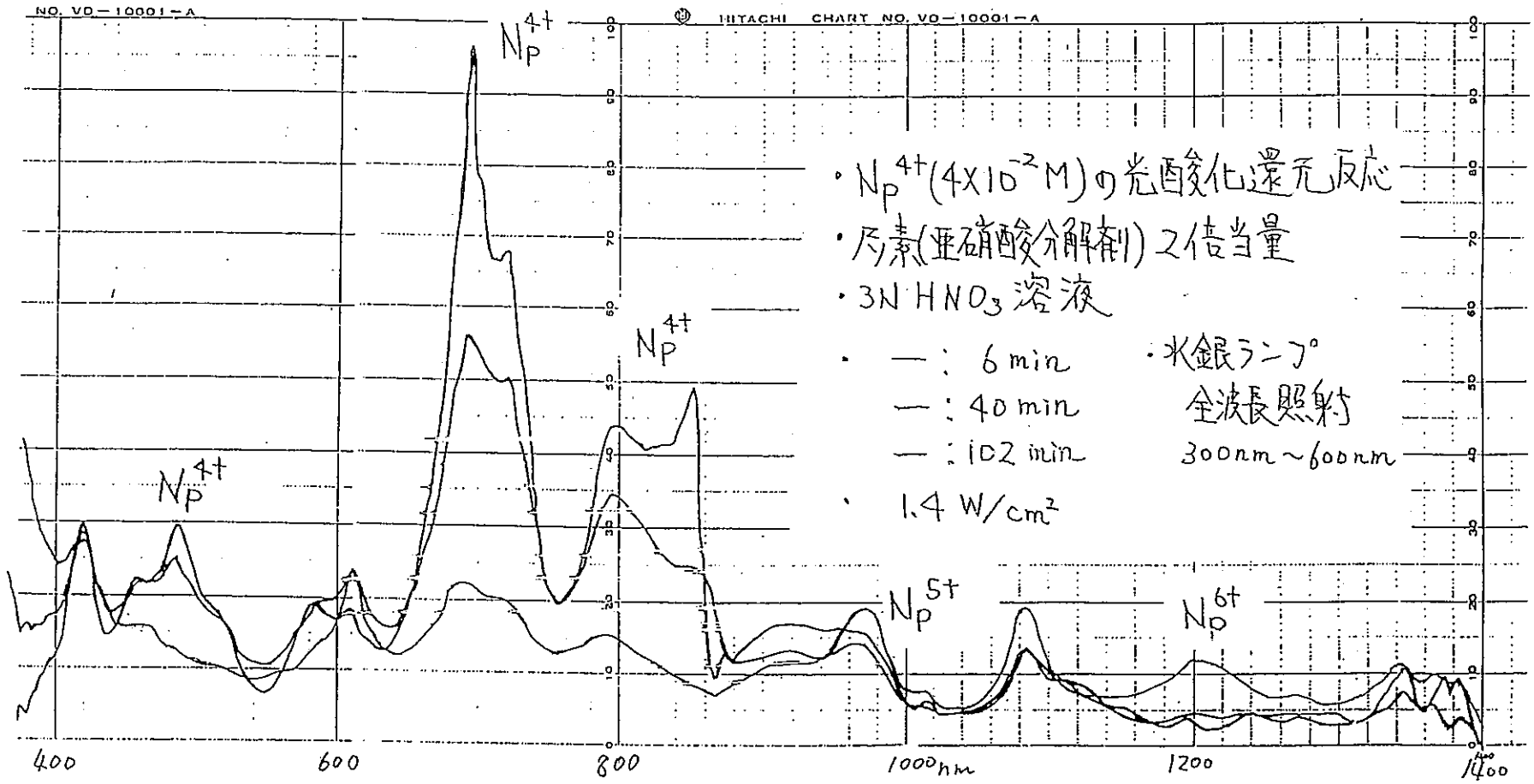
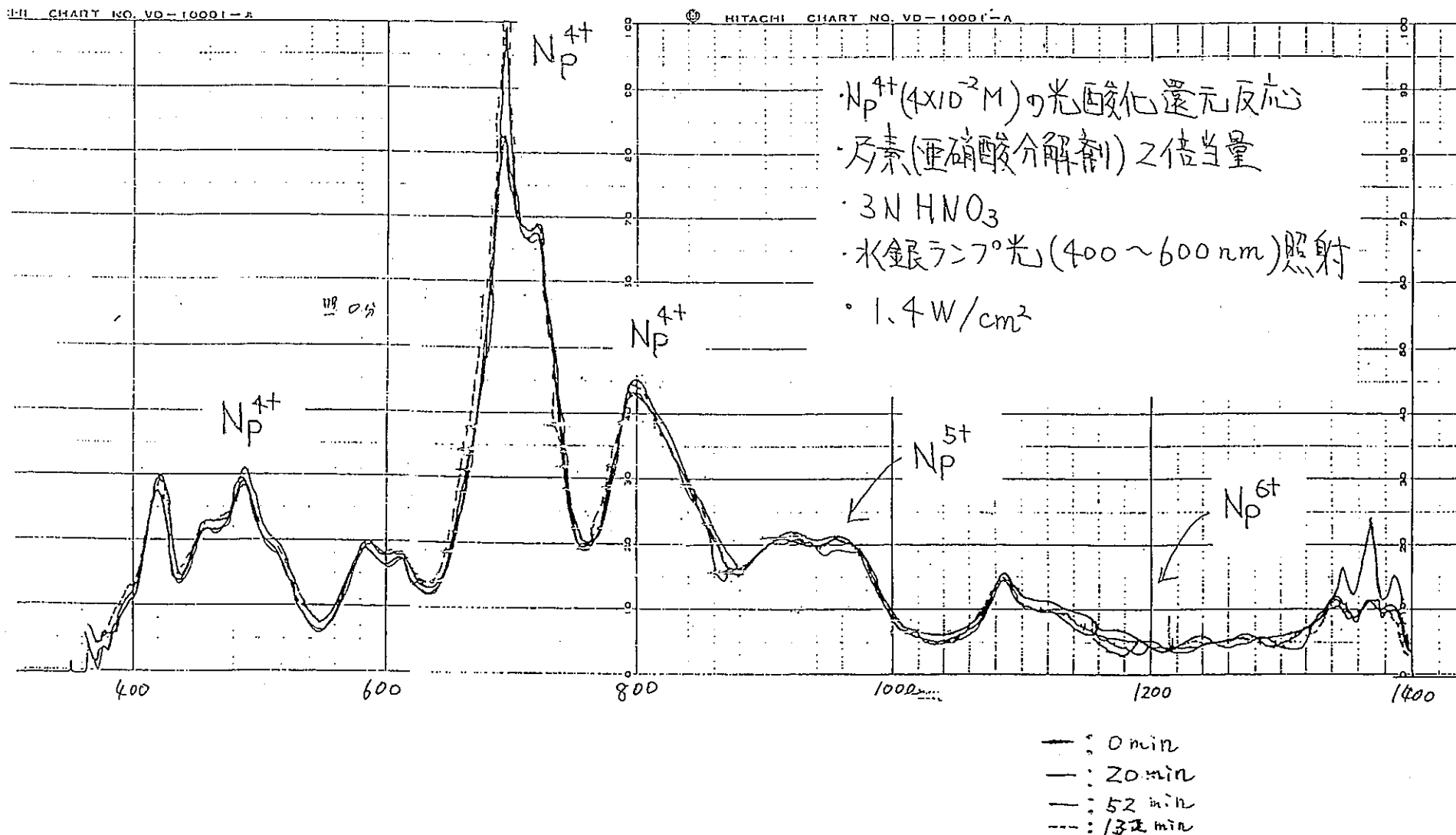


Fig.3 The absorption spectra of neptunium ions in 2 M perchloric acid solution: (a) Np(III); (b) Np(IV); (c) Np(V); (d) Np(VI). 8)



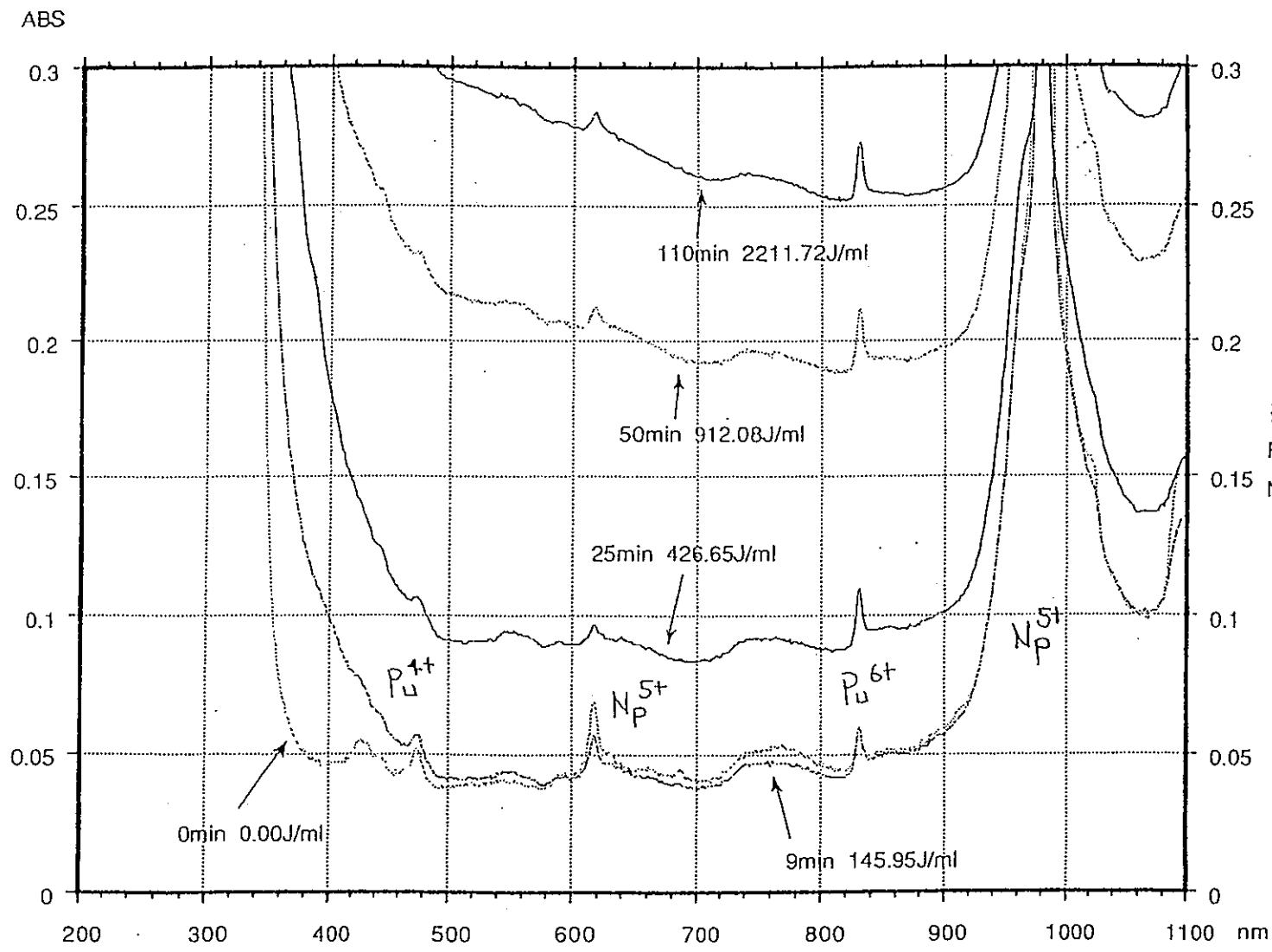
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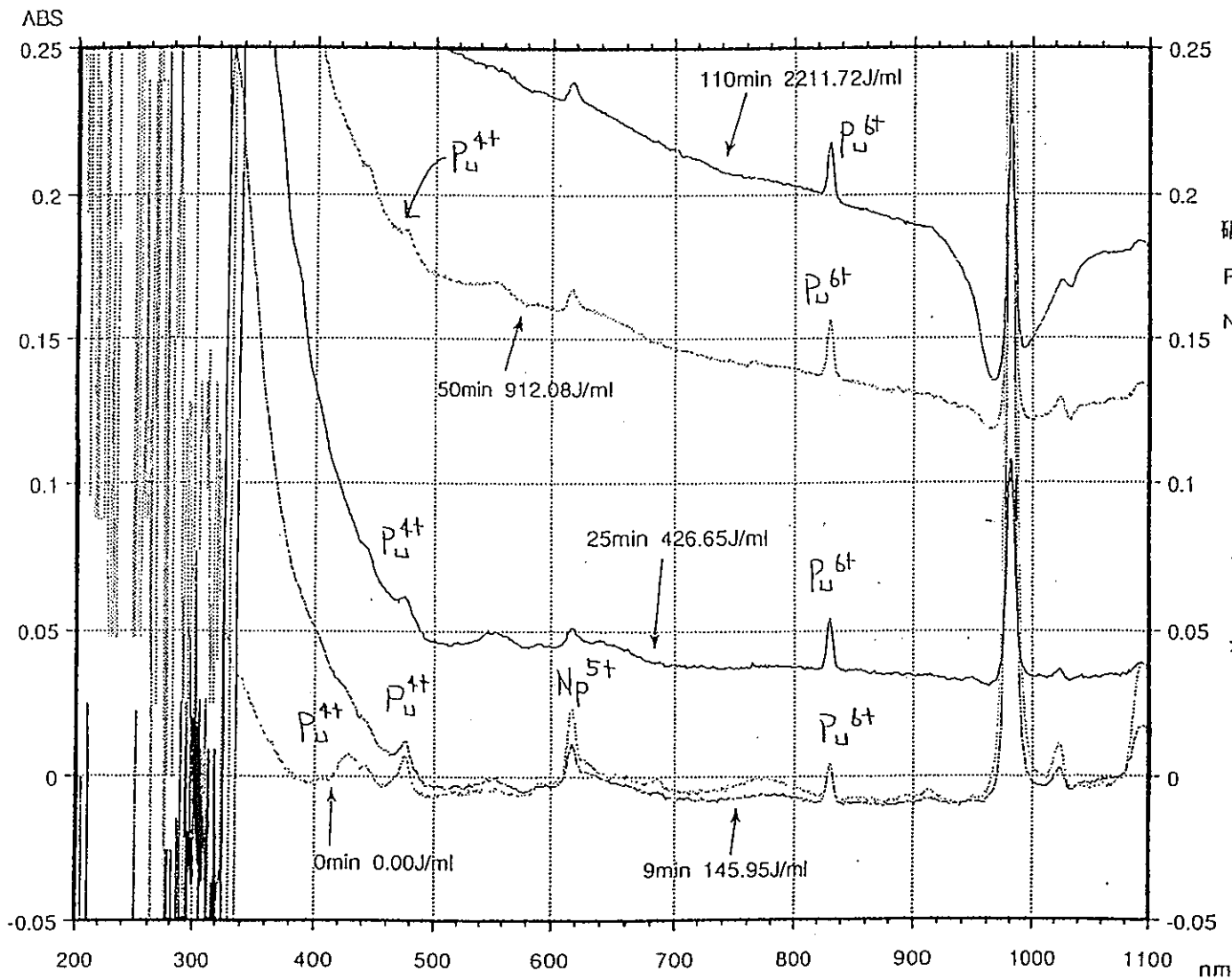


Pu, Np 混合系の
水銀ランプ光(全波長)
照射(0.5 W/cm²)

