論文の内容の要旨

論文題目

STUDIES ON CHARACTERIZATION OF PROCESS SOLUTIONS

IN NUCLEAR FUEL REPROCESSING

－ANALYSIS AND RADIOLYSIS IN HIGHLY RADIOACTIVE SOLUTIONS－

核燃料再処理プロセス溶液のキャラクタリゼーションに係る研究

－高放射性溶液に係る分析および放射線分解－

久野 祐輔

1. 本研究の背景と目的

　ビューレックス再処理法に係わる基礎研究は主に1950年代から行われ
ているが、中でも高放射性溶液の濃縮／貯蔵プロセスにおける「有機相
の生成／分解」や「水の放射線分解による水素の発生」のように同プロ
セス溶液の特異な性質を調べる研究が重要視された。
　濃縮工程における有機相の生成／分解に係る研究の大部分は、トリブ
チル燐酸（ＴＢＰ）／希釈剤が混入した硝酸溶液の加熱時における急激分
解反応事象の検証・解明である。しかしＴＢＰが実際の再処理プロセス
の水溶液中に多量に溶解し、濃縮等の操作により有機相が生成（析出）す
ると仮定した場合（実際の再処理工程ではＴＢＰ洗浄除去が行われるた
めＴＢＰの多量の溶解はない）、ＴＢＰのみならずジブチル燐酸（ＨＤＢ
Ｐ）などの劣化生成物も有機相の生成／分解に関与することが予想でき

る。しかし実工程水溶液におけるＴＢＰの劣化や溶解についての知見は極めて少ない。

　高放射性溶液貯蔵プロセスにおける水の放射線分解による水素の発生についても、いくつかの未研究課題が残されている。高$\beta\gamma$放射性溶液においては、溶液の深さが増すにつれ見かけの$G(H_2)$が減少する事象（以下液深効果と呼ぶ）が報告されているが、高α放射性の系においては同効果を扱った研究は報告されていない。また、既出の報告では相互に矛盾した結果も示されており、必ずしも満足な知見が得られてない。

　一方、再処理高放射性系プロセス溶液の性質を調べる上で基礎となる成分元素／核種等の分析技術については、既出の報告の大部分が、測定分離の比較的容易な元素／核種の定量についての研究であり、同溶液の性質を決める上で重要な元素／核種等のうち、いくつかについては報告がなされていない。

　高放射性プロセス溶液に係わる既存の研究は以上であるが、これらを踏まえて本研究では実際の核燃料再処理の高放射性プロセス溶液の特性をより明確にするため、同溶液のキャラクタリゼーションに係るいくつかの研究を行いまとめた。目的および概要を述べれば次のようになる。

　再処理高放射性プロセス溶液の成分元素／核種等の分析技術は、同溶液のキャラクタリゼーション研究上極めて重要である。本研究では、第一部として同溶液の性質を決定する上で重要な核種／元素等のうちこれまで確立されていないものについて取り上げた。

　蒸発濃縮プロセスにおける有機相生成（分解）に関する研究を実際のプロセスにおける事象として想定する場合、同プロセス溶液におけるＴＢＰの溶解度、溶解特性、放射線分解速度などについての知見が必要かつ

重要となる。また貯蔵プロセスにおける水の放射線分解については、特にα放射性水溶液において上述のような未研究課題／矛盾点が残されており、これ等を解明することは重要である。本論文第2部では、高$\beta\gamma$放射性溶液である高放射性廃液高放射性廃液（HRLW）および高α放射性溶液である硝酸プルトニウム水溶液（PuN）を対象に、TBPの溶解度／溶解特性を調べるとともにTBPの放射線劣化速度、劣化生成物に焦点を置き研究を実施した。さらにPuNにおける水素発生について、これまで報告されていない液深効果やPuの化学的寄与などについて究明した。

2．高放射性溶液に係る分析技術の研究

本研究では、高放射性プロセス溶液の発熱評価上最も重要な^{90}Sr - ^{90}Yの定量、高い核分裂収率を示しプロセス上特異な性質を示す^{99}Tcの定量、そして再処理の高α放射性溶液において化学的性質を決定づけるPuの原子価別定量法ついて取り扱った。さらにTBPを含む高放射性プロセス溶液の特性に関する研究を行う上で重要となる同溶液中のTBP／HDBPの定量技術について扱った。

HRLW中の^{90}Srの定量：キャリア（Sr）および共沈剤（Fe）存在下で溶液を塩基性に変換することにより、^{90}Sr以外の^{90}Yを含む核分裂生成物（FP）を沈澱除去した。炭酸塩として沈澱回収した^{90}Srの周囲を 0.2mmステンレスおよび水で覆った状態でチェレンコフ計測することにより定量した。本法は、1000MWe、3年照射のPWR燃料から発生した200日以上の冷却期間を持つHRLWに含まれる^{90}Srに対し 5%の精度で適用できた。

再処理工程の高放射性溶液に含まれる^{99}Ｔｃの定量：対象溶液を塩基性に変化させＴｃ以外の大部分のＦＰを沈澱除去した。必要に応じ陰イオン交換法による精製を行った。Ｔｃがすべて^{99}Ｔｃである点を利用し、Ｔｃ濃度を高周波誘導プラズマ発光分光（ICPAES）によって測定する方法を採った。使用した発光線は、261.00nmであり、本波長においてＴｃは混入物の有意な妨害なく良好な精度で測定できることが確認できた。

　ＰｕＮ中のＰｕの原子価別定量：定電位クーロメトリーのＰｕへの適用を図ることにより、高精度（0.1%／10mgＰｕ）なＰｕ定量を実現した。また従来法である電位差滴定法において妨害を示すNp, Cr, Amについても影響なく測定できることを確認した。またＰｕ酸化状態組成比については、Ｐｕ(III), (IV), (VI)のみならずＵ(IV), (VI)が混在する硝酸系試料に対し、試料の吸光スペクトルをグラフィック上で演算し個々の成分スペクトルに分解する方法により正確に分析する技術を確立した。

　ＨＲＬＷ／ＰｕＮ中のＴＢＰ／ＨＤＢＰ定量：対象溶液を塩基性に変化させることによりＺｒ，Ｐｕ等と沈澱塩を形成するＨＤＢＰを遊離溶解させるとともに金属イオンを沈澱させた。さらに溶液を酸性とした後、ＴＢＰおよびＨＤＢＰをクロロホルムに抽出させ、ガスクロマトグラフィで測定する方法を採った。カラムにはTENAX GC担体にPEG20M液相をコーティングした充填剤を調製し用いた。本法により、ＨＤＢＰ（>1mg/1）を直接ＴＢＰ（>0.2mg/1）と共に測定できることが確認された。

３．高放射性水溶液に溶解するＴＢＰおよび水の放射線分解に係る研究

　ＰｕＮ及びＨＲＬＷに対するＴＢＰの溶解度を求めた。さらに、次に

示す溶解特性の知見を得た。1)Ｐｕ濃度(0-0.1M)の溶液についてはＰｕがＴＢＰ溶解に対し塩析剤的に働くが、Ｐｕ濃度の上昇に伴いＴＢＰ-Ｐｕ(Ⅳ)間の相互作用と思われる影響を示した。2)低Ｐｕ濃度(0-0.1M)の溶液では、ＴＢＰ・硝酸の形成によると思われる塩溶効果が観察された。3)ＨＲＬＷについてもＴＢＰ溶解度のＦＰ濃度依存性が観察された。4)水および対象溶液における溶解度の比の対数は、ほぼ温度に対し逆比例することが確認された。しかしＰｕ濃度が高くなるにつれ、本関係は直線からはずれる傾向を示した。これについてＰｕのイオン形態の変化から説明した。

　ＰｕＮに溶解するＴＢＰの放射線劣化について研究した。その結果以下に示す知見を得た。1)ＴＢＰの劣化は一次反応的に進む。しかしその劣化速度はＰｕ(Ⅳ)濃度に依存する。2)ＴＢＰ劣化速度はＯＨスカベンジャーである非解離硝酸濃度の増加により減少する。3)ＰｕＮにおけるＴＢＰの放射線劣化をＰｕおよび非解離硝酸の濃度を用い定量的に表すことができた。4)Ｐｕ(Ⅲ)溶液とＰｕ(Ⅳ)溶液では、溶解するＴＢＰの劣化速度が異なることがわかった。よって非解離硝酸以外にＰｕもＯＨスカベンジャーとしてＴＢＰの分解遅延に関与しているものと考えた。

　ＨＲＬＷに溶解するＴＢＰの放射線劣化について研究を行った。得られた結果は次の通りである。1)ＴＢＰの劣化速度は、上記非解離硝酸および NOxより高い酸化還元電位を示すＦＰ(Ce, Ru, Ag, Pd, Brなど)の存在により減少する。2)本効果はＴＢＰ－ＯＨ反応への各元素の寄与により説明できる。3)劣化生成物であるＨＤＢＰの分解速度は非常に遅いにもかかわらずＨＤＢＰの生成速度はＴＢＰ分解速度と一致しない。よって水相ではＨＤＢＰ以外の劣化物がかなり生成されていることがわかった。

4)ＨＤＢＰ以外の主要な生成物の定性を試みた。その結果、主な劣化生成物の形態を見い出すことができた。

　ＰｕＮにおける水の放射線分解を研究した。その結果以下の知見を得た。1)Ｐｕ(Ⅳ)は水素発生に化学的に関与する。ＰｕＮにおける$G(H_2)$は、他報における^{244}Cm(硝酸系)による$G(H_2)$と一致しないが、これについてはＰｕの化学的寄与により説明できる。2) $G(H_2)$における液深効果が確認できたが、その効果は$\beta\gamma$系の場合の液深効果に比べ明らかに小さい。3)ＯＨスカベンジャーである非解離硝酸およびＰｕ(Ⅳ)の濃度が液深効果に影響するため、同効果には、$H_2 - OH$反応が関与していることがわかった。その他、ＰｕＮにおける$G(O_2)$への影響因子についても知見が得られた。

4．結論

　ピューレックス再処理の濃縮貯槽プロセスにおける高放射性水溶液の特性を明確にするため、同溶液の分析技術および同水溶液中に溶解するＴＢＰおよび水の放射線分解について研究を行った。その結果、重要な核種／元素等について分析技術を確立した。また、蒸発濃縮工程における有機相の生成事象を実際の系において想定する場合必要となるＴＢＰの溶解度およびその放射線劣化速度に関し新たな知見が得られた。さらに高放射性溶液中の水の放射線分解に関し、水素等の生成に係る影響因子や反応機構などについて解明した。本研究の実施により再処理高放射性プロセス溶液の特性が明確化された。

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i

TABLE OF CONTENTS

PART 1

STUDIES ON ANALYTICAL TECHNIQUES FOR

HIGHLY RADIOACTIVE SOLUTIONS

PART 2

STUDIES ON RADIOLYSIS OF DISSOLVED TBP AND WATER IN HIGHLY RADIOACTIVE AQUEOUS SOLUTIONS

ABSTRACT

The PUREX (Plutonium Uranium Refining by EXtraction) is the
only technique for nuclear fuel reprocessing industrially
established at the present time. The important problems related
to the PUREX type reprocessing have been almost investigated,
resulting in the basis for the establishment of a safe flowsheet
for the reprocessing. The information so far reported, however,
does not completely satisfy the requirements for the
clarification of the phenomena which could occur in the practical
field. In this respect, further study on the characterization of
process solutions, especially from the processes of concentration
(evaporation) and storage where the dominant issues on the
reprocessing are present, is hence required for better nuclear
technology. Although the establishment of analytical techniques
is a basic issue for the characterization, the determination
methods for some of important nuclides/elements/species in highly
radioactive solutions have not been completed. The investigation
of dissolution property of tri-butylphosphate (TBP: the principal
organic material in the PUREX) and its radiolysis in aqueous
nitrate solutions of the practical reprocessing processes, on the
other hand, has been demanded for solving the problem of the
formation of the organic phase in the evaporation process
although the formation never occur in practical plants taking
protections. The study of the radiolysis of water in the
radioactive solutions is also important because ealier studies on
some parts of the radiolysis were not always consistent and
because of the unsatisfactory information available.

Based upon the above requirements, this dissertation emphasizes
the studies of the analytical techniques, and radiolysis of

dissolved TBP and water in the highly radioactive solutions.

In Chapter 1 the purpose/significance of this study is stated, followed by Part 1 (Chapter 2 - Chapter 5) which describes the analytical techniques for the determination of the important but unestablished items.

The determination of $^{90}Sr/^{90}Y$ in highly radioactive solutions, which is a predominant exothermic nuclide, bearing nearly half of the energy evolved in the solution from the spent fuels cooled for several years, is described in Chapter 2. The fission products including ^{90}Y possibly interfering with this method, were quantitatively removed by co-precipitation with ferric hydroxides during the alkaline precipitation stage, leaving ^{90}Sr in the supernatant in the presence of inactive strontium as the hold-back carrier. ^{90}Y freshly grown from the ^{90}Sr recovered as a carbonate precipitate from the supernatant was measured by Cerenkov radiation counting 2 hours after the separation. ^{90}Sr in the solutions was found to be determined with little deviation.

The species as major ingredients may chemically characterize the solutions of concern. The determination of the elements of high fission yield in highly radioactive solutions is of importance in this regard. Although the separation and measurement methods for almost all the elements have been established, the determination of technetium (^{99}Tc) has not been reported. Chapter 3 describes the study of the determination of ^{99}Tc in highly radioactive solutions, which was roughly isolated from other elements by changing the acidity to alkaline. After making the supernatant liquid acidic, inductively coupled plasma emission spectrometry (ICPES) was employed for the measurement. Sensitive determination of ^{99}Tc has been established.

