Order Number 8914805

Distribution of fission products in the homogeneous liquid-liquid extraction of uranium

Xu, Jizhang, Ph.D.

City University of New York, 1988

U·M·I
300 N. Zeeb Rd.
Ann Arbor, MI 48106

Distribution of Fission Products in the Homogeneous Liquid-Liquid Extraction of Uranium

by

Jizhang Xu

A dissertation submitted to the Graduate Faculty in Chemistry in partial fulfillment of the requirments for the degree of Doctor of Philosophy, The City University of New York.

1988

This manuscript has been read and accepted for the Graduate Faculty in Chemistry in satisfaction of the dissertation requirement for the degree of doctor of Philosophy.

April 28, 1988
Date

Harmon L. Finston
Chairman of Examining Committee

May 9, 1988
Date

A. M.
Executive Officer

Evan T. Willan

Orest Popovych

Selman A. Berger
Supervisory Committee

The City University of New York

Abstract

Distribution of Fission Products in the Homogeneous Liquid-Liquid Extraction of Uranium

by

Jizhang Xu

Advisor: Professor Harmon L. Finston

The radioactive products from uranium fission constitute a serious health hazard due to the possibility of entry into the food chain and uptake by humans. The processing of spent uranium fuels and the separation of uranium from the fission products and their subsequent safe storage is of great concern to the nuclear industry.

Separation of uranium from fission products by homogeneous liquid-liquid extraction of uranium from one molar nitric acid solution with addition of ferric nitrate as salting-out reagent, into propylene carbonate has been performed. Uranium(VI) was quantitatively extracted into propylene carbonate from an aqueous medium of 0.5 g/l $Fe(NO_3)_3 \cdot 9H_2O$ and 1 M HNO_3 at 99°C, then quantitatively stripped from the organic phase with 0.1 M sodium carbonate at pH 9. Final separation of uranium(VI) was obtained by

extracting uranium(VI) into 0.1 M dibenzoyl methane in propylene carbonate using the homogeneous technique at pH 7.

Precipitation of ferric hydroxide from the initial aqueous phase after extraction of uranium, and also from the aqueous sodium carbonate phase after stripping uranium from the propylene carbonate phase affords efficient decontamination from significant fission products.

The representative fission product elements, molybdenum, strontium, ruthenium, zirconium, and cerium, remained in the aqueous solution after extracting uranium(VI) into propylene carbonate to an extent greater than 97 %; i.e., less than three percent of the respective elements were found in the carbonate stripping solution. After the final separation step, the extraction of uranyl ion into propylene carbonate containing dibenzoyl methane, these fission product elements were no longer detectable. Ten percent of the original concentration of iodide was found in the carbonate stripping solution. However, it was removed in the final separation step.

This uranium extraction method can be applied as a practical method for separating uranium from fission products to recover the uranium from spent fuel elements. The capacity of ferric hydroxide for adsorption of fission products and the ability to convert to the somewhat refractory ferric oxide also promises convenience for long term storage.

Acknowledgement

I wish to extend my appreciation to Professor Harmon L. Finston for his excellent guidence, accessibility, encouragement, understanding and friendship throughout this work.

I like to thank Professor Selman A. Berger, Professor Orest Popovych, Professor Evan T. Williams, members of my examining and advisory committee for their aid and advice.

I am also grateful to Professor Dominick A. Labianca, Professor P. Gray Mennitte, Professor Darryl G. Howery, Professor Richard D. Pizer, and Professor George Moriber for their helpness during my graduate work.

I am indebted to Bill Knoop, Gloria Schnitzer, Barbara Fudge, Harriet Weinrieb, Beatrice Zucker, Joseph Fedullo, Aileen Fedullo, Carl Paparella, Kenneth Kennelty, Lloyd Benjamin, Ottmar Safferling and others for their friendship and assistance during my years at Brooklyn College.

I also like to thank my wife, Rong, and daughter, Jin, without whose love, patience and support this work could never have happened.

Contents

List of Tables

List of Figures

Chapter I

INTRODUCTION

1.1 Uranium Fission

Fission was discovered in 1938 by Otto Hahn and Fritz Strassman when they observed that the bombardment of uranium with neutrons produced several radioactive nuclides which were isotopes of much lighter elements. These nuclides could be formed only by the splitting of the uranium nucleus into two parts of comparable size.

Heavy nuclei which are excited to an energy equal to the barrier height, or above, can undergo fission almost instantaneously. The potential barrier for fission of ^{236}U is 6 Mev. The capture of slow neutrons by nuclei of ^{235}U produces the compound nuclei ^{236}U with 6.24 Mev of excitation energy. Some of the excited ^{236}U nuclei decay to the ground state by emission of γ-rays, but the majority of them are destroyed by fission before they have had time to emit photons.

The neutron to proton ratio N/Z of a heavy nucleus lying near the β-stability line is much greater than the ratio for a stable, medium-weight nucleus. For example, N/Z for ^{236}U is 144/92 or

1.57, whereas for the stable nucleus ^{138}La it is only 1.42. If the fission of a ^{236}U compound nucleus produced a nucleus of lanthanum with the same neutron to proton ratio as ^{236}U, it would have to be ^{147}La, which is very far on the neutron excess side of the line of β-stability. Even allowing for the escape of two or three neutrons, it is clear that the products of fission must be neutron-rich, and therefore will, for the most part, be unstable to β^--decay.

The fissioning nuclei in a given system do not all divide in the same way. In all cases, the total numbers of protons and neutrons are unchanged before and after the division, but the division may take place in many different ways. It has required a great amount of skillful radiochemical work to measure the yields of each of the many different fission products for each of a large number of different initial fissioning systems.

In practice, it is not often possible to determine the atomic numbers of the two primary fragments, because their β-decays are usually extremely rapid. ^{118}Ag with a β^- half life of only 4 seconds, is very difficult to separate by chemical means from the dozens of other fission products formed simultaneously, in time to measure its radiation. However ^{118}Ag decays to ^{118}Cd, whose half life is 50 minutes, and which is also formed in fission, so that a measurement of its radiation will give the sum of the amounts of ^{118}Ag and ^{118}Cd formed in fission (plus the amounts of any other nuclides with

A = 118 which decay rapidly to ^{118}Ag and thence to ^{118}Cd). A series of products with the same mass number A is called a fission product chain, and instead of obtaining the yields of the separate nuclides, it has been the aim of most radiochemical experiments to measure the cumulative chain fission yield, Y(A). This quantity is defined by the equation

$$Y(A) = \frac{\text{(Number of product nuclei of mass number A) x 100 \%}}{\text{(Number of fissioned nuclei)}}$$

Obviously the chain yield Y(A) is equal to the sum of all the independent yields of the various members of the chain. Since each fission act produces two fragments, the sum of all the chain yields must be 200 %, not 100 %. A plot of chain fission yield against A is called a fission yield curve, which is shown in Figure 1.1 for the fission of ^{235}U at fairly low excitation.

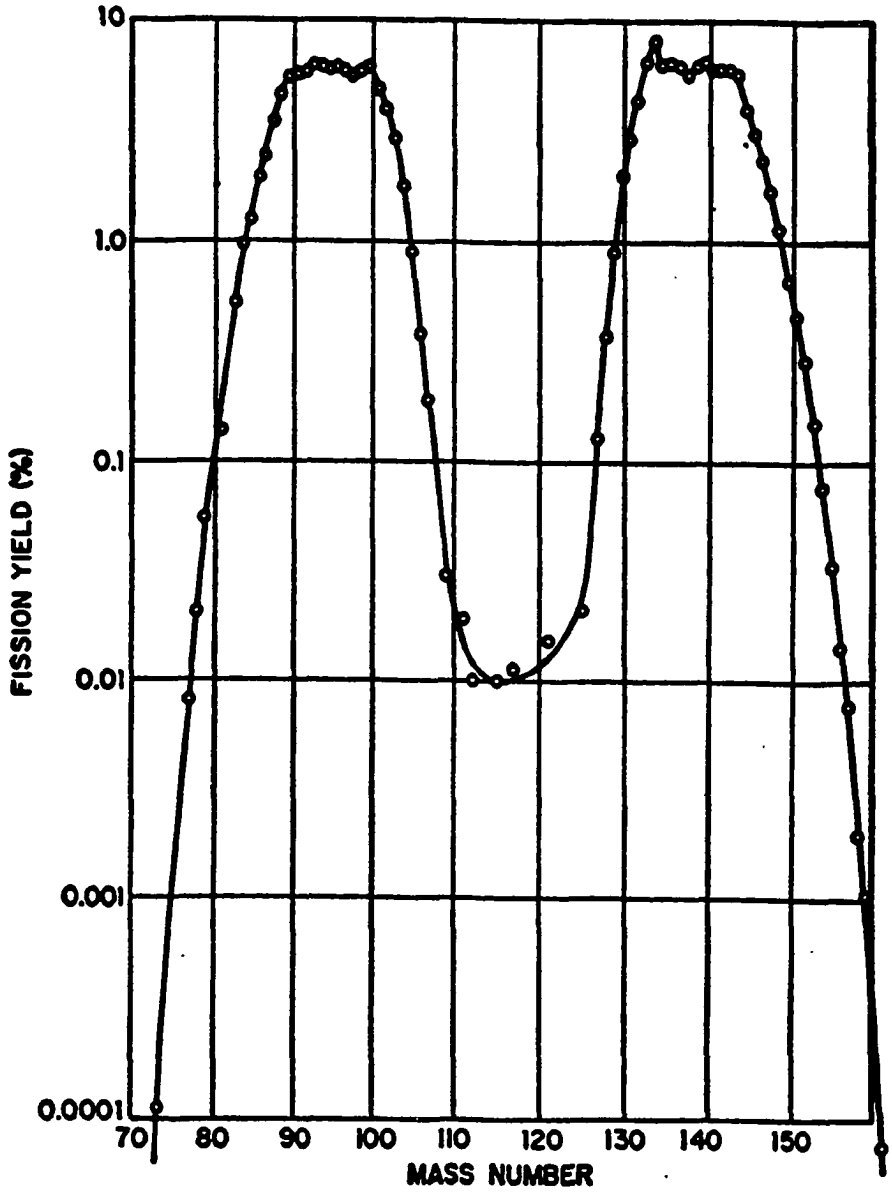


Fig. 1.1 Typical fission yield curve at fairly low excitation

The most striking feature of Figure 1.1 is the presence of the two large maxima with a very deep minimum between them. The minimum falls at an "A" value corresponding to division of the ^{236}U fissioning nucleus into two fragments of equal size, and the low fission yields in the region of A = 117 show that this symmetrical division is very unlikely to occur. The most probable division, as the positions of the maxima show, is into fragments with masses 95 and 138.

The fission yield curve of Figure 1.1 is very nearly symmetrical about the minimum, as of course it should be, since the yield of any mass number must be the same as the yield of the complementary fragment on the other side of the curve. However, the sum of the masses of a fragment and its partner is about 233 rather than 236, because on the average 2.47 neutrons are emitted in the fission of ^{235}U induced by slow neutrons.

The two small spikes near the maxima of the fission yield curve are associated with mass numbers 100 and 134. Their high yields may be due to shell model effects, but they are not fully understood. The primary fragments with 82 neutrons should have mass number in the vicinity of 134 and because of the extra stability associated with the 82 magic number*, they might be

---

*magic number:
The investigation of nuclear stability shows that certain nuclei are particularly stable. For example, the energy required to remove

formed in the initial fission process in high yield.

The complementary fragments of mass of about 100 would therefore also be formed in high yield. In addition, the bonding energy of the 83rd neutron is unusually low, and if, in many cases, fragments with this neutron number lose a neutron by evaporation, then fragments of mass 135 will end up in the mass 134 chain, so that the yield of mass 134 will be enhanced at the expense of the yield of mass 135.

---

a neutron from the various isotopes of lead drops very sharply between ^{208}Pb (126 neutrons) and ^{209}Pb (127 neutrons). ^{208}Pb is therefore much more stable than ^{209}Pb. The energies required to remove a neutron from the various lead isotopes are shown in the following table:

Isotope	Neutron number	Energy to Remove One Neutron
^{205}Pb	123	6.64 Mev
^{206}Pb	124	8.16 Mev
^{207}Pb	125	6.73 Mev
^{208}Pb	126	7.38 Mev
^{209}Pb	127	3.87 Mev
^{210}Pb	128	5.23 Mev
^{211}Pb	129	3.77 Mev

This result and much additional evidence suggests that the structure of the ^{208}Pb nucleus (with 126 neutrons) is particularly stable. Throughout the periodic table there are other cases of a similar nature, each associated with a particular number of protons or neutrons. These numbers are called "magic numbers". The magic number of protons are 2; 8; 20; 28; 50; 82, and of neutrons are 2; 8; 20; 28; 50; 82, and 126. ^{208}Pb with 82 protons and 126 neutrons is doubly magic, and so is ^{56}Ni with 28 nucleous of each type. They are particularly stable.

The depth of the central valley in the mass yield curve is a function both of the excitation energy and the mass number of the fissioning nucleus. As the excitation energy is increased, the depth of the valley decreases until finally no valley remains, and the most probable division is into two fragments of equal mass.

As the fission yield curve shows, the highest yield fission products are ^{90}Sr, ^{90}Y, ^{95}Zr, ^{99}Mo, ^{131}I, ^{106}Ru, ^{137}Cs, ^{140}La, ^{140}Ba, ^{144}Ce etc.

The Chinese scientist, Chien Chung, at Tsing Hua University in Taiwan reevaluated the independent fission yield in thermal-neutron fission of ^{235}U by using physical and radiochemical techniques(1) in 1986. In this work, a total of 625 experimently determined independent fission yields in ^{235}U, covering 224 recently reported fission products in 62 mass chains, are reviewed and compared to the predicted values from recent evaluations and model calculations. The contribution of independent fission yield to overall chain yield is small amounting to as much as 5 % only in the case of ^{95}Zr; usually it is about 1 % or less.

The fission yield and half lifes of the high yield fission products are shown in Table 1.1

Table 1.1 Fission yields and half lives of the high yield fission products

Fission Product	Fission Yield %	Half Life
^{90}Sr	5.9	29 y
^{90}Y	5.9	64.0 h
^{95}Zr	6.5	65.5 d
^{99}Mo	6.1	66.02 h
^{131}I	2.77	8.04 d
^{106}Ru	0.39	369 d
^{137}Cs	6.23	30.1 y
^{140}La	6.3	40.23 h
^{140}Ba	6.3	12.79 d
^{144}Ce	5.45	284.4 d

1.2 Atmospheric Contamination

Radioactive elements can enter our environment from fallout deposition which may result from routine or accidental releases from nuclear power plants and nuclear fuel-cycle facilities, as well as from nuclear explosions, and also because of inadequate storage of fission product wastes and subsequent seepage into ground water. Radioactive fallout presents a short-term risk due to its direct deposition on agricultural crops, as well as a long-term risk resulting from its deposition on soil and subsequent uptake by crops. Contamination of agricultural food chains is one mechanism which causes irradiation of the population following the deposition of radioactive fallout in the environment.

The transfer processes of radionuclides through food chains can be described as follows(2).

(a) Atmospheric fallout is deposited onto the crop canopy and the ground. Part of the fraction intercepted by plants is retained, while the remainder is deposited on the ground.

(b) Retained fallout is removed from plant surfaces by weather factors such as wind and rain, and by plant factors such as the shedding of aging leaves or the removal of protective waxy layers during growth.

(c) After absorption of the radionuclides through plant surfaces, a fraction is translocated to inner tissues. This mechanism is very significant when edible parts are not directly exposed to

fallout.

(d) Material that deposits on the ground may be re-suspended, mainly by the wind, and then deposited on plant surfaces, or it may penetrate from the superficial soil layer into the root zone.

(e) In the root zone, radionuclides are absorbed by plant roots, depending on soil, plant and radioelement properties, and from there into the inner tissues of the plants.

(f) If the harvested crops are intended for human consumption, it is possible to considerably reduce the external radioactivity by food preparation or processing methods, such as washing leafy vegetables or paring fruits and vegetables.

(g) If harvested crops are consumed by animals (forage crops), a fraction of the ingested radioactivity is absorbed from the digestive system into the blood and transferred to various tissues or organs, which are consumed by humans, or to milk and eggs, which are also consumed by humans.

(h) After the consumption of contaminated food by humans, the radionuclides concentrate in certain organs, irradiating them and also adjacent organs.

The scheme of the different processes of radioactivity transfer in the food chain is shown in Figure 1.2.

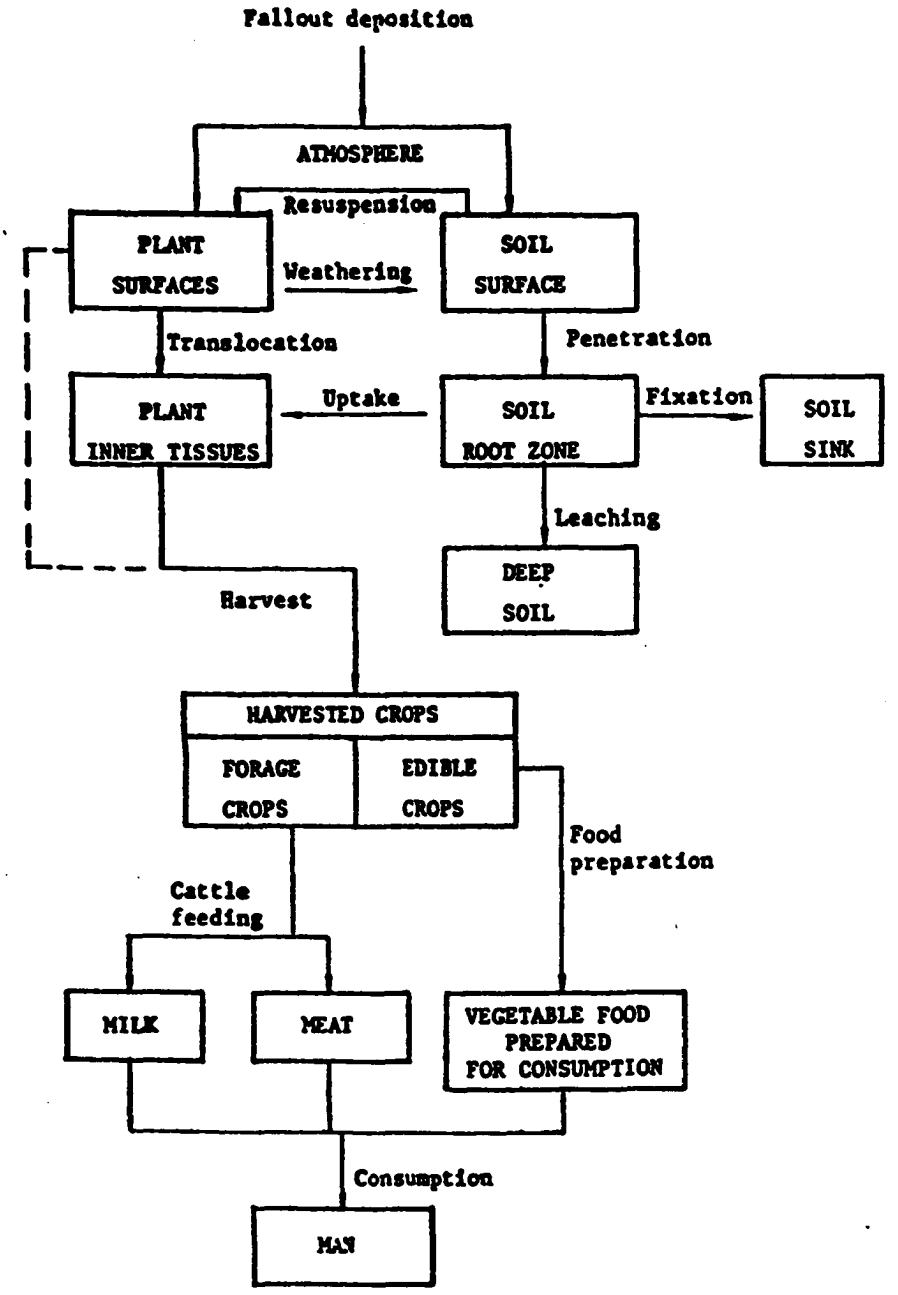


Fig. 1.2 The different processes of radioactivity transfer in the food chain

(Koch, J.; Tadmor, J., Health Physics, 1986, 50(6), 721)

The Israeli scientists, J. Koch and J. Tadmor(2), evaluated the transfer of radionuclides through the food chain, the corresponding individual and collective radiation doses and the health effects following a large release of radioactivity into the environment. A sample calculation was also performed. The uniform contamination of an urban area (with a population density of about 10,000/km^2) surrounded by a rural, but relatively heavily populated area (with a population density of about 800/km^2), was assumed. Initial contamination levels due to critical radionuclides are shown in Table 1.2.

Considering the fission yields, half-lives, and levels of contamination, we can see that some of the fission products, such as ^{90}Sr, ^{90}Y, ^{95}Zr, ^{99}Mo, ^{106}Ru. ^{131}I, ^{137}Cs, ^{140}Ba, ^{144}Ce, are significant hazards which should require isolation and safe storage after uranium is separated from fuel elements in nuclear reactors. All the fission product elements we studied have high fission yields, long half-lives and are serious contaminants in the food chain.

Table 1.2 Radioactive contamination levels in food chain

Radionuclide	Radioactivity per unit area (MBq/m^2)
^{89}Sr	1.85×10^{1}
^{90}Sr	1.85×10^{-1}
^{91}Y	5.55×10^{1}
^{95}Zr	5.55×10^{1}
^{106}Ru	1.85×10^{1}
^{131}I	5.55×10^{2}
^{133}I	1.85×10^{3}
^{137}Cs	5.55×10^{-1}
^{140}Ba	5.55×10^{2}
^{144}Ce	1.85×10^{1}

1.3 Chemical Processing by Solvent Extraction

Solvent extraction on a micro or macro scale is a well-established process for the separation of organic or inorganic substances. It is of interest historically to note that the use of diethyl ether for the separation of uranium as uranyl nitrate from the other constituents of pitchblende for both analytical and large-scale production purposes in the Manhattan Project can be traced back to the use of ether by Peligot in 1842 to purify uranyl nitrate obtained from pitchblende(3). The classical application to analytical chemistry is, of course, the extraction of ferric chloride from hydrochloric acid solution by diethyl ether introduced by Rothe in 1892(4). Today, with a variety of ways available for accomplishing solvent extraction, almost every element in the periodic table has been found to undergo solvent extraction under suitable conditions. Many contributions to the development of methods, theory, and techniques of solvent extraction of inorganic substances have originated in the problems arising since the 1930s in connection with target chemistry associated with the production of artificial radioactivity, and recently in connection with the utilization of nuclear energy for peaceful and military purposes.

