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Annual report 2009

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Nuclear Chemistry
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Abstract

The long-lived elements in the spent nuclear fuels are mostly actinides, some fission products (^{79}Se, ^{87}Rb, ^{99}Tc, ^{107}Pd, ^{126}Sn, ^{129}I and ^{135}Cs) and activation products (^{14}C, ^{36}Cl, ^{59}Ni, ^{93}Zr, ^{94}Nb). To be able to destroy the long-lived elements in a transmutation process they must be separated from the rest of the spent nuclear fuel for different reasons. One being high neutron capture cross-sections for some elements, like the lanthanides. Other reasons may be the unintentional production of other long lived isotopes. The most difficult separations to make are those between different actinides but also between trivalent actinides and lanthanides, due to their relatively similar chemical properties. Solvent extraction is an efficient and well-known method that makes it possible to have separation factors that fulfil the highly set demands on purity of the separated phases and on small losses. In the case of a fuel with a higher burnup or possible future fuels, pyro processing may be of higher advantage due to the limited risk of criticality during the process.

Chalmers University of Technology is involved in research regarding the separation of actinides and lanthanides and between the actinides themselves as a partner in several European frame work programmes. These projects range from NEWPART in the 4th framework via PARTNEW and EUROPART to ACSEPT in the present 7th programme. The aims of the projects have now shifted from basic understanding to more applied research with focus on process development. One process, the SANEX (Selective ActiNide EXtraction) is now considered to be working on a basic scale and focus has moved on to more process oriented areas. However, since further investigations on basic understanding of the chemical behaviour are required, we have our main focus on the chemical processes and understanding of how they work. Our work is now manly focussed on the so called GANEX (Group ActiNide EXtraction) process. We have proposed a novel process along these concept lines and continue to optimise it. In this work process considerations have been taken into account which has lead to synthesis of new molecules for preventing undesired extraction of different fission products. A substantial effort has also been made in the understanding of the radiolytic behaviour of the solvents used both in our own GANEX process and also for the processes suggested by our partners in ACSEPT.

Sammanfattning

De långlivade ämnena i det använda kärnbränslet består till största delen av aktinider, en del fissionsprodukter (^{79}Se, ^{87}Rb, ^{99}Tc, ^{107}Pd, ^{126}Sn, ^{129}I, ^{135}Cs) och aktiveringsprodukter (^{14}C, ^{36}Cl, ^{59}Ni, ^{93}Zr, ^{94}Nb). För att kunna förstöra de långlivade ämnena i en transmutationsprocess måste de separeras från resten av det använda kärnbränslet. En av anledningarna är det höga tvärsnitt för neutroninfångning som finns hos bland annat lantaniderna. Andra anledningar kan vara en önskan att inte framställa andra långlivade isotoper från nu stabila eller kortlivade ämnen. De svåraste separationerna att göra är de mellan trevärda aktinider och lantanider, på grund av deras relativt liknande kemi, samt de mellan aktiniderna själva. Vätskeextraktion är en effektiv och välkänd metod som gör det möjligt att uppnå separationsfaktorer som uppfyller de högt ställda kraven på renhet i de separerade faserna och små förluster i processen. Om man i stället skulle ha ett högutbränt bränsle eller vissa möjliga framtida bränslen kan en så kallad pyroprocess vara att föredra. I detta fall är kriticitetsrisken under upparbetningen väsentligt lägre.

Chalmers tekniska högskola deltar i forskningen rörande separationen av aktinider och lantanider och mellan aktiniderna själva, genom att vara en partner i flera ramprogram finansierade av EU. Dessa projekt sträcker sig från NEWPART i det 4:e ramprogrammet via PARTNEW och EUROPART till ACSEPT i 7:e ramprogrammet. Målet med arbetet har under denna tid flyttats från grundläggande förståelse till mer tillämpad forskning med processberäkningar och test med riktigt använt kärnbränsle. En process, SANEX (Selective ActiNde EXtraction), anses nu fungera på labskala varför dess utveckling nu i huvudsak förs inom den mer processorienterade forskningen. Dock behövs fortfarande grundläggande kunskaper varför vår fokus fortfarande ligger på grundläggande kemiska frågor och förståelse för ingående processer. I nuläget fokuserar vi mest på den så kallade GANEX-processen (Group ActiNide EXtraction). På grund av nyrekryteringar kommer vi nu även att utveckla och syntetisera nya extraktionsreagenser. Detta kommer att minska svarstiden mellan tillverkning av ett nytt reagens och testen av dess effektivitet.

Contents

1 Introduction

The Partitioning and Transmutation (P&T) group at Nuclear Chemistry and Industrial Materials Recycling, Department of Chemical and Biological Engineering at Chalmers University of Technology investigates the separation of different chemical elements in spent nuclear fuel, for purification and/or recovery in a future transmutation process.

Solvent extraction is used already today in e.g. France, UK and Russia in the reprocessing of spent nuclear fuel, i.e. the recirculation of uranium and plutonium back into the fuel cycle. This means that a lot of expertise on how to handle highly active aqueous and organic solutions already exists. Solvent extraction is also a good technique to use considering the high efficiency of separation that can be achieved.

Internationally, other processes such as molten salt electrolysis and chromatographic methods are also investigated. These so called pyro processes are of particular interest when it comes to high burnup fuel and possible future fuel types due to the very limited risk of criticality in the developed process.

The Chalmers group has been involved in the separation for transmutation research throughout three different European Union framework programmes*;* NEWPART (1996–1999), PARTNEW (2000–2003) and EUROPART (2004–2007). During this time the focus has changed slightly although the main content has remained the same. As time has passed the main effort has been more and more focussed on process development. In the early years there was a search for suitable extracting agents for separation of trivalent lanthanides from trivalent actinides following the CHON principle (only containing carbon, hydrogen, oxygen and nitrogen). This separation, the so called SANEX (selective Actinide EXtraction) is now considered to be working on an acceptable level, which is why the basic research is now redirected towards other, more sophisticated separation schemes, e.g. the GANEX (Group Actinide Extraction). The SANEX research has now continued in a different direction. Instead of improving the basic characteristics of the extracting ligand a further and closer collaboration with process expertise is made to make sure that the molecules not only have good separation capabilities but also work practically in a process. In addition, extra focus has been put on the whole organic system since by changing the diluent the hydrolytic and radiolytic stability can be increased as well as the separation factor enhanced. To further work towards an industrial process, Chalmers is since 2008 a partner in the 7th European Union framework programme ACSEPT (2008–2012).

A substantial collaboration has started in Sweden between Chalmers and KTH on the issue of fuel fabrication. Present a fuel fabrication lab is prepared at Chalmers which will be in connection to the existing separation lab and thus the border between the fuel and separation research will be significantly decreased.

The main experimental work at Chalmers concerns the extraction properties and other basic chemical characteristics of extraction ligands. The department also house the development and synthesis of new ligands in the organic laboratory. Typical factors studied at Chalmers are, among others: the influence on extraction of pH, kinetics, ionic strength and media, absorbed dose and concentration of the involved species are studied in combination with modelling of the systems using e.g. solubility parameters. The role of the diluent used has been investigated in some detail and during 2009 a thesis dealing with this subject was presented. A new GANEX process has been designed and related issues have been investigated in depth. We have further spent a significant work on the radiolytic behaviour of BTBP based extraction systems ranging from basic studies of the effect of dose on the distribution of different metals to deep chemical investigation aimed at understanding the basics of the degradation process and identifying pathways and products.

2 Research

During 2009 typically three to four PhD students have worked in the project. Teodora Retegan finished her work on "the effect of side groups of the extracting ligands and the diluent effects". She defended her thesis on the subject the 13th of March 2009. Catharina Nästrén made most of her work at ITU in 2005–2007 and her appointment at Chalmers ended in April 2009. She will defend her thesis in 2010. Anna Fermvik is studying the effects of radiolysis on several selected extraction systems. She will be on maternity leave during part of 2010 and then present her thesis during 2011. Emma Aneheim has mainly been working with most aspects of a novel GANEX extraction system. A new PhD student, Elin Löfström-Engdahl, was recruited in November 2009. She will in the beginning study the experimental findings presented by Teodora Retegan and investigate the possibility of theory building of diluent and side group effects mainly in BTBP based extraction systems.

Dr. Mark Foreman is working 50% within this project and 50% with other material recycling issues. The main part of his work this year has been on synthesis of suppressing ligand for several fission and corrosion products that are extracted by our novel GANEX solvent.

A diploma worker, Karin Wald, started to work in the P&T group during 2008 but due to maternity leave her work is not yet finished. She is studying the behaviour of a synergic mixture often used as a model system a decade ago, α-bromodecanoic acid and terpyridine in tributylbenzene (TBB), in collaboration with Zoltan Szabo at KTH.

Sofie Englund is working at OKG AB but is still involved in this project at about 10% intensity.

The ACSEPT project started in March 2008 and during 2009 there were two meetings: a 1st Annual Meeting in Madrid in March and a Half Yearly Meeting in Bologna in September. The first meeting included presentations of work done during the first year of ACSEPT, while the second meeting was primarily dedicated to education and training by workshops and seminars on e.g. radiolysis and GANEX, organised by the Domain 4 group (Education & Training).

3 General information

Below are some definitions that will be used throughout the report to minimise the need for repetition and hence increase the readability.

3.1 Extraction

Throughout the report the concepts of distribution ratio (D) and separation factor (SF) are frequently used in the context of extraction and they are defined as follows:

$$D = \frac{[A]_{org}}{[A]_{aq}}$$

D = the ratio of the total concentration of a substance, A, in the organic phase to its concentration in the aqueous phase.

$$SF_{A/B} = \frac{D_A}{D_B}$$

$SF_{A/B}$ = the ratio between the distribution ratios of two different ions (A and B) in the same system.

3.1.1 Standard extraction experiment

Most extraction experiments presented in this report are performed in a similar manner and therefore a standard experimental procedure is stated here and will be referred to in the text.

Almost exclusively 3.5 mL glass vials are used for the extraction experiments. The volumes most commonly used are therefore 200–500 µL of organic phase and 200–500 µL of aqueous phase. Due to the mutual solubility of some of the diluents used (e.g. cyclohexanone) and the acidic water phases (e.g. water with 1 M nitrate concentration), both phases used for extraction are pre-equilibrated with the corresponding aqueous and organic solution. The organic phase contains 0.005–0.01 M extractant dissolved in a selected diluent and the aqueous phase contains HNO_3 of various concentrations and the metals to be extracted. When radioactive isotopes are used the metals are added in trace amounts by spiking the aqueous phase with concentrated stock solutions (often 10–20 µL are added). The phases are contacted either by vigorously hand-shaking in an isolated canister in which the vials are placed or in a shaking machine connected to a thermostatic bath. The contact time depends on how long time it takes for the extraction system to reach equilibrium. After contact, the phases are left to separate either by gravitation or by centrifuging. When the phases are completely separated samples from each phase are taken for analysis and prepared in different ways depending on the detection method used.

^{241}Am and ^{152}Eu are commonly used as radiotracers to act as analogues for trivalent actinides and trivalent lanthanides, respectively.

3.2 Detection

The equipment most commonly used for analysis will only be described in detail here and in the rest of the text just referred to by name.

HPGe 1: High Performance Germanium detector for γ-radiation (Ortec, GEM 15180-S)

HPGe 2: High Performance Germanium detector for γ-radiation (Ortec, Gamma Analyst GEM 23195) with automatic sampler

Liquid Scintillator 1: Liquid scintillation detector for α- and β-radiation (Wallac 1414 WinSpectral)

Liquid Scintillator 2: Liquid scintillation detector for α- and β-radiation (LKB Wallac 1219 Rackbeta)

NaI: NaI(Tl) scintillation well detector (Intertechnique GC-4000)

ICP-OES: Thermo iCAP 6500 Inductively Coupled Plasma Optical Emission Spectrometer

ICP-MS: ELAN 6000 Inductively Coupled Plasma Mass Spectrometer

Spectrophotometer 1: Perkin Elmer Lambda 19 UV/VIS/NIR spectrometer

Spectrophotometer 2: Ocean Optics Inc LS-1 Tungsten Halogen Lamp

3.3 Gamma irradiation sources

^{60}Co-source: A ^{60}Co-source (Gamma cell 220 from Atomic Energy of Canada ltd) at Chalmers with a calibration certificate from 1961-12-28 with the activities (uncertainty 3%):

Central position: 556,000 rad/h
Top position: 513,000 rad/h
Bottom position: 522,000 rad/h

The estimated dose given to samples put in the source is now approximately 10 Gy/h.

In December 2009 the irradiation source was transported to Germany to be recharged up to 0.913 PBq, which will correspond to a maximum dose rate of approximately 20 kGy/h.

^{60}Co-source: A ^{60}Co-source (Issledovatel) at Instytut Chemii I Techniki Jadrowej, Poland with an approximate dose rate of 0.939 kGy/h (April 2009).

In the end of 2009 the ^{60}Co-source was sent off to be recharged. It will be returned to Chalmers in the spring 2010 and will then give a maximum dose rate of approximately 20 kGy/h. In addition, during 2009 Chalmers took over six ^{137}Cs-sources of 111 GBq each. They will be used to build a "low dose irradiator", which will give 5–10 Gy/h. Thus, it will more or less correspond to the "old" ^{60}Co-source.

3.4 Extraction processes

A number of different extraction processes have been suggested for the partitioning of spent nuclear fuel. The processes of concern in this report are:

PUREX: (**P**lutonium **U**ranium **R**edox **EX**traction). A well established process used for many years to recover uranium and plutonium from spent nuclear fuel. The metals are co-extracted from an acidic solution using TBP in kerosene and then separated by selective stripping using redox control.

DIAMEX: (**DIAM**ide **EX**traction) /29/. Co-extraction of actinides and lanthanides from PUREX raffinate using diamides as extracting agents, e.g. DMDOHEMA /49/.

r-SANEX: regular SANEX (**S**elective **A**cti**N**ide **EX**traction) /30/. This process aims at extracting trivalent actinides into an organic phase with the use of a nitrogen donor ligand as extractant. The lanthanides are left in the aqueous phase and a good An/Ln separation is achieved. The r-SANEX feed consists of the extract stream from the DIAMEX process.

i-SANEX: innovative SANEX (**S**elective **A**cti**N**ide **Ex**traction). A further development of r-SANEX. Actinides and lanthanides are co-extracted into an organic phase followed by selective back extraction of the actinides with a hydrophilic complexing agent.

GANEX: (**G**roup **A**cti**N**ide **Ex**traction) /35/. As the name suggests, the idea behind this process is to simultaneously remove all the actinides from the dissolved spent fuel. This renders a separation of the actinides from the lanthanides as well as the rest of the fission and corrosion/activation products in one step. This separation can be done either from dissolved fuel where the bulk part of the uranium already has been removed or directly from the dissolved spent fuel.

4 BTBP-chemistry

The use of nitrogen-containing heterocyclic molecules following the CHON-principle (should contain only carbon, hydrogen, oxygen and nitrogen) has been shown to efficiently separate actinides and lanthanides using solvent extraction /15/. One of the latest groups of molecules to be designed and developed was the BTBPs.

4.1 BTBP

BTBP is an abbreviation for *bis*-triazin-*bi*-pyridine, which refers to the nature of the central core common to all the molecules in the family (see Figure 4-1). This is a group of molecules that can act as tetradentate ligands to metal ions and a high selectivity towards trivalent actinides over trivalent lanthanides has been observed /37, 24, 38/.

The extracting properties of the molecules and their possibilities to be used in a process are dependent on factors like the extraction and separation ability, solubility, kinetics of extraction, stability towards irradiation, etcetera. Depending on the side groups (denoted R, in Figure 4-1) and different attachments to the BTBP core-molecule these properties change /45, 14/.

The different BTBP's referred to in the report are shown below in Figure 4-2 with molecular structures.

Various experiments have been performed to further explore the general chemistry of the BTBPs, mainly focussed on properties that are of importance in solvent extraction processes. Some of the different studies are presented below:

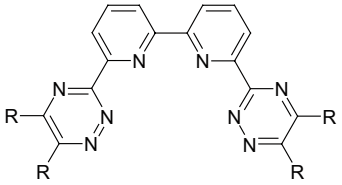


Figure 4-1. *The bis-triazin-bipyridine, or BTBP, core molecule.*

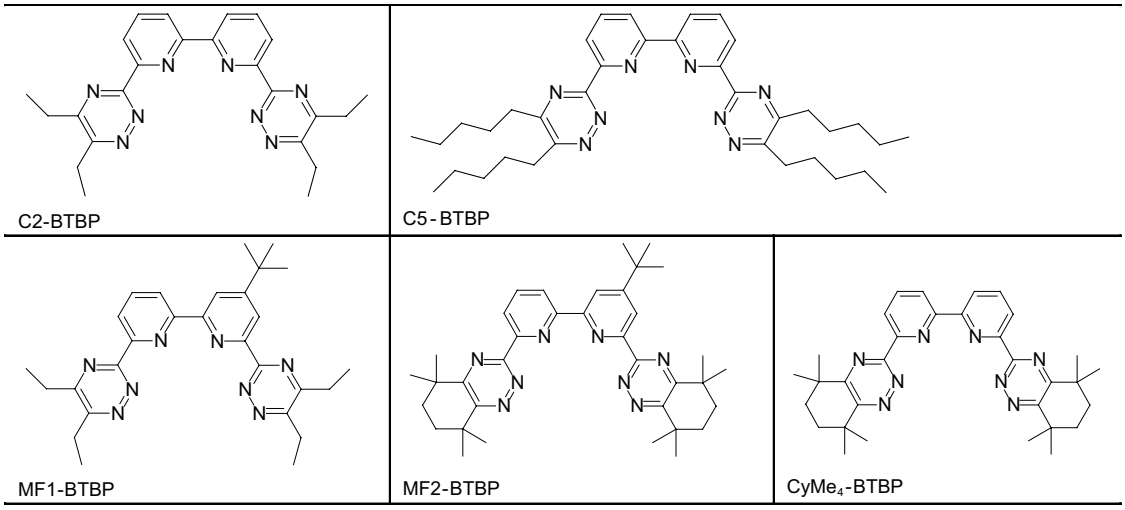


Figure 4-2. *Molecular structures of the BTBP molecules discussed in this report.*

4.2 Extraction of Cu, Ag and Cd

Extraction experiments were done with the extractant C_2-BTBP and the metals silver, cadmium and copper to establish in which proportions the extracted ligand-metal complexes are built up. Cyclohexanone was used as organic diluent and five different concentrations of extractant was used. The aqueous phases used were nitric acid (Ag and Cd) and perchloric acid (Cu) with varying metal content. The experiments were performed as the standard extraction experiment described above but with the volumes adjusted to 1 mL organic phase and 1 mL aqueous phase. The aqueous phase before and after contacting was analyzed with ICP-OES. Analyzes were repeated twice and all extractions were made in double samples.

4.2.1 Silver

Figure 4-3 shows the results for silver. The linear regressions for both series give a mean slope of 0.2573 ± 0.174 for series 1 and 0.2605 ± 0.148 for series 2, with the confidence 95%. Due to these broad confidence intervals the extractions will be performed once again and analyzed with ICP-MS and radioactive tracer ^{110}Ag. This will hopefully increase the reproducibility of the results.

4.2.2 Cadmium

The log-log graph for cadmium is shown in Figure 4-4. Linear regression gives an average slope of 1.259 ± 0.645 for series 1 and 1.196 ± 0.257 for series 2, with the confidence 95%. Due to these broad confidence intervals and the fact that cadmium has very high D-values (> 500 for high BTBP concentrations), which decreases the reliability of the results, the extraction experiment will be repeated and analyzed with ICP-MS and radioactive tracer ^{109}Cd.

4.2.3 Copper

Figure 4-5 shows the measured values for copper. The linear regression gives an average slope of 0.605 ± 0.383 for series 1 and 0.5663 ± 0.383 for series 2, with the confidence 95%. Also these measurements will be repeated and analyzed with ICP-MS to lower the detection limit and to decrease the uncertainty.

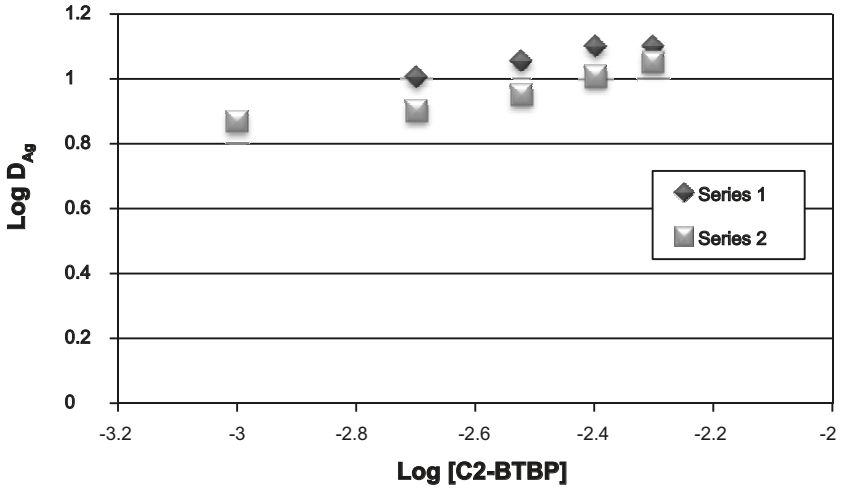


Figure 4-3. *Log-log curve for silver extracted from an aqueous phase with C_2-BTBP in cyclohexanone. Uncertainties are included in the sample points.*

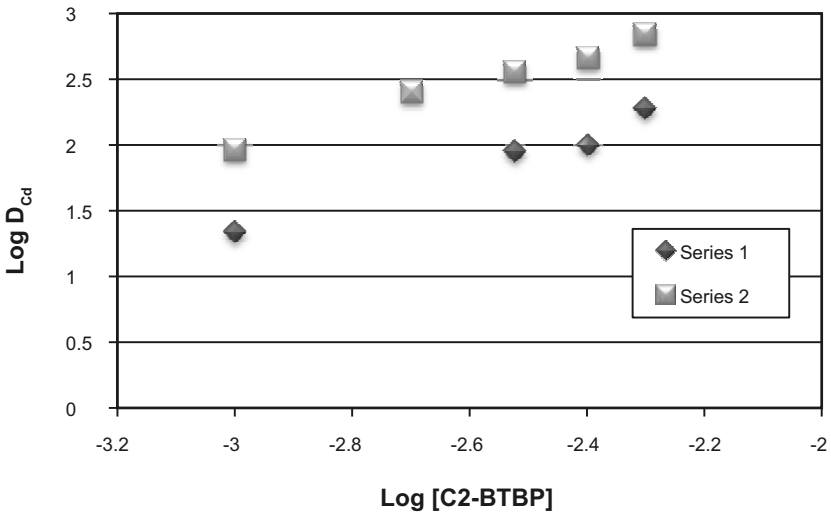


Figure 4-4. *Log-log curve for cadmium extracted from an aqueous phase with C_2-BTBP in cyclohexanone. Uncertainties are included in the sample points.*

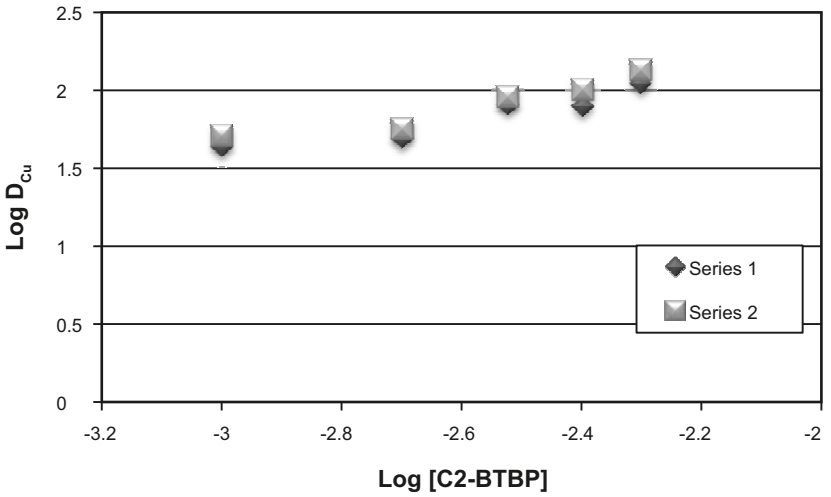


Figure 4-5. *Log-log curve for copper extracted from an aqueous phase with C_2-BTBP in cyclohexanone. Uncertainties are included in the sample points.*

4.3 Crystal structures of BTBP complexes with Cu, Ag and Cd

Single X-ray diffraction was performed on the metal complexes of Cu, Ag and Cd with C2-BTBP and the aim was to compare crystallographic results with the results from the extraction experiments presented above. The analyses were performed at the University of Reading by Professor Michael Drew. The crystals used were obtained by the vapour diffusion of diethyl ether into acetonitrile solutions of the metal complexes.

The crystallographic results suggest that for copper it is possible to form both 1:1 and 1:2 complexes with BTBP. If the perchlorate oxygen atoms are ignored, the copper in the 1:1 complex is in a square planar complex (see Figure 4-6). The perchlorate oxygens are over 2.3 Å from the copper atom while the four nitrogens are on average less than 2.0 Å from the copper atom. This suggests that in a strong donor solvent such as water, the perchlorates will only weakly coordinate to the copper atom.

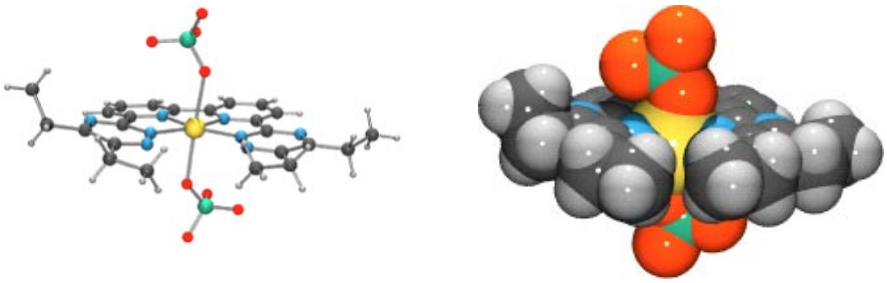


Figure 4-6. *Two views of the 1:1 copper complex.*

The 1:2 complex has a distorted octahedral coordination geometry around the copper (see Figure 4-7). The distortion can be explained by the Jahn-Teller effect which is well known to occur in copper(II) complexes. The coordination can be described as four equatorial nitrogen atoms (on average 2.04 Å from the copper) with two axial sites occupied by nitrogen atoms which are 2.30 and 2.41 Å from the copper atom.

The results ($d \log_{10}(D_{Cu})/d \log_{10}[BTBP] = 0.605$ or 0.566) from the solvent extraction experiments suggest that over the concentration range used, the extraction of copper is at least in part controlled by the affinity of the copper to the BTBP. On a 95% confidence level we cannot neglect the hypothesis that the 1:1 complex dominates in solution.

In the solid state the cadmium is bonded to eight nitrogens from two different BTBP molecules (see Figure 4-8). This *bis* η4-BTBP cadmium complex is likely to be similar to that of yttrium, or a smaller f-block metal. Hence it is reasonable to expect that two BTBP molecules will be required for the extraction of each cadmium atom.

However the slope ($d \log_{10}(D_{Cd})/d \log_{10}[BTBP]$) is only 1.2, suggesting that likely both 1:1 and 1:2 complexes exist, but the 1:1 is the dominating structure for the cadmium:BTBP complex.

The solid state structure of the 2:2 silver complex is a short double helix which is reminiscent of the structure of DNA (see Figure 4-9). The graph of the silver distribution ratio as a function of the BTBP concentration suggests that it may be possible that the partitioning of the silver BTBP complex between the two phases is largely responsible for determining the distribution ratio ($d \log_{10}(D_{Ag})/d \log_{10}[BTBP] = 0.25$).

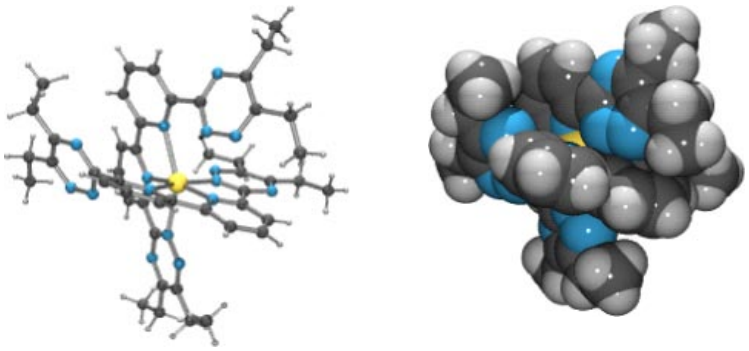


Figure 4-7. *Two views of the 1:2 copper complex.*

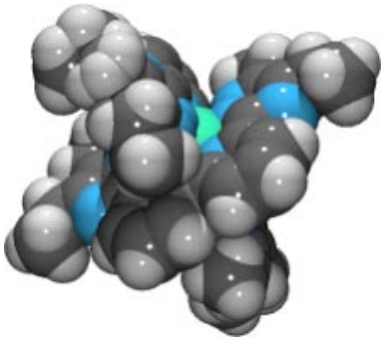


Figure 4-8. *A view of the 1:2 cadmium complex.*

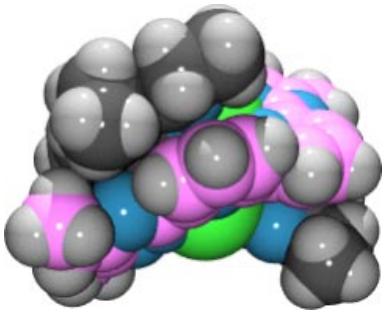


Figure 4-9. *A view of the di-silver complex showing the carbons of one BTBP in pink and the other with grey carbons.*

4.4 Thermodynamics of dissolution

An important aspect when using the BTBP molecules as extractants is the solubility of the molecule in the selected diluent. Different BTBPs have previously shown different solubility in various diluents and therefore dissolution experiments with C2-, $CyMe_4$-, C5-, MF1- and MF2-BTBP in cyclohexanone and octanol at different temperatures were performed to obtain entropy and enthalpy of dissolution.

