



Belgian Nuclear Higher Education Network

*Vrije Universiteit Brussel • Universiteit Gent • Katholieke Universiteit
Leuven • Université de Liège • Université Catholique de Louvain •
Studiecentrum voor Kernenergie – Centre d'Étude de l'Énergie Nucléaire*

Separation of trivalent lanthanides and actinides by extraction chromatography

Ing. Huys Thomas

Academic year 2004-2005

Promotor: Prof. Dr. Ir. P. Mathieu, *Université de Liège*

Thesis submitted in partial fulfilment
of the requirements for the degree of
Master of Science in Nuclear
Engineering





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Master of Science in Nuclear Engineering

Thesis Summary Page

Name of the student:

Ing. Huys Thomas

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Abstract:

One of the most critical steps in the Partitioning and Transmutation strategy is the separation of the lanthanides and actinides that are present in nuclear waste streams. Since these elements are chemically very alike the separation of these elements is nearly impossible through the use of conventional techniques.

Extraction chromatography seems to offer several advantages over the use of liquid-liquid extraction. Therefore it was decided to apply this technique for the lanthanide/actinide separation. CMPO, a powerful extractant for both the lanthanides and concerned actinides was loaded onto porous silica particles and was tested with regards to the lanthanide/actinide separation. To improve the poor selectivity of CMPO for this separation, water soluble complexing agents were added to the extraction chromatographic system. Experiments were carried out to examine the influence of the different complexing agents on the distribution of the lanthanides and actinides between the resin and the aqueous phase. Six different complexing agents participated in the experiments, but none was found to be satisfactory. In highly concentrated nitric acid media most complexing agents were unable to form complexes with metal ions. In dilute nitric acid solutions only dipicolinic acid seemed to be capable of retaining metal ions from the resin. Unfortunately dipicolinic acid tends to show very little distinction between lanthanides and actinides. Because of this fact no separation factor larger than 1.5 was found as a result of the experiments.

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ABSTRACT

One of the most critical steps in the Partitioning and Transmutation strategy is the separation of the lanthanides and actinides that are present in nuclear waste streams. Since these elements are chemically very alike the separation of these elements is not possible through the use of conventional techniques.

Extraction chromatography seems to offer several advantages over the use of liquid-liquid extraction. Therefore it was decided to apply this technique for the lanthanide/actinide separation. CMPO, a powerful extractant for both the lanthanides and concerned actinides was loaded onto porous silica particles and was tested with regards to the lanthanide/actinide separation. To improve the poor selectivity of CMPO for this separation, water soluble complexing agents were added to the extraction chromatographic system. Experiments were carried out to examine the influence of the different complexing agents on the distribution of the lanthanides and actinides between the resin and the aqueous phase. Six different complexing agents participated in the experiments, but none was found to be satisfactory. In highly concentrated nitric acid media most complexing agents were unable to form complexes with metal ions. In dilute nitric acid solutions only dipicolinic acid seemed to be capable of retaining metal ions from the resin. Unfortunately dipicolinic acid tends to show very little distinction between lanthanides and actinides. Because of this fact no separation factor larger than 1.5 was found as a result of the experiments.

ABSTRACT

Waarschijnlijk is de scheiding van de trivalente actiniden en de lanthaniden die aanwezig zijn in bestraalde kernbrandstof de meest kritische stap in het hele Partitie en Transmutatie scenario. Deze elementen gedragen zich chemisch bijna identiek waardoor ze moeilijk te scheiden zijn door middel van klassieke scheidingsmethoden.

Extractiechromatografie lijkt verschillende voordelen te bieden ten opzichte van de klassiek toegepaste vloeistof-vloeistof extractie. Hierdoor werd beslist om deze techniek toe te passen op de lanthanide/actinide scheiding. Een krachtig extractant, CMPO, werd hiervoor op een poreus silica dragermateriaal aangebracht en getest op de efficiëntie van de lanthanide/actinide scheiding. Om de slechte selectiviteit van CMPO voor de scheiding te verbeteren werden wateroplosbare complexanten aan de oplossingen toegevoegd. Verschillende experimenten werden uitgevoerd om de invloed van deze complexanten op de verdeling van de metaalionen tussen de waterige fase en het hars te bepalen. Zes verschillende complexanten werden onderzocht, maar geen enkele complexant bracht enige merkbare verbetering toe aan de scheiding. In sterk geconcentreerde salpeterzuur oplossingen zijn de meeste complexanten niet in staat om complexen te vormen. In verdunde salpeterzuur oplossingen was enkel dipicolinic acid in staat om de metaalionen merkbaar van het hars te weerhouden. Spijtig genoeg toonde deze complexant weinig onderscheid tussen de lanthaniden en de actiniden. Hierdoor werd in de experimenten geen scheidingsfactor groter dan 1,5 bekomen.

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ABBREVIATIONS

CMPO	Octyl[phenyl]-N, N-diisobutylcarbamoymethylphosphine oxide
CYANEX 301	Extractant composed chiefly out of Bis (2,4,4, -trimethylpentyl) dithiophosphinic acid
DIAMEX	DIAMide EXtraction; a typical process flowsheet based on diamide extractants for MA separation
DIDPA	Di-isodecylphosphoric acid
DMDBTDMMA	Di-methyl-di-butyltetradecylmalonamide
DPA	Dipicolinic acid
DTPA	Di-ethylenetriaminepentaacetic acid
EDTA	Ethylenediaminetetraacetic acid
EXC	Extraction chromatographic system
GWD	Gigawatt day
HAR	Highly active raffinate
HDNNS	Di-nonylnaphthalenesulfonic acid
HEDTA	Hydroxyethyl-ethylenediaminetriacetic acid
HETP	Height Equivalent of a Theoretical Plate
HLLW	High Level Liquid Waste
ICP_MS	Inductively Coupled Plasma combined with a Mass Spectrometer
LLFP	Long-Lived Fission Products
MA	Minor Actinides
MAREC	Minor Actinides Recovery from. HLLW by Extraction Chromatography
MGY	Mega-Gray; Gray is the SI unit of absorbed dose.

ODP	1,8-octanediol-O,O'-diphenyl phosphonic acid.
P&C	Partitioning and conditioning
P&T	Partitioning and transmutation
PMT	Photomultiplier Tube
PTFE	Polytetrafluoroethylene, also better know under the trade name Teflon®
PUREX	Plutonium (and Uranium) Recovery by Extraction; a number of chemical processes for the recovery of U and Pu from spent nuclear fuel.
PYROREP	European research project that assess Pyro-metallurgical processes for separation of Minor Actinides (MA) from Lanthanides
PYROX	Pyrochemical Treatment of Spent Light Water Reactor Oxide Fuel
SETFICS	Solvent extraction for trivalent-f-elements intra-group separation in CMPO complexant system
SIR	Solvent Impregnated Resin
TALSPEAK	Trivalent Actinide-Lanthanide Separation by Phosphorus reagent Extraction from Aqueous Complexes
TBP	Tributylphosphate
tHM	Metric ton of heavy metal
TOPO	Trioctylphosphine oxide
TPEN	Tetrakis-(2-pyridylmethyl)ethylenediamine
TPTZ	Tripyridyltriazine ligand
TRPO	Trialkylphosphine oxide
TRUEX	TransUranium Extraction; a typical process flow sheet based on CMPO for MA separation.
UOX	Uranium OXide

1. INTRODUCTION

In order to develop nuclear energy as a sustainable energy source, a solution to the waste problem has to be found. One of the most attractive solutions seems to be the strategy of partitioning and transmutation. Hereby a cascade of separation processes partitions the nuclear waste into different fractions. Fissile and fertile materials are recycled and reused. Short lived radionuclides are conditioned and stored. Long-lived fission products and the minor actinides are introduced in thermal reactors, fast reactors or accelerator driven systems. Herein they are transmuted through various nuclear reactions into stable or short-lived isotopes. To achieve this partitioning into different fractions one has to design a number of ingenious separation processes. Probably the most difficult separation is the separation between the trivalent lanthanides and the also trivalent actinides. Since they are chemically very alike they are difficult to separate through conventional techniques.

Extraction chromatography seems to offer several advantages over the use of liquid-liquid extraction. Therefore it was decided to apply this technique for the lanthanide/actinide separation. A powerful extractant was loaded onto porous silica particles and was tested with regards to the lanthanide/actinide separation. To improve the poor selectivity of CMPO for this separation, water soluble complexing agents were added to the system. To examine the influence of the different complexing agents the distribution of the lanthanides and actinides between the resin and the aqueous phase was determined experimentally.

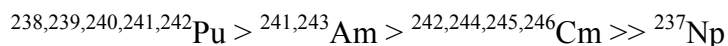
2. PARTITIONING AND TRANSMUTATION

The word transmutation originates from the never-realized goal of ancient alchemists to transform, or to transmute, the base metals into gold. Today's research focuses on finding pathways to transmute radioactive waste into non-radioactive elements, thereby eliminating the radiological hazards and waste disposal problems to a certain extent.

A challenging aspect of the waste management strategy is the required waste partitioning. Just as domestic wastes must be partitioned into categories before they are recycled, radioactive waste must preferably be sorted before being recycled back into nuclear reactors. One particularly challenging task involves the minor actinide and lanthanide elements. Minor actinide and lanthanide elements are chemically similar and thus very difficult to separate efficiently from each other. Depending on the burn-up, type of fuel and the reactor type the mass ratio lanthanides/(minor actinides) can be of a factor 10 to 50. As most lanthanide isotopes are stable and only a few are long-lived isotopes, little incentive exists to invest neutrons in these elements for transmuting them. However, some lanthanides have an enormous cross section for thermal neutron capture and will so prevent efficient transmutation of americium and curium. Improved methods for separating lanthanides from actinides are needed to reach the goal of actinide transmutation. The former problem will be addressed in this work.

2.1. Why partitioning and transmutation?

Nuclear power generates steadily a mass of spent fuel, which contains apart from the short-lived fission products, a significant amount of actinides and long-lived fission products (LLFP) with a very high radiotoxicity. These elements are responsible for the radioactive waste problem on the long term basis, beyond 10^4 years. Even after only seven years of discharge from the reactor the following ranking in terms of hazard factors can be made ^[1]:



Conventional reprocessing recycles most of the major actinides (uranium and plutonium), while most of the minor actinides (neptunium, americium and curium) and the long-lived fission products are vitrified before being disposed. Partitioning of the minor actinides and a few selected fission products will lower the radiotoxicity of the waste with a factor proportional to the separation yield. The separated minor actinides would then be recycled into the nuclear fuel cycle. Inside the reactor they will be transmuted into stable or short-live isotopes. In the same manner the long-lived fission products can be burned. The technique of

partitioning and transmutation is in principle capable of reducing the radiotoxicity period to a few hundreds of years, the decay time for the short-lived isotopes. Before P&T can become available on an industrial scale a number of practical problems will have to be tackled. One should be aware of the fact that never only one nuclear reaction will take place during transmutation. There are always multiple reaction pathways with different reaction products, sometimes leading to very radiotoxic nuclides with medium-long half lives. Another problem is, as said before, the separation of the different partitions of the waste streams. Some parts are already well developed, such as the PUREX process for separating the major actinides, while other parts are still in research phase. For the separation of the minor actinides from the high level waste, resulting from the PUREX process, some very efficient techniques are developed. Regrettably most of them are not well suited for industrial application because of the fact that they are too sensitive to radiation damage or they make use of non-combustible products, resulting in even more waste. The ideal partitioning system should be able to be easily connected to the waste stream of the PUREX process and extract the minor actinides and some long-lived fission products with high efficiency and a minimum of operations needed.

Nowadays partitioning is almost always associated with transmutation, but this does not always have to be the case. Another step after partitioning can be the conditioning of the waste, so-called partitioning and conditioning (P&C). After a careful separation the high level waste is divided into several groups, depending on their radiotoxicity and half-life, which can be conditioned in a matrix adapted to the specific group.

3. LANTHANIDES AND ACTINIDES

3.1. General properties ^[2]

The fifteen elements with an atomic number between 57 (lanthanum) and 71 (lutetium) are called the lanthanide series. The elements in this series are characterised being the filling of the 4f shells. The lanthanide ions are primarily in the III oxidation state because electrons in outer orbitals significantly shield the f electrons. Other stable oxidations states observed with lanthanide ions include II and IV. The sizes of the trivalent lanthanide ions are similar due to the lanthanide contraction and range from 1.216 Å for La(III) to 1.032 Å for Lu(III). Due to the decreasing size of the lanthanide ions across the series, the charge density of the ion increases across the series. Because of the similar charge and size, most lanthanide(III) ions behave similarly both physically and chemically. Lanthanide(III) ions are more similar to alkali and alkaline earth metals than to d-block metals, preferring to bind to hard acids like oxygen and fluorine donors rather than to soft donors like nitrogen and sulphur. Lanthanide(III) ions can form both inner and outer sphere complexes. The coordination is primarily ionic with a solution coordination typically ranging from 8 to 9, depending on properties of the ligands, solvent and concentration.

Before World War II only the first four actinides were known to mankind. At the mid-forties G. Seaborg introduced the actinide concept. Seaborg stated that there would be another series like the lanthanide series, but now the 5f shell was being filled instead of the 4f shell. Just as the lanthanide series is named after its first element, the new series was called ‘the actinides’. The elements in the series are all radioactive and after plutonium none occurs in nature. They show very similar chemical properties with the lanthanides just above them in the periodic table. This behaviour is expressed as chemical analogues. For example, neodymium has more or less the same chemical behaviour as uranium. Concerning nuclear waste problems the only significant actinides are uranium, plutonium, neptunium, americium and curium. The lower actinides are absent, the higher actinides have a short half-life and thus a low abundance.

57	58	59	60	61	62	63	64	65	66	67	68	69	70	71
La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
89	90	91	92	93	94	95	96	97	98	99	100	101	102	103
Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

Figure 3.1: The f-elements (top: the lanthanides, bottom: the actinides)

3.2. Comparison between the trivalent lanthanides and the actinides

The trivalent charge that is commonly observed for most lanthanide ions is not the most stable oxidation state for the actinides. The most stable oxidation states for uranium and plutonium are VI and IV. Neptunium can have either V or VI as stable oxidation state, while the other minor (transplutonium) actinides only have the stable III oxidation state. The lanthanide(III) ions are similar in size and are commonly used as analogues for actinide(III) ions. The 5f orbitals are significantly shielded from binding interactions similarly to the 4f orbitals. The actinide 5f orbitals have greater spatial distribution compared to the 7s and 7p orbitals than the spatial distribution of the lanthanide 4f orbitals compared to the 6s and 6p orbitals. The larger spatial distribution increases the possibility that actinide bonding has a small degree of covalent nature compared to lanthanide bonding. The increased covalence results in actinide elements having a slightly higher affinity for soft electron donors, such as amines. The increased affinity for soft donors can be used to separate lanthanide and actinide elements by use of a soft donor system like a ligand with both hard and soft donor groups such as aminocarboxylates ^[3]. Generally, materials with an increased potential for covalent interactions will have significantly larger probability to enhance the lanthanide/actinide separation.

3.3. The lanthanides of interest

From the calculation that will be made in section 4.3 it will become clear that only 4 lanthanides are responsible for the majority of the neutron captures by lanthanides in nuclear reactor systems. Because of this the experiments will use only these four lanthanides. Consequently this paragraph will discuss europium, samarium, neodymium and gadolinium ^[4] to give an idea of the properties and possible applications of these elements.

3.3.1. Europium (Eu)

In 1890 Boisbaudran obtained basic fractions from samarium-gadolinium concentrates which had spark spectral lines not accounted for by samarium or gadolinium. These lines subsequently have been shown to belong to europium. The discovery of europium is generally credited to Demarcay, who separated the rare earth in reasonably pure form in 1901. The pure metal was not isolated until recent years. Like other rare-earth metals (except for lanthanum) europium ignites in air at about 150 to 180°C. Europium is about as hard as lead and is quite ductile. It is the most reactive of the rare-earth metals, quickly oxidizing in air. It resembles

calcium in its reaction with water. Bastnasite and monazite are the principal ores containing europium. Europium has been identified spectroscopically in the sun and certain stars. More than 25 isotopes are now recognized of which only two are stable. Europium isotopes are good neutron absorbers and are being studied for use in nuclear control applications.

Europium oxide is now widely used as a phosphor activator and europium-activated yttrium vanadate is in commercial use as the red phosphor in colour TV tubes. Europium-doped plastic has been used as a laser material. With the development of ion-exchange techniques and special processes, the cost of the metal has been greatly reduced in recent years. Europium is one of the rarest and most costly of the rare-earth metals.

3.3.2. Samarium (Sm)

In nature samarium is found together with other rare-earths in many minerals, including monazite and bastnasite. These minerals are the commercial sources of this element. Recent developments in separation techniques such as solvent extraction and ion-exchange made it possible to isolate the element in a relatively pure form. Samarium has a bright silver lustre and is reasonably stable in air. Three crystal modifications of the metal exist, with transformations at 734 and 922°C. The metal ignites in air at about 150°C. The sulphide has excellent high-temperature stability and good thermoelectric efficiencies up to 1100°C.

About thirty isotopes of samarium exist. Natural samarium is a mixture of several isotopes, three of which are unstable with very long half-lives.

Samarium, along with other rare earths, is used for carbon-arc lighting for the motion picture industry. SmCo_5 has been used in making a new permanent magnet material with the highest resistance to demagnetization of any known material. Samarium oxide has been used in optical glass to absorb the infrared. Samarium is used to dope calcium fluoride crystal for use in optical masers or lasers. Compounds of the metal act as sensitizers for phosphors excited in the infrared; the oxide exhibits catalytic properties in the dehydration and dehydrogenation of ethyl alcohol. Misch metal which contains a mixture of rare-earths is used in lighter flints and steel production contains up to 1% samarium. In nuclear applications the element is especially known for its absorptive behaviour towards neutrons.

3.3.3. Neodymium (Nd)

Mossander separated a previously unknown rose coloured oxide from cerite in 1841. He believed that the oxide contained a new element which he named didymium, as it was the

inseparable twin brother of lanthanum. In 1885 von Welsbach separated didymium in two elemental compounds, praseodymium and neodymium.

It would take until 1925 before neodymium could be isolated into a relative pure form. Just as for samarium, the commercial sources for the element are the minerals monazite and bastnasite. Neodymium can be refined by separating Nd-salts from other rare earths by ion-exchange and solvent extraction. Neodymium metal can be obtained by the reduction of anhydrous halides such as NdF_3 using calcium metal. Freshly cut neodymium metal has a bright metallic lustre. Because it is one of the most reactive rare-earths, it will oxidise quickly when exposed to air. Natural neodymium consists of seven different isotopes while more than twenty radioactive isotopes are recognised. Perhaps the main use for neodymium is as a colorant for glasses. When added to glass it can produce colours ranging from pure violet through wine red and warm grey. It is also added to glass to remove the green colour induced by the presence of iron. Neodymium containing glasses can be used for astronomical work to produce sharp bands for the calibration of spectral lines, as a filter for infrared radiation and as an alternative to ruby in lasers for producing coherent light. Similarly didymium is used for making the glass that goes into welders' goggles and neodymium is used as a colorant for enamels. Another application of the element is in magnets, such as computer disk drives.

3.3.4. Gadolinium

This rare-earth is found in the minerals gadolinite, monazite and bastnasite. With the development of different new separation techniques such as solvent extraction and ion exchange, gadolinium has become widely available. Gadolinium present in nature consists out of seven isotopes and about twenty other isotopes can be created artificially. The isotopes with mass number 155 and 157 have enormous cross sections for the thermal neutron capture reaction. The element has the highest thermal neutron capture cross-section of any known metal. This property enables the use of these elements in nuclear control applications, although they have a very fast burn-out rate. Just as most other lanthanide metals is gadolinium a silvery white, ductile metal with a bright metallic lustre. It is relatively stable in dry air, but tarnishes in moist air. The metal reacts slowly with water and dissolves in dilute acid. Gadolinium is used in microwave applications and the element is incorporated in phosphors used in cathode ray tubes of colour televisions. The metal is ferromagnetic and has a Curie temperature (above which ferromagnetism vanishes) which is situated around room temperature. This makes it possible to use the metal as a magnetic device that senses the difference between 'cold' and 'hot'.

3.4. The minor actinides of interest

The minor actinides are considered to be neptunium (Np), americium (Am) and curium (Cm). They are produced by successive neutron capture from the nuclei in the fuel elements. Apart from plutonium the minor actinides are the most radiotoxic components of the spent fuel radiotoxic inventory. For this reason these elements are the main target for transmutation. Neptunium will not be discussed in this work because after a small modification of the PUREX [5] process neptunium can be easily extracted together with plutonium and uranium and later separated from these elements. In the experiments the only minor actinide used is americium. Handling curium should be avoided as much as possible because of its extremely high radiotoxicity and low availability.