From the same respect as the technetium, the precise determination of plutonium for each oxidation state is an important issue for the chemical characterization of plutonium solution. New analytical techniques for the above requirements have been developed. The application of controlled-potential coulometry to plutonium, regarded as the most precise deterination technique for elements having an electrochemically reversible couple, is described in Chapter 4. Spectrophotometric study for determining the oxidation states is also shown in Chapter 4, where satisfactory results were presented.

The determination of TBP and DBP in the solutions of interest is absolutely necessary to investigate the characteristics of the solutions relating to the formation of organic phase. The methods commonly used for the this requirement were time-consuming and difficult to apply to highly radioactive samples. Chapter 5 describes a simple determination method for TBP and DBP in the highly radioactive solutions by gas chromatography which does not require any troublesome preparation. It was found that this method can be applied to samples not only of the solutions containing TBP/DBP but also the solutions having a precipitate of a DBP-metal compound with high sensitivity.

Part 2, consisting of four chapters and entitled "Studies on radiolysis of dissolved TBP and water in highly radioactive aqueous solutions", deals with the solubility of TBP, the radiolytic degradation of TBP and the radiolysis of water in the aqueous reprocessing solutions.

Chapter 6 describes the solubility of TBP dissolved in the solutions of the highly radioactive processes with variation of several parameters such as concentrations of species involved and

temperature. It was found that plutonium or fission product(FP) simply acted as an electrolyte in the solutions of low concentration of Pu/FP for the salting-out of TBP while the dissolution of TBP showed a different tendency with increasing concentration of Pu/FP due probably to some interactions A dependency of TBP solubility on presence of HNO_3 was observed. The dependency of TBP solubility on temperature was also confirmed to be theoretical for low concentration of Pu in plutonium nitrate solution. The dissolution properties of TBP such as the interaction between TBP and the species involved or the change of ionic form are discussed.

The radiolytic degradation of TBP in the solutions of plutonium nitrate and highly radioactive liquid waste is described in Chapters 7 and 8, respectively. The former chapter focuses on the effect of plutonium on the degradation of TBP. The retardation of the degradation of TBP was found to be described only by the concentration of Pu and HNO_3, which indicates the retardation is primarily due to the presence of the competitive reactions between OH and HNO_3 / OH and Pu(IV). In Chapter 8, a kinetic study of the TBP degradation was extensively conducted in addition to an investigation of the effect of FP metal ions on the degradation. The formation of DBP in highly radioactive liquid waste solution has been also studied in order to clarify the major product(s) of the degradation of TBP in aqueous solutions. The possibility of other degradation products is discussed in the same chapter. Throughout both chapters evidence for the mechanism of the radiolytic degradation of TBP in aqueous solutions, namely due primarily to the reaction between OH and TBP, is given.

Chapter 9 describes hydrogen and oxygen gases generated radiolytically in a nitrate system by alpha-radiation. The influence of plutonium on the $G(H_2)$ was studied for an explanation of the consistent difference in G-values in $^{244}Cm-HNO_3$ solution and $Pu-HNO_3$ solution. The effect of solution height on the hydrogen generation was observed to be small but was still significant in the presence of alpha radiation. The reaction between OH and H_2 was found to be involved in the effect of solution height on hydrogen generation. The investigation of oxygen generation in PuN solution is also described for reconfirmation of the G-value of oxygen which disagreed in the previous studies.

Finally the conclusion of this study is presented in Chapter 10.

ABBREVIATIONS

TBP   Tri-(n)-butylphosphate

DBP   Di-butylphosphate

HDBP   Di-butylphosphoric acid

H_2MBP Mono-butylphosphoric acid

PuN   Plutonium nitrate

HRLW   Highly radioactive liquid waste

FP(s)   Fission product(s)

FP metal-ions Fission product/metal-ions involved

G(TBP)   G-value of TBP decomposition

G(DBP)   G-value of DBP formation

$G(H_2)$ G-value of hydrogen generation

$G(O_2)$ G-value of oxygen generation

CHAPTER 1

INTRODUCTION

1.1 Research on Characterization of Highly Radioactive Process
     Solutions in Nuclear Fuel Reprocessing

The nuclear fuel reprocessing technique called PUREX (Plutonium
Uranium Refining by EXtraction) is the only technique established
and used commercially at the present time. Based upon the basic

research on the recovery of uranium and plutonium[1] proposed by American chemists, several PUREX process flowsheets were investigated in the early 1950s[2]. Finally 30% TBP-diluent flowsheets became commonly used. This extraction method by TBP has several advantages, e.g., complete recovery of uranium and plutonium with high decontamination factors of FPs, and has resulted in outstanding success. Various basic studies for the use of an organic/aqueous solution system in the nuclear industry were required to establish a safe flowsheet. There was special concern regarding safe operations relating to the highly radioactive solutions in the processes of concentration (evaporation) and storage because the specific characteristics of the solutions were observed in the processes. Two major issues of concern were i) the formation of an organic phase in the concentration process, resulting in exothermic decomposition when heated exceedingly, and ii) hydrogen generation resulting from radiolysis of water in highly radioactive solutions. Several studies on the characterization of the process solutions were undertaken from the 1950s through the 1970s.

The organic phase mentioned above has been known to be a complex, dense mixture of organic compounds. In particular condition, it causes exothermic reactions between certain heated TBP solutions and aqueous nitrate solutions containing actinides[3]. A few problems have occurred in the evaporators/denitrators[4-7].

These indicate that the reaction could take place when the aqueous solutions containing TBP are concentrated at high temperature[8]. From this viewpoint, the properties of the organic compounds and the safety of the evaporation processes in the reprocessing plant were studied[7, 9-18]. Consequently, the safety of the plant-scale evaporator has been guaranteed in practice by controlling certain operational conditions[19, 20]. It was reported that the explosive chemical decompositions were commonly observed in the presence of an organic phase primarily containing metal nitrate·TBP/HNO$_3$·TBP species[20]. The formation of the organic phase during the concentration of solutions, on the other hand, should also be associated with the presence of degradation products of TBP. The appearance of an organic phase composed of uranium, TBP and DBP that resulted from the TBP degradation in an uranium evaporator was reported[21].

In spite of the fact that the presence of the degradation products such as HDBP can also be related to the formation of organic phase, there is very little information about the dissolution/degradation of TBP in aqueous nitrate solution of nuclear reprocessing. Most of the studies concerning the degradation were hydrolysis of TBP and its radiolysis carried out with anhydrous TBP, TBP-diluent or mixtures of TBP-diluent plus aqueous solution. Especially the latter has lasted for three decades and the results have been summarized by Schultz et al.[3].

The radiolysis mechanism of TBP in the organic phase in the presence of water can be described as follows;

$$O=P(-O-C_4H_9)_3 \rightarrow O=P(-O-C_4H_9)_2 + \cdot C_4H_9$$
$$|$$
$$O\cdot$$

$$O=P(-O-C_4H_9)_2 + H_2O \rightarrow O=P(-O-C_4H_9)_2 + \cdot OH$$
$$| \qquad\qquad\qquad |$$
$$O\cdot \qquad\qquad\qquad OH$$

or

$$H_2O \rightarrow \cdot OH + \cdot H$$
$$\cdot OH + O=P(-O-C_4H_9)_3 \rightarrow O=P(-O-C_4H_9)_2 + \cdot OC_4H_9$$
$$|$$
$$OH$$
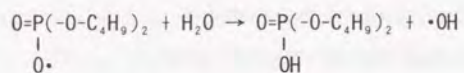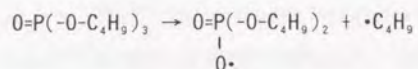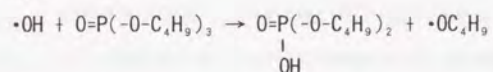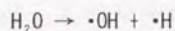
The latter is thought to be predominant in total degradation of TBP[22]. Brodda et al. stated that the degradation of TBP was initiated by OH as a radiolytic product of water from the hydrous form[23]. This is based on the result that an increase in the concentration of HNO_3, by which hydrated H_2O would be replaced, decreased the degradation of TBP. Clay et al. reported on the degradation of TBP in nitric acid solution where the chemical attack was also primarily due to the radiation-produced OH radicals and the degradation was influenced by the presence of HNO_3[24]. However, he suggested that HNO_3 acted differently as an OH scavenger for the degradation in aqueous solution. This implies that the degradation products of TBP in a single aqueous phase could be different from those in an organic phase or an organic/aqueous system. No further study on the TBP degradation, especially applicable for the practical aqueous solutions of the nuclear fuel reprocessing, has been reported. Although the G-values of the formation of degradation products of TBP in several systems involving many discussions were reported and summarized[3], only one paper by Becker et al. showed the G-value of TBP degradation in pure water or aqueous nitric acid solution[25]. That, however, cannot be directly applied to the practical solutions including e.g., plutonium or FP metal-ions, because the indirect degradation by radicals should be influenced by some species involved.

It is known for the control of hydrogen generated from highly radioactive solutions that hydrogen composition in the gas phase must be kept at less than 4.1 vol.%. The $G(H_2)$ for gamma radiation reported by Mahlman[26,27] has often been used for safety evaluations. The safety of the processes of concern has been guaranteed in practice by maintaining appropriate ventilation, taking into account the G-value. A lower G-value for the PUREX reprocessing solutions is expected from the radiation chemistry, taking into account the various species involved. The typical G-values for gas generation in the nitrate systems reported are summarized in Table 1.1. It can be seen that the G-values in the practical high beta, gamma-radioactive waste solutions were considerably lower than those in laboratory

Table 1.1 Hydrogen (oxygen) yield from nitric acid solution

Isotopic source	total [nitrate](M)	$G(H_2)$ $(G(O_2))$	Remarks	Literature cited
γ (^{60}Co)	2.0	0.05-0.06		27
$\beta\gamma$ (FP)	0.08	0.2	HCOOH added	28
$\beta\gamma$ (FP)	5.2	1.4×10^{-3}	4 cm (height)	29
α (Pu)	1.0	ca. 0.25		30
	5.8	(0.03)	not agitated	
α (Pu)	1.0	ca. 0.37		31
	6.1	(0.03)	not agitated	
α (^{210}Po)	1.0	0.45		32
	6.0	(0.75)	not agitated	
α (^{244}Cm)	1.0	0.44		33
	5.6	(0.75)	agitated	
α (Pu+^{244}Cm)	10.1	(0.94)	agitated	33

experiments[29]. The height of the solutions in the practical system was found to contribute to the decrease in G-value[29]. Although this may be due primarily to the reaction between molecular hydrogen and OH radicals[34, 36], no evidence has been given. Hydrogen generation by gamma radiolysis, including that observed in nuclear fuel reprocessed waste solutions, was summarized by Specht[34]. The hydrogen generation by alpha radiolysis in nitric acid solutions was investigated for plutonium[30, 31], curium-244[33] and polonium-210[32]. Weiss et al. summarized the reported G-values for plutonium[35]. As can be seen in Table 1.1, the $G(H_2)$ values with ^{244}Cm (^{210}Po) were consistently higher than that with plutonium, as Bibler[33] pointed out, but a further discussion was not given. He also studied the mechanism of oxygen generation in alpha radiolysis, where he showed disagreed results with others'[30, 31]. No information about the effect of solution height in PuN solutions has been reported, although less effect of solution height is expected to be observed in alpha radiolysis because of the lower OH radical density than that in gamma radiolysis.

Besides the investigation of the characteristics of highly radioactive process solutions mentioned above, the study of analytical techniques for constituent species/elements/nuclides has been a basic issue for the characterization of the solutions of interest. The determination methods for some of important

items, however, have not been established. The incompleteness of the analytical techiques in this field may be due primarily to the extremely high radioactivity in addition to the difficulty in handling.

1.2 Contents and Significance of this Study

The studies on the characterization of highly radioactive solutions stated above are situated at positions in the safety evaluation of PUREX reprocessing as summarized in Fig. 1.1, from which required and remaining items for the safety study on PUREX reprocessing can be found.

It is obvious from Fig. 1.1 that the above-mentioned establishment of analytical techniques is essential for the characterization. The determination methods for some of important but incomplete items for the highly radioactive solutions are first of all dealt with in this study as Part 1 (Chapter 2 - Chapter 5).

Yttrium-90 in HRLW solutions of reprocessing is a predominant exothermic nuclide, bearing nearly half of the energy evolved in the solution from the spent fuels cooled for several years, so that determination of ^{90}Sr, present at radioactive equilibrium with ^{90}Y, is of importance for the calorific evaluation of the HRLW solution. Difficulties in the determination of ^{90}Sr arose in
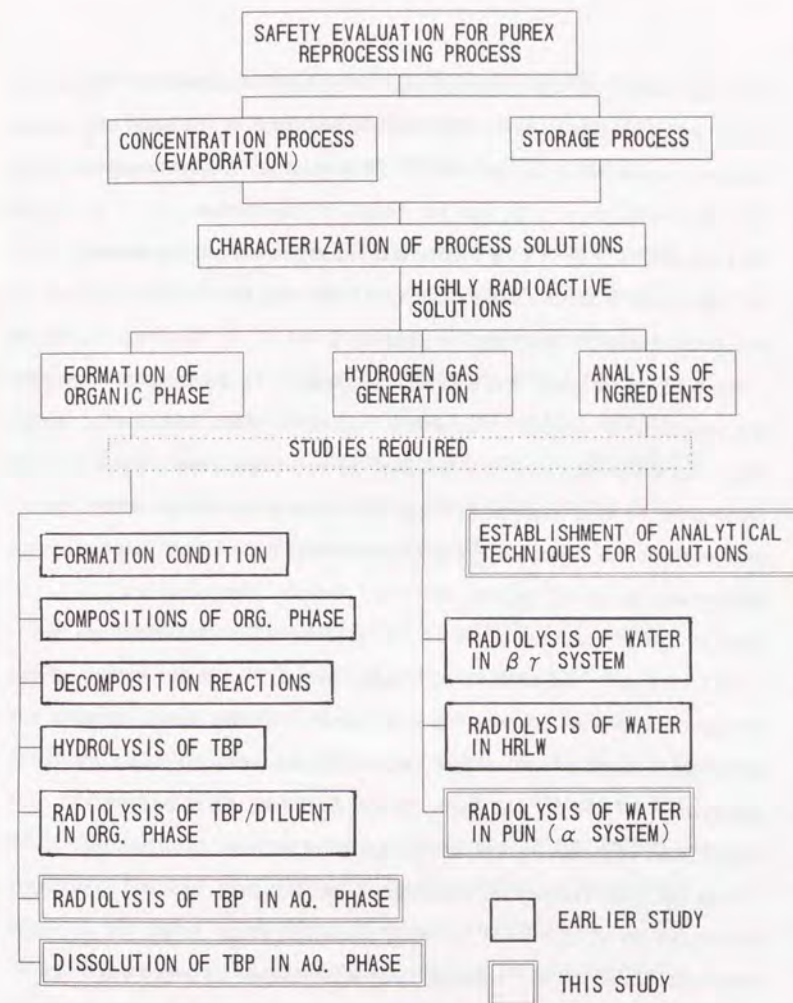
Fig. 1.1 Systematic description of studies on characterization of highly radioactive solutions in safety evaluation of PUREX reprocessing.

the requirement of its complete separation/recovery because ^{90}Sr (^{90}Y) emits only beta rays. The methods proposed in the earlier studies, which might be applied for HRLW solution, take long time for the isolation of ^{90}Sr and for reaching radioactive equilibrium of ^{90}Sr-^{90}Y. A simple and rapid determination method of ^{90}Sr in HRLW solution that can easily be applied for the practical field is described in Chapter 2.