4.4.1 Theory

The dissolving process of a solid phase in reaction (1) can be described by the solubility constant K_s in equation (2).

$$BTBP(s) \rightarrow BTBP(l) \tag{1}$$

$$K_s = \frac{\{BTBP(l)\}}{\{BTBP(s)\}} = \frac{[BTBP(l)] \cdot \gamma_{BTBP(l)}}{\{BTBP(s)\}} \tag{2}$$

where {BTBP(l)} and {BTBP(s)} are the chemical activities of the molecule dissolved in a diluent and in solid state, [BTBP(l)] and $\gamma_{BTBP(l)}$ are the concentration and the activity coefficient of dissolved molecule in diluent, respectively. The activity of the solid state is equal to 1 and it is also assumed that the activity coefficient of the dissolved molecule $\gamma_{BTBP(l)}$ is equal to 1, since the molecule in the solution is not charged and the activity coefficient $\gamma_{BTBP(l)}$ strongly depends on the charge interactions in the solution. With this assumption the solubility constant equals the concentration of dissolved BTBP molecule.

The Gibbs free energy change (ΔG^0) during the dissolution can be calculated by using either the solubility constant, K (3), or the change in enthalpy and entropy (4). Values of enthalpy (ΔH^0) and entropy (ΔS^0) at standard state can be determined by measuring the solubility (= solubility constant) at a number of different temperatures (5). However, this requires that the enthalpy and entropy are temperature independent in the specific temperature range:

$$\Delta G^0 = -RT \ln K_s \quad (3)$$

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \quad (4)$$

$$\ln K_s = -\frac{\Delta H^0}{R} \cdot \frac{1}{T} + \frac{\Delta S^0}{R} \quad (5)$$

where R is the molar gas constant, T is the absolute temperature, ΔH^0 is the enthalpy change for the dissolution and ΔS^0 is the entropy change for the dissolution. Here it is assumed that the solubility is sufficiently low in order to make ligand-ligand interaction negligible compared to ligand-diluent interactions. The enthalpy and entropy of dilution are also neglected compared to those for dissolution.

4.4.2 Experimental

BTBP molecules forms colored complexes with iron and the degree of light absorption, determined in spectrophotometer 2, by these colored complexes can be used to estimate the BTBP concentration. A calibration curve was constructed for each BTBP using solutions with known concentrations. The absorbance was measured for three samples containing 10 mL 95% ethanol, 0.5 mL iron(II) solution and 0.4 mL solution of known BTBP concentration. The iron(II) solution was prepared using an excess of $FeSO_4$ (pro analysi, Merck) in equal amounts of 95% ethanol and MilliQ water (Millipore®, > 18 MΩ). This solution is sensitive towards ageing, i.e. oxidation of the Fe(II) to Fe(III) and had to be freshly prepared for each sampling. It was shown that that the shape of the calibration curve does not depend on the type of diluent and thus the calibration curve for each BTBP molecule was constructed using cyclohexanone as diluent. Naturally the background for each case was the same as the sample but without BTBP. Thus the dependence of the diluent was cancelled out.

The first experiments were performed at a temperature of 10°C. The diluents: cyclohexanone, octanol and hexanol, were cooled down in a fridge and a few milliliters of the diluents were put in glass vials containing an excess of solid phase. The glass vials were shaken at the desired temperature for approximately two days and were then left for 2–3 days in a water bath of the same temperature to allow settling. Small samples of liquid phase were then diluted with ethanol and iron(II) solution as described above and analyzed with the spectrophotometer. This procedure was repeated 2–4 times for each of the different temperatures 10°C, 20°C and 30°C. The absorption peak for the Fe-BTBP complex was measured at a wavelength of 598.27 nm for MF2-, C5- and $CyMe_4$-BTBP and at a wavelength of 608.12 nm for MF1- and C2-BTBP.

4.4.3 Results/discussion

All measured values of solubility in cyclohexanone at the three different temperatures can be seen in Table 4-1. It is clear that MF2-BTBP is the most soluble ligand in this series, with a maximum concentration of 304 ± 35 mM at 20°C, followed by C5-BTBP with a solubility of 83 ± 4 mM at the same temperature. The least soluble ligand is C2-BTBP with a maximum concentration of 11.1 ± 0.1 mM. The uncertainties given throughout the paper are derived using the chi-square method outlined by Meinrath and Ekberg et al. /34/.

Table 4-2 gives the corresponding values when the diluent was octanol. Note that only three out of the five molecules were tested in octanol. The mutual order of solubility is the same as for cyclohexanone if one excludes MF2-BTBP and C2-BTBP, i.e. that C5-BTBP is the most soluble ligand, followed by MF1- and $CyMe_4$-BTBP.

Table 4-1. Solubility of BTBP molecules in cyclohexanone at three temperatures.

System		Concentration [mM] at temperature [K]		
		283	293	303
$CyMe_4$-BTBP	cyclohexanone	8.7 ± 1.4	17 ± 1.6	25 ± 1.5
C5-BTBP	cyclohexanone	38 ± 2.0	83 ± 4.3	246 ± 16
C2-BTBP	cyclohexanone	9.2 ± 0.06	11 ± 0.06	16 ± 0.06
MF1-BTBP	cyclohexanone	17 ± 0.5	26 ± 0.6	52 ± 0.9
MF2-BTBP	cyclohexanone	34 ± 5.3	304 ± 35	1106 ± 73

Table 4-2. Solubility of BTBP molecules in octanol at three temperatures.

System		Concentration [mM] at temperature [K]		
		283	293	303
$CyMe_4$-BTBP	octanol	4.3 ± 1.1	8.2 ± 0.8	13 ± 1.0
C5-BTBP	octanol	11 ± 1.2	24 ± 1.5	45 ± 2.5
MF1-BTBP	octanol	6.1 ± 0.2	9.9 ± 0.2	17 ± 0.2

An interesting result that comes out from the solubilities shown in Table 4-2 is that several experiments in the literature have been performed with BTBP concentrations close to the maximum solubility. This means that there is a risk of super saturated solutions. The reason for this is that the precipitation of the BTBPs is extremely slow. Oversaturated samples have been left for more than a week without reaching the equilibrium solubility, with the concentrations of BTBP slowly decreasing all the time. In order to visualize the actual linearity, Figure 4-10 shows the values presented in Table 4-1 and 4-2 plotted as the natural logarithm of the solubility versus 1/T.

From the slopes and intercepts of these curves the values of standard enthalpies and entropies of dissolution can be calculated using equation 5. The values are shown in Table 4-3, together with corresponding R^2 values.

The changes in enthalpies of all systems are positive, which means that the dissolution is an endothermic process requiring energy from outer environment, i.e. the bonds between the molecules are more energetic. The lower values of the change in enthalpy for some diluents most likely indicate that the bonds between the BTBP molecules and these diluents are stronger. Therefore if two systems have similar values of ΔS^0 the system with lower value of enthalpy will be more soluble.

This explanation could be applied to the systems with $CyMe_4$-BTBP dissolved in cyclohexanone and octanol. The values of entropies are very similar (92 and 99 J/mol, respectively) and the system with cyclohexanone has a lower enthalpy. This suggests that $CyMe_4$-BTBP is more soluble in cyclohexanone, a behavior that is supported by practical experience. One part of the explanation to this could be the geometrical structure of the molecule and the diluents. The structure of cyclohexanone is more similar to the $CyMe_4$-BTBP molecule than what the chain structure of the octanol molecule is /43/.

In the case of C5-BTBP, the lower value of enthalpy is found in the system with octanol as diluent. This could indicate that C5-BTBP would be more soluble in octanol. This conclusion can however not be drawn since the entropies of the two systems with cyclohexanone and octanol differ too much. The solubility of C5-BTBP in cyclohexanone is actually 4–5 times higher than in octanol.

Comparing the cyclohexanone systems containing $CyMe_4$-BTBP vs. MF2-BTBP and C2-BTBP vs. MF1-BTBP some trends can be found. By adding a tert-butyl group to the structure of the BTBP molecules the values of entropies increased around three times, i.e. the level of disorder in the solution is much higher for the molecules containing a tert-butyl group. At the same time the values of enthalpies are approximately doubled, which can indicate that the bonds between the diluent and the molecules are weaken by the added assymetry of the BTBP.

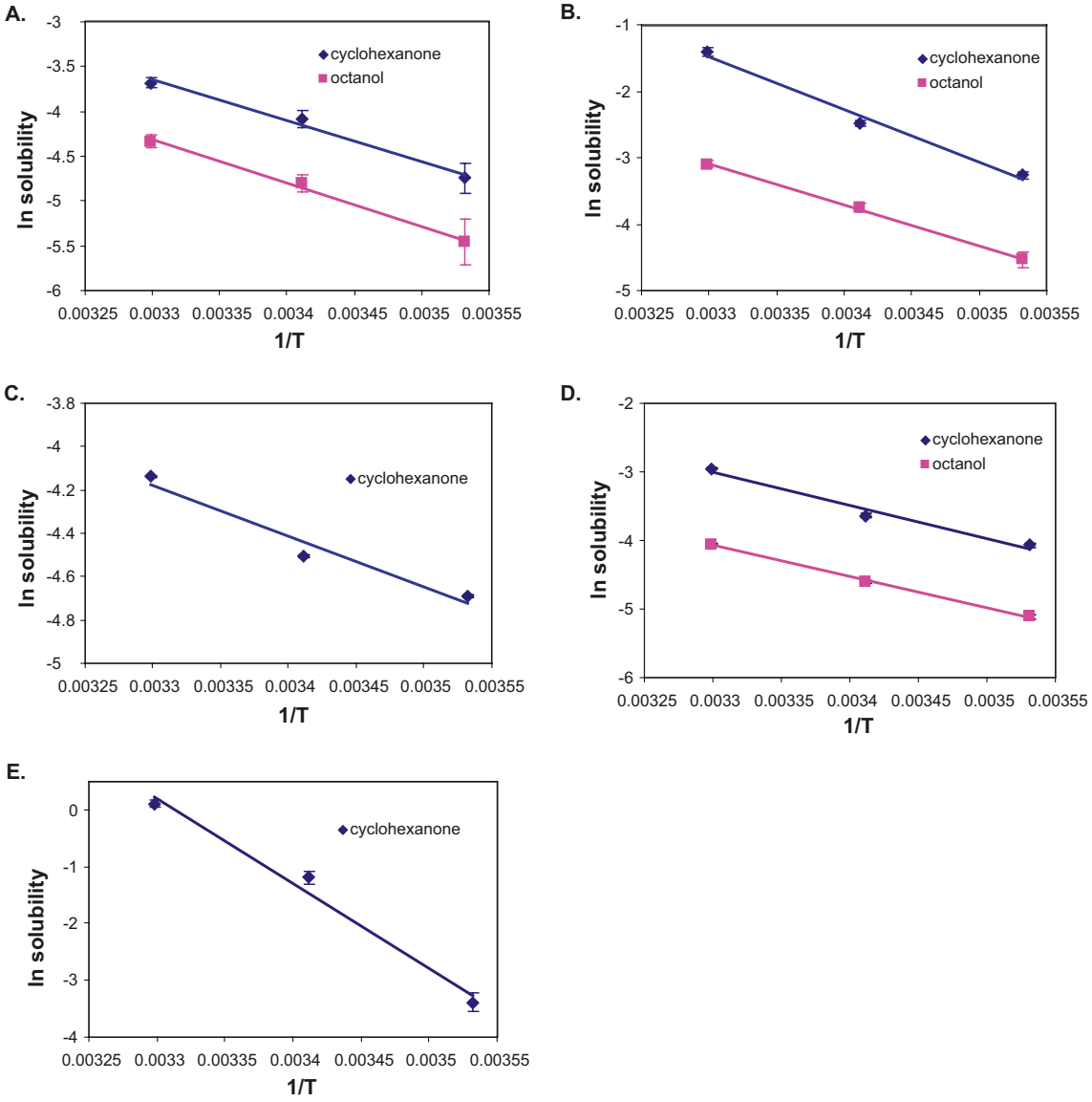


Figure 4-10. *Dependences of logarithm solubility of different systems vs 1/T. A. represents $CyMe_4$-BTBP, B. C5-BTBP, C. C2-BTBP, D. MF1-BTBP and E. MF2-BTBP in cyclohexanone and octanol.*

Table 4-3. Standard enthalpies and entropies of dissolution of several systems containing BTBP molecule dissolved in diluent (cyclohexanone, octanol). The uncertainties present one standard deviation.

System		ΔH (kJ/mol)	ΔS (J/mol)	R^2
$CyMe_4$-BTBP	cyclohexanone	37.2 ± 0.7	92 ± 2	0.987
	octanol	41.0 ± 0.8	99 ± 3	0.9945
C5-BTBP	cyclohexanone	66.6 ± 0.5	207 ± 2	0.9875
	octanol	51.4 ± 0.4	143 ± 1	0.999
C2-BTBP	cyclohexanone	22.3 ± 0.3	40 ± 1	0.9561
MF1-BTBP	cyclohexanone	44.8 ± 0.5	123 ± 2	0.9779
	octanol	37.7 ± 0.2	90 ± 1	0.997
MF2-BTBP	cyclohexanone	106 ± 2	346 ± 6	0.9836

4.5 ESI-MS investigation of BTBP – lanthanide(III) and actinide(III) complexes

In order to gain an understanding of the mechanism involved in the extraction process, complex formation of actinides and lanthanides with BTBPs, an experiment was carried out with the help of Electrospray Ionization Mass Spectrometry (ESI-MS). The focus of the experiment was to study the influence of the side groups on the extraction, but also how the diluents used in the respective systems affected the extracted complexes. Two extractants were used: C5-BTBP and $CyMe_4$-BTBP and three different diluents: nitrobenzene, octanol and cyclohexanone. The experiment was carried out in the ATALANTE facility, Marcoule, France due to an ACTINET cooperation grant.

4.5.1 Experimental conditions

Organic solutions consisted of 0.005 M $CyMe_4$-BTBP and C5-BTBP, respectively, dissolved in cyclohexanone, nitrobenzene or octanol. The solutions containing cyclohexanone and nitrobenzene were pre-equilibrated with 1 M HNO_3 before the experiments. The aqueous solution consisted of $8.7 \cdot 10^{-4}$ M ^{241}Am in 1 M HNO_3 and for the nitrobenzene and cyclohexanone samples the aqueous solutions were pre-equilibrated with pure diluents before the start of the experiments.

A separate experiment was carried out for the Eu extraction, with $2 \cdot 10^{-3}$ M stable Eu and 2 M $LiNO_3$ in 1 M HNO_3. The 2 M $LiNO_3$ was added to increase the concentration of complexes in solution in order to facilitate the detection by ESI-MS.

Another separate experiment was carried out with pure diluents, without any extractant, to check the possible formation of complexes or associations with the diluent alone. The aqueous phase was the same as above and the pre-equilibration procedure was carried out in the same manner as above.

The organic and aqueous solutions were mixed together in vials for 2 h at 20°C in a thermostated shaking device (own design existing in CEA-ATALANTE facility, France). Aliquots of 20 µL from each phase were diluted 3×1/100 into acetonitrile/water (50/50) or (80/20) in the case of nitrobenzene (since the other solution was not able to dissolve the nitrobenzene properly) before analysis by ESI-MS.

An example of typical spectra resulting from ESI-MS experiments are presented below in Figure 4-11 and Figure 4-12.

It was found that the change of the diluent and the substituent on the BTBP moiety does not modify the stoichiometry of the complexes which is $L_2M(NO_3)_3$. Due to this result it has been proposed that one nitrate is bonded to the metal ion whereas the two other nitrates probably exist in the outer coordination sphere.

The difference observed in extracting properties /44, 45, 46/ is probably due to the solvation of the complexes by the diluent. The non-covalent force that holds complexes together is likely to be largely governed by electrostatic interactions even if the hydrophobic exterior of the complexes might play an important role in the complexation/extraction mechanism.

4.6 Recovery of BTBP from the organic phase

As an alternative to the evaporation of the diluent when using cyclohexanone a low temperature method operating at ambient pressure has been devised and tested. By treatment of a solution of a BTP or BTBP in cyclohexanone with an aqueous solution of sodium hydrogen sulphite ($NaHSO_3$) it is possible to convert the cyclohexanone into a crystalline solid that is less soluble in organic solvents without altering the extractant molecule. As the product of cyclohexanone and sodium hydrogen sulphite (the sodium salt of 1-hydroxy-cyclohexanesulfonic acid) is soluble in water, under suitable conditions it is possible to convert a cyclohexanone solution of a BTBP (or BTP) into an aqueous solution of the sodium salt of 1-hydroxy-cyclohexanesulfonic acid and solid BTBP. The BTBP can then be collected by filtration, washed with water and dried before being reused.

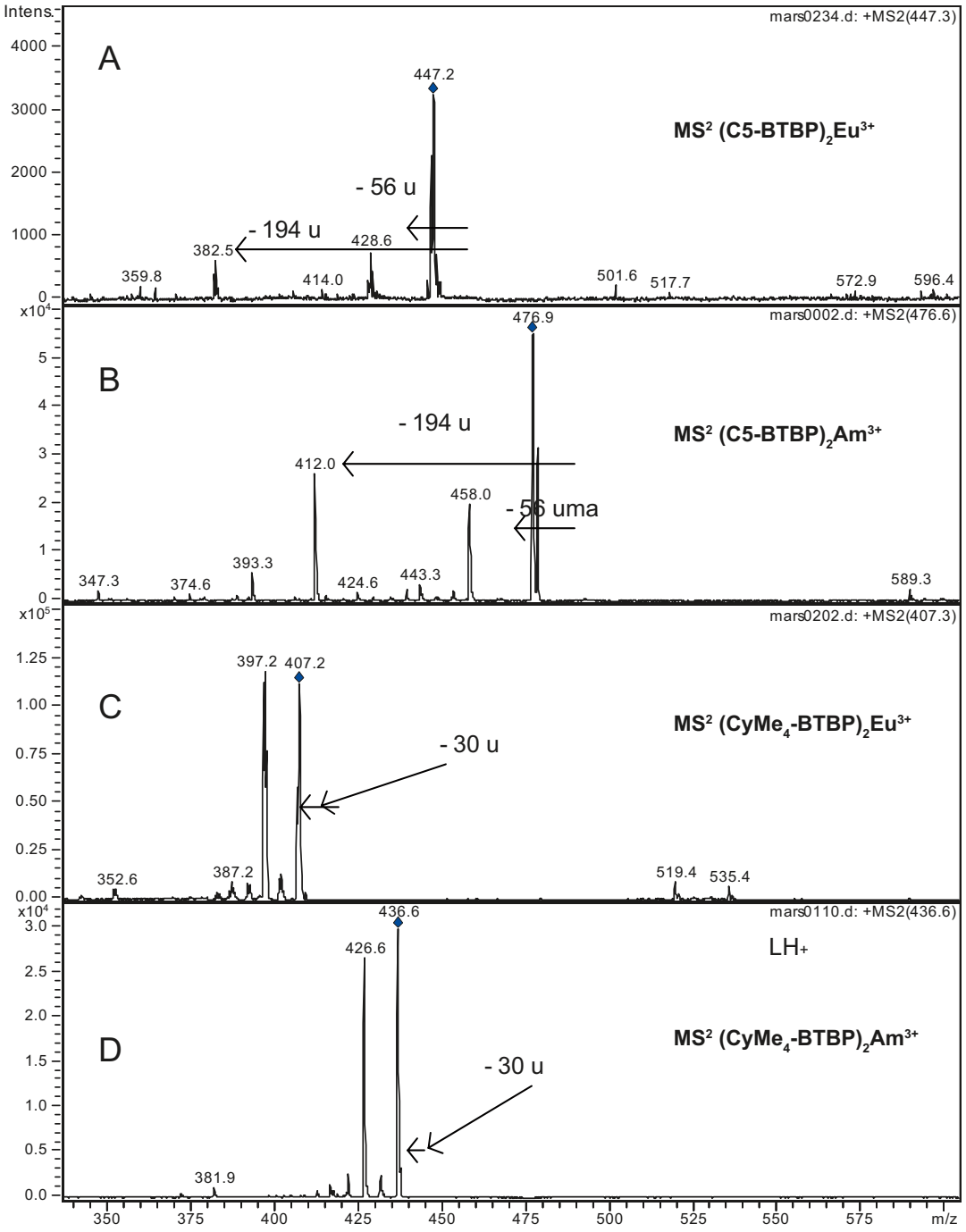


Figure 4-11. *MS^2 spectrum of L_2M^{3+} complex observed in the organic phase after extraction by BTBP.* ◆ *indicates the precursor ion.*

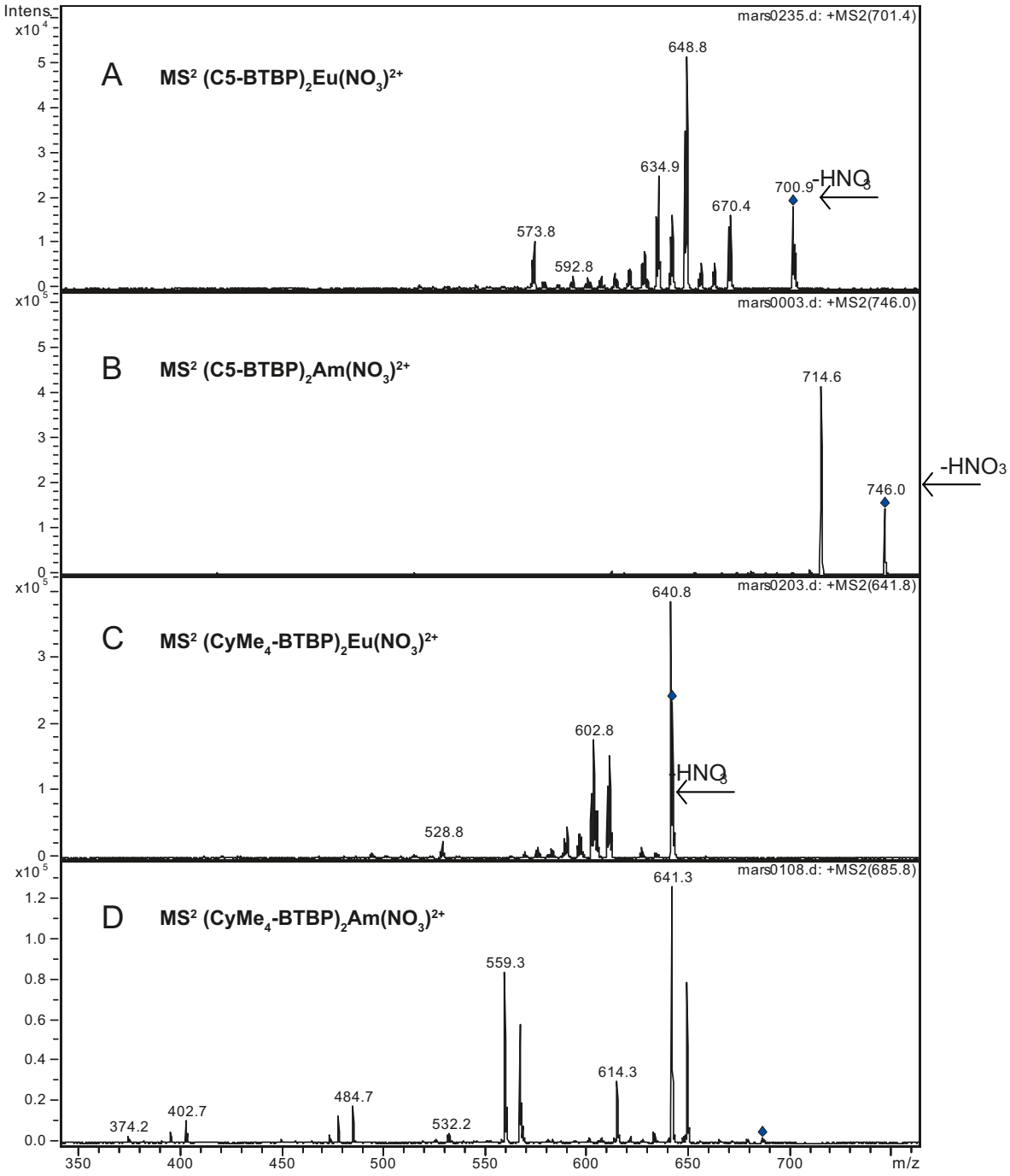


Figure 4-12. *MS^2 spectrum of $L_2M(NO_3)^{2+}$ complex observed in the organic phase after extraction by BTBP. ◆ indicates the precursor ion.*

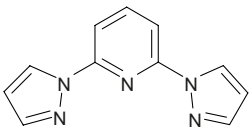
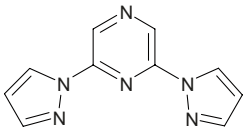
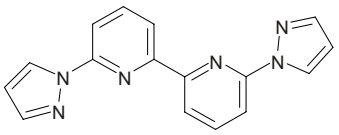
5 Screening of new extractants for r-SANEX

Three new extractants intended for the r-SANEX process were synthesized by CSIC (Consejo superior de investigaciones científicas) in Spain and sent to Chalmers to be tested within the ACSEPT project requirements (see Appendix A). The structure of the molecules are given in Table 5-1.

The screening included a dissolution test in cyclohexanone and an extraction test with ^{241}Am and ^{152}Eu. First, the solubility of the extractants was investigated by trying to dissolve 5 mM of the extractants in cyclohexanone. The solutions were prepared without further problems except for the solution of N-DPBP, which needed to be heated up with warm water.

These solutions of 5 mM were then used for the extraction tests. The experiments were performed as described in the general section, using an aqueous phase of 1 M HNO_3, and shaken for 60 minutes in the shaking device. Extraction properties of the new molecules are shown in Figure 5-1. It can be seen that the distribution ratios of ^{152}Eu and ^{241}Am are low, which means that almost no extraction took place. Although the D of americium for N-DPBP (D_{Am} = 0.0041) is almost twice the D_{Am} for the other two molecules the values are still too low and not applicable for an industrial process. No separation between Am and Eu occurred in the systems with N-DPP and N-DPPz where the separation factors in both cases were equal to 1. However, the $SF_{Am/Eu}$ for the system with N-DPBP is 1.7 which indicates a slight separation between the elements. The low distribution ratios and no significant separation, indicate that these systems are not suitable for further investigation. However, the extractants might be useful if e.g. a synergist like bromodecanoic acid was used. Similar effects have previously been shown for the terpyridine system /50, 41, 3/.

Table 5-1. Molecular structure and chemical name of N-DPP, N-DPPz and N-DPBP.

		
a. 2,6-di(pyrazol-1-yl)pyridine (N-DPP)	b. 2,6-di(pyrazol-1-yl)pyrazine (N-DPPz)	c. 2-pyrazol-1-yl-6-(6-pyrazol-1-yl-2-pyridyl) pyridine (N-DPBP)

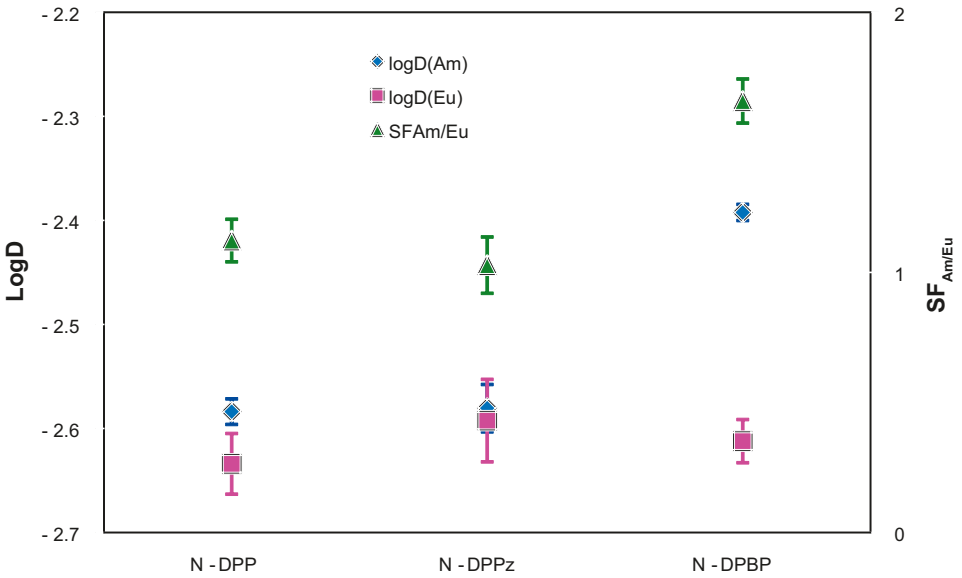


Figure 5-1. *Extraction behaviour of 5 mM N-DPP, N-DPPz and N-DPBP solutions in cyclohexanone (aqueous phase: 1 M HNO_3, shaking intensity: 1,500 rpm, contact time: 60 minutes).*

6 Investigations of a ternary system for GANEX applications

Investigations of a ternary system containing cyclohexanone as diluent and the two extractants BTBP and TBP for GANEX purposes have been performed.