硝酸濃度 : 3 N
Pu 濃度 : 1E-04 M
Np 濃度 : 1E-03 M



H5-Light-04

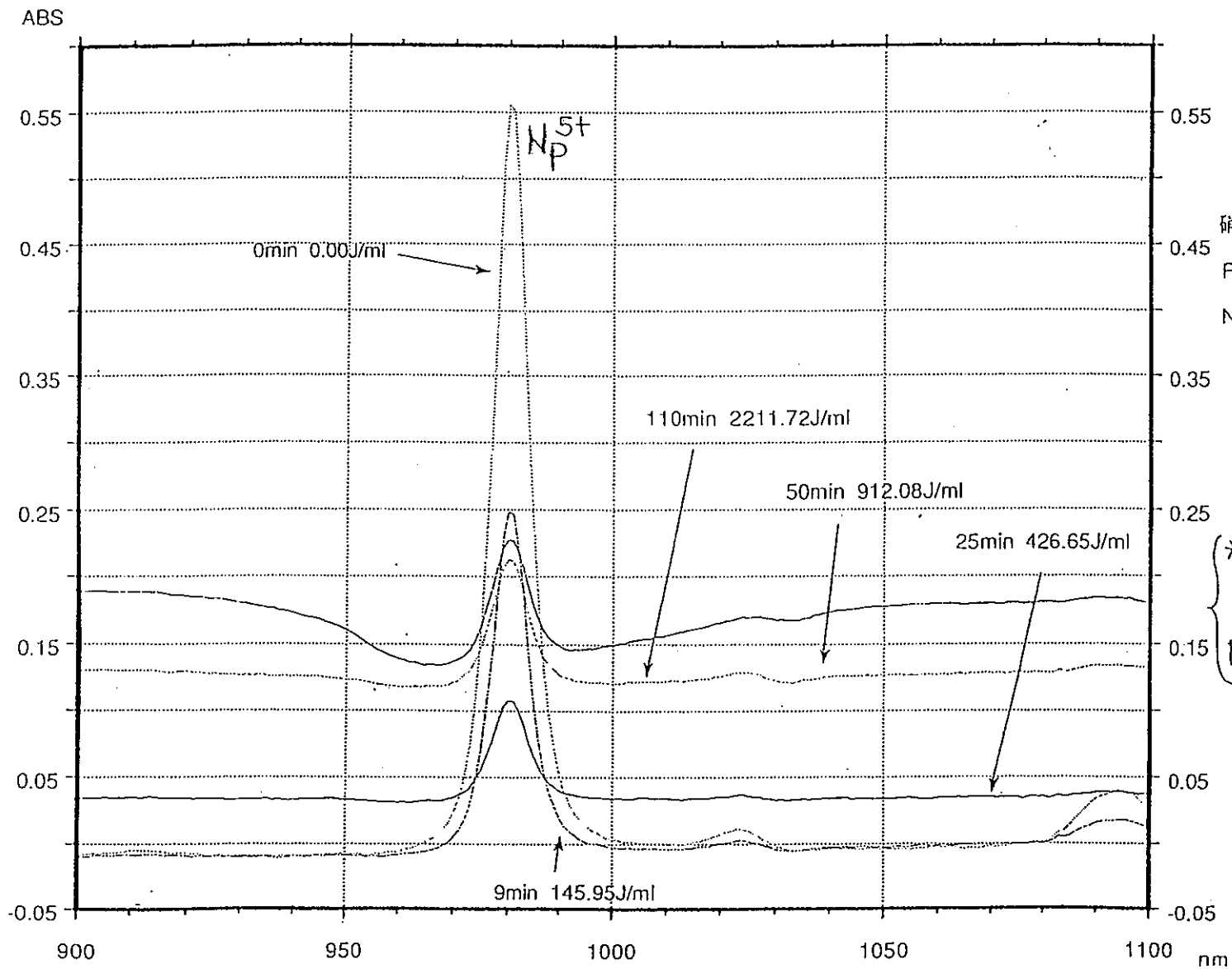


硝酸濃度 : 3N
 Pu濃度 : $1E-04$ M
 Np濃度 : $1E-03$ M

Pu, Np 混合系の
 水銀ランプ光(全波長)
 照射($0.5W/cm^2$)

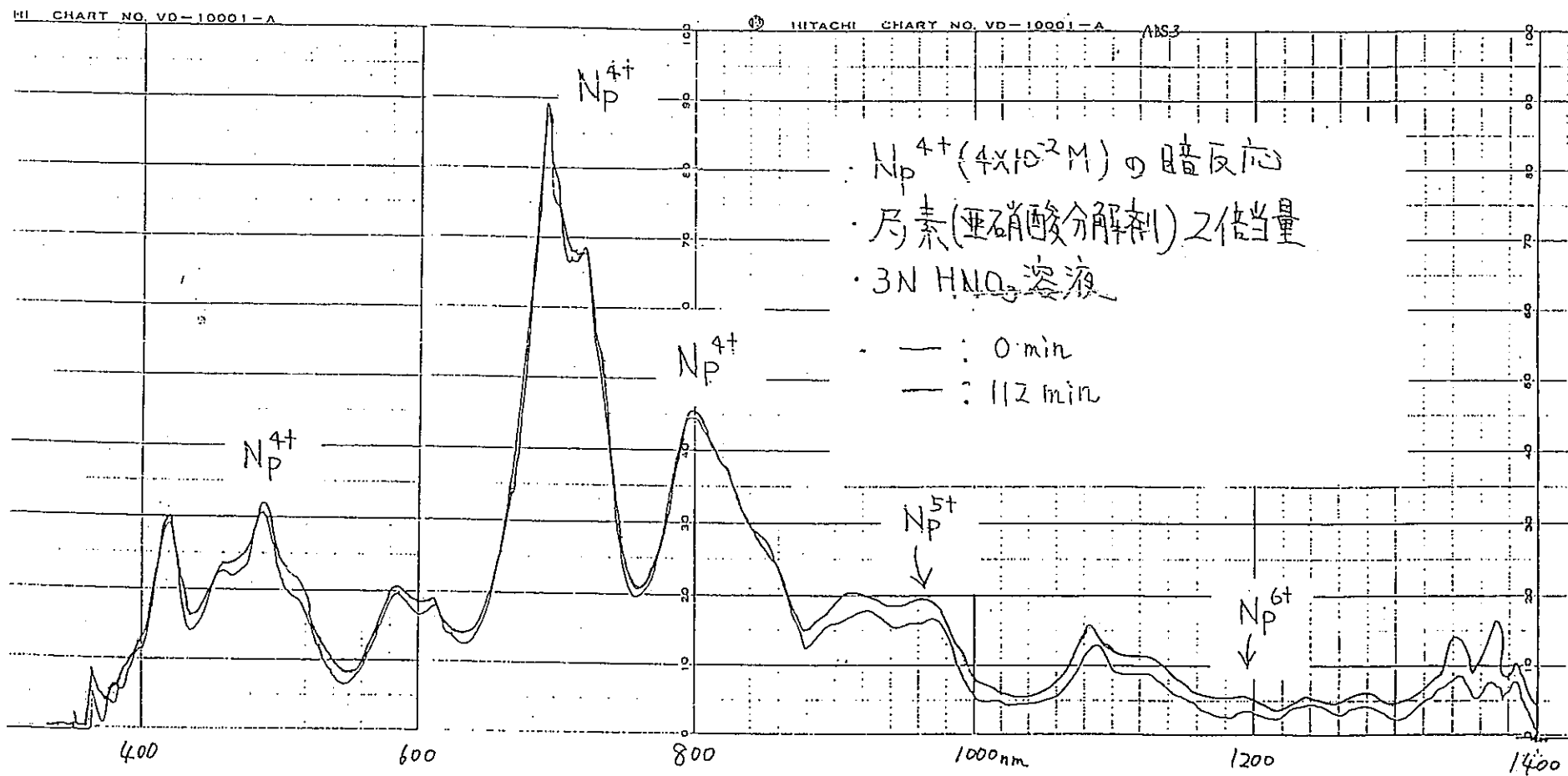
H5-Light-04

硝酸吸収スペクトル補正済



H5-Light-04

硝酸吸収スペクトル補正済



3-1 Np(V)の不均化反応における光励起効果

② Basic Photochemical Study of Plutonium and Neptunium

BASIC PHOTOCHEMICAL STUDY OF PLUTONIUM AND NEPTUNIUM

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ABSTRACT

Photochemical technologies are generally expected that it will contribute to advanced nuclear fuel reprocessing process technologies by means of using selective excitation of objective elements with photon energy and following redox reactions in solution.

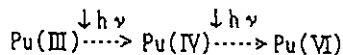
In this work, as the beginning of the basic photochemical studies in the field of nuclear fuel reprocessing, feasibility studies of separation between Pu and Np by using photo-oxidization, reduction reactions have been carried out. The results indicate that there is a possibility of photochemically induced valency adjustment to separate Np from Pu in nitric acid solution.

INTRODUCTION

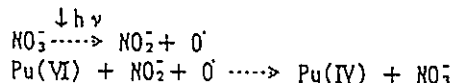
In the conventional nuclear fuel reprocessing technologies, chemical redox reagents have been used to adjust valencies of U, Pu. For example, U(IV) produced by electrolytic reduction or hydroxylamine(HAN) and sodium nitrite are used to adjust Pu valencies to Pu(III) and Pu(IV) respectively. However, these chemical reagents cause secondary waste solution.

The several studies of redox reaction using photochemical technologies for nuclear fuel solution as substitutes for these reagents have been reported. In these reports, there are two kinds of studies which are basic photochemical studies of U, Pu and Np^{1,2,3)} and its application studies to nuclear fuel reprocessing^{4,5,6)}. The applicabilities of the photochemical technologies have been confirmed from the these

studies. However, photo-redox reactions are generally complicated and such as complex reactions which are consist of direct reactions



and also indirect reactions,



are simultaneously occurred by photon energy.

Therefore, basic data concerning a variation of the oxidization-reduction potential by photon-excitation, the rate of reaction and other fundamental theories have to be accumulated to control the valencies of objective elements arbitrarily.

In this work, the several basic tests of light exposure for Pu and Np in nitric acid solution were carried out to evaluate the photochemical behaviors of their valencies. The valencies of Pu and Np in nitric acid solution are ordinarily Pu(III), Pu(IV), Pu(VI) and Np(IV), Np(V), Np(VI).

The distribution coefficients of their valencies between 30% TBP/dodecane and nitric acid are shown in Fig. 1^{7,8)}. As shown in this Fig., Pu(IV), and Np(VI) are easily extracted to TBP. However, Pu(III) and Np(V) which are not shown in it are scarcely extracted and their distribution coefficients are about 10⁻¹ and 10⁻² respectively. Therefore, if their valencies can be controlled into the following like conditions ① Pu(IV)-Np(V) or ② Pu(III)-Np(VI), their elements are effectively mutually separated.

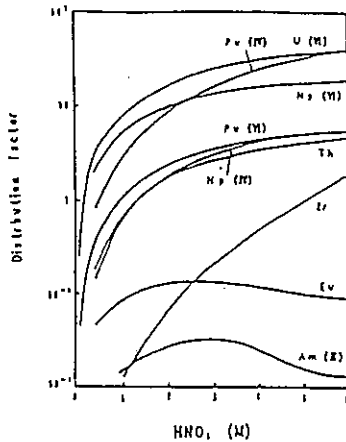


Fig. 1 Plutonium and Neptunium distribution coefficient between 10%TBP/dodecane and nitric acid

EXPERIMENTAL CONDISION

A : Preparation of Test Sample

The concentrations of Pu and Np test nitric acid solutions were adjusted to 1×10^{-4} mol and 1×10^{-3} mol respectively and they were mixed. The purity of α -radioactivity of Np-237 in Np test sample solution was 99.8 %.

Pu test sample solution were prepared by dissolving NBS-949 Pu metal of which abundance ratio of Pu-239 and Pu-241 were about 97 atom % and 0.065 atom % respectively. Therefore, the α -activity contribution of Am-241 compared to the total α -activity of Pu is lower than 1 %.

The valencies of Pu and Np test mixed solution were completely adjusted to Pu(III) and Np(V) with hydroxylamine(NH₂OH) and hydrazine(N₂H₄) as shown in Fig.2 which was the result analyzed by the extraction chromatographic method.

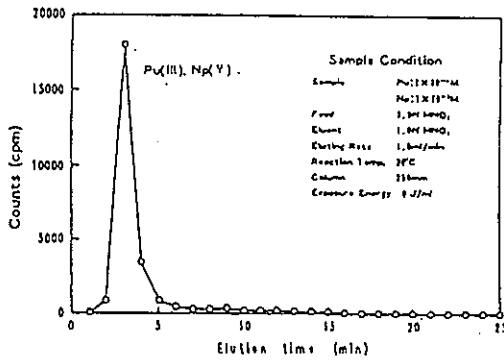


Fig. 2 Valency analysis of mixed solution with Pu and Np by extraction chromatograph

B : Test Instrument

The light exposure instrument system which was used in this work is shown in Fig.3. This system consists of the Hg lamp light source and the part of a sample cell with a temperature stabilizer and a mixing stirrer to stabilize the temperature of the sample solution and to homogenize it during light exposure.

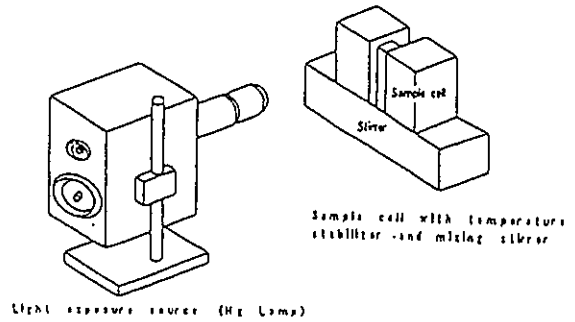


Fig. 3 Outline of instrument of light exposure test

C : Analytical Method

C-1 : Extraction Chromatograph

As a conventional technique of the valency analysis of Pu and Np, colorimetry method has been usually used. However, if concentration of an objective element in a sample solution is less than 10^{-4} mol, the method is not generally applicable.

Therefore, the new method which consisted of the extraction chromatograph and the radioactivity analysis of an each valency fraction was used.

First of all, a sample solution is injected into the extraction chromatograph column which is filled with Gas-Chrom Q made by Applied Science Corp. and impregnated with TBP. Each valency fraction of Pu and Np is obtained according to specific retention time with the fraction collector.

Then, α -radioactivity of the each fraction is measured by α counting system with ZnS detector. Consequently, the extraction chromatograph as shown in Fig.4 is obtained. The horizontal and vertical axis show an elution time and α -radioactivity(CPK) respectively.

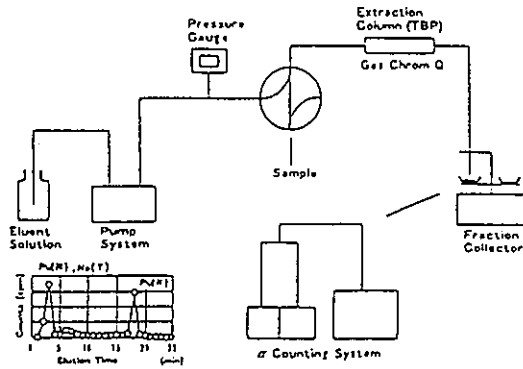


Fig. 4 Schematic diagram of extraction chromatography setup

Fig.5 shows the result of the extraction chromatographic analysis of the Pu,Np mixed solution which contains Pu(III),Pu(IV),Pu(VI) and Np(V). Each valency is eluted in opposite order of an adsorption tendency with TBP.

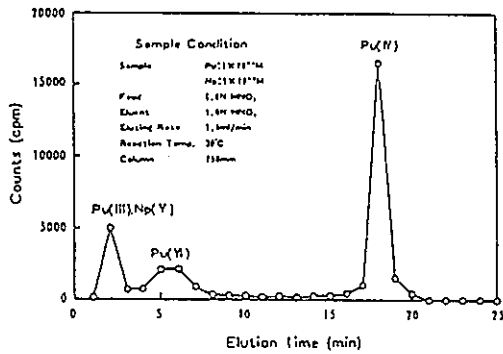


Fig. 5 Valency analysis of mixed solution with Pu and Np by extraction chromatograph

C-2 : Pulse Height Analysis

The fraction of Pu(III) and Np(V) mixed solution of which valencies are simultaneously eluted as shown in Fig.5 is analyzed by α spectrometry to distinguish between Pu(III) and Np(V). Fig.6 shows the result of α spectrometric analysis. As shown in this Fig.,Pu and Np are distinguished according to α ray energy from their nuclides and the mixture ratio is quantitatively determined.

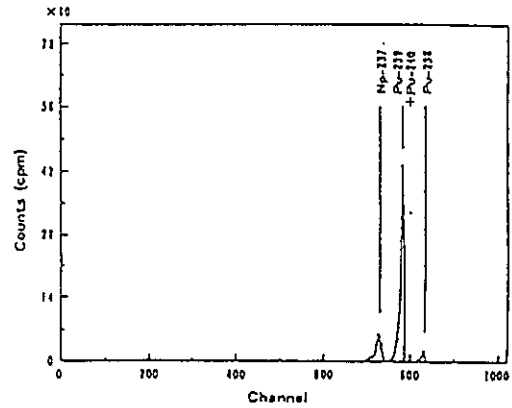


Fig. 6 Pulse height analysis of α -ray from Pu and Np

RESULTS AND DISCUSSION

Fig.7 shows the step flow of the light exposure tests for Pu and Np in this work. First,the initial valencies condition of Pu,Np mixed sample was adjusted to Pu(III),Np(V) and their concentrations were 1×10^{-4} mol, 1×10^{-3} mol respectively .

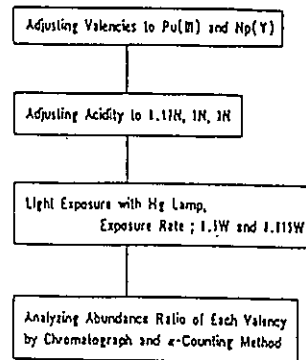


Fig. 7 Step flow of light exposure tests

At the second step,the acidities of several aliquots of the initial sample were adjusted to about 0.2N,1N and 3N.

Next,the light exposure tests were carried out with the exposure rates of 0.5W and 0.015W using the Hg lamp.

At the final step,the radioactive analyses of the each fraction from the extraction chromatograph column were carried out. As shown in this fig.,the parameters of these tests are the acidity of the sample solution and the rate of light exposure.

Fig.8 shows the results of the light exposure tests under the conditions of which the parameters are 3N nitric acid and 0.5W exposure rate.

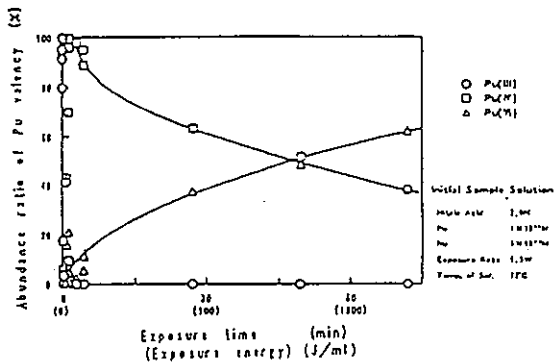


Fig. 8 Redox reaction of Pu by light exposure

The horizontal and the vertical axis in this Fig. show the exposure time(energy) and the abundance ratio(%) of the each valency in the element respectively.