The species as major ingredients may chemically characterize the solutions of concern. The determination of the elements of high fission yield in highly radioactive solutions is of importance in this regard. Although the separation and measure- ment methods for almost all the elements have been established, the determination of technetium (^{99}Tc) has not been reported. Chapter 3 describes the study of the determination of technetium (^{99}Tc) in highly radioactive solutions. Since ^{99}Tc emits low energy beta rays which requires highly pure ^{99}Tc for measurement, alternative method, inductively coupled plasma emission spectrometry (ICPES), was employed for the measurement because ICPAES does not require strict isolation of ^{99}Tc.

From the same respect as the technetium, the precise determination of plutonium for each oxidation state is an important issue for the chemical characterization of plutonium solution. New analytical techniques for the above requirement have been developed. The application of controlled-potential coulometry to plutonium, regarded as the most precise

determination technique for elements having an electrochemically reversible couple, is described in Chapter 4. Spectrophotometric study for determining the oxidation states is also shown in Chapter 4.

The determination of TBP and DBP in the solutions of interest is absolutely necessary to investigate the characteristics of the solutions relating to the formation of organic phase. The methods commonly used for the this requirement were time- consuming and difficult to apply to highly radioactive samples. Chapter 5 describes a simple determination method for TBP and DBP in the highly radioactive solutions by gas chromatography which does not require any troublesome preparation.

The important radiolysis occurring in the PUREX reprocessing can be considered the radiolysis of organic materials used for the chemical extraction and of water in the aqueous nitrate solutions based on the discussion given above. As stated in 1.1, the radiolysis of TBP, as the principal organic material in the PUREX reprocessing, has been dealt with for over three decades. Those are, however, mostly the radiolytic studies on the organic phase or the mixed organic/aqueous phases. The radiolysis of TBP in aqueous reprocessing solutions is required for the research concerning the safety of processing highly radioactive solutions. The study of the formation of the organic phase of TBP complexes applicable to the practical reprocessing solution system is of

importance to know precisely the phenomena which could occur in PUREX although the formation never occurs in practical plants taking some protections. The mechanism/formation conditions and the properties of the organic compounds have already been determined as stated in 1.1. The chemical degradation (hydrolysis) of TBP in aqueous nitrate solutions has also been elucidated[3, 37]. Since the concentrations of not only TBP but its degradation products such as DBP would be essential for estimating the formation of the compounds, the remaining studies to be required are i) how TBP degrades radiolytically in aqueous nitrate solutions of reprocessing, and ii) how much TBP can contaminate the solutions of interest, as shown in Fig. 1.1. The former study would provide information on the rate of TBP degradation occurring in the solutions before evaporation, and also the rate of formation of degradation products is expected to be known. As for the latter study, on the other hand, the information on the possible solubility of TBP and on the appearance of an organic phase accompanied by concentrating solution is expected to be obtained. With respect to the degradation products of TBP in aqueous nitrate solution, the expected major product, HDBP, is formed by attack at the alpha-carbon position[24] of TBP as shown below.

$$OH + C_4H_9-O-P(-O-C_4H_9)_2 \rightarrow C_2H_5CH_2CH\cdot-O-P(-O-C_4H_9)_2$$
$$\quad\quad\quad\quad \underset{O}{\overset{\|}{}} \quad\quad\quad\quad\quad\quad\quad\quad \underset{O}{\overset{\|}{}}$$
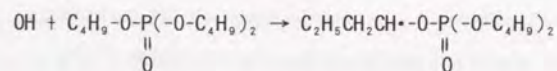
The addition of oxygen to the radical site results in the decomposition of the TBP radical into DBP in the presence of oxygen[24]. However, the other TBP radicals, namely having radical site at beta or gamma carbon position are also probably generated in some conditions. These TBP radicals must react in a different way. This may produce a lower yield of DBP. The investigation of the formation of DBP and other degradation products of TBP in aqueous solutions is of significance from this viewpoint.

The radiolysis of water is another important issue on the safety evaluation of reprocessing, as can be seen from Fig. 1.1. Although the results of earlier studies on the radiolysis by gamma radiation are almost consistent, those on alpha radiolysis do not always show good agreement, for example, the consistent difference in $G(H_2)$ between plutonium and Cm/Po and the disagreement of $G(O_2)$ in the earlier reports as shown before. Moreover, we have a lack of information on the effect of solution height on alpha radiation.

This dissertation deals with the radiolysis of dissolved TBP and water in highly radioactive aqueous solutions in Part 2.

The highly radioactive solutions relating to the processes of evaporation/storage dealt with in this study are i) PuN solutions and ii) HRLW solutions. Chapter 6 focuses on the solubility and the dissolution property of TBP in both the solutions; whereas,

the radiolytic studies of TBP in the solutions of PuN and HRLW
are described in Chapter 7 and Chapter 8, respectively. The
formation of degradation products in the aqueous solutions is
also discussed in Chapter 8. Studies on the remaining problems on
hydrogen/oxygen generation shown above are required for a more
precise evaluation of gas generation in reprocessing solutions.
Hence, the generation of hydrogen and oxygen from PuN solutions,
especially focusing on the specific problems mentioned above was
studied and its results are shown in Chapter 9.

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PART 1

STUDIES ON ANALYTICAL TECHNIQUES FOR
HIGHLY RADIOACTIVE SOLUTIONS

CHAPTER 2

DETERMINATION OF STRONTIUM-90 IN HIGHLY RADIOACTIVE
LIQUID WASTE SOLUTION

2.1 INTRODUCTION

Determination of ^{90}Sr in HRLW solutions is of importance for
the calorific evaluation due to ^{90}Y as mentioned in Chapter 1.
Simple and rapid determination for ^{90}Sr in HRLW solutions is
required because most of the determination ways taking long time

for the isolation of ^{90}Sr and for reaching the radioactive equilibrium of ^{90}Sr-^{90}Y are not appropriate for the analytical method in a practical reprocessing field.

Numerous methods have been reported for the determination of radio-strontium in biological/environmental samples. Very few methods for determining ^{90}Sr in HRLW solutions, however, have been published. Many efforts have been made for the separation and purification of Sr. Those that showed satisfactory results needed long processing times. The precipitation methods[1, 2] require repeated operations for good recovery of Sr, while ion exchange procedures[3, 4], moreover, require careful pH adjustment. Extractions[5-14] are frequently used for the separation of radio-strontium, although use of an organic solvent in a hot cell is undesirable for remotely controlled analytical operations with a manipulator. Most of these procedures are to separate Sr from calcium which may interfere with the subsequent beta-counting. Recently, the use of dicyclohexano-18-crown-6[5-9] and dibenzo-18-crown-6[9] have been proposed for Sr separation from calcium. However, these can not be applied to highly acidic solution samples. In addition, Sr picrate used in these methods is restricted in nuclear facilities from a safety viewpoint. An improvement has been made by Horwitz et al.[10]; they reported a method using crown ether which can extract Sr from nitric acid without using picrate. This method, however, requires the additional separation of actinides prior to Sr recovery when applied to HRLW solutions. Di-2-ethylhexyl phosphoric acid (HDEHP), proposed[11-14] to selectively separate Y also may not perform the separation of ^{90}Y in the samples of interest with a single extraction procedure.

One advantageous chemical property of Sr is that Sr is not precipitated in alkaline, where most metal ions are precipitated.

HRLW solutions have a high concentration of ^{90}Sr, which can also be advantageous to achieve a rapid determination because a relatively large amount of ^{90}Y can be generated in a short waiting time after the separation of ^{90}Sr. Cerenkov radiation counting may be the most appropriate method for the samples of ^{90}Y containing inactive impurities because ^{90}Y emits high-energy beta particles. In the present work, a rapid determination method for ^{90}Sr in HRLW solutions with the above advantages has been studied.

2. 2 EXPERIMENTAL

2. 2. 1 Reagents and Apparatus

Radionuclides such as ^{90}Sr and ^{147}Pm were purchased from Amersham Corporation. All other reagents were of analytical-reagent grade. The HRLW solution used was obtained from the Tokai Reprocessing Plant.

All counting was done with an ALOKA LSC-1000 Liquid

Scintillation System.

2. 2. 2 Procedure

A carrier solution containing inactive Sr and ferric nitrates
is added to an aliquot of diluted HRLW solutions. A hundred times
dilution of an original HRLW solution corresponding to the order
of 10^7 Bq/ml, which would provide a high count rate for the
Cerenkov radiation counting even for measuring ^{90}Y generated in a
short grow-in time, would be appropriate. Sr is left in the
supernatant after ^{90}Y, uranium, plutonium and many other major
fission products (FPs) are precipitated with 25-28% ammonia water.
Minor FPs such as ruthenium would also be coprecipitated with
ferric hydroxide during the same stage. The supernatant is
filtered off, the selective precipitation of strontium carbonate
with the addition of ammonium carbonate[16] follows. The
precipitate is packed in the bottom of a plastic vial (10 mmϕ,
40 mmh) directly or after being dissolved in nitric acid solution,
and then surrounded by stainless steel. This sample is placed in
the center of a glass vial (20 mmϕ, 40 mmh) filled with water.
^{90}Y which has freshly grown-in during the operation/waiting time
of approximately two hours after the precipitation, which should
be exactly recorded, is measured by Cerenkov radiation counting.
The concentration of ^{90}Sr is finally calculated from the ^{90}Y
found and the grow-in time. The detailed procedure is given in
Fig. 2. 1.

Take an aliquot (1 ml of HRLW)
|
Dilute to 100 ml
|
Take an aliquot (1 ml)
|
Add 50 mg Sr carrier, 50 mg Fe carrier
and 10 mg Y carrier.   Operate in
| shielded cell
Adjust pH>10 with NH₄OH
|
Stir and leave for 5 min. and
remove precipitate with JIS-5C filter
|
Add 2 ml of saturated (NH₄)₂CO₃   Operate in
(record time)   glove box
|
Obtain precipitate using JIS-5C filter
and pack it in plastic vial
(surrounded by 0. 2 mm stainless steel + water)
|
Measure 5 min. (record time at 2. 5 min.)

Fig. 2. 1 ^{90}Sr sample preparation for Cerenkov radiation counting.

2.3 RESULTS AND DISCUSSION

2.3.1 Decontamination of FPs and recovery of ^{90}Sr

Potentially interfering diverse nuclides present in HRLW during the Cerenkov radiation counting of ^{90}Y generated after 2 hours grow-in time were estimated using the activity ratio of each FP to ^{90}Y and the counting efficiency of beta particles of each FP. This method assumed that ^{90}Sr is quantitatively recovered and that no chemical separation of each FP was made. It was found that the ten nuclides shown in Table 2.1 had to be removed for ^{90}Sr determination in the typical HRLW. Table 2.2 shows the effect of alkaline precipitation in the presence of an iron carrier on the removal of interfering nuclides. The decontamination factors of FPs by a combination of alkaline precipitation and carbonate precipitation are also given in the table. It is obvious that the coprecipitation with ferric hydroxide effectively functions for the quantitative separation of Ru, Cs, Ce, Pm and Eu. ^{106}Rh decays to a negligible activity within 2 hours after ^{106}Ru is precipitated. Decontamination of Pr, Sn and Sb with the proposed procedure is confirmed with natural elements using ICP spectroscopy. The decontamination factors (DFs) of these were better than 10^3, although worse DFs were obtained without coprecipitation with ferric hydroxide. It can be concluded that the FP nuclides involved are decontaminated to

Table 2.1 Estimate of interfering diverse nuclides with the counting of ^{90}Y generated in grow-in time (2 hr)

Interference nuclide[a] (Error %[b])
^{106}Ru-^{106}Rh(>100), ^{123}Sn(3), ^{125}Sb(5), ^{134}Cs(>100), ^{137}Cs(>100) ^{144}Ce-^{144}Pr(>100), ^{147}Pm(41), ^{154}Eu(60)

a) Estimated from the table of fission yield of 1000MWe PWR, 3-year-irradiation[1], half-lives and β-energy emitted, assuming that the ratios of relative efficiency of Cerenkov counting to that of ^{90}Y(2.3MeV) are 10^{-3}, 10^{-2}, 10^{-1} and 1 for <0.1MeV, 0.1-0.5MeV, 0.5-1MeV and >1MeV, respectively[1].

b) Error(%) is given relative to ^{90}Y generated in 2 hours from ^{90}Sr. Calculated for 1000-day-cooling time. Nuclides not shown in the above table interfere with less than 0.5% of ^{90}Y.