TBP already has a well documented ability to extract uranium and plutonium directly from dissolved spent fuel /7/. BTBPs on the other hand are known to be able to separate trivalent and pentavalent actinides from trivalent lanthanides /45, 12/. By combining these two molecules the intention is to be able to extract all actinides from the dissolved spent fuel without any redox control and at the same time separate them from the lanthanides as well as from the fission and corrosion/activation products.

6.1 Experimental

6.1.1 Analysis methods

In all experiments in this section the following methods for analysis of metals have been used:

The samples with ^{152}Eu, ^{235}U and ^{241}Am have all been analyzed using HPGe 1 and 2.

The samples with ^{63}Ni, ^{234}Th, ^{238}Pu and ^{238}U were analyzed with Liquid Scintillation 1 (the uranium loading samples with ^{238}Pu were however analysed with HPGe 1 due to the inability to measure the U-Pu mixture with liquid scintillation and since the α-spectrometer was out of order. This however renders somewhat unreliable results since ^{238}Pu have quite weak γ-peaks).

The ^{237}Np samples were for all the extractions from acidity/nitrate concentration lower than 4 M measured with Liquid Scintillation 1 but since this rendered a lot of difficulties with psa-stepping (used to separate the α-counts from ^{237}Np from the β-counts from ^{233}Pa) the NaI detector was used for the other extractions. The NaI-measurements were repeated up to 4 half lives of ^{233}Pa ($t_{1/2}$ = 27d) until the D was found stable. This was done to take the extraction of ^{233}Pa into account.

The inactive metals were analyzed with ICP-OES by comparing the aqueous phase before and after extraction. With this method, very small distribution ratios can sometimes appear as negative. Since this is not a possible scenario these negative ratios have been considered to be small and therefore given the fictive value of D = 0.01 giving log D = –2.

6.1.2 Experiments

All extraction experiments described below were performed as described in Section 3.1.1 – Standard extraction experiment, unless otherwise stated. The ternary system that was used as a starting point for these investigations contained 0.01 M of BTBP and 30 vol% TBP in cyclohexanone. Two different BTBPs were used and the solvent containing C5-BTBP will from now on be referred to as TS1 while the solvent with $CyMe_4$-BTBP will be referred to as TS2.

Chemicals

All inactive chemicals used in the following experiments are presented in the Table 6-1 and 6-2 below.

Table 6-1. List of inorganic chemicals used in the experiments.

Substance	Brand	Purity (if available)
$AgNO_3$	May & Baker	pro analysi > 99.9%
$Ba(NO_3)_2$	Merck	> 99%
$Cd(NO_3)_2x4H_2O$	Fischer Scientific	certified reagent
$Ce(NO_3)_3x6H_2O$	Fluka	puriss
$Co(NO_3)_2x6H_2O$	Fluka	purum p.a. > 99.0%
$Cr(NO_3)_3x9H_2O$	Riedel de Haën AG.	pure cryst.
$CsNO_3$	Merck	extra pure
$Fe(NO_3)_3x9H_2O$	Merck	pro analysi > 99%
HNO_3	Sigma Aldrich	69% puriss p.a.
$KMnO_4$	Merck	pro analysi
$La(NO_3)_3x6H_2O$	Riedel de Haën AG	> 99%
$MnSO_4x1H_2O$	Merck	pro analysi > 99%
MoO_3	Fluka	purum p.a. 99.7%
$NaCO_3$	Fluka	wasserfrei purum p.a.> 99.0%
$NaNO_3$	Riedel de Haën AG	p.a.
$Nd(NO_3)_3x6H_2O$	Fluka	puriss
$Pd(NO_3)_2x2H_2O$	Fluka	purum > 97%
$RbNO_3$	Merck	99%
Sb_2O_3	Fluka	purum ≥ 99.5%
SeO_2	Fluka	purum
$Sm(NO_3)_3x6H_2O$	Fluka	purum > 98%
SnO_2	Fluka	purum
$Sr(NO_3)_2$	Merck	pro analysi, wasserfrei 99%
Te	Fluka	puriss > 99.999%
$Y(NO_3)_3$	Fluka	puriss 99%
$ZrO(NO_3)_2x5H_20$	ICN K&K Laboratories inc.	–

Table 6-2. List of organic chemicals used in the experiments.

Substance	Brand	Purity
cyclohexanone	Acros Organics	99.8% extra pure
TBP (tri-butyl phosphate)	Fluka	purum > 97%
ethanol	BDH Pro Labo	95%
dichloromethane	Acros Organics	pure > 99%
tri-ethyl amine	Riedel de Haën AG	purum > 99%

6.2 Interaction tests

First, tests had to be done to investigate whether the BTBP and the TBP molecules could coexist in a solution without reacting with each other and thereby hampering their separate complex-formation abilities. It is also possible that the two molecules could merely associate with each other in which case the complex formation ability still could be affected, but this would be more difficult to detect.

A Thin Layer Chromatography (TLC)-test is a fast and easy way to see if the BTBP and the TBP react with each other. The following TLC-tests were all performed by placing a small volume (a spot) of the sample and the reference samples on a straight line on a silica plate. The plate was then placed with the samples above the surface of a mobile phase specially designed to be able to separate the molecules in the samples. The distance between the base line and the detected spots (containing the molecules) is the R_f value. This value is molecule specific and also depends on the composition of the mobile phase. In the tests, samples of TS1 are compared to samples of pure BTBP and pure TBP. The BTBP is easy to detect with a short wave UV-lamp and if the BTBP and

the TBP in TS1 would have reacted, another spot representing the new molecule might appear on the chromatogram with an R_f value not corresponding to either the TBP or the BTBP and if the spot corresponding to BTBP would not appear at all this would suggest that the molecule has been totally decomposed.

Several tests were made to determine the composition of the mobile phase for the final TLC-test using different concentrations of ethanol and dichloromethane. A mobile phase consisting of 25 vol% ethanol in dichloromethane with a drop of triethylamine added was chosen. The triethylamine was added to diminish the blurriness of the dots by making the BTBP bind harder to the acidic sites of the silica on the TLC-plates /53/.

The TS1 was prepared, diluted with dichloromethane and then subsided to several TLC tests.

The first test was performed similar to the TS1. A spot of TS1 was compared with a spot of pure C5-BTBP dissolved in acetone and also with a double spot where pure C5-BTBP and TS1 had been put on top of each other. The TLC-test was performed and the plate dried before the spots of BTBP were detected with a short wave UV lamp. The plate was also developed by dipping it in a colouring solution ($KMnO_4$ and $NaCO_3$ in water) and heated to visualise the spots of TBP. From this the conclusion could be drawn that the BTBP and the TBP had not reacted with each other but was left intact.

The TS1 was then left over night in room temperature to investigate any possible reaction kinetic between the BTBP and TBP. The TLC-experiment was repeated the next day but this time also with the addition of a sample of pure TBP (diluted in dichloromethane) to ensure that the spot developed with the colouring solution actually was TBP. As can be seen in Figure 6-1, detection with UV-lamp and dipping showed neither addition of extra spots nor any lack of expected spots resulting in the same conclusion as earlier; both the BTBP and TBP were intact.

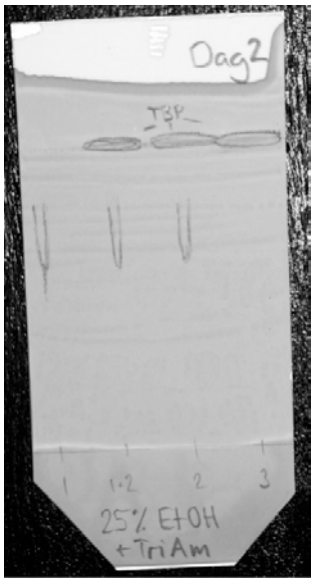


Figure 6-1. *Spot 1 – 0.01 M BTBP in cyclohexanone. Spot 2 - 0.01 M BTBP +30 vol% TBP in cyclohexanone. Spot 1+2 = Spot 1 + Spot 2 on the same place on the plate. Spot 3 - 30 vol% TBP in cyclohexanone. All solutions were diluted with DCM before addition to the plate.*

6.3 Stability of BTBP and TBP towards nitric acid

In many extraction experiments as well as a real life GANEX process the aqueous phase will consist of nitric acid. Therefore it also has to be investigated whether the mixture of BTBP and TBP stays stable in the presence of strong nitric acid. Both BTBP and TBP can extract nitric acid into the organic phase. A 1:1 complex is formed with TBP and HNO_3. Using 30% TBP in kerosene in contact with 4 M nitric acid the concentration of nitric acid in the organic phase is app. 0.8 M /1/. Then on the other hand both TBP and cyclohexanone also have a mutual solubility of water. The solubility of water in TBP is 4.67 weight % at 25°C and the solubility of water in cyclohexanone is 8.0 weight % at 25°C /33/.

It is already known that C5-BTBP is degrading in the presence of nitric acid (due to attack on the benzylic carbons of radicals from the nitrous acid which is present in nitric acid) but this is not true for all BTBPs. For instance the $CyMe_4$-BTBP is stabile towards nitric- and hence also nitrous acid /26/. TS2 is not used in the experiments because of the limited amounts of $CyMe_4$-BTBP available. Due to this the problem with degradation of BTBP from nitric acid can be taken somewhat lightly as long as the TBP is not responsible. It is possible that even though the TBP itself doesn't participate in the degradation of the BTBP, the larger amount of nitric acid present in the system due to the TBP extraction could be contributing. This would indirect make TBP responsible for the systems instability in the presence of nitric acid. It is however not only BTBP that is degraded by nitric acid but also TBP. This degradation only occurs to a very small degree so this is not taken into account in these investigations. The products formed by the degradation of TBP are di-butyl phosphate (DBP), mono-butyl phosphate (MBP) and phosphoric acid /8/.

The reaction between BTBP and TBP ought to be more or less the same for all BTBPs since the side groups should not be involved in the reaction. If the BTBP's and the TBP had reacted it would have been the nitrogens on the BTBP molecule that would have been attacked by the TBP but since this has already been shown not to happen it is not an issue. In the reaction with nitric acid though it is the side groups that are affected and it is therefore that different BTBP's act in different ways in the presence of nitric acid. The side group on the $CyMe_4$-BTBP doesn't give the nitrous acid radicals any opportunity for hydrogen abstraction on the benzylic carbon and is therefore stable.

The TS1 was freshly prepared and pre equilibrated with an equal amount of 1 M nitric acid. After the two phases had separated the organic phase was carefully removed and a TLC-test was made. Unfortunately, dichloromethane could not be used for dilution this time due to the solvated nitric acid. Instead the sample was diluted with acetone and the mobile phase used consisted of a solution of 21% ethanol in dichloromethane with a drip of trietylamine (the lower amount of Ethanol used in this test was an attempt to slightly increase the R_f value). The test showed that directly after the calibration there had been no degradation of the TBP and the BTBP which were contacted with nitric acid (see Figure 6-2).

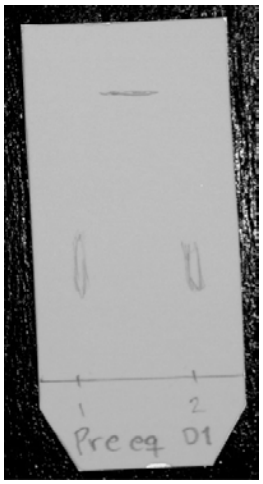


Figure 6-2. *Spot 1 – 0.01 M BTBP in cyclohexanone. Spot 2 – 0.01 M BTBP +30 vol% TBP in cyclohexanone. Both solutions were diluted with acetone before addition to the plate.*

The TS1 was therefore left to stand for approximately 72 hours and then the test was remade. By this time the organic solution had shifted colour from being bright yellow to apricot-orange suggesting even before the test was made that a reaction had occurred. The TLC-test (using the same mobile phase as in the previous test) now showed two spots from the TS1 of which none corresponded to the standard of C5-BTBP. To see if this degradation had anything to do with the presence of TBP and not only the nitric acid, a sample of C5-BTBP (0.01 M) in cyclohexanone was prepared, pre equilibrated with 1 M nitric acid in the same manner as the TS1 and left for 72 hours. The TLC-test that was made (with the same mobile phase as the previous two) showed almost exactly the same result as the test done with the pre calibrated TS1, suggesting that it is the nitric acid alone that causes the degradation of C5-BTBP and that the larger amount present in the system due to TBP does not play a significant role (see Figure 6-3).

6.4 Stability towards radiolysis

The stability of new BTBP-TBP-cyclohexanone systems toward radiolysis was tested. For an application as a GANEX solvent the radiolytic stability of a system is very important due to the large dose it will receive from the dissolved spent fuel.

6.4.1 Low dose rate

The stability tests were done by comparing the systems separation ability of actinides and lanthanides after different received doses.

Since it is well known that the C5-BTBP is not only unstable towards nitric acid but also towards radiolysis the experiments were performed with both C5-BTBP and $CyMe_4$-BTBP. The latter is known to be more stable /18, 43/.

TS1 and TS2 were placed inside a ^{60}Co-source with low dose rate (app. 11.5 Gy/h) after a small amount from each solution had been withdrawn as a reference sample. The solution was irradiated for a total of 3,745.5 hours which corresponds to a total dose of 43.07 kGy. This also gave an opportunity to see if the system would be ageing over a long period of time. During the time of irradiation samples were withdrawn at different times from both the irradiated solutions and the reference solutions and extractions of ^{241}Am and ^{152}Eu were performed. The extraction experiments were performed as stated in Section 3.1.1 with a spiked 1 M nitric acid solution as the water phase and hand shaking of the samples for 10 minutes.

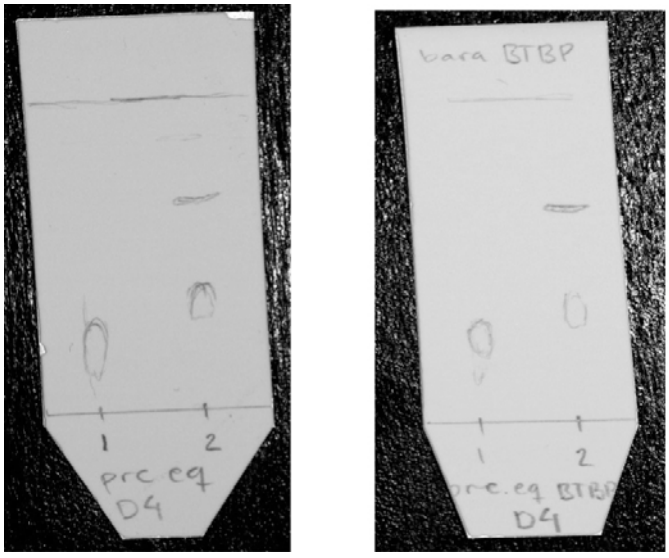


Figure 6-3. *Picture to the left: Spot 1 – reference 0.01 M BTBP in cyclohexanone. Spot 2 – 0.01 M BTBP +30 vol% TBP in cyclohexanone pre eq. with nitric acid (1 M). Picture to the right: Spot 1 – reference 0.01 M BTBP in cyclohexanone. Spot 2 – 0.01 M BTBP in cyclohexanone pre eq. with nitric acid (1 M).*

The results obtained by analysis with HPGe1 are shown in Figure 6-4 and 6-5. As can be seen, the effect of both ageing and radiolysis is clearly much larger for TS1 than TS2 as expected. What is somewhat surprising though is that when comparing these results for TS1 to results obtained from irradiated solutions containing only C5-BTBP in cyclohexanone (see Figure 6-6) it can be seen that the TS1 degrades a lot more and faster both by irradiation and ageing than the C5-BTBP without TBP present does. TS2 on the other hand behaves very similar to $CyMe_4$-BTBP without TBP present (see Figure 6-7).

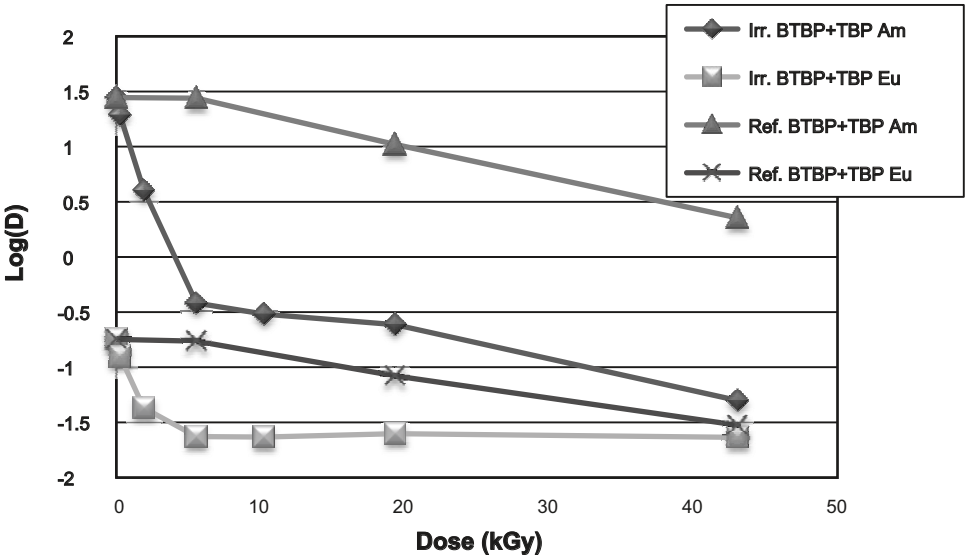


Figure 6-4. *C5-BTBP (0.01 M) + 30% TBP in cyclohexanone irradiated with γ-radiation. Samples taken at different times and tested for extraction of Am and Eu. Dose rate: 11.5 Gy/h.*

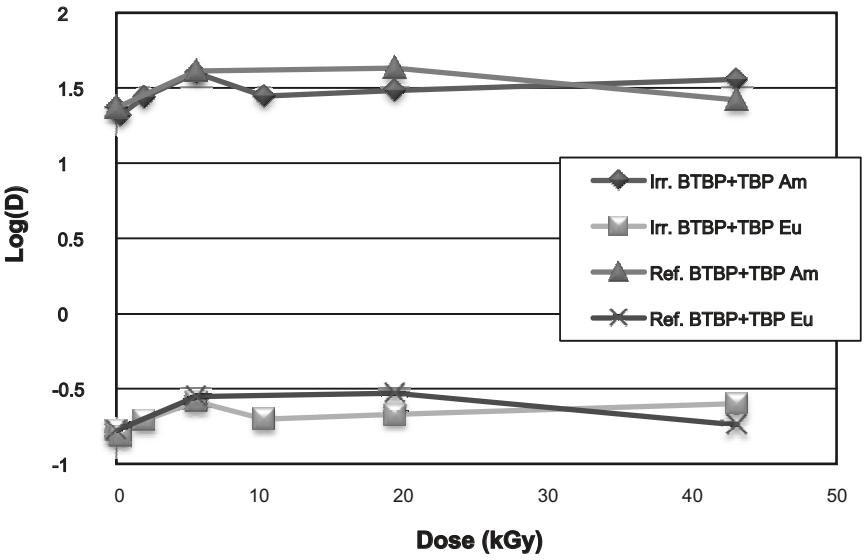


Figure 6-5. *$CyMe_4$-BTBP (0.01 M) + 30% TBP in cyclohexanone irradiated with γ-radiation. Samples taken at different times and tested for extraction of Am and Eu. Dose rate: 11.5 Gy/h.*

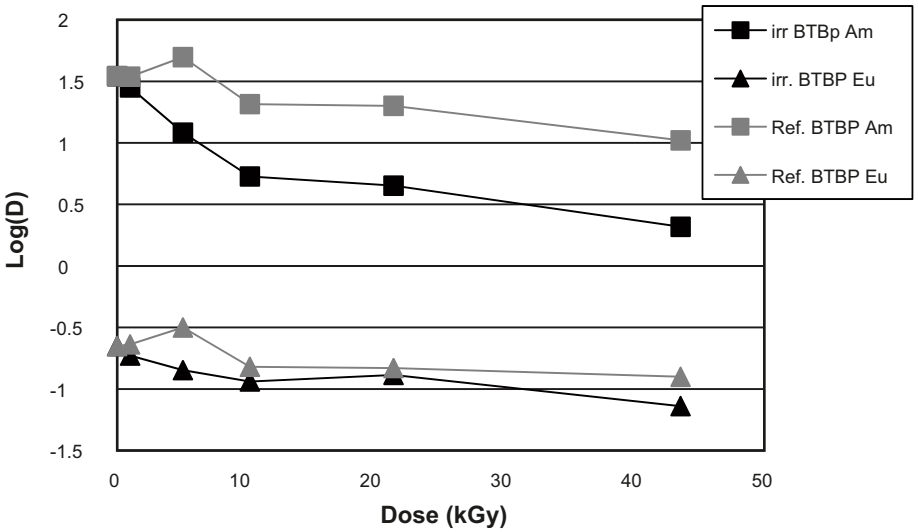


Figure 6-6. *C5-BTBP (0.01 M) in cyclohexanone irradiated with γ-radiation. Samples taken at different times and tested for extraction of Am and Eu. Dose rate: 15.4 Gy/h.*

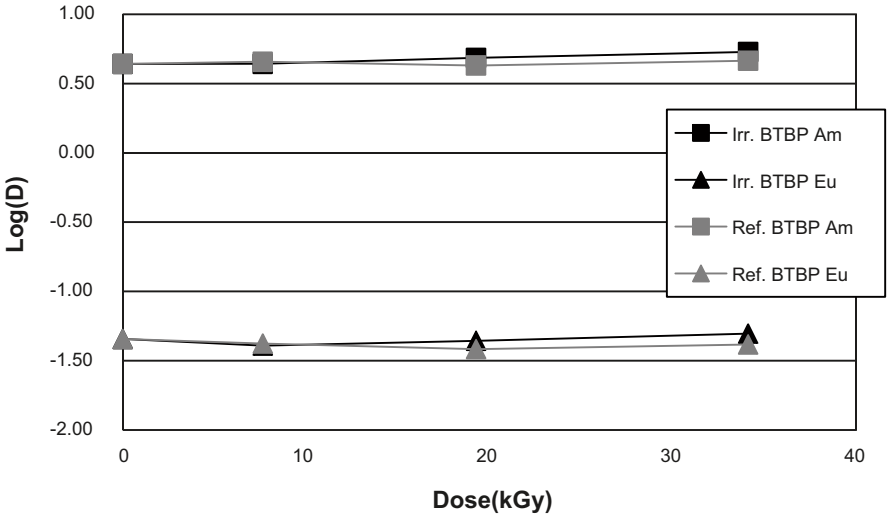


Figure 6-7. *$CyMe_4$-BTBP (0.005 M) in cyclohexanone irradiated with γ-radiation. Samples taken at different times and tested for extraction of Am and Eu. Dose rate: 12.7 Gy/h.*

6.4.2 High dose rate

In a real life scenario in a GANEX process the dose rate would be much higher than in the previous radiolysis tests and the total received dose would also be much larger. In a process case the solvent would also be in contact with strong nitric acid during this period of irradiation. Because of these factors two different irradiations with conditions closer to the real life case has been performed.

Two sets of solutions were sent to ICHTJ (Instytut Chemii i Techniki Jadrowej, Poland) for irradiation. One set consisted of pure TS2 and the other of TS2 in contact with an equal amount of 4 M nitric acid. The solutions were given various doses up to 200 kGy with a dose rate of app. 0.9 kGy/hour.

The extraction experiments were performed as stated in Section 3.1.1 with hand shaking of the samples for 10 minutes and the water phase consisted of 4 M nitric acid.

As can be seen when comparing Figure 6-8 to Figure 6-9 the presence of nitric acid during irradiation of the solvent promotes a resistance towards radiolysis. Without acid present the distribution ratio first goes up and then it starts to decrease while the D with acid present stays almost exactly the same.

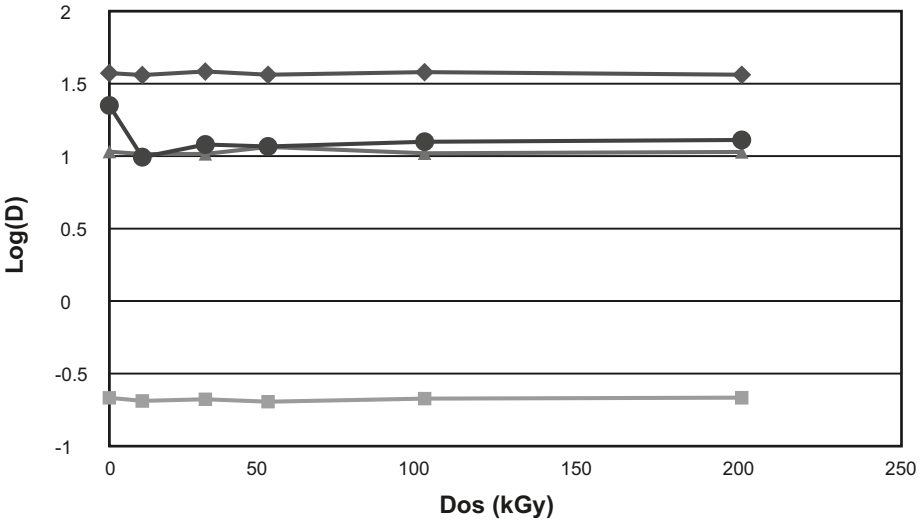


Figure 6-8. *Extraction of ^{241}Am, ^{152}Eu, ^{238}Pu and ^{235}U from 4 M HNO_3 with 6 different organic phases: $CyMe_4$-BTBP(0.01 M) +30% TBP in cyclohexanone given different doses from a ^{60}Co-source when in contact with an equal amount of 4 M HNO_3.*

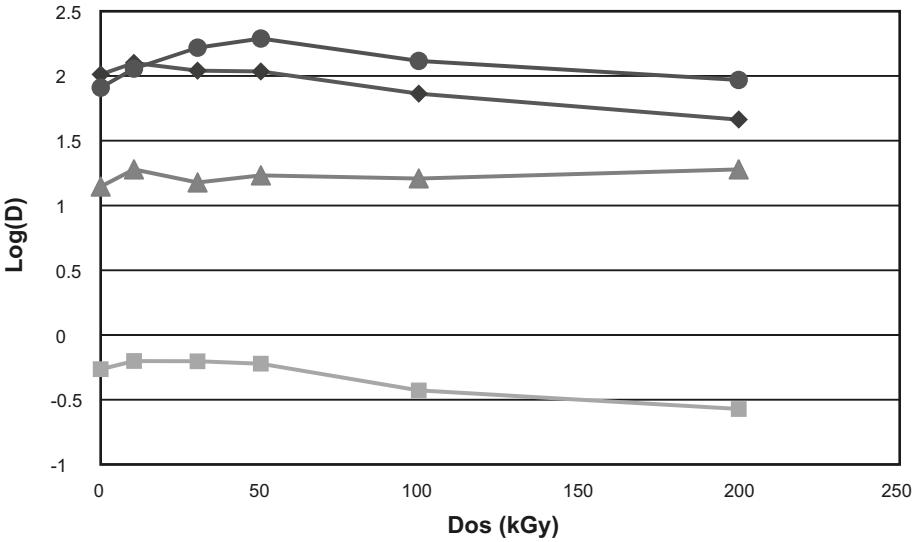


Figure 6-9. *Extraction of ^{241}Am, ^{152}Eu, ^{238}Pu and ^{235}U from 4 M HNO_3 with 6 different organic phases: $CyMe_4$-BTBP(0.01 M) +30% TBP in cyclohexanone given different doses from a ^{60}Co-source.*

6.5 Stability towards hydrolysis

It was already indicated during the high dose rate radiolysis tests that the TS2 solvent is stable towards hydrolysis. However, to be able to ensure that no major acid decomposition of neither BTBP nor TBP occurs, an additional test was done. A TS2 solution was left to stand in contact with 4 M nitric acid at room temperature for a long time period. Aliquots of the organic phase were removed after different times and extraction tests were done. The extraction tests were performed as stated in Section 3.1.1 with hand shaking and using a fresh 4 M nitric acid as the water phase.

As can be seen in Figure 6-10 the D-values for both Am and U are stable over time while the D for Eu is slowly decreasing, rendering an increase in $SF_{Am/Eu}$.

6.6 Separate extractions

Distribution ratios for the TS1 solvent was compared to corresponding ratios for pure BTBP in cyclohexanone and for pure TBP in cyclohexanone, as well as for pure cyclohexanone. By comparing the extraction of actinides, lanthanides and fission products it can be seen if the extraction potential is increased or decreased when the two extractants are combined into one solvent. There is a possibility that a ternary complex is formed between the metal and both TBP and BTBP. This is not an ideal situation for the developed process and needs to be investigated.