This result indicates that 0.5W of the light exposure rate was too strong so that Pu(III) momentarily decreased until about zero percent level and Pu(IV) oppositely momentarily increased. After several minutes, Pu(IV) gradually decreased and on the contrary, Pu(VI) gradually increased. In other words, it shows that Pu(III) was momentarily oxidized to Pu(IV) and seemingly, Pu(IV) was gradually oxidized to Pu(VI) under such as the conditions due to the equilibrium of the oxidation-reduction reaction.

Fig.9,10,11 show the results of the light exposure tests under the conditions of the light exposure rates; 0.015W and of the acidities; 0.17N, 1N, 3N. These Fig. show that Pu(III) was more slowly oxidized to Pu(IV) than at the case of Fig.8 and the rates of these oxidizations became faster according to the increase in acidity.

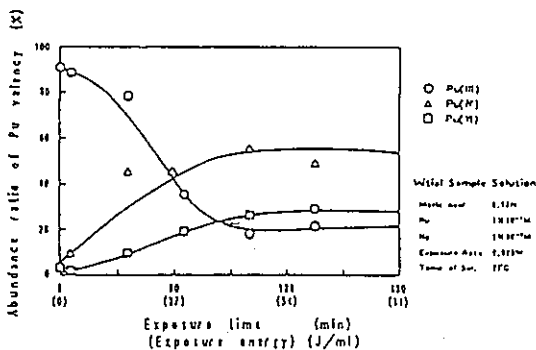


Fig. 9 Redox reaction of Pu by light exposure

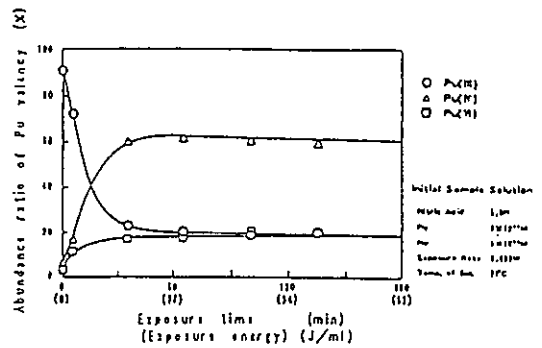


Fig. 10 Redox reaction of Pu by light exposure

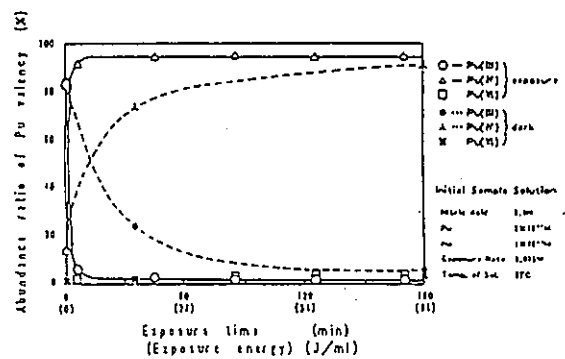


Fig. 11 Redox reaction of Pu by light exposure

Particularly, the results of Fig.11 were characteristic in the redox reaction because Pu(III) was momentarily completely oxidized to Pu(IV). Furthermore, there was little Pu(III) and Pu(VI) issued from the oxidization of Pu(IV) and the equilibrium state reached within about 10 minutes after the beginning of light exposure.

The result of the dark test without light exposure was also shown in Fig.11. This result shows that Pu(III) was very slowly oxidized to Pu(IV) and it took about two hours until the equilibrium state.

Fig.12 shows the result of the extraction chromatographic analysis of the sample at the equilibrium state when the exposure energy was 56 J/ml in Fig.11. From this result, it was also found that the valencies of Pu were controlled to Pu(IV) and there was little Pu(III) and Pu(VI).

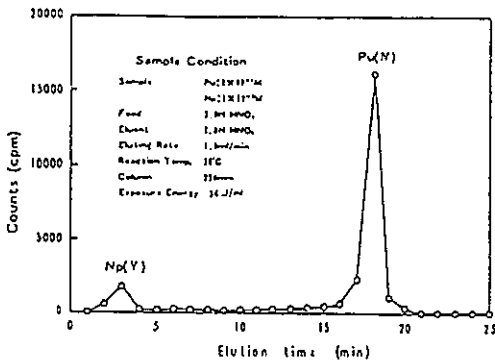


Fig. 12 Valency analysis of mixed solution with Pu and Np by extraction chromatograph

Then, this Fig. shows that Np(V) in the initial sample was not oxidized and also was not reduced by light exposure under these conditions.

Such as controlled valencies condition, Pu(IV) and Np(V), is most suitable for the separation between Pu and Np.

These photochemical behaviors were caused by the direct excitation with photon energy for an objective ion, redox reactions with the photolytic products such as HNO_2 , NO , from HNO_3 , and other excited species.

The supposed theories for these results should be discussed in several aspects of the standard electrode potentials for all of coexisting element species, excitation level by photon energy and wave length characteristic of exposure light, etc on the basis of the data obtained from furthermore detail photochemical tests.

CONCLUSION AND R&D PLAN IN THE NEXT STEP

From this work, following conclusions were obtained

◆ Results of Photochemical Behaviors of Pu and Np

- ① Pu · Pu(III) is oxidized to Pu(IV) and until Pu(VI) by light exposure.
 - As to the oxidization of Pu(III)→Pu(IV), the more the acidity of nitric acid solution increase, the more the reaction is easily proceed in the range of 0.1N→3N HNO_3 .
 - On the other hand, in the case of the reaction of Pu(IV)→Pu(VI), the more the acidity decrease, the more the generation rate of Pu(VI) increase in the range of 0.1N→3N HNO_3 .

- ② Np · Np(V) is not oxidized to Np(VI) and also is not reduced to Np(IV) by light exposure in HNO_3 of 0.1N→3N.

◆ Conclusion

- It is defined that there is a possibility of removal of Np from Pu, Np mixed solution which is adjusted to Np(V) and Pu(III) by using photochemical reactions with the adequate rate of light exposure and the adequate acidity of HNO_3 .

From above the discussions and conclusions, following R&D of the next step are planned.

◆ R&D Plan in The Next Step

- The continued photochemical studies for the removal technologies of several percent of Np contained in Pu production solution simulating the reprocessing process.
- The studies of photochemical behaviors of U, Pu and Np in a mixed nitric acid solution.
- The studies of selective separation technologies of objective elements (U, Pu, TRU and FP) by using photochemical techniques with a selective wave length of laser.
- The development of the quantitative analysis method of trace amounts of an objective element by the laser-induced thermal lensing spectroscopy.

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3-2 U(V)の不均化反応における 光励起効果

① Laser Enhanced Reductions of Uranium(VI) Ion in Aqueous Phosphoric
Acid Solutions

LASER ENHANCED REDUCTIONS OF URANIUM(VI) ION
IN AQUEOUS PHOSPHORIC ACID SOLUTIONS

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ABSTRACT

Photochemical reactions of U(VI) ions with inorganic anions (I^- , Br^- , Cl^- , NCS^-) and organic compounds (1-hexene, cyclohexene, pyridine) in phosphoric acid were studied for the purpose of finding an efficient method of adjusting the oxidation states of uranium ions in nuclear fuel reprocessing. The formation of U(IV) was observed in the photo-reactions with I^- , Br^- and NCS^- , but not with Cl^- . The yield of U(IV) increased in the order, $Br^- < NCS^- < I^-$. This order was the same as the quenching rate constants of the excited U(VI) ions with these anions, and the reverse of their standard redox potentials. The rates of the formation of U(IV) in the presence of Br^- were measured spectrophotometrically. It was found that the rate equation was first order in both $[U(VI)]$ and $[Br^-]$. The results were reasonably interpreted by a series of reaction processes involving U(V) and Br radical. With organic molecules, 1-hexene, cyclohexene, and pyridine, the formation of U(IV) were observed. The yield of U(IV) increased in the order pyridine $<$ 1-hexene $<$ cyclohexene. This order is the reverse of their vertical ionization potentials, suggesting an electron

transfer mechanism between these organic molecules and excited U(VI).

INTRODUCTION

The application of photo-reaction to the adjustment of oxidation states of uranium ions in nuclear fuel reprocessing has become of interest, because redox reactions of metal ions are effectively catalyzed by photo-irradiation. In spite of a number of studies on photo-reactions of U(VI)(refs. 1-7), little has been known with respect to the photo-reaction of U(VI) by inorganic anions. Schneider first studied quantitatively the photo-reactions between U(VI) and I^- ion, and proposed an energy transfer mechanism from excited uranyl ions to I^- ions for the primary process of quenching(ref. 1). Later, Weiss interpreted Schneider's results in terms of an electron transfer mechanism involving U(V) and I radical(ref. 2). Burrows et al. studied the photo-oxidation of inorganic anions with U(VI) by the flash photolysis method(ref. 3). They observed directly decay traces of transient radical anions produced by the photo-reaction between U(VI) and these anions. Matsushima measured

the luminescence intensity of U(VI) in aqueous solutions containing inorganic anions and reported that the quenching rate constants of excited U(VI) correlate with the reduction potentials of quenchers(ref. 6). Although I^- ion has been known to be photo-oxidized by U(VI) in aqueous solutions(refs. 1-5), the formation of U(IV) is not clearly established. However, we found that U(VI) is photo-reduced to U(IV) by various halogen and pseudohalogen anions in the phosphoric acid solutions under irradiation of nitrogen laser.

The present paper deals with the kinetics of the photo-reduction of U(VI) by halogen ions. Moreover, in order to investigate the reactivity of excited U(VI) in phosphoric acid, we also studied the photo-reaction of U(VI) with some organic compounds which are not reactive in perchloric acid or nitric acid.

EXPERIMENTAL

Stock solution of uranium(VI) perchlorate was prepared by a method described previously(ref. 8). All other chemicals were reagent grade and used without further purification. Water purified by ion exchange resin was distilled twice before use. Oxygen free solution was obtained by bubbling nitrogen gas for 30 min in an optical cell. Decay rates of uranyl luminescence were measured by the laser photolysis method described previously (ref. 8). Photo-chemical reactions were carried out in 2 M ($M = \text{mol dm}^{-3}$) phosphoric acid solutions under irradiation of the nitrogen laser (Molelectron UV-22). The concentrations of U(IV) were measured spectrophotometrically at 660 nm. Quantum yields were determined by chemical actinometer method using potassium ferrioxalate actinometer(ref. 9). The solutions were stirred by a magnetic stirrer during the irradiation. Temperature was kept at 25°C in all experiments.

RESULTS

UV-visible absorption spectra of the U(VI) solutions containing I^- , Br^- or NCS^- changed with the laser irradiation, and new

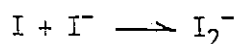
absorption appeared in the wavelength between 600 and 700 nm. The new peaks at 620, 640 and 660 nm were consistent with the absorption of U(IV)(ref. 10), indicating that U(VI) is photo-reduced to U(IV). Therefore, the concentration of U(IV) was determined by measuring the absorbance at 660 nm. (the extinction coefficient of U(IV): $32.07 \text{ M}^{-1} \text{ cm}^{-1}$ at 660 nm). The quantum yields for the formation of U(IV) by the photo-reactions with I^- , Br^- and NCS^- are listed in Table 1 together with the standard electrode potentials between halogen X_2 and its anion X^- ($1/2X_2/X^-$) and the quenching rate constants $k_q(X^-)$ of these anions.

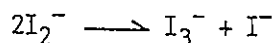
Table 1. The quantum yields of U(IV) by the photoreduction of U(VI) with various inorganic anions(X^-) in 2 M phosphoric acid solutions.

anions X^-	quantum yield ^a $\phi_{U(IV)}$	standard potential ^b / V	quenching constant ^c $/10^9 \text{ M}^{-1} \text{ s}^{-1}$
Cl^-	0	1.36	0.045
Br^-	6.0×10^{-3}	1.07	0.85
I^-	1.3×10^{-2}	0.54	2.0
NCS^-	1.0×10^{-2}	0.77	1.6

a) Quantum yields were determined under the condition; $[U(VI)]_0 = 0.05 \text{ M}$, $[X^-] = 2.0 \text{ M}$, and at 25°C b) ref. 11 c) ref. 8.

In Table 1, the yield of U(IV) increases in the order, $Br^- < NCS^- < I^-$. This order is the same as that of $k_q(X^-)$ and the reverse of the standard potentials of these anions. The results show that photo-reaction between U(VI) and X^- proceed through an electron transfer between excited uranyl ion and X^- in the primary process. In the U(VI) - I^- and U(VI) - NCS^- systems, the photo-reactions were accompanied by a formation of some products other than U(IV), which showed absorption in the visible region. Particularly, in U(IV)- NCS^- system, insoluble species were produced with the long irradiation. Burrows et al.(ref. 3) reported in their flash photolysis study that I radical is converted into stable I_3^- as follows:





and that NCS radical reacts with NCS^- to form $(NCS)_2^-$ or oxidized species $(NCS)_2$. It is likely that the decomposition of $(NCS)_2$ or $(NCS)_2^-$ could produce the insoluble species. Such species produced in $U(VI) - I^-$ and $U(VI) - NCS^-$ systems showed absorptions in the visible region overlapping with that of $U(IV)$, while in the irradiation of $U(VI)-Br^-$ system no absorption other than those of $U(IV)$ and $U(VI)$ was observed in the visible region. Hence, $U(VI)-Br^-$ system was studied kinetically in detail.

Fig. 1 shows plots of $-\ln(1 - [U(IV)]/[U(VI)]_0)$ vs. t_{irr} for the photo-reaction of $U(VI)-Br^-$ system at various concentrations of Br^- in oxygen free solutions, where $[U(IV)]$ refers to the concentration of $U(IV)$ at time t_{irr} and $[U(VI)]_0$ is the initial concentration of $U(VI)$.

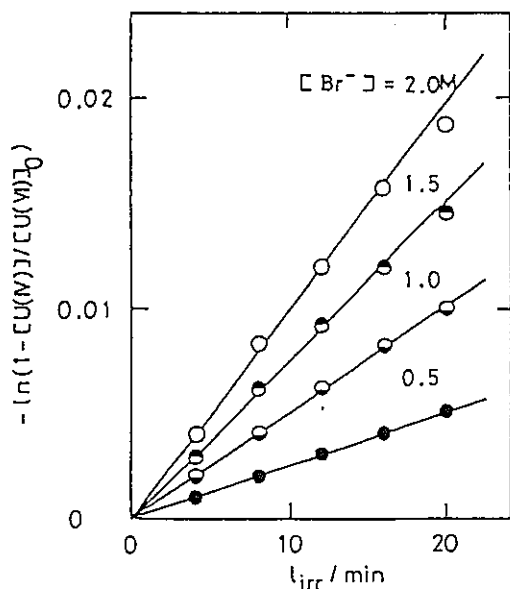


Fig. 1. Plots of $-\ln(1 - [U(IV)]/[U(VI)]_0)$ vs. t_{irr} at 25°C for the photo-reaction of $U(VI)-Br^-$ system in the oxygen free solutions. $[U(VI)]_0 = 5.0 \times 10^{-2}$ M, $[H_3PO_4] = 2$ M.

The plots in Fig. 1 are linear and indicate that the pseudo-first-order treatment can be applied under the conditions, $[Br^-] \gg [U(VI)]_0$:

$$d[U(IV)]/dt = k_{obsd} [U(VI)] \quad (1)$$

where k_{obsd} denotes the observed-first-order rate constant. Fig. 2 shows a plot of k_{obsd} vs. $[Br^-]$ and indicates that k_{obsd} is expressed by Eq. (2).

$$k_{obsd} = k_{Br} [Br^-] \quad (2)$$

where k_{Br} is the second-order rate constant (first order in $[U(VI)]$ and in $[Br^-]$, respectively). In oxygen-saturated solutions, the first-order plots were also closely linear, but the rates were nearly half as slow as those in the oxygen-free solutions.

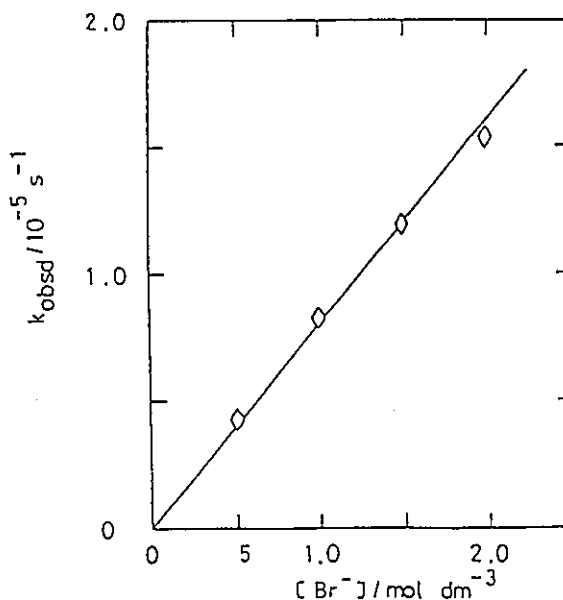


Fig. 2. Plot of k_{obsd} vs. $[Br^-]$. The experiments were carried out under following condition: $[U(VI)]_0 = 5.0 \times 10^{-2}$ M, $[H_3PO_4] = 2$ M, and at 25°C.