Chapter II

A REVIEW OF EXTRACTION METHODS FOR URANIUM FROM FISSION PRODUCTS

2.1 Basic Theory of Solvent Extraction

2.1.1 The Principles

a. Phase Rule

All the recently developed separation techniques, such as chromatography and ion exchange, as well as solvent extraction, involve the distribution of matter between two different phases. For all phase distributions, the classical phase rule of Gibbs can be applied.

$$P + V = C + 2$$

where P is the number of phases, V the variance or degrees of freedom, and C the number of components. In the particular case of solvent extraction, we are dealing basically with two essentially immiscible solvents and one solute distributed between them, so that P = 2 and C=3. Under constant temperature and pressure, if we choose the concentration of the solute in one phase, the solute

concentration in the other phase is fixed. Hence, there is a definite relation between the solute concentration in each of the solvent phases which is described by the distribution law.

b. Distribution Law

The distribution law was first stated by Berthelot and Jungfleish(5) in 1872 and elaborated in 1891 by Nernst(6). For a solute, X, distributing between solvents 1 and 2, we have

$$X_1 \rightleftharpoons X_2$$

$$K_D = [X_2]/[X_1]$$

where K_D is the distribution coefficient, a constant independent of total solute concentration, where the brackets denote concentrations in moles/liter. A solute will distribute between two essentially immiscible solvents in such a manner and achieve an equilibrium. The ratio of concentrations of solute in these two phases, at a particular temperature and pressure, will be a constant, provided that the solute has the same molecular weight in each phase.

c. Distribution Ratio

In general, the overall or stoichiometric distribution of the component of interest between the phases, is better described by the distribution ratio, D, which is a more practical quantity. For

the extraction of metal ion from aqueous phase into organic phase, the D is defined by the equation

$$D = \frac{\text{Total concentration in organic phase}}{\text{Total concentration in aqueous phase}}$$

If we are aware of all the significant interactions of the distributing species, it is usually possible to evaluate them in order to obtain D as a function of the experimental parameters. When there are no interactions of the distributing species, D and K_D are identical.

d. Degree of Extraction

The degree of extraction, %E, is a more useful concept in practice than is the distribution ratio D. For example, for values of R between 99 and 100 %, denoting essentially complete extraction, the corresponding value of D ranges from 99 to infinity (for equal phase volumes) and is rather more difficult to express. The relation of %E and D can be expressed as follows:

$$\%E = \frac{W_o}{(W_o + W_a)} = \frac{D}{D + (V_a/V_o)} \times 100\ \%$$

where W_o, V_o, and W_a, V_a represent the weight and volume of the organic and aqueous phases, respectively.

e. Process of Extraction

Although details of the specific nature of the interactions obviously must differ from one system to another, a helpful organizational pattern may be adopted, based on three essential aspects of every metal extraction process.

The first step involves reactions of metal ion in the aqueous phase leading to the formation of an extractable species. Complex formation may be accomplished by coordination, including chelation, and simple coordination, or by ion association.

The second aspect is the distribution of the extractable complex. This is by far the easiest to understand from the mathematical standpoint, since the distribution of the extractable species between the two liquid phases follows the distribution law. However, factors affecting extractability are quite complex.

The third aspect is the interactions of the complex in the organic phase; for example, polymerization or dissociation; and interaction with other components, such as the reagent as well as the solvent comprising the organic phase. The organization pattern for the extraction process applies just as well for extraction of organic compounds with the possible simplifying modification that many such compounds are directly extractable without the necessity for a complex-forming reagent.

2.1.2 Formation of Metal Complexes

Since the formation of an extractable complex is a vital step in the extraction process, the nature of metal complexes and the factors governing their formation will now be explored.

a. Coordination Complexes

Our understanding of the metal complexes that may be termed coordination compounds derives from Werner's concept of the coordination of ions or groups in a definite geometric arrangement about a central ion which was translated in terms of the G. N. Lewis electronic theory by Sidgwick(7) and Lowry(8).

The application of Lewis' electronic theory of acid and bases to the consideration of coordination compounds is very useful. According to this theory, acid-base reactions involve the formation of a coordinate-covalent bond between an acid, defined as an electron-pair acceptor, and a base, or electron-pair donor. A metal cation, being electron-pair deficient, is considered as an acid capable of reacting with several basic entities, the number of which is related to the coordination number of the metal.

The basic entities, characterized by possessing at least one unshared pair of electrons, are usually either neutral or negatively charged. The nature of the bonds between the acidic metal cation and the basic coordinated groups, called ligands, ranges from almost

completely covalent, to the other extreme of essentially electrostatic, with a large number of coordination complexes having bonds of intermediate character. The transition between electrovalent and covalent bonding is considered in terms of the polarizabilities of the ions or groups involved(9). When a cation and a ligand approach each other, a deformity, or polarization, is induced in the ligand due to interaction with the highly charged metal cations, which have a non-inert-gas electronic configuration.

According to the Lewis theory, we can anticipate that the stability of a metal coordination complex will depend on (a) factors related to the "acidity" of the metal ion, (b) those related to the "basicity" of the coordinating ligand, and (c) special factors related to the configuration of the resultant complex.

Among the many metal complexes of interest in extraction, several types may be distinguished. First, there are **simple coordination complexes** in which metal ions combine with mono-dentate ligands in a number equal to their coordination number. Some of these complexes are extractable or, if charged, can associate with other ions to form extractable species.

A second category derives from the interaction of metal ions with poly-dentate ligands that can each occupy more than one position in the coordination sphere of the metal. These complexes are called **chelates.**

A third category, of which **heterpoly acids** are an illustration, is distinguished by the presence of a central complex ion rather than a central monatomic ion. Heteropoly acids, many of which are extractable into organic solvents, form a large group of oxygen-containing acids possessing an atom of an element such as boron, silicon, phosphorus, or arsenic in combination with a number of atoms of another element, such as molybdenum or tungsten.

b. Chelate Complexes

Chelating reagents play an important role in extraction of metals because they comprise an impressive body of both useful extraction agents and masking agents. The latter are sequestering agents, which form soluble complexes preventing the interference of certain ions in other reactions. Metal chelates represent a type of coordination compound in which a metal ion combines with a poly-dentate ligand capable of occupying two or more positions of the coordination sphere of the metal ion to form a cyclic compound. The functional groups of the base must be so situated in the molecule that they permit the formation of a stable ring, generally five- or six-membered.

The physical and chemical properties of a metal chelate will of course depend on factors related to the basic nature of the chelating agent and the acidic nature of the metal, as well as on factors inherent in the metal chelate itself.

Chelating agents may be conveniently classified according to the charge type of the basic groups present. If both basic groups of the reagent are uncharged, positively charged metal chelates are formed. If the reagent has one anionic group, neutral chelates usually result. The presence of a multiple negative charge on the chelating agent may result in negatively charged chelates. All types of chelating agents find useful application in metal extraction procedures. As a class, the neutral chelates are those most easily extracted into organic solvents. Some cationic chelates by pairing with certain anions, form uncharged species, i.e., ion pairs, which can then be extracted into organic solvents. The great usefulness of reagents forming anionic chelates resides in their "masking" action. The use of an extraction agent and a masking agent in combination can result in a marked increase in the selectivity of the extraction system.

c. Ion-Association Complexes

A major fraction of the extractable species other than those that are chelates exist in the organic solvent as associated ionic aggregates. Although, in ion-pair formation the forces of attraction are physical, as contrasted to the chemical forces involved in the formation of coordination complexes, both types behave in accord with the law of mass action. Hence, for two ions A^+ and B^- which associate to form (A^+, B^-) according to the equation

$$A^+ + B^- \rightleftharpoons (A^+, B^-)$$

the equilibrium expression is

$$K = \frac{[(A^+, B^-)]}{[A^+] [B^-]}$$

The existence and behavior of such complexes was predicted by N. Bjerrum(10), whose theory relates the value of the ion-pair formation constant K to the dielectric constant of the solvent ε, to the temperature, and to the size of the ions involved. Thus,

$$K = \frac{4 \pi N}{1000} \frac{e^2}{\varepsilon k T} Q (b)$$

$$b = \frac{e^2}{a \varepsilon k T}$$

where N is Avogadro's number, e is the unit of charge, k is the Boltzmann constant, T is the absolute temperature, Q (b) is a calculable function, and a is an empirical parameter which has been interpreted as representing the distance between charge centers of the paired ions when in contact.

2.1.3 Distribution of the Extractable Species

a. Solubility and Distribution

It must be pointed out that to uncritically equate the ratio of solubilities of a solute in each of two solvents to the distribution coefficient of the solute distributing between the same two solvents could lead to serious errors. Despite the fact that the underlying mechanisms in both cases are quite similar, it would almost always be incorrect to expect a quantitative agreement of the solubility ratio and the distribution coefficient. Two major factors are responsible for the disparity.

The first of these arises from the changes that occur in the activity coefficients of the solute in each phase as the total solute concentration changes. The second cause for discrepancies between distribution coefficients and solubility ratio is the effect of the presence of the second solvent on the solubility of the solute in the first solvent. Since the solvent pair is essentially immiscible, it is a reasonable assumption that the low mutual solubility does not appreciably alter the activity of either solvent. However, the solute may react with the second solvent to form a new species (e.g., a solvate) which may have solubility characteristics completely different from those of the original solute.

b. Factors Affecting Solubility

The process of solvation which consists of solute molecules forcing themselves between solvent molecules may be classified by the type of bonds involved(11).

The first type of bond is the **electrostatic bond,** which involves forces between two ions, two dipoles, or an ion and a dipole. The solubility of electrolytes in a highly polar medium, such as water, is aided by electrostatic forces. A comparison of the solubilities having the same or similar free energies of formation indicates the primary role of electrostatic forces. In such a comparison, lattice energies are useful in seeking factors that govern solubility.

The second type of bond is the **hydrogen bond** which is essentially electrostatic, but exceptional enough to warrant separate consideration. Much of the solvent action of water is attributable to its hydrogen-bonding capacity. The solubility of a substance in water or alcohol is determined more by its ability to form hydrogen bonds than by its polarity as measured by dipole moment.

The third type is the **chemical bond.** These bonds depend upon the specific system and, in general, are temperature dependent. In this category, acid-base interactions are of particular interest to us. The solvent action of water, alcohols, and ethers on many salts reflects the basic character of these solvents in the Lewis sense.

c. Solubility Characteristics of Chelates

Most chelating agents used as extraction agents are of the type that contain one uncharged and one anionic basic functionality so that both the electrovalency and maximum coordination of the metal ion is satisfied in the chelate formed. The metal chelates are essentially covalent compounds and are far less soluble in water than in organic solvents, which they resemble structurally.

The intermolecular forces affecting the solubility of many of the organic-like metal chelates in organic solvents are characterized as being relatively weak, and as being physical, rather than chemical, in nature. For such solutions, in which specific chemical forces are absent, the classical dictum of "like dissolves like" and Hildebrand's theory of regular solutions(12) can be applied.

In this theory, a quantity, δ, called the solubility parameter, is introduced, defined as the square root of the heat of vaporization of the liquid per unit volume. The solubility parameters of solvent and solute are compared. It is a measure of cohesive energy density or "internal pressure". The solubility increases with increasing similarity of the solubility parameter values since the heat of mixing of the solute and solvent depends on the difference of their δ values. For the solubility of a solid solute, the heat of fusion of a solid and temperature affect its solubility in all solvents; so these same consideration lead to the choice of the best solvent.

d. Solubility Characteristics of Ion-Association Compounds

Ion-association compounds can be considered as polar molecules, i.e., those having dipole moments, whose solubility in organic solvents depends in large measure on their structural resemblance to those solvents. Thus, if the ions involved contain large organic groups, then solubility in organic solvents is a reasonable expectation.

Oxonium systems occupy a special place among ion-association systems because of the participation of the solvent molecules in the formation of the extractable complex. Oxygen-containing organic liquids serve effectively as solvents for a number of metal salts because the basic character of the oxygen atom enables the incorporation of the solvent molecule in the coordination sphere of the metal ion, giving rise to an ion-association compound that bears a structural resemblance to the solvent.

The ability of oxonium solvents to compete successfully with water for the acidic metal ion depends on the basicity of the oxygen in the molecule. The basicity, in turn, reflects the steric availability of the electrons at the oxygen atom as well as the electron density. Steric considerations are of particular importance in coordination with metal ions which are much larger than protons. At the same time, the competitive strength of water may be reduced by the use of high concentrations of salts and acid. High electrolyte concentration helps extraction in three ways: (a) by the mass action

effect, if the electrolyte possesses suitable coordinating anions (the high anion concentration makes the replacement of water by the anion easier), (b) by greatly reducing the water activity; and (c) by lowering the dielectric constant, thus favoring ion-pair formation.

The relative basicity of solvents can be evaluated by infrared spectroscopic measurements(13). The observed decrease in base strength of a series of oxonium solvents follows the order: alcohols > ethers > ketones. However, with regard to effectiveness for coordination to metals, the position of ethers and ketones is sometimes reversed because the carbonyl oxygen, being more remote from the hydrocarbon side chains than the ether oxygen, is less subject to steric interference to coordination.

The term "salting-out" agents is applied to those electrolytes whose addition greatly enhances the extractability of complexes, particularly those encountered in oxonium extractions, where salting-out agents play a most important role. The use of such salts added to the aqueous phase to improve the extraction has meant the difference between success and failure in many oxonium extraction systems. The functions of the salting-out agent are, at first, providing a higher concentration of complexing anion which, by mass action, increases the concentration of the complex, and thus improves the extraction. Secondly, differences in salting-out agents also depend upon their influence on the activity coefficients of the

ions participating in the formation of the complex. Another important factor is the binding of water by the ions of the salting agent. Water is probably bound as a shell of oriented water dipoles around the ion and thus becomes unavailable as a free solvent. Finally, it is noteworthy that the dielectric constant of the aqueous phase decreases with increasing salt concentration, which will favor the formation of the ion-association complex.

2.1.4 Chemical Interactions in the Organic Phase

Chemical interactions of the extractable species in the organic phase owe their importance to their effect on the concentration of the complex and, hence, on the extent of extraction.

One of the most important types of organic-phase reactions is polymerization of ion-association complexes. By their very nature, virtually all ion-pair complexes tend to form higher aggregates as the concentration increases. Naturally, since polymerization tends to reduce the activity of the extractable species in the organic phase, the overall extraction equilibrium is shifted in favor of higher distribution ratios. It should follow that the extent of most ion-association extractions depend on the concentration of the metal involved, which is found to be the case in practice.

Dissociation of ion-association complexes may also occur in very dilute solutions, particularly in the more polar solvents(14)(15).

This reaction would result in increased extraction at very low metal concentrations(16).

Since extractable metal chelates are essentially covalent compounds, their solutions in neutral organic solvents are relatively free from chemical interaction. One noteworthy exception arises when buffers that have extractable components are used. For example, an acetic acid-sodium acetate buffer used to adjust the pH of the aqueous medium could easily result in extraction of acetic acid into the organic phase. The acetic acid might react with either the chelating reagent or the chelate itself and thereby affect the course of the extraction.

2.2 Several Typical Methods of Solvent Extraction

Liquid-liquid extraction is, of all the various separation techniques for uranium from fission products which have appeared in the past decades, the one that has been used almost universally. Extractions of uranium utilizing ion-association systems tend to be more specific than extractions utilizing the chelate systems, and, of these, the extractions of nitrate complexes probably constitute the most specific systems. Examples are the ethyl acetate-nitrate salting system, the ether-nitrate salting system, the tributyl phosphate system, the phosphine oxide system, and the methyl isobutyl ketone system.

2.2.1 Tri-n-butyl Phosphate (TBP)

The use of tri-n-butyl phosphate (TBP) as a separating agent in the solvent extraction of uranium has been developed to a considerable extent, and there are many solvent extraction methods employing this reagent in current use.

TBP is a colorless liquid with a boiling point of 177 to 178°C at 27 mmHg, a flash point of 146°C, a viscosity of 3.41 centipoises, and a specific gravity at 20°C of 0.973. Its solubility in water is 0.4 g/liter at 25°C, the solubility of water in TBP at 25°C is about 7 per cent. The material is not very corrosive and can be stored in most common laboratory containers.

The separation of uranium from other materials with TBP is based on the fact that inert diluents decrease the distribution coefficients in general, thus, if the proper TBP to diluent ratio is selected, the uranium distribution coefficient, although decreased, will still be significantly higher than the coefficients of the metals that extract similarly to uranium. In this way, the absolute amounts of impurities extracted will be decreased.

The uranium complex $UO_2(NO_3)_2(TBP)_2$ appears to be stronger than the analogous complexes of thorium, plutonium, cerium(IV), and zirconium, which extract in a similar manner to uranium.

Since extractions are usually made from nitric acid solutions, the stability of TBP in the presence of nitric acid is important. Acid concentrations up to 16 M at room temperature were found to have no effect. However, the presence of hydrolysis products, notably dibutyl and monobutyl phosphates, markedly decreases the efficiency of stripping the uranium from the solvent because of the rather stable complexes of these hydrolysis products with uranium. Pretreatment of the TBP with 1 M sodium hydroxide effectively removes hydrolysis products.

The type of solvent used to dilute the TBP affects the distribution of uranium. For example, if one uses carbon tetrachloride, the uranium extraction coefficient (organic/aqueous) is 20.1; if benzene is used, the extraction coefficient is 13.2; and if chloroform is used, the coefficient is decreased sharply to 3.22(17).

In general, kerosene-type solvents, such as Varsol (a mixture of aliphatic hydrocarbons), carbon tetrachloride, hexane, and hexone are employed in chemical analysis, and processing of uranium.

Various factors influence the extraction of uranium. The extraction efficiency varies inversely with the temperature, with a change in the distribution coefficient of uranium by a factor of 2 when the temperature is varied from 10 to 50°C. The uranium distribution coefficient, when no salting agent is present, increases with the concentration of nitric acid up to about 5 M, but it is also a function of the total nitrate concentration. Salting agents have a marked effect on the uranium distribution coefficient, and various salting agents, such as aluminum nitrate, ammonium nitrate, calcium nitrate, ferric nitrate, and sodium nitrate have been used.

The distribution coefficient of uranium is reduced by dilution of the TBP with an inert solvent. The distribution coefficients of metals with extraction mechanisms similar to uranium show a similar reduction with decreased TBP concentration. Therefore, it is possible to separate uranium from these metals by utilizing an optimum TBP concentration.

Various solutions have been used for the recovery of uranium from the TBP solution, such as sodium carbonate, ammonium sulfate(17), and ammonium acetate(18), as well as hot water. Contrary to one statement(19), uranium is rather readily stripped from TBP in a hydrocarbon diluent with sodium hydroxide and

hydrogen peroxide(20) or with ammonium hydroxide and hydrogen peroxide.

A different approach to stripping uranium from TBP (20 % in kerosene) solution has been made by Petrement Eguiluz and Palomares Delgodo(21), who employed 2 N sulfuric acid and granular metallic cadmium. The cadmium reduces the hexavalent uranium to the tetravalent form, which goes into the sulfuric-acid layer. The method was especially applicable for the separation of traces of uranium. No emulsions were formed, as sometimes happens when sodium or ammonium carbonate solutions are used for stripping. The efficiency of stripping with sulfuric acid and cadmium was greater than with water, 2 N sulfuric acid, or solutions of sodium carbonate, ammonium carbonate, or sodium sulfate.

2.2.2 Diethyl Ether

Diethyl ether was used for the separation of uranyl nitrate by solvent extraction to a great extent in the early phases of the work on nuclear energy problems both in plant processes and in analytical chemistry. This solvent is no longer used to the extent that it formerly was, but it is still employed in some separations in analytical chemistry. Uranyl nitrate is soluble in diethyl ether, but, for complete recovery from interfering elements, it is necessary to use salting agents. The early work of Furman and coworkers(22,23) described the effects of various salting agents.

Scott(24) made a thorough study of the effects of salting agents, acid concentration, and interfering anions as applied to analysis of uranium.

Among the various salts, calcium and ammonium nitrate have been used extensively as salting agents, and zinc, copper, ferric, lithium and aluminum nitrates are also very effective for this purpose. The efficiency of various salting agents are shown in Table 2.1(25).

Table 2.1 The efficiency of various salting agents in the extraction of uranium with diethyl ether

Formula	NO_3^- normality from salting agent	U distribution coefficient (org./aq)	U extracted %
NH_4NO_3	10.07	1.31	56.7
$NaNO_3$	7.72	2.85	74.0
$LiNO_3$	10.50	85.2	98.8
$Ca(NO_3)_2$	10.57	165.4	99.4
$Zn(NO_3)_2$	10.68	259	99.6
$Cu(NO_3)_2$	9.31	162	99.4
$Mg(NO_3)_2$	3.03	0.448	30.9
$Th(NO_3)_4$	5.54	1.71	63.2
$Al(NO_3)_3$	4.85	3.95	79.8
$Fe(NO_3)_3$	7.37	74.7	98.7

The nitric acid content is also important; with increasing nitric acid content, up to about 5 N, the percentage of uranium extracted increases(24). Acidities higher than 6 N nitric acid may lead to reaction between the ether and the nitric acid. The elements which extract in varying amounts and which may cause problems are cerium(IV), vanadium, iron, if present in large amounts, thorium, zirconium, and molybdenum, if present as silico or phosphomolybdic acid. Nitric acid is also extracted, and additional nitric acid should be added either to the extraction funnel, or to the continuous extractor, depending on which method is used.

Certain anions cause difficulty in the separation, either by extracting other elements, such as ferric ion when chloride is present, or by decreasing the uranium distribution, such as happens when fluoride, sulfate, and phosphate ions are present in certain amounts. This was investigated by Scott(24) who determined the percent of uranium extracted from solutions containing varying quantities of the common anions, introduced as the sodium salts, that were 3 N with respect to nitric acid and 1 M with respect to ferric nitrate. If the foreign anions do not reduce the percentage of uranium extracted below 79 per cent in a single extraction, no modification of the routine procedure using three extractions is required to achieve 99 per cent recovery of uranium. Although calcium nitrate can be used to offset the effect of sulfate, it is the usual practice to precipitate the uranium with CO_2-free ammonium hydroxide and to redissolve the precipitate in nitric acid. The

separation as the hydroxide is not always complete in the presence of phosphate ion. Phosphate can be removed by precipitation with zirconium nitrate in a nitric-acid medium(23), but the zirconium phosphate precipitate is inclined to be gelatinous, and some uranium may be occluded. Aluminum nitrate or ferric nitrate can be used to overcome the influence of phosphate. A saturated ferric-nitrate solution as the salting agent has proven satisfactory for this purpose(23).

Both continuous extraction and batch extraction have been employed with this solvent.

2.2.3 Methyl Isobutyl Ketone (MIBK)

The use of methyl isobutyl ketone for the extraction of uranium from nitrate solutions was used as far back as 1945 by Kraus(26). The use of this reagent in plant separations has been quite extensive, but recently, this reagent has only been used for analysis. Paley(27) used methyl isobutyl ketone in a nitrate solution with ammonium nitrate as a salting-out agent to separate uranium prior to a colorimetric determination with thiocyanate. Nietzel and DeSesa(28) modified this procedure for the same purpose, in connection with the separation of uranium from fission products. Booman and coworkers(29,30) also made a rather complete study of the use of methyl isobutyl ketone in analytical chemistry. From their studies it appears that the use of aluminum nitrate as a salting-out

agent is preferred. The acidity of the aluminum nitrate salting solution affects the distribution of fission products in a liquid-liquid extraction system. At constant concentration of aluminum nitrate, fission product extraction is increased 50-fold between 0.1 N acid deficiency and 0.1 N free acid. An acid-deficient nitrate solution is defined as one that contains less nitrate ion than a solution of the stoichiometric salt, i.e., it contains hydrolyzed species. Zirconium and niobium hydrolyze in an acid-deficient solution to give a species that does not extract. Ruthenium and rhodium also have lower extractability from an acid-deficient solution. A value of 1 N acid-deficient aluminum nitrate was selected as optimum for the system because in the concentration range from 2.4 M to 2.8 M it provided the degree of buffering required for the range of acidity expected in samples and it did not cause emulsification of the two phases as did the more highly acid-deficient solutions(30).