Table 2.2 Decontamination factors (DFs) of FPs and recovery of Sr in 1)alkaline precipitation and in 2)both precipitations by alkaline/carbonate of proposed scheme

Nuclides	^{106}Ru	^{137}Cs	^{144}Ce	^{147}Pm	^{154}Eu	^{90}Y	^{90}Sr
Initial conc.(Bq/ml)	2.4x10^7	7.1x10^8	3.8x10^7	$-$[a]	6.0x10^7	3.7x10^8	3.7x10^8
DF/recovery in 1)	>1.6x10^8	1.7x10^5	2.5x10^4	>5.0x10^2	3.2x10^4	>1.0x10^5	0.96±0.04[c]
		4.4x10^{3}[b]	2.5x10^{4}[b]	1.5x10^{5}[b]	1.1x10^{1}[b]	2.0x10^{5}[b]		0.96±0.03[b,c]
DF/recovery in 2)	>1.6x10^8	5.9x10^8	2.9x10^8	>5.0x10^2	>4.8x10^8	>1.0x10^5	0.96±0.04[c]

a) Examined in synthetic HRLW solution containing 10^3 Bq/ml of ^{147}Pm.
b) Coprecipitation stage with ferric hydroxide was excluded.
c) Calculated from 3 repeated runs.

negligible levels for Cerenkov radiation counting of ^{90}Y generated after 2 hours grow-in time by the proposed chemical procedure.

A good recovery of ^{90}Sr was also observed in Table 2.2. It was confirmed that ^{90}Y freshly grown after alkaline precipitation was not precipitated during the carbonate precipitation stage of Sr. This indicates that the grow-in time of ^{90}Y should be counted from the moment of carbonate precipitation.

2.3.2 Cerenkov Radiation Counting for ^{90}Y Generated During Grow-in time

^{90}Sr recovered as a precipitate was dissolved in nitric acid solutions for Cerenkov radiation counting. The effect of acidity on the count rate is given in Fig. 2.2, where a slight difference in acidity of the solution influences the count rate. The relation between the count rate and the concentration of ^{90}Sr during the direct counting of the Sr precipitate packed in a plastic vial surrounded by water is also given in the same figure. This relation indicates that the precipitate provides a stable and reproducible result although the precipitation must be carefully placed at the same position in the vial. Taking into account the possibility of color quenching by some ions, which could be observed at the resolution of the recovered precipitate, the direct measurement with precipitate proves to be advantageous.

The count rate (C) at time (t) in the Cerenkov method due
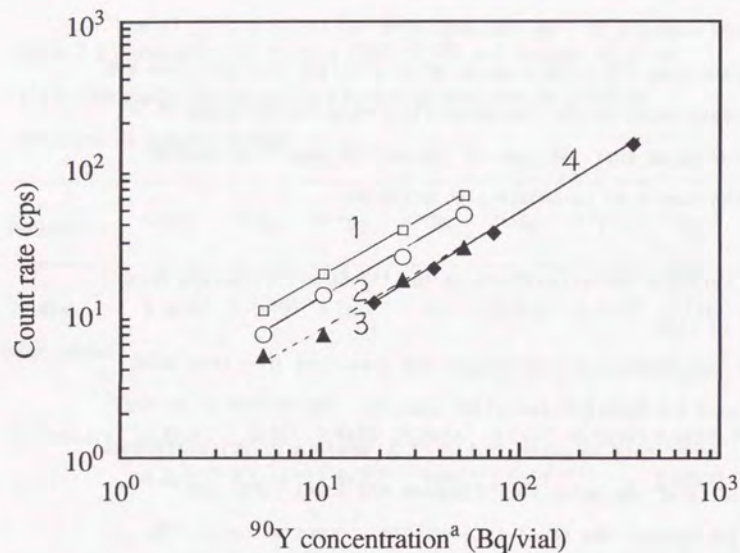
Fig. 2.2 Effect of acidity of sample solutions on Cerenkov radiation counting. 1: ^{90}Sr-^{90}Y dissolved in 0.8M HNO_3, 2: ^{90}Sr-^{90}Y in 1.0M HNO_3, 3: ^{90}Sr-^{90}Y in 1.2M HNO_3, 4: ^{90}Sr-^{90}Y precipitate. a: ^{90}Y generated from ^{90}Sr for grow-in times of 4 hrs for lines 1-3 and for 2.5 hrs for line 4. All were measured without stainless steel cover.

mainly to ^{90}Y freshly grown from separated ^{90}Sr before its radioactive equilibrium is given by Eq. (1).

$$C=[^{90}Sr][f_1 \cdot exp(-\lambda_1 t)+\{f_2 \cdot \lambda_2/(\lambda_2-\lambda_1)\}$$
$$\cdot\{exp(-\lambda_1 t)-exp(-\lambda_2 t)\}] \qquad (1)$$

where $[^{90}Sr]$, f_1, f_2, λ_1, λ_2 are, respectively, the radioactivity of ^{90}Sr, efficiency of ^{90}Sr and ^{90}Y in Cerenkov radiation counting, and decay constants of ^{90}Sr and ^{90}Y. The count rate at radioactive equilibrium of ^{90}Sr/^{90}Y is given by Eq. (2).

$$C = [^{90}Sr](f_1 + f_2) \qquad (2)$$

The low energy beta particles from ^{90}Sr are expected to be completely shielded by a 0.2mm stainless steel cover. Figure 2.3 shows C versus ^{90}Sr radioactivity at 3.5 hours after Sr separation and that at radioactive equilibrium. The efficiencies, f_1 and f_2, were obtained, respectively, to be nearly zero and 3.80×10^{-2} from the two straight lines fitted to Eq. (1) and Eq. (2). The activity of ^{90}Sr at time t (hr) can be expressed as follows.

$$[^{90}Sr(Bq)] = C / [\{f_2 \cdot \lambda_2/(\lambda_2-\lambda_1)\} \cdot \{exp(-\lambda_1 t)-exp(-\lambda_2 t)\}]$$
$$= C(cps) / 3.80 \times 10^{-2}\{exp(-2.75 \times 10^{-6} t) - exp(-1.08 \times 10^{-2} t)\} \quad (3)$$
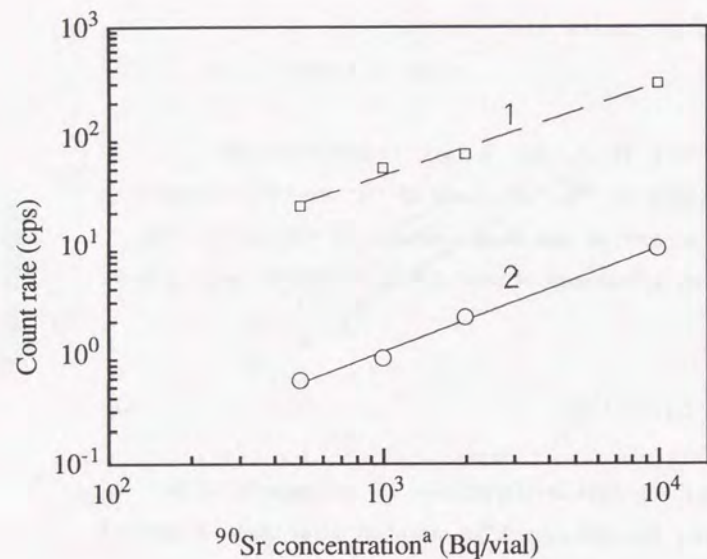
Fig. 2.3 Relation between count rate and radioactivity of precipitate. Both lines were obtained with 0.2 mm stainless steel cover. 1: ^{90}Sr-^{90}Y radiative equilibrium, 2:^{90}Y generated from ^{90}Sr for grow-in time of 3.5 hrs. a: given in ^{90}Sr activity originally contained.

The Cerenkov radiation counting for ^{90}Y-^{90}Sr with the proposed procedure thus showed a linear relationship in the range of 10 to 3×10^5 Bq/vial with a regression coefficient of 0.999, which implies that the grow-in time of ^{90}Y for a proper measurement must be less than three hours when the dilution factor of HRLW ($\sim 10^9$ Bq^{90}Sr/ml) is a hundred as given in Fig. 2.1.

2.3.3 Validity of Proposed Procedure

The validity of the proposed procedure for ^{90}Sr in the practical HRLW solutions was confirmed by two approaches. The time-course of the count rate of the sample prepared from a diluted HRLW solution plotted in Fig. 2.4 is in accord with the curve obtained from Eq. (3) with the average content of ^{90}Sr ($(3.20 \pm 0.07) \times 10^5$ Bq/vial). This would be evidence for the validity of the proposed procedure, because the curve should deviate from the relation given in Eq. (3) in case the sample is contaminated by other FPs.

Another approach was taken using the method of standard addition, by which the accuracy of the method would be confirmed. The concentrations of additional ^{90}Sr found are in good agreement with ^{90}Sr added within 2% at 10^4 Bq/vial as shown in Table 2.3. The error due to the correction of grow-in time (from the time of strontium carbonate precipitation to that of the intermediate moment of counting period) was estimated to be less than 1% when a 2-hour grow-in is employed.
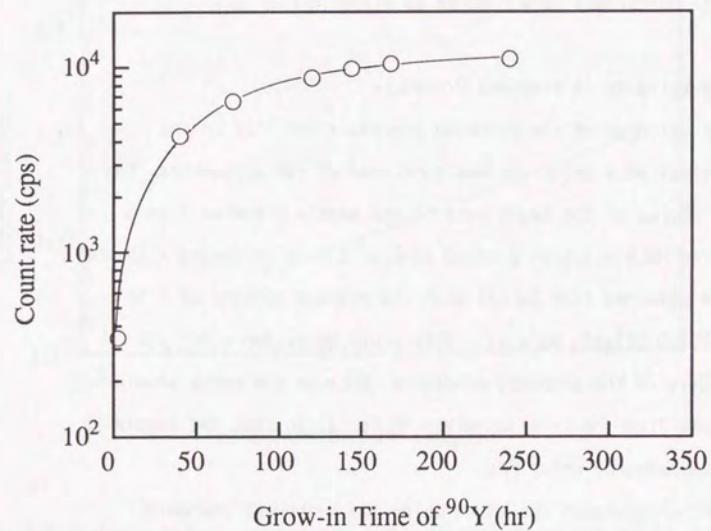
Fig. 2.4 Time-course of Cerenkov radiation counting for ^{90}Sr separated from HRLW solution. Plots are measured data and solid line shows theoretical curve described by Eq.(3) with average concentration of ^{90}Sr calculated from the plots.

Table 2.3 Determination of ^{90}Sr added in HRLW samples[a]

[90]Sr added (Bq/ml)	[90]Sr found (Bq/ml)[b]
9.9×10^3	$(9.5 \pm 0.5) \times 10^3$
1.98×10^4	$(2.00 \pm 0.1) \times 10^4$
3.96×10^4	$(3.92 \pm 0.2) \times 10^4$

a) ^{90}Sr originally present in the HRLW sample was adjusted to 4.0×10^3 Bq/ml by dilution because ^{90}Sr standard available for the addition was limited. No further dilution was made after ^{90}Sr standard was added.

b) ^{90}Sr originally present was excluded. Mean value±av. dev. for two results.

The procedure was reproducible to approximately 4.1% on 5 repeated independent determinations (5 min. counting each) for the practical samples ($\sim 10^5$ Bq/vial).

2.3.4 Application for HRLW Solutions Having a Short Cooling Time

The proposed method is available for the determination of ^{90}Sr in typical HRLW solutions with 1000 hours of cooling time. The influence of other FPs should be considered if the waste solution having a shorter cooling time is used. When the cooling time is presumed to be 150 days, ^{95}Zr, ^{110m}Ag, ^{110}Ag, ^{140}Ba, ^{160}Tb and ^{140}La would only slightly interfere with the method, taking into account the DFs previously discussed. The minimum cooling time in which the above method is directly applicable with an error of less than 0.5% was estimated to be 200 days from ^{140}Ba, based on the same approach shown in Table 2.2, since Zr, Ag, La and Tb were confirmed to be removed as precipitates.

2.4 SUMMARY

A method for simply and rapidly determinating ^{90}Sr in HRLW solutions from nuclear fuel reprocessing has been established. The majority of FPs including ^{90}Y are precipitated in an alkaline medium leaving ^{90}Sr in the supernatant in the presence of inactive strontium as the hold-back carrier. ^{90}Y freshly grown-in from the ^{90}Sr is measured by utilizing Cerenkov radiation counting technique with stainless steel shielding 0.2 mm thick that cuts off any low energy beta particles, after strontium is recovered as a carbonate precipitate from the supernatant. Only two hours is sufficient for ^{90}Y grow-in because the large amount of ^{90}Sr can be present in the final precipitation. The concentration of ^{90}Sr is calculated from the ^{90}Y detected and its grow-in time. The nuclides potentially interfering with this method, ^{106}Ru, ^{134}Cs, ^{137}Cs, ^{144}Ce, ^{144}Pr, ^{147}Pm, ^{155}Eu, ^{125}Sn and ^{125}Sb, are quantitatively removed by co-precipitation with ferric hydroxides during the alkaline precipitation stage. The relative standard deviation (n=5) is better than 5%. The time required for one determination is less than three hours.

