

## **Partitioning and transmutation**

### **Annual report 2006**

Isabelle Dubois, Christian Ekberg, Sofie Englund,  
Anna Fermvik, Jan-Olov Liljenzin, Denis Neumayer,  
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## Abstract

The long-lived elements in the spent nuclear fuels are mostly actinides, some fission products ( $^{79}\text{Se}$ ,  $^{87}\text{Rb}$ ,  $^{99}\text{Tc}$ ,  $^{107}\text{Pd}$ ,  $^{126}\text{Sn}$ ,  $^{129}\text{I}$ ,  $^{135}\text{Cs}$ ) and activation products ( $^{14}\text{C}$ ,  $^{36}\text{Cl}$ ,  $^{59}\text{Ni}$ ,  $^{93}\text{Zr}$ ,  $^{94}\text{Nb}$ ). 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. The most difficult separations to make are those between trivalent actinides and lanthanides, due to their relatively similar chemical properties, and those between different actinides themselves. These separations are necessary to obtain the desired efficiency of the transmutation process and in order not to create any unnecessary waste thus rendering the process useless. 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.

Chalmers University of Technology is involved in research regarding the separation of actinides and lanthanides and between the actinides themselves as a partner in the EUROPART project within the European Union sixth framework program. This is a continuation of the projects we participated in within the fourth and fifth framework programmes, NEWPART and PARTNEW, respectively. The aims of the projects have now shifted from basic understanding to more applied research with focus on process development. However, since the basic understanding is still needed we have our main focus on the chemical processes and understanding of how they work. Work is progressing in relation to a proposal for the 7th framework programme. This proposal will be aiming at a pilot plant for separation for transmutation purposes.

## Sammanfattning

De långlivade ämnena i det använda kärnbränslet består till största delen av aktinider, en del fissionsprodukter ( $^{79}\text{Se}$ ,  $^{87}\text{Rb}$ ,  $^{99}\text{Tc}$ ,  $^{107}\text{Pd}$ ,  $^{126}\text{Sn}$ ,  $^{129}\text{I}$ ,  $^{135}\text{Cs}$ ) och aktiveringsprodukter ( $^{14}\text{C}$ ,  $^{36}\text{Cl}$ ,  $^{59}\text{Ni}$ ,  $^{93}\text{Zr}$ ,  $^{94}\text{Nb}$ ). För att kunna förstöra de långlivade ämnena i en transmutationsprocess måste de separeras från resten av det använda kärnbränslet. De svåraste separationerna att göra är de mellan trevärdade aktinider och lantanider, på grund av deras relativt liknande kemi, samt de mellan aktiniderna själva. Dessa separationer är nödvändiga för att uppnå den önskade effektiviteten i transmutationsprocessen samt för att undvika extra avfall som skulle göra hela processen överflödig. 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.

Chalmers tekniska högskola deltar i forskningen rörande separationen av aktinider och lantanider och mellan aktiniderna själva, genom att vara en partner i EUROPART, ett projekt inom EU:s sjätte ramprogram. Detta projekt är en fortsättning på tidigare projekt vi deltagit i inom det fjärde och femte ramprogrammet, nämligen NEWPART och PARTNEW. Målet med arbetet har under denna tid flyttats från grundläggande förståelse till mer tillämpad forskning med processberäkningar och test med riktigt använt kärnbränsle. Dock behövs fortfarande grundläggande kunskaper varför vårt fokus fortfarande ligger på grundläggande kemiska frågor och förståelse för ingående processer. Arbeta pågår med att färdigställa en ansökan för 7:e ramprogrammet. Detta projekt kommer att ha som mål att bygga upp en pilotanläggning för separation för transmutationsändamål.

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# Introduction

The Partitioning and Transmutation (P&T) group at Nuclear Chemistry, Department of Chemical and Biological Engineering at Chalmers University of Technology investigates the separation of different chemical elements in the 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 deal with highly active aqueous and organic solutions already exists. It is also a good technique to use considering its high efficiency of separation.

Internationally other processes, such as molten salt electrolysis and chromatographic methods, are also investigated.