2.2.4 Trialkyl Phosphine Oxides (TOPO)

In the course of a systematic study of organic complexing agents for uranium, investigators at Oak Ridge National Laboratory(31) found a number of promising reagents among the organophosphorus compounds. One class of these compounds, the tri-n-alkyl phosphine oxides, was found to have an extremely high extraction coefficient for uranium, significantly greater than the coefficients for iron, aluminum, thorium, and vanadium.

On the basis of this work, White and Ross(32) made a qualitative investigation of the extraction of some 40 additional metal ions from acidic solutions by tri-n-octyl phosphine oxide (TOPO) to obtain a general picture of the selectivity of these compounds as extractants.

The neutral alkyl phosphine oxides (R_3PO), and the phosphinates [$R(RO)_2PO$] can be grouped with the familiar alkyl phosphate, tributyl phosphate (TBP), with regard to their extraction behavior.

These organophosphorus reagents, however, offer a greatly increased range of extraction power. TOPO extracts uranium with a coefficient that is five orders of magnitude higher than TBP and extractions can be achieved from sulfate and phosphate solutions in which TBP is completely ineffective. The phosphinates and phosphonates are intermediate between these extremes. In all cases nitrate is the most favorable aqueous medium, with rapidly decreasing extraction from chloride to sulfate solutions. As with the acid compounds, reagent concentration is an important variable in determining extraction coefficients. Uranium coefficients, for example, vary with the second power of the uncomplexed phosphine oxide concentration.

An important consequence of the high extractability from nitrate solutions is that, by the introduction of relatively small amounts of nitrate in much less favorable aqueous solutions (e.g. sulfate and phosphate), uranium can be effectively extracted by a phosphine

oxide. This is to be contrasted with the inhibiting effect that small concentrations of sulfate and phosphate have on extractions with TBP from concentrated nitrate solutions(33).

It is interesting to note that the variation of uranium extraction with reagent type and with aqueous anion roughly parallels the extraction of mineral acids by these reagents. Thus, all these neutral reagents extract phosphoric acid, sulfuric acid, hydrochloric acid, and nitric acid from aqueous solutions, the extraction increasing roughly in that order. In addition, the extent of extraction of a given mineral acid increases in the order: phosphate, phosphonate, phosphinate, phosphine oxide. An important property of the dialkyl phosphoric acids is that in combination with neutral organophosphorus reagents, a strong enhancement (synergism) of U(VI) extraction can be obtained(33).

The other organic solvents, such as ethyl acetate, dibutoxytetraethylene glycol (penta ether), dibutyl carbitol, diethyldithiocyarbamate, acetylacetone etc., are also used as extractants for the separation and determination of uranium from fission productions(25).

2.2.5 Synergistic Extraction

The term synergism was first introduced by C. A. Blake et al.(34) to describe the enhanced extraction of uranium with

dialkylphosphate and some organophosphorus esters. The phenomenon has been explained by an organic-phase reaction in which one or two moles of phosphate ester add to the neutral thenoyltrifluoroacetone (TTA) complex(35).

The most intensively studied systems are of the following types: (a) a chelating agent such as TTA or IPT (β-isopropyltropolone) and a solvating solvent such as TBP, MIBK, DBSO (dibutyl sulphoxide), and (b) a dialkylphosphoric acid and a neutral organophosphorus ester. Considerable work has been done in the area of chelating agent-solvating solvent system. Irving and Edgington(36) postulated that the conditions for synergic extraction are: (a) one of the active reagents (HX) should be able to neutralize the charge on the metal ion, preferably by forming a chelate; (b) the solvent should displace any residual coordinated water from the neutral metal complex, rendering it less hydrophilic; (c) the solvent should not itself be hydrophilic and coordinated less strongly than HX; and (d) the maximum coordination number of the metal and the geometry of the ligands should be favorable. These postulates appeared valid for the U(VI)-TTA-TBP(TOPO) system but not for the trivalent lanthanides and actinides, which are apparently coordinatively saturated. With U(VI)-TTA-TBP and U(VI)-TTA-TBPO (tributylphosphine oxide) mixtures, synergic enhancement factors of the order of 10^3 and 10^4 respectively were observed. The extracted species were assigned the compositions UO_2X_2TBP and $UO_2X_2(TOPO)_3$ respectively(37,38,39), from isopiestic and infrared

measurements. The studies were extended to plutonium(VI), americium(III), europium(III) and thorium, and the species identified were $PuX_3(TBP)_2$, $AmX_3(TBP)_2$, AmX_3TBPO, $ThX_3(NO_3)TBP$ and $ThX(NO_3)_3TBPO$.

Healy(40) reported the synergic extraction of uranium(VI), thorium, lanthanides(III), actinides(III) and alkaline earth metal with TTA-TBP, TTA-TBPO and TTA-TPP; TPP is triphenyl phosphate. The extracted species are $UO_2(TTA)_2S$, $UO_2(TTA)_2S_2$, $Th(TTA)_4S$, $Pm(TTA)_3S_2$, $Am(TTA)_3S_2$, $Cm(TTA)_3S_2$ and $Ca(TTA)_2S$, where S is an organophosphorus ester. It was observed that the synergic effect increases with increasing basicity of the ester, i.e., in the order TOPO > TBP > TPP.

Newman and Klotz(41), in their study of the extraction of thorium with TTA and tri-n-octylamine, demonstrated that $Th(TTA)_4R_3NHCl$ is the extractable species. H. L. Finston and Y. Inoue(42) observed synergism in the system Fe(III)-TTA-SCN and attributed this to a kinetic effect rather than to formation of some mixed ligand complex. Synergic extractions of gallium and cobalt(II) with TTA and tetraphenylarsonium chloride from acetate medium also have been done by M. S. Rahaman and H. L. Finston(43,44). E. Gnizi(45) investigated the effect of SCN^- on the extraction of Zr-TTA complex. The extraction system Zr-TTA-SCN^- was studied, using ^{95}Zr tracer, with two solvents systems. It was found that in benzene, the rate of zirconium extraction was increased by SCN^-,

but no synergic effect was observed. When mixtures of hexone and benzene were used as solvent, in addition to the rate promoting effect, SCN^- also had a synergic effect on the extraction in those systems where Zr-SCN was itself extractable. This result was attributed to a mechanism for the synergic effect that was the same as for the Fe(III)-TTA-SCN^- system.

More recently, Chinese scientists, Dong Zhou and Jinwen Ding(46) separated uranium, thorium, iron and rare earth elements in monazite by using a multistage counter-current extraction with dimethylheptylmethylphosphonate (DMHMP) and TBP in kerosine and stripping with $(NH_4)_2SO_4$ + H_2SO_4. This process is characterized by simple operation and high economic efficiency and a recovery of 99.5 % U(VI), Th(IV), and rare earth metals from HCl and HNO_3 solution.

The Romanian scientists, Nistor Perescu, Anca Ionescu, Danut Bujoreanu and Valeriu Balan(47) developed the Thorex acid process. This process consists of solvent extraction of aqueous solution containing Th(IV) (220 g/l), U(IV) (32.75 g/l), HNO_3 (3 M), and Al(III) (0.25 M), using as solvent a mixture of TBP 30 %, dodecane 60 %, and diethylbenzene 10 %. The Th(IV) and U(VI) are both extracted from the aqueous solution in eight stages of extraction, then the organic extractant phase is reprocessed, the Th(IV) being separated by extraction with dilute aqueous solution of 0.02 M HNO_3. The products of the process are an organic phase containing

U 12 g/l and Th < 50 mg/l and the aqueous phase containing Th 56 g/l and U < 10 mg/l.

J. Duarte Neto(48) recovered uranium from phosphoric acid by synergistic extraction. The extracting mixture was bis(2-ethylhexyl) phosphoric acid (D_2EHPA) and trioctylphosphine oxide (TOPO). A micro-pilot scale installation was made to get data for a continuous process. The recovery of uranium from phosphoric acid by two extraction processes was also studied. Uranium was reduced to tetravalent state and extracted by dioctypyrophosphoric acid. The stripping was made with concentrated H_3PO_4 and an oxidizing agent. Then, uranium was extracted by D_2EHPA and TOPO(49).

R. Misiak and M. Tlalka(50) determined the optimum condition for precipitation of ammonium uranyl carbonate and reported a precipitation recovery of 97-98 % uranium for the synergistic extraction system of 0.3 M D_2EHPA and 0.075 M TOPO.

2.2.6 Homogeneous Extraction

The liquid-liquid extraction method has been extensively applied to studies of chemical equilibria, the separation of different elements, and the synthesis of inorganic compounds. However, some problems do remain in solvent extraction, e.g., slow extraction rates and incomplete extractions. Murata et al. have devised a new homogeneous liquid-liquid extraction method and obtained

satisfactory results in the extraction of molybdenum(VI) with a simple procedure(51). This method is based on the high solubility of an organic solvent in water at higher temperature and is characterized by immediate formation of the complex (with a suitable complexing agent) upon attaining a state of homogeneous solution consisting of water and the organic solvent during the procedure. At elevated temperature, there is a transition to a single homogeneous phase which separates into the two phases again upon cooling. During these sequential procedures, the species in the aqueous phase transfers into the organic phase, i.e., the extraction is achieved. This method of equilibration by achieving a homogeneous state is different from the common mechanical shaking method. Molecules of the organic solvent enter into the aqueous solution rather freely, and consequently, the water structure of the aqueous media and the environment of solute species will be altered remarkably by participation of the organic solvent molecules. This "unshielding" of the environment may affect extraction; such a condition is not satisfied in the conventional extraction method.

Propylene carbonate, which has found recent use in solvent extraction and also in electrochemical studies, is a most suitable organic solvent for homogeneous liquid-liquid extraction. It has a high dielectric constant (65 at 25°C), low vapor pressure, high boiling point, high flash point, and the unique property of being completely miscible with aqueous solutions above 71°C and becoming immiscible again upon cooling. Another special advantage of

propylene carbonate is that it permits a direct comparison of analyte concentration in each phase with a standard. Propylene carbonate/aqueous/ethanol medium in the ratio 2:2:1 yields a single homogeneous phase.

The only disadvantage of propylene carbonate as an extractant is the relatively high solubility of propylene carbonate in water. The phase diagram of the propylene carbonate-water system was investigated(52) at atmospheric pressure and the phase behavior is shown in Figure 2.1. Although propylene carbonate is soluble in water, the chelate complex which has been extracted remains in the organic phase. Large-scale processing of aqueous media could result in significant losses of propylene carbonate. The possibility of recovering propylene carbonate from aqueous solutions was investigated.

C. Hong(52) studied the homogeneous liquid-liquid extraction of TTA complexes of some metal ions, such as Fe(III), Cu(II), Ni(II), Zn(II) etc., and a variety of chelate and ion association complexes of iron, such as iron complexes with β-diketones, 8-quinolinol, cupferron, thiocyanate, benzoate, chloride, bromide etc.. The extraction rate was in all cases very rapid compared to the slow rate of conventional extraction. All those metal complexes can be extracted into propylene carbonate quantitatively.

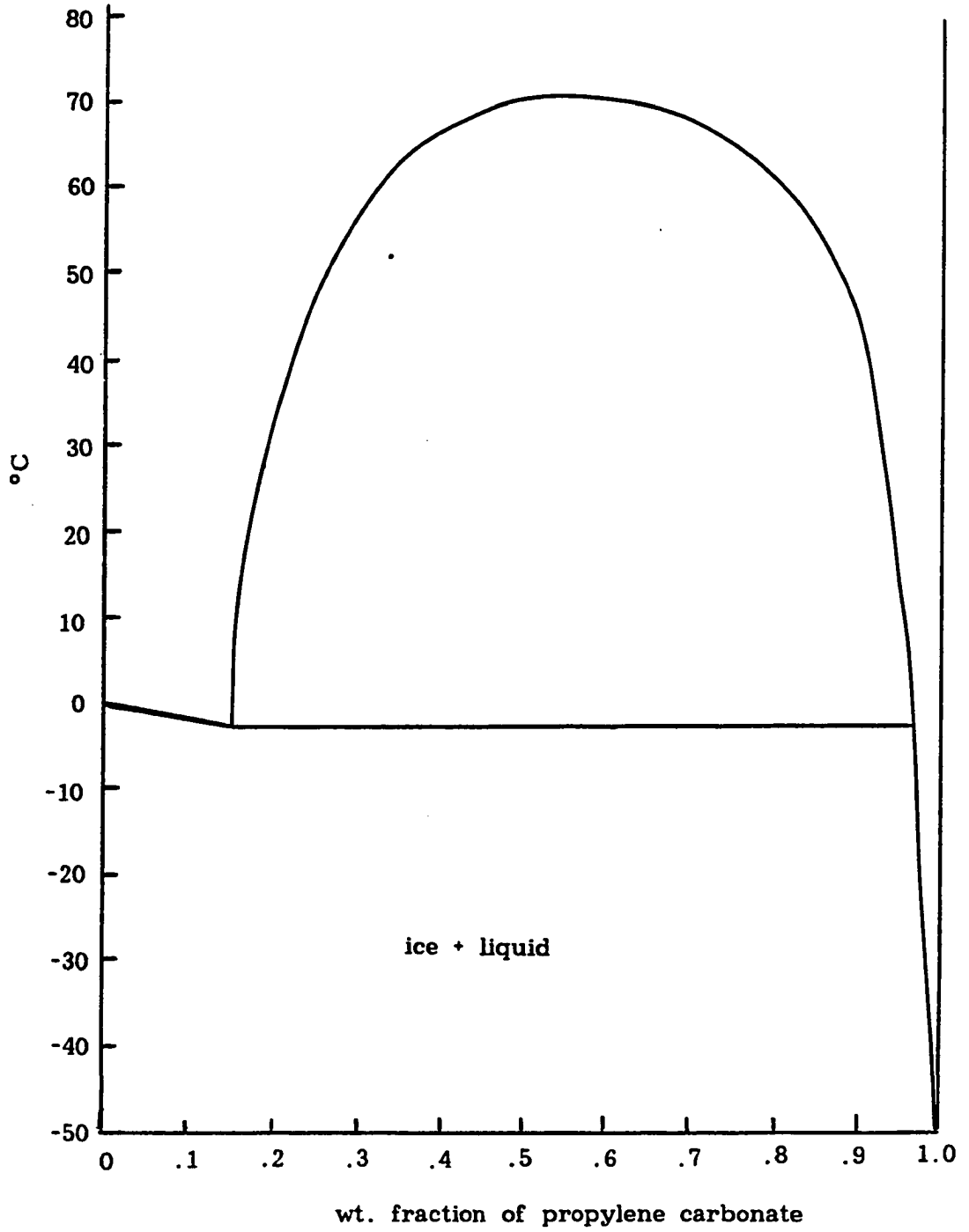


Fig. 2.1 Phase diagram of propylene carbonate-water system

N. Rajapakse(53) studied the homogeneous liquid-liquid extraction of some metal chelate complexes, such as TTA chelates of Fe(III), Co(II), Cu(II), at near neutral pH (6 to 8) by propylene carbonate. The extractions were very rapid and quantitative under optimum conditions. The systems studied included Cu(II), Co(II), Fe(III) complexed with tartaric acid as auxiliary ligand, and both TTA and acetylacetone in propylene carbonate as extractants. The advantage of TTA over acetylacetone does not exist at these higher pH's. TTA is a stronger acid than acetylacetone and consequently is more highly dissociated at low pH than is acetylacetone. However, at pH > 6 the difference may not be significant.

The homogeneous liquid-liquid extraction of uranium as uranyl nitrate also had been done in this study. Uranyl ion was extracted into propylene carbonate from uranyl nitrate solution supersaturated with ammonium nitrate as a salting-out reagent by heating (to 99°C) and stirring equal volumes of aqueous and propylene carbonate phases. The uranium extracted from nitrate solution into propylene carbonate was stripped from the organic phase with sodium carbonate solution at varying pH values. The final separation step consisted of extraction of uranyl ion into propylene carbonate containing dibenzoyl methane (DBM). The carbonate complex was first destroyed by heating the aqueous phase with nitric acid, and pH was adjusted from 6 to 8 before the extraction. The recovery of uranyl nitrate by extraction into propylene carbonate with ammonium nitrate as a salting-out agent was 97 %

under optimum condition.

The uranium(VI) extraction by propylene carbonate shows promise for separation of uranium from fuel elements. However, the optimum conditions and the behavior of typical high-yield fission product elements had not been studied.

It was the purpose of this study to determine the behavior of the significant fission products and to determine optimum conditions for an efficient and economic separation of uranium by homogeneous solvent extraction.

CHAPTER III

EXPERIMENTAL

3.1 Reagents

Uranyl nitrate, ammonium molybdate and strontium hydroxide (A.C.S. certified reagents) were obtained from J. T. Baker Chemical Company.

Ruthenium(III) chloride (49.1% Ru) and zirconium metal powder (M3N) were obtained from Morton Thiokol, Inc..

Cerous nitrate (reagent grade) was obtained from G. Frederick Smith Chemical Company.

Ferric nitrate and sodium carbonate (A.C.S. certified reagents) were obtained from Fisher Scientific Company.

Propylene carbonate, MCB reagents, 98 % by GC, was distilled under reduced pressure (b.p. 92°C at 4.5 mmHg) for purification.

All the other chemicals such as nitric acid, hydrochloric acid, ethanol, ammonium hydroxide, etc., were the highest purity grade available and used as such.

3.2 Apparatus

Metal cation concentrations were determined by visible spectrophotometry using a Perkin Elmer Lambda 3B UV/Visible spectrophotometer coupled to the PE 3600 data station and by atomic absorption spectrometry using a Perkin Elmer 372 atomic absorption spectrophotometer.

pH measurements were made with a Beckman ϕ43 pH meter using glass and calomel electrodes.

3.3 Procedures

3.3.1 Preparation of Model Solutions of Uranium and Fission Product elements

Uranium solutions were prepared by dissolving uranyl nitrate in 1 M nitric acid, which were then mixed with solutions of the different fission product elements, and adjusted to the desired concentration.

Molybdenum solutions were prepared by dissolving ammonium heptamolybdate tetrahydrate in 1 % ammonium hydroxide solution, which was then diluted with nitric acid, and adjusted to 1 M nitric acid solution.

Strontium solutions were prepared by dissolving strontium hydroxide in 1 M nitric acid and adjusting to the desired concentration.

Ruthenium solutions were prepared by dissolving ruthenium(III) chloride in a minimum volume of concentrated hydrochloric acid, which was evaporated to incipient dryness, with the residue dissolved in 1 M nitric acid solution.

Metallic zirconium powder was heated with concentrated sulfuric acid and concentrated hydrofluoric acid to fumes in a platinum vessel. After cooling, the walls of the vessel were rinsed with water

and the solution evaporated again to white fumes. The residue was cooled and dissolved in a minimum amount of water with heating, and the solution made 1 M in nitric acid.

Cerium solutions were prepared by dissolving the cerium(III) nitrate in 1 M nitric acid solution and adjusting to the desired concentration.

3.3.2 Extraction of Uranium in the Presence of Fission Product Elements

Uranyl ion was extracted into propylene carbonate from uranyl nitrate solution containing different fission product elements with ferric nitrate as a salting-out reagent by heating (to 99°C) and mixiup equal volumes of the aqueous and propylene carbonate phases in a 125 ml erlenmeyer flask. A "cold-finger" condenser placed in the neck of the flask minimized any loss of solution by evaporation. When a single homogeneous phase was achieved, the mixture was cooled to room temperature.

The uranium extracted from nitrate solution into propylene carbonate was stripped from the organic phase with 0.1 M sodium carbonate solution which had been previously equilibrated with propylene carbonate before stripping to minimize the loss of propylene carbonate. The pH of the stripping solution was adjusted to 9 by adding anhydrous sodium carbonate, which resulted in the

formation of a ferric-hydroxide precipitate. The mixture of organic phase, aqueous phase and precipitate was filtered off using a fine filter under reduced pressure (vacuum pump). The filtrate, a mixture of organic and aqueous phases was transferred to a separatory funnel for separation. The uranium was concentrated in the aqueous phase, i.e., the stripping solution.

3.3.3 Determination of the Recovery of Uranium

The uranium concentration in the stripping solution was determined by absorption spectrophotometry using the dibenzoyl methane method(53). The absorbance was compared with calibration standards prepared by mixing propylene carbonate:uranium concentration standard:ethanol solution of 0.1 M dibenzoyl methane in the ratio 2:2:1 to yield a single homogeneous phase. The pH of the homogeneous phase was adjusted to 7.0 before spectrophotometric determination.

The uranium carbonate complex in the stripping solution was first destroyed by heating the aqueous phase with nitric acid to incipient dryness. The residue was dissolved in dilute nitric acid, and mixed with propylene carbonate, an ethanol solution of dibenzoyl methane in the proper ratio, and the pH adjusted to 7.0 for determination of the uranium concentration.

The concentration of uranium in the stripping solution was

compared with the concentration in the original aqueous phase to determine the fraction of uranium recovered.

3.3.4 Determination of Fission Product Elements

The concentrations of fission product elements in both the aqueous phase after extraction and the stripping solution were determined by various methods. The methods selected for the analysis of the fission product elements and of the uranium were free from mutual interference according to the reference and the results which were checked in this study.

The concentrations of molybdenum, ruthenium(III) and strontium in the stripping solution, and the concentrations of ruthenium(III), strontium in the aqueous phase, after extraction, were determined by atomic absorption. For each determination, the reference solution is identical with the sample except for the element which would be determined.

The concentration of molybdenum in the aqueous phase after extraction could not be determined by atomic absorption because of interference of the large quantity of Fe(III). It was determined by absorption spectrophotometry using the thiocyanate method(54). The procedure consists of adding 30 ml of weakly acidic sample solution containing not more than 0.1 mg of Mo, to a separatory funnel, followed by addition of 5 ml of concentrated HCl, 5 ml of 20 % citric

acid solution, 5 ml of 10 % potassium thiocyanate solution, and, with swirling, 5 ml of stannous chloride solution (10 % $SnCl_2 \cdot 2H_2O$ solution in HCl). After 5 minutes, the solution was extracted with two portions of isoamyl alcohol, which were then combined and diluted to the mark with the solvent in a 50 ml volumetric flask.The absorbance was measured at 460 nm, using the solvent as reference. Fe(III) does not interfere in the determination of molybdenum since, under the reaction conditions, it is reduced to Fe(II) by stannous chloride. Large quantities of uranium interferes; but in the aqueous phase after extraction, the uranium is present only in trace amount and also, the molybdenum is separated from uranium by extracting into isoamyl alcohol, thus, it does not interfere with the determination.