3.4.1. Americium

The actinide with atomic number 95 was named after America (the Americas). In the general properties of the f-elements it was discussed that every actinide has its lanthanide analogue. In case of americium this analogue is europium. Americium was the fourth transuranic element to be discovered. The isotope ^{241}Am was identified by Seaborg, James, Morgan, and Ghiorso late in 1944 at the wartime metallurgical laboratory at the University of Chicago as the result of successive neutron capture reactions on plutonium isotopes in a nuclear reactor. More than ten isotopes of the element are recognised and all of them are radioactive, just like all other actinides. Half-lives vary up to a couple of thousands of years. The lustre of freshly prepared americium metal is white and more silvery than plutonium or neptunium prepared in the same manner. It appears to be more malleable than uranium or neptunium and tarnishes slowly in dry air at room temperature. Americium must be handled with great care to avoid personal contamination. The alpha activity from ^{241}Am is about three times that of radium. When gram quantities of ^{241}Am are handled, the intense gamma activity makes exposure a serious problem. ^{241}Am has been used as a portable source for gamma radiography. It has also been used as a radioactive glass thickness gauge for the flat glass industry and as a source of ionization for smoke detectors. For some nuclear applications a mixture of americium with beryllium is used as a neutron source.

The important isotopes in the perspective of partitioning and transmutation are ^{241}Am and ^{243}Am , with respectively a half-life of 432 and 7370 years. Both isotopes decay by emission of a α -particle.

3.4.2. Curium

In the summer of 1944 G.T. Seaborg, R.A. James and A. Ghiorso, working at the Manhattan Project, performed a careful chemical fractionation on a sample of plutonium which had been irradiated with 32 MeV helium ions at the University of California. A new radioactive isotope was found, which emitted 4.7 MeV alpha particles and was chemically separable from plutonium and neptunium. It was the third transuranic element to be discovered. Both nuclear and chemical evidence indicated that the activity could be ascribed to an isotope of a new element with atomic number 96. In tribute to the brilliant pioneering achievements of Pierre and Marie Curie in the field of radioactivity the new element was named curium (Cm).

Minute amounts of curium probably exist in natural deposits of uranium, as a result of a sequence of neutron captures and beta decays sustained by the very low flux of neutrons naturally present in uranium ores. The presence of natural curium, however, has never been detected. ^{242}Cm and ^{244}Cm are available in multigram quantities. ^{248}Cm has been produced only in milligram amounts. Curium is similar in some regards to gadolinium, its rare earth analogue, but it has a more complex crystal structure. Most compounds of trivalent curium are faintly yellow in colour. In the literature 16 radioisotopes of curium are listed, decaying by alpha emission, electron capture or spontaneous fission.

Both ^{242}Cm and ^{244}Cm are used in the thermoelectric generation of power for the operation of instruments at remote terrestrial locations or in space vehicles. ^{242}Cm generates about 3 watts of thermal energy per gram, while ^{238}Pu only generates 0.5 watt of thermal energy per gram.

Curium is one of the most radiotoxic elements known to mankind. In the human body, curium tends to accumulate in the bones. The short-lived isotopes are extremely radiotoxic due to the destruction of the red cell forming mechanism. The maximum permissible human body burden of ^{244}Cm is 2 nano-grams.

4. ACTINIDE / LANTHANIDE SEPARATIONS

Because of the fact that some lanthanides have large cross sections for thermal neutron capture and that they are in relatively large amounts produced in fission reactors, effective separation methods are needed to separate these elements from the actinides. Another reason for this separation is the fact that most lanthanides are stable and only few are long-lived so there is little incentive to invest neutrons in these elements. Another drawback of having lanthanides in nuclear fuels is the fact that during irradiation they tend to segregate on the grain boundaries and so introducing microscopic inequalities in the heat production of the fuel elements.

4.1. General considerations

Most of the classical applications of the lanthanides require little or no separation of the metal ions. About 15% of the commercial rare-earth production is under the form of Misch-metal, which is used as flints in cigarette lighters and in steel production. In Misch-metal the proportion of the lanthanides is the same as they occur in the ore. A few large scale applications require a more extensive degree of separation. A few examples are: high-temperature superconducting oxides, permanent magnets, rare-earth phosphors. Of the lanthanide ores, bastnasite and monazite are concentrated sources of the lighter lanthanides, while xenotime contains generally heavier lanthanides.

The actinides uranium and thorium occur in nature as primordial matter, their decay products actinium and protactinium occur as trace amounts. Plutonium and neptunium are present in minute amounts in nature due to neutron absorption reactions on lighter actinides. Higher actinides found in nature originate from anthropogenic sources such as nuclear detonations, nuclear fuel reprocessing, etc. Since the beginning of their discovery separation chemistry has been central to their isolation and purification. The continued application of separation science has resulted in the availability of weighable quantities of the actinides up to fermium.

A very serious obstacle in the further development and expansion of the nuclear industry, especially the nuclear power industry is the absence of a completely accepted solution to deal with the high-level radioactive waste. Burying this waste in geological repositories is a widely accepted strategy. Much research is carried out in finding methods to transmute a significant part – from the viewpoint of radiotoxicity – of this waste to make it less long-lived and radiotoxic. As will be discussed below (4.3.), separation of the actinides from the lanthanides is critical to implement transmutation successfully in the nuclear fuel cycle.

4.2. The basics of separation chemistry

Typical industrial separation methods based on volatility, e.g. distillation, are of little importance in lanthanide/actinide separations. Precipitation and other two-phase separation methods are by far the most useful to accomplish the separation. In the early days fractional crystallisation was the principal method to separate the lanthanides from the actinides. An important drawback due to the small difference in solubility between the different species is the fact that hundreds or even thousands of repetitions are needed to separate the elements to a reasonable degree of purity. The disadvantage prohibits the application of fractional crystallisation onto an industrial level. This led to the development of ion exchange and solvent extraction techniques for the separation of the 4f from the 5f-elements. Precipitation can be used to separate the actinides from most of the high-level radioactive waste, but because of its insensitivity to subtle changes in ionic radii, this technique is not useful to separate the actinides from the lanthanides. Methods based on the co-precipitation of actinides with lanthanide fluoride are able to selectively remove the tri- and tetravalent species from the penta- and hexavalent actinides. The main difficulty in the separation of the trivalent lanthanides from the actinides is the separation of the trivalent species. It is known that all lanthanides have a stable III oxidation state, together with the trans-plutonium elements. The targeted actinides for this kind of separation are the ones with mass number 95 and 96, americium and curium. The separation process in solvent extraction consists, in its most elementary form, of the transfer of a charged metal ion or a metal complex from a polar aqueous phase to an immiscible, non-polar phase. The effectiveness of any separation process is a function of the ability of the reactions to accomplish phase transfer and the relative affinity of the counter-phase for the species to be separated. In the case of the trivalent lanthanides and actinides, the latter aspect must exploit the slight difference in ionic radii and covalence of metal ions.

4.3. Actinide/lanthanide separations from a neutronic point of view

In the literature^[6] compositions of spent fuel assemblies are listed. As an example uranium oxide fuel with 4% (²³⁵U) initial enrichment, 50GWd/tHM burn-up and 3 years of cooling was chosen. To evaluate the importance of all isotopes, the absorptive behaviour was calculated according to equation 4.1.

$$AB = \text{conc}_{La} \cdot \frac{N_A}{A} \cdot \sigma_{\text{capt,th}} \left[\frac{\text{cm}^2}{\text{tHM}} \right] \quad (4.1)$$

For example:

$$^{139}\text{La} \Rightarrow \text{AB} = \frac{1818.050 \text{ g}}{\text{tHM}} \cdot \frac{6.02 \cdot 10^{23} \text{ mol}^{-1}}{139 \text{ g} \cdot \text{mol}^{-1}} \cdot 8.93 \cdot 10^{-24} \text{ cm}^2 = 70.31 \frac{\text{cm}^2}{\text{tHM}}$$

The relative absorptive behaviour (R.A.B) per isotope was calculated by dividing the absorptive behaviour of the isotope by the sum of the absorptive behaviour of all isotopes. Because the separation methods discussed in this work don't make a distinction between the isotopes of an element, it is possible to add the absorptive behaviour per element. A graphical representation of the result of the calculations can be found in figure 4.1.

This analysis makes clear that only four elements are responsible for the majority of the neutron absorptions by lanthanides (more than 95%) in a thermal spectrum. These elements are samarium, neodymium, gadolinium and europium. Three other elements (Pr, La, Pm) exhibit a more moderate absorptive behaviour and are responsible for more than 4% of the thermal neutrons captured by lanthanides. The behaviour of all other lanthanides is negligible compared to the previously mentioned lanthanides. Clearly, the use of the most important lanthanides during the experiments is most representative for later applications of the technique. With regards to the fast spectrum, the results are more or less the same. Again, the same elements as in the thermal spectrum are responsible for the majority ($\approx 85\%$) of the neutron loss by the (n,γ) reaction. One should also be aware of the fact that the probability for radiative capture is much smaller in the fast spectrum, from a factor 10 up to 10^5 smaller.

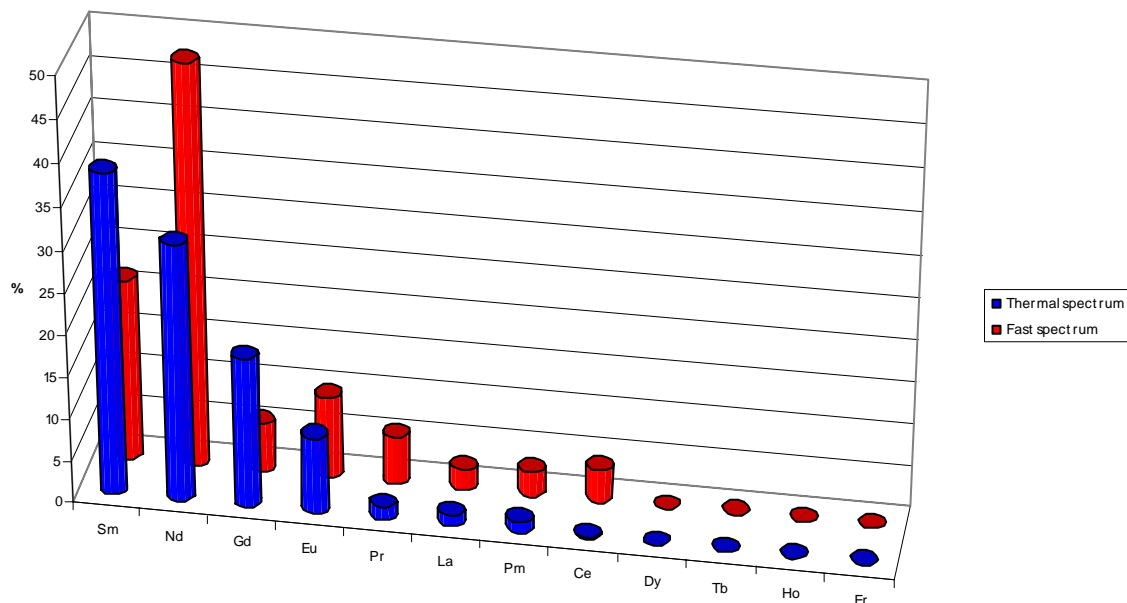


Figure 4.2: Relative absorptive behaviour of the lanthanides produced in UOX fuel.

The cross sections of the n,γ reaction with thermal neutrons were extracted from the Nudat database. The JENDL 3.3 database was consulted for cross section data for the radiative

capture of fast neutrons by the lanthanides. All these databases were accessed through the JANIS program, obtained from the Nuclear Energy Agency [7].

4.4. Aqueous separation techniques

The stable oxidation state of Am and Cm in the high active raffinate (HAR) resulting from the PUREX process is +III. This is also the oxidation state of the lanthanides, which represent about one third of the total mass of fission products in the HAR. As mentioned previously, the major problem is the separation of the trivalent actinides and lanthanides. This is complicated by the fact that:

- these elements have very similar chemical properties
- the mass ratio Ln/Ac is high (between 10-50, depending on several parameters)

Currently there are two separation strategies that can be used to separate these elements. Both of them will extract the lanthanides and trivalent actinides in a first step. The first strategy is the co-extraction of the lanthanides and the actinides, followed by selective stripping of the actinides with complexants. The goal of this work is to find more effective complexants that will allow a selective stripping of the trivalent actinides. A second strategy followed for the Ln/Ac separation is the selective extraction of the actinides by an extractant with a high selectivity. In the following paragraphs the most recent schemes of these techniques with their advantages and possible drawbacks will be discussed. One should remark that when in the literature is spoken about lanthanide/actinide separations, the actinides of interest are mainly americium and curium (the minor actinides or MA's). All other actinides can more or less easily be removed by the PUREX process. A lot of the information mentioned in this section can be found in the report "Actinide and Fission Product Partitioning and Transmutation" published by the Nuclear Energy Agency (NEA) [8].

4.4.1. Co-extraction of lanthanides and actinides

The principle of this separation technique is to extract the minor actinides together with some of the fission product that are present in the HAR. After the extraction the different elements are partitioned by selective stripping.

TALSPEAK and DIDPA

Two processes, both based on very similar or identical chemical reagents, are the so-called TALSPEAK [9] and DIDPA [10] processes. In both processes the co-extraction is carried out

by an organophosphorous extractant, di-ethyl-hexyl-phosphoric acid (HDEHP) for TALSPEAK and di-isodecylphosphoric acid (DIDPA). The actual Ln/An partitioning is accomplished by means of aqueous stripping with a solvent containing complexing agents. These complexing agents can be alcohol-carboxylic acids and diethylenetriaminepentaacetic acid (DTPA). It is generally believed that the selective stripping of the actinides is due to the fact that these complexants form more stable complexes with the actinides than with the lanthanides. Since these organophosphorous extractants are cation exchangers, the nitric acid concentration of the HAR has to be drastically reduced. This can be achieved by denitration with formic acid^[11]. The advantage of the DIDPA process compared to the TALSPEAK process resides in the higher affinity of DIDPA for metal ions, allowing a more acidic environment. This allows to minimize a major drawback of these processes, the precipitation of some fission products which can retain a fraction of the transuranic elements.

Tests with real HLLW showed that the DIDPA process is able to recover more than 99.99 % of the minor actinides^[10].

TRUEX

The Trans Uranium EXtraction or TRUEX process is based on the use of neutral organophosphorous bidentate extractant: n-octyl-di-isobutyl-carbamoylmethyl-phosphine-oxide (CMPO). It was developed in the 80s by Horwitz et al^[12] to cope with the huge amount of actinide-contaminated waste accumulated in the US during the Cold War in defense nuclear material production sites such as Hanford. This process is also studied by Japan, Italy and India for the partitioning of commercial wastes. CMPO displays high and low affinities for An(III) and Ln(III) nitrates at high and low nitric acid concentrations, respectively. To cope with third phase formation problem, the solvent contains a high concentration of TBP, used as modifier. CMPO mixed with TBP allows the extraction of most important actinide and the process is directly applicable to the HAR as it results from the PUREX process. CMPO is such a powerful extractant that quantitative stripping of most extracted species is difficult. Americium can be recovered, but it will be accompanied by curium and the bulk of the lanthanides. The TRUEX process has to be complemented by a process that is able to perform these separations, such as TALSPEAK.

One drawback of the process is the effect of solvent degradation products in the process. Some of these products are cation exchangers which prevent the efficient stripping of the trivalent Ln/An fraction. Another problem is the difficulty in stripping U(VI) and tetravalent actinides due to their high affinity with CMPO.

Currently it was demonstrated that the Am(III) could preferentially be stripped with Cm(III) and heavier Lns by DTPA-NaNO₃ solution and that a partial fractionation was possible by this system named SETFICS [13]. This has also been demonstrated in the MAREC [14] process which applies extraction chromatography in stead of liquid-liquid extraction.

TRPO

The trialkyl phosphine oxide or TRPO process, developed by Zhu, Song et al, is based on the use of a mixture of TRPO and kerosene in an extraction process [15]. The affinity of TRPO for trivalent actinides and lanthanides is the reverse in comparison to CMPO. TRPO has a high affinity for these elements at moderate aqueous nitric acid concentration (1M) and low affinities in highly concentrated nitric acid solutions. This process requires a neutralization of the nitric acid in the HAR solution to 1M. Stripping of the Ln(III)/An(III) fraction is done with a 5M nitric acid solution. The process was developed in the Republic of China and successfully tested at the Institute for TransUranium elements (ITU) at Karlsruhe with dilute HLLW. The decontamination factors for transuranium elements range from 10³ to 10⁴ in 1M nitric acid. The great advantage of the method is its reversibility in extraction and stripping, its miscibility with TBP and especially its loading capacity. However, the extraction requires additional separation steps since certain fission products tend to interfere with the separation. Another drawback is the high concentration of nitric acid in the An/Ln fraction resulting from the process because almost all An/Ln separation processes require relative low HNO₃ concentrations.

DIAMEX

The DIAMide EXtraction process was developed by Musikas et al at CEA and Madic and Hudson in a joint European Research program involving the CEA and the University of Reading [16]. This process is based on the use of malonamide extractants. The reference substance developed for the first version process is di-methyl-di-buthyltetradecylmalonamide (DMDBTDMA). This reagent has up to now the most promising chemical and physical properties for the use as an extractant. The diamide extractant is used in solution with an aliphatic diluent.

The DIAMEX process has some advantages over the TRUEX process:

- The degradation products, produced by radiolysis or hydrolysis, are less troublesome than those in the TRUEX extractant.

- The DIAMEX extractant fully complies with the CHON principle, making it totally burnable and hence no secondary solid waste is generated.

The DIAMEX process was successfully tested in 1993 on real HAR at the Fontenay-aux-Roses Research center. The process continues to be developed and an optimization of the diamide formula is underway. Also Japan, the UK, the US Switzerland and India are expressing their interest in these diamide extractants.

4.4.2. Selective extraction of actinides

These one-step processes will try to leave all the fission products in the HAR and extract only the trivalent actinides from the aqueous solution. Because of this they are supposed to generate smaller amounts of secondary waste.

TPTZ

Tripyridyltriazine (TPTZ) is a terdentate nitrogen-donor ligand which can selectively extract trivalent actinide species from a mixture of actinides and lanthanides when used in a synergistic combination with an organic cation exchanger. This system was first studied in the 80s by Vitorge ^[17]. Good separation factors were obtained for An(III) vs. Ln(III) using TPTZ with HDNNS (di-nonylnaphtalenesulphonic acid) or TPTZ with alpha-bromocapric acid. Improvements to the process are underway in an European research program. Recently Kolarik et al designed a very efficient family of molecules related to TPTZ able to extract selectivity An(III) over Ln(III) from aqueous nitric acid solutions.

CYANEX 301™

Zhu et al in Tsinghua University (Republic of China) recently published extraordinary results for the separation of An(III) over Ln(III) using CYANEX 301 extractant ^[18] This extractant consists mainly of bis (2,4,4-trimethylmethyl dithiophosphinic acid). The commercial product contains many impurities of which some are detrimental to the extraction of metal ions. In fact when the product is not purified, no separation of An(III) over Ln(III) is observed. After purification of CYANEX 301 by precipitation of its ammonium salt, tremendously high separation factors are obtained, up to 5900. Nevertheless, one of the major drawbacks of the process is the fact that the aqueous solutions must be adjusted to a rather high pH of 3.5 to 4. Modification of the molecule and the use of a synergist (trioctylphosphine oxide or TOPO) can partially overcome this problem ^[19].

New methods

Kulyako et al proposed in 1996 that the An/Ln separation can be carried out by the selective precipitation of the actinides from an aqueous acidic medium by the addition of potassium ferricyanide^[20].

Picolinamides are N and O chelating agents which selectively complex or extract An(III) over Ln (III)^[21].

Goto et al recently reported that, using novel organophosphorous bifunctional ligands in which no soft nitrogen or sulfur donor atoms are incorporated, exhibit high selectivity for the inter-lanthanide separation and the Eu/Am separation at acidic medium. A promising candidate is ODP (1,8-octane-diol-O,O'-diphenyl phosphonic acid)^[22].

4.5. Non-aqueous methods

Non-aqueous processes have been used in reprocessing plants to separate materials for nuclear weapons and in plants for reprocessing spent reactor fuels, mostly to clean up the uranium product. Some of these processes are high-temperature processes and they are referred to as either pyrochemical or pyrometallurgical processes^[23]. Large-scale non-aqueous processes to produce uranium hexafluoride, a compound unstable in the presence of water, are used routinely on a scale of tons per day to produce feed for the gaseous diffusion process used for the enrichment of uranium. When it was found that plutonium also formed a volatile hexafluoride with characteristics very similar to those of uranium hexafluoride, it became apparent that uranium and plutonium might theoretically be recovered from irradiated fuels on an industrial scale by taking advantage of the fact that few other elements form volatile fluorides and that fluoride volatility processing might also theoretically be used to recover neptunium as NpF₆. However, volatile actinide fluorides other than uranium are unstable, and fluoride volatility processing is only practical for recovery and purification of uranium (Benedict et al., 1981).