The Chalmers group has been involved in the separation and transmutation research throughout three different European Union framework programmes, *i.e.* NEWPART (1996–1999), PARTNEW (2000–2003) and EUROPART (2004–2007). During this time the focus has changed slightly although the main content is still 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 following the CHON principle (only containing carbon, hydrogen, oxygen and nitrogen). This search has continued but now in more close collaboration with process expertise to make sure that the molecules not only have good separation capabilities but also survive practically in a process. In addition, it has been shown recently that the whole organic system is of interest since changing the diluent the hydrolytic and radiolytic stability can be increased as well as the separation factor can be enhanced. The research can be divided into three different areas:

- Co-extraction of actinides and lanthanides from acidic high active raffinate – DIAMEX process (**DIAM**ide **EX**traction).
- Separation of actinides and lanthanides – SANEX process (**Se**lective **ActiN**ide **EX**traction).
- Separation of Am and Cm.

The EUROPART project also involves the former European Union projects PYROREP and CALIXPART. Their main focus was to deal with pyroprocesses and processes involving extraction with calixarenes mainly for Cs removal from the nuclear waste.

The main experimental work at Chalmers concerns the extraction properties and other basic chemical characteristics of ligands synthesized in Reading, UK. The influence 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. Recently the role of the organic diluent has been investigated as well as detailed studies on the effect of small changes in the molecular structure of the ligands used for the separation. However, Chalmers is also involved in process development and flow sheet calculations. One of our PhD students is currently working at ITU in Germany with real waste solutions to increase the experience and verify the modelling tool developed at Chalmers previously.

## Research

During 2006 two PhD students have worked full time in the project, Teodora Retegan and Anna Fermvik. The former is studying the effect of the diluent on the extraction ligand as well as the effect of small changes in the molecular changes in the structure of the ligand on extraction, stability and separation. Anna Fermvik is studying the effect of radiolysis and which products are produced. As a part she also investigates how to inhibit this radiolysis. Sofie Englund is now working at OKG AB but is still involved in this project at about 10 % intensity. Daniel Magnusson is working in Germany (ITU) on process experiments on real high active raffinate from the PUREX process.

The EUROPART meetings have been as scheduled, i.e. in January in Aachen and in June in Rome. A French diploma worker, Isabelle Dubois worked in the P&T group. She studied and compared BTBP ligands with different properties to try to increase the understanding of the importance of side groups on the extractant.

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

$D = \frac{[A]_{org}}{[A]_{aq}}$ . I.e. the ratio of the total concentration of a substance, A, in the organic phase to its concentration in the aqueous phase.

$SF = \frac{D_A}{D_B}$ . I.e. the ratio between the distribution ratios of two ions in the same system.

# 1 BTBP chemistry

The use of nitrogen-containing heterocyclic molecules following the CHON-principle (contain only carbon, hydrogen, oxygen and nitrogen) has been shown to efficiently separate actinides and lanthanides using solvent extraction. The basic structure has changed over the years and currently the BTBP family is the most promising one. BTBP stands for *bis*-triazin-bipyridine, which refers to the nature of the central core common to all the molecules in the family. The molecules extracting properties and possibilities to be used in a process are dependent on factors like the solvent, solubility, kinetics, stability towards irradiation etcetera. The chemistry of the BTBPs is not sufficiently known and this chapter includes studies of various properties for a number of BTBP molecules developed over the past years, as well as screening studies of newly synthesized molecules.

## 1.1 Screening studies

### 1.1.1 MF1-BTBP

A new ligand, called MF1-BTBP, was received from Reading University, UK. The following screening tests were performed:

- Solubility.
- Extracting capacity.
- Kinetics.
- Concentration dependence.

The general experimental conditions were:

- aqueous phase consisted of 1 M HNO<sub>3</sub> spiked with trace amounts of <sup>152</sup>Eu, <sup>241</sup>Am, and <sup>244</sup>Cm,
- organic phase consisted of the ligand at a concentration of 0.01 M unless stated otherwise, dissolved in a chosen diluent (usually cyclohexanone, pre-equilibrated with 1 M HNO<sub>3</sub>),
- the experiments were carried out in duplicates,
- 400 µL of each phase were placed in 3 mL glass vials and shaken for 5 minutes by hand (except for the kinetics experiments) and centrifuged for 10 minutes at 800 g,
- aliquots of 200 µL were taken from each phase and the activities of <sup>152</sup>Eu and <sup>241</sup>Am were measured in a HPGe detector (Oretec, Gamma Analyst GEM 23195).

#### **Solubility**

A range of diluents was chosen for solubility experiments. All of them were previously used in dissolution tests for other molecules, so a comparison was possible. The experimental conditions were as stated above. The results of the dissolutions are shown in Table 1-1, where a comparison with other dissolution tests is made /8/. The new molecule seems to dissolve fairly easy in the diluents used, showing a better solubility than the previous molecules.