The concentration of zirconium in the stripping solution was determined by absorption spectrophotometry using the Alizarin S method(54), since the sensitivity of atomic absorption for determination of zirconium is too low. The procedure consists of acidifying the stripping solution with HCl to 0.1 M hydrochloric acid solution, containing not more than 0.5 mg of Zr in a 50 ml volumetric flask, to which is then added 1 ml of 1 % gum arabic solution, 5 ml of 0.05 % Alizarin S aqueous solution, and the mixture is diluted with 0.1 M HCl to the mark, and mixed well. After 15 minutes, the absorbance is measured at 520 nm, using a reagent blank as reference. Large amounts of Fe(III) should be reduced to Fe(II), preferably with ascorbic acid. Uranium does not interfere in

the determination of zirconium by the Alizarin S method. Thus, this method can even be used for detecting zirconium in uranium alloys.

The concentration of zirconium in the aqueous phase after extraction, was determined by absorption spectrophotometry using the Arsenazo III method(54). The procedure consists of adding 4 ml of 0.05 % Arsenazo III aqueous solution and 37 ml of concentrated HCl to the acidic sample solution in a 50 ml volumetric flask containing not more than 0.04 mg of Zr; the solution is then dilited with water to the mark and mixed well. The absorbance was measured at 665 nm, using a reagent blank as reference. Over the acidity range 2-10 M HCl, only thorium and uranium(IV) interfere; other metals do not react with Arsenazo III in strongly acid medium.

The concentrations of cerium(III) in both stripping solution and aqueous phase after extraction were determined by absorption spectrophotometry using the 8-hydroxyquinoline method(54), because the sensitivity for determination of cerium by atomic absorption is too low. For the stripping solution, the procedure is to acidify the sample solution containing not more than 0.5 mg of Ce(III), which is then diluted with water to 10-15 ml, followed by addition of 1 ml of the 1 % solution of 8-hydroxyquinoline in ethanol, 2 drops of 1 % solution of phenolphthalein in ethanol, and ammonia solution (1 + 1) until a red color appears, and then 1 ml more of the ammonia solution is added (the pH of the solution should be within the range 9.9-10.6). The solution was quantitatively transfered to a

separatory funnel, and the cerium extracted with two successive portions of chloroform, equilibrated for 5 minutes each. The extracts were combined and diluted with chloroform to the mark in a 50 ml volumetric flask and the absorbance of the solution measured at 485 nm against the solvent. Cerium in the aqueous solution, was first separated as the oxalate from the huge amount of iron solution, to avoid interference. This was done by adding 20 ml of 8 % oxalic acid solution and 6 mg of lanthanum (in the form of a salt solution), then adjusting the pH of the solution to 2-3, heating the solution to 70-80°C, and maintaining it at this temperature for 1 hour. After 2-3 hours, the precipitate was filtered off and washed thoroughly first with 1 % oxalic acid solution and then with water. Finally, the precipitate was ignited to the oxide and dissolved in a small amount of hot 4 M HCl for determination of cerium by absorption spectrophotometry as described.

Chapter IV

RESULT AND DISCUSSION

4.1 Extraction of Uranium

The methodology for extraction of uranium has progressed to a great extent during the past four decades with the development and growth of nuclear power to meet worldwide energy demands. As early as 1842, Peligot(3) found that uranium in nitric acid is extractable into diethyl ether. Since that time, the extraction of uranium with many other solvents has been studied by many investigators and a modern technology for uranium extraction now exists. However a number of techniques have been, or are being, developed which could further improve the efficiency of uranium extraction, lower costs or reduce environmental impact. Recently, Fathi Habashi(55) pointed out that a major breakthrough in hydrometallurgy was the introduction of an "in-situ" leaching process for uranium ore in which sodium carbonate is pumped directly into the deposit to remove uranium, thus obviating ore transport, and solvent extraction was used for recovering the uranium. More recently, a number of advanced methods for extraction of uranium have been achieved by many

investigators(46-50).

It has been shown in this laboratory that uranium(VI) can be extracted into propylene carbonate from nitrate medium and the uranium(VI) in the organic phase can be stripped into aqueous phase using aqueous carbonate solutions. The final separation of uranium(VI) can be achieved by extracting uranium(VI) into dibenzoylmethane in propylene carbonate(53).

4.1.1 "Salting-Out" Agent

Historically, the extraction of uranyl nitrate into organic solvents, e.g. ether, TBP, MIBK, etc. has always required a salting-out agent, and Rajapakse(53) has verified that this was also the case for extraction into propylene carbonate.

Various salting-out agents have been investigated for extraction of uranyl nitrate into propylene carbonate. Previously it was found that ammonium nitrate as a salting-out reagent at a concentration of 2 g/ml in 1 M nitric acid solution gave 97 % recovery of uranium. However, this concentration of ammonium nitrate corresponds to a supersaturated solution at room temperature, and when the homogeneous solution cools down after extraction, the ammonium nitrate crystallizes out, causing some practical difficulty. The following salts, at the concentrations given, can all be used in relatively low concentration as salting-out reagents, but they all,

except for ferric nitrate, increase the solubility of propylene carbonate in water. The results obtained in this study are shown in Table 4.1.

Ferric nitrate offers the following advantages:

(a) Ferric hydroxide can be precipitated at pH > 2. The precipitate is a very effective scavenger due to its large surface area which can adsorb and carry down fission products thus providing a decontamination step in the overall extraction of uranium. It may also serve as a useful matrix for long term storage of radioactive fission products.

(b) A lower concentration of ferric nitrate rather than the higher concentration of ammonium nitrate can be used, which simplifies the practical procedures.

(c) As is the case with ammonium nitrate, the moderate solubility of propylene carbonate in the aqueous phase is acceptable.

The optimum concentration of ferric nitrate was determined; the results are shown in Table 4.1.

Finally, 0.5 g/ml $Fe(NO_3)_3 \cdot 9H_2O$ was selected as the optimum salting-out agent in this system.

Table 4.1 Optimum condition of salting-out agent for the extraction of uranium.

UO_2^{2+} concentration (moles/l)	Salting-out reagent	% Extracted
10^{-4}	0.35 g/ml $Al(NO_3)_3$	Solubility of PC in water increases*
10^{-4}	0.87 g/ml $Ca(NO_3)_2$	Solubility of PC in water increases*
10^{-4}	1.56 g/ml $Zn(NO_3)_2 \cdot 6H_2O$	Solubility of PC in water increases*
10^{-4}	0.72 g/ml $LiNO_3$	Solubility of PC in water increases*
10^{-4}	0.10 g/ml $Fe(NO_3)_3 \cdot 9H_2O$	35
10^{-4}	0.25 g/ml $Fe(NO_3)_3 \cdot 9H_2O$	68
10^{-4}	0.50 g/ml $Fe(NO_3)_3 \cdot 9H_2O$	97
10^{-4}	1.00 g/ml $Fe(NO_3)_3 \cdot 9H_2O$	97

* In these cases, the % Extracted was not determined; the solubility of PC in water in the presence of these salting-out reagents made them impractical.

The addition of nitric acid to the aqueous phase favors the extraction of uranium by preventing or decreasing the hydrolysis of uranyl ion and by increasing the nitrate ion concentration(56). However, large concentrations of nitric acid are generally not desirable; the formation of $HNO_3 \cdot S_n$ complexes reduces the amount of free solvent; the extraction of other elements is enhanced; and the danger of an explosive reaction between solvent and acid is increased(57). The optimum matrix for uranyl nitrate extraction into propylene carbonate was a medium 1 M in HNO_3 containing 0.5 g/ml $Fe(NO_3)_3 \cdot 9H_2O$.

4.1.2 Optimum pH for Stripping Uranium from Propylene Carbonate

Uranium was stripped from propylene carbonate with a sodium carbonate solution rather than with water or acidic solutions because it has the advantage that many cations (e.g. those of the transition metals) are insoluble in a solution with a moderate to high carbonate concentration, thus further eliminating a number of fission products. It has been long known that uranyl compounds show considerable solubility in sodium carbonate solutions, indicating the formation of stable complex ions. This unique property of uranium has been useful in analytical separation procedures and in industrial uranium separation processes. As early as 1842, the particular compound sodium uranyl tricarbonate, $Na_4UO_2(CO_3)_3$, had been prepared and identified by M. Ebelman(58), and its solubility

had been measured in 1947 by W. E. Bunce and coworkers(59). In addition, Haldar(60) observed discontinuities in conductometric titrations of uranyl nitrate with carbonate solutions at points corresponding to carbonate:uranium mole ratio of 3:1 and 2:1. C. A. Blake and coworkers(61) investigated protions of the phase digram for the four components system UO_3-Na_2O-CO_2-H_2O at 26°C. Solubilities were determined for UO_2CO_3 in sodium carbonate solutions and for $Na_4UO_2(CO_3)_3$ in sodium carbonate and other salt solutions as a function of the concentration of co-solute. A solubility of 320 gU/l was obtained at molar ratio CO_2:Na:U close to 2:2:1 and pH close to 7. From solubilities and spectrophotometric measurements, evidence was obtained for the existence of $UO_2(CO_3)_2^{-2}$ and $UO_2(CO_3)_3^{-4}$, with an estimate of the stability of the latter, and also for an additional complex ion having the molar ratio CO_2:U = 0.5.

Stripping uranium from propylene carbonate by sodium carbonate is incomplete at low pH, which may be due to the low concentration of carbonate ion, insufficient to form the complex. The effect of pH on the stripping of carbonate is shown in Table 4.2.

Table 4.2 The effect of pH on stripping of uranium by carbonate solution

pH of Stripping	Recovery of Uranium %
6	11.25
7	45
8	63.75
9	97
10	97

The results shown in Table 4.2 can be illuminated mathematically. The fractional concentration of the carbonate ion (i.e., the fraction of total carbonate species that exist as CO_3^{-2}), α_2, can be expressed as follows:

$$\alpha_2 = \frac{[CO_3^{2-}]}{[H_2CO_3] + [HCO_3^-] + [CO_3^{2-}]}$$

$$= \frac{1}{\frac{[H_2CO_3]}{[CO_3^{2-}]} + \frac{[HCO_3^-]}{[CO_3^{2-}]} + 1}$$

$$= \frac{1}{\frac{[H^+]^2}{K_1K_2} + \frac{[H^+]}{K_2} + 1}$$

$$= \frac{1}{10^{(pK_1+pK_2-2pH)} + 10^{(pK_2-pH)} + 1}$$

Here K is ionization constant, and pK = -logK. For carbonic acid, $pK_1 = 6.34$ and $pK_2 = 10.36$. So,

$$\alpha_2 = \frac{1}{10^{(16.7-2pH)} + 10^{(10.36-pH)} + 1}$$

When pH = 8,

$$\alpha_2 = \frac{1}{10^{0.7} + 10^{2.36} + 1} = 4.3 \times 10^{-3}$$

If pH = 9,

$$\alpha_2 = \frac{1}{10^{-1.3} + 10^{1.36} + 1} = 4.2 \times 10^{-2}$$

Thus, as pH increases from 8 to 9, the fractional concentration rises 10-fold, i.e., the concentration of carbonate ion increases ten times, and the stripping of uranium from propylene carbonate will be complete.

The success of the carbonate stripping is due to the large overall formation constant for uranyl-carbonate complexes(62).

$$UO_2^{2+} + 3CO_3^{2-} \rightleftharpoons [UO_2(CO_3)_3]^{4-}$$

$$\beta_3 = 2 \times 10^{18}$$

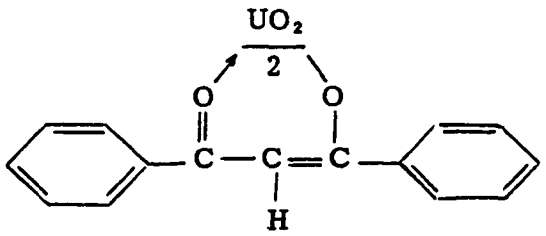
$$UO_2^{2+} + 2CO_3^{2-} \rightleftharpoons [UO_2(CO_3)_2 \cdot 2H_2O]^{2-}$$

$$\beta_2 = 4 \times 10^{14}$$

Unfortunately, the stability of the complexes limits the possibility of a quantitative reaction between uranium and any known colorimetric reagent(63). Thus, it is necessary to free the uranium from the carbonate complex by adding nitric acid and boiling to eliminate the CO_2. The uranium liberated from the carbonate complex reacts with the colorimetric reagent quantitatively.

In the final separation step, the uranyl ion is extracted into propylene carbonate containing dibenzoyl methane, at pH between 6 to 7; the extraction is complete. As the pH of the aqueous solution increases above 7, the percent extraction decreases(53,64), which

may be due to increasing hydrolysis of uranyl ion. The effect of initial aqueous pH on the homogeneous extraction of uranyl-dibenzoylmethane into propylene carbonate is shown in Figure 4.1(53). It is known that the dibenzoyl methane exists in the enolic form $C_6H_5COCH{=}COHC_6H_5$(65) at pH = 7, and the structure of the yellow complex is given(66) as:



in alcohol-water medium. The absorption spectrum of uranium dibenzoyl methane is shown in Figure 4.2. The maximum which is measured against a reagent blank occurs at 405 nm. The medium is a 2:2:1 ratio of propylene carbonate:aqueous phase:ethanol, at pH 7. Yoe et al.(66) also reported the same spectrum in ethanol-aqueous medium at pH 7. The calibration curve for determination of uranium using dibenzoyl method is shown in Figure 4.3.

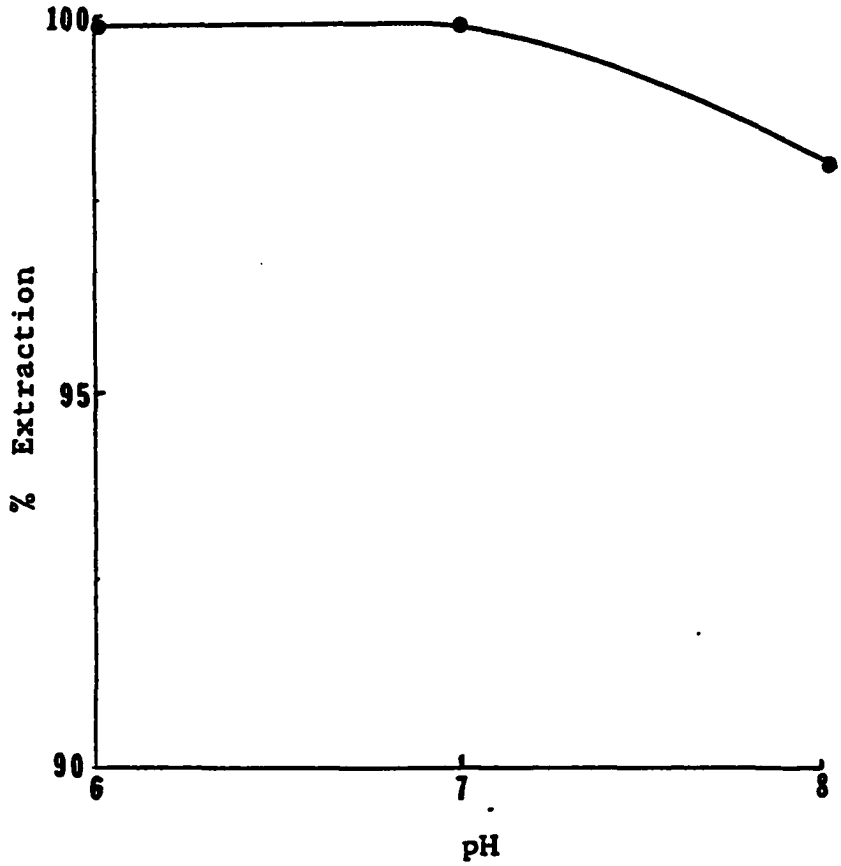


Fig. 4.1 The effect of initial aqueous pH on the homogeneous extraction of uranyl-dibenzoylmethane into propylene carbonate

$[UO_2^{+2}] = 4.4 \times 10^{-4}$ [DBM] = 0.1 M

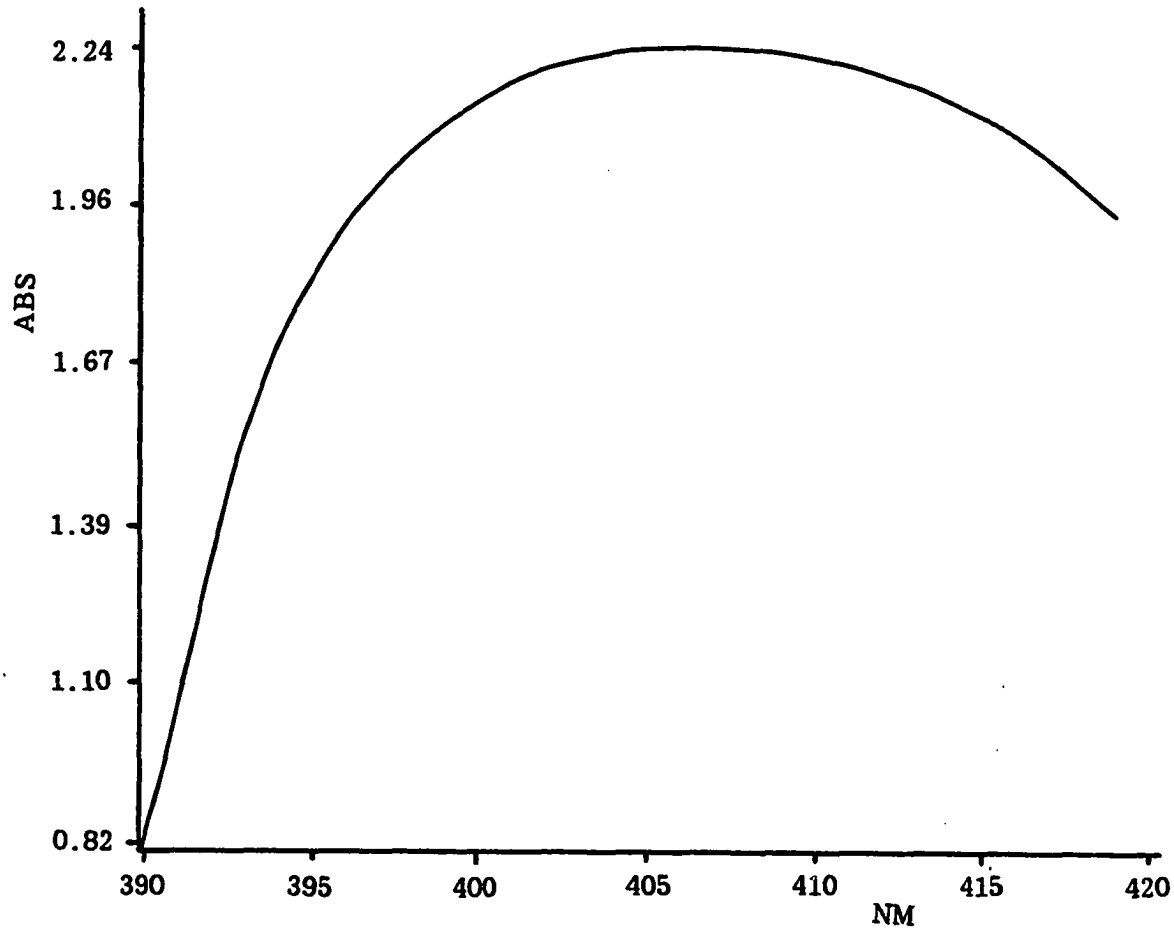


Fig. 4.2 Absorption spectra of uranium-dibenzoyl methane in 2:2:1 ratio of PC/aqueous/ethanol at pH 7

$[UO_2^{+2}]$ = 10 ppm

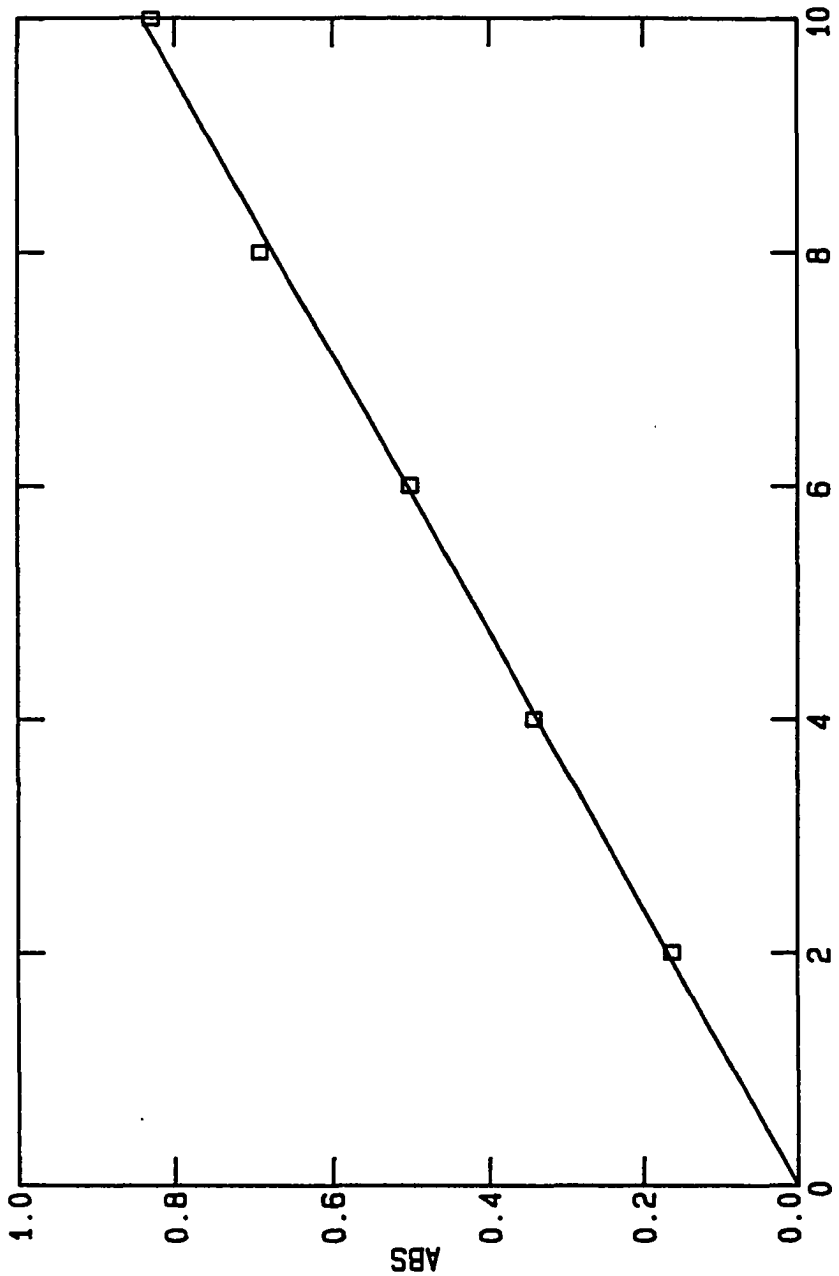


Fig. 4.3 The calibration curve for determination of uranium using dibenzoyl methane method

4.1.3 Effect of Fission Product Elements on the Recovery of Uranium

The effect of some fission product elements, such as Mo(VI), Sr(II), Ru(III), Zr(VI), Ce(III) and mixtures of all these elements, on the homogeneous extraction of uranium was investigated. The optimum matrix for uranyl nitrate extraction into propylene carbonate was 0.5 g/ml $Fe(NO_3)_3 \cdot 9H_2O$ + 1 M HNO_3. The pH of solution for stripping of uranium from propylene carbonate with 0.1 M sodium carbonate was 9. After filtering off the precipitate of ferric hydroxide, the uranium(VI) is homogeneously extracted into a solution of 0.1 M dibenzoyl methane in propylene carbonate at pH = 7.