In addition, photo-reaction of $U(VI)$ with various organic compounds (cyclohexene, 1-hexene, pyridine) were also investigated in 2 M phosphoric acid solutions. It is known that these organic compounds do not react with excited uranyl ions in perchloric acid or nitric acid solution (ref. 12). However, in phosphoric acid, we found that $U(IV)$ is formed by the photo-reaction between $U(VI)$ and these organic compounds. The yields of $U(IV)$, $[U(IV)]/[U(VI)]_0$, are listed in Table 2 with

the vertical ionization potential of the organic compounds.

Table 2. The yields of U(IV) by the photo-reaction of U(VI) with various organic molecules in 2 M phosphoric acid solutions.

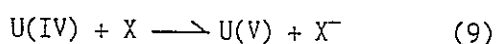
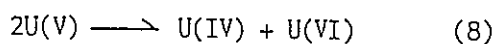
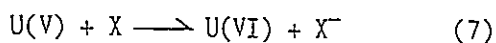
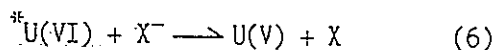
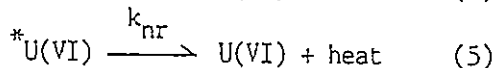
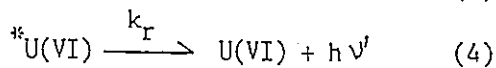
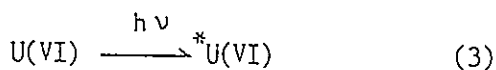
organic molecule	yield of U(IV) [U(IV)]/[U(VI)] ₀	vertical ionization potential/eV
cyclohexene	0.075	9.12
1-hexene	0.016	9.59
pyridine	0.008	9.67

Yields of U(IV) were determined under the condition; [U(VI)]₀=0.01 M, [Org.] = 1.0 × 10⁻³ M, t_{irr} = 30 min, and at 25°C.

In Table 2, the yield of U(IV) increases in the order, pyridine < 1-hexene < cyclohexene. This order is the reverse of the vertical ionization potentials of these organic molecules.

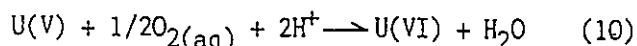
DISCUSSION

In view of earlier studies on reactions of the excited uranyl ions, the following reaction processes are of essential importance for the photo-reduction of U(VI) (refs. 2, 4, 6):

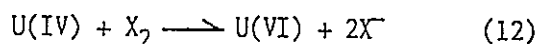


where the reaction (3) is the photo-excitation of U(VI), the reactions (4) and (5) the radiative and non-radiative deactivation

processes of ^{*}U(VI), respectively, and the reaction (6) one electron transfer process from anion X⁻ to ^{*}U(VI). In the case of U(VI) - I⁻ system, most of X⁻ could exist in a form of I₃⁻ after the irradiation (ref. 5) as described before. Reaction (6) initiates the present photo-reaction followed by reactions (7), (8), and (9). In solutions containing oxygen, U(V) is oxidized by:



A combination of halogen radicals X yields X₂, which may oxidize U(IV):



In U(VI) - I⁻ and U(VI) - Br⁻ systems, however, reaction (12) should be ignored by the reasons that U(IV) exists stably in the solutions after the laser irradiation and moreover U(IV) was not oxidized by adding extra I₂ and Br₂ under the present experimental conditions. On the other hand, in U(VI) - Cl⁻ system, the formation of U(IV) was not observed even after the long irradiation. This can be explained by the following reasons: U(V) formed by reaction (6) is oxidized quickly to U(VI) by reaction (7) without producing U(IV) or U(IV), if produced by the disproportionation of U(V) (reaction (8)), is oxidized to U(VI) by reaction (12). Therefore, in U(VI) - Cl⁻ system reaction (12) can not be ruled out.

Based on the above mechanism, the rate of the formation of U(IV) can be expressed by:

$$d[U(IV)]/dt = k_8[U(V)]^2 - k_9[U(IV)][X] \quad (13)$$

The steady state approximation should be applied for unstable U(V):

$$\begin{aligned} d[U(V)]/dt = & k_6[{}^*U(VI)][X^-] - k_7[U(V)][X] \\ & - k_8[U(V)]^2 + k_9[U(IV)][X] \\ & - k_{10}[U(V)][O_2(aq)] = 0 \quad (14) \end{aligned}$$

where the last term is zero in the oxygen free solutions. On the assumption that $k_8[U(V)]^2 \gg k_7[U(V)][X]$, Eqs. (13) and (14) give Eq. (15):

$$d[U(IV)]/dt = k_6[^*U(VI)][X^-] \quad (15)$$

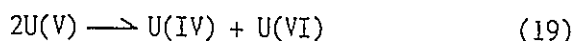
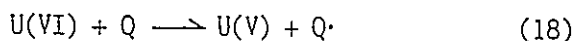
Since $[^*U(VI)]$ is regarded to be proportional to the laser intensity and to $[U(VI)]$, Eq. (15) can be written by:

$$d[U(IV)]/dt = AI_a k_6 [U(VI)][X^-] \quad (16)$$

where A refers to a constant, which consists of quantum yield of U(VI) and various quenching rate constants, and I_a is laser intensity. Eq. (16) is basically the same as Eq. (1) connected with Eq. (2). These results support that the above assumption $k_8[U(V)]^2 \gg k_7[U(V)][X]$ is valid in the present experimental conditions. In the oxygen saturated solutions, the rates are considerably slower than in the oxygen free solutions. This fact suggests that the reaction (10) becomes consecutive with the reaction(8). In this case, the rate equation is expressed by Eq. (17).

$$d[U(IV)]/dt = k_6[^*U(VI)][X^-] - k_{10}[U(V)][O_{2(aq)}] \quad (17)$$

The photo-reaction occurring on irradiation of the U(VI)-organic system in phosphoric acid can be explained by the following mechanism:



In U(VI)-cyclohexene system, we observed the cyclohexene radical by ESR measurements for irradiated sample at 77K. Therefore, it is reasonable that the photo-reaction proceed through an electron transfer from organic molecule to $*U(VI)$.

A question arises why U(VI) is photo-reduced by halogen and pseudohalogen anions in only phosphoric acid solutions. There are two plausible reasons: One is that the life-time of $*U(VI)$ is much longer in phosphoric acid solutions than in $HClO_4$ or HNO_3 solution (the decay constant is $6.9 \times 10^3 \text{ s}^{-1}$ in the phosphoric acid solution, and $5.2 \times 10^5 \text{ s}^{-1}$ in the perchloric acid solution(ref. 8)).

Hence, the average concentration of $*U(VI)$ is expected to be much higher in the phosphoric acid solution than in other solutions. Another is that the produced U(IV) is stabilized by the formation of a phosphato complex of U(IV).

ACKNOWLEDGEMENT

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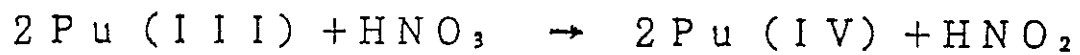
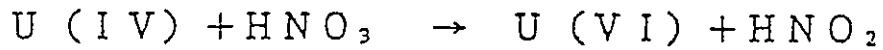
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3-3 硝酸および亜硝酸とアクチノイド元素の光励起効果

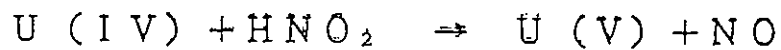
- ① 硝酸溶液中におけるウラン、プルトニウムおよびネプツニウム
(ドラフトデータ)

硝酸と亜硝酸の反応

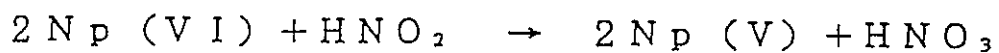
酸化剤としての硝酸

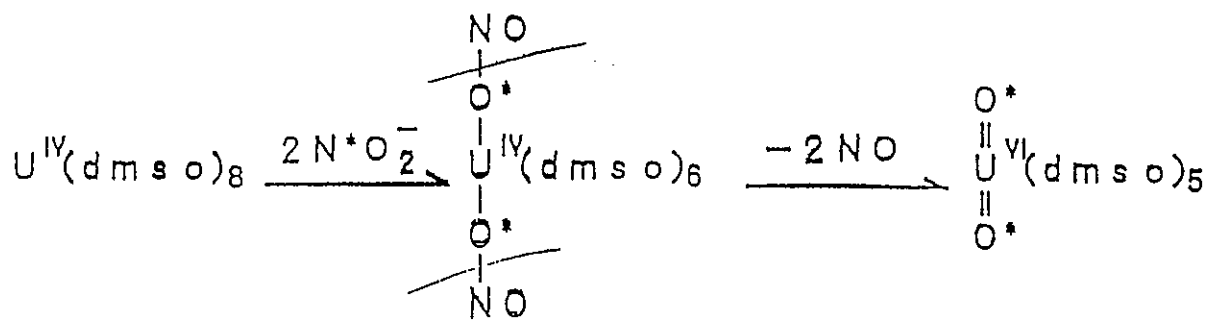


酸化剤としての亜硝酸



還元剤としての亜硝酸





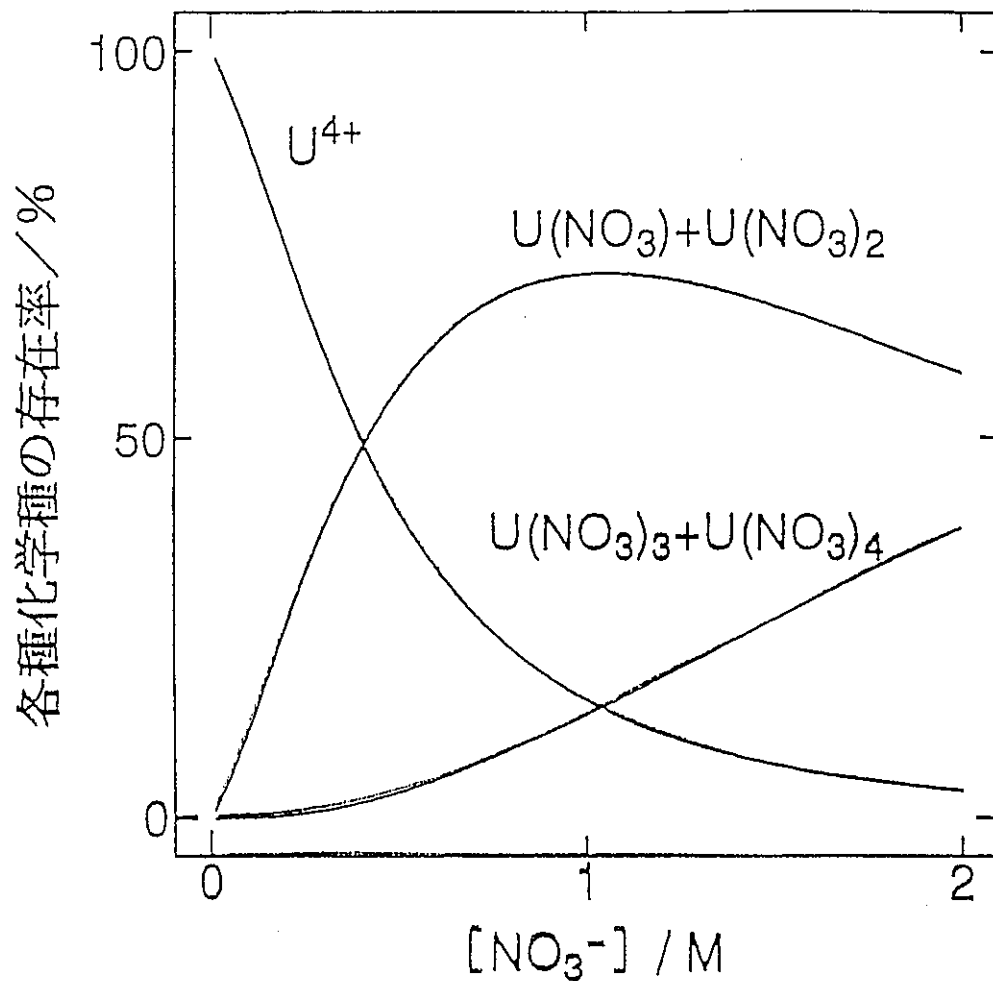


Fig U(IV)-NO₃⁻系内における硝酸イオン濃度と各化学種の存在率-2

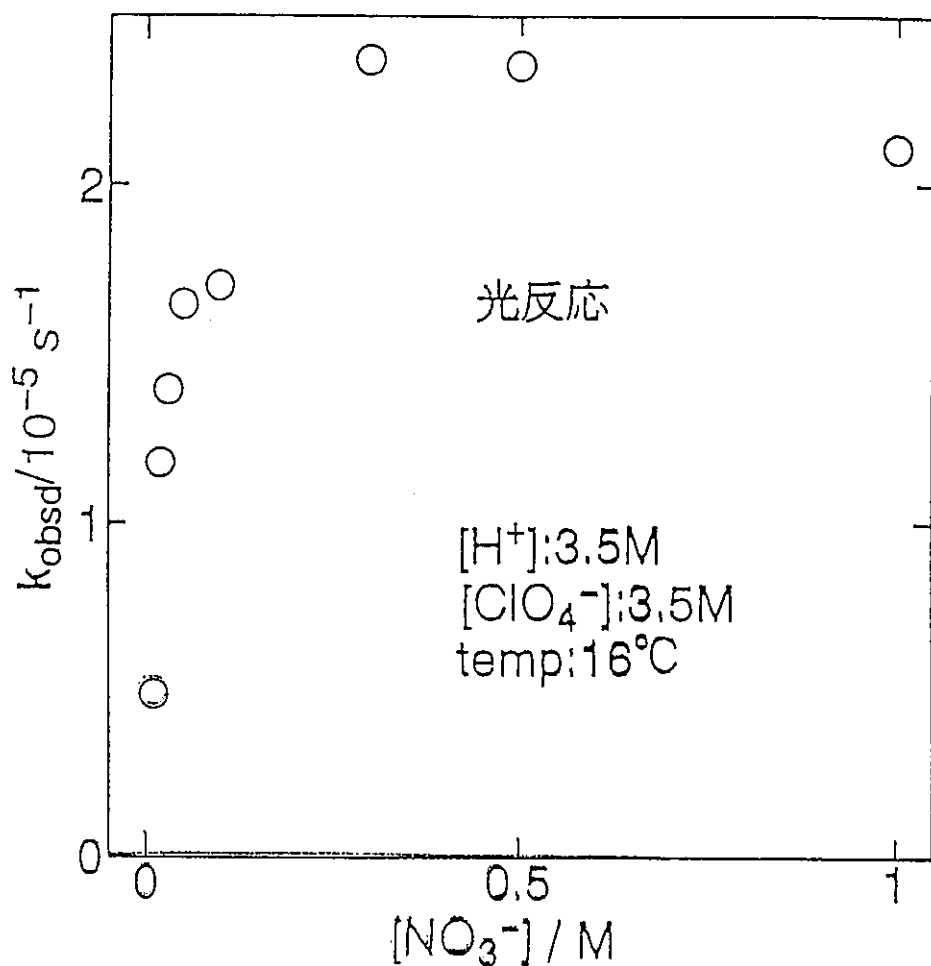


Fig 光反応における k_{obsd} の硝酸イオン濃度依存性

NO_3^- : 0.01~1M, H^+ : 3.5M, ClO_4^- : 3.5M
温度範囲: 16°C

Table 光反応における k_{obsd} の波長依存性 a) c)