A technique known as plutonium electrorefining was developed for actinide systems in the mid-1960s as a way to purify the plutonium metal alloys that were proposed as fuel for the Los Alamos Molten Plutonium Reactor Experiment (LAMPRE) project. Electrorefining is classified as a pyrochemical process for the purposes of this discussion, since it uses a molten chloride salt as the ion transport medium between an impure metal anode and a much purer metal cathode (the collected product). The basic electrorefining technique has been adapted for purifying plutonium from essentially all elements, including americium, and for preparing

pure uranium and plutonium metals for both the weapons and the breeder reactor fuels programs. The development of pyrochemical reprocessing methods requires accurate knowledge about the chemical and electrochemical behaviour in molten salt at elevated temperatures > 450 °C. The basic electrochemical behaviour of actinide and lanthanide ions in chloride media is investigated using transient electrochemical techniques such as cyclic voltammetry and chronopotentiometry. Such investigations yield information about the oxidation/reduction mechanisms occurring and the transport behaviour (diffusion) of the actinide ion in the salt melt. In addition some thermochemical properties can be calculated such as standard potentials and activity coefficients in salt and metal phases. Pure An chlorides are often not available and the starting material is often the An metal which has to be chemically oxidised and dissolved in LiCl-KCl eutectic salts. The difference in the reduction potentials of the actinides compared to other elements can be used for a separation by electrolysis. Enough difference in reduction potential between the Ans and Lns is necessary for their difficult separation. Also the choice of the material onto which the actinides are deposited is of considerable importance.

At Argonne National Laboratory the PYROX process is under development. This non-aqueous process separates the uranium into one stream. All other actinides are kept together for recycling into advanced reactor fuel. Keeping the plutonium together with americium and curium makes it unsuitable for direct weapon applications and thus lowers the proliferation risk. It also looks like the PYROX process is able to make the reprocessing of spent fuel less expensive. A European Research project, PYROREP is developing reprocessing methods for future nuclear fuel cycles. Another important advantage of pyroprocessing is its ability to handle fuels that have been out of the reactor for much less than a year. The inventory build up is lower and the operations are on a smaller mass flow scale relative to the PUREX process. The non-aqueous nature of the process reduces the radiolysis problems. The high decay heat may even be an advantage since pyroprocessing typically is performed at process temperatures of 500 to 800°C. However, it requires structural materials that can withstand the high temperatures and the corrosive molten salts.

5. EXTRACTION CHROMATOGRAPHY

5.1. Principles of extraction chromatography

An extraction chromatographic (EXC) system is composed out of three major constituents; the mobile phase, the stationary phase and an inert support for this material. The porous inert support that is coated with the liquid stationary phase – the extractant – is called a solvent impregnated resin (SIR). The material is loaded in a column where the mobile phase flows through. Under the right conditions, metal ions of the mobile phase are absorbed by the stationary phase. If one changes the properties of the mobile phase to a certain extent (e.g. by increasing the acidity) the mobile phase will release the metal ions. By carefully choosing the extraction chromatographic system and the right conditions, it is possible to selectively extract a metal or a group of metals from a complicated matrix (e.g. spent nuclear fuel). The use of extraction chromatography possesses numerous advantages over ‘traditional’ liquid-liquid extraction:

- Solvent Impregnated Resins provide the selectivity of traditional extraction systems, combined with the ease of operation of solid ion exchange equipment such as fixed bed columns.
- Problems dealing with phase separation (e.g. formation of a third phase) are eliminated
- The ease of preparation of the resins

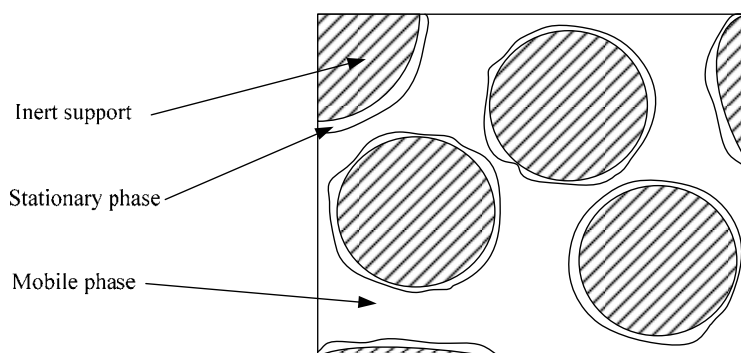


Figure 5.1: *Extraction chromatographic system*

A solvent impregnated resin can be defined as ‘a liquid complexing agent that is dispersed homogeneously in a solid polymeric medium’. For an ideal SIR the extractant must be in the liquid state or should be brought to this state by adding a diluent. Another requirement for the extractant is that its solubility in the mobile phase should be as little as possible. From the support it is asked that it will fully expand during impregnation and that it will retain this state. Also a good mechanical stability and inertness is demanded from the support.

Almost any organic extractant that can be used in liquid-liquid extraction is applicable into extraction chromatography. The inert support consists mostly out of silica particles or organic polymers. In literature the use of porous silica, magnetic silica, polyacrylonitril,... is extensively discussed. The particles are most of the time between 5 and 150 micrometer, although much smaller and bigger particles are being studied for special purposes. The mobile phase consists mostly out of an aqueous solution with a relative high acidity. In some cases organic complexants such as oxalic acid are added to enhance the selectivity or to mask interfering ions. When such a chromatographic column is fed with a solution containing different metal-ions that are extractable by the resin and the concentration of these metal-ions is monitored at the outlet of the column after a certain time one will notice a number peaks arising. Each of these peaks will correspond with a certain metal-ion. The first peak represents the metal-ion that is the least retained by the stationary phase, the last peak corresponds to the metal-ion that is the strongest retained by the stationary phase. This behaviour can be expressed by many formulas and equations, but a serious drawback is the fact that these mathematical expressions need to be fed by a lot of parameters. Most of these parameters need to be experimentally determined or to be estimated, what reduces the accuracy significantly. So the behaviour of metal-ions in a chromatographic column can be mathematically modelled, but the results are most of the time a poor approximation of the reality^[24]. Hereunder some relevant chromatographic terms are discussed.

The capacity factor can be calculated from the position of the peak maximum by:

$$k' = \frac{V_{\max} - v_m}{v_m}$$

where V_{\max} is the eluate volume to peak maximum or retention volume and v_m is the void volume of the resin. The distribution coefficient K can be determined from k' or v_m by means of following equations:

$$K = k' \cdot \frac{v_m}{v_s}$$

$$K = \frac{V_{\max} - v_m}{v_s}$$

where v_s is the volume of the stationary phase.

The height equivalent to a theoretical plate H or HETP is the volume can be derived from the following equation:

$$N = \frac{L}{H} = 8 \cdot \left(\frac{V_{\max}}{W} \right)^2$$

Where N is the number of theoretical plates, V_{\max} the volume of eluate to peak maximum, W the width of the peak at $1/e$ times the maximum solute concentration and L is the total height of the column bed. Another experimental technique to determine the affinity of the resin for a metal is the determination of batch distribution coefficients. In this technique a known quantity of resin is added to a known quantity of metal in solution and the concentration in the aqueous phase is measured before and after mixing. This coefficient is an equilibrium measure of the overall ability of the solvent impregnated resin to remove an ion under set conditions. The value of the batch distribution coefficient can be calculated by:

$$K_d = \frac{C_0 - C_e}{C_e} \frac{V}{m}$$

where C_0 is the initial concentration of the metal ion and C_e is the equilibrium concentration. V is the volume of the solution and m is the mass of the resin used in the batch experiment. When the mass of the dry resin is used in the formula above, the coefficient is commonly called the dry weight distribution coefficient.

5.2. Principles of chelation

5.2.1. The nature of chelation

When a metal ion associates with another species, a ligand, a metal complex is formed. The ligand is mostly an anion or a polar molecule. All metals form complexes, although the extent of formation and the nature of these complexes are strongly depending on the electronic structure of the metal [25]. The concept of a metal complex originates in the work of Alfred Werner. Werner stated that a metal ion can be characterised by two valence numbers, the principal and auxiliary valence. Nowadays the principal valence number is called the oxidation state and the auxiliary valence number represents the coordination number. The coordination number is the number of ligand atoms or molecules associated with the central metal atom. Most metals in their lower oxidation state (I, II, III) have usually a coordination number of 4 or 6. The nature of the bond can be described by treating the ligand as an electron-pair donor and the metal ion as an electron-pair acceptor. In other words, the metal behaves as a Lewis acid and the ligand as a Lewis base. When the ligand donates a pair of electrons to the metal ion, a coordination bond is established. Orbitals on the metal and the ligand of σ -symmetry will overlap to give rise to a σ -bonding molecular orbital which contains the lone pair of electrons from the ligand. Sometimes, when the symmetry is appropriate, also π -bonding can come into play. Ligands can be classified by the number of donor-atoms they contain. Molecules like ammonia that only contain one such atom are called

unidentate (one-toothed) ligands. Other molecules like ethylenediaminetetraacetic acid (EDTA) contain multiple donor atoms and are called multidentate ligands.

When certain ligands form a bond with a metal, a heteroatomic ring structure is established. The process of ring formation is known as chelation, derived from the Greek word ‘chele’ meaning a lobsters claw. These ligands are called chelating agents and the complexes they form metal chelates. Chelating agents can be neutral molecules, but mostly they contain carboxyl groups that, when they lose their protons, will help coordinate the ligand to the metal atom. For a chelating agent, containing α donor atoms, $\alpha-1$ chelate rings will be formed. The stability of a complex will increase with the number of chelate rings formed. This phenomenon is called the chelate effect.

5.2.2. Properties of ligands

A ligand that contains at least two donor atoms, capable of bonding to the same metal atom, is a chelating agent. Electron donating elements are situated on the right-hand side of the periodic table, mostly Group V and VI elements. Donor atoms can be part of an acidic or basic group of the chelating agent. In the case of a basic group, the donor atom will carry a lone pair of electrons. A few important functional groups and their structure are listed in table 5.1 (basic groups) and table 5.2 (acidic groups).

Functional group	Lewis structure
Amino	-NH ₂
Heterocyclic nitrogen	-N=
Carbonyl	=O
Ester, ether	-O-
Substituted phosphine	-PR ₂
Alcohol	-OH
thioether	-S-

Table 5.1: Basic functional groups

Functional group	Lewis structure
Carboxylic	-CO ₂ H
Sulphonic	-SO ₃ H
Phosphoric	PO(OH) ₂
Enolic/phenolic	-OH
Thioenolic/thiophenolic	-SH

Table 5.2: Acidic functional groups

Another condition for chelation is that the functional groups must be so located that it is sterically possible to form the chelate ring structure. Carbon-carbon σ -bonds between multiple functional groups in the ligand will provide some degree of flexibility, but they must not separate these groups too much. Probably, inductive and mesomeric effects could increase the electro-negativity of the electron-donating atom. Alkyl groups like methyl, ethyl, isopropyl, isobutyl will increase the electro-negativity of the donor atom significantly when bonded to this atom.

5.2.3. Properties of metals

The most convenient way to classify metals is via their electronic structure. Two main categories can be distinguished. In the first category all metals that have completely filled subshells. Examples of this category are: lithium, beryllium, alkali metals, alkali earths, copper, zinc, tin, gallium, ... The second category is filled with those metals that have incompletely filled subshells. These are the transition metals, lanthanides and actinides. The valence electrons of these elements are in more than one shell and because of this they usually exhibit more than one oxidation state.

An alternative classification of metals is into two classes α and β . The metals of the first class will form their most stable complexes with ligands containing elements from the first row of Group V, VI and VII. These elements are nitrogen, oxygen and fluorine. Most metals in their common oxidation state belong to this class. The second class elements form stable complexes with the second row of Group V, VI and VII, phosphorus, sulphur and chlorine. Class α metals are not easy polarisable while a class β metal is highly polarised.

A ligand behaves as a Lewis base and the metal as a Lewis acid. To describe interactions between the two species, the concept of hardness and softness is developed. A hard acid is one that retains its valence electrons strongly. Hence it is not easily polarisable, hard acids can roughly be compared to class α metals. Soft acids will quickly loose their valence electrons. These are the same elements that can be found in class β metals. Generally, most stable complexes result from the formation of a complex between a soft acid and a soft base or from a hard base with a hard acid. Such differences in 'hardness' of metal ions can be exploited to separate them.

The concept of ionic size is invaluable for the interpretation of most experimental data regarding metal complexes. The size of an ion is not invariant but depends on its coordination number, oxidation state, bonding partners and many more parameters. In table 5.3 the ionic radii of some trivalent lanthanides and actinides in an octahedral coordination are given.

La ³⁺	Ce ³⁺	Pr ³⁺	Nd ³⁺	Pm ³⁺	Sm ³⁺	Eu ³⁺	Gd ³⁺
106.1	103.4	101.3	99.5	97.9	96.4	95.0	93.8
Ac ³⁺	Pa ³⁺	U ³⁺	Np ³⁺	Pu ³⁺	Am ³⁺	Cm ³⁺	
118	113	106	104	100	101	98	

Table 5.3: ionic radii of trivalent metal ions in octahedral coordination ^[26]

Cations of the lanthanide elements show class α behaviour. Complexes with oxygen bearing ligands are most known. Coordination with nitrogen donors is mostly found in association with oxygen bearing ligands. In case of ligands that donate solely via nitrogen, the lanthanides will form preferential bonds with the oxygen atoms of the aqueous solution. The relatively large size of the lanthanide ions will allow coordination number as high as 8 or 9, and in a few cases, up to 10. Because the interaction between the ligand and the lanthanide is mostly of electrostatic nature the stability of the complexes will increase by decreasing size. As shown in table 5.3, heavier lanthanides will form more stable complexes.

The actinides generally resemble the lanthanides in their complexes. Again, high coordination numbers are possible. One difference is the fact that actinides have a higher affinity for nitrogen than lanthanides. This difference is introduced by the larger spatial distribution of the outer f-orbital by the actinides compared to the lanthanides.

5.3. Solvent Impregnated Resins

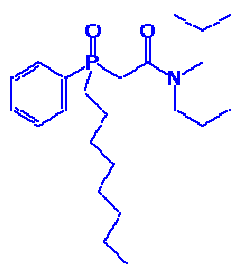
As mentioned above, solvent impregnated resins contain two fundamental components, the stationary phase – the extractant – and the inert support material. Both components are of considerable importance to the efficiency of the resin. Roughly, one can say that the stationary phase determines the stationary state (capacity ...) and the support material will control the kinetics of the extraction. If the resin particles are more porous, more mobile phase will be able to enter these pores and enhance the reaction rate. In the following section the properties of a specific resin are discussed more into detail.

5.3.3. CMPO/SiO₂-P resin

The inert support of the CMPO/SiO₂-P resin consists of porous silica particles that are coated with a polymer. The stationary phase is made of a carbamoylmethylphosphineoxide (CMPO), which makes up one third of the weight of the resin..

CMPO

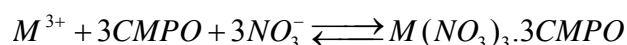
The development of CMPO and other carbamoylmethylphosphonate extractants can be traced ultimately to the work of Siddall [27, 28] in the mid 1960's. Much research effort was expended at Argonne National Laboratory (ANL) by Horwitz et al on the optimization of the basic extractant structure. The major goal of the research was to develop a reagent that was readily compatible with the PUREX process. During the 1980's the TRUEX process was developed at ANL. The reference extractant for this process is octyl(phenyl)-N,N-diisobutyl-carbamoylmethylphosphine oxide (figure 5.2).



CMPO

Figure 5.2: Octyl(phenyl)-N,N-diisobutyl- carbamoylmethylphosphine oxide

This molecule is able to extract almost all actinides and lanthanides in nitric acid solution with high efficiency by following reaction:



wherein M stands for metal ions like Am³⁺, Nd³⁺, Eu³⁺, ...

A major drawback of this carbamoylmethylphosphine is the fact that it makes little distinction between the lanthanides and actinides, hampering their separation. Currently much research effort is put into the synthesis of new carbamoylmethylphosphines with higher selectivity for lanthanides and actinides.. The extractant is extensively tested on its physico-chemical properties and stability. CMPO possesses a moderate resistance to radiolytic and hydrolytic degradation.

SiO₂-P

The support consists of a macro porous composite system of a polymer embedded in porous silica particles. These particles have an average diameter of 50 μm and a pore size of 0.6 μm . The polymer is a copolymer of styrene and divinylbenzene. The resin contains about 11 to 12 mass percent of polymer and 55 to 56 mass percent of silica.

Capacity

The resin used during the experiments is developed in the Institute for Research and Innovation (IRI) in Japan by Y. Wei et al. IRI has been investigating the capacity of the resin for neodymium [29]. Because of the strong mutual similarity between the lanthanides and the actinides, it can be expected that they all will show more or less the same capacity. The capacity of the resin for Nd^{3+} is plotted in figure 5.3.

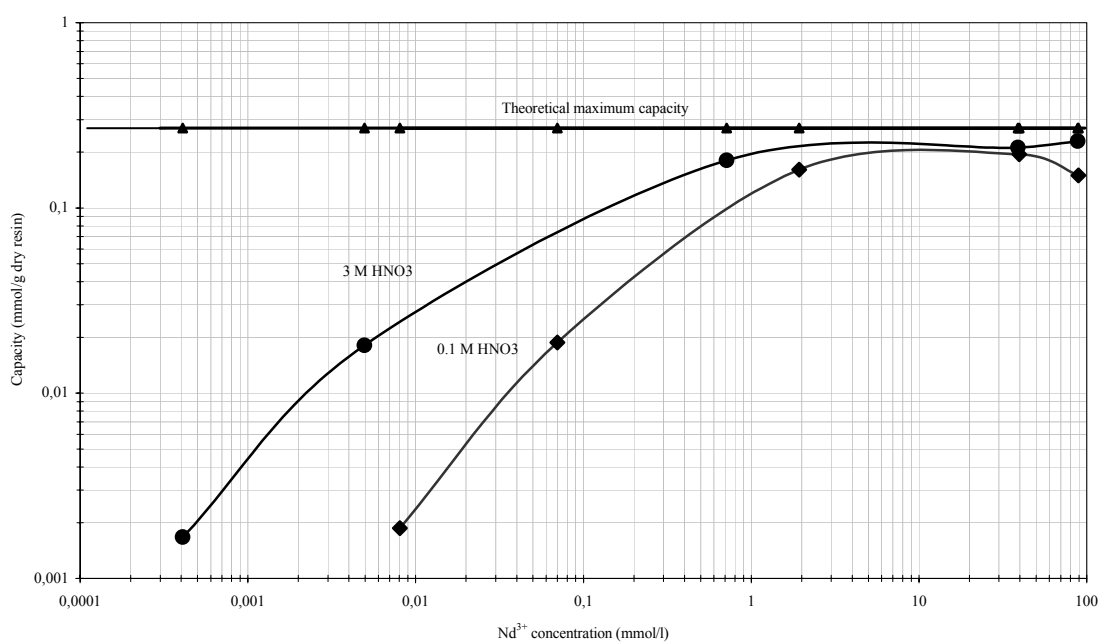


Figure 5.3: Capacity of CMPO/SiO₂-P resin versus Nd^{3+} concentration.

It is also possible to calculate the theoretical maximum capacity of the resin. Since we know the content of CMPO in the resin (33 w/o), the molar mass of the molecule (~407g/mol) and the fact that each trivalent metal needs 3 CMPO molecules to form a stable complex, we can easily deduce the theoretical maximum capacity. A short calculation shows that theoretically the resin can absorb up to 0.27mmol metal ions per gram of resin. In practice the reaction rate of the complexation or the diffusion step will reduce the capacity. Figure 5.3 shows very clearly that at high nitric acid concentration the actual capacity is very close to the theoretical maximum capacity. Also it can be noticed that there exists a strong dependency on the concentration of the metal ion.

Stability

Recently, different experiments are carried out in order to investigate the stability of the CMPO/SiO₂-P resin. For potential industrial applications in the future, it is of great important to understand the behaviour of the resin towards temperature, acids and radiation. In the Institute for Research and Innovation, Zhang and co-workers have investigated these degradation processes ^[30]. They showed that the resin has an excellent resistance towards nitric acid media and heat. It is known that high radiation fields are capable of destroying organic molecules such as CMPO. Nash et al reported in 1988 that in the presence of relatively high gamma sources a fraction of CMPO decomposed in different kinds of acidic or neutral organophosphorous molecules. This was confirmed by the study of Zhang et al. Radiation doses over several MGy will decrease the amount of metal ions that can be extracted by irradiated CMPO significantly.