The effects of Mo(VI), Sr(II), Ru(III), Zr(VI), and Ce(III) respectively and all these five ions together in the overall procedure are shown in Table 4.3.

The recovery of uranium in the presence of fission product elements by homogeneous extraction of uranium is satisfactory.

Table 4.3 The recovery of uranium in the presence of fission product elements

[Fission Products]	$[UO_2^{+2}]$ initial	$[UO_2^{+2}]$ found	% U recoverd
[Mo(VI)] = 30 ppm	4.40×10^{-4} M	4.13×10^{-4} M	93.6
[Sr(II)] = 100 ppm	4.40×10^{-4} M	4.40×10^{-4} M	100
[Ru(III)] = 50 ppm	4.40×10^{-4} M	4.09×10^{-4} M	93.0
[Zr(II)] = 50 ppm	4.40×10^{-4} M	4.27×10^{-4} M	97.0
[Ce(III)] = 100 ppm	4.40×10^{-4} M	4.29×10^{-4} M	97.5
All five of above 10 ppm of each	4.40×10^{-4} M	4.14×10^{-4} M	94.1

4.2 Distribution of Fission Products in the Extraction of Uranium

4.2.1 Distribution of Some Significant Fission Product Elements

The separation of uranium from fission products by extraction, requires a suitable extractant system which can extract the uranium completely and give adequate separation from the fission products. Propylene carbonate was selected for study as the solvent for separating the uranyl nitrate complex. The distributions of some typical fission product elements, such as Mo(VI), Sr(II), Ru(III), Zr(VI) and Ce(III), between propylene carbonate and aqueous nitrate solutions were investigated.

a. Molybdenum

There are four radioisotopes of molybdenum, ^{99}Mo, ^{101}Mo, ^{102}Mo, and ^{105}Mo, which are formed from uranium fission; the half lives are 66.0 hr, 14.6 min., 11.1 min., and 0.9 min., respectively. The only significant radioisotope based on half life is ^{99}Mo with a corresponding overall fission chain yield of 6.1 %. Molybdenum has six oxidation states: 0, +2, +3, +4, +5, and +6. The +6 oxidation state is the one most commonly found in aqueous solution. Molybdenum is generally considered to exist in solution as an oxygenated anion in the +6 state. Water soluble compounds of molybdenum(VI) include the ammonium, sodium, potassium and

magnesium salts of normal molybdates.

The extraction of molybdenum from an aqueous solution into an organic solvent has been studied by many investigators for different systems. Molybdenum in dilute acid in the presence of a reducing agent, such as stannous chloride, forms a red-colored complex with thiocyanate. This reaction has been used for many years as a means of determining molybdenum colorimetrically. Hiskey and Meloche(67), in a study of the complex, stated that it consisted of thiocyanate:molybdenum(V) in the ratio 3:1. R. Bock(68) made a detailed investigation of the extraction of various metal thiocyanates at 0.1 M concentrations into ethyl ether from 0.5 M hydrochloric acid solutions which were 1 to 7 M in ammonium thiocyanate. Molybdenum can be separated from a number of fission products, uranium(VI), and other elements by varying the ammonium thiocyanate concentration, volume ratios, etc..

Molybdenum can also be extracted into ethyl ether from halogen acid solutions. Swift(69) reported 80-90 % extraction from 6 M HCl. Other investigators reported 54 %, 9.7 %, and 6.5 % extraction from 6 M HBr(70), 3.5 M HF(71), and 6.9 M HI(72) solutions respectively. A rapid separation of molybdenum and technetium from fission products and from each other was effected by extracting molybdenum(VI) with ethyl ether from a 6 M HCl solution of irradiated uranium, precipitating the molybdenum as the 8-hydroxyquinolate and separating or "milking" the technetium from

molybdenum by precipitating nitron pertechnetate with rhenium as the carrier(73).

Tributyl phosphate (TBP) is an excellent extractant for molybdenum. Nelidow and Diamond(74) reported distribution coefficients $(Mo)_{org.}/(Mo)_{aq.}$ of 4.0 and 65 respectively, from 1 M and 2 M hydrochloric acid solutions, with distribution coefficients increasing with increasing acid concentration. Gerlit(75) reported distribution coefficients of 8.5 and 21.6 from neutral medium, and from 2 N sulfuric acid solutions, respectively. TBP is used for the solvent recovery of uranium and plutonium, from fission products.

More than 99 % of molybdenum(VI) was extracted from uranium leach liquors by 0.4 M DDPA (mono ester of dodecylphosphoric acid) in kerosene(76). Extraction coefficients larger than 1000 were observed for molybdenum(VI) when sulfuric acid solutions (pH = 2) containing about 3 mg Mo/ml were contacted with an approximately equal volume of 0.1 M solutions of the amines, dilaurylamine, 1-(3-ethyl-pentyl)-4-ethyloctylamine, and methyl dilaurylamine, respectively in an aromatic hydrocarbon diluent. However, these amine extractions have the characteristic that as the concentration of molybdenum in the aqueous phase decreases, so does its distribution coefficient(77).

White(78) studied the extraction behavior of over forty elements with the trialkylphosphine oxides. Molybdenum(VI) was completely extracted from 1 M hydrochloric or sulfuric acid solutions by 0.1 M

tri-n-octylphosphine oxide (TOPO) in cyclohexane and partially extracted from the same aqueous media by 0.1 M tris-2-ethylhexylphosphine oxide.

Molybdenum(VI) was not extracted into propylene carbonate from uranyl nitrate solution with 1 M nitric acid and 0.5 g/ml ferric nitrate. After extraction of uranium into propylene carbonate and stripping uranium by sodium carbonate solution, the concentrations of molybdenum(VI) in both the stripping solution and the original aqueous phase were determined to get the distribution of molybdenum in the homogeneous extraction of uranium. The result is shown in Table 4.4.

Table 4.4 Recovery of fission product elements in their co-extraction with UO_2^{+2}

[Fission Products Cation]			
initial (ppm)	Found in aqueous (ppm)	Found in organic (ppm)	% Extracted
[Mo(VI)] = 30	29.64	0.6	2.0
[Sr(II)] = 100	97.50	2.5	2.5
[Ru(III)] = 50	49.15	0.6	1.2
[Zr(II)] = 50	48.00	1.25	2.5
[Ce(III)] = 100	96.60	2.8	2.8

notes: 1. $[UO_2^{+2}] = 4.40 \times 10^{-4}$ M

2. Determined after stripping with 0.1 M Na_2CO_3 at pH 9

The concentration of molybdenum(VI) in the stripping solution was determined by atomic absorption spectrophotometry which uses the reagent as a reference blank. The standard curve is shown in Figure 4.4.

The concentration of molybdenum in the aqueous phase after extraction of uranium cannot be detected by atomic absorption spectrophotometry due to the interference of large amounts of ferric nitrate. It was determined by UV/Visible spectrophotometry using the thiocyanate method(54). The absorption spectrum of the molybdenum(V) complex with thiocyanate is shown in Figure 4.5. The maximum which is measured against a solvent blank occurs at 460 nm. The calibration curve for determination by UV/Visible spectrophotometry is shown in Figure 4.6.

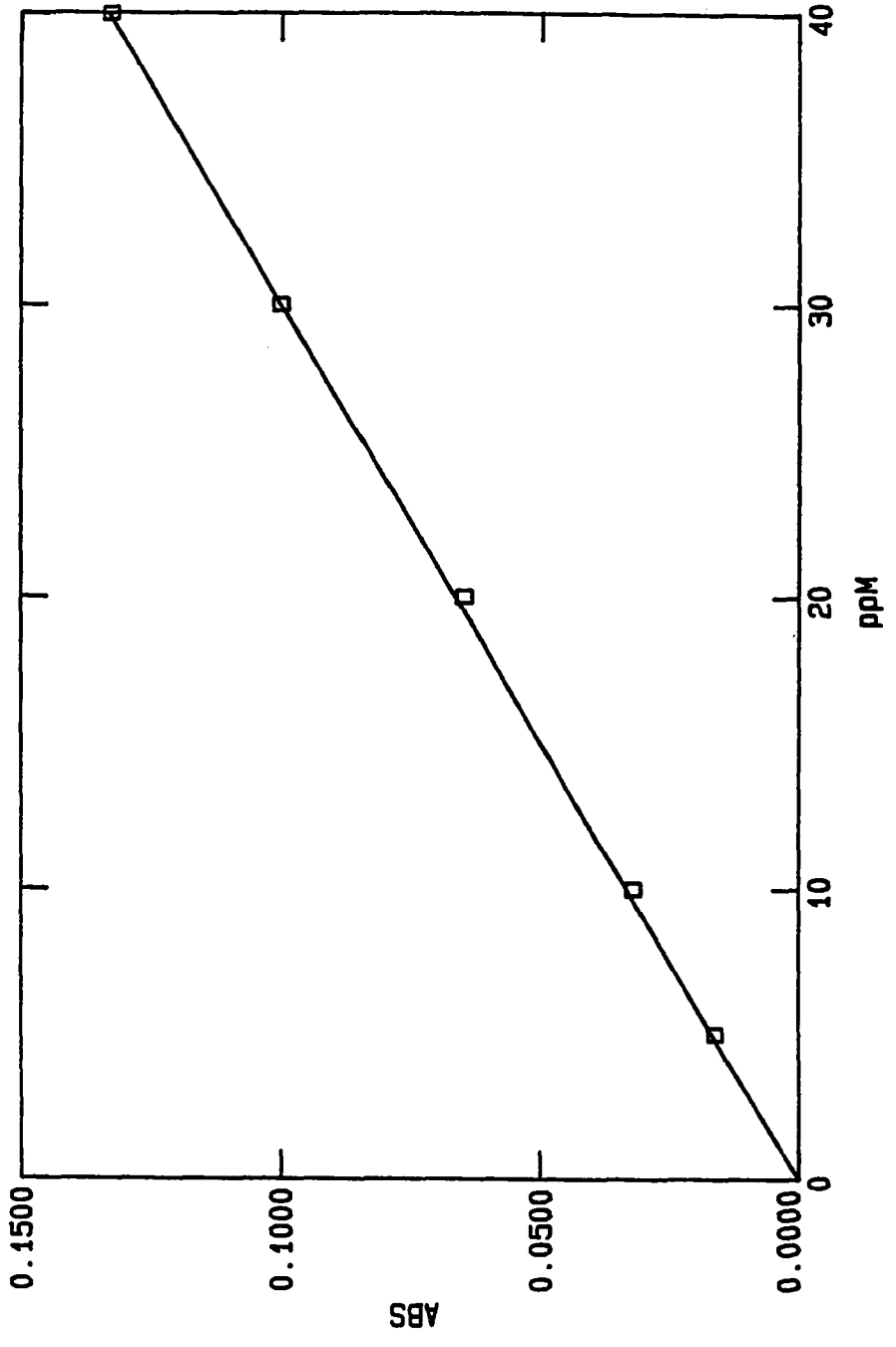


Fig. 4.4 The calibration curve for determination of molybdnum using atomic absorption spectrophotometry

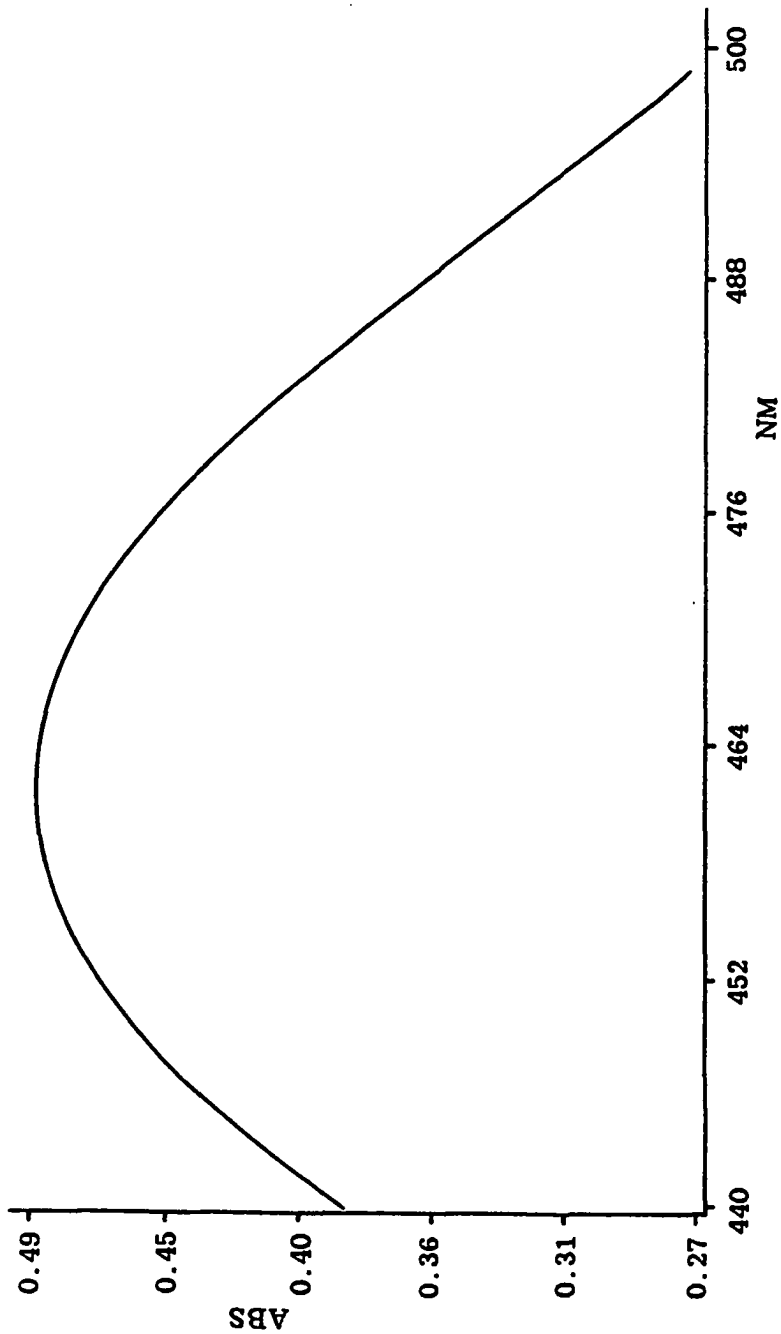


Fig. 4.5 Absorption spectra of the molybdnum(V) complex with thiocyanate

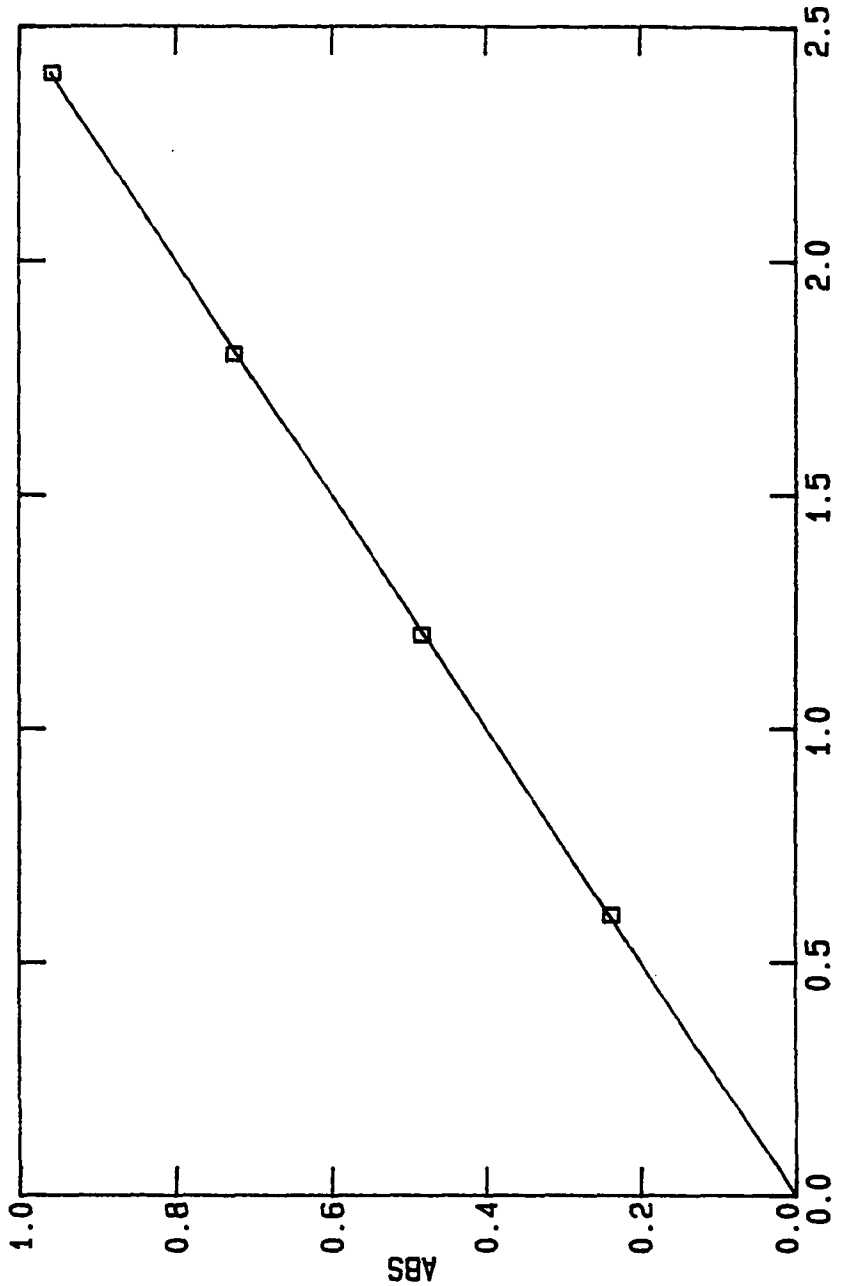


Fig. 4.6 The calibration curve for determination of molybdnum(V) using UV/Visible spectrophotometry

b. Strontium

There are nine radioisotopes of strontium produced in fission of uranium, namely ^{89}Sr, ^{90}Sr, ^{91}Sr, ^{92}Sr, ^{93}Sr, ^{94}Sr, ^{95}Sr, ^{96}Sr, and ^{97}Sr, which have half lives of 50.5 days, 29 yrs, 9.5 hrs, 2.7 hrs, 7.5 min., 1.3 min., 26 s, 4 s, and < 0.2 s, respectively. The most significant, because of half life and fission yield is ^{90}Sr. The soluble salts of strontium include the acetate, halides (except SrF_2), nitrate, permanganate, sulfide, chlorate, bromate, and perchlorate.

Strontium(II) can form a complex with thenoyltrifluoroacetone (TTA) which is extracted into organic solvents. For example, strontium has been extracted at pH greater than 10 into a 0.02 M solution of TTA in benzene(79). The equilibrium constant for this extraction is 7.5×10^{-15}. The equilibrium constant of extraction is defined by

$$K_{Sr} = \frac{(SrT_2)_B(H^+)^2_A}{(Sr^{+2})_A(HT)^2_B}$$

where B and A represent the benzene and aqueous phases, respectively. A TTA extraction at pH 5 has been used to separate Y^{90} from Sr^{90}(80-82). Yttrium extracts into a benzene solution of TTA at this pH, but strontium does not. Kiba and Mizukami(83) reported the extraction of strontium at pH 8 into a 0.05 M solution of TTA in hexane. Strontium may be separated from other metals by extraction with TTA in MIBK(84,85) or with TTA and TBP in carbon tetrachloride(86).

Strontium can also be extracted into a 1 M solution of 8-quinolinol in chloroform(87). An aqueous solution of less than 0.1 mg of strontium is brought to a pH of 11.3 with sodium hydroxide and diluted to 16 ml. This is shaken with the organic solvent, and approximately 96 % of the strontium is extracted.

A 1.5 M solution of di-(2-ethylhexyl)-orthophosphoric acid (HDEHP) in toluene has been used to separate Y^{90} from Sr^{90}. The Y^{90} is extracted by this reagent from a 0.1 M HCl solution leaving most of the strontium in the aqueous phase. The distribution ratio for strontium in this system is 1.6×10^{-2} and that for yttrium is greater than 10^{4}(88).

Similarly to molybdenum(VI), strontium(II) is also not extracted into propylene carbonate from 1 M nitric acid solution containing uranyl ion and ferric nitrate. The concentrations of strontium(II) in both the stripping solution and the original aqueous phase after extraction of uranyl nitrate into propylene carbonate were determined by atomic absorption spectrophotometry. The results are shown in Table 4.4.

There was no interference from ferric ion in the detection of strontium using a reagent blank containing ferric nitrate as a reference, even though the concentration of ferric nitrate was higher in the aqueous phase than in the "stripping solution". The calibration curve for the determination of strontium by atomic absorption spectrophotometry is shown in Figure 4.7.

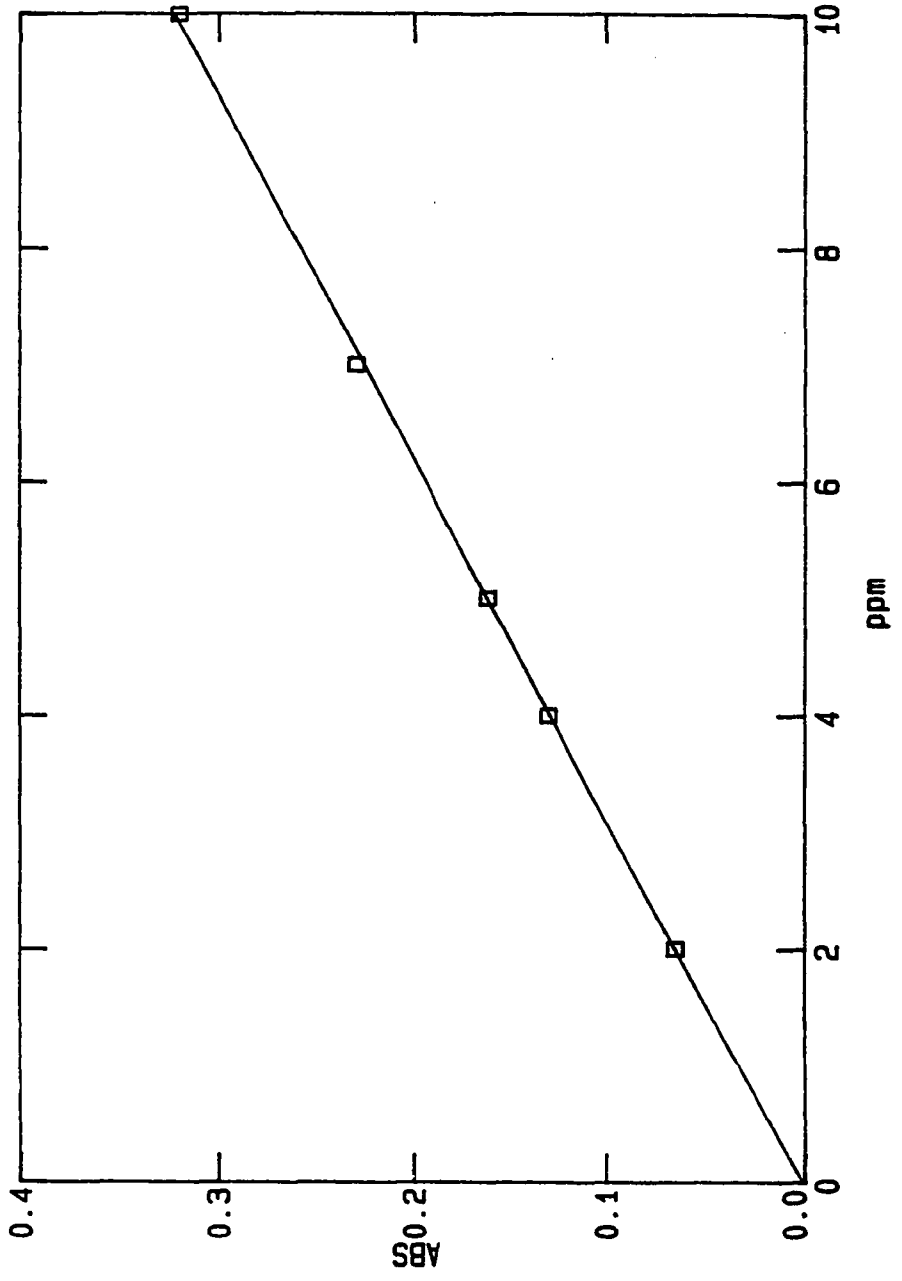


Fig. 4.7 The calibration curve for determination of strontium by atomic absorption spectrophotometry

c. Ruthenium

^{103}Ru and ^{106}Ru which have rather long half lives of 39.6 days and 369 days respectively, are the important radioisotopes of ruthenium produced in uranium fission.