波長領域 nm	k_{obsd} s ⁻¹	測定温度 °C
全領域	2.4×10^{-5}	16.0
420nm～長波長 b)	3.5×10^{-6}	16.0
暗反応	3.6×10^{-6}	17.3

a)キセノンランプ使用, b)フィルターL42

c) NO_3^- : 0.3M, H^+ : 3.5M, ClO_4^- : 3.5M

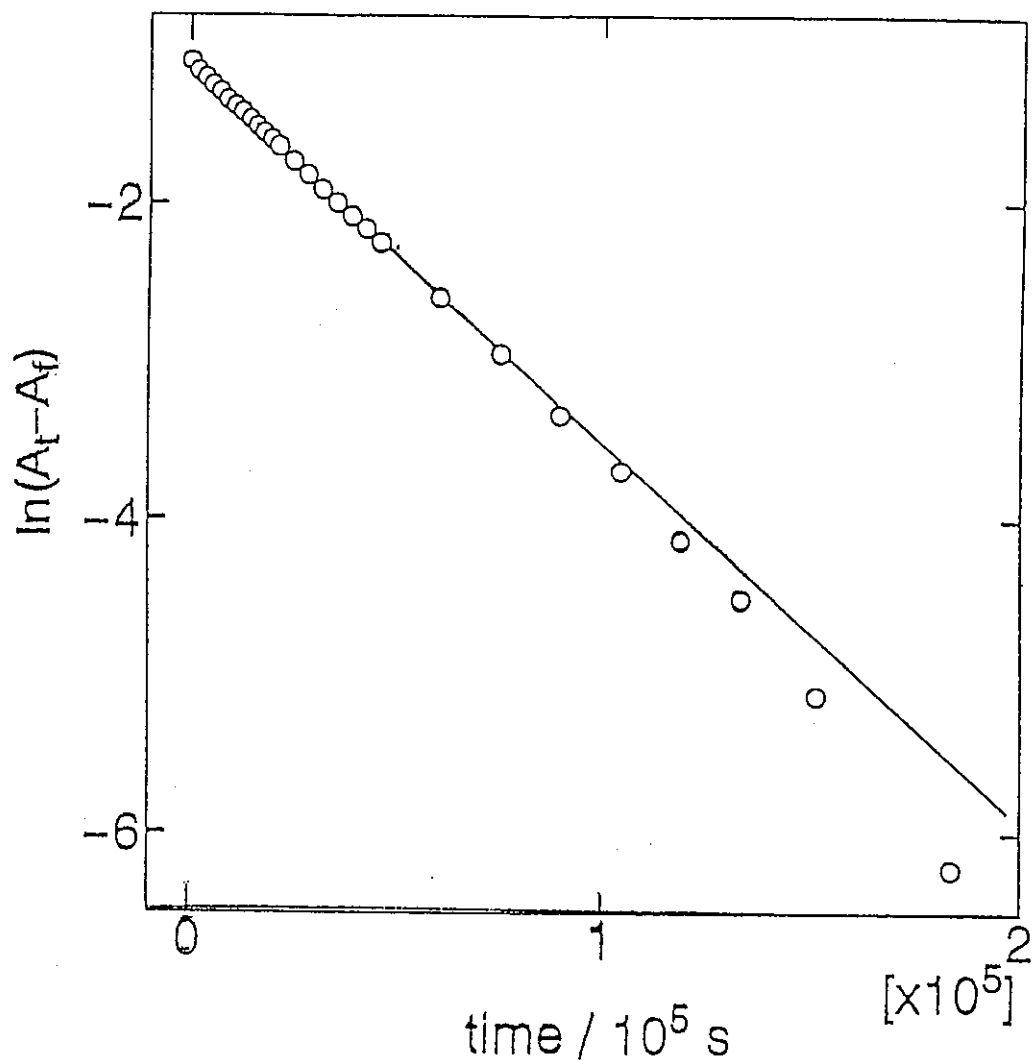


Fig 光反応における擬一次プロット
 $\text{NO}_3^-: 0.3\text{M}, \text{H}^+: 3.5\text{M}, \text{ClO}_4^-: 3.5\text{M}, 21^\circ\text{C}$

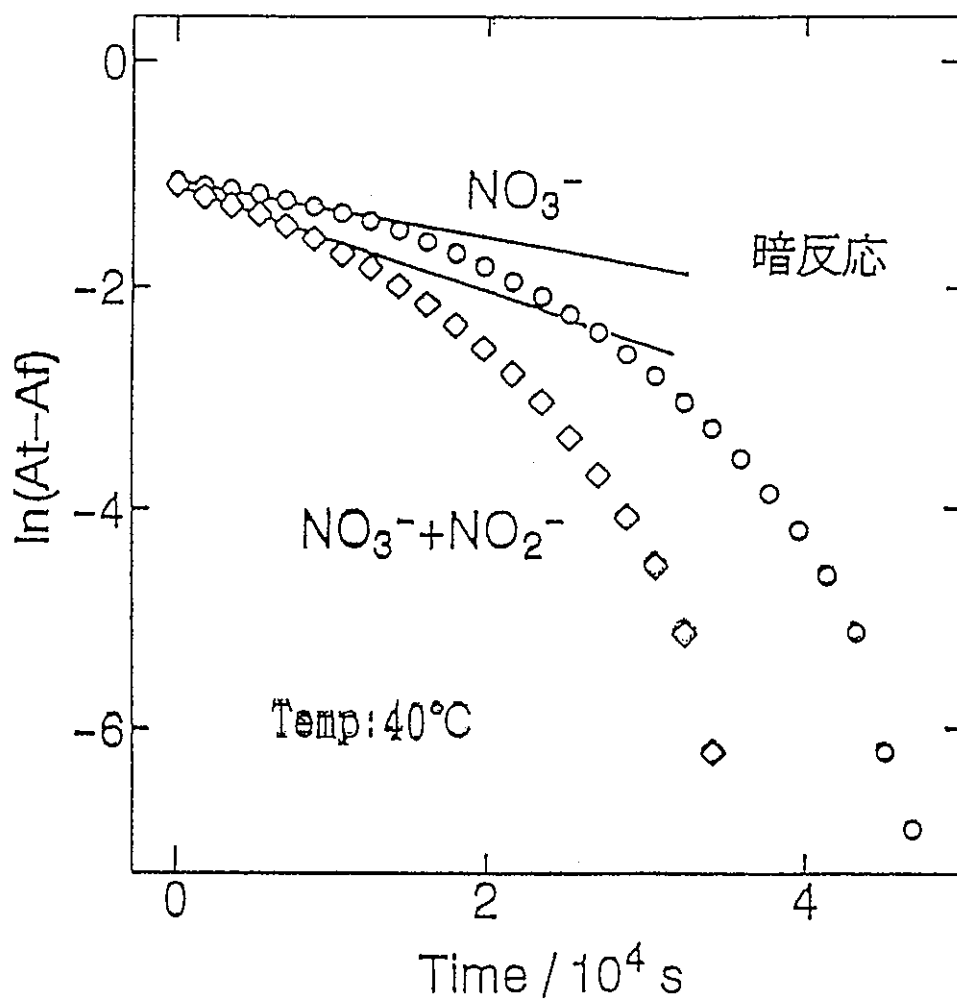
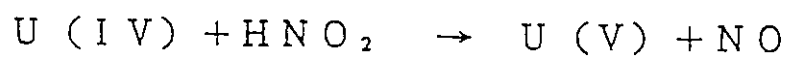
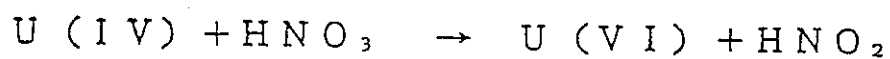
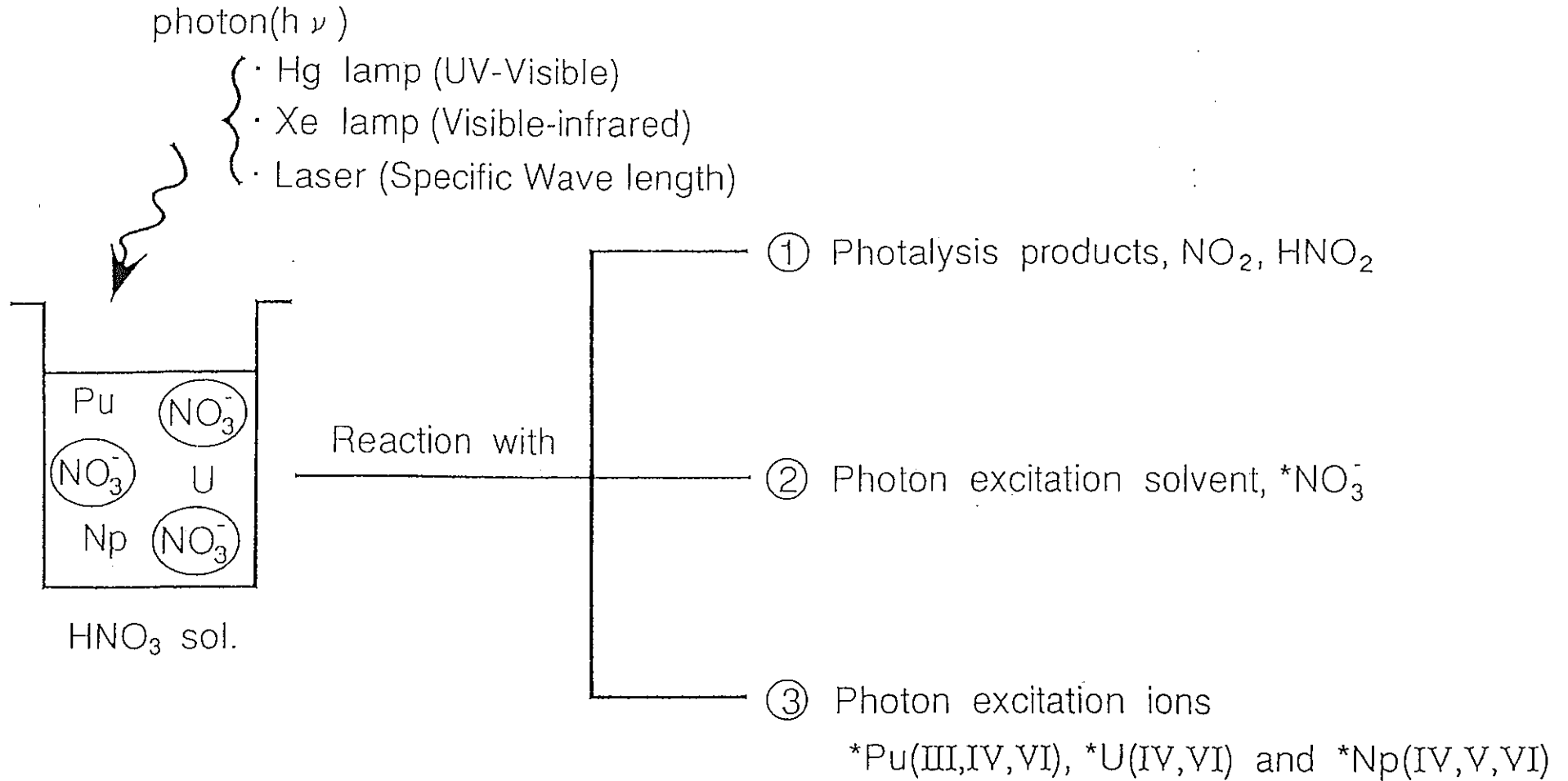


Fig 硝酸によるU(IV)の酸化反応における擬一次プロット

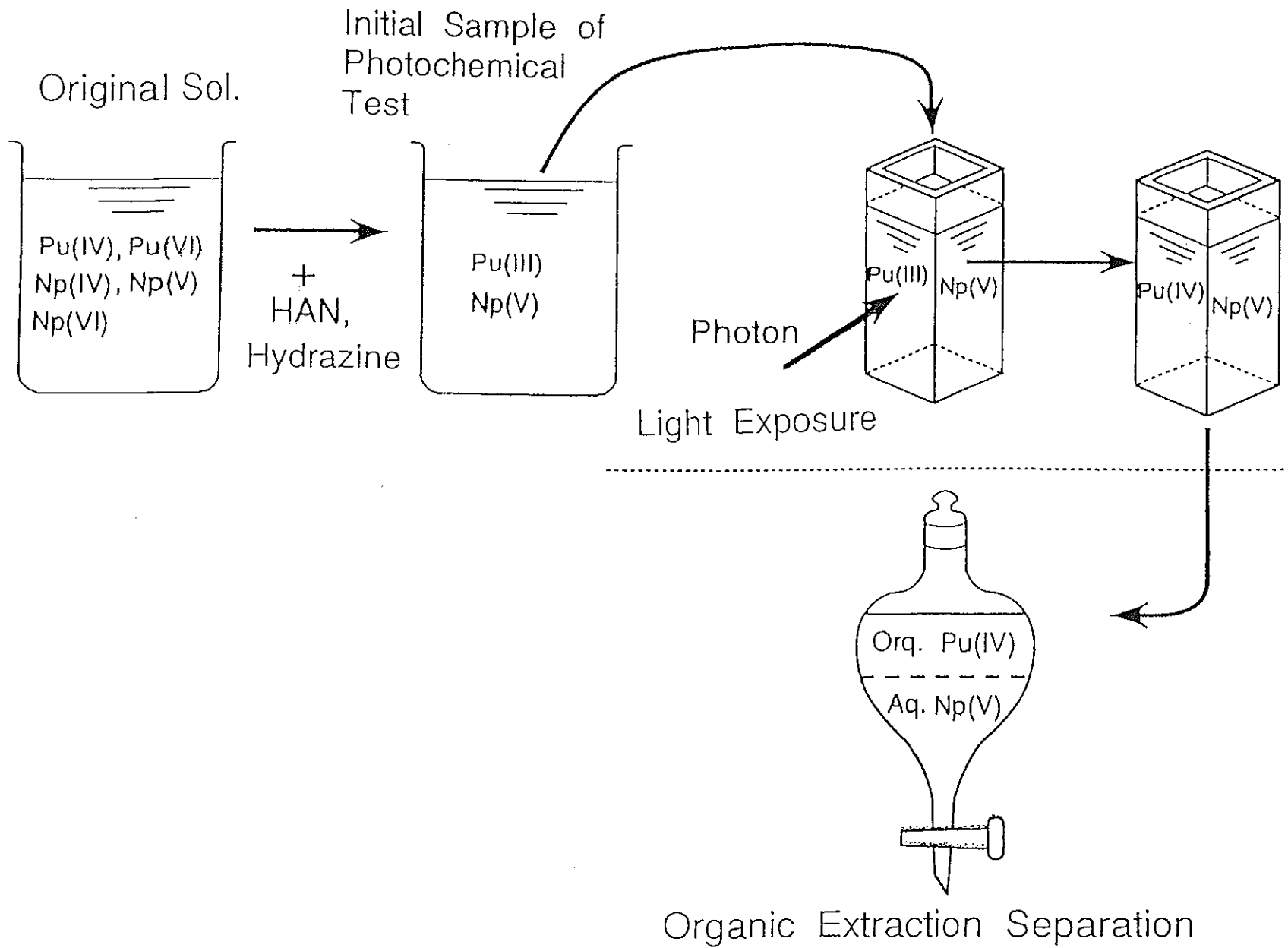
暗反応

$\text{NO}_3^-: 0.3\text{M}, \text{H}^+: 0.5\text{M}, \text{ClO}_4^-: 3.5\text{M}$