6.6.1 Uranium

The extractions shown below were performed as described under Standard extraction experiment (Section 3.1.1) with hand shaking for 10 minutes. A 1 mM UO_2^{2+} solution was used as the water phase and created by dissolving uranyl nitrate ($UO_2(NO_3)_2 \times 6H_2O$) made from natural uranium in 1 M nitric acid. In this case the uranium is most likely present as U(VI) and hence is expected to be extracted by the TBP.

As can be seen in Figure 6-11 the extraction of U is caused by the TBP as expected and there is no participation of the BTBP. It is expected that under the conditions used the U(VI) will dominate completely over the U(IV).

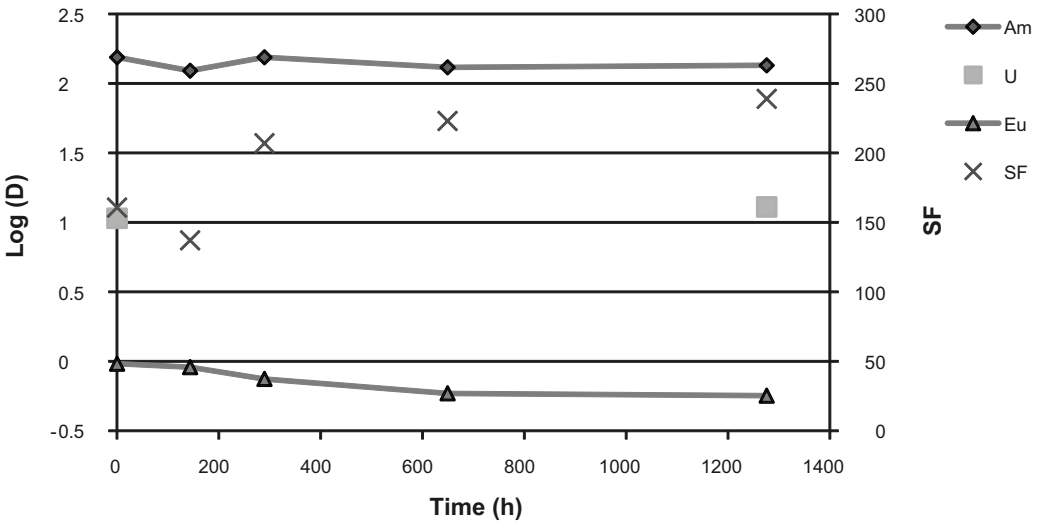


Figure 6-10. *Extraction of ^{241}Am, ^{152}Eu and ^{235}U after different periods of time from 4 M HNO_3 with $CyMe_4$-BTBP (0.01 M) +30% TBP in cyclohexanone that have been standing in contact with 4 M HNO_3.*

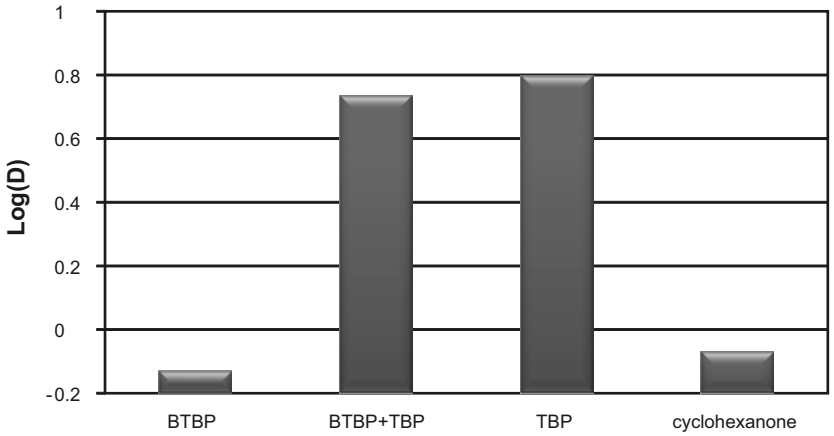


Figure 6-11. *Extraction of 1 mM uranium (natural) in 1 M HNO_3 with four different organic phases. Organic phase BTBP: C5-BTBP(0.01 M) in cyclohexanone. Organic phase BTBP+TBP: C5-BTBP(0.01 M)+30% TBP in cyclohexanone. Organic phase TBP: 30% TBP in cyclohexanon. Organic phase cyclohexanone: 100% cyclohexanone.*

6.6.2 Neptunium

The extractions below were performed as described in Section 3.1.1 with hand shaking for 10 minutes and a water phase of 1 M nitric acid. Neptunium has three different oxidation states and can exist as either Np(IV), Np(V) or Np(VI) in a nitric acid solution. The most part is however expected to exist in the form of Np(V) and hence be extracted by the BTBP.

As can be seen in Figure 6-12, Np is extracted by BTBP and there is no difference between the TS1 solvent and the pure BTBP and hence the molecules are extracting independently.

Since the distribution ratios for neptunium is somewhat modest a test with different concentrations of BTBP was made to see to what extent the D could be increased by increasing the BTBP-concentration in the ternary system.

As can be seen in Figure 6-13 the slope is close to one which indicates that one BTBP-molecule accompanies one Np-atom into the organic phase, as was previously shown in /45/.

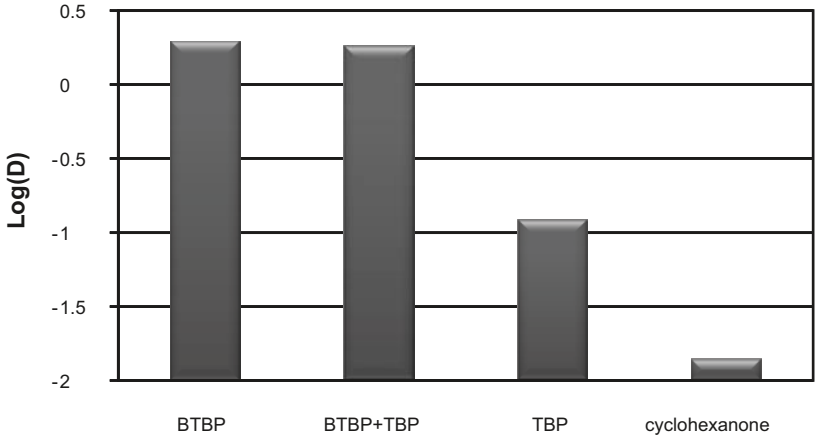


Figure 6-12. *Extraction of ^{237}Np in 1 M HNO_3 with four different organic phases. Organic phase BTBP: C5-BTBP(0.01 M) in cyclohexanone. Organic phase BTBP+TBP: C5-BTBP(0.01 M)+30% TBP in cyclohexanone. Organic phase TBP: 30% TBP in cyclohexanon. Organic phase cyclohexanone: 100% cyclohexanone.*

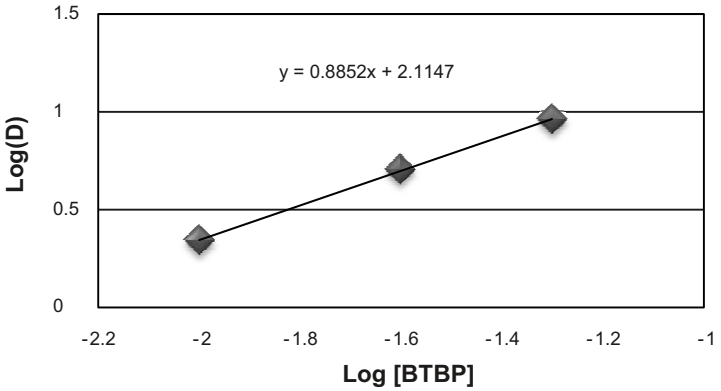


Figure 6-13. *Extraction of ^{237}Np with three different organic phases (0.05 M C5-BTBP, 0.025 M C5-BTBP and 0.01 M C5-BTBP) all containing 30% TBP in cyclohexanone from 2 M nitric acid.*

6.6.3 Americium

The extractions below were performed as described in Section 3.1.1 with hand shaking for 10 minutes and a water phase of 1 M nitric acid.

Americium is known to be extracted by BTBP and the interesting part was now to see how the extraction was affected by the presence of TBP in this ternary system.

As can be seen in Figure 6-14 the extraction of americium decreases slightly with the addition of TBP to the system and almost nothing is extracted by TBP or cyclohexanone as expected.

6.6.4 Europium

The extractions were performed as described in Section 3.1.1 with hand shaking for 10 minutes and a water phase of 1 M nitric acid. Europium is known to be unfavoured for extraction by BTBP type molecules. Since TBP only extract metals with the oxidation states (IV) and (VI) the europium was not expected to be extracted to a great extent with any of the used systems. As can be seen in Figure 6-15 Europium was not extracted to a great extent by any of the organic phases as expected but the extraction that did occur was caused by the BTBP.

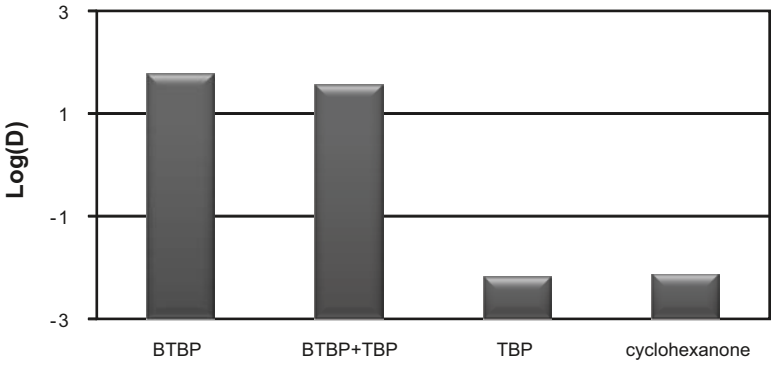


Figure 6-14. *Extraction of ^{241}Am in 1 M HNO_3 with four different organic phases. Organic phase BTBP: C5-BTBP(0.01 M) in cyclohexanone. Organic phase BTBP+TBP: C5-BTBP(0.01 M)+30% TBP in cyclohexanone. Organic phase TBP: 30% TBP in cyclohexanon. Organic phase cyclohexanone: 100% cyclohexanone.*

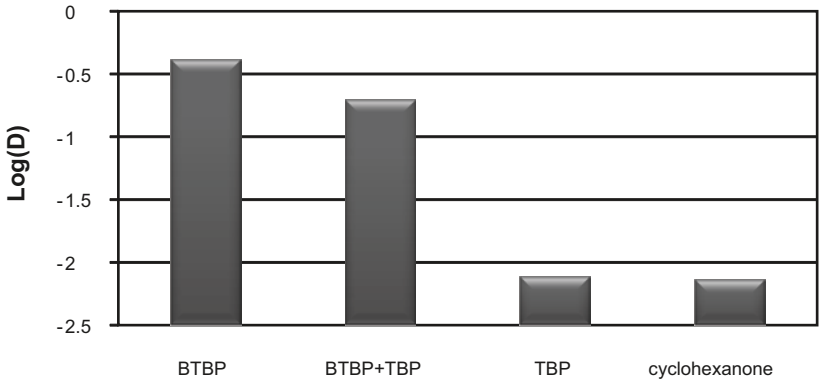


Figure 6-15. *Extraction of ^{152}Eu in 1 M HNO_3 with four different organic phases. Organic phase BTBP: C5-BTBP(0.01 M) in cyclohexanone. Organic phase BTBP+TBP: C5-BTBP(0.01 M)+30% TBP in cyclohexanone. Organic phase TBP: 30% TBP in cyclohexanone. Organic phase cyclohexanone: 100% cyclohexanone.*

6.6.5 Thorium

The extractions below were performed according to the Standard extraction experiment described in Section 3.1.1, with hand shaking for 10 minutes and a water phase of 1 M nitric acid.

As can be seen in Figure 6-16 the extraction of Th is very low and almost exactly the same with both the ternary system as well as with pure BTBP and TBP in cyclohexanone. This is somewhat surprising since another 4+ ion Pu(IV) is known to be extracted with TBP in the PUREX-process. The results suggest a different behavior of thorium compared to plutonium.

6.6.6 Comparing Th and Pu

Th was chosen as an analogue for plutonium (Pu) but it is possible that this analogy does not apply partly due to the fact that Th in comparison to Pu lacks the f-orbitals that give Pu some of its special features but most likely since thorium is much larger than plutonium. That Th(IV) is a very poor analogue to Pu(IV) has previously been pointed out by Ekberg et al. /13/.

To see if Th acts as an analog for Pu or not in this case, an extraction experiment was performed where ^{238}Pu and ^{234}Th were extracted with TS1 from 2 M nitric acid. The extraction was performed as stated in Section 3.1.1 with hand shaking for 10 minutes.

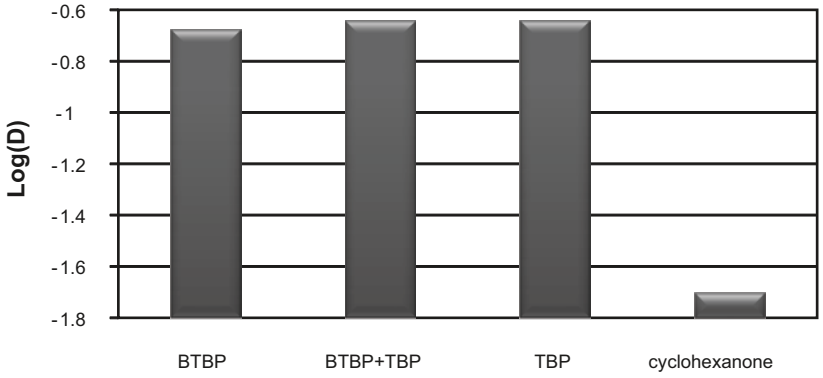


Figure 6-16. *Extraction of ^{234}Th in 1 M HNO_3 with four different organic phases. Organic phase BTBP: C5-BTBP(0.01 M) in cyclohexanone. Organic phase BTBP+TBP: C5-BTBP(0.01 M)+30% TBP in cyclohexanone. Organic phase TBP: 30% TBP in cyclohexanon. Organic phase cyclohexanone: 100% cyclohexanone.*

This experiment showed much higher D for Pu (D_{Pu} = 34.06; log (D_{Pu}) = 1.53) than for Th (D_{Th} = 0.52; log (D_{Th}) = –0.28) rendering the conclusion that Th is not a suitable analogue to Pu and that the data collected on thorium not should be believed to be valid also for Pu.

6.6.7 Fission products – TS1 solvent

To see how the TS1 solvent extracts different metals commonly present in spent nuclear fuel, two different mixtures of nitrate salts or oxides of these were prepared. The chosen metals were: Ba, Cs, Mo, Nd, Rb, Ru, Sr, Y, Zr, Pd, Ag and Cd. One aqueous solution was prepared containing only trace levels (~50 ppb) of palladium, silver and cadmium in a 1 M nitrate solution (0.99 $NaNO_3$ + 0.01 M HNO_3). The other solution containing the rest of the metals was prepared with quantities of metals close to those in real dissolved spent fuel /49, 32, 25/ and a total nitrate concentration of 1 M (see Table 6-3).

The results from the first extraction of Ag, Pd and Cd were obtained by using ICP-MS determination of only the aqueous phases, comparing the aqueous phase before extraction with the aqueous phase after. Since the distribution ratios are very high this is a somewhat uncertain result and hence should only be used as an indication that all three of these metals are extracted to a great extent by TS1. This is mostly because of the BTBP which can be seen in the comparison of the other organic phaces. The results from the extraction of the other metals were obtained by using ICP-OES. The ICP-OES however give low relative intensity and spectral interferences for Ru and Cs so these two metals were measured again with ICP-MS. The indication that can be seen in Figure 6-17 is that the metals are not extracted to any great extent and that molybdenum is the only one that with any certainty can be said to be extracted by the TS1 solvent. Extraction of Rb is only observed with TS1 and not with any of the other three systems. This might indicate that the distribution ratio is just the result of a measurement error. All these results are showed in Figure 6-17.

Fission and corrosion products – TS2 solvent

Another independent extraction of fission products was performed but this time with TS2 and a higher acidity and nitrate concentration in the water phase, to resemble process like conditions. The reason for keeping the ionic strength high but the acidity low was because it was observed that without TBP present, cyclohexanone and 4 M nitric acid was almost completely miscible. In this test three major corrosion products /11/ were also extracted.

The extractions were performed with four different organic phases: 0.01 M $CyMe_4$-BTBP +30% TBP in cyclohexanone (organic phase 1), 0.01 M $CyMe_4$-BTBP in cyclohexanone (organic phase 2), 30% TBP in cyclohexanone (organic phase 3) and pure cyclohexanone (organic phase 4). The aqueous media consisted of 1 M HNO_3 and 3 M $NaNO_3$ for the radioactive tracers (^{152}Eu and ^{63}Ni). Three additional aqueous phases was prepared with the inactive metals: Mo, Pd, Mn, Co, Ag, Cd, Sb, Sm. Mo and Pd were prepared in two separate solutions and the rest of the metals were put into a third solution. The solutions were done by dissolving the oxides/salts in 1 M HNO_3 and adding $NaNO_3$

Table 6-3. Approximate metal concentrations in aqueous phase.

Metal	App. concentration (g/dm^3)
Rb	0.12
Sr	0.28
Y	0.15
Zr	1.24 *
Mo	1.18
Ru	0.40
Cs	1.26
Ba	0.59
Nd	1.42

* uncertain concentration due to incomplete dissolution of the salt.

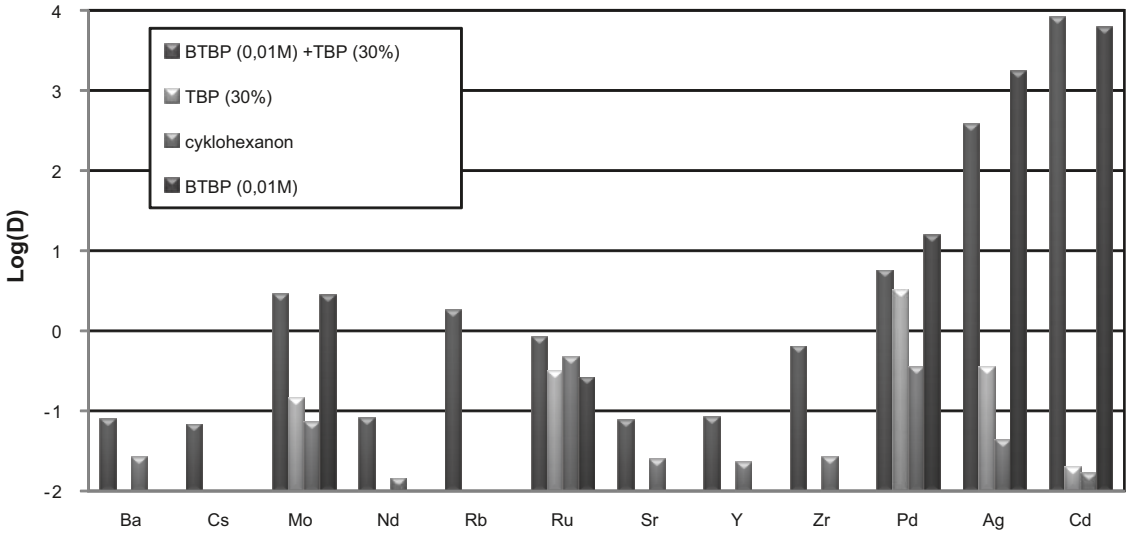


Figure 6-17. *Data from extraction of metals with three different organic phases performed in two steps. Trace amounts of Ag, Cd and Pd in one extraction and larger amounts of Ba, Cs, Mo, Nd, Rb, Ru, Sr, Y and Zr in another extraction. Organic phase BTBP+TBP: C5-BTBP(0.01 M)+30% TBP in cyclohexanone. Organic phase TBP: 30% TBP in cyclohexanone. Organic phase BTBP: C5-BTBP(0.01 M) in cyclohexanone. Organic phase cyclohexanon: 100% cyclohexanone.*

until a total nitrate concentration of 4 M was reached. To avoid loading, the metal concentrations were kept close to 0.001 M for Mn, Ag, Cd, Sb and 0.0006 M for Co and Sm. All of these extractions were then performed as stated in Section 3.1.1. The samples with radiotracers were shaken by hand for 10 minutes and the samples with inactive metals were shaken with the thermostated shaker for 60 minutes (20°C).

As can be seen in Table 6-4 it is the BTBP molecule that is responsible for all the extractions of the fission and corrosion products, except for antimony which also to a small amount is extracted with TBP. The distribution ratios are somewhat lower with TS2 than with pure BTBP which in this case is a good sign since these extractions are all unwanted.

To make sure that the results above not only apply to a water phase of 4 M nitrate concentration but also to an aqueous phase with 4 M nitric acid concentration, which would be the real case, an extraction with TBP in cyclohexanone was made and compared to the extraction with TS2. The results that can be seen in Table 6-5 are well in coherence with that obtained earlier in Table 6-4 ensuring an independent extraction even under process conditions.

Table 6-4. Log (D) from the extraction of metals (in 4 M nitrate concentration (1 M HNO_3 + 3 M $NaNO_3$)) with four different organic phases (BTBP+TBP: 0.01 M $CyMe_4$-BTBP + 30% TBP in cyclohexanone. BTBP: 0.01 M $CyMe_4$-BTBP in cyclohexanone. TBP: 30% TBP in cyclohexanone. Cyclohexanone: pure cyclohexanone).

	BTBP+TBP log (D)	BTBP log (D)	TBP log (D)	Cyclohexanone log (D)
Eu	0.55	0.09	–0.94	–1.82
Ni	1.83	2.85	–2.99	–2.58
Pd	1.33	2.11	–0.84	–0.76
Mo	1.21	1.46	–0.99	–1.13
Ag	1.78	1.72	–0.79	–0.76
Cd	*	*	–1.11	–1.46
Co	4.06	4.02	–1.09	–1.38
Mn	3.49	3.47	–1.00	–1.23
Sb	3.05	3.14	0.06	–0.08
Sm	–0.38	–0.73	–0.52	–1.32

* D value too high to measure with the equipment.

Table 6-5. Log (D) from the extraction of metals from 4 M HNO_3 with two different organic phases (BTBP+TBP: 0.01 M $CyMe_4$-BTBP + 30% TBP in cyclohexanone. TBP: 30% TBP in cyclohexanone).

	BTBP+TBP	TBP
Eu	–0.02	–1.35
Zr	–0.02	–0.43
Mo	0.86	–2.00
Ag	2.92	–0.88
Cd	4.26	–1.10
Sb	0.82	–0.94
Mn	0.01	–2.00
Co	–0.30	–2.00
Sm	–0.18	–1.22

6.7 Varying the ternary system

To see how the systems extraction abilities correlates to the composition, the amount of TBP has been varied from the until now used 30% to 20 and 40%. The nitric acid concentration in the aqueous phase has also been varied from 1 M to 2 and 3 M to see how this affects the extractions.

All extractions were performed as stated in Section 3.1.1 with hand shaking for 10 minutes.

6.7.1 Americium

As can be seen in Figure 6-18 below the distribution ratio for Am is decreased when increasing the nitric acid concentration when the organic phase consists of 20% TBP + 0.01 M C5-BTBP in cyclohexanone. In the opposite way the D is increased when increasing the nitric acid concentration when the organic phase consists of 40% TBP + 0.01 M C5-BTBP in cyclohexanone. The organic phase with 30% TBP on the other hand shows a peak in distribution ratio at a nitric acid concentration of 2 M. How the amount of TBP in the organic phase affects the extraction therefore highly depends on the nitric acid strength in the water phase.

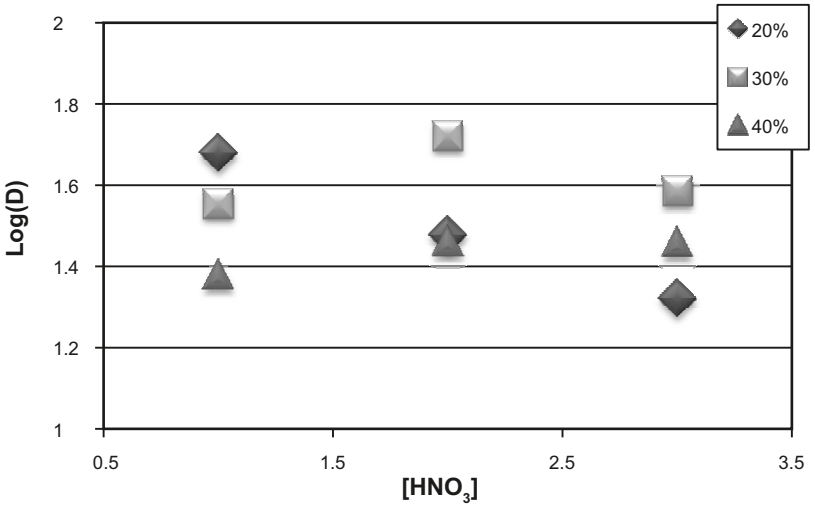


Figure 6-18. *Extraction of ^{241}Am from 1, 2 and 3 M HNO_3 with three different organic phases: C5-BTBP(0.01 M)+20% TBP in cyclohexanone, C5-BTBP(0.01 M)+30% TBP in cyclohexanone and C5-BTBP(0.01 M)+40% TBP in cyclohexanone.*

6.7.2 Europium

The extraction of Eu (see Figure 6-19) shows an almost identical behavior as the extraction of Am. This is not surprising since the elements display a very similar chemical behavior and therefore the extraction of both elements is caused by the BTBP molecule and not the TBP.

6.7.3 Neptunium

As can be seen in Figure 6-20 below, the extraction of neptunium is increased for all organic phases when increasing the nitric acid concentration from 1 to 2 M and then the D reaches a plateau. On the contrary to D_{Am} and D_{Eu} the D for Np is always higher when the TBP content in the organic phase is lower. This goes for the lower acidities (1 and 2 M HNO_3) but at 3 M HNO_3 the D_{Np} for 20% and 30% TBP in the organic phase is almost the same.

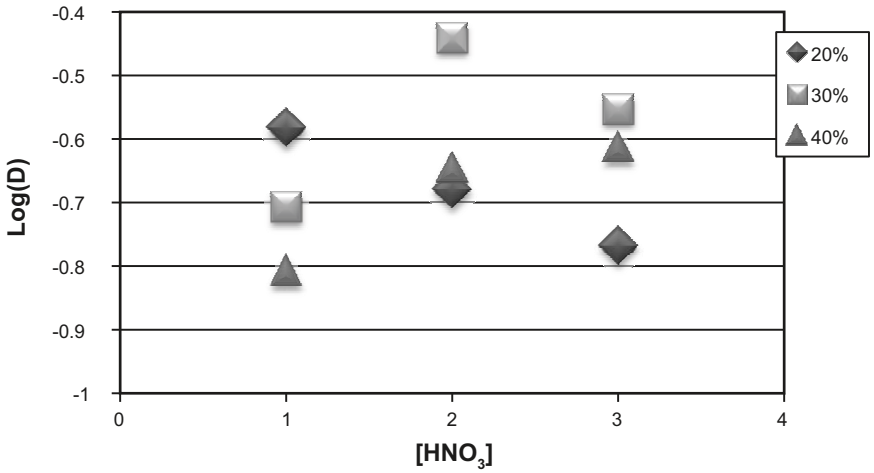


Figure 6-19. *Extraction of ^{152}Eu from 1, 2 and 3 M HNO_3 with three different organic phases: C5-BTBP(0.01 M)+20% TBP in cyclohexanone, C5-BTBP(0.01 M)+30% TBP in cyclohexanone and C5-BTBP(0.01 M)+40% TBP in cyclohexanone.*

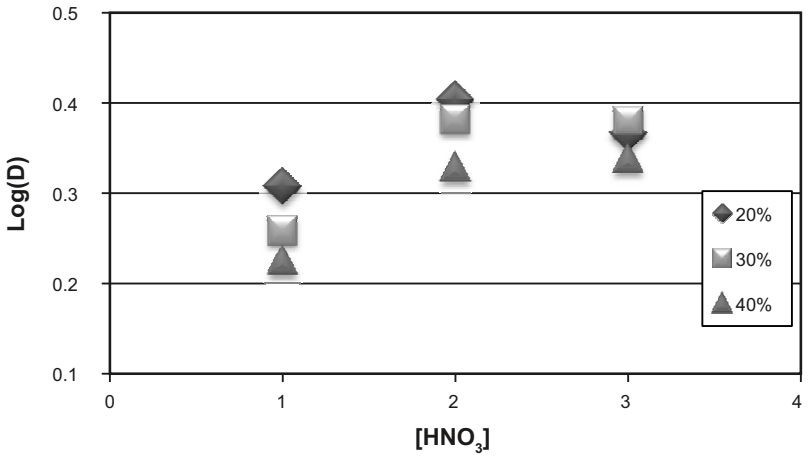


Figure 6-20. *Extraction of ^{237}Np from 1, 2 and 3 M HNO_3 with three different organic phases: C5-BTBP (0.01 M)+20% TBP in cyclohexanone, C5-BTBP(0.01 M)+30% TBP in cyclohexanone and C5-BTBP (0.01 M)+40% TBP in cyclohexanone.*

6.7.4 Thorium

As can be seen in Figure 6-21 thorium display a very simple behavior compared to the two other actinides. The distribution ratio is increased when the TBP content in the organic phase is increased and in the same way the D is increased when the nitric acid strength is increased.