Ruthenium belongs to subgroup VIII, the platinum metals. In radiochemical processes, ruthenium may be present as Ru(II), Ru(III), Ru(VI), Ru(VI), Ru(VII), or Ru(VIII). Ru(V) exists but is unlikely to be encountered. The chemisty of ruthenium is complicated because of its many valence states. The metal is usually dissolved by means of alkali-metal nitrate and peroxide fusion; acids and mixtures of acids have little dissolution effect. The fluorination or chlorination of ruthenium at high temperatures yields various soluble fluorides or chlorides. Ruthenium is analogous to the transition elements cobalt, iron, and nickel in its formation of numerous coordination complexs with the ligands, O^{-2}, Cl^{-1}, NO, NO_2^{-1}, NO_3^{-1}, OH^{-1}, OH_2, CN^{-1}, SCN^{-1}, etc.. Specific halogen compounds and complexs of di-, tri-, and tetravalent ruthenium are known. The chlorination of ruthenium metal produces ruthenium trichloride and possibly ruthenium tetrachloride, but pentachloride has not been isolated. Commercial ruthenium chloride is usually a mixture of trichloride and tetrachloride(89).

The oxides of ruthenium that are encountered most often in radiochemistry are the tetroxide, RuO_4, and the dioxide, RuO_2. The tetroxide is formed in acid solutions by strong oxidants. The oxide,

RuO_4, has been isolated, and its chemical and physical properties have been determined(89). Ruthenium tetroxide melts at about 26°C and begins to volatilize at 45°C; the volatilization is nearly complete at 110°C. The volatility of the tetroxide has been used extensively in radiochemistry(90). Ruthenium can be decontaminated from the other fission products by distillation as ruthenium tetroxide, especially if perchloric acid is the oxidizing agent. The high boiling point of $HClO_4 \cdot 2H_2O$ (200°C) ensures the complete distillation of ruthenium tetroxide. Halogens that distil under these conditions can be oxidized to their nonvolatile oxyacids by adding sodium bismuthate before the distillation(89).

Ruthenium(IV) in the system, HCl-5% triisooctylamine-xylene, has been found to extract efficiently from dilute hydrochloric acid concentration(91). The extraction of nitrosyl ruthenium nitrates by trilaurylamine and di(tridecyl)amine in toluene has also been described(92). Increasing extraction of ruthenium with decreasing acidity was observed over the range of 8 N nitric acid to 2 N nitric acid + 4 N sodium nitrate in the trilaurylamine- toluene system.

In the homogeneous extraction of uranium in the propylene carbonate system, ruthenium(III), which is a common valence form of radioruthenium(93), has no affinity for propylene carbonate. More than 98 % of ruthenium(III) remains in the aqueous phase, thus affording separation from uranium. Concentrations of ruthenium in both the stripping solution and the original aqueous phase, after

extraction of uranium, were determined by atomic absorption spectrophotometry. The results are shown in Table 4.4.

The interference of high concentrations of ferric ion in atomic absorption were overcome by adding ferric nitrate into the reagent as a reference blank. The calibration curve for determining ruthenium by atomic absorption spectrophotometry is shown in Figure 4.8.

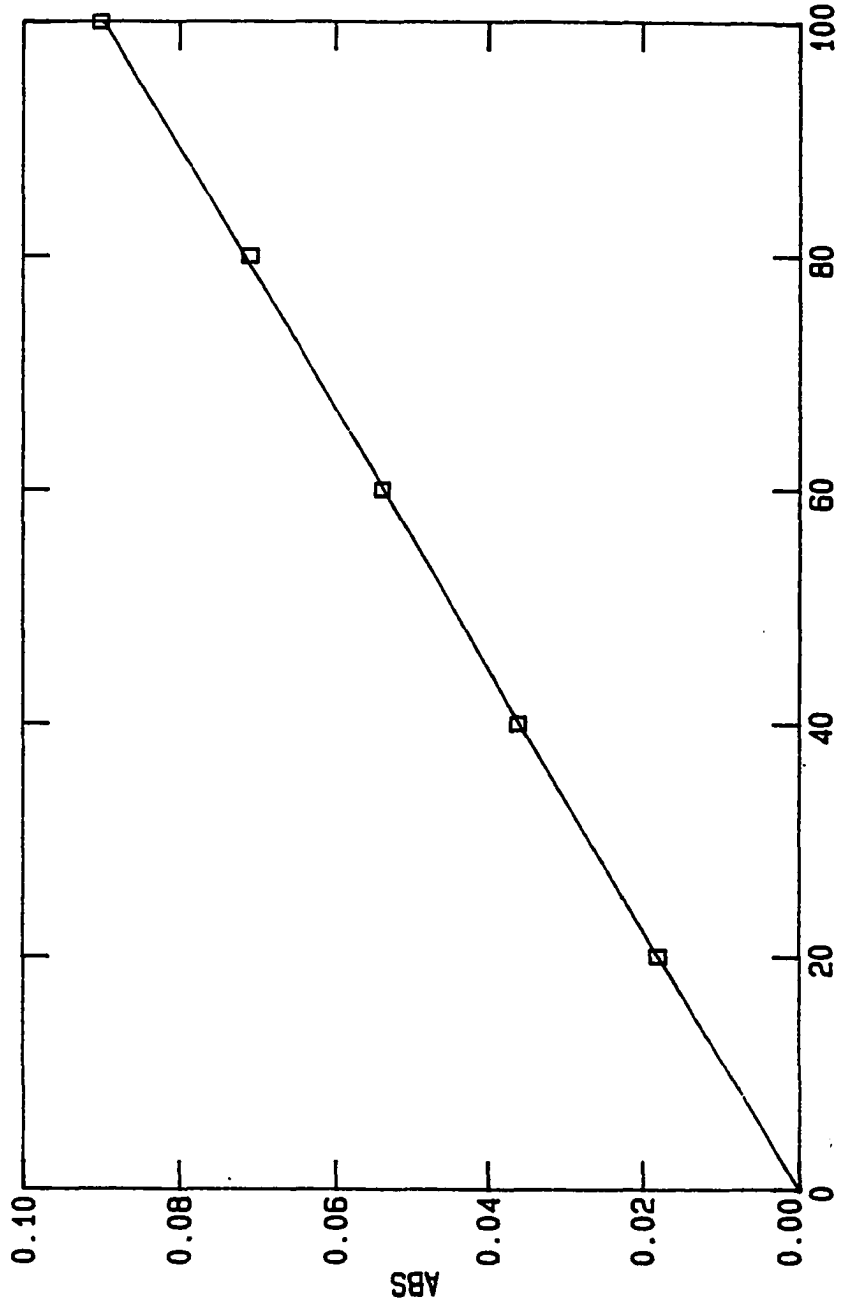


Fig. 4.8 The calibration curve for determination of ruthenium by atomic absorption spectrophotometry

d. Zirconium

Uranium nuclear fission produces the zirconium radioisotopes ^{93}Zr, ^{95}Zr, ^{97}Zr, ^{98}Zr, and ^{99}Zr; their half lives are 1.1×10^6 yrs, 65 days, 17.0 hrs, 1 min. and 35 sec., respectively. The significant health hazard is ^{95}Zr. Zirconium has very high melting point and reacts vigorously at high temperature with carbon, oxygen, and nitrogen. The dry metal powder is pyrophoric and should be moistened for safe handling. In compact form, and at low temperature, the zirconium metal is very inert chemically, being attacked appreciably only by HF, aqua regia, and fused KNO_3.

The solution chemistry of zirconium is not very well understood, and considerable confusion exists in the literature regarding the ionic species present in aqueous solutions. This results mainly from the formation of colloids and the fact that zirconium ions undergo extensive hydrolysis and polymerization, strongly dependent on pH and concentration(94). The only important oxidation number is +4. The nitrate, chloride, bromide, iodide, perchlorate, and sulfate salts of zirconium are all soluble in acid solution. Zirconium can form complex ions with many substances. As is the case with the hydrolysis products, the species present in solution are not well established. Connick and McVey(95) have studied the complexing ability of a number of substances, and have indicated that the fluoride is by far the most stable complex; among the dicarboxylic acid, oxalic has a much greater complexing power than can be

accounted for simply by a comparison of the acid dissociation constants.

The formation of chelate complexes of zirconium with acetylacetone, TTA, trifluoroacetylacetone (TFA), 8-quinolinol, and cupferron etc., which are soluble in organic solvents, has been of great importance to the development of radiochemical separation procedures(95-99).

The common solvent, ethyl ether, is effective for the extraction of many elements from halide systems. Extraction of zirconium, however, is not appreciable, the fluoride being extracted to the extent of only 2.9 % and the other halides even less(100). The distribution of Zr(IV) between aqueous HNO_3-$Ca(NO_3)_2$ solutions and hexone has been studied by Rydberg and Bernstrom(101). Distribution ratios approaching unity were obtained for zirconium from solutions 3.5-4.0 M in $Ca(NO_3)_2$ and about 3 M in HNO_3. Scadden and Ballou(102) investigated the di-n-butylester of phosphoric acid (DBPA), alone and in a mixture with the monoester (as in commercial "butylphosphoric acid"), as extractants for zirconium and niobium. Both tracer and macro levels of zirconium were found to extract quantitatively from aqueous solutions 1 M in HNO_3, HCl, $HClO_4$, or H_2SO_4. A 0.06 M solution of the dibutylphosphoric acid in di-n-butylether extracted > 95 % of the Zr and < 5 % of the Nb. Tri-n-butylphosphate (TBP) is an excellent extractant for zirconium. It may be used pure or with an inert

diluent such as n-butylether, ether, kerosene, benzene, or CCl_4. The extractability increases with acid strength, and a distribution ratio of about 100 is observed from 8 M HCl and 1000 from 13 M HNO_3(103).

Propylene carbonate does not extract zirconium(VI) from uranyl nitrate solution with 1 M nitric acid and 0.5 g/ml ferric nitrate. The concentrations of zirconium in both stripping solution and aqueous phase, after extraction of uranium, were determined to get the distribution of zirconium ion in this system. The results are shown in Table 4.4.

It was difficult to use atomic absorption spectrophotometry for determining the concentration of zirconium in both stripping solution and aqueous phase after extraction of uranium due to its low sensitivity (about 500 ppm). The concentration of zirconium in the stripping solution was determined by UV/Visible spectrophotometry using the Alizarin S method. Alizarin S reacts with zirconium ions in acid medium (pH 0.5-1.0) to form a purple-red compound which is sparingly soluble in water. Moderate quantities (1-10 mg) of Fe do not interfere at pH around 1. The sensitivity of this method is 4-10 ppm. The spectrum of the zirconium complex with Alizarin S is shown in Figure 4.9. The maximum which is measured against a reagent blank occurs at 520 nm. The calibration curve for the Alizarin S method is shown in Figure 4.10. The concentration of zirconium in the aqueous phase

after extraction of uranium was determined by UV/Visible spectrophotometry using the Arsenazo III method. Zirconium reacts with Arsenazo III in strongly acidic medium (2-10 M HCl) to form an emerald green water-soluble complex. Only thorium and uranium(IV) interfere over the acidity range 2-10 M HCl; other metals do not react with Arsenazo III in strongly acid. Thus, this method can detect zirconium in cast iron and steels. The sensitivity of this method is 2-8 ppm. The spectrum of the zirconium complex with Arsenazo III is shown in Figure 4.11. The maximum, which is measured against a reagent blank, occurs at 665 nm. The calibration curve for Arsenazo III method is shown in Figure 4.12.

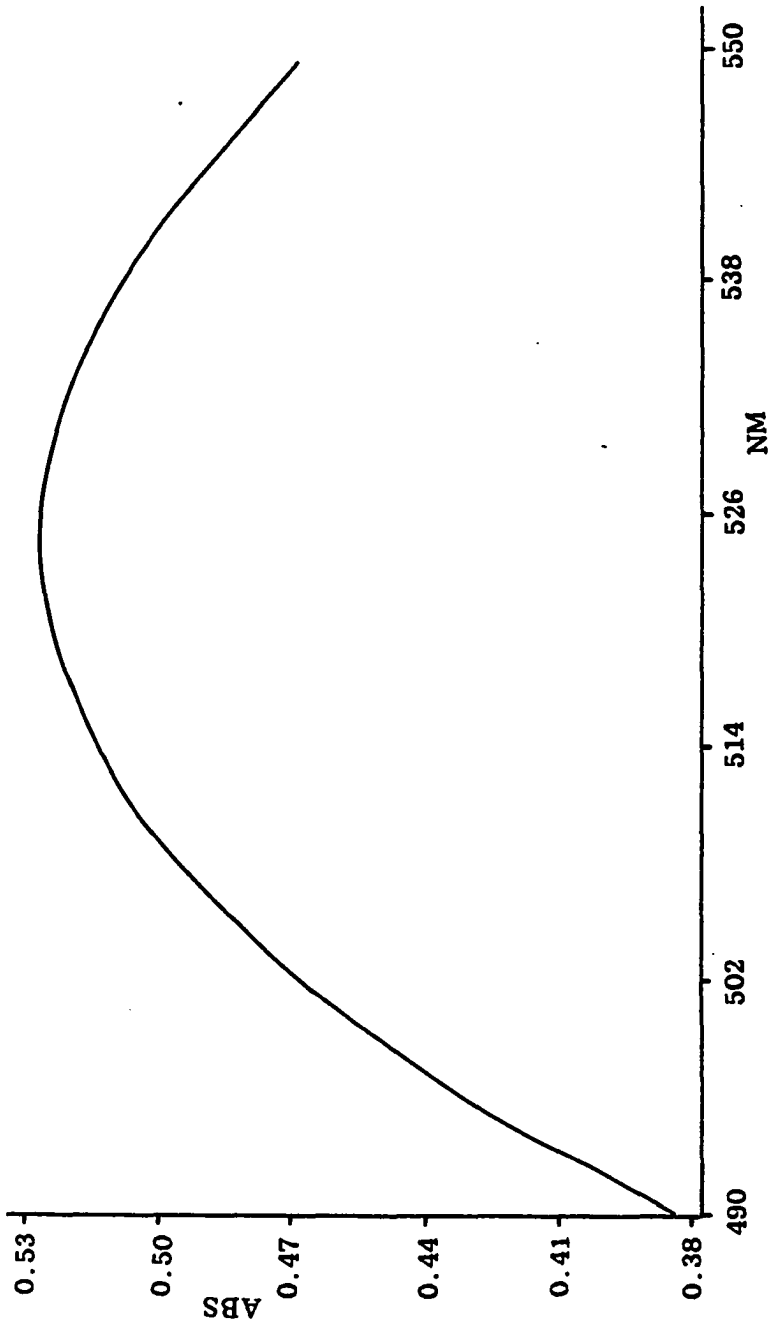


Fig. 4.9 Absorption spectra of the zirconium complex with Alizarin S

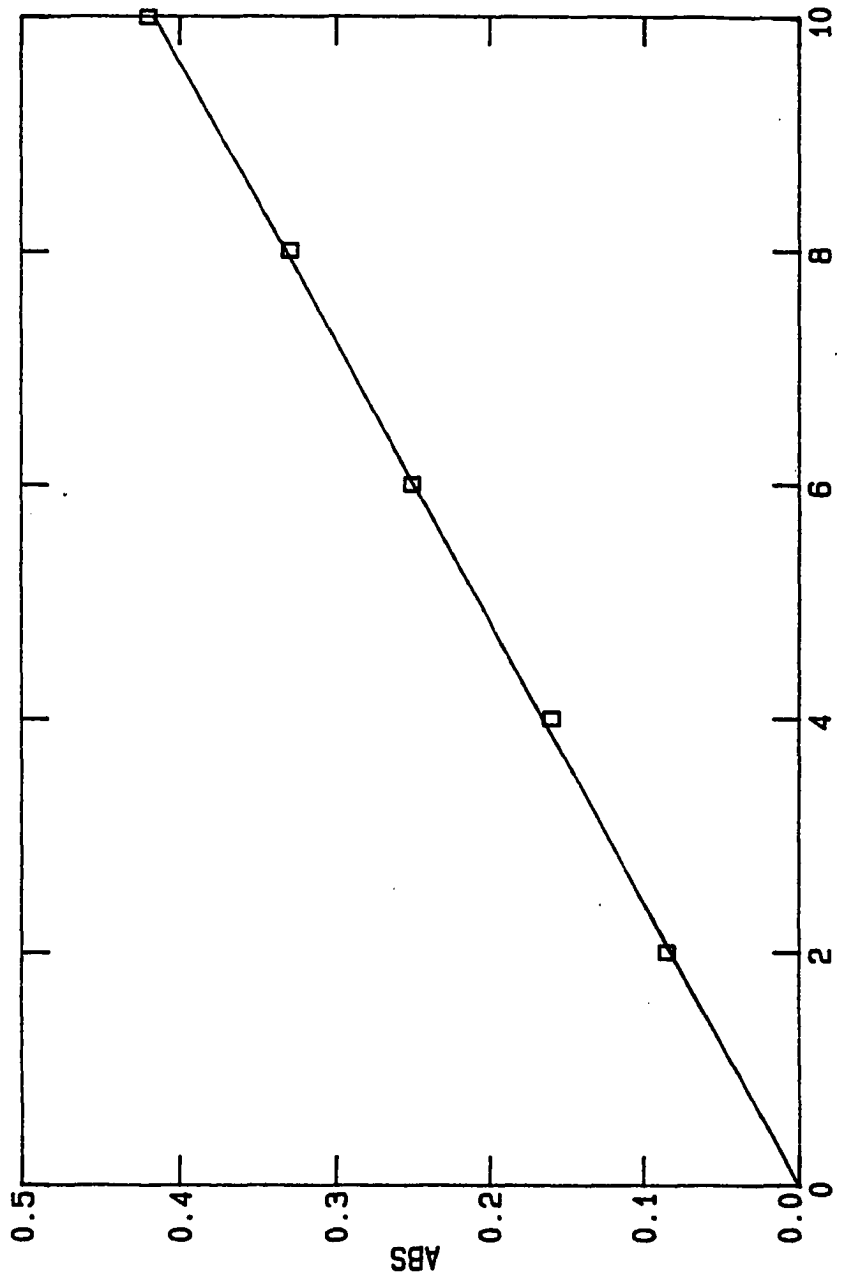


Fig. 4.10 The calibration curve for the determination of zirconium using Alizarin S method