5.4. Chelating agents

In section 5.2.1 it was already mentioned that a chelating agent is a molecule that is able to form several bonds with a metal ion. After the complexation reaction a more or less stable ring structure is formed. This stabilization can be expressed by means of the stability constant. Before discussing some chelating agents, two commonly used definitions of constants are given [31]. For metal ion complexation either the stepwise stability constants K_n defined as:

$$K_n = \frac{[ML_n]}{[ML_{n-1}][L]}$$

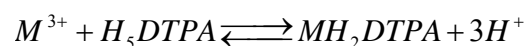
or the overall stability constants, β_n

$$\beta_n = \frac{[ML_n]}{[M][L]^n}$$

are used.

5.4.1. DTPA

Diethylenetriaminepentaacetate or DTPA is a multi-dentate chelating agent containing five carboxyl and three amine groups capable of being protonated. It can also form quite stable one to one complexes with many trivalent metal ions in a weakly acidic solution according to the following equation:



The overall stability constant is given by:

$$\beta_1 = \frac{[MH_2DTPA]}{[M^{3+}][H_5DTPA]}$$

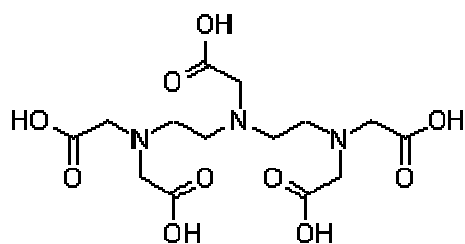


Figure 5.4: Molecular structure of DTPA

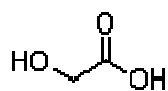


Figure 5.5: Molecular structure of glycolic acid

5.4.2. Glycolic acid

2-hydroxyacetic acid or glycolic acid is a naturally occurring hydroxy acid. The structure is represented in figure 5.5. Hydroxycarboxylic acids contain two donor groups, the hydroxyl and the carboxylate function, and therefore they are all potential bidentate ligands. The ability to complex a metal ion depends strongly on the relative position of the two donor groups in the molecule. The presence of the electron-withdrawing hydroxyl group makes the carboxyl group significantly more acidic. This effect decreases with the length of the aliphatic carbon chain of the molecule. Another disadvantage of long carbon-chains in these molecules is the fact that the hydroxyl groups will not participate anymore in the chelation process. Only the carboxylate group will then coordinate to the metal ion.

Up to four glycolate molecules can coordinate to a trivalent metal ion, providing four β -values:

$$\beta_1 = \frac{[M.GLYCOLATE^{+2}]}{[M^{3+}][L^-]} \quad \beta_2 = \frac{[M.GLYCOLATE_2^{+1}]}{[M^{3+}][L^-]^2}$$

$$\beta_3 = \frac{[M.GLYCOLATE_3]}{[M^{3+}][L^-]^3} \quad \beta_4 = \frac{[M.GLYCOLATE_4^{-1}]}{[M^{3+}][L^-]^4}$$

In figure 5.6 a few stability constants are shown for the elements concerned in this work. The working medium in which the constants were determined is aqueous 0.5 molar NaClO_4 solutions. It can be expected that the values are near those in 1.0 molar NaNO_3 solutions, certainly the trend will be the same.

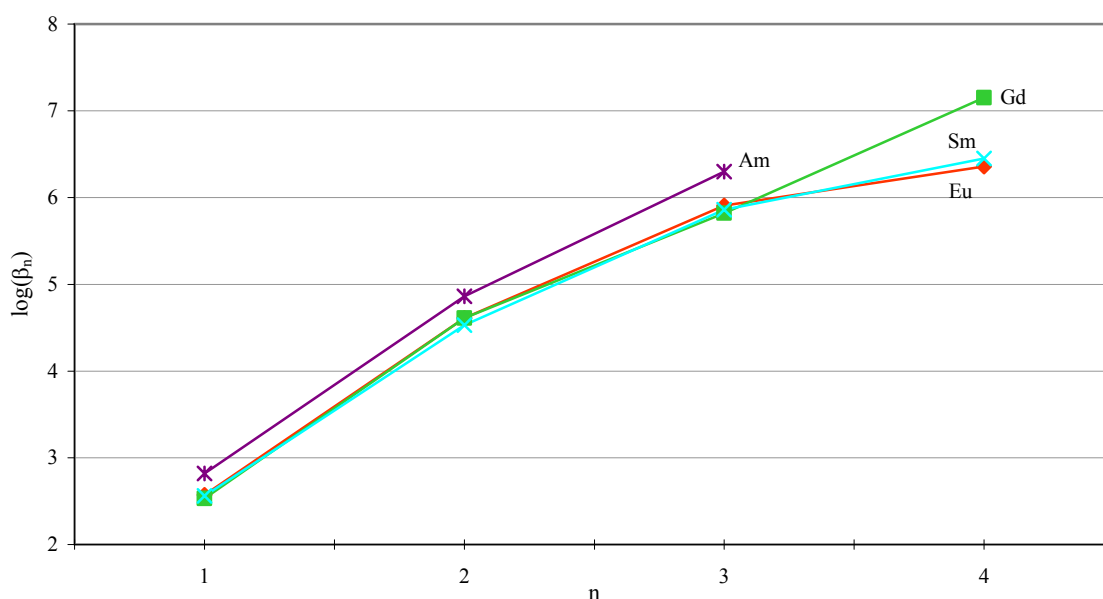
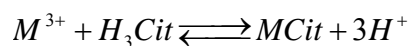


Figure 5.6: Overall stability constants of complexes of trivalent metal ions and glycolic acid in 0.5 M NaClO_4 solutions ^[31]

5.4.3. Citric acid

Citric acid is a naturally occurring organic acid that is commonly used as a chelating agent. It contains three carboxyl groups and one hydroxyl group, making it a quadridentate ligand. It plays a very important role in the metabolism of some organisms, namely in the breakdown of glucose for the production of energy.

The equation governing the chelation reaction is given by:



The first overall stability constant is given by:

$$\beta_1 = \frac{[MCit]}{[M^{3+}][H_3Cit]}$$

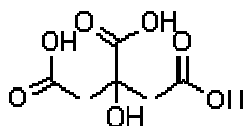
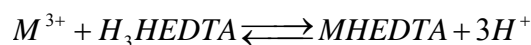


Figure 5.7: Molecular structure of citric acid

5.4.4. HEDTA

HEDTA is like DTPA multi-dentate chelating agent containing three carboxyl and two amine groups capable of being protonated. It is known to form relatively strong complexes with trivalent metal ions through following equation:



The overall stability constant is given by:

$$\beta_1 = \frac{[MHEDTA]}{[M^{3+}][H_3HEDTA]}$$

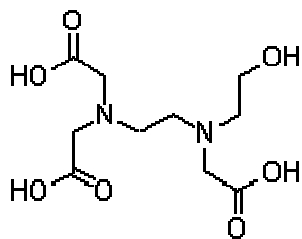


Figure 5.8: Molecular structure of HEDTA.

5.4.5. Dipicolinic acid

Several literature references [2] make notice of dipicolinic acid as a good complexing agent for the f-elements. Therefore dipicolinic acid (DPA) was included into the experiments.



Figure 5.9: Molecular structure of dipicolinic acid.

5.4.6. TPEN

If the lanthanide/actinide separation should be based on the usage of soft donor systems, then TPEN appears to be an ideal ligand. TPEN, a hexanitrogen donor is the 2-pyridylmethyl analogue of EDTA. Previous measurements show that the molecule is able to form stable complexes with the f-elements despite the presence of water molecules [32].

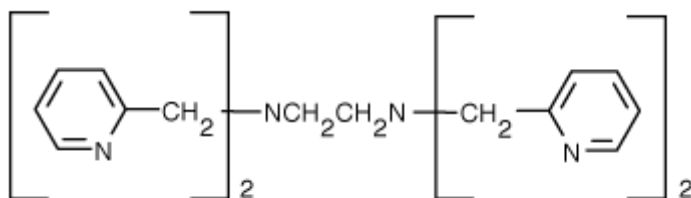
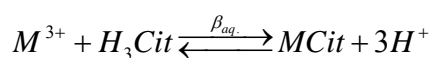
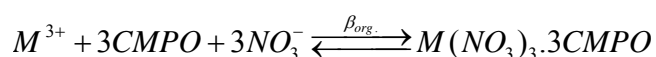


Figure 5.10: Molecular structure of TPEN.

5.5. Trans-complexation

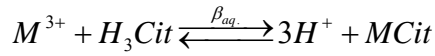
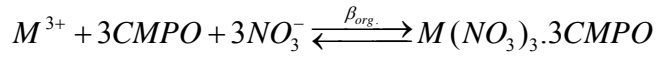
If there is more than one chelating agent present in the extraction chromatographic system, they will compete with each other to form a complex with the metal ions. The distribution at equilibrium will depend on the overall stability constant of the complexing agents, the concentration of all species and the environment. In our case there is most of the time one chelator in the organic (stationary) phase and a different one in the aqueous phase. Carbamoylmethylphosphine oxide will act as chelator in the organic phase and suppose that citric acid is the chelating agent in the aqueous phase.

The system can be expressed under the form of following reactions:

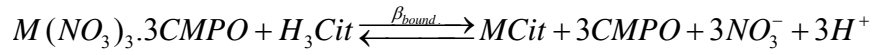


From the moment that $\beta_{aq.} > \beta_{org.}$ metal ions will start to transfer to the aqueous phase. The criteria can be achieved by e.g. controlling the acid concentration.

On the boundaries of the organic and aqueous phase following reaction takes place:



$$\beta_{org.} = \frac{[M(NO_3)_3 \cdot 3CMPO]}{[M^{3+}][3CMPO]} \quad \beta_{aq.} = \frac{[MCit]}{[M^{3+}][H_3Cit]}$$



$$\beta_{bound.} = \frac{[MCit][CMPO]^3}{[M(NO_3)_3 \cdot 3CMPO][H_3Cit]} = \frac{\beta_{aq.}}{\beta_{org.}}$$

This leads to the conclusion that when the value of β_{bound} is larger than unity, the aqueous solution will be able to strip the metal ions from the resin. The difficult part is to find a chelating agent and the conditions wherefore β_{bound} is smaller than unity for the lanthanides and preferably much larger than unity for the trivalent actinides or vice versa. Because of the absence of relevant data in the literature, the search for a suitable ligand has to be carried out by experiments.

6. MEASUREMENT TECHNIQUES

One of the most problematic aspects during this work was to find a suitable way to detect and measure the lanthanides in highly concentrated nitric acid solutions. A lot of literature research was carried out in order to find a suitable analysis technique. ICP-MS was selected as analysis technique, because of its ability to handle these acidic solutions without any problem. The determination of the americium content in the samples is carried out by liquid scintillation counting.

6.1. Spectrophotometry

First we looked at the spectrophotometric determination of the lanthanides. Unfortunately extinction coefficients are too low to allow a direct detection of the elements at the concerned concentrations. Therefore complexation with colour-reagents is required. Readily difficulties arose because of the fact that this method makes almost no distinction between the lanthanides mutually. Secondly, the matrix was too complex to make one calibration line. In fact, it turned out that each sample needed its own calibration line, what results in the need for a few hundreds of calibration lines. The complexity of the matrix is mainly caused by two reasons. First of all, nitric acid is widely known to interfere with spectrophotometric analysis in the ultraviolet and visible region. This behaviour was experimentally confirmed. At the other hand the colour-reagent makes use of a complexation reaction to form a detectable coloured complex. Adding other chelating agents to this solution will result in a trans-complexation and systematically to low lanthanide concentration are measured because of the masking effect of the other chelating agents. Because of all these interferences spectrophotometry is found unsuitable as analysis technique.

6.2. ICP-MS

Inductively Coupled Plasma combined with a Mass Spectrometer or commonly called ICP-MS is nowadays a very popular analysis technique. This is mainly due to its capability for multi element analysis and the fast transit of samples. Almost any element from the periodic table can be analysed into the ppt range (ppt: parts per trillion or ng/kg) with this technique. It can be applied for quantitative or qualitative determinations, or even both. The mass spectrometer can also be used to determine isotopic ratios of an element.

6.2.1. Principle

Most samples are in their liquid state before they are analysed by ICP-MS, but even solid samples can be used in the system. Before analysis these samples are vaporised using a laser, a technique called laser ablation.

Nebuliser

Liquid samples are pumped into the nebuliser, where they form together with argon gas an aerosol. Hereafter the aerosol passes through a spray chamber to obtain a more homogeneous aerosol. The argon gas will transport the aerosol into the plasma. Most of the time nebulisers are equipped with coolers to reduce the amount of solvent that reaches and lowers the temperature of the plasma.

Plasma torch

The plasma is formed by argon gas that flows through concentric tubes made of quartz glass. The torch is surrounded by a water cooled coil on which an alternating voltage with high frequency is applied. The frequency of the voltage is up to several MHz and is generated by a radiofrequency generator. This intense electromagnetic field arising from electromagnetic induction causes the gas to heat up. With this method, temperatures up to 10000K can be reached. An argon flow around the outer tube keeps the plasma away from the torch. Inside the plasma the aerosol droplets start to dry up, vaporise and finally decompose into single atoms. These atoms all lose an electron, resulting in ions with a single positive charge. The energy to lose such an electron is called the ionisation energy of an atom and differs per element. The time span of this process to occur is in the order of a few milliseconds. The produced ions are then sucked through a small orifice in the sampling cone and enter the expansion chamber with a supersonic speed.

Ion lenses

Because all ions are positively charged they repulse each other constantly. In the middle of the ion bundle the heavier ions are found. Somewhat further from the centre the more mobile lighter ions are situated. To focus the ion bundle a set of ion lenses is necessary. These lenses are made of a set of metal rings to which a voltage is applied. The electrical fields force the ion bundle into a curved motion, rejecting all neutral particles.

Quadrupole

The term quadrupole is derived from the fact that it is made out of four metal bars (two by two, parallel to each other) whereupon a combination of alternating and direct current is

applied. The instrument filters ions based on their mass to charge ratio (m/z). There exists a certain combination of both potentials by which only ions with a fixed m/z value can travel through the quadrupole and reach the detector. All other ions disappear between the bars and never reach the detector. In practice the instrument scan over a range of potential combinations, called a sweep. Performing such a sweep takes only a tenth of a second. If this is done multiple times, the results can be integrated.

Detector

The ions are measured by an secondary electron multiplier (SEM) and are counted for each mass. The electron multiplier consists of a number of dynodes coated in a semi-conductor. A dynode liberates electrons when an ion or another electron impinges on it. These electrons will hit another dynode and steadily the numbers of electrons increases until a measurable current is produced. This signal is further amplified and finally recorded.

Mass spectrum

Finally the peripherals of the ICP-MS apparatus produce a mass spectrum. On the horizontal axis the m/z ratio is plotted and the vertical axis represents the intensity of the signal. After calibration, the peak height can be used to determine the concentration of a sample. This technique has a linear concentration range from ppt (ng/kg) till ppm (mg/kg) level.

Element	atomic number	atomic weight	Abundance (%)	Halflife (y)	Decay mode
Nd	60	142	27,2	Stable	–
Nd	60	143	12,2	Stable	–
Nd	60	144	23,8	2,29E+15	α
Nd	60	145	8,3	Stable	–
Nd	60	146	17,2	Stable	–
Nd	60	148	5,7	Stable	–
Nd	60	150	5,6	> 6,8E+18	β^-
Sm	62	144	3,07	Stable	–
Sm	62	147	14,99	1,06E+11	α
Sm	62	148	11,24	7,00E+15	α
Sm	62	149	13,82	> 2E+15	α
Sm	62	150	7,38	Stable	–
Sm	62	152	26,75	Stable	–
Sm	62	154	22,75	Stable	–
Eu	63	151	47,81	Stable	–
Eu	63	153	52,19	Stable	–
Gd	64	152	0,2	1,08E+14	α
Gd	64	154	2,18	Stable	–
Gd	64	155	14,8	Stable	–

Gd	64	156	20,47	Stable	–
Gd	64	157	15,65	Stable	–
Gd	64	158	24,84	Stable	–
Gd	64	160	21,86	> 1,3E+21	β^-

Table 6.1: Naturally occurring isotopes of some selected lanthanides and their abundance and half-life.

6.2.2. Isobaric interference

A potential drawback of the use of a mass spectrometer is the occurrence of isobaric interference. Isobaric nuclides are nuclides with the same atomic mass but a different number of protons, thus a different chemical nature. The mass spectrometer measures only the mass of the atom, regardless of its chemical nature. As the lanthanides have a lot of naturally occurring isotopes this should be kept in mind when looking at the result of an analysis. Table 6.1 lists all isotopes of the lanthanides used in this work that occur in nature. The table shows also the natural abundance and the half-life of those lanthanides.

It appears from table 6.1 that there are ten nuclides that behave isobaric towards one or more other nuclides. As long as each lanthanide has one isotope that has no isobars in the sample, the concentration of this nuclide can be used from the calculation of all the others since their relative abundance is known. When analysing spent fuel derived solutions, the situation is different and fission yields have to be taken into account.

6.3. Liquid scintillation counting

Liquid scintillation counting is probably one of the most used measurement techniques for the determination of radionuclides that decay through α - and β -emission. The method involves the incorporation of these radionuclides into a liquid medium, capable of converting the kinetic energy of the emitted particles into electromagnetic radiation. The radiation has a wavelength under 400nm, just outside the visible range, in what is called the ultra-violet region. By means of a photomultiplier tube (PMT) this radiation can be detected and converted into an electric signal. By measuring the number of pulses per unit of time, and of course calibrating the device, it is possible to determine the activity of a sample.

Nowadays, sophisticated liquid scintillation counters exist that have the possibility to discriminate between α - and β -decay and measure both phenomena simultaneously.

6.3.1. Principles

In order to obtain an efficient energy transfer from the emitted particle to the scintillation liquid, both are intimately mixed. In a first step of the scintillation process, a particle is

emitted. Within a few nanoseconds the particle dissipates all its kinetic energy by colliding with the scintillation medium and comes to rest. The energy is dissipated through three pathways, heat, ionisation and excitation. Liquid scintillation counting relies on the dissipation of energy through excitation. When a particle hits a scintillation molecule, a fraction of its kinetic energy will be used to excite this molecule. In fact, it are the orbital electrons that are excited. It is commonly known that when an excited electron returns towards its ground state, it emits a photon. These photons will be captured by a photomultiplier and generate an electric signal. It should be noted that a variety of processes happen inside the scintillation liquid, but summarized it comes down to the excitation of molecules by particles and emission of UV-light when these molecules return to their ground state. A photomultiplier tube is an instrument that is capable of converting photons into electrons and multiplying those electrons. It consists out of a photocathode that, by means of the photoelectric effect, emits electrons when photons impinge onto the material. Hereafter the number of electrons generated by the photocathode is multiplied by a chain of dynodes. These dynodes consist of an electron-absorbing material with enhanced secondary electron emission. Electrical fields are applied between the dynodes to accelerate and guide the electrons towards the next dynode.

For example, suppose that a single alpha-decay liberates 10 photons and each dynode has a multiplication factor of 10 and there are 10 dynodes between the photocathode and anode. 10 electrons impinge on the first dynode and one hundred take off to the second dynode. After the last dynode, about one hundred billion electrons would impinge onto the anode. The process is schematically represented in figure 6.1.

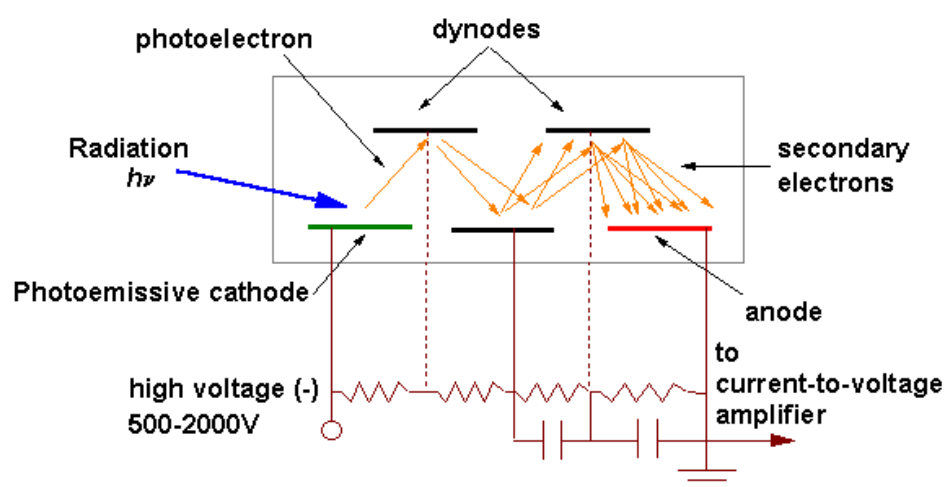


Figure 6.1: Schematic representation of a photomultiplier

A microprocessor will translate the number of pulses and the height into a number of counts per time unit. Commonly used are 'counts per minute' or 'counts per second'.