6.7.5 Uranium

For uranium only the TBP-content in the organic phase was varied since the extraction was not performed from a spiked water phase hence making nitric acid variation more difficult.

As can be seen in Figure 6-22 the distribution ratio for uranium is increased when increasing the TBP-content, as expected.

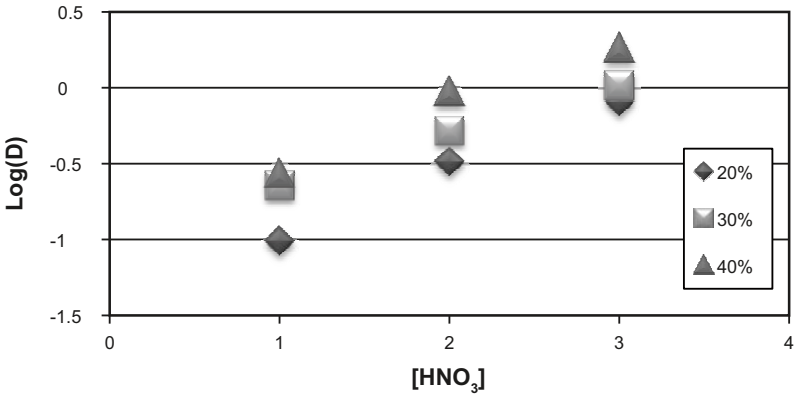


Figure 6-21. *Extraction of ^{234}Th from 1, 2 and 3 M HNO_3 with three different organic phases: C5-BTBP(0.01 M)+20% TBP in cyclohexanone, C5-BTBP(0.01 M)+30% TBP in cyclohexanone and C5-BTBP(0.01 M)+40% TBP in cyclohexanone.*

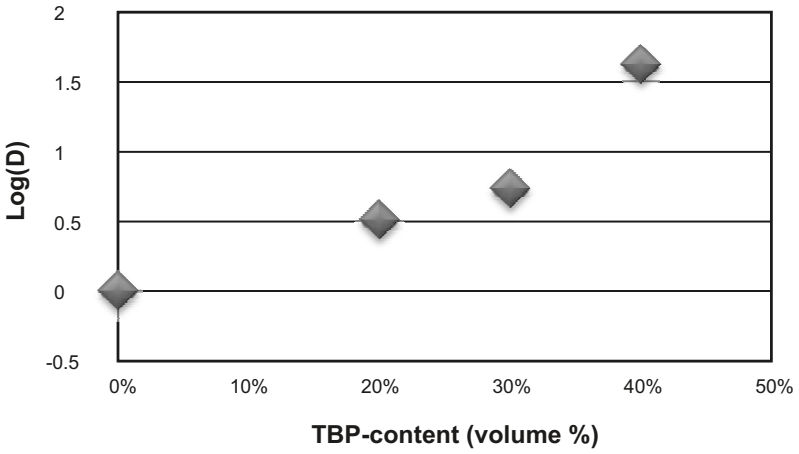


Figure 6-22. *Extraction ^{238}U from a 1 mM UO_2^{2+} (natural uranium) solution in 1 M HNO_3 with three different organic phases: C5-BTBP (0.01 M) + 20% TBP in cyclohexanone, C5-BTBP (0.01 M) + 30% TBP in cyclohexanone and C5-BTBP (0.01 M) + 40% TBP in cyclohexanone.*

6.8 Extraction under process like conditions

The studies performed above have given important information on the ternary system containing TBP-BTBP and cyclohexanone. Most investigations were made with C5-BTBP and due to this also with lower acidity than what would be the case in a real GANEX process was used. To see how the system would act under more realistic process conditions with high acidity (4 M nitric acid) extractions of actinides, lanthanides, fission products and corrosion products were performed. Besides the radioactive isotopes used (^{235}U, ^{237}Np, ^{238}Pu, ^{241}Am, ^{152}Eu and ^{63}Ni) all metals were present in quantities close to those in real dissolved spent fuel /49, 32, 25, 11/ (see Table 6-6).

As can be seen in Figure 6-23 the actinides are readily extracted from 4 M nitric acid and could also be separated from the lanthanides which are not extracted to any greater extent (see Figure 6-24).

Some of the fission and corrosion products are also extracted (see Figure 6-25 and 6-26), which is undesirable.

6.9 Pd and other fission products

As could be seen in the section above, some fission products were extracted by the ternary system. This problem can either be dealt with through pre extraction were the troublesome elements are removed in an extraction step before the actual GANEX process or through suppression by adding a water soluble complexant that stops the elements in question from being extracted by the GANEX solvent.

Table 6-6. Concentrations of Fission products and Corrosion products (measured with ICP-OES) used in the extraction experiments.

Substance	Conc. (ppm)	Conc. (mM)
Ba	480	3.5
Ce	930	6.6
La	480	3.5
Nd	1,360	9.4
Cs	1,200	9.0
Rb	100	1.2
Sm	230	1.5
Sr	240	2.7
Te	1,470	11.5
Y	110	1.2
Ag	60	0.5
Cd	30	0.3
Rh	40	0.4
Sb	10	0.08
Sn	1	0.008
Co	300	5.1
Cr	260	5.0
Fe	270	4.8
Mn	330	6.0
Zr	1,500	16
Pd	450	4.2
Mo	650	6.8
Ru	400	3.9

Focus were put on the elements that have a high abundance in spent fuel and that have a distribution ratio close to or above 1 (Zr, Mo and Pd). It was reported earlier /4/ that Pd precipitates in the presence of a ketone like cyclohexanone and due to this, special focus was put on Pd.

All extractions in this section were performed according to the standard extraction experiment described in Section 3.1.1 with metal concentrations close to those in Table 6-6. All samples with Pd as well as the An and Ln were shaken by hand for 10 minutes while the samples with the other inactive metals were shaken with a thermostatic shaker for 60 minutes (20°C).

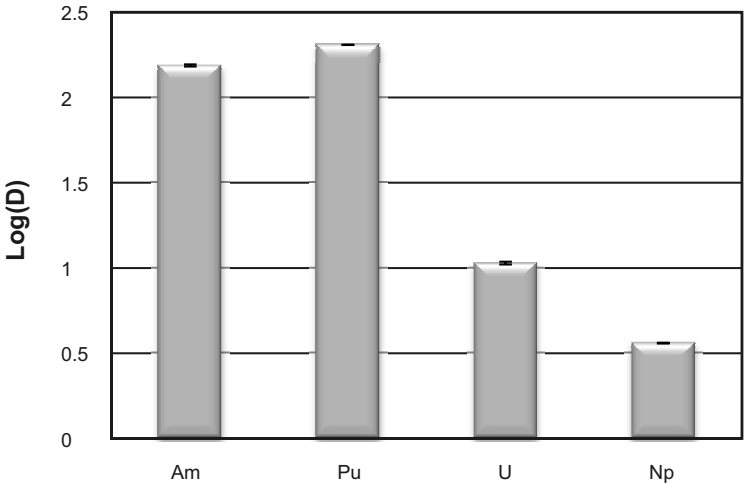


Figure 6-23. *Extraction of actinides (^{235}U, ^{237}Np, ^{238}Pu, ^{241}Am) from 4 M nitric acid with 0.01 M $CyMe_4$-BTBP and 30% TBP in cyclohexanone.*

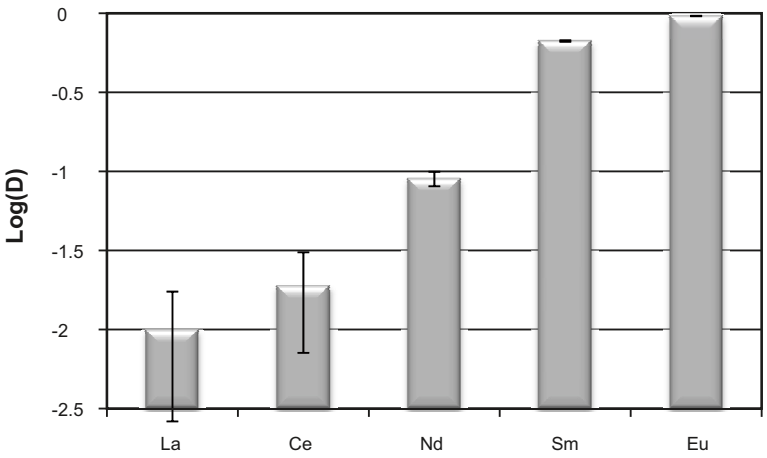


Figure 6-24. *Extraction of lanthanides (^{152}Eu, the rest as non radioactive metal salts) from 4 M nitric acid with 0.01 M $CyMe_4$-BTBP and 30% TBP in cyclohexanone.*

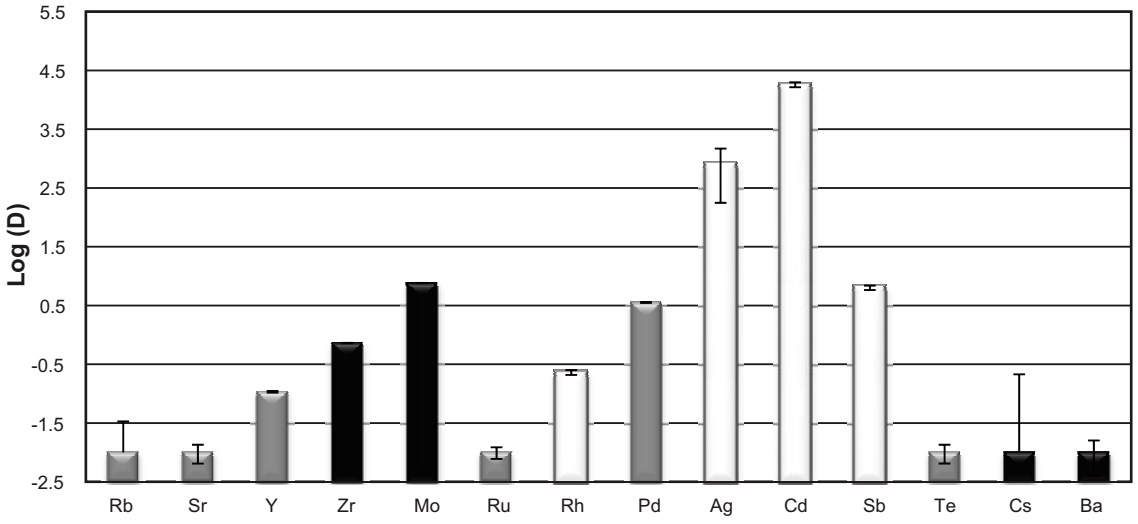


Figure 6-25. *Extraction of fission products from 4 M nitric acid with 0.01 M $CyMe_4$-BTBP and 30% TBP in cyclohexanone. White bars-concentrations well below 100 ppm in dissolved fuel. Grey bars-concentrations between 100–600 ppm in the dissolved fuel. Black bars-concentrations above 1,000 ppm in dissolved fuel.*

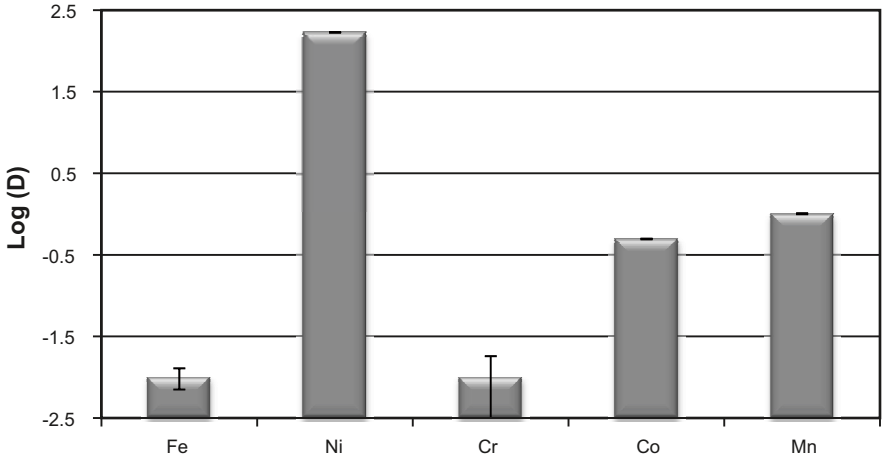


Figure 6-26. *Extraction of corrosion/activation products from 4 M nitric acid with 0.01 M $CyMe_4$-BTBP and 30% TBP in cyclohexanone. Metal concentrations of 0.005 M.*

6.9.1 Pre extraction

As was previously reported by Aneheim et al. /4/ dioctyl sulfide could be used to pre extract Pd and other troublesome fission products. These earlier tests were however made with cyclohexanone as a diluent that besides precipitating Pd also extracted U and Pu, which is undesired in a pre extraction step. Due to this new extraction tests with dioctyl sufide (0.5 M) in kerosene (Solvent 70) instead of cyclohexanone have been performed. This time the extractions were also made from 4 M nitric acid to resemble process like conditions.

As can be seen in Figure 6-27, Pd is readily extracted by the system. Also Mo is extracted but not to any greater extent. To make sure that this extraction not would disturb the actinide chemistry an extraction of Am, Pu and U with dioctyl suldfide in kerosene was performed. As can be seen in Table 6-7 none of the actinides were extracted.

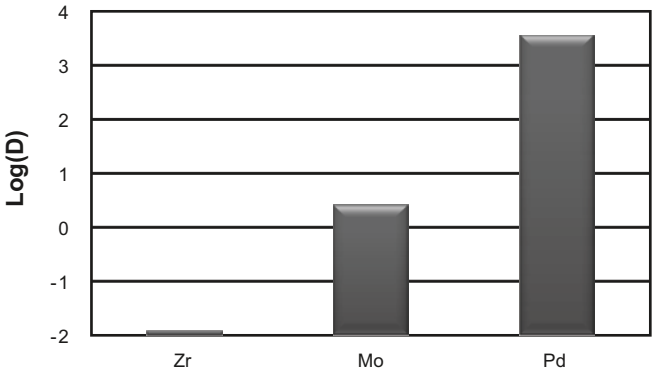


Figure 6-27. *Extraction of Zr, Mo and Pd from 4 M nitric acid with 0.5 M dictyle sulfide in kerosene.*

Table 6-7. Extraction of ^{241}Am, ^{238}Pu and ^{235}U from 4 M nitric acid with 0.5 M dioctyl sulfide in kerosene.

Element	Log(D)
Am	< –3
Pu	–5
U	–3

6.9.2 Suppression

Methionine

It was previously reported by Aneheim et al. /4/ that methionine in high enough concentrations could be used to stop the precipitation of metallic Pd from a Pd nitrate solution in the presence of cyclohexanone.

Now this amino acid has also been used as a water soluble complexing agent to try and stop the unwanted extraction of Pd with the ternary system. By using different concentrations of methionine dissolved in an aqueous palladium nitrate solution, the effect of the methionine concentration upon the palladium distribution ratio for the TS2 solvent was investigated.

Extractions of Pd from two different nitrate solutions (1 M nitric acid and 4 M nitric acid) were performed. As can be seen in Figure 6-28 methionine effectively prevents the Pd extraction from 1 M nitric acid while it is evident in Figure 6-29 that the methionine addition does not prevent the extraction from 4 M nitric acid.

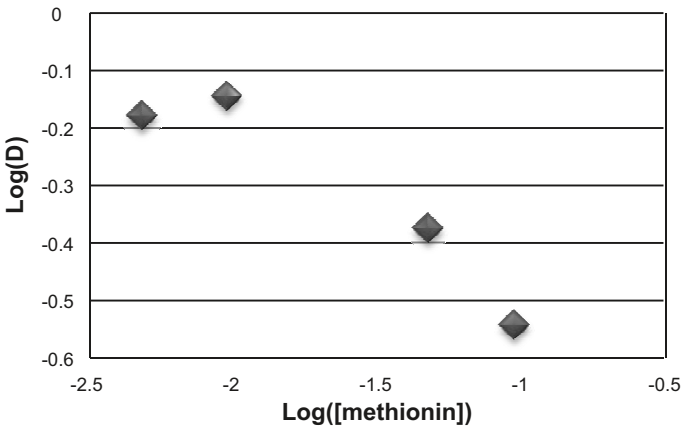


Figure 6-28. *Extraction of Pd with 0.01 M CyMe$_4$-BTBP + 30% TBP in cyclohexanone from 1 M nitric acid.*

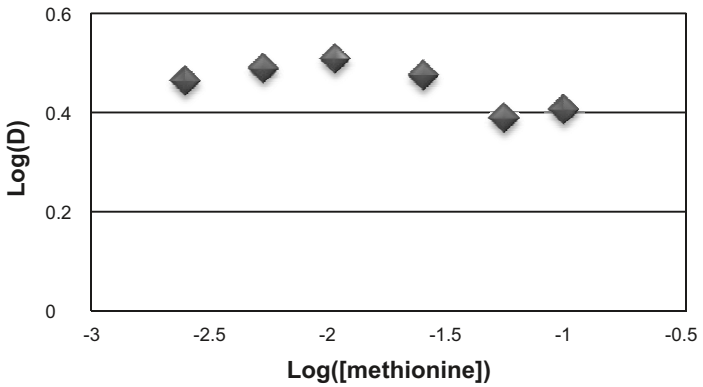


Figure 6-29. *Extraction with 0.01 M $CyMe_4$-BTBP + 30% TBP in cyclohexanone from 4 M nitric acid.*

Mannitol

When looking at two other fission products, Zr and Mo, it was found that the addition of mannitol to an aqueous phase of 4 M nitric acid caused the distribution ratios for both these two metals with the TS2 solvent to be decreased (see Figure 6-30). The decrease for Mo is only minor while on the other hand the extraction of Zr with TS2 is completely suppressed.

Bimet

Since it was discovered earlier that methionine cannot stop the Pd-extraction from 4 M nitric acid, another molecule based on methionine was designed and synthesised. The advantage of the chelate effect was taken into account and employed on a palladium binding agent with two sulfur atoms; bi-methionine (bimet) (see Figure 6-31). This compound was made by the reaction of methionine with ethylene dibromide (1,2-dibromoethane) in hot concentrated hydrochloric acid. When using bimet as a water soluble complexing agent instead of methionine it was found that even low concentrations were able to prevent the precipitation of metallic palladium in contact with cyclohexanone. Bimet was also able to stop the extraction of Pd with the TS2 solvent from both 1 M nitric acid (see Figure 6-32a) and 4 M nitric acid (see Figure 6-32b).

To make sure that the addition of bimet to the water phase does not alter the actinide chemistry and the lanthanide separation an extraction experiment with Am, Eu, U and Pu from a bimet containing water phase was performed. As can be seen in Figure 6-33 the bimet addition does not affect the distribution ratios for the actinides or the lanthanides.

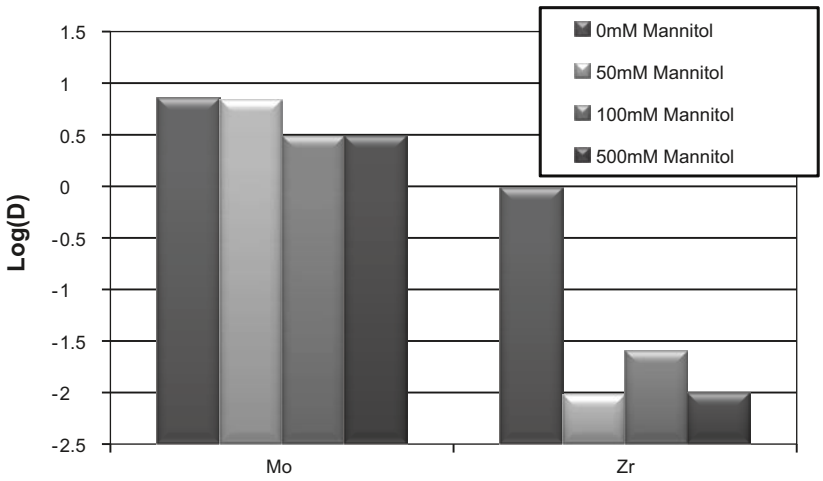


Figure 6-30. *Extraction with 0.01 M $CyMe_4$-BTBP + 30% TBP in cyclohexanone from 4 M nitric acid with different additions of mannitol.*

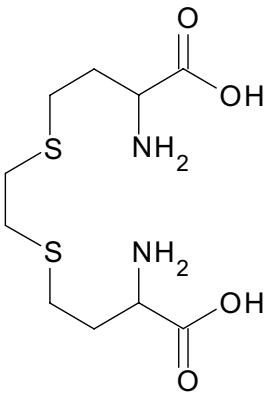


Figure 6-31. *molecular structure of bi-methionine (bimet).*

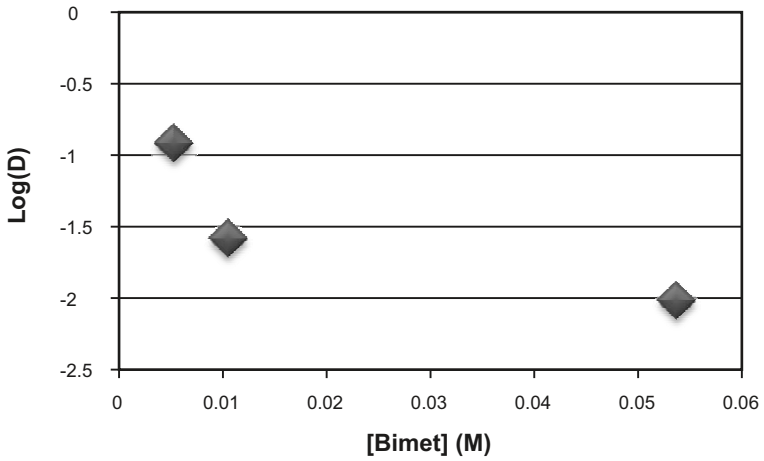


Figure 6-32a. *Extraction of Pd with 0.01 M $CyMe_4$-BTBP + 30% TBP in cyclohexanone from 1 M nitric acid.*

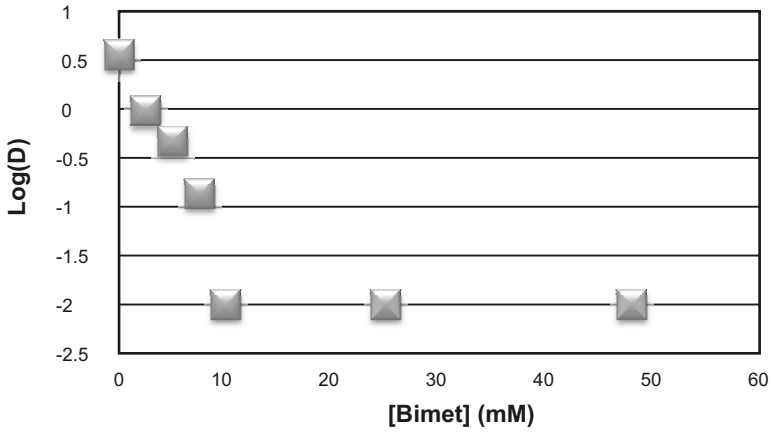


Figure 6-32b. *Extraction of Pd with 0.01 M $CyMe_4$-BTBP + 30% TBP in cyclohexanone from 4 M nitric acid.*

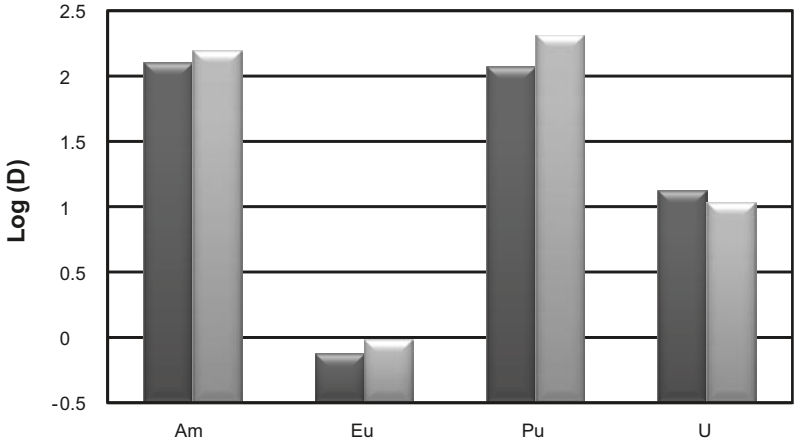


Figure 6-33. *Extraction with 0.01 M $CyMe_4$-BTBP + 30% TBP in cyclohexanone from 4 M nitric acid with and without the addition of 10 mM Bimet.*

The effect of Bimet on the extraction of Zr and Mo with the ternary system was also tested. With an addition of 50 mM of Bimet to the water phase (4 M nitric acid) the distribution ratio for Zr was slightly decreased ($\log(D_{Zr}) = -0.5$) but the D for Mo was unaffected.

6.9.3 Conclusion

The extraction of Pd can effectively be suppressed by the addition of Bimet to the water phase. Also the extraction of Zr can be diminished with Bimet but totally stopped if adding Mannitol. The effect on Mo-extraction with Bimet addition to the water phase has to be investigated.

6.10 Loading

Distribution ratios in a solvent extraction process are highly affected by the possible loading situation in the organic phase. To see how this affects the primary extraction of the actinides and their separation from the lanthanides, two different sets of tests were performed.

6.10.1 Metal loading

The extraction experiments were performed as stated in Section 3.1.1 – standard extraction experiment, with 10 minutes of hand shaking. One metal solution was prepared by dissolving the metal salts/oxides of: Rb, Sr, Y, Zr, Mo, Rh, Pd, Ag, Cd, Sb, Cs, Ba, La, Ce, Nd, Sm and Te (in approximately the same concentrations as seen in Table 6-6) in 4 M HNO_3. The total metal concentration was then over 9,000 ppm. ^{235}U, ^{237}Np, ^{238}Pu, ^{241}Am and ^{152}Eu was then extracted with TS2 from the metal solution.

As can be seen in Figure 6-34 the D for U is unaffected by the loading conditions, just like the D for Np. It can also be seen that the D for both Am and Pu is lowered but still sufficiently high for an extraction process, especially since the D for Eu also was lowered. This in fact renders a total raise in SF for all actinides except Am (see Table 6-8).

6.10.2 Uranium loading

In the previous investigations of this ternary system the future scenario has exclusively been a GANEX process where the bulk part of the uranium in the spent fuel has been removed. A preliminary test was also made simulating a case where the uranium bulk is not removed.

A highly concentrated solution of uranium (approx. 0.1 M) spiked with traces of americium, europium and plutonium was subsided to extraction with TS1. The extractions were performed according to the standard extraction experiment (Section 3.1.1) with 10 minutes of hand shaking.

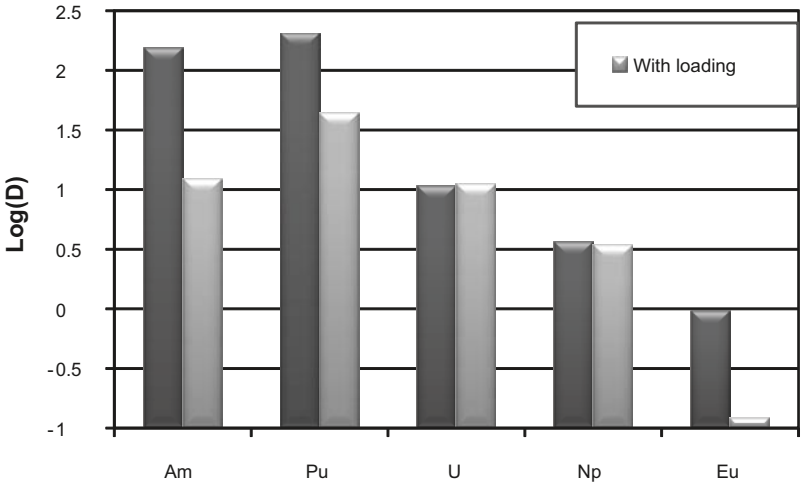


Figure 6-34. *Extraction of ^{235}U, ^{237}Np, ^{238}Pu, ^{241}Am and ^{152}Eu from a 4 M nitric acid-metal loaded aqueous phase with 0.01 M $CyMe_4$-BTBP and 30% TBP in cyclohexanone. Total metal concentration: > 9,000 ppm.*

Table 6-8. Separation factors for the actinides (U, Np, Pu, Am) and one lanthanide (Eu) after extraction from metal loaded 4 M HNO_3 (metal content > 9,000 ppm) with 0.01 M $CyMe_4$-BTBP + 30% TBP in cyclohexanone.

Elements	Separation factor
Am / Eu	101
Pu / Eu	363
U / Eu	91
Np / Eu	28

As can be seen in Figure 6-35 the extractions of Am, Eu and Pu are somewhat suppressed with the high concentration of uranium present in the water phase but the distribution ratios and separation factors for these elements are still high enough. This test however has to be remade with process like conditions, i.e. higher acidity (4 M HNO_3) in the aqueous phase and the TS2 solvent, to be able to draw any final conclusions whether or not the new GANEX system could be implicated on a water phase where the uranium bulk not has been removed.