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CHAPTER 3

DETERMINATION OF TECHNETIUM
IN HIGHLY RADIOACTIVE SOLUTION

3.1 INTRODUCTION

The fission yield of technetium-99 amounts to about 6%. Its content in the spent fuel of a light water reactor is about to be 0.1% by weight[1]. In a reprocessing process of the spent fuel, most technetium exists in HRLW solutions. The determination of this sort of major element in HRLW solution is of importance for the discussion on the chemical characterization of the solution, as mentioned in Chapter 1. A certain amount of technetium is also present in the insoluble residue and some in the product streams of plutonium/uranium. The investigation on technetium behavior is another important issue for the sound operation of a large-scaled reprocessing plant. There remain many problems to be solved in the behavior of technetium in such a plant[1]. Technetium works as an unfavorable catalyst to decompose hydrazine being added to the plant streams to scavenge nitrous compounds[2]. Though a few examinations[1, 3, 4] about the technetium behavior in reprocessing have been made on a laboratory scale, a detailed investigation has not been done for a large-scaled reprocessing of a light water reactor fuel. This delay is mainly due to the difficulties in its separation from the fission products (FPs) and heavy metals.

Several methods have been reported for the determination of technetium, including the separation from FPs. Technetium was separated from FPs and precipitated as tetraphenylarsonium pertechnetate in the presence of perchlorate[5] However, it is difficult to perform the precipitation and the dissolution of technetium by a remote operation in a hot cave. Among various solvent extraction methods, the use of such extractants as tertiary amines or quarternary ammonium salts seems to be most efficient for the separation of technetium from FPs[6, 7, 8]. Under

the conditions suitable for the separation, however, plutonium is co-extracted. Ferguson and Kyffin[3] suggested that the precipitation of the heavy metals and the co-precipitation of certain FPs in alkaline media prior to the extraction were effective for the separation of pertechnetate, which is stable in both alkaline and acidic media.

A chromatographic method using an ion exchange resin could be the most appropriate for the separation from the viewpoint of remote-controlled operation. Rimshaw[9] has reported the needed conditions for the technetium separation with anion exchange resins in sodium hydroxide media.

Almost complete separation of technetium is required before its radiometric, electrochemical or spectrophotometric measurement. The interference due to impurities in the case of the inductively coupled plasma emission spectrophotometry (ICPES) is much less than that for the other methods described above. Therefore, ICPES would appear most promising as a way to solve the difficulties involved in the complete separation of technetium from FPs. Although very few reports had been published on the determination of technetium by ICPES, the method has been introduced recently for technetium in the field of environmental analysis[10].

In this study, the separation of technetium based on the precipitation of diverse elements in alkaline media or on the anion exchange after the precipitation and the measurement of

technetium with ICPES have been dealt with to allow the determination of technetium in not only HRLW solutions but also other solutions of the reprocessing process.

3.2 EXPERIMENTAL

3.2.1 Apparatus

The inductively coupled plasma (ICP) spectrometer used and the operating conditions adopted are given in Table 3.1. The ICP source was installed in a glove-box of stainless steel, as illustrated in Fig. 3.1, so as to prevent potential releases of radioactive elements; a spectrometer was separately set just beside the glove-box. The Emission spectrum was measured through a glass window of the glove-box. The fine particulates in an ICP exhaust stream were removed by filtration with high-efficiency particulate air filters inserted after a gas cooling device.

3.2.2 Reagents

Ammonium pertechnetate (Dupont Tc-99 in 1M HNO_3, isotopic purity of 99.00%) was purified chemically by the anion exchange method[11]. Other reagents were of analytical-reagent grade. The anion exchange resin used, BIO-RAD AG1-X8, was 100-200 mesh and was conditioned to be nitrate form.

Table 3.1 Instrumental operating conditions

ICP source	Shimadzu ICPS-2H
Nebulizer	Concentric glass nebulizer
Plasma operating power	1.2 kw
Argon flow rate	
coolant	10.5 l/min
auxiliary	1.5 l/min
carrier	1.0 l/min
Observation height	15 mm above load coil
Integration time	20 s
Spectrometer	Shimadzu GEW-170
slit width	50 μm - 6 mm
Analytical line	Tc(II) 261.00 nm
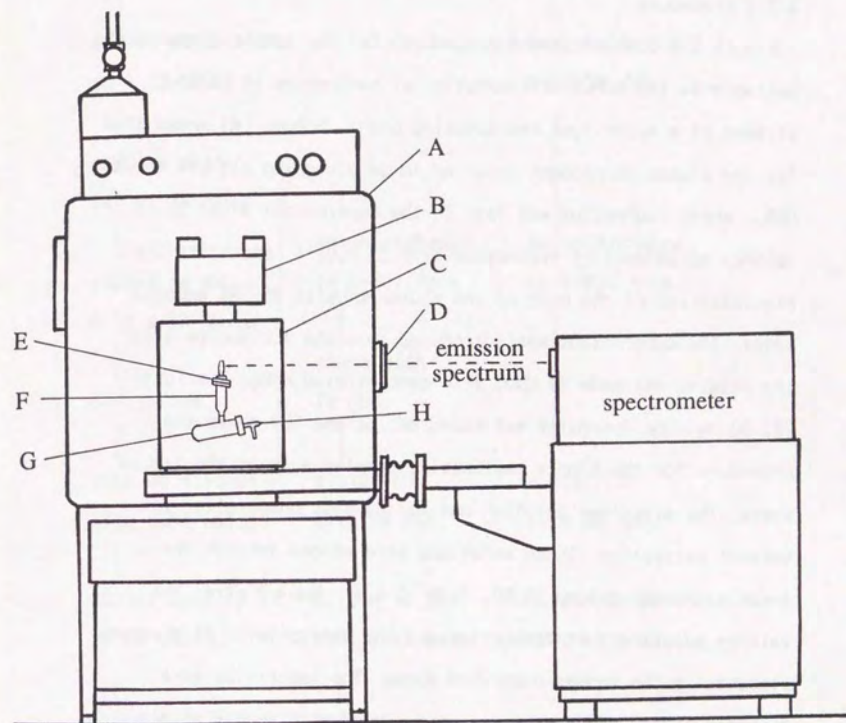
Fig. 3.1 Inductively coupled plasma emission spectrometer enclosed in a glove-box. A, glove box; B, gas cooling device; C, inductively coupled plasma source; D, glass window; E, high-frequency generator; F, plasma torch; G, chamber; H, nebulizer.

3. 2. 3 Procedure

Figure 3. 2 summarizes the procedures for the sample preparation suitable to the ICPES determination of technetium in various streams of a spent fuel reprocessing plant. Scheme (A) shows that for the plutonium product solution to be plutonium nitrate in 7M HNO_3, where technetium was left in the supernatant after the valency adjustment of technetium with 3% H_2O_2 [2] and after the precipitation of the bulk of the plutonium with 25-28% ammonia water. The supernatant was introduced into the ICP source after its acidity was made 2M HNO_3 with concentrated HNO_3. The Tc II 261.00 nm line intensity was measured. Scheme (B) shows the procedure for the highly radioactive samples such as the liquid waste, the dissolver solution and the aqueous phase after the solvent extraction. Those solutions were passed through the anion exchanger column (R-NO_3 form, 0.5 ml, 5mmφ) after the valency adjustment of technetium and the precipitaion of diverse elements in the manner described above. The impurities were directly eluted and the resins were rinsed with weakly acidic media (1M HNO_3). After the elution of technetium with 8M HNO_3, the acidity of the eluate was adjusted to 2M HNO_3 with water. The technetium in the eluate was determined by the ICPES. Scheme (C) is for the organic phase after the solvent extraction. Technetium in the phase was back-extracted with 8M HNO_3. The solution back-extracted was introduced into an anion exchanger column where little pertechnetate was adsorbed, while heavy metals slightly
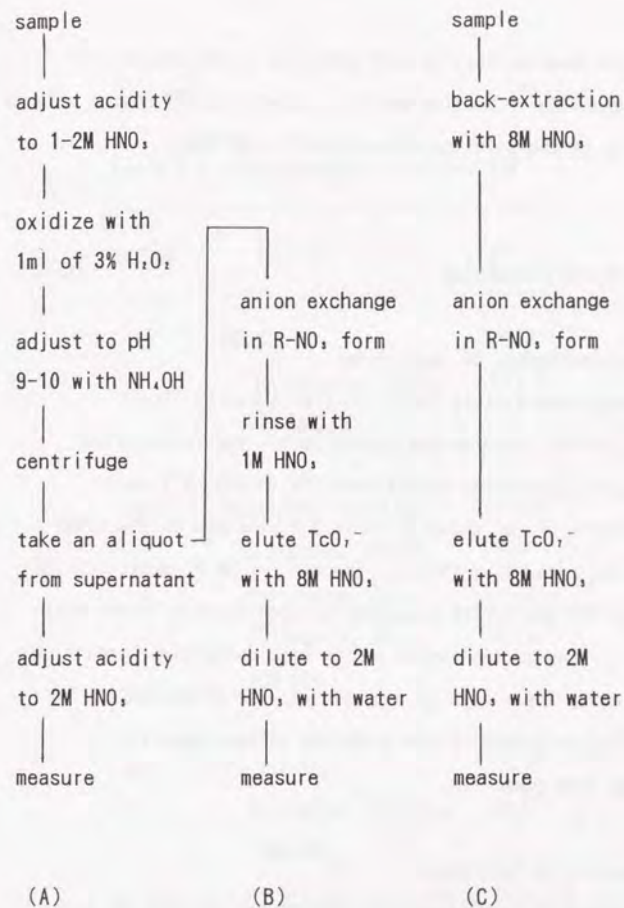
Fig. 3.2 Tc sample preparation for ICPES. (A): separation of Tc from other elements by the alkaline precipitaion, (B): separation of Tc by the alkaline precipitaion, followed by the anion exchange, (C): separation of Tc by the back-extraction from organic phase, followed by the anion exchange.

mixed in the back-extraction were adsorbed in the resins. The eluate containing technetium was introduced into ICP source after the acidity of the solution was adjusted to 2M HNO$_3$.

3.3 RESULTS AND DISCUSSION

3.3.1 Decontamination of Impurities

Decontamination factors (DFs ; initial activity/final activity) of FPs, uranium and plutonium for the isolation of technetium by procedures (A), (B) and (C) in Fig. 3.2 were sufficiently high, as shown in Table 3.2. The DFs of the total FPs were estimated from those of the typical FP elements, Cs-137, Ce-144, Eu-155 and Ru-106 by gamma-ray spectrometry. Since most gamma-activities in the sample can be eliminated by procedure (B) in a hot cave, these results suggest that the determination by ICPES can be performed in the glove-box without special shieldings from gamma-ray.

3.3.2 Recovery of Technetium

The recovery of technetium after procedures (A) and (B) was examined. Samples containing technetium and ten other elements, whose concentrations were about 100 times as high as that of technetium, were prepared for the experiment. Table 3.3 gives the results obtained from 4 replicate determinations; these results

Table 3.2 Decontamination factor (DF)

Method[a]	Sample	DF
(A)	HRLW FPs:approx. 50g/l /2M HNO$_3$	1×10^4 (FP) [b]
(B)	Dissolver solution U:approx. 200g/l Pu:approx. 2g/l FP:approx. 5g/l /3M HNO$_3$	1×10^4 (FP) [b] $>1\times10^1$ (U, Pu)
(C)	Pu product Pu:approx. 200g/l /8M HNO$_3$	2×10^3 (Pu)

a) (A)(B)(C) correspond to those in Fig. 3.2.
b) DF on gamma activity

Table 3.3   Recovery rate of Tc

Method	Sample	Recovery rate(%)
Alkaline prec. [a]	Tc 20 mg/l /3M HNO₃	101.7 ± 2.0
Alkaline prec. + ion exch. [a]	Tc 20 mg/l /3M HNO₃	97.7 ± 2.4

a)Sample contains following elements besides Tc;
   Fe, Ni, Cr, Mo, Ba, Ce, Na, Zr, Eu and Sm.

suggest that almost perfect recovery of technetium can be attained by the proposed procedures. The results also imply that no co-precipitation of technetium occurs during the procedures, in accordance with the results reported in ref. 3.

3.3.3 Effect of Nitric Acid

The effect of acidity on ICPES is shown in Fig. 3.3(a). The degradation of relative emission intensity was within 10 % even when the neutral solution was changed to be 2M HNO_3. On the other hand, the smallest dilution factor of the eluent, which should be 8M nitric acid, was needed to obtain a high response of technetium in ICPES. Two molar nitric acid was, thereby, chosen in the present work. Two molar HNO_3 was also employed to obtain the calibration curve of technetium in ICPES.

3.3.4 Effect of Sodium Hydroxide and Ammonia Water

Sodium hydroxide has usually been used for the separation of technetium by basic anion exchange resins[9] ; the effect of sodium hydroxide on ICPES was therefore studied and compared with that of ammonia. Sodium hydroxide seriously affects the emission intensity of technetium, but ammonia does not, as seen in Fig. 3.3 Ammonia seems to be available for both separation methods; the alkaline precipitation and the basic anion exchange. The separation of technetium with the anion exchanger based on the procedure (B) in Fig. 3.2 from molybdenum, which is also adsorbed
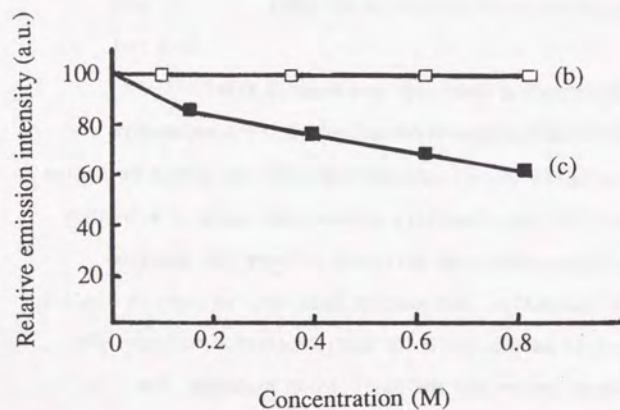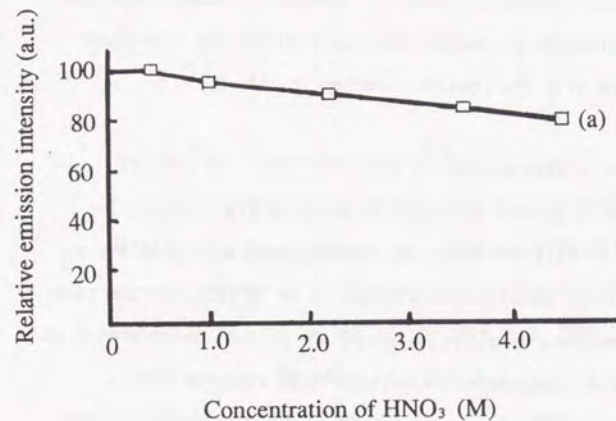
Fig. 3.3 Effect of nitric acid (a), sodium hydroxide (b) and ammonia (c)
on emission intensity of technetium.

in the exchanger from alkaline media and a major interference on
ICPES of technetium, showed almost the same performance as that
using 0.5M sodium hydroxide instead of ammonia in the above
procedure.