Supposed Photochemical Reactions Concepts



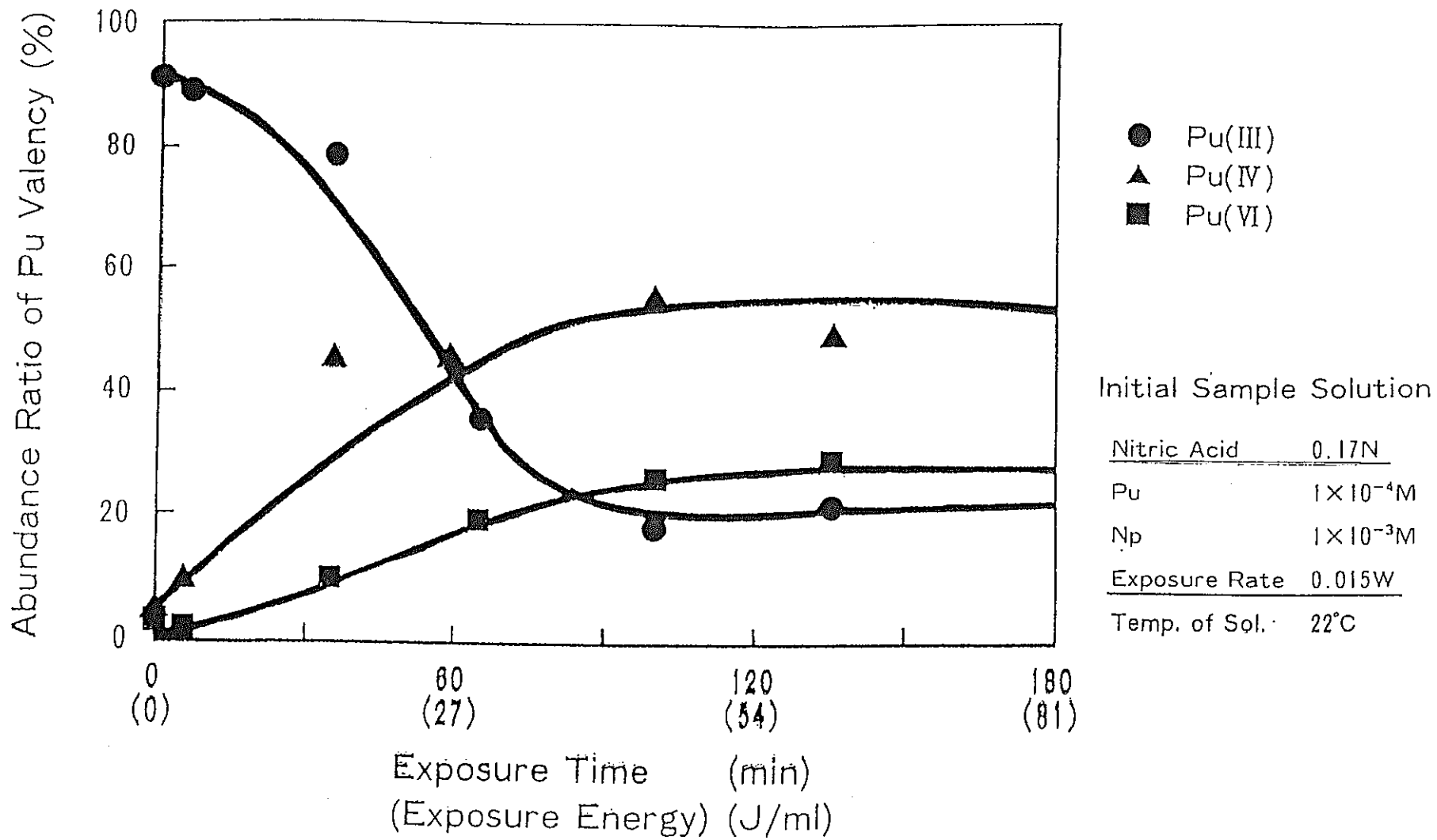


Fig. Redox Reaction of Pu by Light Exposure

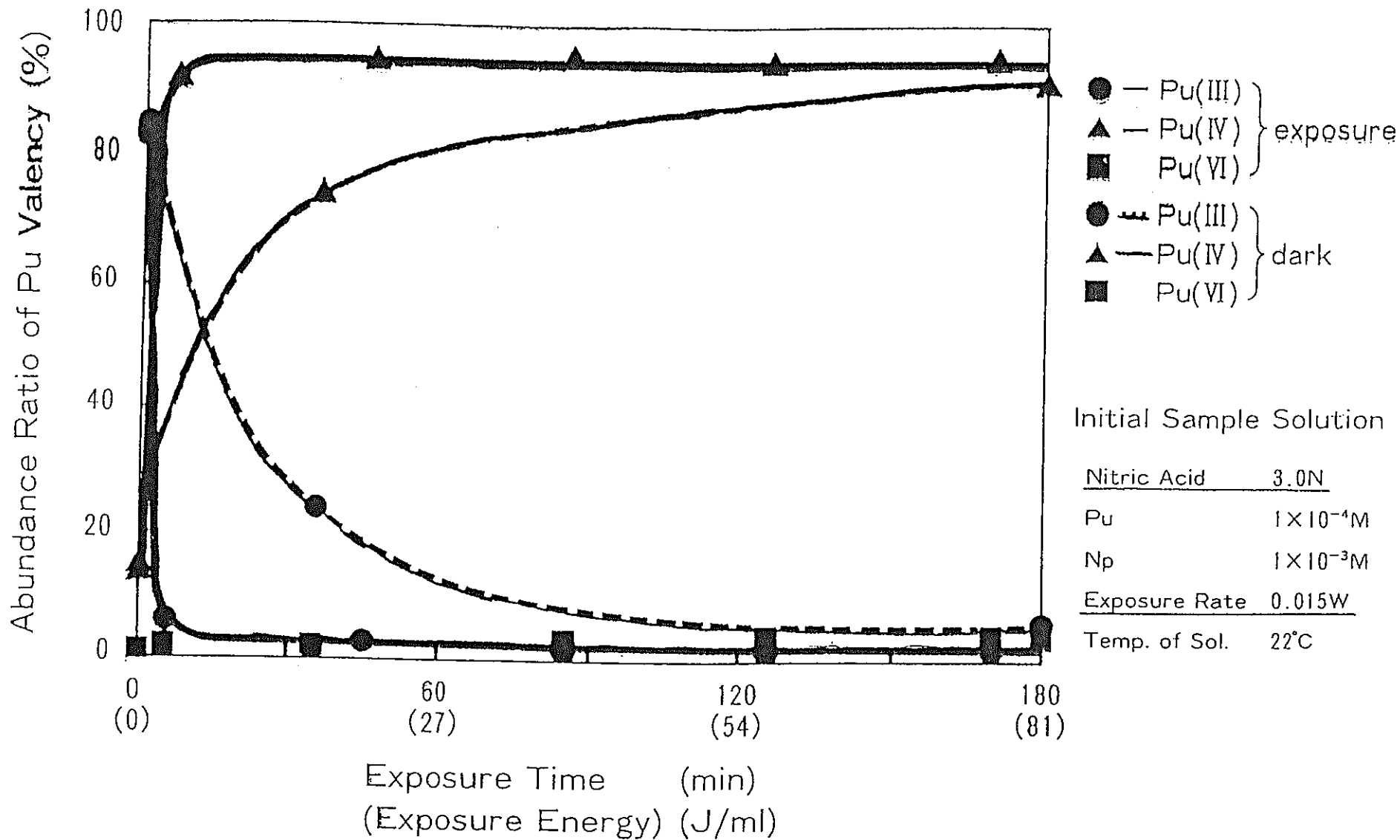


Fig. Redox Reaction of Pu by Light Exposure

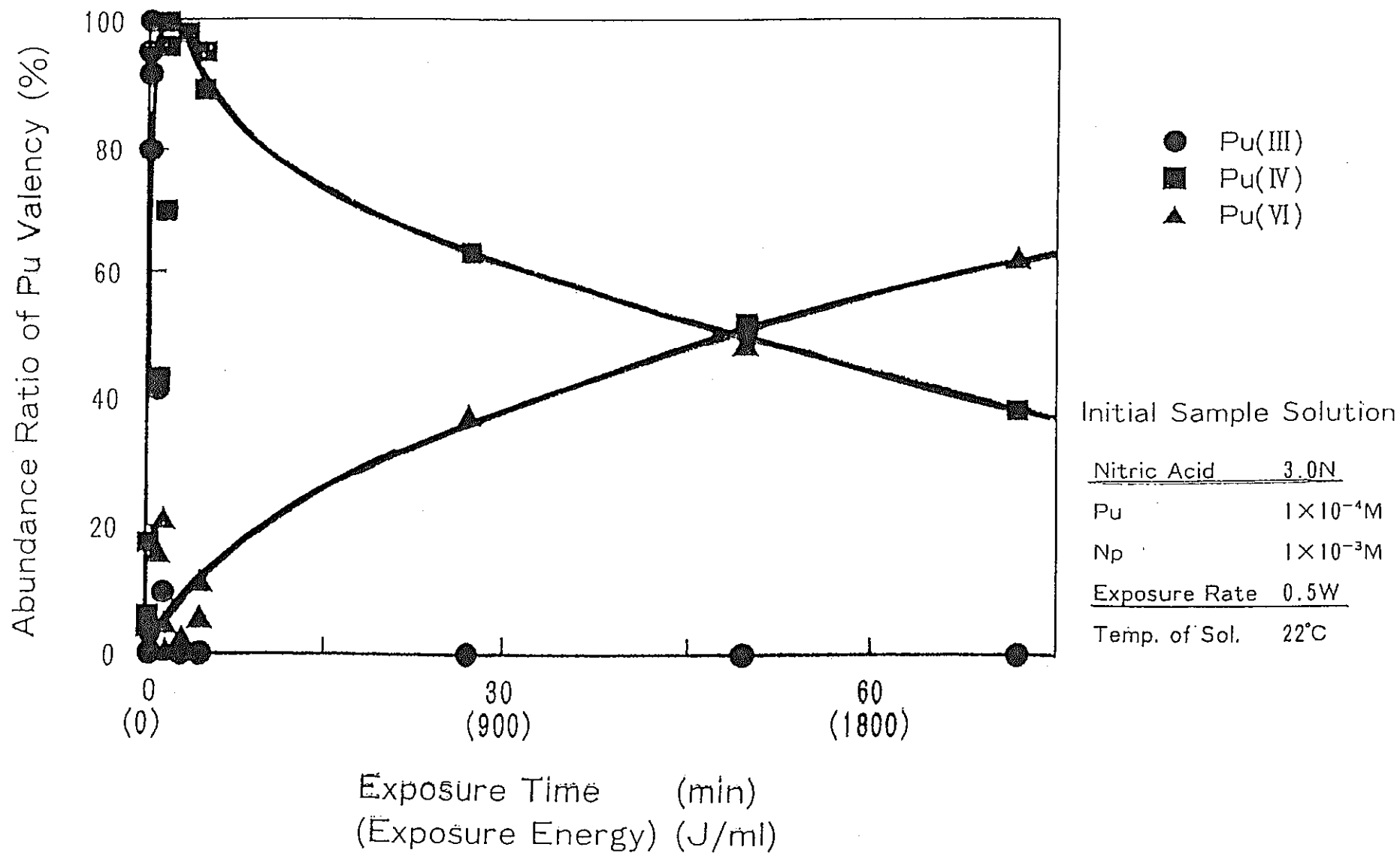


Fig. Redox Reaction of Pu by Light Exposure

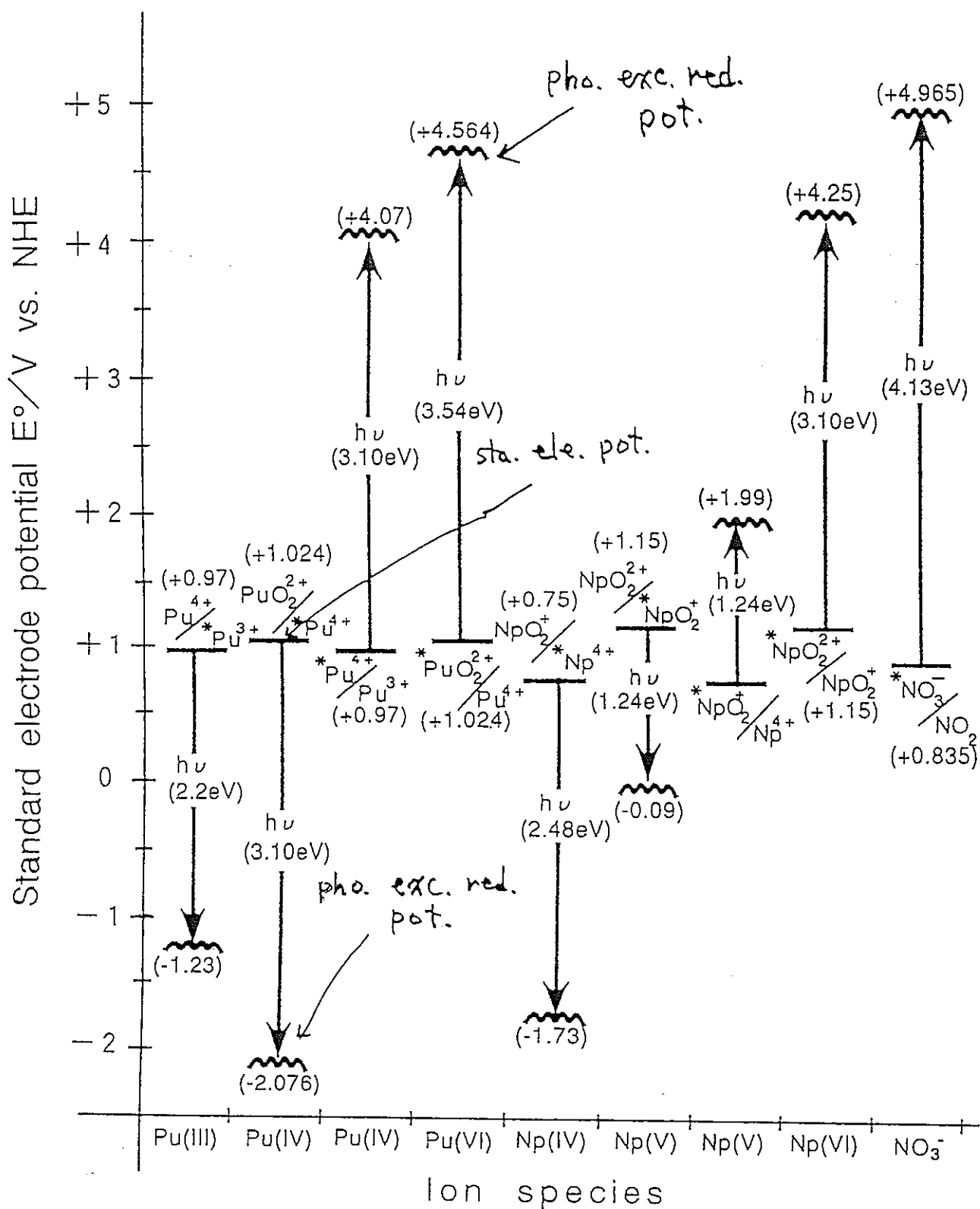


Fig.23

Variation of standard electrode potential by photo-excitation

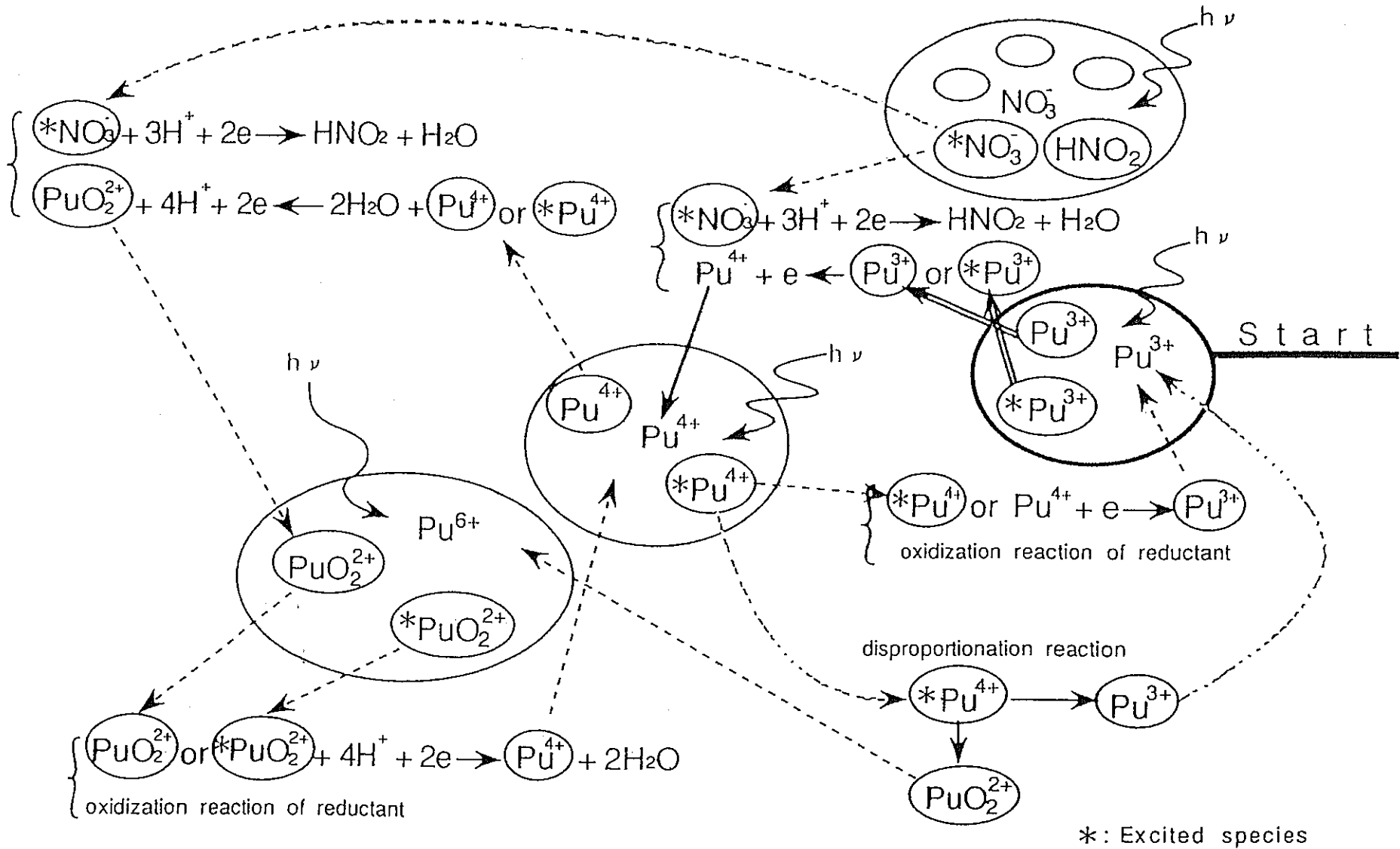


Fig.1 Photo-redox reaction chain of Pu valency by light irradiation

$$V_{3 \rightarrow 4} = 2.74 \times 10^2 [*Pu(III)]^{1.96} + 9.08 [Pu(III)]^{1.96} \quad \left\{ \begin{array}{l} 3H \text{ HNO}_3 \text{ のとき} \\ 0.015W \end{array} \right\}$$

$$V_{3 \rightarrow 4} = *k_{3 \rightarrow 4} [*Pu^{3+}]^2 [*NO_3^-][H^+]^3 + k_{3 \rightarrow 4} [Pu^{3+}]^2 [HNO_2][H^+]^3$$