These instruments are capable of measuring photons with a wavelength between 100 and 1100 nm. It should be mentioned that the efficiency will not be the same for every photon within this range. It is clear that more energetic photons will generate more electrons what finally will result in a stronger signal.

There is a whole range of so-called scintillation cocktails commercially available. The choice of the scintillation cocktail depends on different factors such as the radionuclide that one wants to measure and the medium in which these nuclides are situated. Alpha-particles can be counted with almost 100% efficiency, while e.g. for tritium roughly only one out of three beta-decays will be counted.

7. EXPERIMENTS

The experiments carried out in this work are split into two different phases. The first phase involved the determination of the distribution coefficients of the lanthanides on CMPO/SiO₂-P resin. Secondly the distribution coefficient of americium on the resin was determined. But, due to the relatively high activity of ²⁴¹Am used in the experiments it was necessary to perform these experiments in a glove box. The advantage of this splitting is the fact that in the first phase no radioactive elements are used. This led to fewer constraints with regards to radioprotection so that this phase could be carried out more rapidly. It also gave the opportunity to optimize the technique for the determination of distribution coefficient without producing radioactive waste. Problems encountered during the initial experiments could be much easier solved and the procedure was optimized for the next phase.

7.1. Motivation

As mentioned above, a chelator has to be found that has the property of withdrawing the trivalent actinides from the resin while it leaves the lanthanides in this resin. It is very likely that this property will only occur under a combination of certain conditions such as temperature, ionic strength, acidity, etc. Therefore the distribution coefficients were determined at various acid concentrations. Experiments have been carried out at relatively low nitric acid concentrations and at high nitric acid concentrations. Most other references tend to work only at high nitric acid concentrations. The disadvantage of using high nitric acid concentrations is the fact that, most likely, under these conditions the actinides are too strongly withheld by the resin. If one keeps in mind the enormous extractive potency of CMPO at high nitric acid concentrations, it is easy to believe that – even strong – chelating agents will not be able to withdraw actinides at such high nitric acid concentrations. Another problem is the fact that at high nitric acid concentrations, almost all chelating agents are fully protonated and thus unable to form complexes with any metal ions. For this reason, experiments are also carried out at low acid concentrations. However lower distribution coefficients – due to the lower efficiency of CMPO in these media – are likely to be found.

7.2. First phase

To determine the distribution of lanthanides on the CMPO/SiO₂-P resin several experiments were carried out. The concentration of the lanthanides in the aqueous phase was chosen to be in the range of the PUREX raffinate, between 5×10^{-4} mol/l and 5×10^{-5} mol/l of each

lanthanide. Nitric acid concentrations were varied over a broad interval, starting from 0.01 up to 5 mol/l. Every experiment was carried out six times; to five test tubes different complexants were added while one test tube served as a blanc. The concentration of these complexing agents in the test tubes was chosen to be 0.005 mol/l. An amount of CMPO/SiO₂-P resin between 150 and 250 mg was mixed during several hours with 20 ml of the lanthanide solution. Mixing was carried out by means of a rotating mixer at a speed of 30 rpm. Hereafter the test tubes containing the mixture were placed in a centrifuge for 15 minutes at 1000 rpm. Afterwards samples were taken from the supernatant and filtered through a 0.20µm PTFE syringe filter and analyzed by ICP-MS. With knowledge of the initial lanthanide concentration, the concentration at equilibrium and the dry weight of the resin, one can calculate the dry weight distribution coefficient.

7.3. Second phase

Due to the radiotoxic nature of americium and the relatively large amounts that had to be handled it was necessary to carry out the experiments in a glove box. Again, the concentration of americium was chosen to be alike the one in the PUREX raffinate (for UO₂ fuel), 1×10^{-6} mol/l. Identical to the first phase, nitric acid concentrations range from 0.01 up to 5 mol/l. The concentration of the complexants was chosen to be 0.005 mol/l. Microtubes of 2 ml were used to contact 1 ml of ²⁴¹Am solution with a suitable amount of resin. The mixing process was carried out in the same way as during the experiments with the lanthanides, with a rotating mixer at 30 rpm for 3-4 hours. After the mixing process, the resin was allowed to settle down before samples were taken from the supernatant. Hereafter the samples were filtered through 0.2µm PTFE syringe filters.

To validate the results of the experiments of the first phase it was decided to add also lanthanides to the americium solution. The samples taken after the experiment were divided into two parts. One fraction was simply diluted and sent to the ICP-MS and analyzed for the lanthanides. The other fraction was diluted with scintillator liquid to measure ²⁴¹Am by means of liquid scintillation counting. When knowing the ²⁴¹Am activity in the initial solution and at equilibrium together with the mass of resin, one can calculate the dry weight distribution coefficient.



Figure 7.1: Experimental work in the glove box

7.4. Boundary conditions

In table 7.1 the boundary conditions under which the different experiments are performed are listed. One aspect that is not previously mentioned is the safety factor that was calculated during the preparation of the experiments. It was introduced to ensure that the experiments were not performed with an under capacity of resin. The safety factor can be determined through a small, straightforward calculation. As an example the calculation is carried out for Experiment A.

	$C_{Ln} / \text{mol.l}^{-1}$	$C_{\text{Complex}} / \text{mol.l}^{-1}$	$m_{\text{CMPO}} / \text{mg}$	V / ml	n_{Ln} / mol	$\text{Cap}_{\text{CMPO}} / \text{mol}$	Safety factor
Experiment A	5.00E-04	0.005	200	20.0	4.00E-05	5.56E-05	1.39
Experiment B	5.00E-05	0.005	250	20.0	4.00E-06	6.94E-05	17.4
Experiment C	5.00E-05	0.005	150	10.0	2.00E-06	4.17E-05	20.8
Experiment D	5.00E-05	0.005	100	1.000	2.00E-07	2.78E-05	139
Experiment E	5.00E-05	0.005	100	1.0	2.00E-07	2.78E-05	139

Table 7.1: Boundary conditions of the experiments

In the experiment 200 mg of CMPO/SiO₂-P resin is used, of which one third is actually CMPO. Since the molar mass of CMPO is 407 g/mol, 1.64×10^{-4} mol of the organic molecule is available in the experiment. From several references it is known that there are on average three CMPO molecules needed to complex a trivalent metal ion, so in theory 200 mg of resin can extract 5.46×10^{-5} mol trivalent metal ions. In a volume of 20 ml this corresponds with a concentration of 2.73×10^{-3} mol/l. During the experiment 5×10^{-4} mol/l of four lanthanides are present or 2×10^{-3} mol/l of trivalent lanthanides are in the solution. Comparing the theoretical maximum capacity with the actually present concentration gives a safety factor of 1.39.

8. RESULTS AND DISCUSSION

8.1. First phase – high acidity: Experiment A

From the results of Experiment A (Appendix I) several interesting trends become clearly visible. One is the fact that the efficiency of the resin follows the nitric acid concentration up to a maximum. Hereafter the efficiency seems to decrease. It is believed that these high nitric acid concentrations the resin will start to extract nitrate species that thus compete for extraction with metal ions. Another interesting fact is the observation that the extraction of light lanthanides seems to be preferred over the heavier ones by the CMPO resin. This effect can possibly be related to the decreasing ionic radius over the lanthanide series. In section 5.2.3 it was said that heavier lanthanides will experience stronger electrostatic interactions than the light lanthanides what should lead to more stable complexes. The outcome of these experiments therefore supports the theory that there exists some kind of covalent bonding between the lanthanides and ligands.

Unfortunately, things are not so clear when it comes down to the effect of the complexing agents. It is clearly visible from figures 8.1 until 8.4 that some complexing agents, especially glycolic acid and HEDTA, tend to improve the extraction of lanthanides from the aqueous phase. Normally, complexing agents will “mask” the metal ions from the resin and thus decrease the distribution coefficient. Therefore, an explanation has to exist for this behavior. One strange thing is that HEDTA seems to act as glycolic acid and not as DTPA nonetheless they have almost the same chemical structure. Another curious phenomenon is the fact that in the presence of complexing agents the distribution coefficient seems to converge at high acid concentrations. To verify these results Experiment B was prepared and carried out.

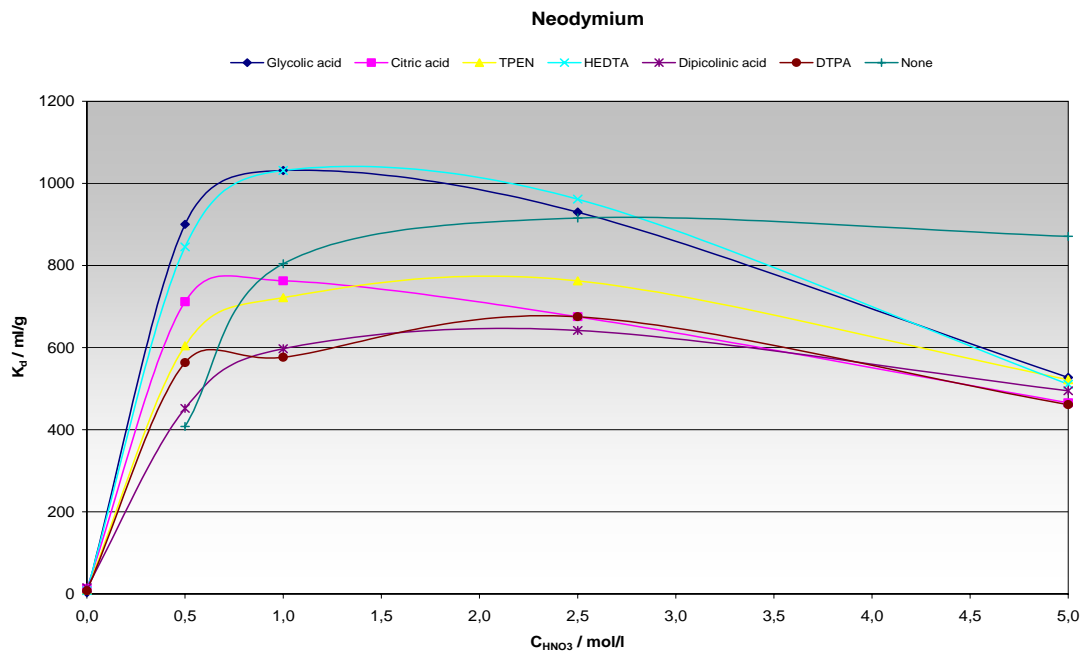


Figure 8.1 : Effect of complexing agents on the distribution of neodymium on the CMPO resin in concentrated nitric acid solutions.

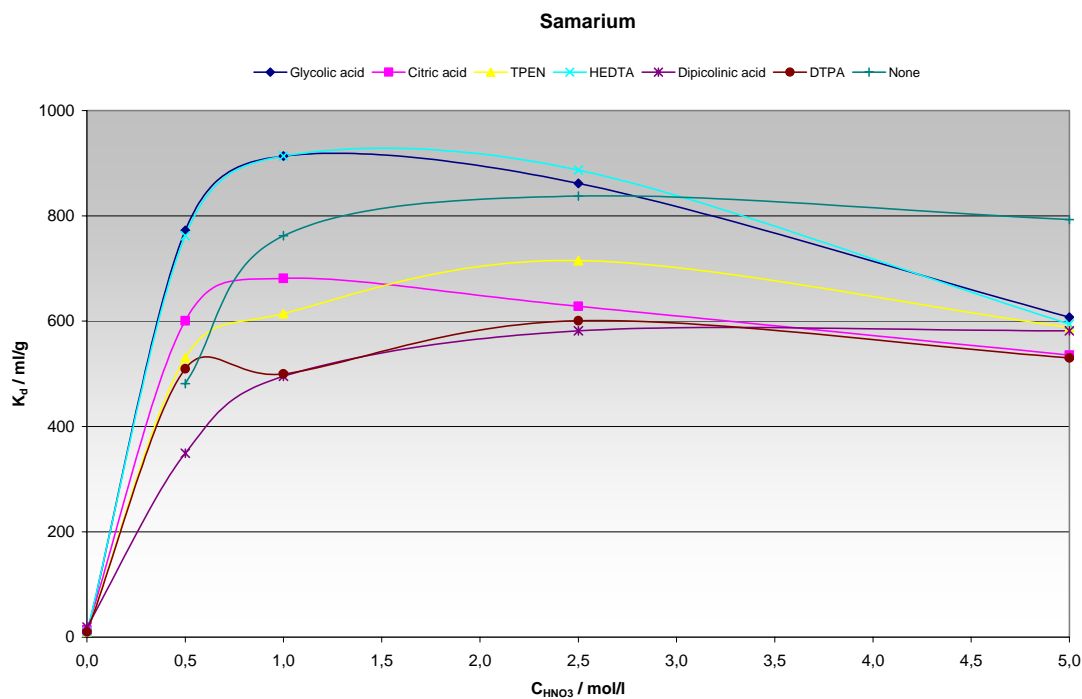


Figure 8.2 : Effect of complexing agents on the distribution of samarium on the CMPO resin in concentrated nitric acid solutions.

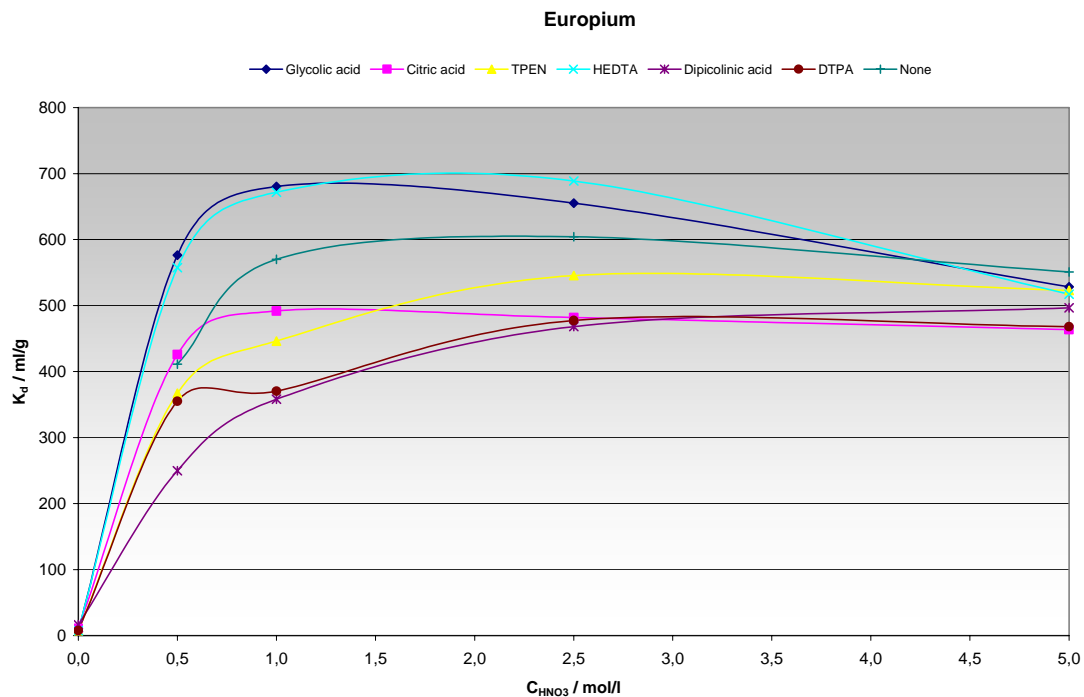


Figure 8.3 : Effect of complexing agents on the distribution of europium on the CMPO resin in concentrated nitric acid solutions.

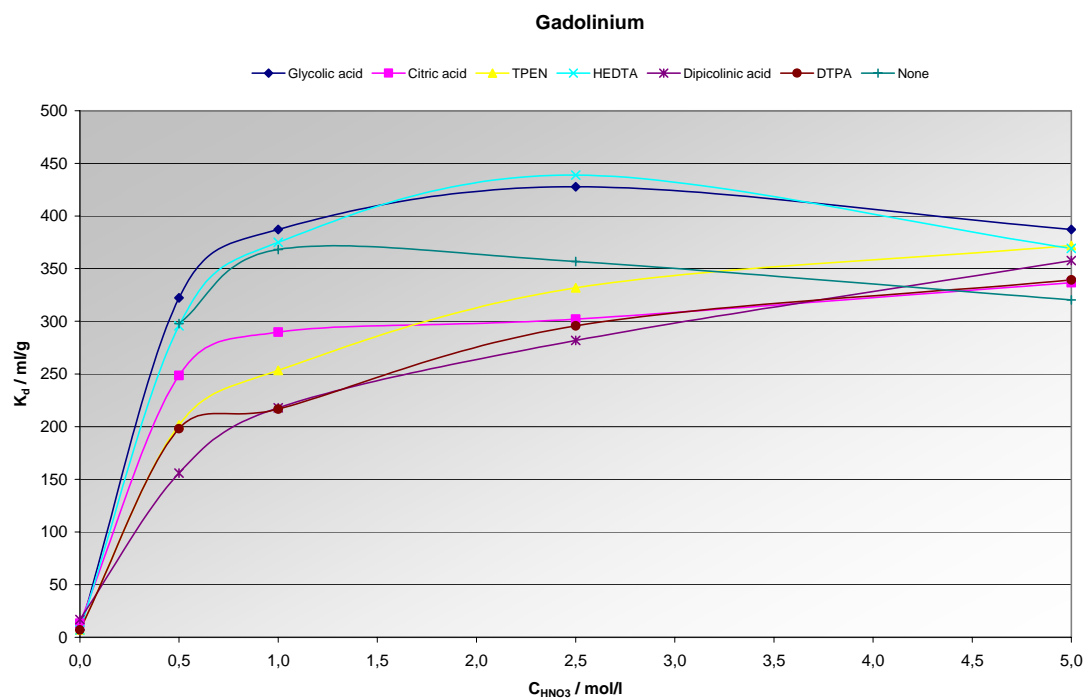


Figure 8.4 : Effect of complexing agents on the distribution of gadolinium on the CMPO resin in concentrated nitric acid solutions..

8.2. First phase – verification of Experiment A: Experiment B

In order to find an explanation for the somewhat strange results of Experiment A another experiment was carried out (Appendix II). Some fear existed that possibly there wasn't enough resin present and that the result could be related to an under-capacity of the resin. Therefore the lanthanide concentration was lowered by a factor 10 and the mass of resin was increased by 25% during the subsequent experiment. The experiment was carried out at following nitric acid concentrations: 0, 0.5, 1.0, 2.5, 5.0 mol/l without the addition of any complexing agents. Besides this, one sample was prepared with 0.005 mol/l glycolic acid at a nitric acid concentration of 1.0 mol/l.

Figure 8.5 confirms the trends that were noticeable in Experiment A, a decrease of extractability with the atomic weight of the lanthanides. Remarkable is the large decrease of efficiency of the resin towards gadolinium when compared with lighter lanthanides. The second part of the experiments, to verify the positive influence of glycolic acid on the extraction, seems to confirm that the effect decreases as the atomic number of the lanthanide ions increases. The results of this experiment can be found in figure 8.6. In Experiment A the positive effect was present for all four lanthanides while in Experiment B only the extraction of the lightest lanthanide, neodymium, was promoted by glycolic acid. Experiment B was thus not able to fully confirm this strange effect and therefore further investigations are needed. One can also notice the increase in distribution coefficient between Experiment A and B which can be explained by the increased safety factor.