3.3.5 Interference

The effects of diverse elements on the determination of
technetium (2 mg/l) by ICPES are given in Table 3.4. The
impurities possibly present in the samples dealt with are some
major FPs, uranium, plutonium, and corrosion products such as
iron, nickel and chromium. Typical spent fuel, whose burn-up is
assumed to be around 3×10^4 MWDt^{-1}, includes FPs at most 10 times
as heavy as technetium. Since the FPs are repeatedly removed from
the solution by the extraction with 30 % TBP in the Purex
reprocessing, concentrations of FPs in the solution at the end of
the reprocessing process are considered to be very low, about
10^{-7} times the concentration in the dissolver solution. Hence,
there will be no interference from FPs when the sample is the
end-solution in the process. However, for the samples
including significant amount of FPs, such as the dissolver
solution, the separation by procedures (A) or (B) in Fig. 3.2 is
required to avoid the interferences from FPs. Among FPs Ru(IV),
Pd(II) and Mo(VI) may be accompanied by technetium in the
separation because their distribution coefficients to the anion
exchange resins in neutral solutions and solutions with various

Table 3.4 Effect of diverse elements for 2 mg/l of Tc

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(1) Ions which caused no interference at 500 mg/l level
    Ag, Cs, Eu, Gd, La, Na, Ni, Se, Sm, Sr

(2) Ions which caused no interference at 250 mg/l level
    Cd, Cr, Pd, Rh, Ru, Sb

(3) Ions which caused no interference at 50 mg/l level
    Ba, Ce, Fe, Nd, Te, U, Zr

(4) Ions which caused no interference at 10 mg/l level
    Mo, Nb, Sn, Pu

---

concentrations of nitric acid show the same tendency as that of technetium[13]. Referring to Table 3.4 and taking the concentrations of these FPs in the dissolver solution into account, we conclude that only Mo(VI) could cause interference on the practical determination. Molybdenum in the samples is, however, expected to be sufficiently removed by the anion exchanger to perform ICPES of technetium, because the distribution coefficient of molybdenum to the anion exchanger is approximately 2 orders lower[13] than that of technetium. The decontamination factors around 10^5 to 10^6 for uranium and plutonium given in Table 3.2 indicate that technetium in the dissolver and that the product solutions can be isolated from these elements enough to perform ICPES of technetium.

The agreement in the results of ICPES on the practical samples measured at two different wavelengths, discussed later, also suggests that interfering elements were satisfactorily removed before the ICPES of technetium.

3.3.6 Detection Limit and Precision

A linear calibration curve was obtained for the technetium up to approximately 10 mg/l. The detection limit (S/N=3) was 0.1 mg/l, which is sufficient for the practical requirements of technetium determination, although it was rather high because of the use of a glass window between the ICP source and the spectrometer. The relative standard deviations for 10 replicate

measurements were 2.2 % at 9 mg/l and 4.9 % at 0.9 mg/l.

3.3.7 Determination of Technetium in Practical Samples

The accuracy of the method was examined by analyzing practical
samples to which known amounts of technetium had been added. The
analytical results of the standard-added samples are given in
Table 3.5. The values found agreed well with the amounts added.
Here, it should be noted that the results of ICPES detetrmination
of technetium in a dissolver solution and in a plutonium product
solution at 261.00 nm agreed with that at 254.32 nm, the second
technetium emission line, within 3 %. These results imply that
the analytical procedures proposed can be applied to the samples
from the spent fuel reprocessing facility with no serious
interference.

Table 3.5 Determination of Tc recovered from radioactive
samples

Sample	Tc added (mg/l)	Tc found (mg/l) [a]
HRLW	51.0	50.6 ± 0.7
Dissolver solution	31.2	30.9 ± 1.0
Solv. ext. (Aqueous)	10.4	10.8 ± 0.3
Solv. ext. (Organic)	5.2	5.1 ± 0.2
Pu product	10.4	10.1 ± 0.3

a) Mean value ± av. dev. for 2 results. Tc content
   originally contained in samples was subtracted by
   measuring samples without addition of Tc standard.

3. 4 SUMMARY

This chapter describes the determination of technetium in
solutions from spent fuel reprocessing processes. Inductively
coupled plasma emission spectrometry (ICPES) was employed after
alkaline precipitation and/or anion exchange. Technetium in the
form of pertechnetate is roughly separated from other elements by
merely changing the acidity of the sample solution to make it
alkaline. This works because most of the FPs are precipitated
along with the heavy metals in an alkaline medium, whereas
technetium is not. Technetium in some solutions from highly
active processes is further purified with the aid of basic or
weakly acid anion exchange after the alkaline precipitation
mentioned above. The decontamination factors were found to be
more than 10^4 and 10^5 for FPs and for the heavy metals,
respectively. The amount of technetium separated is determined by
ICPES, which measures the Tc II 261. 00 nm line without any
significant interference. The relative standard deviations are
2. 24% at 9 mg/l and 4. 9% at 0. 9 mg/l of technetium. The proposed
method has been applied to samples from various streams of the
Tokai Reprocessing Plant; the highly active liquid waste, the
spent fuel dissolver solution, the aqueous phase of solvent
extraction and the plutonium product solution.

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CHAPTER 4

PRECISE ANALYSIS OF CONCENTRATION AND OXIDATION STATES OF
PLUTONIUM IN PLUTONIUM NITRATE SOLUTION

4.1 INTRODUCTION

Precise determination of plutonium in concentrated PuN solution
is important from the same respect as the technetium in Chapter 3,
namely for the chemical characterization of the solution of
interest. Until recently, the AgO-Fe(II)-Cr(VI) titration method[1]

had been used for this purpose. However, it became obvious that a
few impurities contained in the plutonium product interfered with
the titration method[2, 8]. Yet it was found difficult to correct
for the interference of the impurities because of poor
reproducibility of the interfering impurities in the titration
method[2]. Controlled-potential coulometry, which is expected to
be more accurate with less interference, can be an alternative
method.

The controlled-potential coulometric determination of plutonium
has been studied since the 1960s. Earlier studies were reviewed
and have been published[3]. In many reports, the Pu(III)-(IV)
couple has been adopted to measure plutonium because of its
reversible redox reaction, while the Pu(IV)-(VI) couple has also
been used to correct the interference of iron[4], which should be
contained in almost all plutonium samples, because the
differences in the potentials of Pu(III)-(IV) and Fe(II)-(III)
couples in electrolytes such as sulfuric acid and nitric acid are
not sufficient for the separate electrolysis of Pu/Fe. Use of
hydrochloric acid as an electrolyte has been reported to increase
this difference in potentials, and therefore it has been
confirmed that plutonium can be determined in the presence of
iron without any separation[5]. This method, however, cannot be
applied in the actual industrial field because use of
hydrochloric acid is restricted from the viewpoint of material
corrosion. A recent study[6] shows that two different potential

spans on the Pu(III)-(IV) couple are effective to correct for the interference of iron, where the control of potential/current, however, does not seem to provide easy practical control. Very few applications of coulometry to plutonium in large scale reprocessing plants have been reported. This may be due to the delay in instrumentation and insufficient information on the effects of impurities in recovered plutonium in PUREX reprocessing such as neptunium, americium and corrosion products of stainless steel such as iron, nickel and chromium.

Determination of the oxidation states of plutonium is another important issue for the characterization study. Spectrophotometry seems to be the most appropriate method for this purpose. The mixed spectrum of plural oxidation states, however, varies with the change in nitric acid concentration. MacKay et al. proposed a method of estimating the oxidation states of plutonium/uranium mixture from the ratio of the specific peaks of the spectrum which functionally varies with nitric acid concentration[7]. In their proposed method, the influence of nitric acid on the spectrum, however, cannot be estimated when uranium is not present together with plutonium.

In the present study, the most appropriate and practical application of controlled-potential coulometry to the determination of plutonium in PUREX reprocessing product, including studies of the effects of impurities has been studied. Furthermore, a precise analytical method for determining the

oxidation states of plutonium by graphic operations on mixed spectra has been developed. The technique has also been extended to the determination of mixed oxidation states of Pu(III), Pu(IV), Pu(VI), U(IV) and U(VI).

4.2 METHOD

4.2.1 Apparatus

A controlled-potential coulometry system composed of electrolysis cell, a potentiostat(PAR Model 173) and the coulometer(PAR Model 179) was used for the determination of plutonium content. A gold electroplated platinum mesh electrode, a platinum electrode, and a calomel electrode were used as a working electrode, a counter electrode and a reference electrode, respectively. The counter electrode was isolated from the electrolyte by a vycor frit. They were assembled in the electrolysis cell and installed in a glove box. The sample solution was stirred during the electrolysis, while nitrogen gas was passed onto the surface of the solution. The end point of the reaction was determined with a digital voltmeter by monitoring the current below the appropriate level.

A spectrophotometer, HITACHI MODEL U-3410, capable of graphically handling plural spectra with HITACHI OS No.1321000-07, 1321000-07a, was used for the determination of the oxidation

states. A measurement cell (quartz glass, 10 mm pathlength) installed in a glove box was connected to the spectrometer with a quartz fiber.

4.2.2 Procedure

The Pu(III)-(IV) couple and sulfuric acid electrolyte (0.5M H_2SO_4 + 0.05M HNO_3 + a slight amount of sulfamic acid) were chosen, although the plutonium product of a reprocessing plant generally contains a slight but significant amount of iron as a corrosion product. The controlled-potential coulometry for plutonium using the reversible Pu(III)-(IV) couple has been conducted based on the Nernst's equation;

$$E = E_o' + (RT/nF) \cdot \ln [Pu(IV)]/[Pu(III)], \qquad (1)$$

where E_o' and F are the redox potential of the Pu(IV)-[Pu(III) couple in a given system and the Faraday constant. The plutonium concentration is calculated as follows;

$$[Pu] = (X \cdot M \cdot D \cdot f)/(F \cdot Nc), \qquad (2)$$

where X, M, D, f and Nc are the coulomb number due to plutonium, the average atomic weight of plutonium, the dilution factor of sample preparation, the instrumental factor and the theoretical factor, respectively. The following theoretical factor, Nc, is derived from Eq. (1).

$$Nc = \frac{\exp[(Eox - E_o')/k]}{1 + \exp[(Eox - E_o')/k]} - \frac{\exp[(Ered - E_o')/k]}{1 + \exp[(Ered - E_o')/k]} \qquad (3)$$

The electrode potentials used for the redox reactions are necessarily more than 0.2V above and below the E_o' in order to attain more than 99.9 % electrolysis of the reversible reaction. The wide span of the redox potentials, from 0.27V to 0.72V vs the SCE, is used to quantitatively count the coulomb number of the iron reaction accompanied by that of plutonium, where the values of E_o' for Pu and Fe were observed to be 0.51V and 0.47V vs SCE, respectively. The measured value can therefore be corrected by subtracting the coulomb number due to the iron. The slight amount of iron contained in the plutonium was determined by spectro-photometry without any separation of iron, where the concentration of iron was measured at 508 nm by subtracting the absorbance due to plutonium after the color-producing reagent, o-phenanthroline, had been added. Two unkown parameters, the concentrations of Fe and Pu, were calculated from two simultaneous equations for the coulometry and the spectro-photometry. The background of the sulfuric acid solution was determined prior to the electrolysis and corrected. The measurement flow is given in Fig. 4.1.

BG Measurement

Add Supporting Electrolyte

↓

N₂ Gas on Stirrer on

↓

Meas.(Red.)

↓

Cond.1 — Y

↓

Meas.(Ox.)

↓

Cond.1 — Y

Complete 2nd Meas.? — N / Y

↓

N₂ Gas, Stirrer off

↓

Calc. BG Value

where,

Cond.1 : Condition to judge endpoint of electrolysis

Cond.2 : Condition to judge agreement of measurement data

Fe Determination (Spectro-photometry)

Take Aliquot

↓

Add Reagent

↓

Measure

↓

Calculate

Pu Measurement

Add Supporting Electrolyte

↓

N₂ Gas on Stirrer on

↓

Meas.(Red.)

↓

Cond.1 — Y

↓

Meas.(Ox.)

↓

Cond.1 — Y

↓

Meas.(Red.)

↓

Cond.1 — Y

↓

Meas.(Ox.)