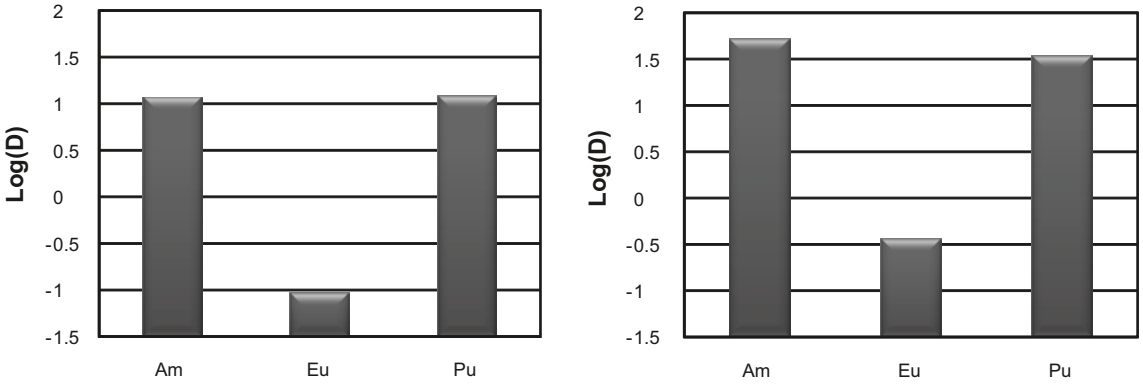


Figure 6-35. *Left: Extraction of ^{241}Am, ^{152}Eu and ^{238}Pu from a uranium-loaded (0.1 M UO_2^{2+}) aqueous phase (2 M nitrate concentration) with C5-BTBP (0.01 M)+30% TBP in cyclohexanone. Right: Extraction of ^{241}Am, ^{152}Eu and ^{238}Pu from an aqueous phase consisting of 2 M HNO_3 with C5-BTBP (0.01 M) + 30% TBP in cyclohexanone.*

7 Radiolysis

Since the separation process using the BTBP molecules takes place in a high radiation flux the solvent, i.e. both the extractant and the diluent, must be resistant to radiation. The radiation will be of different types, e.g. alpha and gamma, and the dose rate will be dependent on the isotopic concentration of minor actinides (MA) /31/. This will in turn be dependent on initial fuel composition and burn-up. During the last years numerous radiolysis studies have been done at Chalmers where the focus has been on how the extraction properties of BTPs and BTBPs are affected by irradiation /39, 40, 18, 21, 22, 43/. Recently, our radiolysis studies have expanded to also include further analysis of irradiated solutions to determine the change in extractant concentration and the increasing concentration of degradation products, as well as to try to identify the formed degradation products. The analysis methods used are HPLC, MS and LC-MS and the analyses have been performed in collaboration with Institute of inorganic chemistry, Academy of sciences, in the Czech Republic.

The aqueous phase used in all radiolysis studies was 0.01 M HNO_3, 0.99 M $NaNO_3$ + radiotracers.

7.1 Decrease in BTBP concentration upon irradiation

A number of organic solvents were analyzed in terms of how the concentration of extractant changed as the solvent was exposed to radiation. The solvents contained a BTBP dissolved in a selected diluent. The change in BTBP concentration as a function of the dose was compared to the change in extraction behavior for the same solvent at similar doses. The following Figures (7-1–7-7) shows the change in BTBP concentration as well as the change in distribution ratios as a function of the received dose for seven different systems. The change is plotted as % of the start value and the start values are given in the caption of each figure. Figure 7-1–7-7 shows the following systems:

7-1 – C5-BTBP in hexanol, irradiated with 12.5 Gy/h
7-2 – C5-BTBP in cyclohexanone, irradiated with 12.5 Gy/h
7-3 – C5-BTBP in cyclohexanone, irradiated with ~1.6 kGy/h
7-4 – $CyMe_4$-BTBP in hexanol, irradiated with 12.5 Gy/h
7-5 – $CyMe_4$-BTBP in hexanol, irradiated with ~1.0 k Gy/h
7-6 – $CyMe_4$-BTBP in cyclohexanone, irradiated with 12.5 Gy/h
7-7 – $CyMe_4$-BTBP in cyclohexanone, irradiated with ~1.0 k Gy/h.

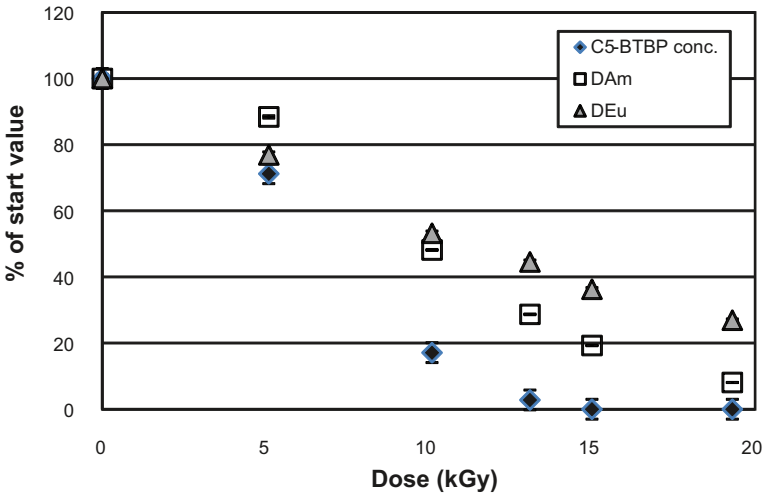


Figure 7-1. *Change in BTBP concentration, D_{Am} and D_{Eu} as a function of the dose for a system containing C5-BTBP in hexanol and irradiated with a dose rate of 12.5 Gy/h (^{60}Co). The start values were: [C5-BTBP] = 0.005 M, D_{Am} = 3.77, D_{Eu} = 0.032.*

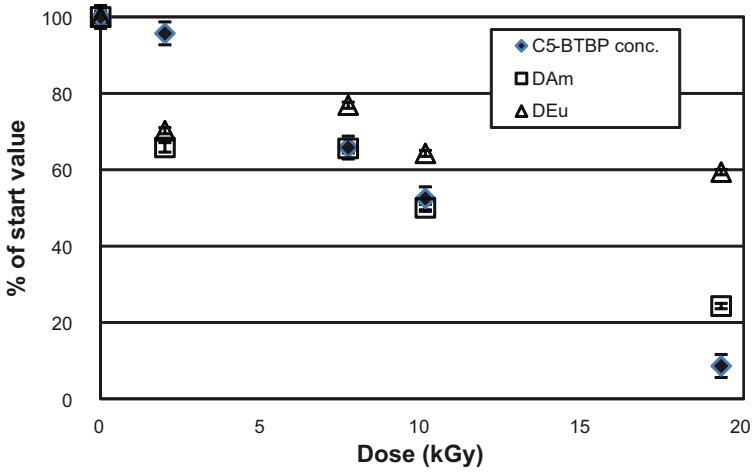


Figure 7-2. *Change in BTBP concentration, D_{Am} and D_{Eu} as a function of the dose for a system containing C5-BTBP in cyclohexanone and irradiated with a dose rate of 12.5 Gy/h (^{60}Co). The start values were: [C5-BTBP] = 0.005 M, D_{Am} = 38.5, D_{Eu} = 0.21.*

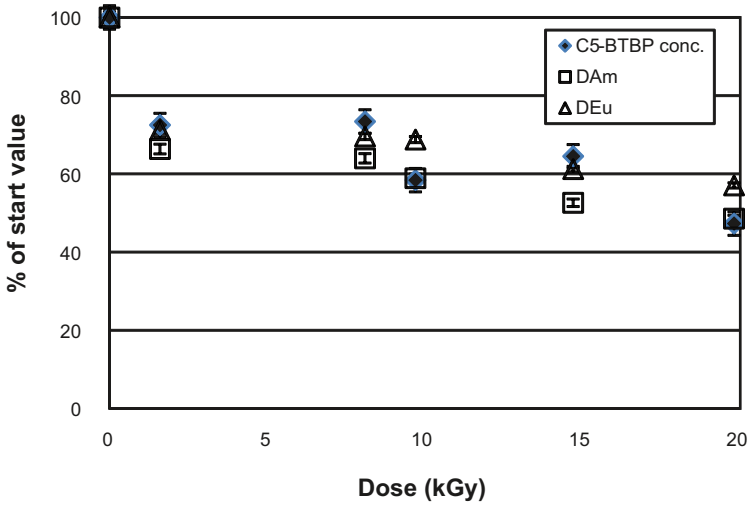


Figure 7-3. *Change in BTBP concentration, D_{Am} and D_{Eu} as a function of the dose for a system containing C5-BTBP in cyclohexanone and irradiated with a dose rate of ~1.6 kGy/h (^{137}Cs). The start values were: [C5-BTBP] = 0.005 M, D_{Am} = 38.5, D_{Eu} = 0.21.*

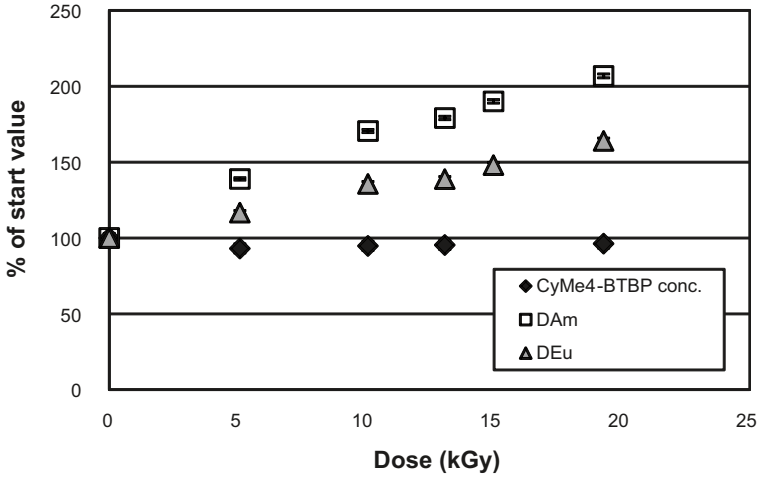


Figure 7-4. *Change in BTBP concentration, D_{Am} and D_{Eu} as a function of the dose for a system containing $CyMe_4$-BTBP in hexanol and irradiated with a dose rate of 12.5 Gy/h (^{60}Co). The start values were: [$CyMe_4$-BTBP] = 0.005 M, D_{Am} = 3.11, D_{Eu} = 0.032.*

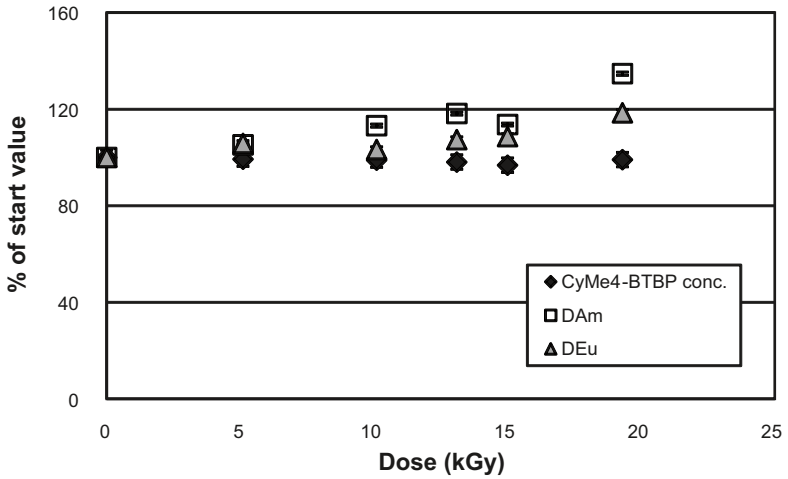


Figure 7-5. *Change in BTBP concentration, D_{Am} and D_{Eu} as a function of the dose for a system containing $CyMe_4$-BTBP in hexanol and irradiated with a dose rate of ~1.0 kGy/h (^{137}Cs). The start values were: [$CyMe_4$-BTBP] = 0.005 M, D_{Am} = 3.09, D_{Eu} = 0.031.*

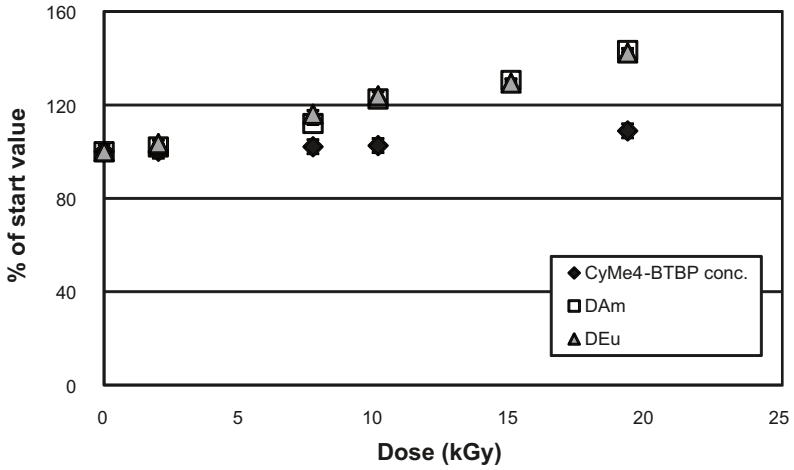


Figure 7-6. *Change in BTBP concentration, D_{Am} and D_{Eu} as a function of the dose for a system containing $CyMe_4$-BTBP in cyclohexanone and irradiated with a dose rate of 12.5 Gy/h (^{60}Co). The start values were: [$CyMe_4$-BTBP] = 0.005 M, D_{Am} = 4.38, D_{Eu} = 0.039.*

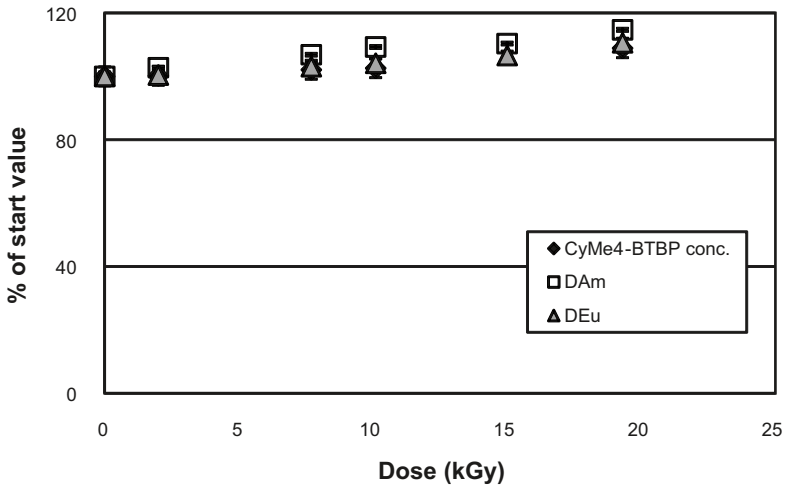


Figure 7-7. *Change in BTBP concentration, D_{Am} and D_{Eu} as a function of the dose for a system containing $CyMe_4$-BTBP in cyclohexanone and irradiated with a dose rate of ~1.0 kGy/h (^{137}Cs). The start values were: [$CyMe_4$-BTBP] = 0.005 M, D_{Am} = 4.38, D_{Eu} = 0.042.*

For C5-BTBP (see Figure 7-1–7-3), the decrease in BTBP concentration more or less follows the decrease in distribution ratios, but when the diluent is hexanol (see Figure 7-1) it can be clearly seen that the decrease, expressed as percentage of the start value, is larger for the BTBP concentration than for the distribution ratios. After 15 kGy there is no C5-BTBP left in the solution, but there is still a certain extraction (D_{Am} at 15 kGy = 0.8), hence, some of the degradation products must also be able to extract the metals.

When it comes to $CyMe_4$-BTBP the situation looks a bit different. In all four systems (see Figure 7-4–7-7), the concentration of BTBP can basically be considered constant when taking uncertainties into account. However, the metal extraction increases, especially in the low dose rate irradiated system with hexanol as diluent.

7.2 Degradation products and their variation with dose

In the annual report for 2008 a study on radiolysis degradation products for a number of systems was presented /4/. During 2009 this study has been expanded and additional analyses have confirmed and strengthened the previous results. The more detailed study is presented in /20/.

7.3 Alpha vs. gamma radiolysis

In the well established PUREX process, which is used to separate uranium and plutonium from the rest of the spent nuclear fuel, the solvent is primarily exposed to gamma radiation. However, for example in the so called SANEX process, suggested as a mean to separate trivalent actinides from trivalent lanthanides, the irradiation mainly originates from nuclides decaying emitting alpha particles. In a SANEX type process the irradiation comes almost exclusively from americium and curium.

When discussing the effect of irradiation, one of the most important features that differ between α and γ irradiation is the Linear Energy Transfer (LET). It describes the rate at which a particle deposits its energy as it moves through a material and is often expressed as keV/µm. ^{60}Co γ-radiation has a typical LET value of 0.2 keV/µm while the value of a ^{241}Am α-particle is 120 keV/µm /28/. A high LET means that all energy is deposited within a short distance, leading to areas of high concentration of various radiolysis products. High LET radiation therefore has a higher probability of interradical reactions (reactions between two radicals) since areas of high concentrated radicals are formed /51/. Deactivation of ionized and/or excited particles by collision is also more likely with high LET radiation /23/. Interradical and deactivation reactions take place in the track formed by the irradiation and compete with the diffusion into the bulk solution and the following reactions with solute molecules /54/. In the case of γ radiation, radicals have a high probability of escaping the track and diffuse into the bulk medium /54/. Thus, alpha radiation results in higher yields of molecular species and lower yields of radicals, compared to gamma radiation /36/.

There are additional differences between α and γ radiation. Among other things the two types of radiation deposit their energy in different ways. The most important way of depositing energy for charged particles, such as α, is the interaction with electrons and atoms in the media, either by excitation or ionization /10/. Radiolysis reactions induced by α particles often include the ejection of secondary electrons and these tend to play an important role in the overall reactions /10/. γ-Rays interact with matter in three different ways: Compton scattering (or Compton effect), photoelectric effect and pair production. The energy of the incoming photon affects the contribution of the different types of interaction. Photons from ^{60}Co (1,173 and 1,332 keV) primarily interact through the Compton effect /6/. The secondary electrons emitted following the interaction of α particles have an average kinetic energy of close to 100 eV and are often assumed to further interact via Compton scattering /48/.

Regarding the difference in ionization between the two types of radiation; alpha radiation produces charged particles directly, while gamma radiation forms charged particles via interactions with the medium, i.e. indirectly /6/. A part of the incident photon energy is transformed into kinetic energy of charged particles and the rest transfers to the secondary γ-rays.

The effect of alpha and gamma radiolysis was compared in a study started in 2008 and thus partly reported in the annual report of that year /4/. Below follows a description of the results from the continuation of those experiments. The radionuclides used were ^{241}Am (α) and ^{60}Co (γ) where the energy of the emitted radiation differs between these two nuclides. The energy of the emitted α particle following a ^{241}Am decay is 5.486 MeV and the photons emitted from a ^{60}Co source have an average energy of 1.2 MeV.

7.3.1 Results for CyMe$_4$-BTBP

In Figure 7-8, the D_{Am} is plotted as a function of the dose for the solvent irradiated with alpha radiation. The radiation originated from an internal source in the form of ^{241}Am initially dissolved in the aqueous phase and then extracted into the organic phase. D is steadily increasing with the dose but no explanation to this has yet been proposed.

CyMe$_4$-BTBP has been shown to be stable with time and stable in contact with dilute nitric acid /26/. Thus it can be assumed that the change in distribution ratio is caused by the irradiation. Figure 7-9 illustrates how the distribution ratio of americium changed as the organic solvent was irradiated with low dose rate alpha and gamma radiation, respectively. Values are plotted as % of the start D, which were 5.1 for the alpha experiment and 4.4 for the gamma experiment. There is no clear difference between the two curves, possibly the gamma radiation affects the system a bit more than alpha does. At least that is the trend indicated from the points between 10 and 20 kGy. This behaviour then coincides with the observation made by Magnusson et al. /31/.

7.3.2 Results for C5-BTBP

It has been shown that C5-BTBP in cyclohexanone is ageing; hence it degrades to a certain extent over time. But by comparing results from irradiated samples with a reference experiment it was concluded that the degradation of the irradiated samples is a combination of both radiolysis and ageing of the solvent. The dose rates used in this study are similar, which means that the total time of irradiation is roughly the same. Thus the samples are ageing to the same extent independent of what irradiation source is used. However, during the alpha irradiation the solvent is in contact with an aqueous phase, and since C5-BTBP has shown to be sensitive towards hydrolysis, this has to be taken into account when comparing the two irradiations done in this study. Figure 7-10 shows the decrease in distribution ratio with time for the solvent exposed to alpha radiation (in contact with aqueous phase during irradiation) and the solvent that was in contact with an aqueous phase but not irradiated (labelled hydrolysis in the figure). The distribution ratio is illustrated as percent of start D.

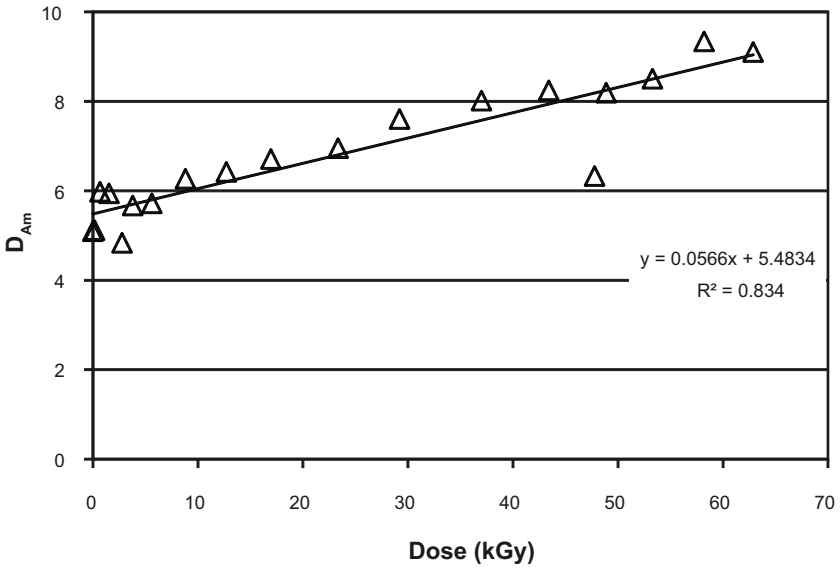


Figure 7-8. *D_{Am} as a function of the absorbed dose for a solvent containing CyMe$_4$-BTBP in cyclohexanone irradiated with α-radiation in the form of ^{241}Am extracted into the organic phase from an aqueous phase.*

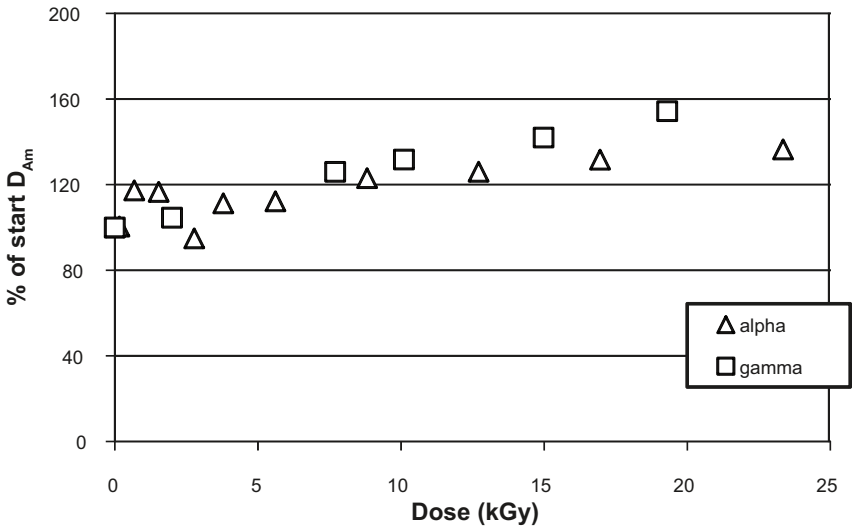


Figure 7-9. *Comparison of the effect of α- and γ-radiation on the extraction of Am by an irradiated solvent containing initially 0.005 M $CyMe_4$-BTBP in cyclohexanone.*

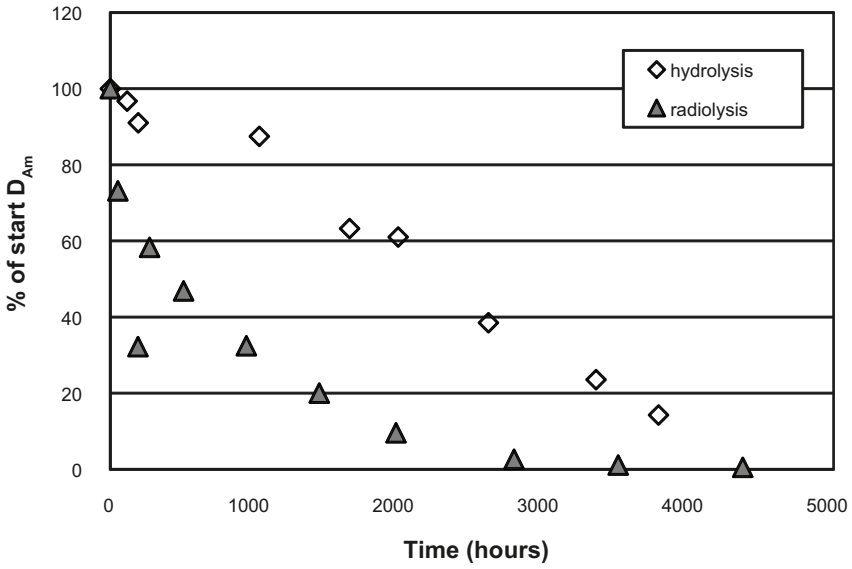


Figure 7-10. *Change in distribution ratio (Am) with time for a solvent containing C5-BTBP in cyclohexanone. The series labelled "hydrolysis" refers to a sample that was left in contact with an aqueous phase (0.01 M HNO_3 + 0.99 M $NaNO_3$). The series labelled radiolysis refers to a corresponding sample with the addition of ^{241}Am in the aqueous phase, resulting in alpha irradiation (thus both hydrolysis and radiolysis).*

The difference between the curves indicates that a large part of the decrease for the irradiated sample is indeed caused by radiolysis, and not by ageing and hydrolysis. Most of the radiolytic degradation appears to take place at the beginning of the irradiation, during the first 2,000 hours, where the D rapidly decreases and the difference between the two curves is the largest. After that, the ageing and hydrolysis accounts for a larger and larger part of the total decrease in D. It should be kept in mind that the dose rate of alpha given to the organic phase decreases with time, as the D decreases, hence the received dose is not a linear increase. If the x-axis is changed to dose (kGy), and the values for the non irradiated sample are plotted as a function of the dose corresponding to a certain time, the figure looks a bit different (see Figure 7-11) but the trends are the same as described above.

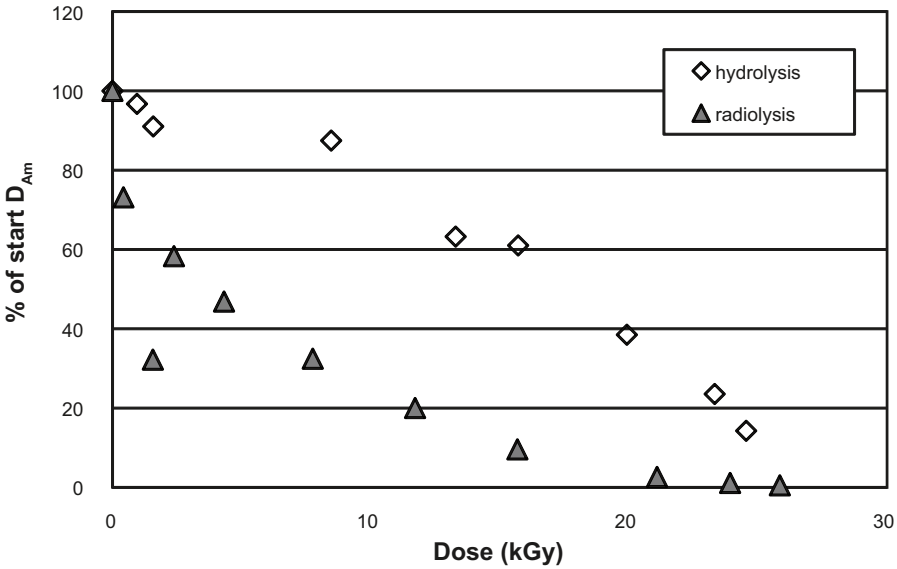


Figure 7-11. *Same as Figure 7-10, but the decrease due to hydrolysis has been subtracted from the total decrease for the irradiated sample. Thus, the values of the "radiolysis series" now represent the decrease due to only radiolysis.*

The distribution ratio of Am is plotted as a function of the received dose for both types of irradiation in Figure 7-12. The distribution ratio is again illustrated as percent of start D. It is clear that the alpha radiolysis affects the solvent to a much higher extent than the gamma radiation does. But this is as discussed before a combination of radiolysis and hydrolysis, since the organic phase was in contact with aqueous phase during the alpha irradiation. Both experiments also include the degradation due to ageing of the organic phase. An attempt was made to correct the values for alpha irradiation by subtracting the decrease in D that is caused by the hydrolysis. This gives the results showed in Figure 7-13. As can be seen, the alpha radiation still seems to cause a larger decrease than what the gamma radiation does. The decrease for the solution irradiated with alpha starts already at the very low doses, reaching less than 80% of start D_{Am} already after 0.5 kGy. The solution irradiated with gamma does not drop to below 80% of start D_{Am} until after 10 kGy.