**Table 1-1. Dissolution experiment with MF1-BTBP. The results are compared with corresponding dissolution experiments for CyMe<sub>4</sub>-BTBP and CyMe<sub>4</sub>-S-BTP /8/.**

Organic diluents	Dissolution CyMe <sub>4</sub> -BTBP	CyMe <sub>4</sub> -S-BTP	MF1-BTBP
TPH	Not soluble	Dissolving after ~ 5 min (room temperature)	Not soluble
1-hexanol	Difficult, required ultrasound bath	Difficult, required ultrasound bath	Dissolving after ~ 1 h (room temperature)
1-heptanol	–	Difficult, required ultrasound bath	Relatively fast ~ 20 min (room temperature)
1-octanol	Difficult, required ultrasound bath	Difficult, required ultrasound bath	Relatively fast ~ 20 min (room temperature)
1-nonanol	–	Difficult, required ultrasound bath	Relatively fast ~ 30 min (room temperature)
1-decanol	Difficult, required ultrasound bath and heating in water bath (60°C) 10 min	Difficult, required ultrasound bath	Dissolving after ~ 2 h (room temperature)
Hexane	Not soluble	Not soluble	–
TBB	Difficult, required ultrasound bath and heating in water bath (60°C) 2 min	Difficult, required ultrasound bath	Dissolving very fast after water bath (60°C) for just some seconds
1,1,2,2-tetra- chloroethane	Very easy and fast	Very easy and fast (room temperature)	–
Anisole	Easy, after 2 min (room temperature)	Easy, after 2 min (room temperature)	–
Benzaldehyde	Easy, after 2 min (room temperature)	Easy, after 2 min (room temperature)	–
Cyclohexanone	Difficult, required ultrasound bath and heating in water bath (60°C) 2 min	Not soluble	Dissolving very fast ~ 1 min (room temperature)
Nitrobenzene	Easy, after 2 min (room temperature)	Very easy and fast (room temperature)	Dissolving very fast (some seconds) (room temperature)

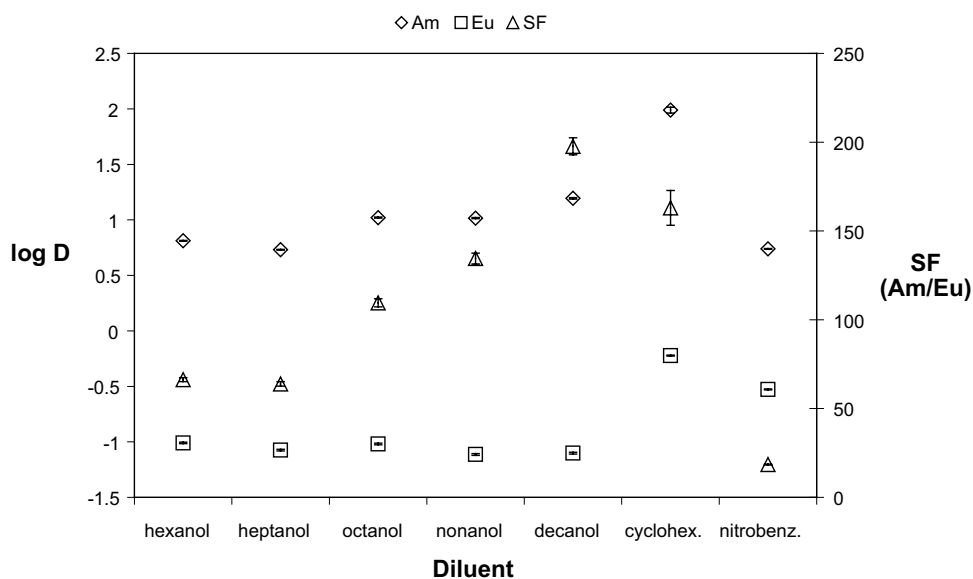
### **Extracting capacity**

After the solubility test, the organic solutions were used for a screening extraction experiment, except the system with TBB, which after contact formed an emulsion that was not broken even after 15 minutes of centrifugation. In Figure 1-1 the D and SF for the different diluents are illustrated. The D is highest for the cyclohexanone system, as expected, but much lower in nitrobenzene than what would be expected. In nitrobenzene, the D is lower than in decanol; this has previously not been observed for other ligands.