↓

Cond.1 — Y

↓

Cond.2 — N / Y

↓

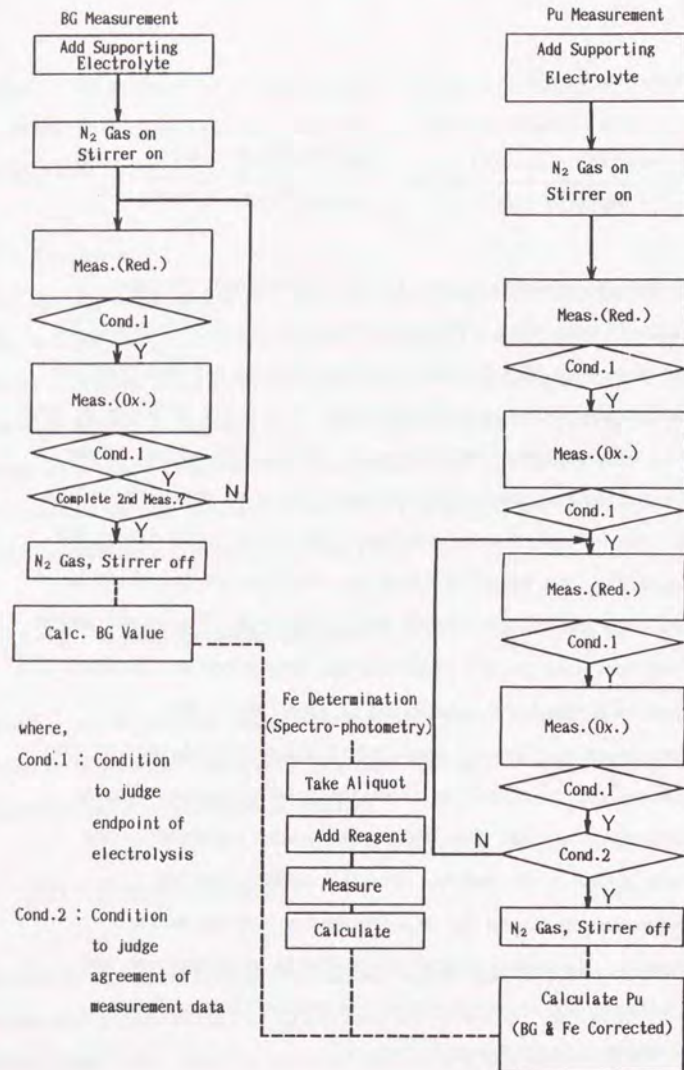N₂ Gas, Stirrer off

↓

Calculate Pu (BG & Fe Corrected)

Fig. 4.1 Measurement flow for the determination of Pu

A procedure for the graphic operations of the spectra was studied for the determination of the oxidation states. The outline of the analytical scheme when both or either of plutonium /uranium is present in the sample is shown in Fig. 4.2. The principal operations involved are as follows;

1)Memorization of a single spectrum of each component.

The spectrum of each single component, Pu(III), Pu(IV), Pu(VI), U(IV) and U(VI) is memorized prior to the graphic operations. The individual spectrum obtained by varying the nitric acid concentration is also memorized in the case where the component is dependent upon the concentration of nitric acid. Fig. 4.3 shows the dependence of nitric acid concentration on the spectra.

2)Estimate of nitric acid concentration

The concentration of nitric acid is estimated by the empirical equations shown below, based upon the relation between the acidity and ratio (R) of the specific peaks, 415nm/427nm-U(VI), 480nm/650nm-U(IV), 812nm/409nm-Pu(III) or 422nm/476nm-Pu(IV).

$[H^+](M) = 330(\log R)^2 - 94 \times \log R + 6$: 415nm/427nm-U(VI)

$[H^+](M) = 77R^2 - 76R + 20$: 480nm/650nm-U(IV)

$[H^+](M) = -8.1R + 11$: 812nm/409nm-Pu(III)

$[H^+](M) = 34R - 8$: 422nm/476nm-Pu(IV)

$0.5M \leq [H^+] \leq 5.5M$

The acidity can be roughly estimated from the original spectrum consisting of plural components or the spectrum obtained at the
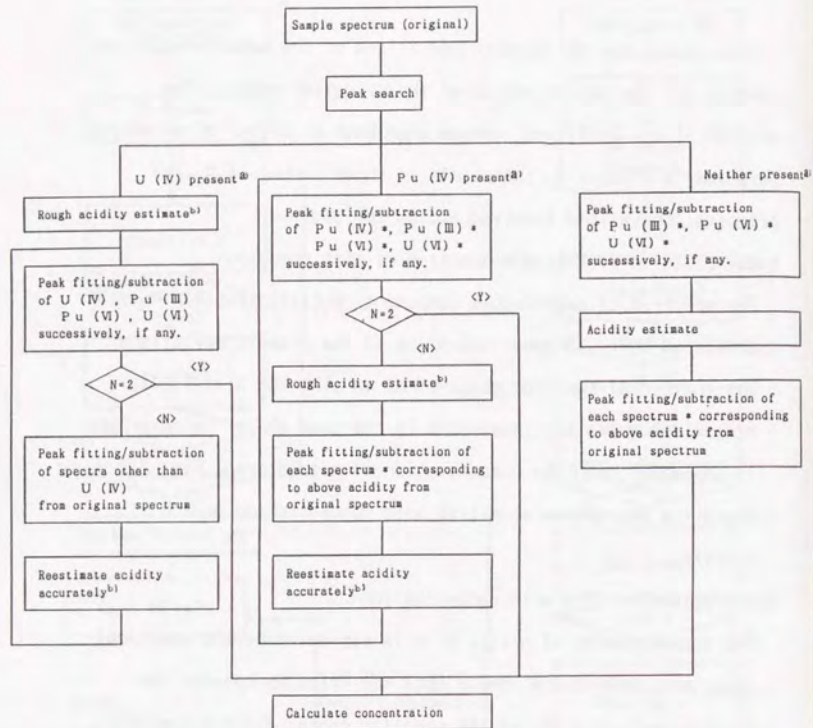
Fig. 4.2 Outline of spectrum data processing flow. a) It is assumed that U(IV) and Pu(IV) can not be present simultaneously. b) Priority of the spectrum used for acidity estimate is as follows; U(IV) U(VI) Pu(IV) Pu(III).
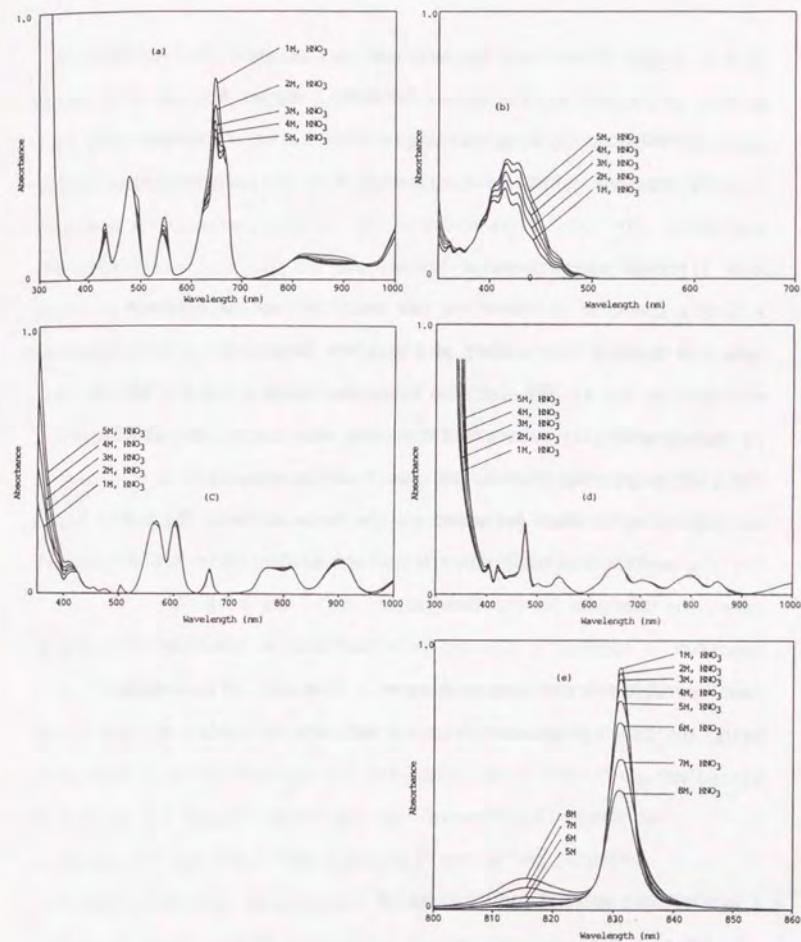

Fig. 4.3 Dependence of nitric acid concentration on spectra of (a) U(IV), (b) U(VI), (c) Pu(III), (d) Pu(IV) and (e) Pu(VI).

initial stage of the peak fitting/subtraction shown below. This acidity may still include a certain error. The acidity is more accurately estimated from the single spectrum of each component finally obtained by the following peak fitting/ subtraction operation.

3)Peak fitting/ subtraction

A single spectrum is fitted to the specific peak of a sample spectrum showing less effect of the other components after multiplying the single spectrum by an appropriate factor, which is then graphically subtracted from the spectrum of the sample. The single spectrum used is the spectrum for acidity corresponding to that estimated by the above method. The peak fitting/subtraction operation is applied successively for the remaining spectrum in the same manner until the original spectrum is completely divided into each single spectrum. The same operation is performed repeatedly from the initial stage using the acidity obtained from the accurate estimate, as stated above.

4. 3 MEASUREMENT RESULTS AND DISCUSSION

(Determination of Plutonium Concentration)

4. 3. 1 Measurement of Plutonium Concentration

The system including coulomb counting was calibrated with a metallic plutonium standard (NBS 949 series). Pure iron metal (JMC 848) was also applied to the calibration of the coulometry system instead of costly metallic plutonium standard because the standard redox potentials of both elements are close, and the potentials used for the measurement quantitatively cover counting both plutonium and iron. The instrumental factor obtained by the iron metal standard was in good agreement with that by the plutonium metal standard within 0. 01%.

The reproducibility of the coulometry was examined. The results obtained from three intermittent runs as examples are shown in Table 4. 1. Each run consisted of five repeated measurements. Good reproducibility within 0. 1% was found among the three runs.

4. 3. 2 Interference

It is essential to examine if impurities possibly contained in the plutonium product of the PUREX type reprocessing plant interfere with the coulometric determination of plutonium. Fig. 4. 4 shows the comparison of the determinations of plutonium products for the Tokai Reprocessing Plant by the proposed coulometry and the conventional titration method[1] where the titration assay consistently gives higher results. This bias may be due to the interference of impurities present in the plutonium products with the AgO-Fe(II)-Cr(VI) titration method, which is consistent with the suggestions shown in the literature cited[2, 8].

Table 4.1 Reproducibility of Pu measurement

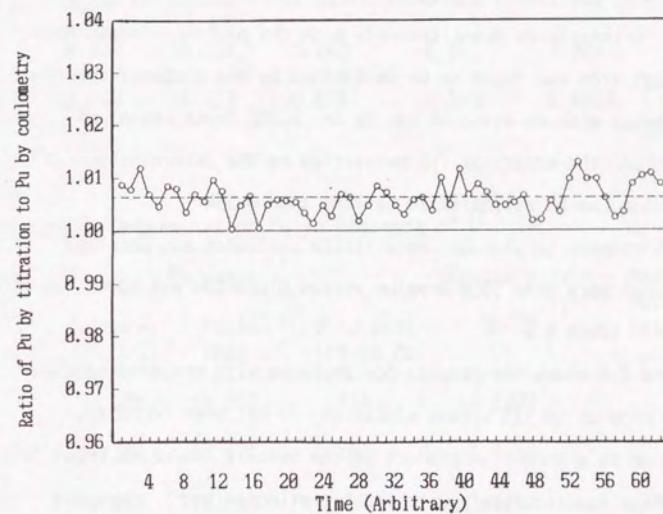| Run No.	Meas. No.	Measured(mg)	Mean (mg) (SD%)
1	1	3.9055	
	2	3.9091	
	3	3.9063	3.9059
	4	3.9074	(0.078)
	5	3.9010	
2	1	3.9050	
	2	3.9057	
	3	3.9080	3.9062
	4	3.9074	(0.037)
	5	3.9048	
3	1	3.9048	
	2	3.9070	
	3	3.9070	3.9054
	4	3.9026	(0.047)
	5	3.9056	
	Overall		3.9058 (0.053)

Fig. 4.4 Comparison between titration and coulometry.

Considering the content of the impurities and their electrochemical potentials, iron, uranium, chromium, neptunium and americium have been chosen for the investigation of the interference(s).

The recovery of iron added to the plutonium sample is shown in Table 4.2. The result indicates that iron can be corrected for since it interferes quantitatively with the plutonium measurement. Although iron was found to be determined by the proposed spectro-photometry with an error of ca. 5% for 1/100 (mass ratio) of plutonium, the effect of its correction on the determination of plutonium can be estimated to be less than 0.05%.

With respect to uranium, very little influence was observed even when more than 200% uranium versus plutonium was added, as shown in Table 4.3.

Table 4.4 shows the results for chromium with prepared samples containing up to 12% versus plutonium. It has been found that chromium as a corrosion product of the vessels, which is known to interfere quantitatively with the titration method[2], does not affect this coulometry determination.