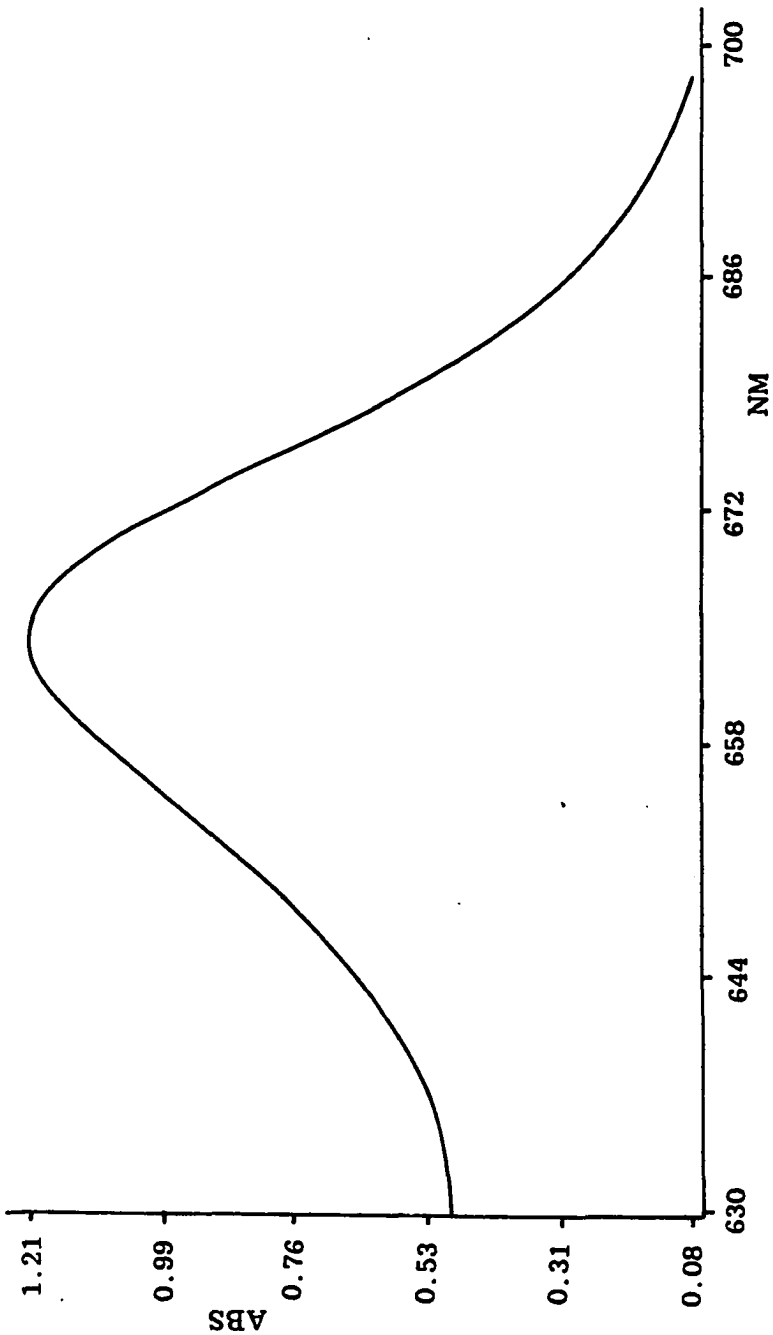


Fig. 4.11 Absorption spectra of the zirconium complex with Arsenazo III

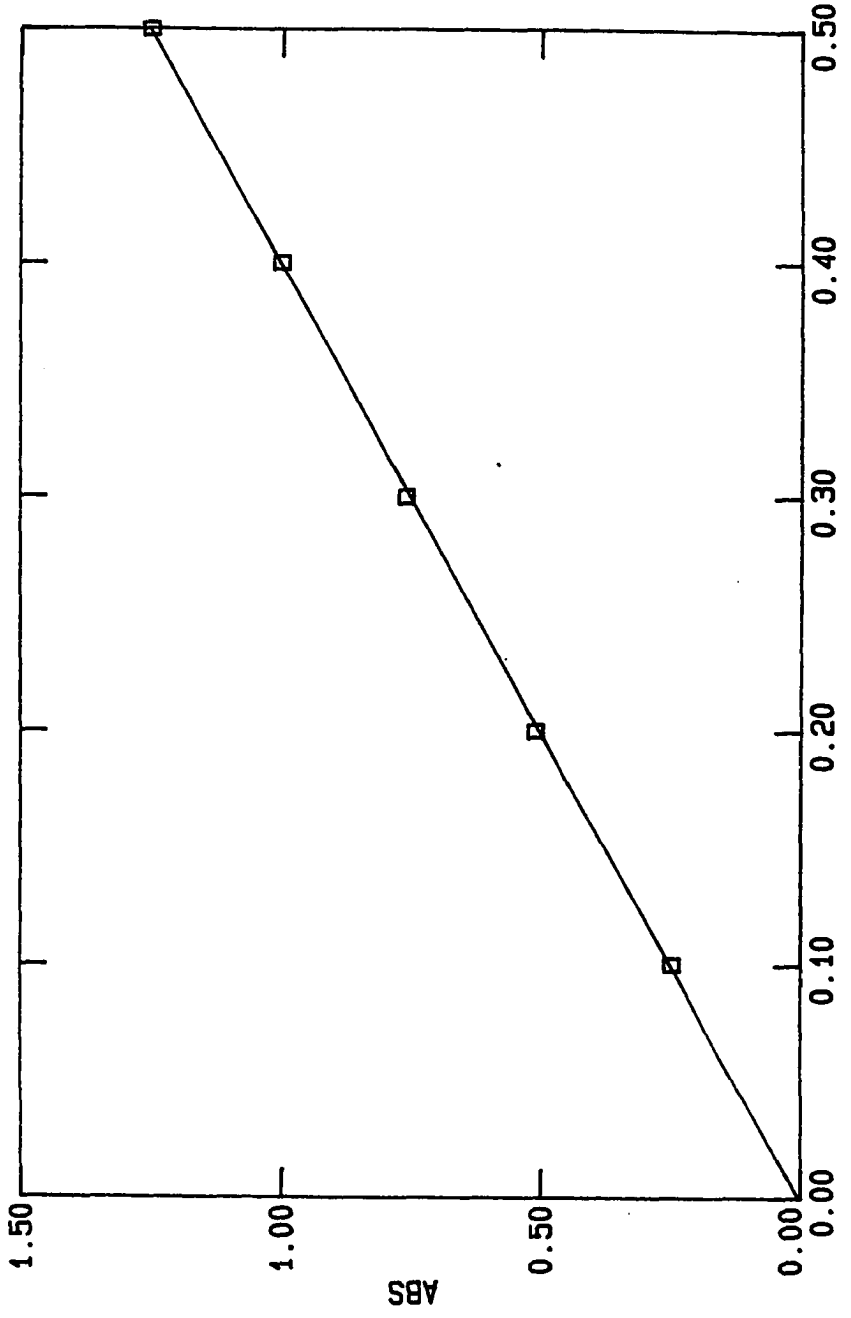


Fig. 4.12 The calibration curve for determination of zirconium using Arsenazo III method

e. Cerium

^{141}Ce, ^{143}Ce, and ^{144}Ce which have half lives of 30 days, 33 hrs, and 284.4 days respectively, are the important radioisotopes of cerium produced in uranium fission. The most significant one is ^{144}Ce.

Cerium is the most common of the rare earth elements. The rare earth elements exist in aqueous solution, under normal conditions only as the trivalent ions. However, some of the rare earths can exist in other than the +3 oxidation state; for example, cerium is the rare earth element which has a useful +4 oxidation state; and this fact is often of value in effecting their separation from other members of the group. Cerium(III) has the same chemical properties as all the other rare earth elements. Cerium(III) can be oxidized in acidic medium with bismuthate, silver(II) oxide, persulphate (in the presence of Ag^{+}) or bromate (in 9 M HNO_3). Cerium(IV) resembles thorium, zirconium, and uranium(IV) in many of its chemical properties but is also a powerful oxidant. However, cerium(IV) is not completely stable, but oxidizes water very slowly. Duke and Anderegg(104) have shown that the reaction is surface catalyzed and Evana and Uri(105) have shown that it is photosensitive, so reasonable precautions must be taken if cerium(IV) solutions are to be kept for any length of time. Like other rare earth elements, cerium(III) can be separated as the sparingly soluble oxalate(106); Calcium, barium, or any of the other rare earth elements (e.g.

lanthanum) can be used as the collector.

Peppard, Faris, Gray, and Mason(107) conducted an extensive study of the extractability of the lighter rare earth elements by TBP. They confirmed the strong dependence of extractability on TBP concentration. Very good extraction of all rare earth elements was noted from 7.2 M $Al(NO_3)_3$-0.2 M HNO_3 and from 10 M NH_4NO_3-0.2 M HNO_3, using 100 % TBP.

TTA is also a successful reagent for extracting rare earth elements. Smith and Moore(108) reported a rapid separation from fission products based on the very high extractability of the Ce(IV) ion by TTA. They extract from 1 M sulfuric acid containing potassium dichromate and sodium bromate, using 0.5 M TTA in xylene, and stripping the cerium with 10 M nitric acid. They also reported severe interference from chloride ion, which effectively prevents the oxidation.

Marsh, Maeck, Booman and Rein(109) developed a solvent extraction method in which cerium in fission product mixtures was oxidized to the quadrivalent state with bivalent silver and extracted as the tetra-n-propylammonium nitratocerate ion-association complex into nitroethane. Cerium was then stripped from the organic phase with H_2O_2-HCl and precipitated as cerous oxalate. This method was applicable to aluminum, thorium, zirconium, and stainless steel nuclear fuel matrices and tolerates up to 1 ml of concentrated nitric, sulfuric, perchloric, hydrochloric, and hydrofluoric acids and

0.25 ml of concentrated phosphoric acid. The total recovery of cerium was 98 %.

Cerium(III) is not significantly extracted into propylene carbonate from nitric acid solution. In the homogeneous extraction of uranium from uranyl nitrate with a high concentration of ferric nitrate, most of the cerium(III), 97 %, remains in the aqueous phase after extraction. The result is shown in Table 4.4.

The concentration of cerium(III) in the stripping solution can be determined by UV/Visible spectrophotometry using the 8-hydroxyquinoline (oxine) which forms a sparingly soluble chelate with cerium ions in ammoniacal media. The red-brown chelate can be extracted into chloroform and also into other organic solvents, thereby allowing the spectrophotometric determination of cerium. Alimarin et al.(110) have found that cerium in the red-brown oxinate is in the +4 oxidation state. In the presence of reducing agents, a pale yellow cerium(III) oxinate is obtained. When reducing agents are absent, the yellow cerium(III) oxinate is rapidly oxidized to the more intensely colored cerium(IV) oxinate by atmospheric oxygen. The spectrum of cerium(IV) complex with oxine in chloroform solution is shown in Figure 4.13. The maximum which was measured against a solvent blank occurs at 485 nm. The calibration curve for determination of cerium by the 8-hydroxyquinoline method is shown in Figure 4.14.

Since a high concentration of ferric nitrate exists in the aqueous phase after extraction of uranium which causes severe interference, it was necessary to separate cerium from the ferric nitrate solution. Cerium can be separated as its oxalate by precipitating with lanthanum as the collector in acidic solution (pH 2-3). After heating and filtering, the precipitate can be ignited to oxide, then dissolved in acidic solution for determination.

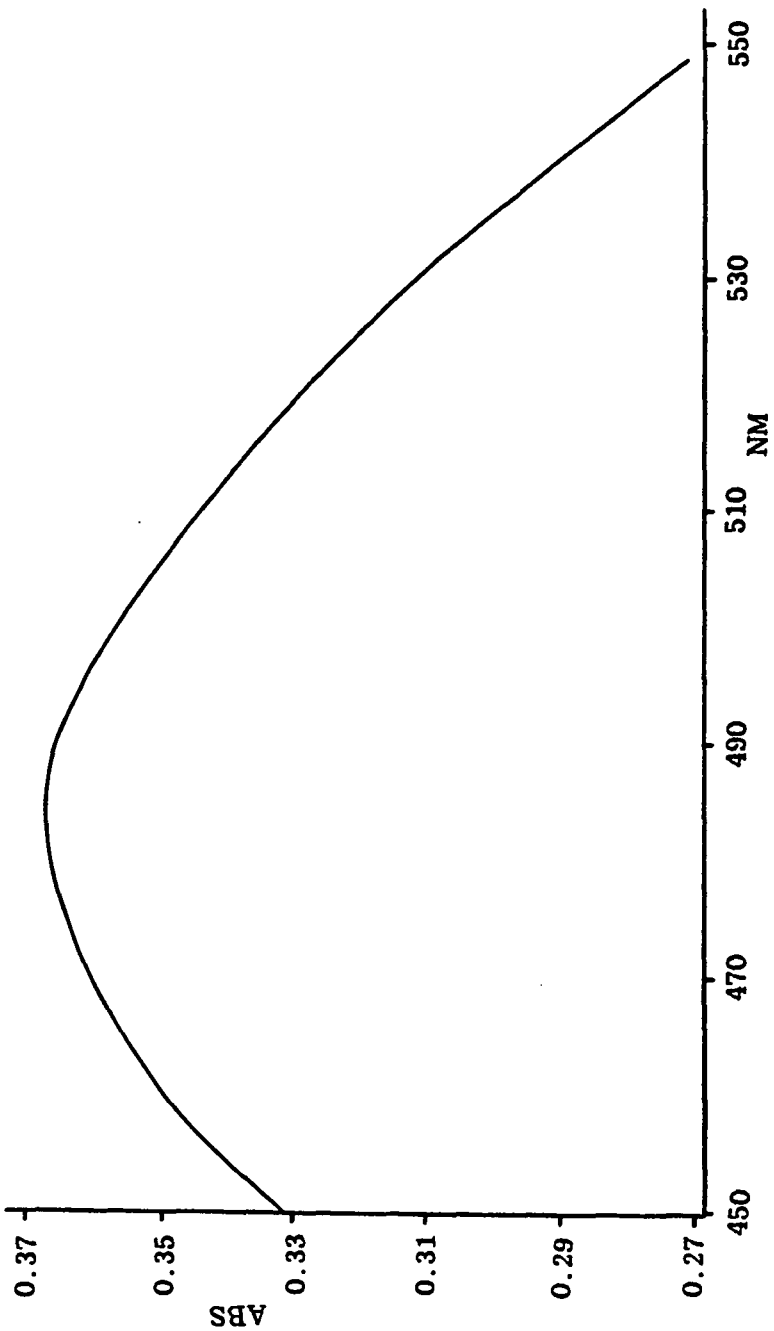


Fig. 4.13 Absorption spectra of cerium(IV) complex with oxine in chloroform solution

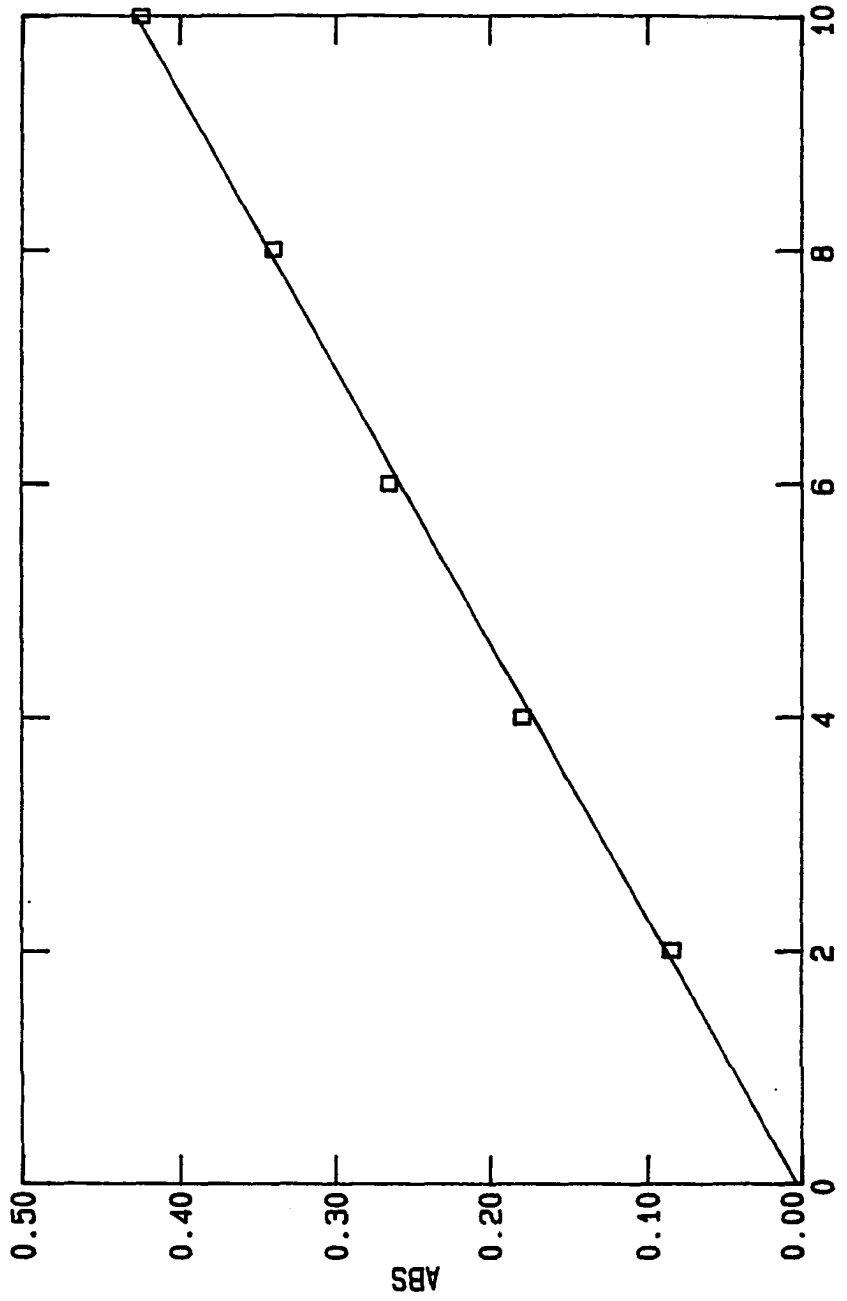


Fig. 4.14 The calibration curve for determination of cerium using 8-hydroxyquinoline method

4.2.2 Behavior of Iodine in the Extraction of Uranium

Iodine is the only environmentally significant non-metal element among the fission prodcts. The major radioisotopes are ^{125}I and ^{131}I with half lives of 59.7 days and 8.04 days respectively.

Iodine is a solid non-metal which is fairly volatile at room temperature and easily sublimed. Iodine dissolves readily in aqueous KI solutions to yield the I_3^- complex, and it is also soluble in organic solutions, e.g., chloroform, carbon tetrachloride, and benzene. It occurs mainly in the -1, +5, and +7 oxidation states, iodide, iodate, and periodate, respectively. Iodide reveals reducing properties, in contrast to iodine, iodate, and periodate which have oxidizing properties.

The behavior and effect of iodide in the recovery of uranium by homogeneous extraction was investigated. The presence of iodide does not effect the recovery of uranium. The total recovery of uranium in the presence of iodine, after three procedures (extracting by propylene carbonate, stripping by sodium carbonate, and final separating with dibenzoyl methane) is 93.5 %.

However, in the presence of a high concentration of ferric nitrate in the initial acidic aqueous solution, the following reaction occurs, where the iodide is oxidized to iodine by Fe(III) ion:

$$2\ Fe^{3+} + 2\ I^- \longrightarrow I_2 + 2\ Fe^{2+}$$

Propylene carbonate shows an affinity for iodine similar to

chloroform, carbon tetrachloride, and benzene. When extracting uranium into propylene carbonate, the iodine enters the organic phase with uranium. After stripping uranium by 0.1 M sodium carbonate at pH = 9, it was found that 10 % of the initial concentration of iodide was in the stripping solution. This phenomenon may be due to reduction of the iodine in propylene carbonate by Fe(II) which is partially extracted into the organic phase as well as some Fe(III). However, residual iodide will be separated from uranium efficiently by the final separation step, i.e., by extracting uranyl ion into propylene carbonate containing dibenzoyl methane. The ferric ions were removed by precipitating ferric hydroxide before the final separation step. Iodide was no longer oxidized to iodine and remained in the aqueous phase during the final separation step.

The concentrations of iodide in the stripping solution both before and after the final separation step were determined by UV/Visible spectrophotometry using the starch-iodine method(54). Iodide can be determined colorimetrically, after oxidation to iodine, as the blue iodine-starch adsorption compound. The sensitivity of the iodide determination is enhanced sixfold if iodide ions are first oxidized to iodate ions which, in turn, are reacted with added potassium iodide in an acidic medium.

$$IO_3^- + 5\ I^- + 6\ H^+ \longrightarrow 3\ I_2 + 3\ H_2O$$

Bromine water is usually used for the oxidation of iodide to

iodate(111). The excess of bromine is removed by brominating phenol. The spectrum of the starch-iodine complex in aqueous phase is shown in Figure 4.15; the maximum occurs at 625 nm after subtracting the reagent blank. The calibration curve for determination of iodide by the starch-iodine method is shown in Figure 4.16.

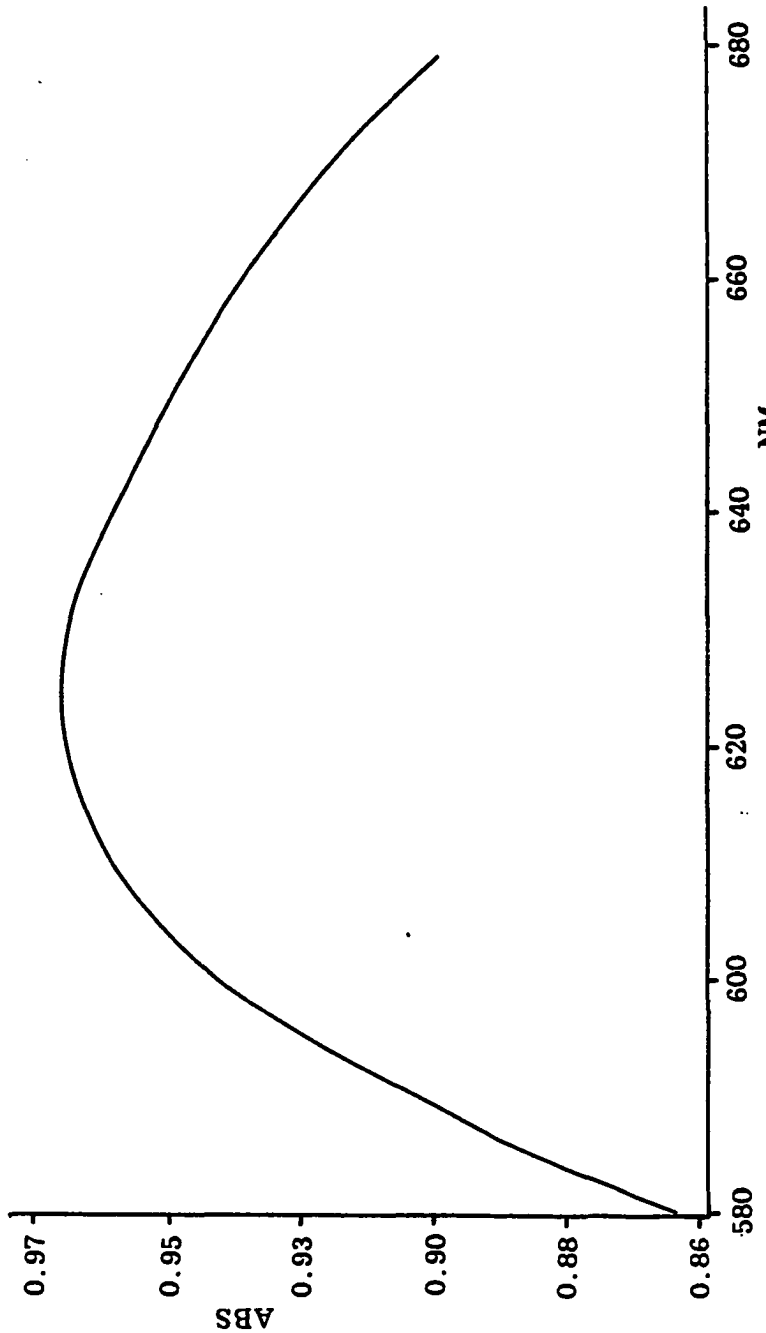


Fig. 4.15 Absorption spectra of the starch-iodine complex in aqueous

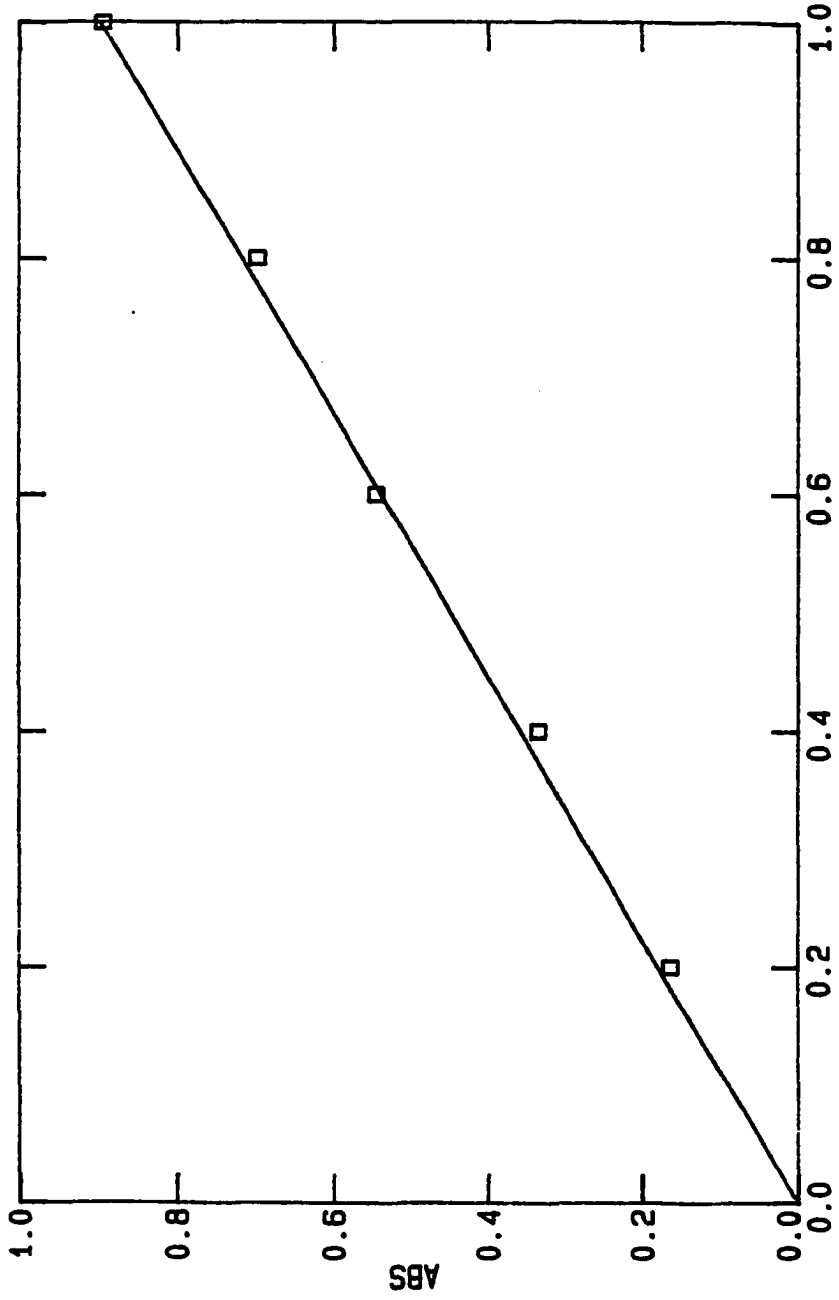


Fig. 4.16 The calibration curve for determination of iodine using starch-iodine method

4.3 Adsorption of Fission Products on Ferric Hydroxide

To evaluate the effectiveness of ferric hydroxide as a scavenger, ferric nitrate (0.05 g/ml) was added to a nitric acid solution of the various fission product elements, and the pH adjusted to 9 by adding anhydrous sodium carbonate. Thus, the ferric hydroxide was precipitated, carrying down the fission product elements. The clear supernatant solution, after centrifugation, was analyzed for each of the fission product elements respectively, by the same methods as applied for the determinations of the fission product elements in the stripping solutions. The results are shown in Table 4.6.