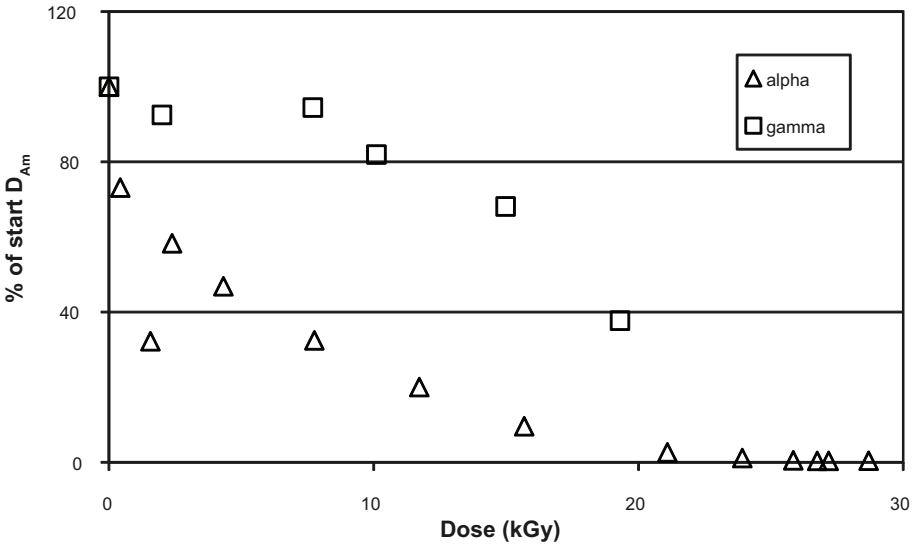


Figure 7-12. *Change in distribution ratio of Am expressed as % of the start D as a function of the received dose. The irradiaiton source was either alpha or gamma radiation. The start D_{Am} was 31 for the alpha experiments and 38 for the gamma experiments.*

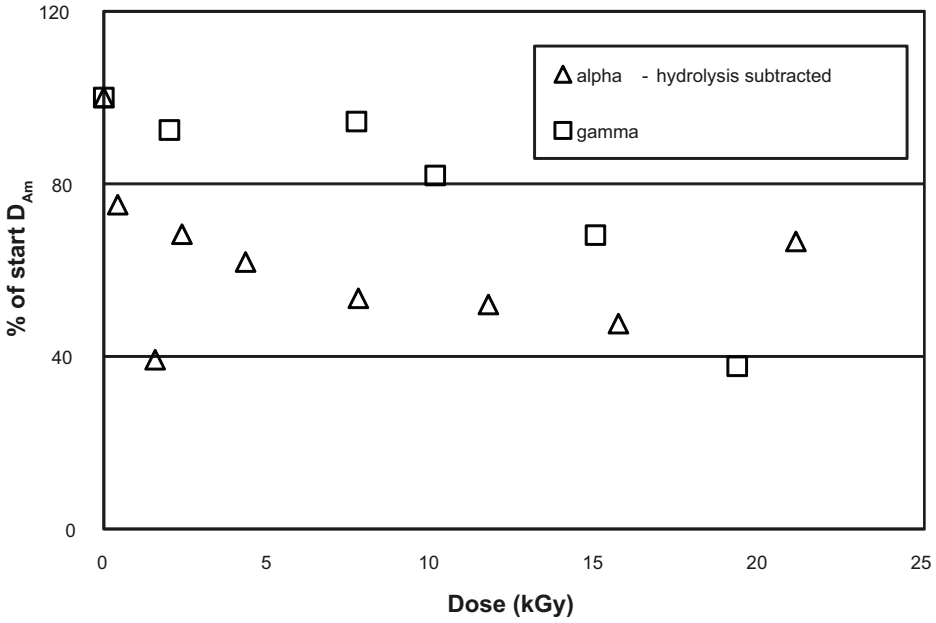


Figure 7-13. *Same as Figure 7-12 but the decrease due to hydrolysis have been subtracted from the alpha values.*

One explanation to the difference between the two irradiations can of course be the presence of an aqueous phase during alpha irradiation. As mentioned above, the radiolysis of water yields many highly reactive intermediates, and these may be expected to react with the organic phase and have drastic effects on the coordinating ability of the BTBP. However, presence of an aqueous phase during irradiation has in some cases proven to lessen the degradation of the organic phase, since the nitrates can scavenge radicals formed during radiolysis. Presence of only water as aqueous phase does not give the same protection towards radiation. In this experiment the HNO_3 concentration is very low and the reactions in the aqueous phase are primarily from water radiolysis, and the amount of nitrates is not enough to scavenge all radicals formed.

7.4 Alpha radiolysis experiments with ^{211}At

A method to perform α-radiolysis experiments with ^{211}At has recently been developed /16/. Due to the short half life and decay chain of ^{211}At, the samples can, after irradiation, be analysed using normal equipment without causing contamination. The method was tested on a solution planned for separation of trivalent actinides from lanthanides based on the BTBP extraction system /12, 24/.

7.4.1 Radionuclide production

^{211}At was produced via the ^{209}Bi(α,2n)^{211}At reaction. A ^{209}Bi target consisting of 99.999% ^{209}Bi metal on an aluminium backing was bombarded with 28 MeV α-particles in the cyclotron (Scanditronic MC32-NI) at Rigshospitalet in Copenhagen, Denmark. After irradiation the target was transported to Salhgrenska University Hospital in Göteborg and ^{211}At isolated in a dry distillation process developed by Lindegren et al. /27/. In this procedure ^{211}At was distilled at 670°C. It was then flushed out with a gentle flow of nitrogen and condensed in a PEEK (polyetheretherketone) loop cooled with dry ice. The astatine was then extracted from the loop with a chloroform solution. The chloroform was then evaporated to give a solid At(0) sample. This sample was transported to Chalmers for further experiments.

7.4.2 Extraction experiments

The aim of these experiments was to study the distribution of astatine between organic and aqueous phases and to establish whether or not the astatine was bound to the BTBP ligand.

A small amount (~3 MBq) of solid ^{211}At was dissolved in 15 mL aqueous phase containing 0.01 M HNO_3 and 0.99 M $NaNO_3$. 500 µL of aqueous phase was contacted with 500 µL of various organic phases in 3.5 mL glass bottles, sealed with a plastic lid. The organic phases were either pure diluents; hexanol, octanol and cyclohexanone, or 0.005–0.01 M of a BTBP type ligand (C5-, $CyMe_4$-, MF1- or MF2-BTBP) dissolved in one of the diluents. The kinetics varies for the different diluents; cyclohexanone require shorter contact times than the hexanol and octanol solvents. Thus, the samples containing cyclohexanone solvents were shaken ten minutes by hand while the rest of the samples were shaken during one hour in a shaking machine. After the required contact time the samples were centrifuged to ease phase separation. 200 µL of each phase were placed in pre-weighed scintillation vials and 10 mL Hionic Fluor Scintillation Liquid was added. Both phases were then measured on Liquid Scintillator 2 and the distribution ratio of astatine could be calculated from the specific activity of the samples. All samples were measured only for a short period of time (10 min) and the corresponding aqueous and organic phases were measured directly after one another. The decay during measurement was not taken into account since these experiments were of a screening nature, not requiring precise measurements. The uncertainty introduced by doing so is < 1.5%.

The extraction of astatine was independent of the absence or presence of BTBP ligands, hence the distribution ratio equals the distribution constant (K_D) and is a result only of the partitioning of astatine between the organic and aqueous phase. Table 7-1 gives the distribution ratios for astatine in hexanol, octanol and cyclohexanone. The aqueous phase was 0.01 M HNO_3 and 0.99 M $NaNO_3$.

Distribution ratios have previously been reported for At in CS_2 solution (D_{At} ~20, aq phase: 1.2 M HNO_3) /52/ and in diisopropylether (DIPE) (D_{At} ~8, aq phase: 1 M HNO_3) /2/.

7.4.3 Irradiation experiments

The aim was to irradiate an organic solvent with alpha radiation and compare the resulting degradation products to those resulting from similar irradiation with gamma radiation.

399 MBq of ^{211}At was available as a deposit on the inside of a small glass container. It was dissolved in 1.9 mL organic solvent containing 0.005 M C5-BTBP in cyclohexanone and 5 µL was measured with a scintillation counter to determine how much of the astatine that was actually dissolved. The solution contained 198 MBq/mL ($1.2 \cdot 10^{-8}$ M), meaning that in total 377 MBq was dissolved. This amount of astatine corresponds to a total alpha dose to the organic phase of 8.4 kGy. After one week the activity of the remaining astatine was approximately 1.8 Bq/mL. The solution, which could now be considered as non-radioactive, was sent to the Institute of Inorganic Chemistry, Academy of Sciences of the Czech Republic for analysis. The analysis of degradation products was performed in the same manner as corresponding analysis of solvents irradiated with gamma radiation /20/.

In the analysis of the α irradiated solution the same degradation products were observed as when a similar solvent was exposed to approximately the same dose of γ radiation /20/. The dose rate during the γ irradiation was ~12.5 Gy/h while it decreased with time from 800 Gy/h down to practically zero for the α irradiation. This implies that the radiolysis effect does not depend strongly on the dose rate within this range.

Table 7-1. Distribution ratio of ^{211}At for three different diluents.

Diluent	D_{At}
hexanol	50 ± 12
octanol	32 ± 6
cyclohexanone	98 ± 10

When comparing α irradiation using an internal source like ^{211}At, which is dissolved in the organic phase, with an internal source like ^{241}Am, which is extracted into the organic phase by the extractants, an important question arises: Are the different states of the radionuclides of importance? In other words, is the degradation of the BTBP molecule dependant on whether the radionuclide is bound to it or if it is dissolved and moving freely in the solvent? To try to answer this question a calculation was made to determine the approximate number of BTBP molecules present in a normal α track. If the number is found to be large, the two BTBPs bound to the radionuclide in the case of e.g. ^{241}Am can be neglected. If, however, the number of BTBPs is found to be small, then the two bounded molecules may be relevant in comparison and hence the radiation may cause a larger effect on the BTBPs than it had if the radionuclides were homogenously distributed in the solvent. A normal α track was estimated to be 53 µm long /42/ with a chemical core radius of 10 nm /10/. Those numbers give a track volume of $1.7 \cdot 10^{-11}$ mm^3 and with a BTBP concentration of 0.005 M this corresponds to more than 50,000 BTBP molecules being present within the track. The two BTBPs that are bound to the radionuclide in the case of extraction of the internal source can thus be neglected, and there is assumed to be no difference between the two modes of α irradiation. The number of BTBPs affected by alpha radiolysis was approximated experimentally by Magnusson et al. /31/. They get about 8,000 affected BTBP molecules per alpha particle for a BTBP concentration of 15 mM. This shows that all the molecules present in the track does not react. However, there are still enough BTBPs affected to make the addition of the two more bound ones negligible.

Preliminary extraction experiments showed the same decrease in extraction of ^{241}Am when a solvent containing C5-BTBP in cyclohexanone was irradiated with α-particles either from dissolved ^{211}At, or from previously extracted ^{241}Am. This confirms the theory presented above, that the state of the internal source in this case does not affect the degree of α radiolysis of the BTBPs.

7.4.4 Conclusion

It was shown that ^{211}At as an internal source for alpha irradiation is a very promising candidate to gain understanding of radiolysis paths and effects. By using this method the detection of radiolysis products may be performed in any specialized lab without being classified for work with radioactive elements. The high solubility of ^{211}At in organic media is also an advantage, since it enables direct dissolution of the radionuclide in the organic phase to be irradiated, avoiding intermediate steps like extraction of the α emitter.

7.5 Radiolysis of a two-phase system

A solvent containing 0.005 M C5-BTBP in cyclohexanone was irradiated in a ^{60}Co source under three different conditions:

1. Irradiation of organic phase alone(– referred to as Solvent 1).
2. Irradiation of organic phase pre-equilibrated with aqueous phase (0.01 M HNO_3 + 0.99 M $NaNO_3$ + ^{241}Am + ^{152}Eu) (– referred to as Solvent 2).
3. Irradiation of organic and aqueous phase in contact (– referred to as Solvent 3).

The solvents were given doses up to 50 kGy and the irradiated samples were used for extraction experiments to study how distribution ratios and separation factors were affected by the dose and the various conditions. They were also analyzed with various MS-techniques to determine the change in C5-BTBP concentration as well as the presence of any degradation products.

All samples were irradiated by γ rays in a ^{60}Co source (Issledovatel) with a dose rate of 0.939 Gy/h. Bottles were removed from the source after various times during 54 hours, resulting in doses between 5 and 50 kGy. Corresponding samples were kept outside the irradiator to act as reference samples. Before and after irradiation, all bottles were kept in a freezer to prevent the ageing of the BTBP /18/.

All extraction experiments were performed after the end of the irradiations and followed the standard procedure described in Section 3.1.1. The samples were shaken during 40 minutes in the shaking device. This time has proven to be sufficient to reach equilibrium for the system.

As mentioned in Section 3.1.1, there is a mutual solubility between water and cyclohexanone (2.3 w% cyclohexanone in water, 8 w% water in cyclohexanone) /33/, hence the phases were pre-equilibrated. For the system in this study, C5-BTBP in cyclohexanone and a weak acid as aqueous phase, it has previously been reported that a pre-equilibrated system gives the same distribution ratios as a non pre-equilibrated system /19/. To confirm this, extraction experiments were carried out both with and without pre-equilibration of the solvent that was irradiated alone (solvent 1). For solvent 3, which had been irradiated in the presence of an aqueous phase, extraction experiments were performed both with the irradiated and with a fresh aqueous phase, to see if it had any effect on the distribution ratios.

The HPLC, MS and LC-MS analyses were performed in collaboration with Institute of inorganic chemistry, Academy of sciences, in the Czech Republic and are described elsewhere /20/.

7.5.1 Extraction

The two extraction experiments with Solvent 1 (with and without pre-equilibration) showed similar distribution ratios, hence confirming that pre-equilibration or not does not affect the values of extraction for this system. Thus, D-values for Solvent 1 are average values of extraction experiments both with and without pre-equilibration. Solvent 3 gave similar distribution ratios whether the irradiated aqueous phase was used or if it was replaced with a fresh pre-equilibrated solution. D-values for Solvent 3 are thus average values of the experiments with irradiated and fresh aqueous phase, respectively. In Figure 7-14 D_{Am} is plotted as a function of the received dose for the three solvents (1–3).

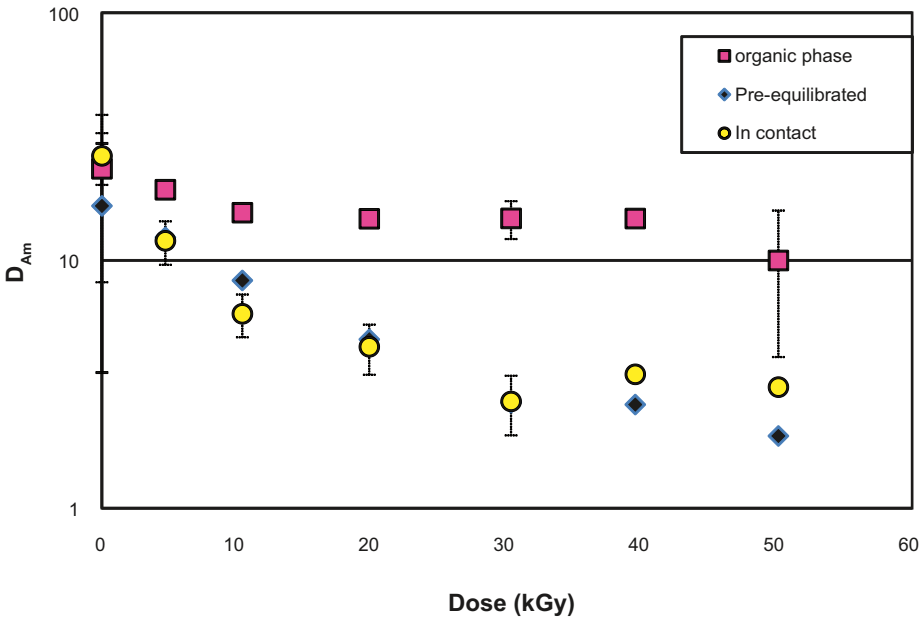


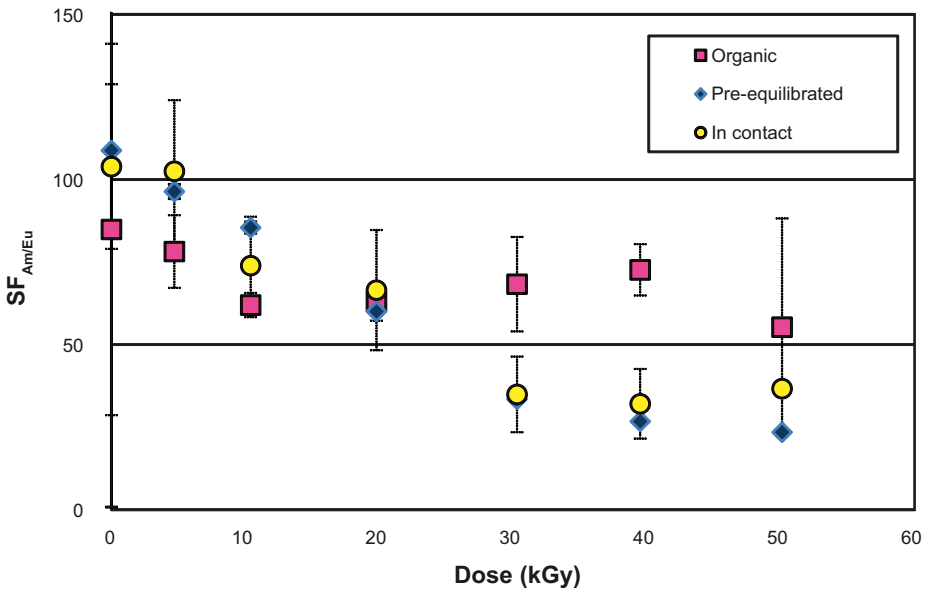
Figure 7-14. *Distribution ratio of americium as a function of the received dose for three similar organic solvents irradiated under different conditions. Labels: organic phase – irradiation of pure organic phase, Pre-equilibrated – organic phase pre-equilibrated with aqueous phase (no metals present) prior to irradiation, In contact – organic and aqueous phase (no metals present) in contact during the irradiation.*

It is clear that the presence of an aqueous solution, either dissolved in the organic phase or present as a separate aqueous phase, enhances the decrease in D_{Am} with dose. For the organic phase that was irradiated alone, the D_{Am} decreases to around 40% of the reference value after a dose of 50 kGy, while the other two series reach levels as low as 10% of the reference value. The reference values are based on samples of solvent that, apart from not being irradiated, was treated in the same way as the irradiated samples in terms of storage time and temperature. Thus, the reference solutions might have aged a bit, a well known behavior for C5-BTBP /18/, and therefore the distribution ratios for the reference solutions (D_{Am} ~20–24) may deviate somewhat from values for freshly prepared solutions (D_{Am} ~38 /18/). But the effect of ageing can be assumed to be the same for all samples, since they were prepared at the same time, stored in similar manner, and extraction experiments performed at the same time. The effect of different storage temperatures on distribution ratios for C5-BTBP systems have previously been studied, and storage in a freezer has proven to be the best option to reduce the ageing /4/.

There is little difference in values between solvent 2 and 3, suggesting that the amount of aqueous phase dissolved in pre-equilibrated solvent is enough to cause the decrease in D_{Am}, compared to the irradiated pure organic phase.

The enhanced decrease in extraction as a result of the presence of an aqueous phase during irradiation is opposite to what was reported for the GANEX radiolysis in Section 6.4. However, the composition of the aqueous phases differed between the experiments. The nitric acid concentration was higher for the GANEX experiments (1 M), and nitrates have previously been suggested to efficiently scavenge radiolysis. In the experiments in this section, the aqueous phase contained only 0.01 M HNO_3, resulting in an aqueous phase very similar to pure water. In addition, C5-BTBP (used in this study) is sensitive towards hydrolysis, while $CyMe_4$-BTBP (used in the GANEX radiolysis study) is not. This likely also affects the consequences of having an aqueous phase present during irradiation.

Distribution ratios for Eu were also decreasing with dose, and the pattern was the same as for Am; that the solvents with aqueous phase present gave a larger decrease. For all three solvents, the distribution ratio for Eu did not decrease to the same extent as it did for Am. This behavior results in a decreasing separation factor between the elements ($SF_{Am/Eu}$), which is illustrated in Figure 7-15 where the change in $SF_{Am/Eu}$ is plotted as a function of the dose for all three solvents (1–3).



Figur 7-15. *$SF_{Am/Eu}$ as a function of the received dose for the three series irradiated under different conditions. Labels: organic phase – irradiation of pure organic phase, Pre-equilibrated – organic phase pre-equilibrated with aqueous phase (no metals present) prior to irradiation, In contact – organic and aqueous phase (no metals present) in contact during the irradiation.*

Solvents 2 and 3 (pre-equilibrated and in contact), showed a larger decrease than the solvent that was irradiated in the absence of any aqueous phase. $SF_{Am/Eu}$ decreased to around 20 and 30% of the reference value for solvent 2 and 3, respectively. The similar dose (50 kGy) yielded a decrease to around 65% of the reference value. Thus, the presence of aqueous phase during irradiation causes both lower extraction capacity and lower selectivity of the solvent compared to if the organic phase is irradiated alone.

7.5.2 HPLC, MS and LC-MS analyses

The concentration of C5-BTBP in irradiated samples is clearly decreasing with dose. As could be expected from the extraction results, the decrease is much more pronounce when aqueous phase is present during irradiation, either as an entire phase (solvent 3) or dissolved in pre-equilibrated organic phase (solvent 2). This is illustrated in Figure 7-16, which shows the concentration change with increased dose. The curves for solvent 2 and 3 are very similar and it cannot be said that one decreases more than the other. For solvent 1, the decrease seems to more or less follow a straight line, and a linear fit of the curve gives an initial G-value of 0.0304 μM/J (R^2 = 0.9846).

HPLC analyses revealed a number of degradation products not observed before, when only organic phases irradiated alone has been analyzed. Figure 7-17 shows the chromatograms for the reference sample and the three samples irradiated with 5, 10 and 20 kGy for all three solvents. The peak with a retention time of around 28 minutes represents the C5-BTBP molecule. It is very obvious how this peak decreases much more for solvent 2 and 3 (middle and bottom figures). A number of structures of degradation products resulting from irradiation of pure organic phase containing C5-BTBP in cyclohexanone have previously been proposed /20, 21/. The chromatograms for solvent 2 and 3 include peaks that have not been observed before, suggesting the presence of other decomposition products. However, the additional peaks are found close to peaks of C5-BTBP and formerly observed degradation products, indicating structural similarity between the compounds.

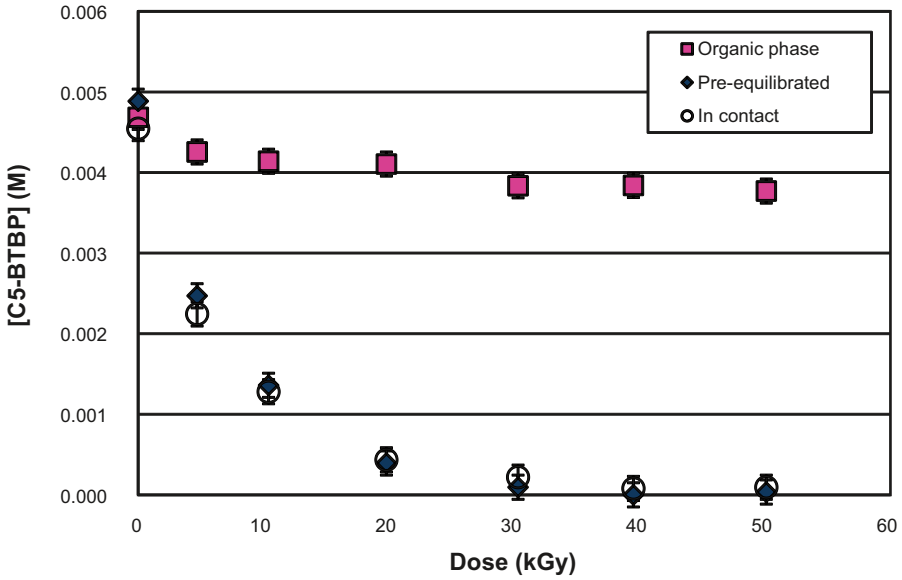


Figure 7-16. *Concentration of the original molecule C5-BTBP as function of the dose received by the solvent. The solvents were irradiated under different conditions: organic phase – irradiation of pure organic phase, Pre-equilibrated – organic phase pre-equilibrated with aqueous phase (no metals present) prior to irradiation, In contact – organic and aqueous phase (no metals present) in contact during the irradiation.*

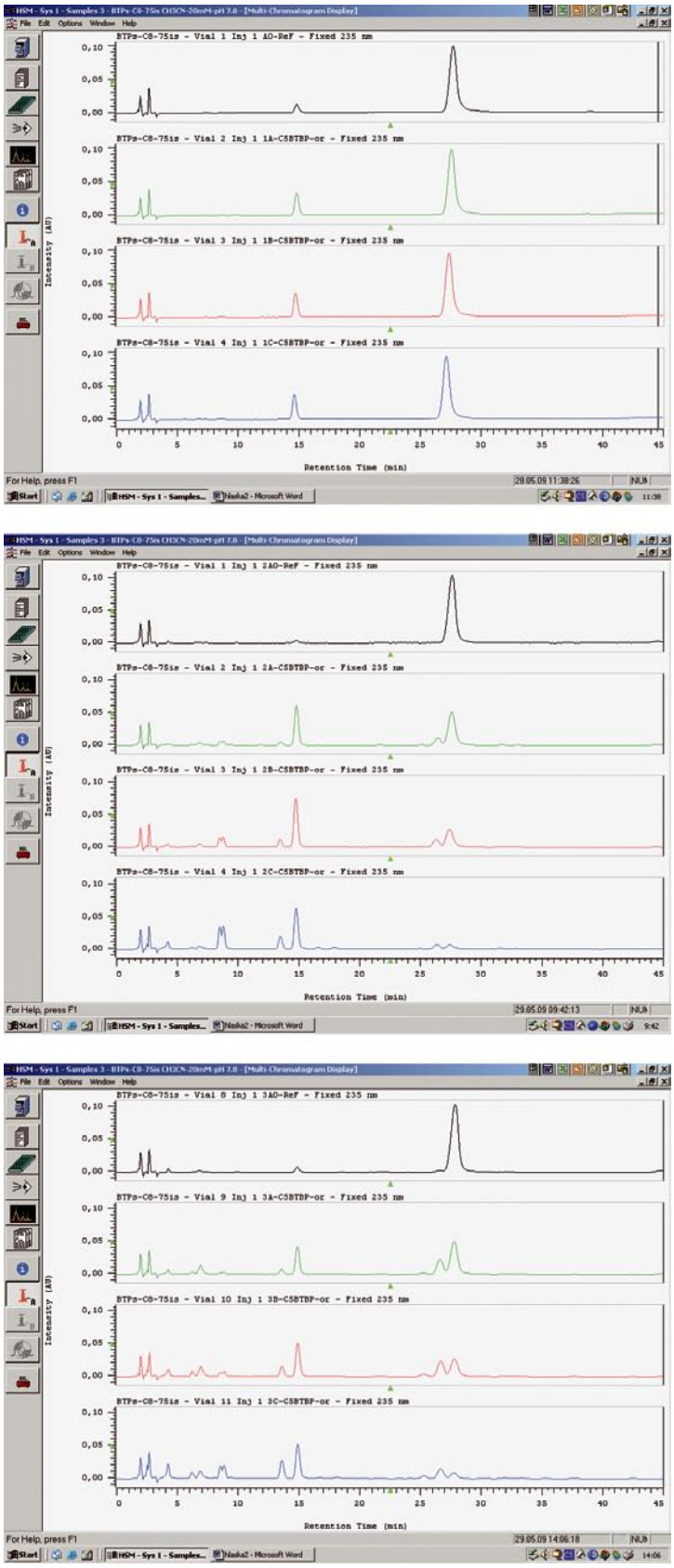


Figure 7-17. *Chromatograms of four samples for each solvent series. The top chromatogram is for solvent 1, followed by solvent 2 in the middle and solvent 3 at the bottom. In each chromatogram the first sample is the reference sample, and then the sample that received 5, 10 and 20 kGy, respectively.*

Concentrations of the various degradation products are calculated based on semi-quantitative measurements where it is assumed that the total peak area corresponds to a concentration of 0.005 M, which was the initial C5-BTBP concentration. To be able to make reliable quantitative measurements pure samples of the degradation products are required and this has not yet been available. Figure 7-18 shows how the presence of various degradation products changes as solvent 1 (pure organic phase) receives more and more dose. The degradation product with m/z = 611 (product A) corresponds to an oxidized form of C5-BTBP, with a hydroxyl group attached at the alpha carbon in one of the C5-chains. The other product (B) observed in solvent 1 corresponds to a further oxidized form of C5-BTBP, with hydroxyl groups on two C5-chains (m/z = 627). The concentration of both degradation products observed increases with dose, but product A reaches a much higher concentration than product B. It has previously been shown that product 611 reaches a maximum and then the concentration starts to decrease; hence it is not stable towards radiolysis /20, 21/.