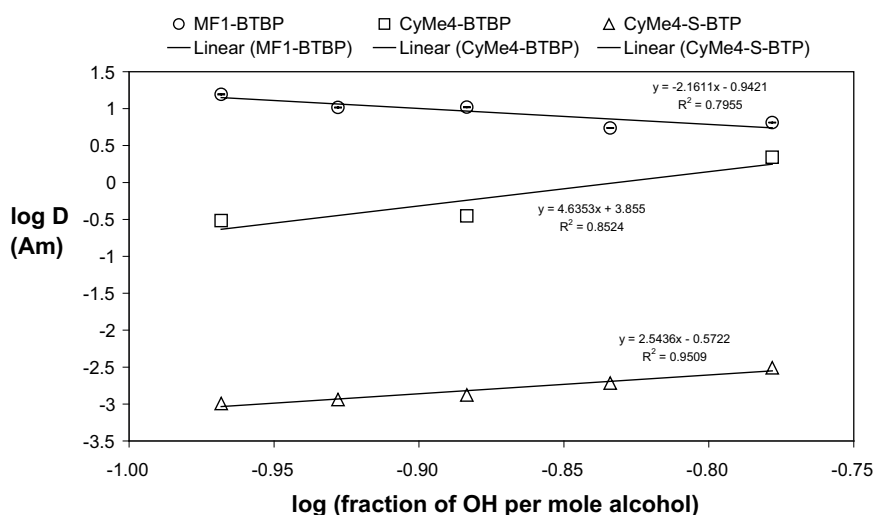
As can be seen in Figure 1-1, the value of D increases with increasing carbon chain length of the saturated alcohols, totally the opposite to what was observed before with other BTBPs. The SF also acts differently, showing very high value, which is unusual for the alcohol systems. It is known to be around 25, see /1/ and /3/. In order to check how the distribution of Am depends on the concentration of OH a plot showing the log D vs. the logarithmic value of the fraction of OH per mole alcohol is presented in Figure 1-2. Three extracting molecules are represented and MF1-BTBP is the only one giving a negative value for the log-log slope. The slope is approximately –2.1 for MF1-BTBP and 4.6 and 2.5 for CyMe<sub>4</sub>-BTBP and CyMe<sub>4</sub>-S-BTP, respectively.

### **Kinetics**

The kinetics experiments were carried out using the same method as stated in the general experimental part, but the contact times were 2, 5, 10, 15, 20 and 30 minutes, respectively. Cyclohexanone pre-equilibrated with 1 M HNO<sub>3</sub> was chosen as diluent for the organic phase. The aqueous phase was pre-equilibrated with pure cyclohexanone. The results of the experiments are presented in Figure 1-3.



**Figure 1-1.** Extraction of Am and Eu with MF1-BTBP in the different organic diluents. TBB is excluded since it after contact formed an unbreakable emulsion.



**Figure 1-2.** Plot illustrating the extraction of Am by different alcohols. The alcohols are represented by their fraction of OH per mole alcohol. Error bars were not available for CyMe<sub>4</sub>-BTBP and CyMe<sub>4</sub>-S-BTP.

It was expected from previous experiments that the kinetics of extraction would be quite fast, since this diluent, being more polar than many others, enhance the extraction and even extracts small quantities by itself /1, 3/. MF1-BTBP proved to have very fast kinetics, equilibrium was reached in only 2 minutes. In previous kinetics work /4/, using the same organic system but a different ligand (C5-BTBP), equilibrium was reached after about 10–15 minutes.

### Concentration dependence

A concentration dependence experiment was carried out in order to establish the best composition of the organic system with respect to the extraction of Am and the SF between Am and Eu. The experiment was carried out using the conditions stated in the beginning of this chapter, but varying the ligand concentration as follows: 0.0005, 0.001, 0.0025, 0.005, 0.0075 and 0.01 M. The results are shown in Figure 1-4.