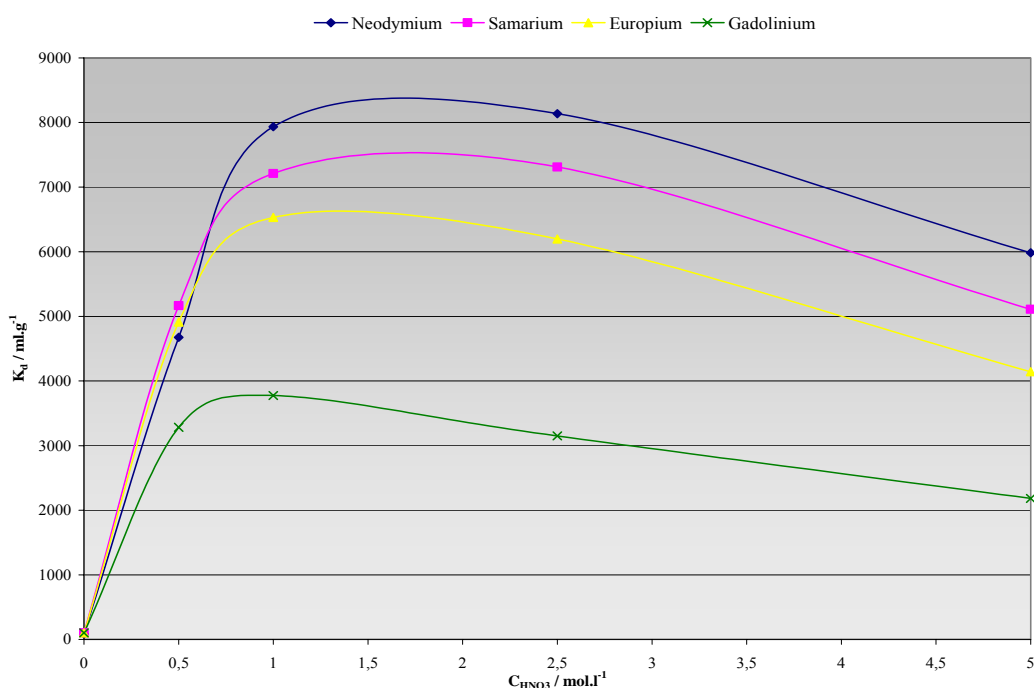


Figure 8.5: Results of Experiment B – no complexing agents

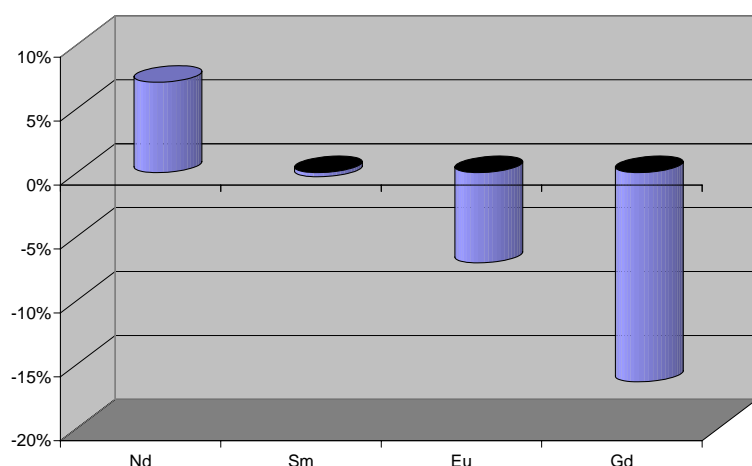


Figure 8.6: Effect of 0.005M glycolic acid on the distribution coefficient in 1M nitric acid.

8.3. First phase – low acidity: Experiment C

The purpose of Experiment C was to examine the effect of complexing agents on the extraction efficiency of the CMPO resin at low acid levels. The nitric acid concentration was therefore varied between 0.01 and 0.1 mol/l. From the results presented in figure 8.7 until 8.10 it is clearly visible that one complexing agent, dipicolinic acid, is extremely effective in retaining the lanthanides from the resin (Appendix III).

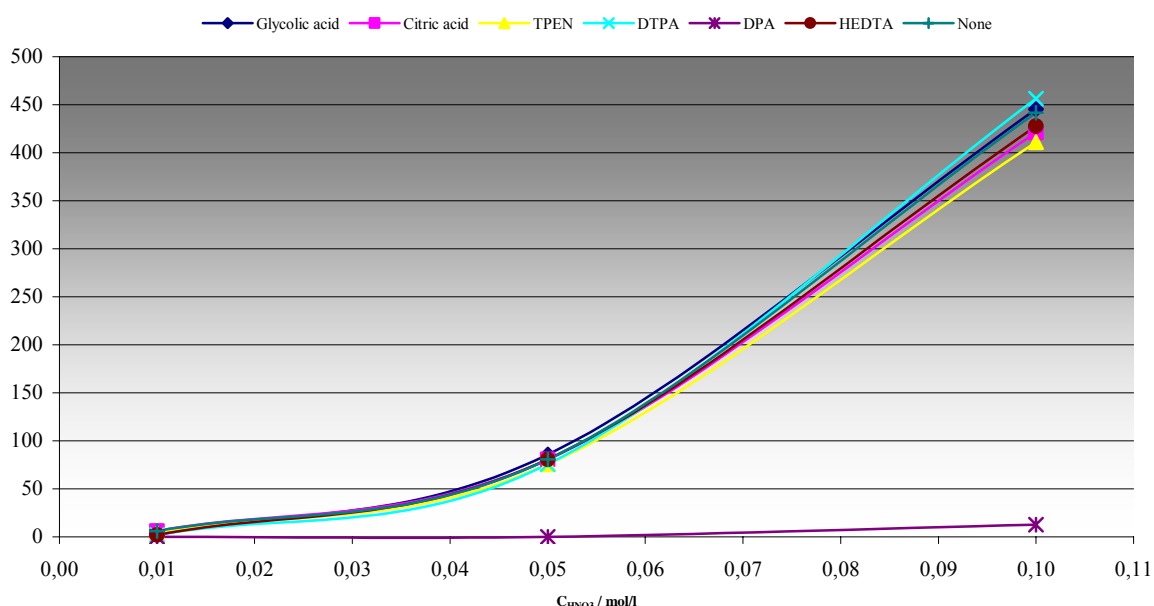


Figure 8.7 : Effect of complexing agents on the distribution coefficient of neodymium on the CMPO resin in dilute nitric acid solutions .

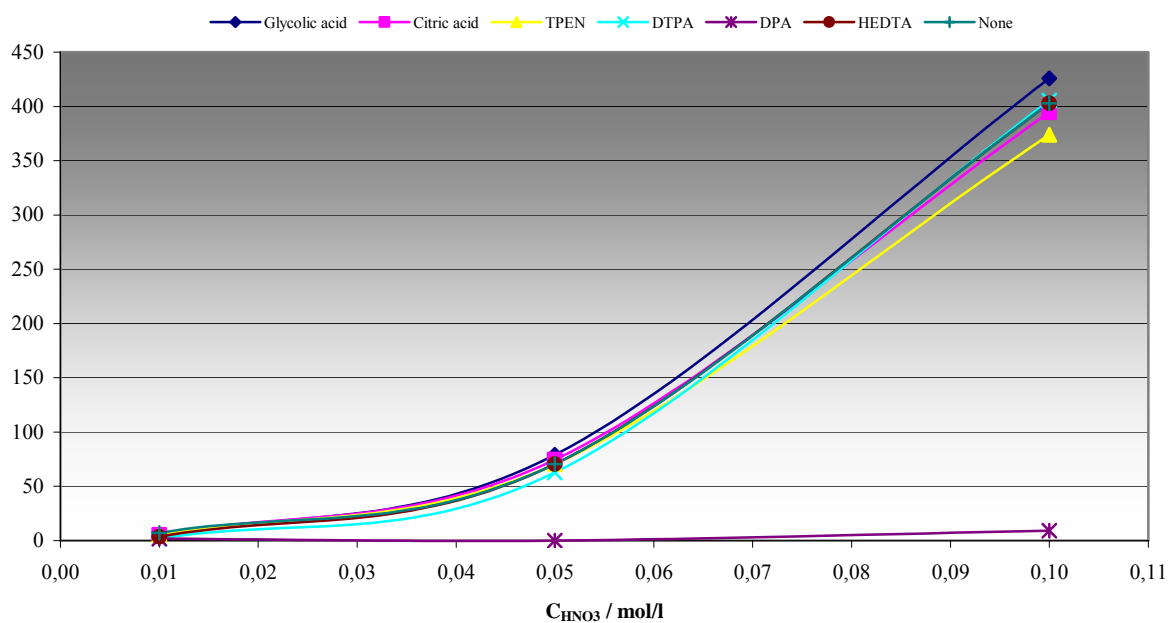


Figure 8.8 : Effect of complexing agents on the distribution coefficient of samarium on the CMPO resin in dilute nitric acid solutions.

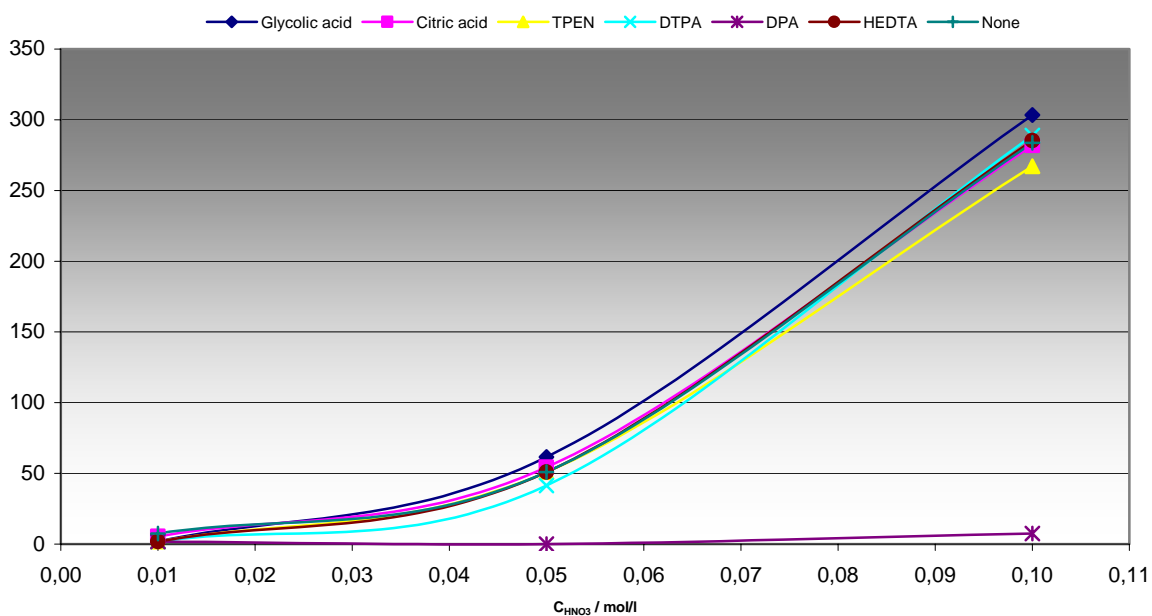


Figure 8.9 : Effect of complexing agents on the distribution coefficient of europium on the CMPO resin in dilute nitric acid solutions.

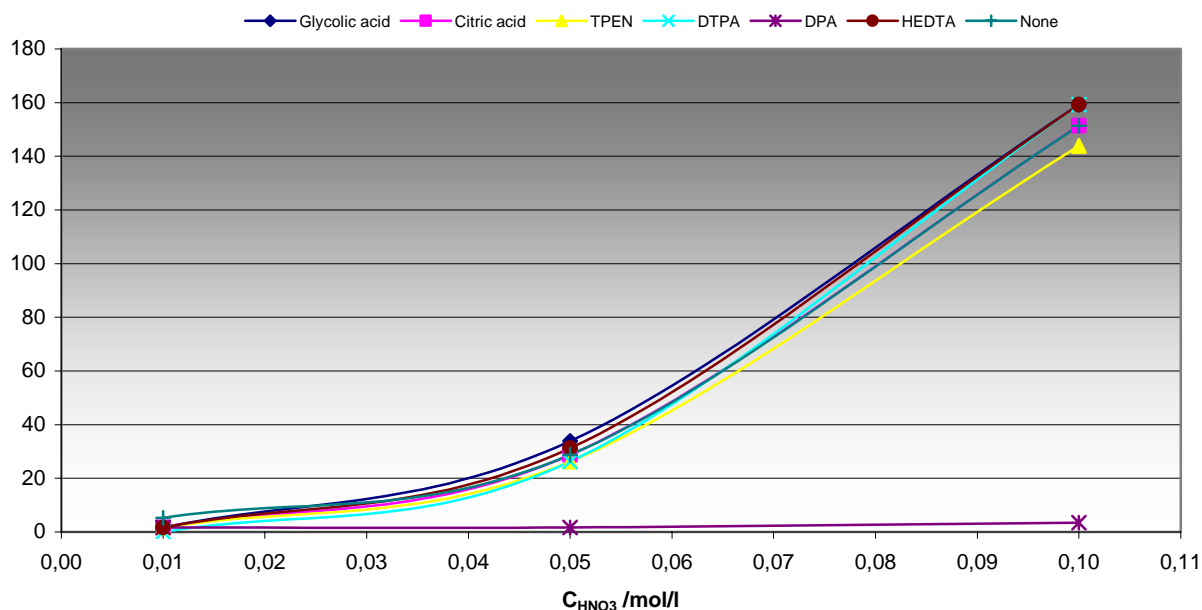


Figure 8.10 : Effect of complexing agents on the distribution coefficient of gadolinium on the CMPO resin in dilute nitric acid solutions.

Again, the preference of the resin for light over heavy lanthanides is noticeable. Except for dipicolinic acid, all complexing agents seem to have little or no effect on the distribution of lanthanides between the resin and the aqueous phase. Statistical analysis was applied to the results [33] and an average experimental uncertainty of 4.15% within a 95% confidence interval was found. Therefore it can be said that under these conditions all tested complexing agents, with the exception of dipicolinic acid, have no noticeable effect on the extraction of lanthanides by CMPO.

The first phase has now come to its end and the next two experiments will involve the use of americium. If it can be shown that dipicolinic acid has a different behavior towards americium than towards the lanthanides, a promising complexing agent is found.

8.4. Second phase – high acidity: Experiment D

The main goal of Experiment D is to investigate the influence of complexing agents on the extraction of americium by the CMPO resin. Lanthanides were also added to the test tubes, in order to confirm the results of the first phase experiments. Numerical values of the measurements can be found in Appendix IV. Hereunder the results of Experiment D are graphically presented in figure 8.11 until 8.16

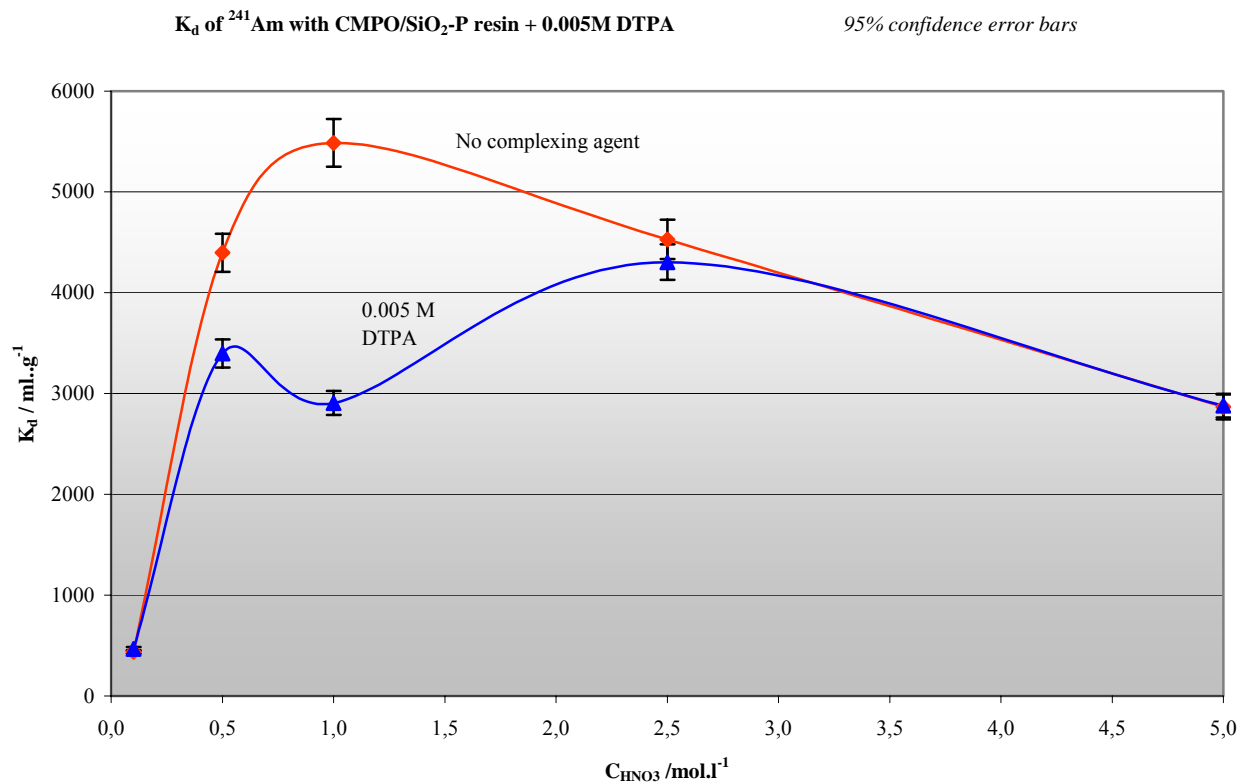


Figure 8.11 : Effect of DTPA on the distribution of americium on the CMPO resin.

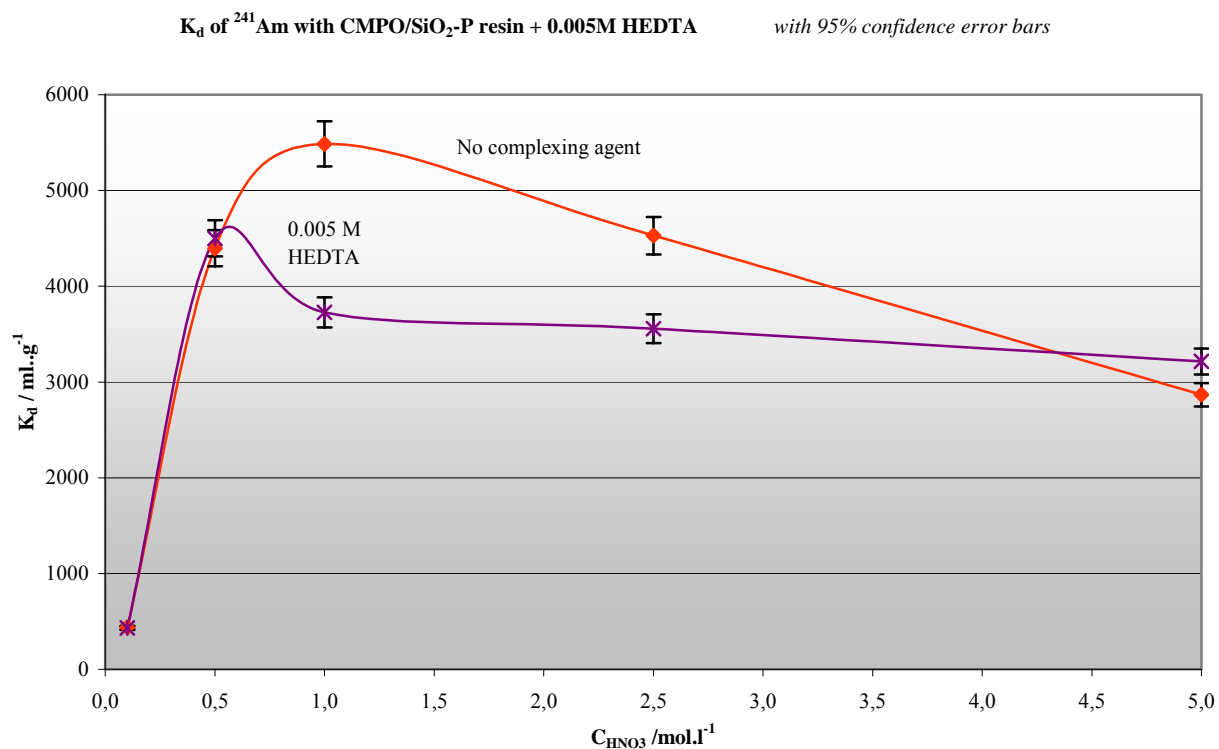


Figure 8.12: Effect of HEDTA on the distribution of americium on the CMPO resin.