Figure 7-19 and 7-20 illustrate the growth of degradation products for solvent 2 and 3, respectively. Note that the scales on the y-axes differ from the scale in Figure 7-18. The additional peaks/degradation products observed in the solvents with aqueous phase present are referred to as C, D, E and F. C represents a product with a structure very similar to product A, probably with a ketone instead of a hydroxyl group attached to the alpha-carbon (m/z = 609). Products D and E both have structures similar to product B: either with one hydroxyl and one ketone group attached on the C5-chains (product D, m/z = 625), or with ketone groups on both chains (product E, m/z = 623). In solvent 3, an additional degradation product was observed, product F. It is similar to product A but one of the C5-chains has been cut off (m/z = 541). Structures of the suggested products, together with their m/z (mass to charge) ratio in APCI-MS, are given in Table 7-2.

Neither C5-BTBP nor any decomposition products were observed by HPLC in the aqueous phases that had been irradiated in contact with the organic phase (solvent 3). Thus, none of the degradation products appear to be soluble in the aqueous phase.

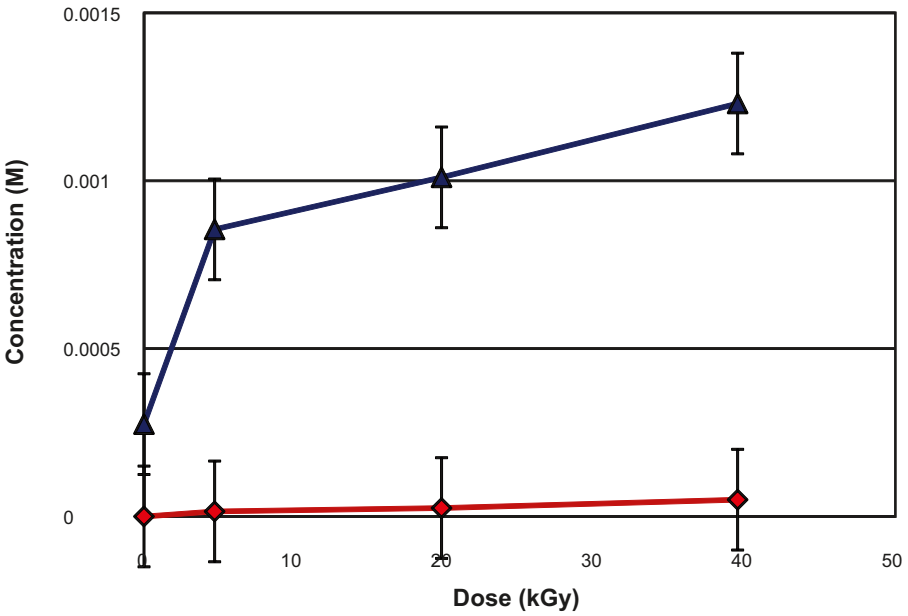


Figure 7-18. *Growth of degradation products with dose for an irradiated solvent containing C5-BTBP in cyclohexanone. Labels A and B refer to the structures given in Table 4-1.*

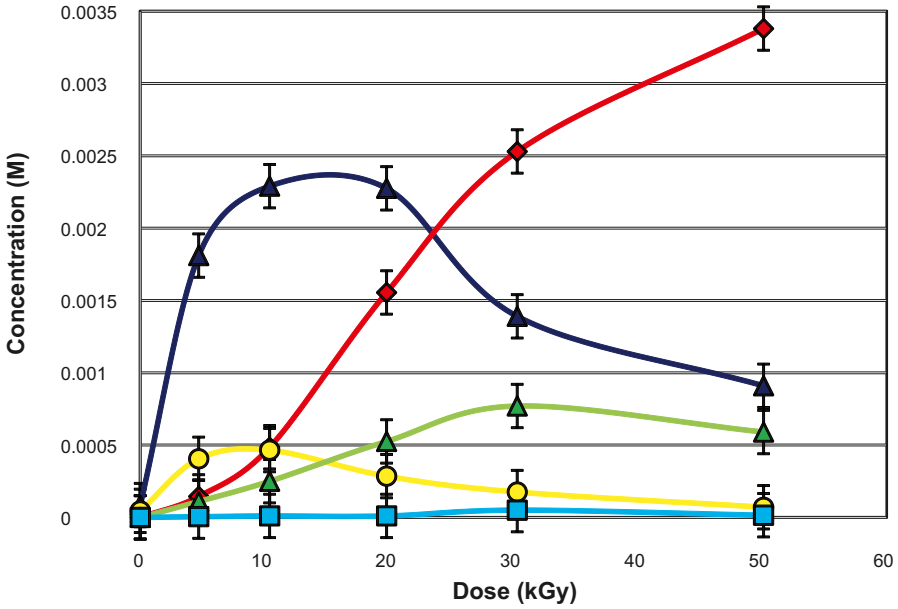


Figure 7-19. *Growth of degradation products with dose for an irradiated solvent containing C5-BTBP in cyclohexanone that was pre-equilibrated with aqueous phase prior to the irradiation.*

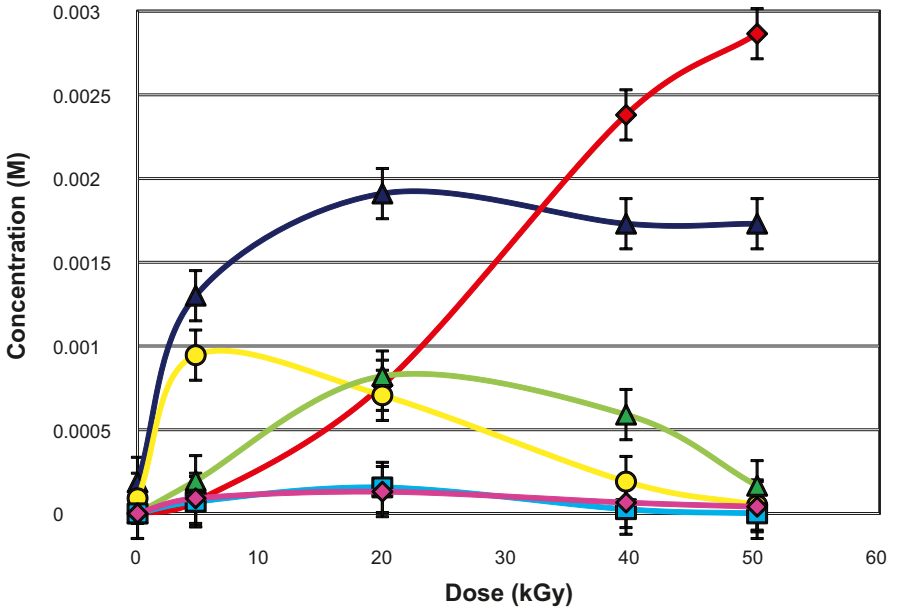
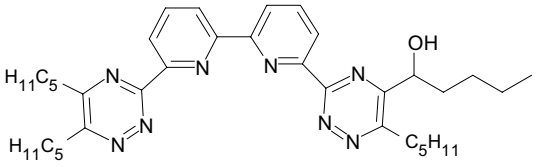
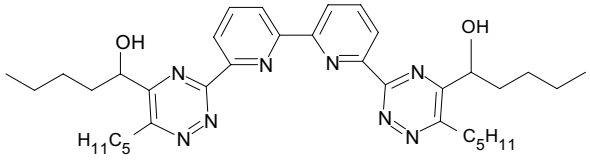
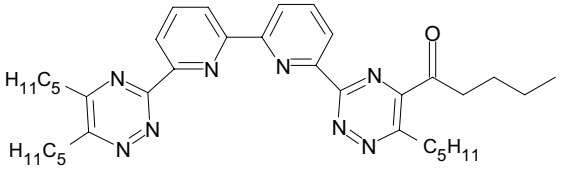
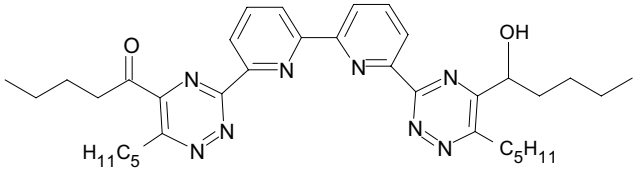
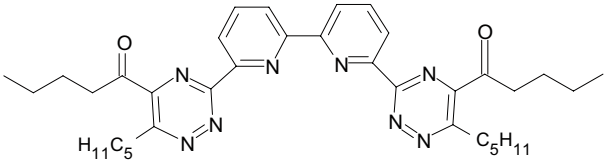
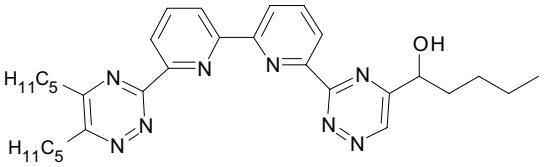


Figure 7-20. *Growth of degradation products with dose for an irradiated solvent containing C5-BTBP in cyclohexanone that in contact with an aqueous phase during the whole irradiation.*

Table 7-2. Proposed structures for degradation products resulting from the irradiation of C5-BTBP in cyclohexanone /20, 21/.

Product	*m/z* ratio	Structure
A	611	
B	627	
C	609	
D	625	
E	623	
F	541	

8 Water-soluble ligands for i-SANEX

Two compounds, Pyridin-2-yl-phosphonic acid (PPA) and (6-Phosphono-pyridin-2-yl)-phosphonic acid (PPPA), both illustrated in Figure 8-1, were designed, synthesized and tested as water soluble An(III) complexing agents for i-SANEX.

8.1 Design and synthesis – PPA and PPPA

As part of the synthesis work an attempt to make two new hydrophilic actinide binding agents was made. For the synthesis work, a reaction similar to the Arbuzov reaction in which triethyl phosphite is reacted with an aryl bromide in the precense of nickel(II) chloride was chosen. The nickel is reduced and the trialkyl phosphaites coordinate to form nickel(0) tetrakis-(triethyl phosphite) which cataylises the formation of the carbon phosphorus bond. Such a reaction forms a dialkyl phosphonate which after treatment with concentrated hydrochloric acid furnishes the target molecule.

Unfortunatley the reaction of 2-bromopyridine, triethyl phosphite and nickel chloride formed a vile intractable mixture. Another synthesis route was tested and a reaction including diisopropyl phosphite, hunig's base (*N,N*-diisopropyl-*N*-ethyl amine) and a palladium complex of 1,1-bis-(diphenylphospino)ferrocene in acetonitrile was used. This reaction was found to conveniently furnish the desired dialkyl phosphonate from 2-bromopyridine (α-bromopyridine). While the literature suggested that chromatography of the product on silica would be required to obtain a pure product /5/, it was found that without chromatography the product was pure. After deprotection with concentrated hydrochloric acid the required pyridin-2-yl-phosphonic acid was obtained. By an analogus procedure starting with 2,6-dibromopyriidne it was able to obtain (6-phosphono-pyridin-2-yl)-phosphonic acid.

8.2 Screening test – PPA and PPPA

The extractions were performed according to ACSEPT project requirements (see Appendix B) and shaken in a thermostatic shaking machine (21°C) for 90 minutes. The organic phase composition was in both cases 0.20 M TODGA (see Figure 8-2) + 5 vol% 1-octanol in kerosene (solvent 70) and the aqueous phase composition was 0.50 M NH_4NO_3 with 0.01 M of PPA or PPPA added. The solubility of the ligand in the water phase was > 12 g/L for PPA and > 9 g/L for PPPA.

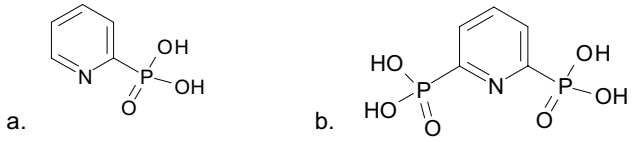


Figure 8-1. *Structure of two water-soluble ligands a) Pyridin-2-yl-phosphonic acid (PPA) and b) (6-Phosphono-pyridin-2-yl)-phosphonic acid (PPPA).*

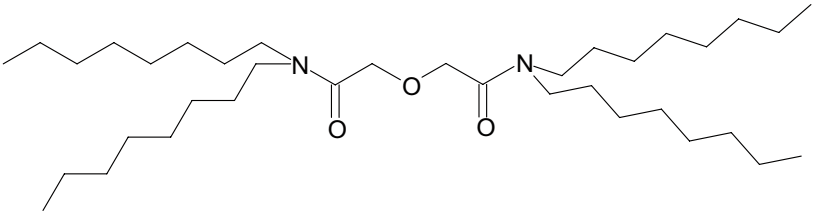


Figure 8-2. *TODGA – (N,N,N',N'-tetraoctyl-3-oxapentane-1,5-diamide) /47/.*

The extraction of Am and Eu with the addition of the two ligands were compared to extraction without any addition under the same conditions. The results (Table 8-1) showed a decrease in distribution ratio for both Am and Eu with both PPA and PPPA. With PPA however, the D for Am was still too high for a separation process plus that there were some third phase formation. With PPPA on the other hand the D for Eu was too low for a separation process even though the $SF_{Eu/Am}$ actually increased.

Table 8-1. Distribution ratios and separation factor for reference sample (no ligand added in aq phase), PPA solution and PPPA solution. The pH at equilibrium is also given.

Substance	pH_{eq}	D_{Am}	D_{Eu}	$SF_{Eu/Am}$
Reference	1.9	30	220	7.3
PPA	1.6	19	110	5.8
PPPA	1.6	0.002	0.03	15

9 Collaborations

The following laboratories are involved in ACSEPT:

- Commissariat à l'énergie atomique (France)
- Alcan centre de recherchers de Voreppe, France
- Compagnie generale des materieres nucleaires SA, France
- Centro de investigaciones energeticas, medioambentales y technologicas-CIEMAT, Spain
- CINC solutions BV, Netherlands
- Centre national de la recherche scientifique (CNRS), France
- Consejo superior de investigaciones cientificas, Spain
- Ceske Vysoke uceni technicke v Praze, Czech Republic
- Charles Univesity in Prague, Czech Republic
- Electricite de France SA, France
- Ente per le nuovo technologie, l'energia e l'ambiente, Italy
- Forschungszentrum Jülich, Germany
- Karlsruhe Institute of Technology, Germany
- Instytut Chemii I Techniki Jadrowej, Poland
- Funda to privada institute Catalá d'investigacio quimca (ICIQ), Spain
- Institute of inorganic chemistry, Academy of sciences, Czech Republic
- Commission of the European community's-directorate general joint research centre – JRC, Belgium
- National Nuclear Laboratory (NNL), UK
- Nuclear research and consultancy group, Netherlands
- Nuclear physics institute ASCR, Czech Republic
- Politecnico di Milano, Italy
- Paul Sherrer Institute, Switzerland
- Rijksuniversiteit Groningen, Netherlands
- Chalmers University of Technology, Sweden
- The University of Edinburg, UK
- Universite de Liege, Belgium
- Universita degli studi di Parma, Italy
- The university of Reading, UK
- Universite Louis Pasteur, France
- Universiteit Twente, Netherlands
- Australian nuclear science and technology organisation ANSTO, Australia
- Central research institute of electric power industry, Japan
- Universite Pierre et Marie Curie – Paris 6, France
- Instituto technologico e nuclear, Portugal

A more intense collaboration with Chalmers exists with:

- CEA, France
- Consejo superior de investigaciones cientificas, Spain
- Forschungszentrum Jülich, Germany
- Institut für Mikrotechnik Mainz, Germany
- Institute of inorganic chemistry, Academy of sciences, Czech Republic
- Instytut Chemii I Techniki Jadrowej, Poland
- Karlsruhe Institute of Technology, Germany
- National Institute of Cryogenics and Isotopic Separation, Romania
- University of Reading, UK

10 International scientific exchange

16–19/3 2009, ACSEPT half yearly meeting in Madrid, Spain.
Participants: E Aneheim, C Ekberg, A Fermvik, M Foreman, J Liljenzin

5–10/4 2009, MARC-VIII – Methods and Applications of Radioanalytical Chemistry, Kona, Hawaii, USA.
Participant: G Skarnemark
Poster and oral presentation entitled: *A Unique Master's Program in Combined Nuclear Technology and Nuclear Chemistry at Chalmers University of Technology*

22–25/6 2009, EuCOMC XVIII – European Conference on OrganoMetallic Chemistry, Göteborg, Sweden.
Participant: E Aneheim

16–19/8 2009, ACS (American Chemical Society) 238th National Meeting & Exposition, Washington D C, USA.
Participants: E Aneheim, C Ekberg, A Fermvik
Oral presentations entitled**:**
Fission product suppression and extraction in a proposed GANEX process (E Aneheim)
ACSEPT – Actinide reCycling by SEParation and Transmutation (C Ekberg)
Identification of degradation products from irradiated C5-BTBP and their influence on the extraction of actinides and lanthanides (A Fermvik)

21–23/9 2009, ACSEPT half yearly meeting in Bologna, Italy.
Participants: E Aneheim, C Ekberg, A Fermvik, M Foreman

15–17/12 2009, CEFOS – Managing Radioactive Waste: International and Interdisciplinary Research Conference, Göteborg, Sweden.
Participants: C Ekberg (expert panel), A Fermvik
Poster entitled: *Separation for Transmutation at Chalmers*

11 Articles and publications

During the past year several reports and articles have been published, submitted for publication or are still in preparation.

Published

Aneheim E, Fermvik A, Ekberg C, Foreman M R S, Retegan T, Skarnemark G: Partitioning and Transmutation in Scandinavia – Chalmers Group, Proceedings of The 10th OECD/NEA Information Exchange Meeting on Actinide and Fission Product Partitioning and Transmutation in Mito, Japan.

Ekberg C, Aneheim E, Fermvik A, Skarnemark G: Using ^{211}At as internal alpha radiolysis source allowing for simple detection of radiolysis products, Accepted for publication in Radiation Physics and Chemistry, 2009.

Fermvik A, Berthon L, Ekberg C, Englund S, Retegan T, Zorz N: Radiolysis of solvents containing C5-BTBP: identification of degradation products and their dependence on absorbed dose and dose rate, Dalton Trans., 2009, 6421–6430.

Fermvik A, Ekberg C, Englund S, Foreman M R S, Modolo G, Retegan T, Skarnemark G: Influence of dose rate on the radiolytic stability of a BTPB solvent for actinide(III)/lanthanide(III) separation, Radiochimica Acta, 97(6), 1–6 (2009).

Magnusson D, Christiansen B, Glatz J-P, Malmbeck R, Modolo G, Serrano-Purroy D, Sorel C: Demonstration of a TODGA based Extraction Process for the Partitioning of Minor Actinides from a PUREX Raffinate, Part III: Centrifugal Contactor Run using Genuine Fuel Solution, Solvent Extraction and Ion Exchange, 27(2), 97–106 (2009).

Magnusson D, Christiansen B, Glatz J-P, Malmbeck R, Modolo G, Serrano-Purroy D, Sorel C: Towards an optimized flow sheet for a SANEX demonstration process using centrifugal contactors, Radiochimica Acta, 97(3), 155–159 (2009).

Magnusson D, Christiansen B, Foreman M R S, Geist A, Glatz J-P, Malmbeck R, Modolo G, Serrano-Purroy D, Sorel C: Demonstration of a SANEX process in centrifugal contactors using the $CyMe_4$-BTBP molecule on a genuine fuel solution, Solvent Extraction and Ion Exchange, 27(1), 26–35 (2009).

Magnusson D, Christiansen B, Glatz J-P, Malmbeck R: Investigation of the radiolytic stability of a $CyMe_4$-BTBP based SANEX solvent, Radiochimica Acta, 97(9), 497–502 (2009).

Retegan T, Berthon L, Ekberg C, Fermvik A, Skarnemark G, Zorz N: Electrospray Ionization Mass Spectrometry Investigation of BTBP – Lanthanide(III) and Actinide(III) Complexes, Solvent Extraction and Ion Exchange, 27, 1–20 (2009).

Retegan T: Investigations of solvent systems based on bis-triazine-bipyridine (BTBP) – class ligands for the separation of actinides from lanthanides, Ph.D. Thesis, Chalmers University of Technology, Göteborg (2009), ISBN: 978-91-7385-239-5.

Skarnemark G, Allard S, Ekberg C, Nordlund A: A Unique Master's Program in Combined Nuclear Technology and Nuclear Chemistry at Chalmers University of Technology, American Institute of Physics Conference Proceeding 1164 – "Current Status, trends, and Needs in Radiochemical Education: the U.S. and Abroad", 78–84 (2009).

Submitted

Aneheim E, Fermvik A, Ekberg C, Foreman M R S: A TBP/BTBP-based GANEX Separation Process – Part 1: feasibility, Submitted to Solvent Extraction and Ion Exchange.

Fermvik A, Gruner B, Kvivalova M, Ekberg C: Variation in concentration of C5-BTBP and its degradation products during γ-irradiation, Submitted to Radiochimica Acta.

In preparation

Aneheim E, Fermvik A, Ekberg C, Foreman M R S: A TBP/BTBP-based GANEX Separation Process – Part 2: fission/corrosion product suppression and pre-extraction.

Ekberg C, Aneheim E, Fermvik A, Foreman M, Spendlikova I, Retegan T: Thermodynamics of dissolution for some BTBP-class ligands in several solvents and its reflection on extraction.

Fermvik A, Gruner B, Kvicalova M, Ekberg C: Radiolysis of C5-BTBP in cyclohexanone irradiated in the absence and presence of an aqueous phase.

A half-yearly report to the ACSEPT project has also been written.

The diploma work by I. Spendlikova is available at Chalmers University of Technology.

12 Future work

The future work will continue along the suggested path of the ACSEPT project. However, we will do as previous years and use the complementary funding from the SKB to focus more on the basic scientific issues arising from the more process oriented studies. This building of knowledge is also the role of a University. In addition we will have a new irradiation source that will facilitate gamma irradiation dose rates up to 23 kGy/h. This together with our novel method of in vitro alpha irradiation using ^{211}At will make the Chalmers facility rather unique in the university world in the context of radiolysis studies. In addition to this a new fuel fabrication lab will be built together with our existing separation laboratory which will make it possible to join both the separation studies and the fuel manufacturing in the same place. The fuel lab will be a collaborative effort with the group of Professor Janne Wallenius at KTH. Our planned work can be listed as follows:

- Partitioning of actinides (different oxidation states, Th-Cm) for advanced dedicated future fuel cycles, like for example ADS nuclear systems. The co-extraction of actinides of different oxidation states will be studied. Mixtures of ligands, bitopic extractants and chromatographic techniques will be used.
- Studies on the radiolytic and hydrolytic stability and detailed investigations of the decay products, their production pathways and their effects on the extraction.
- Investigation of the effect of the diluents on extraction, stripping and selectivity.
- Continue to develop and optimise the extraction system for our novel GANEX (**G**rouped **A**cti**N**ide **EX**traction) system.
- Continue the development of a selective stripping from our GANEX process.
- Start our work in the borderline between the separation process and the fuel fabrication.

Sofie Englund is now working for OKG AB but will continue in the group part time as a co-project leader.

Anna Fermvik will continue her studies on the effect of radiation on the extractant molecules used and what effect the products of radiolysis will have on the extraction. Identification of degradation products and routes will be studied together with Dr. Zoltan Szabo at KTH and Dr. Bohumir Gruner at Academy of Sciences of the Czech Republic. However, she will be on maternity leave for the major part of 2010.

Emma Aneheim will continue her studies of our novel GANEX extraction system including suppression of unwanted extraction and then selective stripping of the separate actinides. She will present her licentiate thesis during 2010.

Elin Löfström-Engdahl will make a literature study of the effects of diluents on the extraction and attempt to develop a predictive theory to BTBP based systems.

A new PhD student will probably be hired for working with the new fuel fabrication lab.

Mark Foreman will work on developing synthesis routes for making new ligands and optimise their production as well as the general problems for a process development.

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Screening protocol for r-SANEX

Actinide reCycling by SEParation and Transmutation
FP7 Collaborative Project 211267

DM1WP2T2

Standard procedure for the 1st screening of new SANEX extractants

Andreas GEIST, FZK-INE

1. Introduction

Up to now (end of September 2008) approx. 20 compounds have been synthesised and distributed in ACSEPT. These are intended to be used as SANEX (i.e., separation of An(III) from Ln(III)) extracting agents. Thus, the extractants must extract An(III) preferentially over Ln(III) from nitric acid. Two relevant SANEX processes are described below (see Chapters 1.1 and 1.2).

A few simple batch extraction screening tests (see Chapter 2) are required to test whether a new compound is suitable for a SANEX application and whether it will be further studied and developed. The goal of the first screening tests is to find out whether the extracting agent is sufficiently soluble and able to preferentially extract the main solutes (i.e., the actinides; here Am(III)). Based on the results, the ACSEPT Hydro Domain and Work Package Leaders decide if a compound is to be further studied, and what processes it may be used for.

The 1st screening tests can be performed by any of the Beneficiaries involved in this Task (i.e., CHALMERS, CIEMAT, CTU, FZJ, FZK-INE, ICHTJ, and POLIMI).

Further tests to be carried out on compound which have passed this first screening will soon be published on the ACSEPT website.

1.1. Regular SANEX (r-SANEX) process

The feed solution for the r-SANEX process is the DIAMEX[1] product solution (i.e., Am(III), Cm(III), Y(III), and Ln(III) in approx. 0.5 – 1 M HNO_3). The r-SANEX process co-extracts Am(III) and Cm(III) from this feed solution, separating them from Y(III) and Ln(III).

Note that further development of this process is generally not supported in ACSEPT since two reference systems (based on CyMe$_4$-BTBP) have been selected. Further development is assigned to the 1c-SANEX process, see below.

1.2. 1-cycle SANEX (1c-SANEX) process

The feed solution for the 1c-SANEX process is the PUREX raffinate (i.e., Am, Cm + fission products + corrosion products in approx. 4 M HNO_3 [assuming that Np is previously separated in the PUREX process]). The 1c-SANEX process directly extracts *only* Am(III) and Cm(III) from this solution. If feasible, a 1-cycle SANEX process would redundantise the DIAMEX process.

[1] The DIAMEX process co-extracts Am(III), Cm(III), Y(III), and Ln(III) (La – Dy) from the PUREX raffinate (Am, Cm + fission products + corrosion products in approx. 4 M HNO_3, considering Np is extracted in the PUREX process).

2. How to test

Organic phase: Dissolve the extracting agent in kerosene, 1-octanol, or kerosene/1-octanol mixture. If the extracting agent does not dissolve in one of these, other diluents may be used.

Aqueous phase: ^{241}Am(III) and ^{152}Eu(III) in 0.1 M / 0.5 M / 1 M / 2 M / 4 M HNO_3.

Contact equal volumes of each organic and aqueous phase on a mechanical shaker. Take into account that some extracting agents may exhibit slow kinetics, so do not select too short contacting time. Centrifuge, sample, and analyse.

Screening protocol for i-SANEX

Actinide reCycling by SEParation and Transmutation
FP7 Collaborative Project 211267

DM1WP2T2

Standard Procedure for the 1st Screening of New *i*-SANEX Hydrophilic Complexing Agents

Andreas GEIST, FZK-INE

1. Introduction

The innovative SANEX (*i*-SANEX) process is an alternative to the regular SANEX process. The feed solution for the *i*-SANEX process is the PUREX raffinate solution (i.e., a solution of all actinides and fission products, with the exception of uranium, neptunium, and plutonium, in approx. 4 M nitric acid). An(III) and Ln(III) are co-extracted by a malonamide (e.g., TODGA). An(III) are selectively stripped from the loaded organic phase with a hydrophilic complexing agent. To keep the Ln(III) in the organic phase, the strip solution must contain a sufficient nitrate concentration. This could be nitric acid, but it is expected that most hydrophilic complexing agents are ineffective in nitric acid. Thus, e.g. ammonium nitrate is added to the strip phase.

A few simple batch extraction screening tests are required to test whether a new hydrophilic complexing agent is suitable for *i*-SANEX application, and whether it will be further studied and developed. The goal of the first screening tests is to find out whether the hydrophilic complexing agent is sufficiently soluble and able to complex actinides (here, Am(III)) preferentially over Ln(III) (here, Eu(III)). Based on the results, the ACSEPT Hydro Team decides if a compound is to be further studied.

The screening tests can be performed by any of the Beneficiaries involved in this Task (i.e., CHALMERS, CIEMAT, CTU, FZJ, FZK-INE, ICHTJ, and POLIMI).

2. How to test

Organic phase: 0.2 M TODGA + 5 % vol. 1-octanol in TPH or kerosene.

Aqueous phase: a) ^{241}Am(III) + ^{152}Eu(III) in 0.5 M NH_4NO_3 of varied *pH* = 1–3
b) same as a) but with hydrophilic complexing agent added.
The hydrophilic complexing agent concentration may be varied.

Contact equal volumes of each organic and aqueous phase on a mechanical shaker. Take into account that complexing kinetics may be slow, so do not select too short a contacting time. Centrifuge, sample, and analyse. Measure *pH* in the aqueous phase.

An efficient hydrophilic complexing agent should reduce Am(III) distribution ratios more efficiently than Eu(III) distribution ratios.