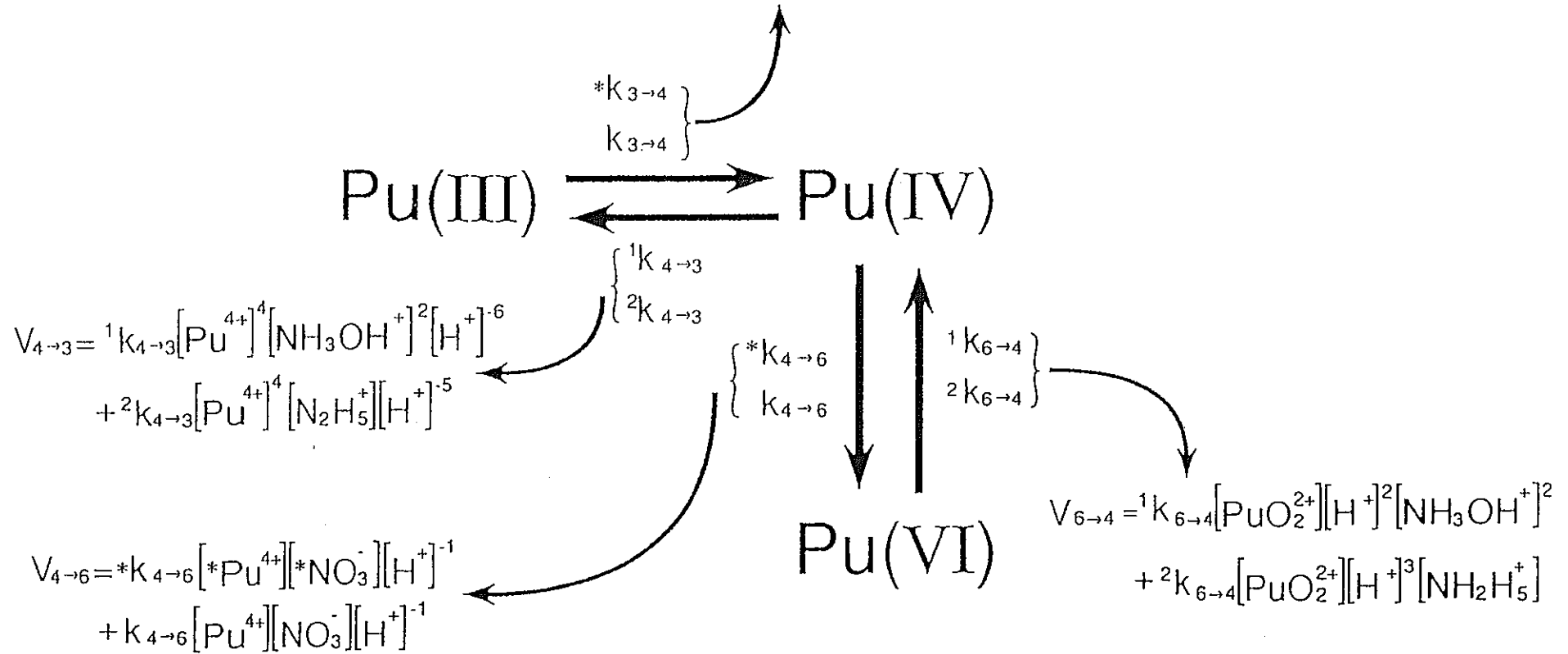


Photo-redox reaction rates of Pu in nitric acid solution

I. 硝酸の光化学

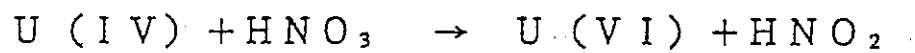
— 原子価調整への応用 —

II. CMP と CMP O の

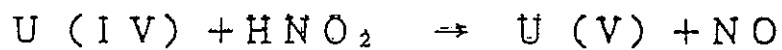
性質と超ウラン元素の分離

硝酸と亜硝酸の反応

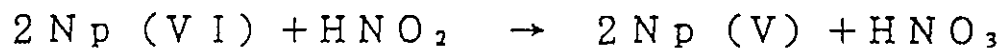
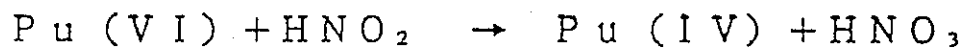
酸化剤としての硝酸



酸化剤としての亜硝酸



還元剤としての亜硝酸



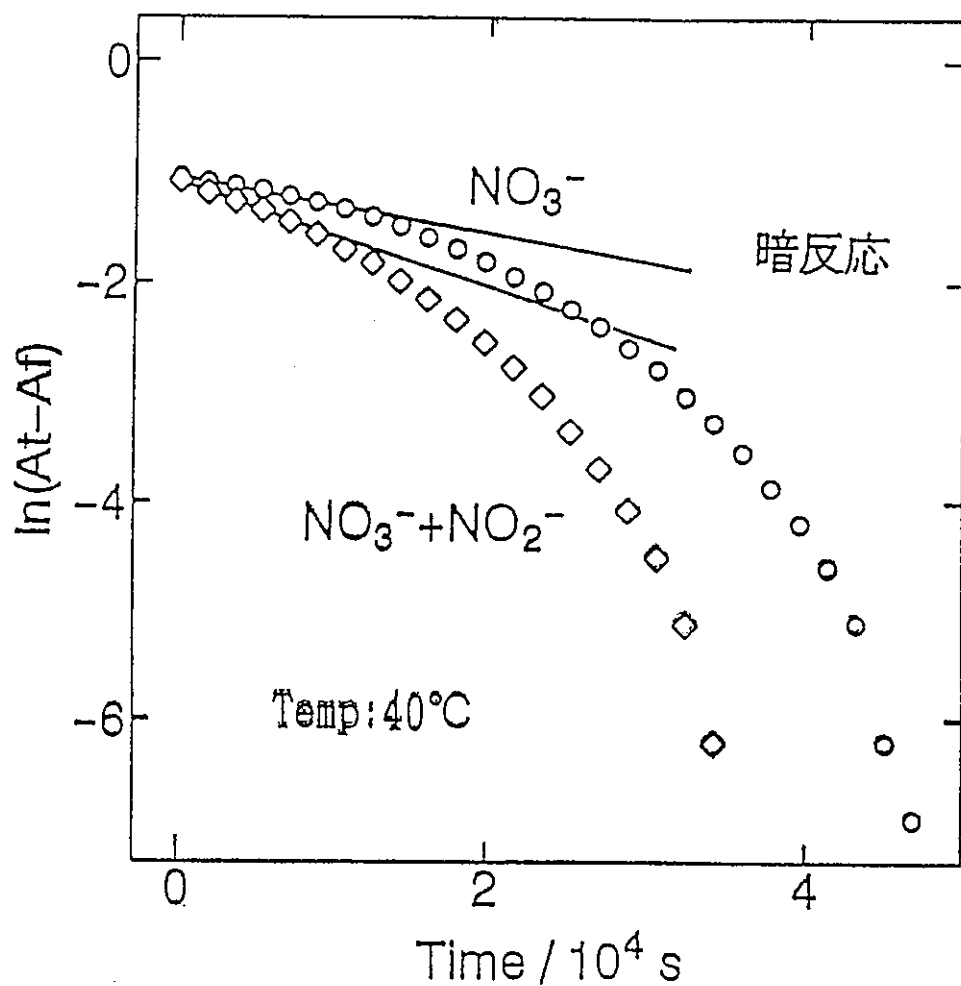
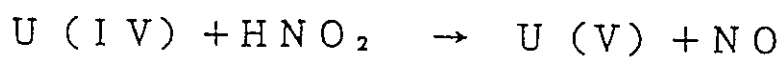
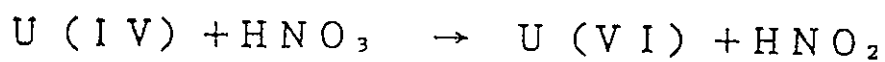


Fig 硝酸によるU(IV)の酸化反応における
擬一次プロット

暗反応

$\text{NO}_3^-: 0.3\text{M}, \text{H}^+: 0.5\text{M}, \text{ClO}_4^-: 3.5\text{M}$



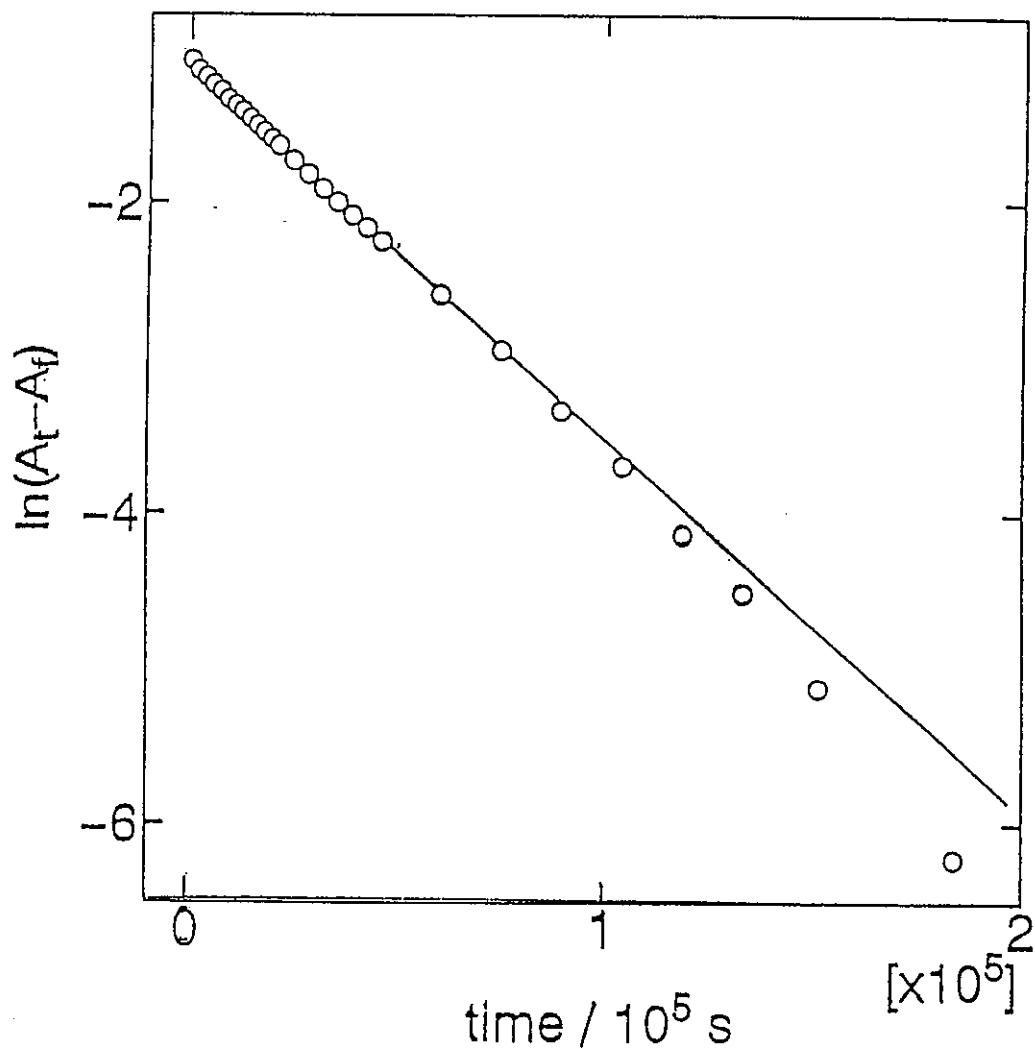


Fig 光反応における擬一次プロット
NO₃⁻:0.3M, H⁺:3.5M, ClO₄⁻:3.5M, 21°C

Table 光反応における k_{obsd} の波長依存性 a) c)

波長領域 nm	k_{obsd} s ⁻¹	測定温度 °C
全領域	2.4×10^{-5}	16.0
420nm～長波長 b)	3.5×10^{-6}	16.0
暗反応	3.6×10^{-6}	17.3

a) キセノンランプ使用, b) フィルター-L42

c) NO_3^- : 0.3M, H^+ : 3.5M, ClO_4^- : 3.5M

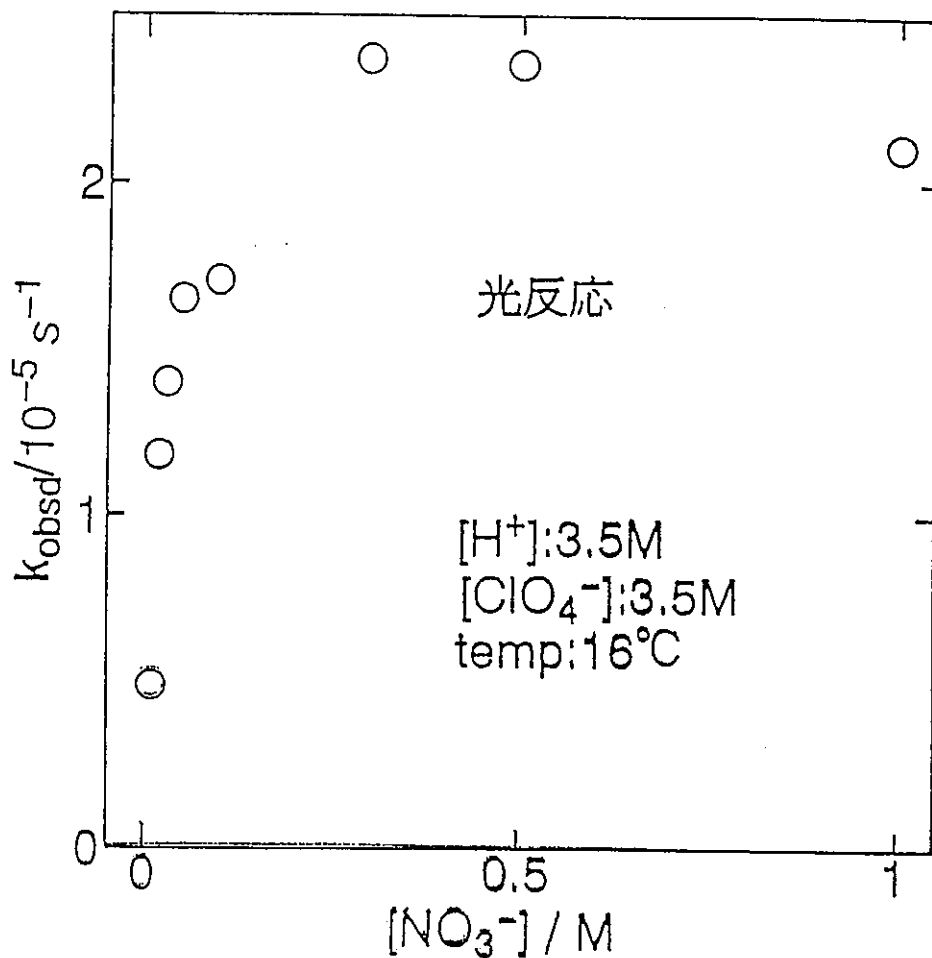


Fig 光反応における k_{obsd} の硝酸イオン濃度依存性

NO₃⁻: 0.01~1M, H⁺: 3.5M, ClO₄⁻: 3.5M
温度範囲: 16°C

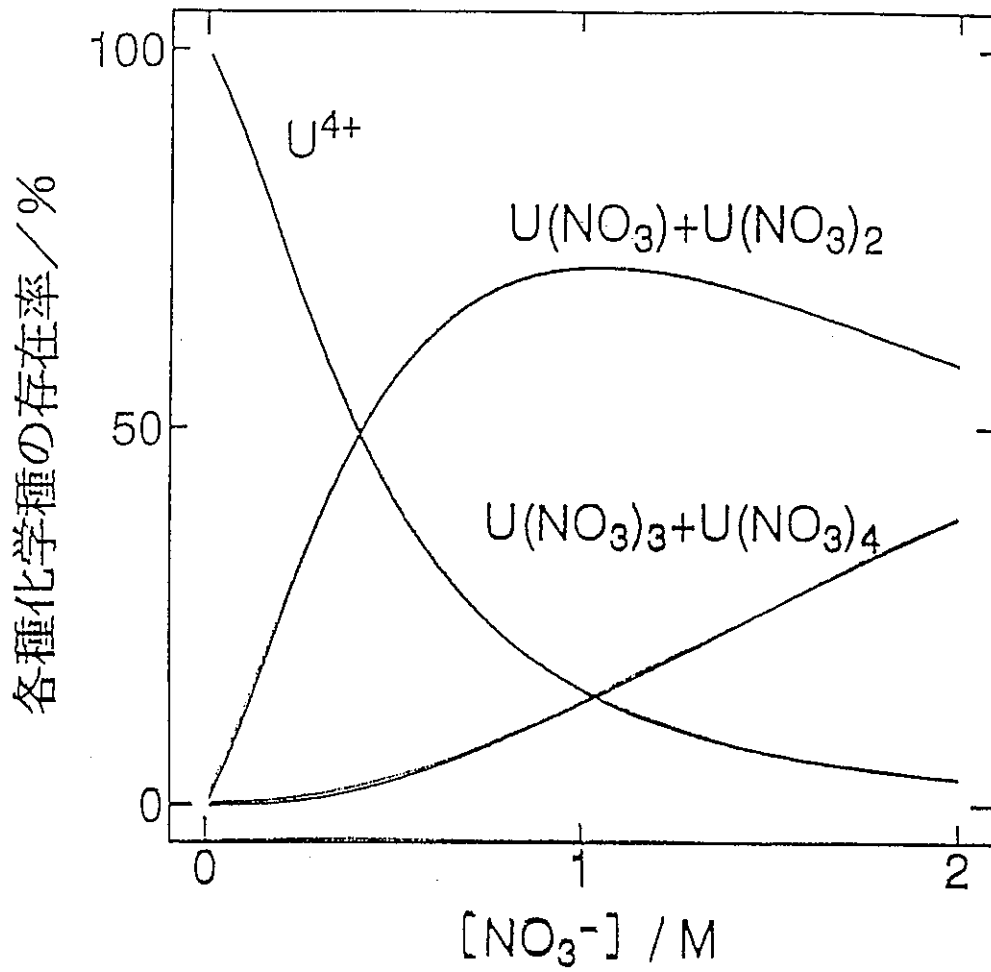
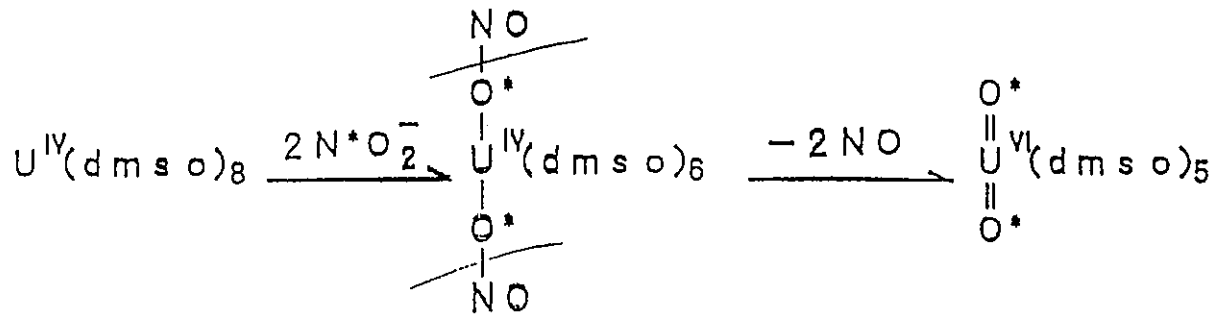