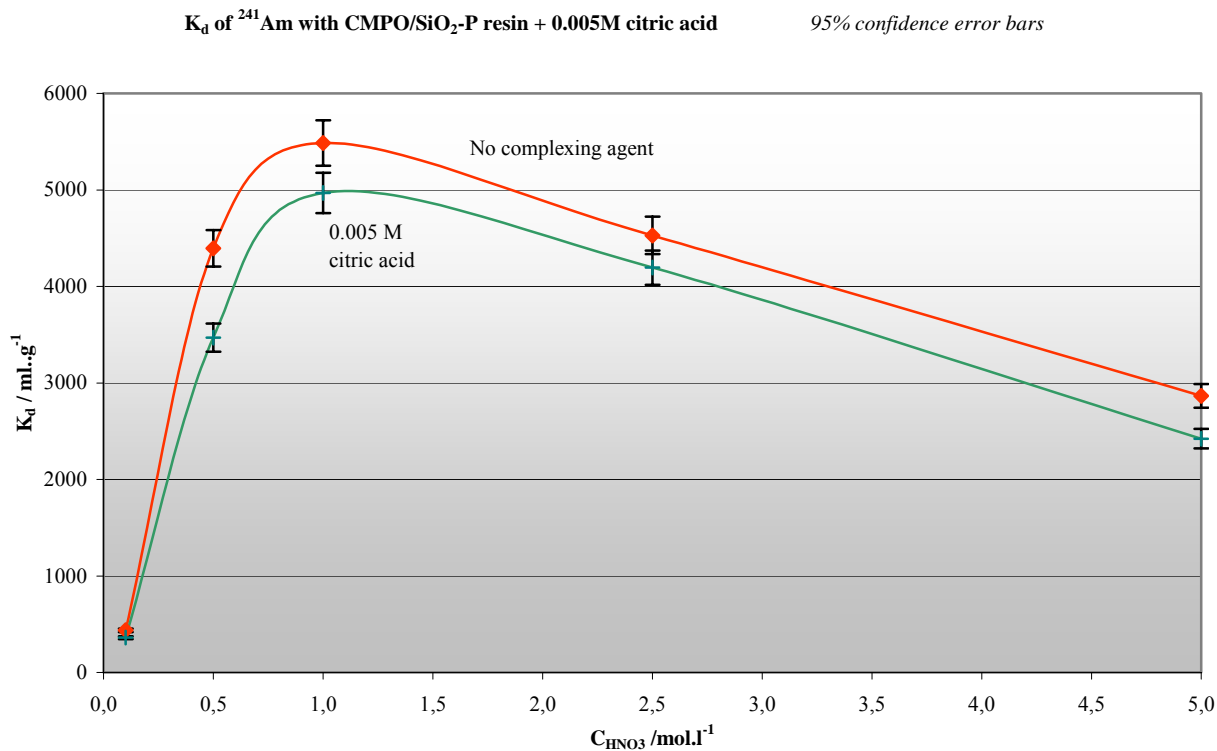


Figure 8.13: Effect of citric acid on the distribution of americium on the CMPO resin.

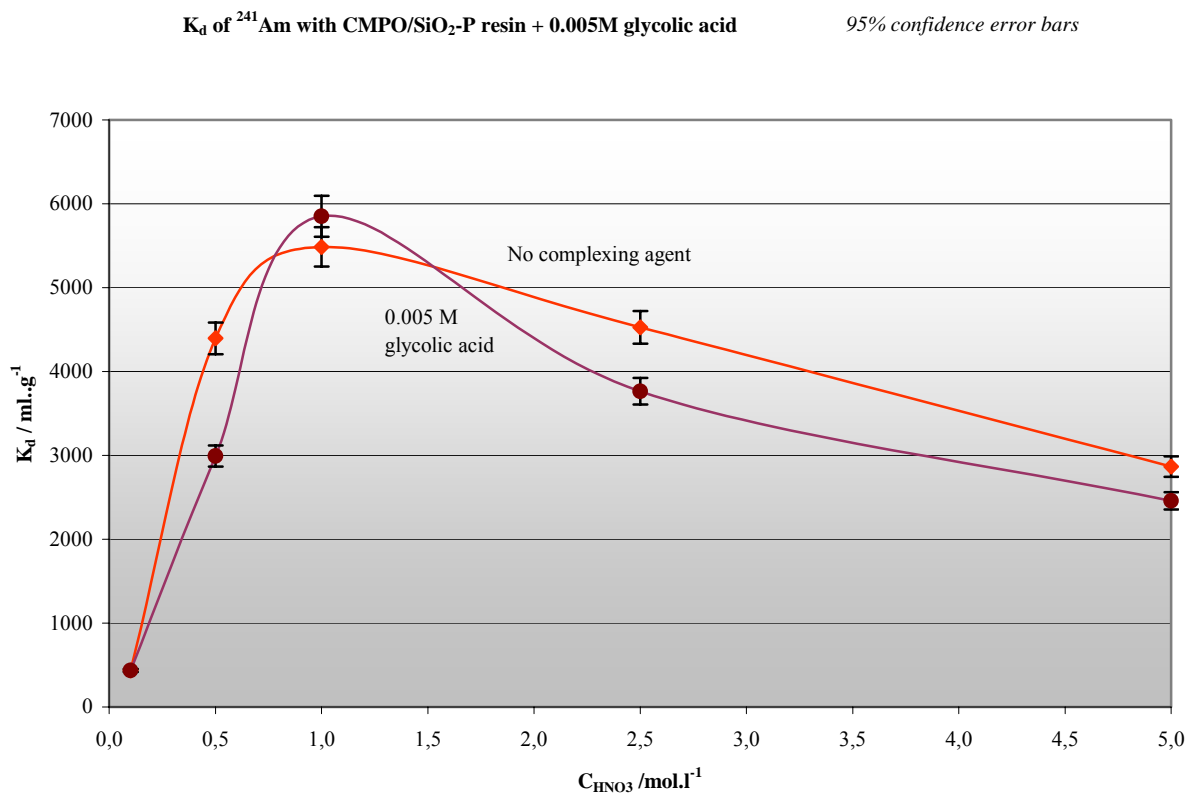


Figure 8.14: Effect of glycolic acid on the distribution of americium on the CMPO resin.

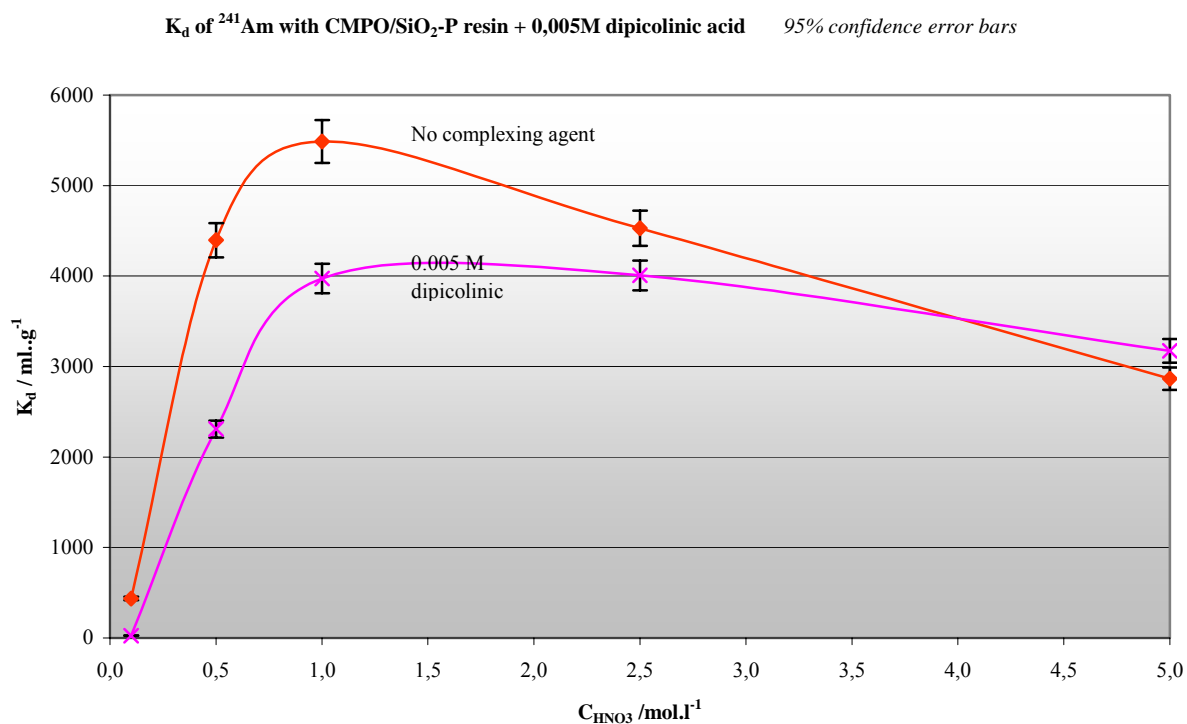


Figure 8.15: Effect of dipicolinic acid on the distribution of americium on the CMPO resin.

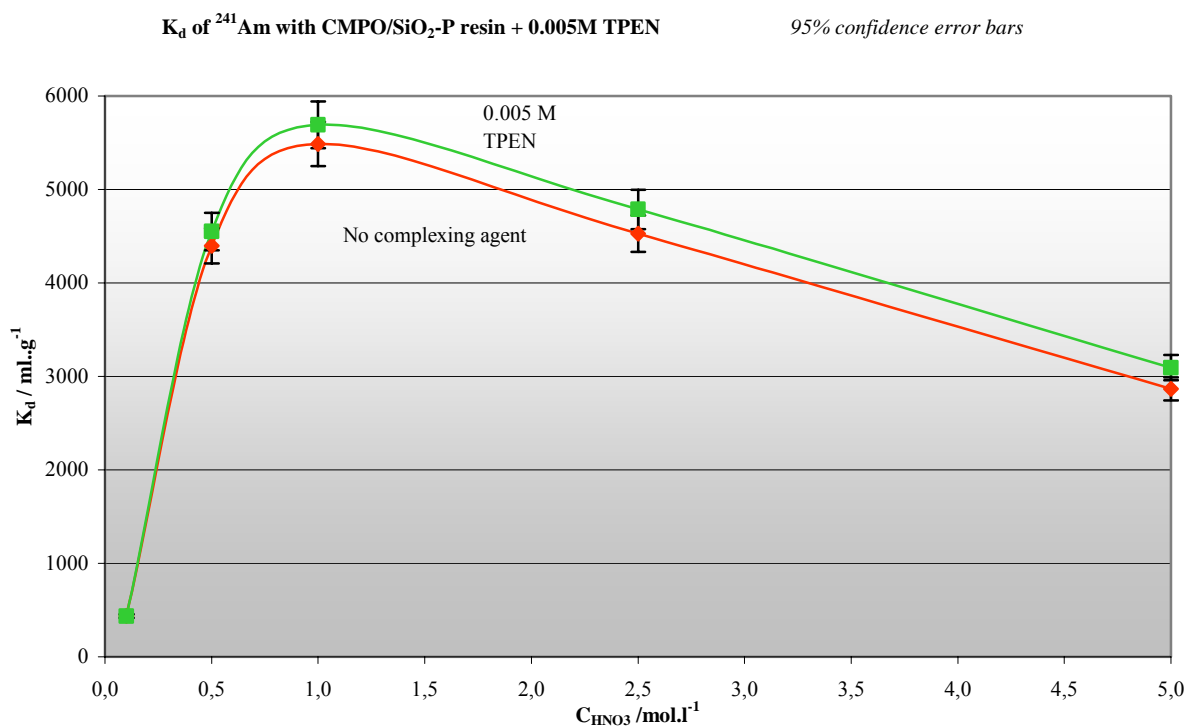


Figure 8.16: Effect of TPEN on the distribution of americium on the CMPO resin.

The complexing agent DTPA seems to have a similar effect on the distribution of americium as it does on the lanthanides. At relatively low and high acid concentrations DTPA seems to have little or no effect. At intermediate acid levels, from 0.5 up to 2.5 M HNO₃, DTPA seems to withhold metal ions from the resin. However, in these kinds of acidic media DTPA is fully protonated [34] and carries a positive charge (H₇DTPA²⁺). Due to Coulomb repulsion metal ions will be repelled from the organic molecule and chelation of the metal ions becomes impossible. Therefore the decrease in affinity for metal ions of the resin cannot be explained by complexation. One possible explanation is the fact that the positively charged DTPA molecules are attracted by the electron-rich sites on the CMPO molecules and so shield off these molecules from the metal ions. HEDTA, with its very similar structure as DTPA, seems to exhibit the same behavior. Even in very acidic media citric acid will not acquire a positive charge due to protonation. Since it is able to complexate trivalent metal ions when it is in its neutral form, citric acid should be able to withhold those ions from the resin. This is in agreement with figure 8.13, where citric acid decreases the distribution coefficient with 10 to 20 %, depending on the acidity.

Glycolic acid seems to decrease the distribution coefficient at most acid concentrations but strangely enough at 1M HNO₃ it increases the distribution coefficient again. Dipicolinic acid is also able to complexate americium up to a certain level of acidity, above which it becomes inactive. The promising complexing agent TPEN seems to be unable to complexate americium at these high acid concentrations.

8.5. Second phase – low acidity: Experiment E

This experiment is almost identical to Experiment C but in this case ²⁴¹Am is added to the test tubes. In this way, it is possible to investigate the distribution of americium on the resin at low acid concentrations. Figure 8.17 shows the results of the experiment (Appendix V).

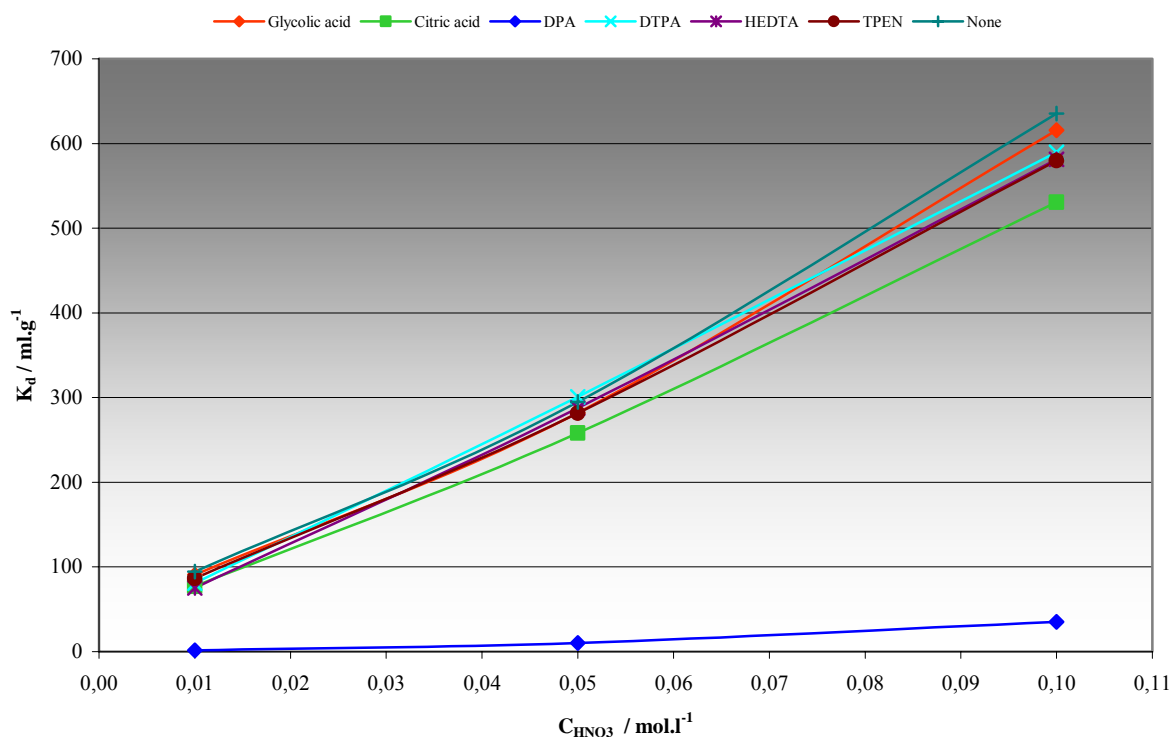


Figure 8.17: Distribution of americium on the CMPO resin at low acidity

Identical to Experiment C it can be seen that only one complexing agent, dipicolinic acid, possesses the ability to influence the distribution of trivalent metal ions between the resin and dilute nitric acid solutions. The concentration of the lanthanides in the samples that contain this complexing agent was determined by ICP-MS measurements and the distribution coefficient was determined. By comparing the distribution coefficients of the lanthanides with the coefficient for americium, one can obtain the separation factor. To obtain a good separation this factor should be considerably larger than unity. Figure 8.18 shows the distribution of some of the f-elements in dilute nitric acid solutions with 0.005 M dipicolinic acid added. The same distribution is plotted in figure 8.19 but without the presence of any complexing agents.

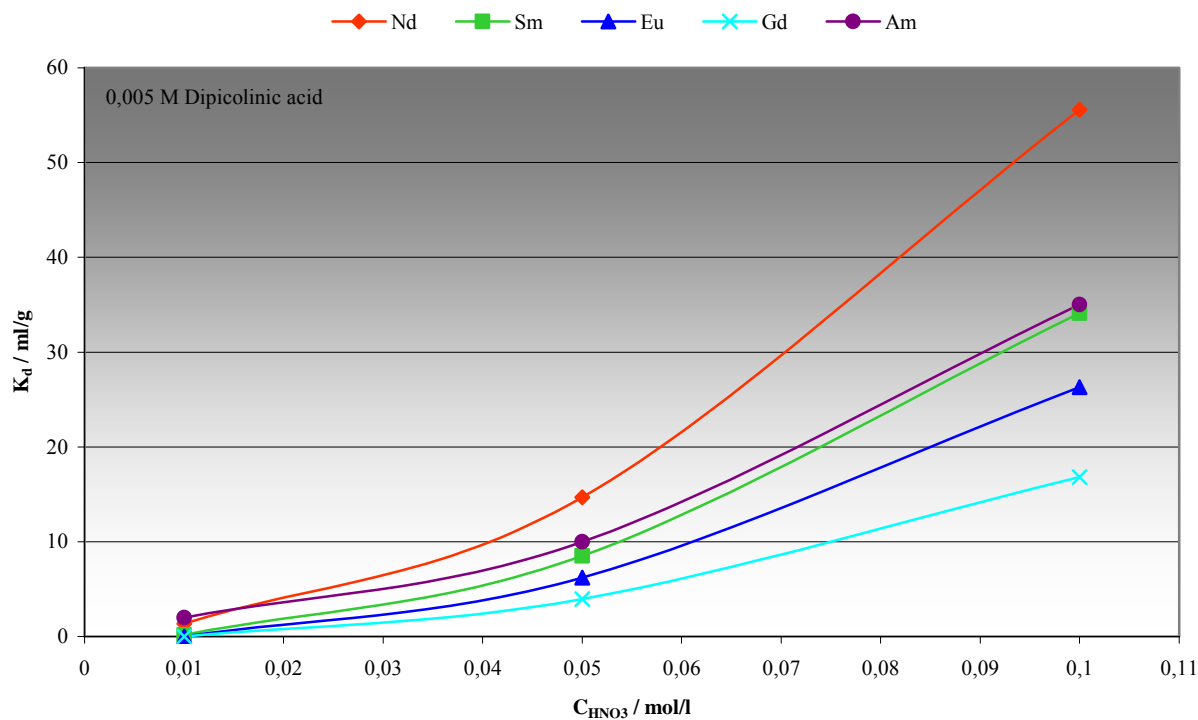


Figure 8.18: Distribution of the f-elements on the CMPO resin in presence of dipicolinic acid.

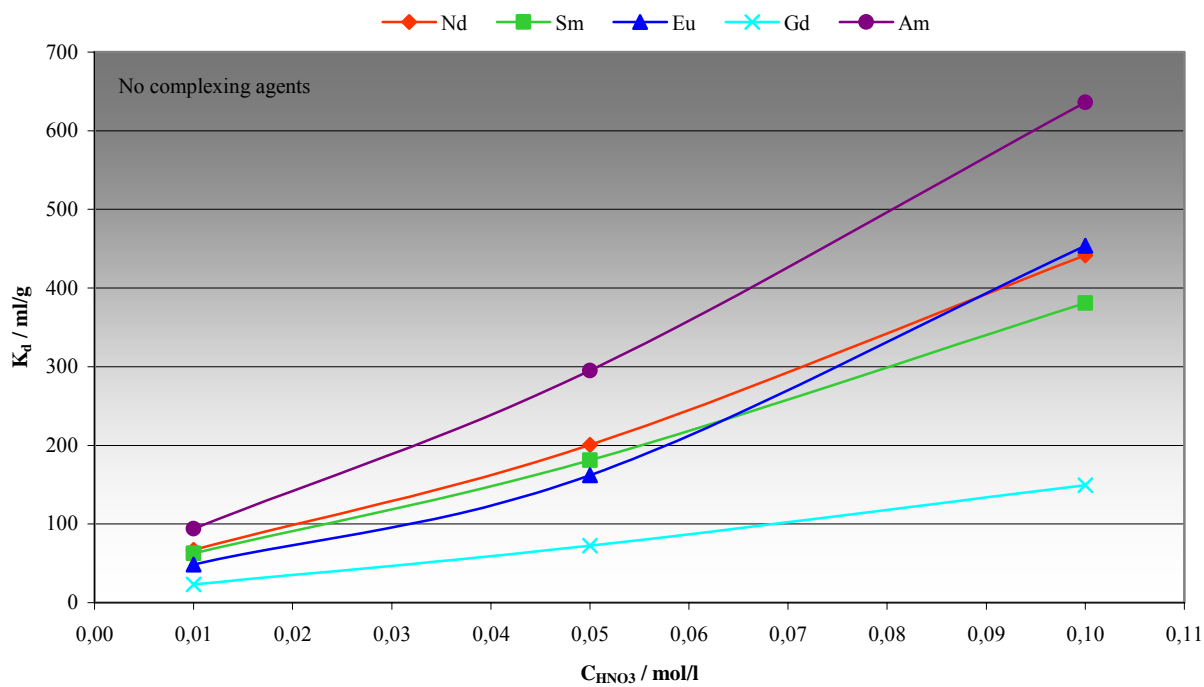


Figure 8.19: Distribution of the f-elements on the CMPO resin without complexing agents.