It has been reported that a significant amount of neptunium present in plutonium samples resulted in the requirement for a different method for determining plutonium[6]. No significant effect of neptunium, an interfering element in the titration method, was detected in the coulometric determination of plutonium even in the case where about 40% neptunium versus

Table 4.2 Effect of Fe on Pu determinatation

Meas No.	Pu assay			Fe recovered (w% vs Pu)	Fe recovery rate	Mean of recovery rate
	Pu taken (mg)	Pu found (mg)	Fe added (w% vs Pu)			
1	16.348	16.435	0.123	0.124	1.008	
2	16.348	16.519	0.246	0.245	0.9959	
3	16.348	16.608	0.369	0.372	1.008	1.003
4	16.348	16.693	0.492	0.492	1.004	
5	16.348	16.777	0.615	0.614	0.9984	

Table 4.3 Determination Pu in presence of U

Meas. No.	Pu assay			Recovery rate	Mean of recovery rate
	Pu taken (mg) ①	Pu(+U) (mg) ②	U content (w% vs Pu)	②/①	
1	10.269	10.268	103	0.9999	
2	10.266	10.270	103	1.0004	
3	10.268	10.268	103	1.0000	
4	10.269	10.276	205	1.0007	1.0005
5	10.266	10.275	205	1.0009	
6	10.268	10.276	205	1.0008	

Table 4.4   Pu determination in presence of Cr

Meas. No.	Pu assay			Recovery rate	Mean of recovery rate
	Pu taken (mg) ①	Pu found (mg) ②	Cr content (w% vs Pu)	②/①	
1	21.756	21.735	4.6	0.9990	
2	21.129	21.149	4.6	1.0009	0.9999
3	21.520	21.560	4.6	1.0019	
4	19.863	19.822	4.6	0.9979	
5	21.756	21.723	11.5	0.9986	
6	21.343	21.350	11.5	1.0003	1.0001
7	21.405	21.438	11.5	1.0015	
8	18.440	18.437	11.5	0.9998	

Table 4.5   Pu determination in presence of Np[a]

Meas. No.	Pu assay			Recovery rate	Mean of recovery rate
	Pu taken (mg) ①	Pu found (mg) ②	Np content (w% vs Pu)	②/①	
1	14.266	14.272	4	1.0004	
2	14.303	14.285	4	0.9987	1.0004
3	14.093	14.107	4	1.0011	
4	14.113	14.132	4	1.0013	
5	14.097	14.115	40	1.0002	1.0010
6	14.106	14.123	40	1.0017	

a) Impurities contained in Np reagent are Am: 1.1×10^{-5} g/l, Pu: 3.5×10^{-4} g/l and Fe: trace amount when Np is 12.8 g/l.

plutonium was added to the sample (Table 4.5). An additional experiment to confirm the potential of the Np(V)-(VI) couple in the given electrolyte was conducted. Fig. 4.5 shows the coulogram of the Np(V)-Np(VI) couple in the electrolyte, namely $0.5M\ H_2SO_4$, $0.05M\ HNO_3$ and a slight amount of sulfamic acid. The potential, $(Eo')_{Np}$ is observed to be 0.90V vs SCE from the figure. The potential of the Pu(III)-(IV) couple is 0.51V vs SCE, whereas that of the oxidation of Pu(III) to Pu(IV) in the same electrolyte in the proposed procedure is 0.72V vs SCE. The predictable error from the viewpoint of thermodynamics can therefore be calculated at maximum of 0.09% using the Nernst equation when 100% neptunium vs plutonium is added. This suggests that the neptunium interference is negligible in the coulometric determination of plutonium, because the plutonium product of the PUREX reprocessing does not contain much neptunium.

Table 4.6 shows the results of the americium effect on the coulometric determination. The samples were prepared by having left the purified plutonium including more than 10% of plutonium-241 for approximately two years. The mean error was 0.15% when the americium content was 1.0 % versus plutonium. Taking into account the level of americium contained in the actual plutonium products, this effect can also be negligible.

4.3.3 Comparison of Performance

In order to confirm the performance of plutonium determination

Table 4.6 Pu determinatation in presence of Am

| Meas No. | Pu assay | | | Recovery rate ②/① | Mean of recovery rate |
	Pu taken (mg)[a] ①	Pu found (mg) ②	Am content[b] (w% vs Pu)		
1	19.33	19.31	1.0	0.9990	
2	19.33	19.30	1.0	0.9984	
3	19.33	19.27	1.0	0.9969	
4	19.33	19.30	1.0	0.9984	
5	19.33	19.32	1.0	0.9995	0.9985
6	19.33	19.28	1.0	0.9974	
7	19.33	19.33	1.0	1.000	
8	19.33	19.31	1.0	0.9990	
9	19.33	19.29	1.0	0.9979	

a) Decay corrected.
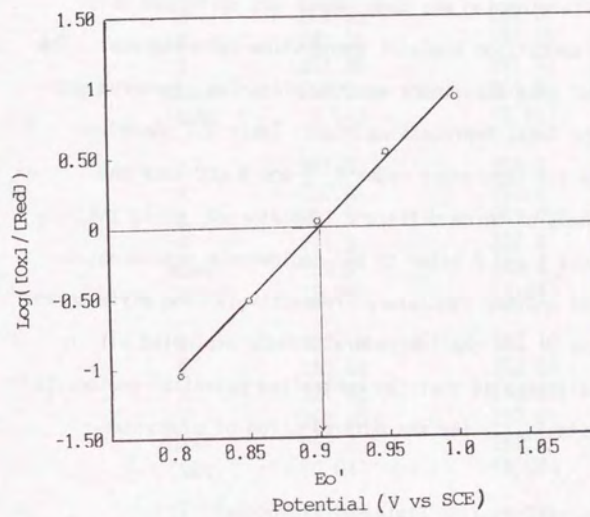b) Calculated as decay produnt.

Fig. 4.5 Coulogram Np(V)-Np(VI) couple. Ox:Np(VI), Red:Np(V)

with coulometry, a comparison among the conventional titration method, isotopic dilution mass spectrometric analysis (IDMS) and coulometric determination was made, which was performed as an international comparison analysis among three laboratories[9]. The sample used for this experiment was the plutonium recovered and purified at the Tokai Reprocessing Plant. Table 4.7 shows the results, where the laboratory codes 1, 2 and 4 indicate the titration methods of three different laboratories, while the laboratory codes 3 and 5 refer to our coulometric determination and the IDMS of another laboratory, respectively. The differences among the means of all the laboratory methods evaluated within 0.17% relatively implies that the controlled-potential coulometry performs satisfactorily for the determination of plutonium.

(Determination of Oxidation States of Plutonium)

4.3.4 Evaluation of the Proposed Scheme with a Synthesized Mixed Spectrum

The performance of the proposed analysis scheme was evaluated with several synthesized spectra composed of some single spectra. An example of spectrum analysis using a mixed spectrum of Pu(III)/U(IV)/U(VI) is shown in Fig. 4.6. A significant spectrum remained in Fig. 4.6(a) after all the spectrum subtractions; whereas, no residual spectrum (a straight line at zero absorbance) was observed in Fig. 4.6(b). This implies that the proposed

Table 4.7 Results of intercomparison analysis

| Laboratory code	Sample No.	Pu concentration (g/l)	
		Preparation 1[a]	Preparation 2[a]
1	1	251.51	251.76
	2	251.95	251.37
	3	252.39	251.35
	4	251.85	251.93
	Mean	251.9	251.6
	(SD%)	(0.14)	(0.11)
2	1	252.3	252.2
	2	252.0	252.0
	3	251.9	252.0
	4	251.9	252.0
	Mean	252.0	252.1
	(SD%)	(0.08)	(0.04)
3	1	252.10	252.10
	2	252.03	252.04
	3	251.88	252.20
	4	252.00	252.04
	Mean	252.0	252.1
	(SD%)	(0.04)	(0.03)
4	1	251.52	252.32
	2	252.12	252.32
	3	251.12	252.12
	4	251.32	251.22
	Mean	251.5	251.7
	(SD%)	(0.17)	(0.22)
5	1	251.94	251.94
	2	252.48	251.64
	3	252.32	251.97
	Mean	252.3	251.9
	(SD%)	(0.11)	(0.07)

a) Pu samples were prepared by different dilution.
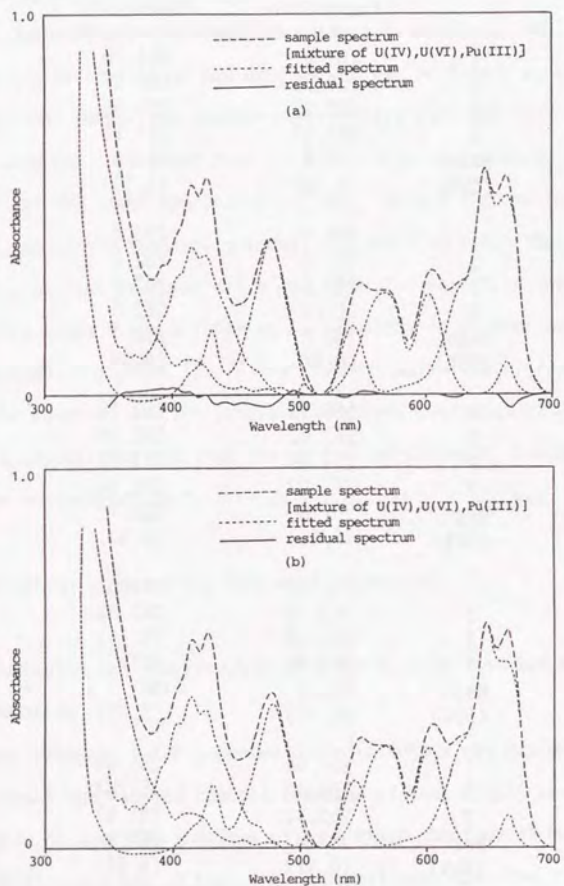
Fig. 4.6 Peak fitting and subtraction without data processing loop(a) and with th loop(b).

analysis flow effectively functions for obtaining a better result. Table 4.8 shows the analytical results for some synthesized spectra including the concentration of nitric acid. It was found that each component can be analyzed with an error of approximate 1 %, while the acidity (3M) was estimated to be 2.92±0.13 M. The analysis of another mixed spectrum synthesized for the 1M HNO₃ system was also examined, where the corresponding errors were 2 % and ±0.2 M, respectively.

4.3.5 Application to Practical Samples

The performance of the analytical scheme was examined by analyzing practical samples. The results were evaluated by comparing them with the total plutonium concentration since it was difficult to determine the composition of the oxidation states without spectrophotometry. The sum of the concentrations of all the components agreed well with the value determined by the coulometry and Davies-Gray method[10] as shown in Table 4.9. It can be concluded that each oxidation state in a mixed sample is determined accurately by the proposed method.

Table 4.8 Results of spectrum analysis.

Components [a]	Concentration analyzed U(IV) (g/l)	U(VI) (g/l)	Pu(III) (g/l)	Pu(IV) (g/l)	Pu(VI) (g/l)	HNO₃ (M)
U(IV)(VI)	4.66	18.2				2.71
U(IV)Pu(III)	4.67		1.67			3.00
U(IV)Pu(VI)	4.68				0.799	2.95
U(IV)(VI)Pu(III)	4.66	18.2	1.68			2.71
U(IV)(VI)Pu(VI)	4.68	18.2			0.802	2.83
U(IV)Pu(III)(VI)	4.69		1.69		0.799	2.92
U(IV)(VI)Pu(III)(VI)	4.69	18.1	1.70		0.802	2.65
Pu(III)(IV)			1.67	0.796		3.08
Pu(IV)(VI)				0.799	0.800	3.07
U(VI)Pu(IV)		18.2		0.807		2.98
Pu(III)(IV)(VI)			1.68	0.796	0.800	2.99
U(VI)Pu(III)(IV)		18.1	1.68	0.807		2.97
U(VI)Pu(IV)(VI)		18.2		0.807	0.803	2.98
U(VI)Pu(III)(IV)(VI)		18.1	1.69	0.807	0.803	3.00
Pu(III)Pu(VI)			1.68		0.799	2.71
U(VI)Pu(III)		18.2	1.68			2.99
U(VI)Pu(VI)		18.2			0.802	2.99
U(VI)Pu(III)(VI)		18.2	1.69		0.802	3.02

a) Some of the spectra of following components were graphically mixed together; U(IV)4.67g/l, U(VI)17.9g/l, Pu(III)1.67g/l, Pu(IV)0.799, Pu(VI)0.799, [H⁺]:3.0M

Table 4.9 Comparison of analytical results

Components		Concentration Other methods [a]	Spectrophotometry
HNO₃	(M)	1. 5	1. 8
U (IV)	(g/l)		7. 08
U (VI)	(g/l)		2. 44
Pu (III)	(g/l)		0. 41
total	(g/l)	9. 90	9. 93
HNO₃	(M)	4. 2	4. 0
U (VI)	(g/l)		6. 49
Pu (III)	(g/l)		0. 49
Pu (IV)	(g/l)		1. 42
total	(g/l)	8. 12	8. 40
HNO₃	(M)	4. 2	4. 5
U (VI)	(g/l)		6. 08
Pu (III)	(g/l)		0. 51
Pu (IV)	(g/l)		1. 41
Pu (VI)	(g/l)		1. 14
total	(g/l)	9. 19	9. 14

a) U and Pu were determined by the methods given in ref.10 and the coulometry shown in this chapter, respectively.

4. 4 SUMMARY

The controlled-potential coulometry was studied for the precise determination of plutonium recovered in the PUREX type reprocessing process. The reliability of plutonium product analysis has been improved by introducing this method which is capable of determining plutonium with better precision and accuracy than the titration method conventionally used. It was found that the impurities such as neptunium, chromium and americium, which are thought to interfere with the AgO-Fe(II)-Cr(VI) titration method, did not affect the proposed controlled-potential coulometry. Iron, which is regarded as an impurity interfering with the coulometry, is properly corrected with a simple measurement procedure using a spectrophotometer. The precision of the method for determining 10 mg-size plutonium was less than 0.1%.

An analytical method for determining the oxidation states of both or either of plutonium/uranium in a nitric acid system has been studied. The proposed method based on spectrophotometry is capable of accurately determining Pu(III), Pu(IV), Pu(VI), U(IV) and U(VI). The spectrum of a mixed solution of the above components is separated into individual spectra of several components with graphic operations. The acidic concentration can also be obtained from the ratio of specific peaks in a spectrum of U(IV), U(VI), Pu(III) or Pu(IV).

The determination of plutonium for each oxidation state was established by a combination of the above two methods, the coulometry and the spectrophotometry.