Fig U(IV)-NO₃⁻系内における硝酸イオン濃度と各化学種の存在率-2



$[\text{UO}_2(\text{NO}_3)_2(\text{CMPO})]=0.400\text{m}$

$[\text{CMPO}]=2.00\text{m}$

$n=2.9$

6°C

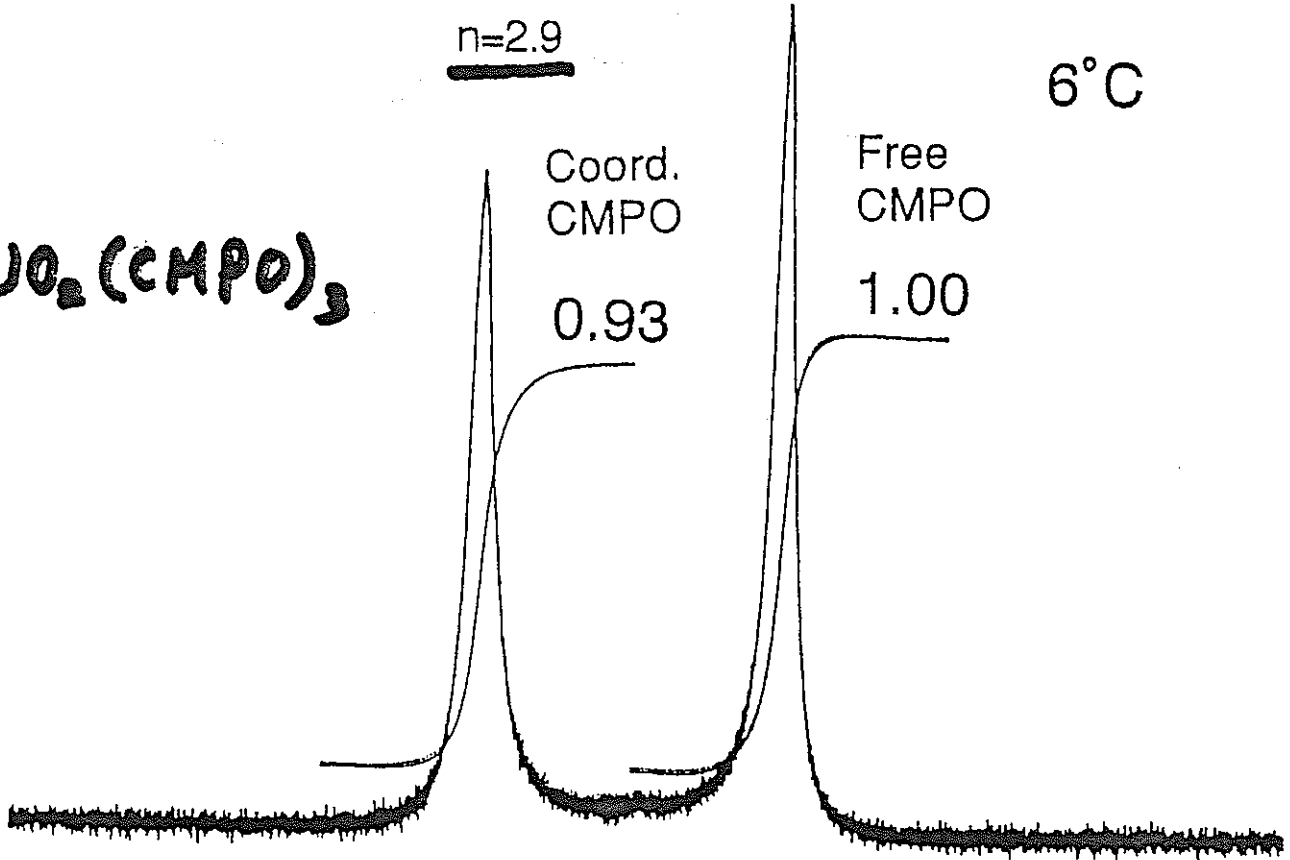
$\text{UO}_2(\text{CMPO})_3$

Coord.
CMPO

Free
CMPO

0.93

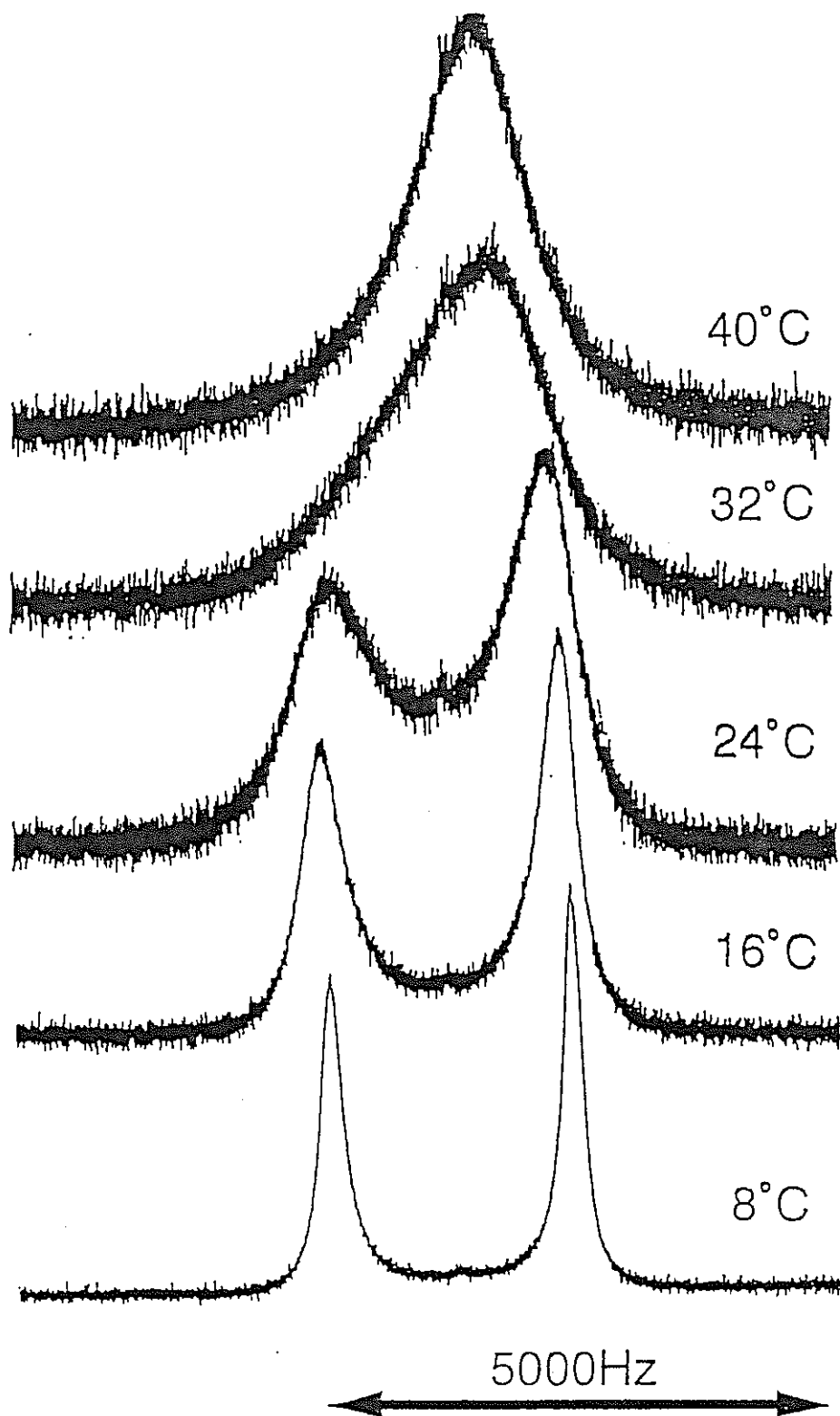
1.00



5000Hz

CMPO ν H

$n = 1$



Experimental ^{31}P NMR lineshapes of a solution containing $\text{UO}_2(\text{NO}_3)_3(\text{CMPO})$ (0.400 m), CMPO (2.00 m), and CD_3COCD_3 (19.2 m).

表 ウラニルCMP, CMPO錯体の配位子交換反応に関する
活性化パラメータ

reaction	k_1/s^{-1}	$k_2/M^{-1}s^{-1}$	ΔH^\ddagger	ΔS^\ddagger
system	25°C	25°C	kJ mol^{-1}	$\text{JK}^{-1}\text{mol}^{-1}$
CMP	-	2.16×10^4	23.0	-84.8
CMPO ¹⁾	2.93×10^3	-	46.2	-23.6

1)宮田, 池田, 朴, 喜安 日本原子力学会1992年秋の大会 H10

抽出剤モデル分子のAtomic Chargeの計算値

	TBP	CMP	CMPO
P	2.1514	2.0916	1.9226
O(PO)	-0.8572	-0.8193	-0.8111
O(RO)	-0.6161	-0.6531	-
O(RO)	-0.6174	-0.6160	-
O(RO)	-0.6172	-	-
N	-	-0.0794	-0.0880
C	-	0.2970	0.3031
O	-	-0.3706	-0.3866

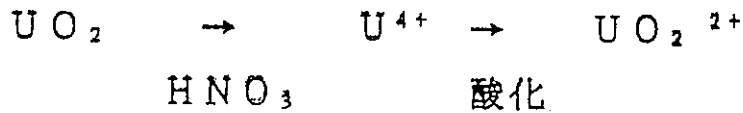
(MOPAC 6; PM3 Hamiltonian による最適化構造での計算値)

酸化物燃料の溶解

現在、酸化物燃料 UO_2 は濃硝酸で溶解する。その際、亜硝酸を加えると溶解が促進されるが、その機構は明らかでない。

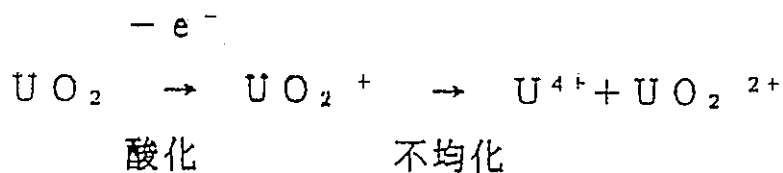
UO_2 の溶解には次の二つの機構が考えられる。

脱酸素化を律速とする機構

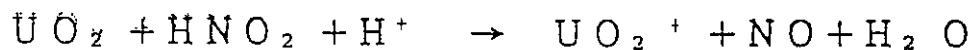


この反応は $U-O$ 結合を切断するため吸熱反応であることが予想される。実際に、溶解は高温で行われる。

電子移動を律速とする機構

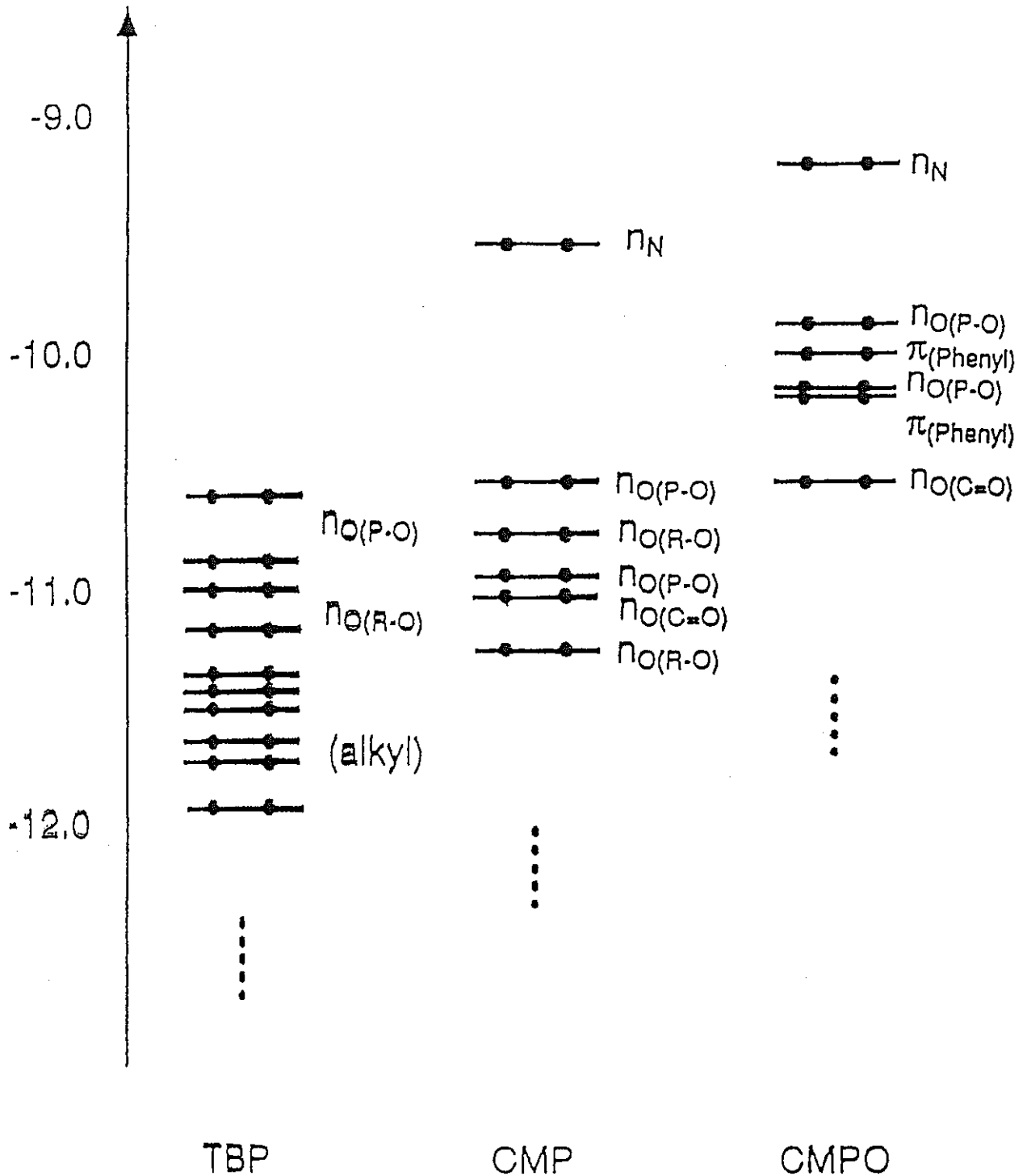


この反応では、酸化剤が必要であるが、常温でも起こる可能性がある。この際、添加した亜硝酸は酸化剤として働く(?)。



^{17}O = NMR 測定の結果、下の機構が正しいことが分かった。すなわち、 UO_2 は酸化剤があれば塩酸でも容易に解ける。

Energy(a.u.)



抽出剤分子の占有軌道エネルギーの比較

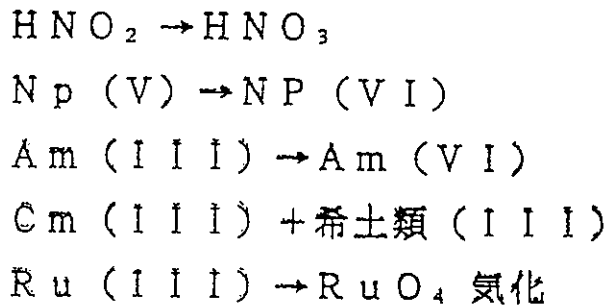
使用済核燃料

溶解 (硝酸)
+ 亜硝酸 (HNO₂)

T B P 抽出

水相	T B P 相
Np (V)	U (VI)、Pu (IV)
FP + Am (III)	
Cm (III)	

オゾンによる酸化



C M P O 抽出

水相	C M P O 相
FP	Am, Cm + 希土類

使用済核燃料

溶解

硝酸 + 酸化剤

オゾン or $C\overset{+}{O}$ (IV)

亜硝酸の酸化

沈殿法

Ru, Pd, Rh

の分離

T B P 抽出

水相

T B P 相

Pu (VI), FP

(Am, Cm)

U (VI), Np (VI)

PuとAmの一部(?)

+ 亜硝酸

T B P 抽出

水相

T B P 相

FP (Am, Cm)

Pu (IV)

C M P O 抽出

水相

C M P O 相

FP

Am, Cm + 希土類