From these figures it can be seen that the addition of dipicolinic acid will make the separation even worse. Americium will then behave in the same manner as samarium while neodymium is more strongly absorbed by the resin. These results show that the addition of dipicolinic acid will not improve the envisioned lanthanide/actinide separation.

If no complexing agents are added to the system than the resin shows some discrimination between the lanthanides and the actinides. The most critical element in this separation seems to be neodymium but no separation factor larger than 1.5 was found as a result of this experiment. However, in order to develop an economically sound separation process, the separation factor will have to be considerably increased.

9. CONCLUSIONS

The powerful extractant octyl(phenyl)-N,N-diisobutyl- carbamoylmethylphosphine oxide (CMPO) shows a strong affinity for the trivalent f-elements. For the experiment a resin, based on porous silica particles that are impregnated with CMPO, was used. However, it is known that CMPO tends to show little distinction towards the lanthanides and actinides. Therefore the goal of this work was to look for a complexing agent that was able to complexate americium selectively and so “strip” this element from the resin. Up to six different complexants participated in the tests, each one containing soft and/or hard donor atoms.

From the experiments it could be seen that the affinity of the resin strongly depends on the nitric acid concentration. The affinity is minimal in the absence of nitric acid, rises to a maximum when the acid concentration increases, and drops when the acid concentration increases further. There was also a relatively large difference in affinity between the different lanthanides noticeable. CMPO has a much stronger affinity for light lanthanides like neodymium and samarium when compared with heavier elements like gadolinium. The former effect seems to support the theory of covalent bonding between the f-elements and soft-donor containing ligands.

In concentrated nitric acid solutions no complexing agent was found that exhibited the envisioned selectivity between the lanthanides and actinides. Some complexing agents, nonetheless they were positively charged due to protonation, seemed to retain trivalent f-elements from the resin. Since these positively charged molecules are unable to complexate any ions, the effect has to be based on another mechanism. Unfortunately, this unknown mechanism does not seem to make any distinction between the lanthanides and actinides. Other complexing agents were also found not to improve the separation of the trivalent lanthanides and actinides into an appreciable extent.

In dilute nitric acid solutions only dipicolinic acid was found to exhibit any noticeable affinity for the f-elements. Unfortunately this complexing agent does not make much distinction between the lanthanides and actinides. As a result of this lack of selectivity only a separation factor of 1.5 was found to be attainable, and this without adding any complexing agent.

As a final conclusion of this work, it can be said that out of the six investigated complexants, none was found to improve the lanthanide/actinide separation significantly. One of the reasons of this outcome is the fact that the promising – nitrogen containing – soft donor complexants are unable to do their job in highly acidic media. Also in dilute nitric acid solutions most of the complexing agents do not seem to work at all. Common complexing

agents need a more or less neutral environment to work efficiently, but this requirement is not compatible with the PUREX process. Therefore it can be suggested that new complexing agents need to be sought and if necessary synthesized. Another solution could be to abandon the use of water-soluble complexing agents and try to modify the extractant on the resin in order to improve the envisioned separation. This route requires however extensive knowledge of computational chemistry, molecular design and organic chemistry. It seems that the problem can be most easily solved through the first route, by adding complexing agents to the aqueous solution. Unfortunately it is not sure that currently there exists a complexing agent that is able to work in the desired acidity range and that at the same time makes a distinction between the lanthanides and actinides.

10. REFERENCES

1. Baetslé, L.H., Role and Influence of Partitioning and Transmutation on the Management of Nuclear Waste Streams, OECD/NEA report on P&T, N°3, August 1992.
2. Fugate, G.A., Complexation of f-elements with aminocarboxylates ligands, PhD thesis, Florida State University, 2004.
3. K. Gschneider, L. Eyring, G.R. Choppin, G.H. Lander, Handbook on the physics and chemistry of rare earths, Volume 18 Lanthanides/Actinides: Chemistry, Elsevier Science B.V., 1994.
4. Periodic table at Alamos National Laboratory, <http://pearl1.lanl.gov/periodic/default.htm>
5. Clefs 46, Sorting: Long-lived radionuclides partitioned at will, CEA, 2002
6. O.W. Hermann, S.M. Bowman, M.C. Brady, C.V. Parks, Validation of the SCALE System for PWR Spent Fuel Isotopic Composition Analyses, Oak Ridge National Laboratory, March 1995.
7. JANIS, A Java based Nuclear Data Display Program, Nuclear Energy Agency, www.nea.fr/janis/
8. Nuclear Energy Agency, "Actinide and Fission Product Partitioning and Transmutation: Status and Assessment Report", OECD Publications, France, 1999
9. Persson G., "Hot test of a TALSPEAK procedure for Separation of Lanthanides and Actinides Using Recirculating DTPA-Lactic Acid Solution", Solv. Extr. Ion Exch, Vol 2, pp. 89-113, 1984
10. Morita Y., "Diisodecylphosphoric acid, DIDPA, as an Extractant for Transuranium elements", International Conference on Evaluation of Emerging Nuclear Fuel Cycle Systems, Global '95, Vol 1, pp. 585 – 594, 1995.
11. Kubota M., "Formation of Precipitate in High-level Liquid Waste from Nuclear Fuel Reprocessing" J. Nucl. Sci & Tech, 17 (10), pp. 783 – 790, 1980.
12. Schulz W.W., Horwitz E.P., "The TRUEX Process and the Management of Liquid TRU Waste, Separation Science and Technology, 23 (12, 13), pp. 1355 – 1372, 1988.
13. Y. Koma et al, "The Concept of Separation Processes For Recovery of Americium and Curium", International Conference on Future Nuclear Systems, Global '97, Vol 1, pp. 598, 1997
14. Development of the MAREC Process for HLLW Partitioning Using a novel silica-based CMPO extraction resin, Yuezhou Wei, Journal of Nuclear Science and Technology, Vol 41, No 3, pp 315-322 (March 2004)
15. Zhu Y., "The Removal of Actinides from High-level Radioactive Waste by TRPO Extraction", Chinese J. Nucl. Sci. Eng., Vol 9, pp. 141 – 150, 1980.
16. Musikas C., "Potentiality of Non-organophosphorus Extractants in Chemical Separations of Actinides", Fifth Symposium on Separation Science and Technology for Energy Applications, Knoxville USA, 1987.
17. Vitorge P., Lanthanides and Trivalent Actinides Complexation by Tripyridyl Triazine, Applications to Liquid-Liquid Extraction, CEA-R-5270, 1984.
18. Zhu Y., "The Separation of Americium from the Light Lanthanides by CYANEX 301 Extraction", Radiochim. Acta, Vol 68, pp. 95-98, 1995.
19. Modolo G., "The Separation of Trivalent Actinides from Lanthanides by Dithiophosphonic Acids from HNO₃ Acid Medium, J. Alloys and Compounds, Vol. 271-273, pp. 248, 1998.

20. Kulyako Y.M., "Study on the Behaviour of Some Trans-plutonium Elements and Rare Earth Elements in Solution of Condensed Phosphate and Potassium Ferricyanide", Fourth International Conference on Nuclear and Radiochemistry, NRC4, St-Malo France, 1996.
21. Cordier P.Y., "De nouvelles Molecules pour la Séparation des Actinides: les Picolinamides", GECOM-CONCOORD '93, France, 1993.
22. Goto M., Novel organophosphorous Bi-functional Extractants for the Separation of Lanthanide and Actinide", International Conference on Future Nuclear Systems, Global '97, Vol 2, pp. 1466, 1997.
23. Nuclear Wastes, technologies for separations and transmutation, committee on separation technologies and transmutation systems, National Academy Press, Washington, 1996
24. E. Philip Horwitz, "Extraction Chromatography of actinides and selected fission products: principles and achievement of selectivity", Eichrom Technologies.
25. Colin F. Bell, Principles and Applications of Metal Chelation, Claredon Press, Oxford, 1977.
26. Shannon, Prewitt, Acta Crystallogr. B 25, 925, 1969.
27. T. H. Siddall, J. Inorg. Nucl. Chem. 25, 883, 1963
28. T. H. Siddall, J. Inorg. Nucl. Chem. 26, 1991, 1964
29. Nogami M., Private Communication, Institute for Research and Innovation, Japan, 2004.
30. Zhang et al, Resistant behavior of a novel silica-based octyl(phenyl)-N,N-diisobutyl carbamoylphosphine oxide neutral extraction resin against nitric acid, temperature and γ -radiation. Radiation Physics and Chemistry, Vol. 72, pp. 455-463, March 2005.
31. Portanova R, Critical evaluation of stability constants for α -hydroxycarboxylic acid complexes with protons and metal ions and the accompanying enthalpy changes part II: Aliphatic 2-hydroxycarboxylic acids, UIPAC Technical Report, 2003
32. Jensen M. P., "Aqueous Complexation of trivalent lanthanide and actinide cations by N,N,N',N'-tetrakis(2-pyridylmethyl)ethylenediamine", Journal of Alloys and Compounds, 303-304, pp. 137-141, 2000.
33. S. L. R. Ellison, M. Rosslein, A. Williams, Quantifying Uncertainty in Analytical Measurement, EURACHEM/CITAC Guide, Seconde Edition, 2000.
34. Visual MINTEQ 2.32, CEAM, EPA, US, 1999.

11. APPENDICES

11.1. Appendix I: Experiment A

Sample	Complexant	C _{HNO3} / mol/l	Nd / µg/l	Sm / µg/l	Eu / µg/l	Gd / µg/l	Kd / Nd	Kd / Sm	Kd / Eu	Kd / Gd
0	-	reference	69000	75000	71000	76000	-	-	-	-
1	Glycolic Acid	0	67000	70000	67000	71000	3	7	6	7
2		0,5	6900	8600	10500	18000	900	772	576	322
3		1,0	6100	7400	9100	15600	1031	914	680	387
4		2,5	6700	7800	9400	14400	930	862	655	428
5		5,0	11000	10600	11300	15600	527	608	528	387
6	Citric Acid	0	61000	66000	64000	67000	13	14	11	13
7		0,5	8500	10700	13500	21800	712	601	426	249
8		1,0	8000	9600	12000	19500	763	681	492	290
9		2,5	8900	10300	12200	18900	675	628	482	302
10		5,0	12200	11800	12600	17400	466	536	463	337
11	TPEN	0	63000	68000	66000	71000	10	10	8	7
12		0,5	9800	11900	15200	25200	604	530	367	202
13		1,0	8400	10500	13000	21500	721	614	446	253
14		2,5	8000	9200	11000	17600	763	715	545	332
15		5,0	11100	10900	11400	16100	522	588	523	372
16	HEDTA	0	64000	68000	66000	71000	8	10	8	7
17		0,5	7300	8700	10800	19200	845	762	557	296
18		1,0	6100	7400	9200	16000	1031	914	672	375
19		2,5	6500	7600	9000	14100	962	887	689	439
20		5,0	11300	10800	11500	16200	511	594	517	369
21	Dipicolinic Acid	0	60000	63000	61000	65000	15	19	16	17
22		0,5	12500	16700	20300	29700	452	349	250	156
23		1,0	9900	12600	15500	23900	597	495	358	218
24		2,5	9300	11000	12500	19900	642	582	468	282
25		5,0	11600	11000	11900	16600	495	582	497	358
26	DTPA	0	64000	68000	66000	71000	8	10	8	7
27		0,5	10400	12300	15600	25500	563	510	355	198
28		1,0	10200	12500	15100	24000	576	500	370	217
29		2,5	8900	10700	12300	19200	675	601	477	296
30		5,0	12300	11900	12500	17300	461	530	468	339

11.2. Appendix II: Experiment B

C _{HNO3} / mol/l	m _{CMPO} / g	Volume / ml	Nd / µg.l ⁻¹	Sm / µg.l ⁻¹	Eu / µg.l ⁻¹	Gd / µg.l ⁻¹	Kd(Nd) / ml.g ⁻¹	Kd(Sm) / ml.g ⁻¹	Kd(Eu) / ml.g ⁻¹	Kd(Gd) / ml.g ⁻¹
0,0	0,2567	20,0	6100	6100	6000	6200	87	105	101	101
0,5	0,2560	20,0	212	213	216	330	4676	5167	4913	3284
1,0	0,2515	20,0	128	156	166	293	7935	7210	6531	3774
2,5	0,2512	20,0	125	154	175	350	8137	7313	6199	3151
5,0	0,2564	20,0	166	215	255	490	5984	5110	4143	2182
1,0	0,2507	20,0	120	157	179	350	8496	7187	6071	3157
ref	0,0000	20,0	12900	14300	13800	14200	-	-	-	-

11.3. Appendix III: Experiment C

Microtube	C _{HNO3} /mol/l	Volume /ml	C _{eq} (Nd) / µg/g	C _{eq} (Sm) / µg/g	C _{eq} (Eu) / µg/g	C _{eq} (Gd) / µg/g	mass CMPO /g	Kd /ml/g	Kd /ml/g	Kd /ml/g	Kd /ml/g	Uncertainty / %
Glycolic acid												
1	0,10	20	1590	1860	2320	3600	0,150	445	426	303	159	3,50%
2	0,05	20	4200	4900	5200	6300	0,150	86	79	62	34	4,31%
3	0,01	20	6800	7600	7500	7800	0,150	2	4	2	2	4,66%
Citric acid												
4	0,10	20	1660	1970	2440	3700	0,150	421	395	282	151	3,53%
5	0,05	20	4300	5000	5400	6500	0,150	81	75	54	29	4,20%
6	0,01	20	6600	7500	7300	7800	0,150	6	5	5	2	4,84%
TPEN												
7	0,10	20	1690	2050	2530	3800	0,150	411	374	267	144	3,53%
8	0,05	20	4400	5100	5500	6600	0,150	76	71	51	26	4,56%
9	0,01	20	6700	7500	7500	7800	0,150	4	5	2	2	4,37%
DTPA												
10	0,10	20	1560	1930	2400	3600	0,150	456	406	289	159	3,41%
11	0,05	20	4400	5300	5800	6600	0,150	76	63	41	26	4,03%
12	0,01	20	6800	7700	7500	7900	0,150	2	2	2	0	4,43%
DPA												
13	0,10	20	6300	7300	7200	7700	0,150	13	9	7	3	3,54%
14	0,05	20	6900	7800	7600	7800	0,150	0	0	0	2	4,30%
15	0,01	20	6900	7700	7500	7800	0,150	0	2	2	2	4,18%
HEDTA												
16	0,10	20	1640	1940	2420	3600	0,150	428	403	285	159	3,53%
17	0,05	20	4300	5100	5500	6400	0,150	81	71	51	31	4,57%
18	0,01	20	6800	7600	7500	7800	0,150	2	4	2	2	4,82%
None												
19	0,10	20	1600	1940	2430	3700	0,150	442	403	284	151	3,53%
20	0,05	20	4300	5100	5500	6500	0,150	81	71	51	29	4,52%
21	0,01	20	6600	7400	7200	7600	0,150	6	7	7	5	4,77%
Reference												
22	0	20	6900	7800	7600	7900	0					

11.4. Appendix IV: Experiment D

Microtube	C _{HNO3} /mol/l	Volume /ml	Counts per minute	mass CMPO /g	K _d /ml/g	Uncertainty /%
Citric Acid						
1	0,1	1,000	5121	0,1001	360	3,50%
2	0,5	1,000	545	0,1001	3470	4,31%
3	1,0	1,000	376	0,1014	4970	4,66%
4	2,5	1,000	448	0,1008	4194	4,48%
5	5,0	1,000	772	0,1011	2423	4,06%
Glycolic acid						
6	0,1	1,000	4246	0,1009	433	3,53%
7	0,5	1,000	626	0,1010	2993	4,20%
8	1,0	1,000	322	0,1006	5851	4,84%
9	2,5	1,000	502	0,1002	3764	4,38%
10	5,0	1,000	769	0,1000	2459	4,07%
HEDTA						
11	0,1	1,000	4290	0,1007	430	3,53%
12	0,5	1,000	416	0,1012	4500	4,56%
13	1,0	1,000	505	0,1006	3727	4,37%
14	2,5	1,000	527	0,1010	3557	4,34%
15	5,0	1,000	587	0,1003	3215	4,25%
DPA						
16	0,1	1,000	52374	0,1005	26	3,41%
17	0,5	1,000	809	0,1012	2309	4,03%
18	1,0	1,000	473	0,1008	3972	4,43%
19	2,5	1,000	468	0,1010	4007	4,44%
20	5,0	1,000	594	0,1004	3173	4,24%
DTPA						
21	0,1	1,000	3957	0,1005	467	3,54%
22	0,5	1,000	553	0,1008	3396	4,30%
23	1,0	1,000	644	0,1011	2906	4,18%
24	2,5	1,000	438	0,1005	4303	4,51%
25	5,0	1,000	654	0,1005	2878	4,17%
TPEN						
26	0,1	1,000	4253	0,1004	435	3,53%
27	0,5	1,000	411	0,1013	4550	4,57%
28	1,0	1,000	329	0,1012	5692	4,82%
29	2,5	1,000	393	0,1007	4787	4,62%
30	5,0	1,000	605	0,1011	3094	4,23%
None						
31	0,1	1,000	4233	0,1004	437	3,53%
32	0,5	1,000	430	0,1002	4396	4,52%
33	1,0	1,000	343	0,1007	5487	4,77%
34	2,5	1,000	415	0,1008	4528	4,56%
35	5,0	1,000	660	0,1000	2866	4,17%
Reference						
36	0,0	1,000	189848	0,0000	nvt	

11.5. Appendix V: Experiment E

Microtube	C _{HNO3} /mol/l	Volume /ml	Counts per minute	mass CMPO /g	Kd /ml/g	Uncertainty / %
Glycolic Acid						
1	0,10	1,000	3000	0,1001	616	3,58%
2	0,05	1,000	6427	0,1001	282	3,48%
3	0,01	1,000	18436	0,1014	91	3,43%
Citric acid						
4	0,10	1,000	3445	0,1009	531	3,56%
5	0,05	1,000	6938	0,1010	258	3,48%
6	0,01	1,000	21456	0,1006	77	3,42%
DPA						
7	0,10	1,000	41420	0,1007	35	3,41%
8	0,05	1,000	93001	0,1012	10	3,42%
9	0,01	1,000	163065	0,1006	2	3,70%
DTPA						
10	0,10	1,000	3120	0,1005	589	3,57%
11	0,05	1,000	5976	0,1012	301	3,49%
12	0,01	1,000	20491	0,1008	81	3,42%
HEDTA						
13	0,10	1,000	3162	0,1005	581	3,57%
14	0,05	1,000	6267	0,1008	288	3,49%
15	0,01	1,000	21826	0,1011	75	3,42%
TPEN						
16	0,10	1,000	3174	0,1004	580	3,57%
17	0,05	1,000	6362	0,1013	282	3,48%
18	0,01	1,000	19260	0,1012	87	3,43%
None						
19	0,10	1,000	2900	0,1004	636	3,59%
20	0,05	1,000	6153	0,1002	295	3,49%
21	0,01	1,000	17882	0,1007	94	3,43%
Reference						
22	0,0	1,000	187948	0,0000	nvt	

Complexing Agent	C _{HNO3} /mol/l	Nd / μg/l	Sm / μg/l	Eu / μg/l	Gd / μg/l	m _{CMPO} / g	V / ml	K _d (Nd) / ml/g	K _d (Sm) / ml/g	K _d (Eu) / ml/g	K _d (Gd) / ml/g
None	0,10	24,1	39	46	66	0,1004	1,000	55,3	34,0	26,2	16,8
None	0,05	64	93	103	127	0,1002	1,000	14,7	8,48	6,20	3,93
None	0,01	139	169	169	182	0,1007	1,000	1,36	0,18	0	0
Dipicolinic Acid	0,10	3,5	4,4	3,6	11,1	0,1007	1,000	438	378	451	148
Dipicolinic Acid	0,05	7,5	9	9,7	21,5	0,1012	1,000	198	179	160	71,5
Dipicolinic Acid	0,01	20,5	23,7	28,6	53	0,1006	1,000	66,7	62,2	48,1	23,3

Reference	0,1	158	172	167	177
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