All of these fission product elements, except molybdenum, can be scavenged by precipitating ferric hydroxide. The incomplete precipitate of molybdenum in strong basic solution may be due to the more soluble complex of molybdenum formed. But molybdenum is not significantly extracted into propylene carbonate, and its half life (66 hrs.) is short, so this procedure will give satisfactory results for separation of uranium from the longer-lived high-yield fission products.

Table 4.5 Adsorption of Fission Products on Ferric Hydroxide

Fission Product Elements	% Remaining after Precipitate of $Fe(OH)_3$
Mo	20
Sr	1.5
Ru	2.0
Zr	1.8
Ce	2.5

4.4 The Capacity for Extraction of Uranium by Propylene Carbonate

The concentration of uranium in these experiments was 4.4 x 10^{-4} M, which is optimal for determination of uranium by spectrophotometry, but not adequate for a practical industrial procedure. In order to determine the capacity for extraction of uranium by propylene carbonate, the concentration of uranium was increased 100-fold, i.e., 4.4 x 10^{-2} M (10.5 g/l), and the extraction performed as previously.

The total recovery of uranium was 93 % after extraction by propylene carbonate, stripping by sodium carbonate and finally separation by extracting uranium into dibenzoylmethane (DBM) in propylene carbonate. Thus, the present uranium extraction method can be applied as a practical method for separating uranium from fission products.

The summary of analytical results for the extraction of UO_2^{+2} in the presence of fission product elements is shown in Table 4.6; and the flow chart of this uranium extraction method is shown in Figure 4.17.

Table 4.6 Summary of analytical results for the extraction of UO_2^{+2} in the presence of fission product elements

[Fission Products]	$[UO_2^{+2}]$ initial	$[UO_2^{+2}]$ found	% U recoverd
[Mo(VI)] = 30 ppm	4.40×10^{-4} M	4.13×10^{-4} M	93.6
[Sr(II)] = 100 ppm	4.40×10^{-4} M	4.40×10^{-4} M	100
[Ru(III)] = 50 ppm	4.40×10^{-4} M	4.09×10^{-4} M	93.0
[Zr(II)] = 50 ppm	4.40×10^{-4} M	4.27×10^{-4} M	97.0
[Ce(III)] = 100 ppm	4.40×10^{-4} M	4.29×10^{-4} M	97.5
All five of above 10 ppm of each	4.40×10^{-4} M	4.14×10^{-4} M	94.1

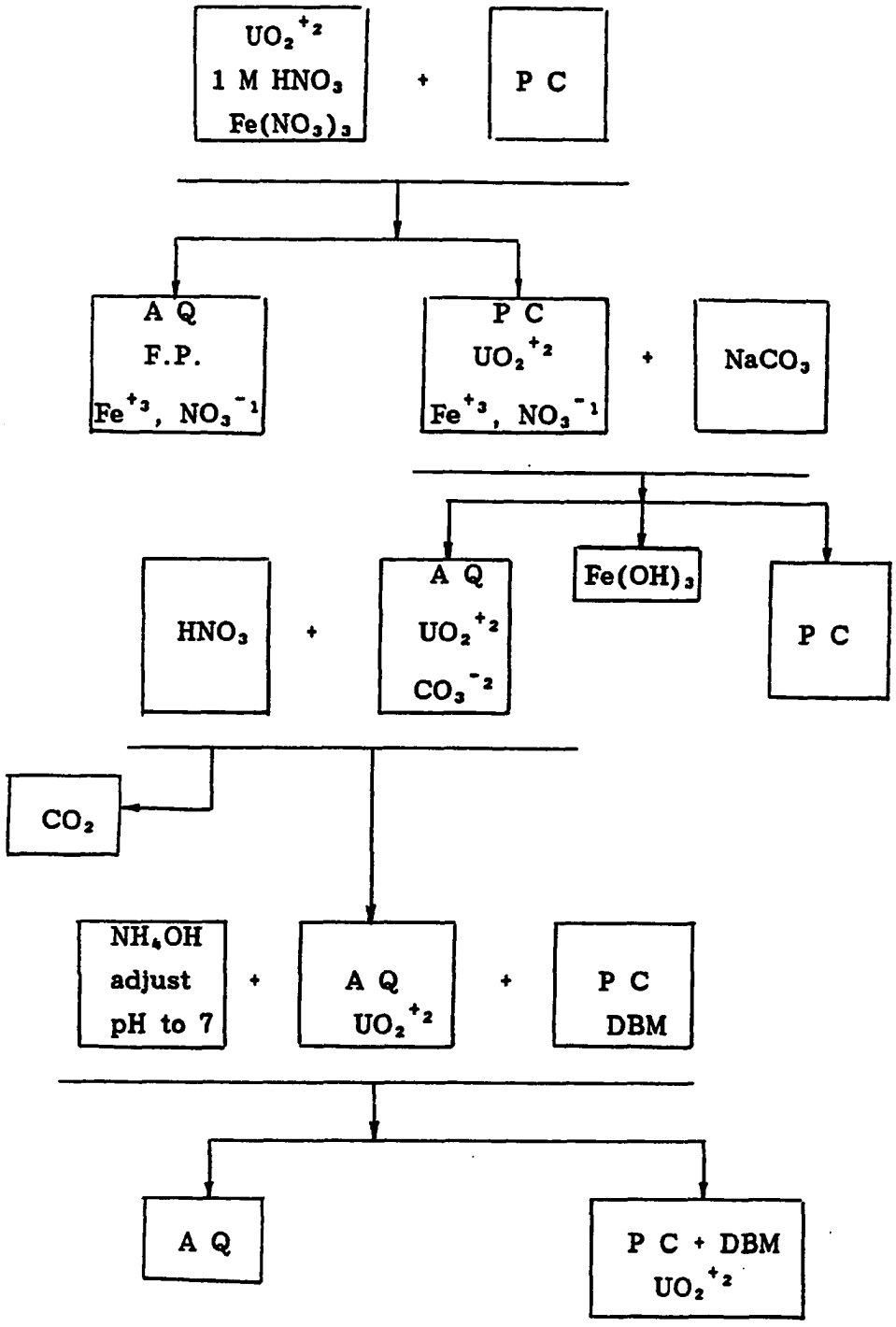


Fig. 4.17 Flow chart of the homogeneous extraction method of uranium

Chapter V
CONCLUSION

Separations of uranium from fission products by homogeneous liquid-liquid extraction of uranium from one molar nitric acid solution with addition of ferric nitrate as salting-out reagent into propylene carbonate have been performed. The distributions of selected typical high-yield fission product elements in the homogeneous extraction of uranium have been investigated.

Uranium(VI) was quantitatively extracted into propylene carbonate from an aqueous medium 0.5 g/ml $Fe(NO_3)_3 \cdot 9H_2O$ and 1 M HNO_3 at 99°C. The uranium(VI) in the organic phase was quantitatively stripped from the organic phase with 0.1 M sodium carbonate at pH 9. Final separation of uranium(VI) was obtained by extracting uranium(VI) into 0.1 M dibenzoyl methane in propylene carbonate using the homogeneous technique at pH 7.

The representative fission product elements, molybdenum, strontium, ruthenium, zirconium, and cerium, remained in the aqueous solution after extracting uranium(VI) into propylene carbonate to an extent greater than 97 %; i.e., less than three

percent of the respective elements were found in the carbonate stripping solution. After the final separation step, the extraction of uranyl ion into propylene carbonate containing dibenzoyl methane, these fission product elements were no longer detectable. Iodide in the original aqueous solution was oxidized to iodine by Fe(III) ion and followed the uranyl ion into propylene carbonate. Ten percent of the original concentration of iodide was found in the carbonate stripping solution. However, it was removed in the final separation step.

The role played by ferric nitrate in the homogeneous extraction of uranium is not only as a salting-out reagent, but also as a scavenger; ferric hydroxide precipitates at pH > 2. As pH is adjusted to 9 by adding anhydrous sodium carbonate, the ferric hydroxide precipitate can carry down more than 97 % of the original concentrations of strontium, ruthenium, zirconium, and cerium in solution. Furthermore, the ferric hydroxide which adsorbed the fission products is easy to ignite to a somewhat refractory oxide which may be readily incorporated into glasses, and/or concretes. This may be one of the best ways for treating the radioactive waste for long time storage.

The capacity for extraction of uranium by propylene carbonate was investigated. As much as 10.5 g/l uranium can be extracted into propylene carbonate efficiently. Thus, the proposed uranium extraction method can be applied as a practical method for

separating uranium from fission products.

The possibility of recovering propylene carbonate from aqueous solutions, in which it has a low but significant solubility, may be achieved by freezing the aqueous solution containing the propylene carbonate. The aqueous phase and propylene carbonate will be separated due to their different freezing point.

The homogeneous extraction of uranium described here can be applied to separate uranium not only from spent fuel elements, but also from ores and sea water. In general, these procedures will result in more effective and rapid extraction, and will enable the design of a commercial extraction process. The conditions for batch and continuous homogeneous extraction of uranium with propylene carbonate will have to be studied.

Bibliography

1. Chung, C., Radiochim. Acta, 1986, 39, 113
2. Koch, J.; Tadmor, J., Health Physics, 1986, 50(6), 721
3. Peligot, E., Ann. Chim. Phys., 1842, 5, 1
4. Rothe, J.W., Chem. News, 1892, 66, 182
5. Berthelot, M.; Jungfleisch, J., Ann. Chim. Phys., 1872, 26, 396
6. Nernst, W., Physik. Chem., 1891, 8, 110
7. Sidgwick, N.V., J. Chem. Soc., 1933, 123, 725
8. Lowry, T.M., J. Soc. Chem. Ind., 1933, 42, 316
9. Fajans, K., Naturwissenschaften, 1923, 11, 165
10. Bjerrum, N., Kgl. Danske Selskab., 1926, 7(9)
11. Hildebrand, J.H.; Rotariu, G.H., Anal. Chem., 1952, 24, 770
12. Hildebrand, J.H.; Scott, R.L., Solubility of Nonelectrolytes, second edition, Reinhold Publishers, New York, 1950.
13. Gordy, W.; Stanford, S.C., J. Chem. Phys., 1940, 8, 170
14. Campbell, D.E., Ph.D. Thesis, Rensselaer Polytechnic Institute, 1952, U.S. Atomic Energy Commission Report, AECU-2313
15. Golden, G.S., B.S. Thesis, Dept. of Chem., Massachusetts Institute of Technology, 1954.

16. Herber, R.H.; Irvine, J.W., Jr., J. Am. Chem. Soc., 1954, 76, 987

17. Wright, W.B., Jr., USAEC Report Y-838, Carbide and Carbon Chemical Co., January 1952.

18. Eberle, A.R.; Lerner, M.W., Anal. Chem., 1957, 29, 1134

19. Steele, T.W.; Taverner, L., Proceedings of the Second International Conference on the Peaceful Uses of Atomic Energy, Geneva, 1958, Vol.3, 510, United Nations, New York, 1959.

20. Guest, R.J., Can. Dept. Mines and Tech. Surveys, Mines Branch, Radioactivity Div. Topical Rept., TR-128/55, May 1955.

21. Petrement Eguiluz, J.C.; Palomares Delgado, F., Junta de Energia Nuclear (Spain), private communication, April 1961.

22. Furman, N.H.; Mundy, R.J.; Morrison, G.H., USAEC Report AECD-2938, Princeton University.

23. Furman, N.H.; Mundy, R.J.; Morrison, G.H., USAEC Report AECD-2861, Princeton University.

24. Scott, T.R., Analyst, 1949, 74, 486

25. Rodden, C.J., Analysis of Essential Nuclear Reactor Materials, U.S. Atomic Energy Commission, 1964.

26. Kraus, C.A., USAEC Report A-2324, Brown University, November 1945.

27. Paley, P.N., in Proc. Intl. Conf. Peaceful Uses At. Energy, 1956, 8, 225

28. Nietzel, O.A.; DeSesa, M.A., Anal. Chem., 1957, 29, 756

29. Booman, G.L.; Holbrook, W.B., Anal. Chem., 1959, 31, 10

30. Maeck, W.J.; Booman, G.L.; Elliott, M.C.; Rein, J.E., Anal. Chem., 1958, 30, 1902

31. Blake, C.A.; Brown, K.B.; Coleman, C.F., USAEC Report ORNL-1964, Oak Ridge National Laboratory, August 1955.

32. White, J.C.; Ross, W.J., USAEC Report CF-56-9-18, Oak Ridge National Laboratory, September 1956.

33. Blake, C.A.; Baes, C.F.; Brown, K.B.; Coleman, C.F.; White, J.C., in Proc. Intl. Conf. Peaceful Uses At. Energy, 1959, 28, 294

34. Blake, C.A.; Baes, C.F.; Brown, K.B.; Coleman, C.F.; White, J.C., ibid. 1550

35. Healy, T.V., J. Inog. Nucl. Chem., 1961, 19,314

36. Irving, H.; Edgington, D.N., ibid., 1961, 20, 314

37. Irving, H.; Edgington, D.N., Proc. Chem. Soc., 1959, 360

38. Irving, H.; Edgington, D.N., Chem. Ind. London, 1961, 77

39. Irving, H.; Edgington, D.N., J. Inorg. Nucl. Chem., 1960, 15, 158

40. Healy, T.V.; Ferraro, J.R., ibid., 1962, 24, 1449

41. Newman, L.; Klotz, P., J. Phys. Chem., 1963, 67, 205

42. Finston, H.L.; Inoue, Y., J. Inorg. Nucl. Chem., 1967, 29, 208

43. Rahaman, M.S.; Finston, H.L., Anal. Chem., 1968, 40, 1709

44. Rahaman, M.S.; Finston, H.L., ibid., 1969, 41, 2023

45. Gnizi, E., M.S. Thesis, City University of New York, Brooklyn College, 1967.

46. Zhou, D.; Ding, J., New Front. Rare Earth Sci. Appl. Proc. Int. Conf. Rare Earth Dev. Appl., 1985, 1, 497

47. Perescu, N.; Ionescu, A.; Bujoreanu, D.; Balan, V., Rev. Chim. (Bucharest), 1985, 36(11), 1039

48. Duarte Neto, J., INIS Atomindex, 1985, 16(23), Abstr. No. 16:080205

49. De Araujo Figueiredo, C.; Duarte Neto, J., ibid., 1985, 16(23), Abstr. No. 16:080203

50. Misiak, R.; Tlalka, M., Pr. Nauk. Inst. Technol. Nieorg. Nawozow Miner. Politech. Wroclaw, 1985, 29, 145

51. Murata, K.; Ikeda, S., Bunseki Kagaku, 1969, 18, 1137

52. Hong, C., Ph.D. Thesis, City University of New York, Brooklyn College, 1980.

53. Rajapakse, N., Ph.D. Thesis, City University of New York, Brooklyn College, 1986.

54. Marczenko, Z., "Spectrophotometric Determination of Elements", Halsted Press, a Division of John Wiley & Sons Inc., 1976.

55. Habashi, F., "Hydrometallurgy", A special report, Chem. & Eng. News, Feb. 8, 1982, 46

56. Norstrom, S.L.G., Svensk. Kem. Tidskr., 1948, 60, 227

57. Gindler, J.E., "Radiochemistry of Uranium", Special Report, 93

58. Ebelman, M., Ann. Chim. Phys., 1842, 5(3), 206

59. Bunce, W.E.; Furman, N.H.; Mundy, R.T., Report M-4238

(revised), May 1947.

60. Haldar, B.C., J. Indian Chem. Soc., 1947, 24, 503

61. Blake, C.A.; Coleman, C.F.; Brown, K.B.; Hill, D.G.; Lowrie, R.S.; Schmitt, J.M., J. Am. Chem. Soc., 1956, 78, 5978

62. Maclaine, L.A., in Proc. Intl. Conf. Peaceful Uses At. Energy, 1956, 8, 26

63. Jablonski, B.B.; Leyden, D.E., Anal. Chem., 1978, 3, 404

64. Stary, J.; Hladky, E., Analytica Chimica Acta, 1963, 28, 227

65. Dufraisse, C.; Gillet, A., Ann. Chim., 1926, 6, 299

66. Yoe, J.H.; Will, F.; Black, R., Anal. Chem., 1953, 8, 1200

67. Hiskey, G.; Meloche, V., J. Am. Chem. Soc., 1940, 62, 1565

68. Bock, R., Anal. Chem., 1951, 133, 110

69. Swift, E., J. Am. Chem. Soc., 1924, 46, 2378

70. Bock, R.; Kusche, H.; Bock, E., Anal. Chem., 1953, 138, 167

71. Kitahara, S., Repts. Sci. Research Inst. (Tokyo), 1949, 25, 165

72. Kitahara, S., ibid., 1948, 24, 454

73. NP-3561, Progress Report, Nov. 1951, 29

74. Nelidow, I.; Diamond, R., J. Phys. Chem., 1955, 59, 710

75. Gerlit, I., in Proc. Intl. Conf. Peaceful Uses At. Energy, 1956, 7, 145

76. Dow-120, Progress Report for July-August 1954, 17 Sept. 1, 1954, available from the Office of Technical Services, Dept. of Commerce, Washington D.C.

77. Coleman, C.; Brown, K.; Moore, J.; Allen, K., in Proc. Intl. Conf. Peaceful Uses At. Energy, 1959, 28, 278

78. White, J.C., First Conference on Analytical Chemistry in Nuclear Reactor Technology, Gatlinburg, Tenn., Nov. 1957, TID-7555, August 1958.

79. Bolomey, R.A.; Wish, L., J. Am. Chem. Soc., 1950, 72, 4483

80. Goldin, A.S., U.S. Atomic Energy Commission Report TID-7517, Part 16, 1956, 323

81. Silker, W.B., Hanford Atomic Products Operation Report HW-55117, May 1958.

82. Goldin, A.S.; Velten, R.J.; Frishkorn, G.W., Anal. Chem. 1959, 31, 1490

83. Kiba, T.; Mizukami, S., Bull. Chem. Soc., Japan, 1958, 31, 1007

84. Johnson, W.C., Jr., Anal. Chem., 1966, 38, 954

85. Akaza, I., Bull. Chem. Soc., Japan, 1966, 39, 971

86. Sekine, T.; Dyrssen, D., Anal. Chim. Acta, 1967, 37, 217

87. Dyrssen, D., Svensk Kem. Tidskr., 1955, 67, 311

88. Peppard, D.F.; Mason, G.W.; Moline, S.W., J. Inorg. Nucl. Chem. 1957, 5, 141

89. Glendenin, L.E., "Improved Determination of Ruthenium Activity in Fission", Paper No. 260, 1549, in Coryell, C.D.; Sygarman, N., Radiochemical Studies: The Fission Products, Book 3, McGraw Hill, New York, 1951.

90. Gilchrist, R.; Wichers, E., J. Am. Chem. Soc., 1935, 57, 2565

91. Moore, F.L., Anal. Chem., 1958, 30, 908

92. Mason, E.A.; Vanghen, V.C., USAEC Report TID-5720, Feb. 26, 1960

93. Wyatt, E.I.; Rickard, R.R., Nuclear Science Series, NAS-NS 3029, 1961.

94. Zielen, A.J.; Connick, R.E., J. Am. Chem. Soc., 1956, 78, 5785

95. Connick, R.E.; McVey, W.H., J. Am. Chem. Soc., 1949, 71, 3182

96. Steinbach, J.F., Ph.D. Thesis, University of Pittsburgh, 1953; USAEC Report NYO-6347

97. Schultz, B.G.; Larsen, E.M., J. Am. Chem. Soc., 1950, 72, 3610

98. Sandell, E.B., "Colorimetric Determination of Traces of Metals", 3rd Ed., Interscience, 1959.

99. Furman, N.H.; Mason, W.B.; Pekola, J.S., Anal. Chem., 1949, 21, 1325

100. Morrison, G.H.; Freiser, H., "Solvent Extraction in Analytical Chemistry", Wiley, 1957.

101. Rydberg, J.; Bernstrom, B., Acta Chem. Scand., 1957, 11, 86

102. Scadden, E.M.; Ballon, N.E., Anal. Chem., 1953, 25, 1602

103. Peppard, D.F.; Mason, G.W.; Maier, J.L., J. INC, 1956, 3, 215

104. Duke, F.R.; Anderegg, J.A., Iowa State Coll. J. Sci., 1953,

27, 491

105. Evana, M.G.; Uri, N., Nature, 1950, 166, 602

106. Rudenko, E.I.; Shvaiger, M.I., Zavodsk. Lab., 1964, 30, 400

107. Peppard, D.F.; Faris, J.P.; Gray, P.R.; Mason, G.W., J. Phys. Chem., 1953, 57, 294

108. Smith, G.W.; Moore, F.L., Anal. Chem., 1957, 29, 448

109. Marsh, S.F.; Maeck, W.J.; Booman, G.L.; Rein, J.E., Anal. Chem., 1962, 34, 1406

110. Alimarin, I.P.; Przheval'skii, E.S.; Puzdrenkova, I.V.; Golovina, A.P., Tr. Komis. po Analit. Khim. Akad. Nauk SSSR, 1958, 8, 152

111. Matthews, A.D.; Riley, J.P., Anal. Chim. Acta, 1970, 51, 295