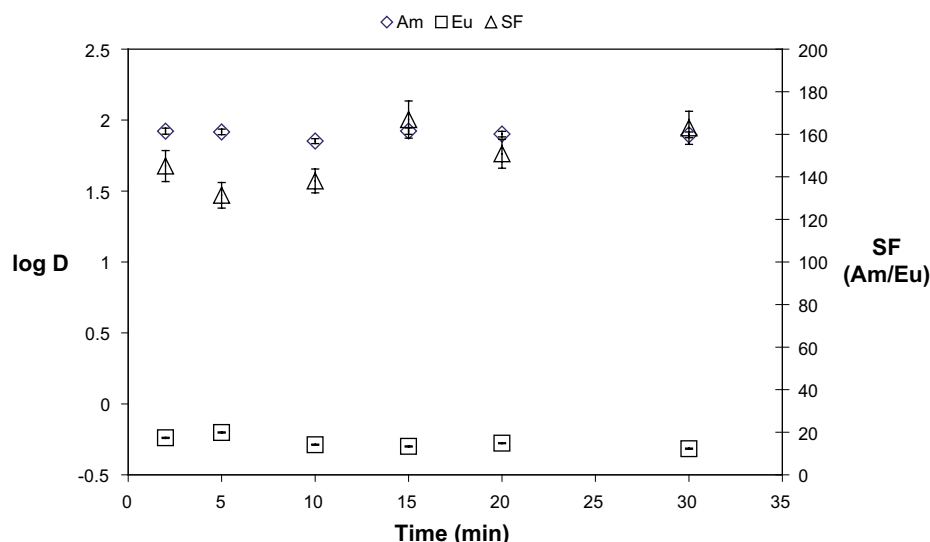


Figure 1-3. Kinetics experiment using 0.01 M MF1-BTBP in cyclohexanone.

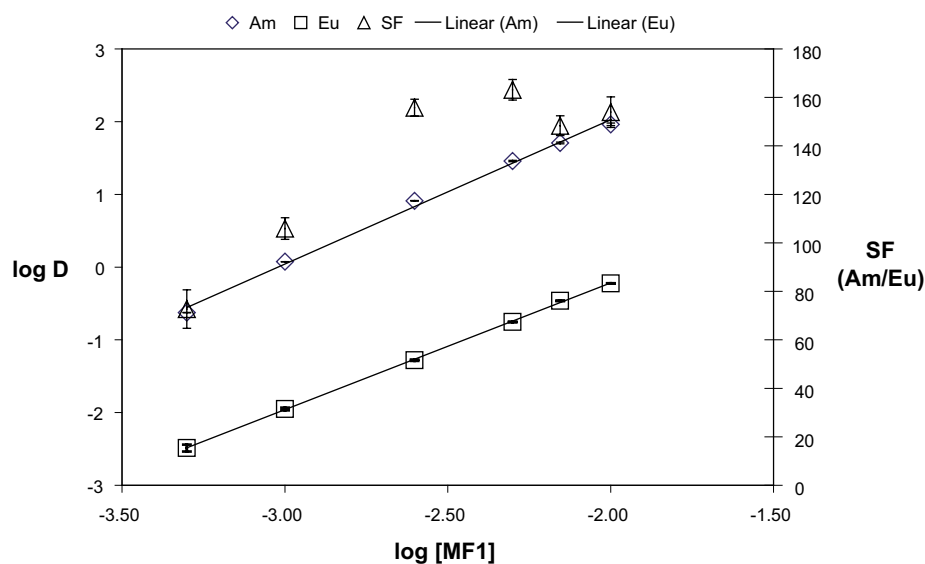


Figure 1-4. Extraction of Am and Eu with varying concentration of MF1-BTBP in cyclohexanone.

The extraction of Am and Eu increases linearly with the increase of ligand concentration. For Am, the calculated slope gives a value of 2 and for Eu, the corresponding value is 1.7. The slopes are very similar to the ones earlier obtained for C5-BTBP /5/.

### 1.1.2 MF2-BTBP

Another newly developed ligand, called MF2-BTBP was received from Reading University, UK.

#### Extraction

Two different organic systems were prepared. One contained 20 mM MF2-BTBP and 0.25 M DMDOHEMA in octanol and one contained 20 mM MF2-BTBP in pre-equilibrated cyclohexanone. The cyclohexanone was pre-equilibrated with 1 M HNO<sub>3</sub>, which constituted the base for the aqueous phase. 5mL of organic phase and 5 mL aqueous phase (1 M HNO<sub>3</sub> + traces of <sup>152</sup>Eu, <sup>241</sup>Am and <sup>244</sup>Cm) was shaken manually for 10 minutes. The samples were then centrifuged for

10 minutes at 800 g and 200  $\mu\text{L}$  aliquots from each phase were measured in a HPGe detector (Oretec, Gamma Analyst GEM 23195).

Figure 1-5 illustrates the result of the extraction experiments. The cyclohexanone system show higher D for both Am and Eu but it has a SF between Am and Eu of 174, while the SF for the DMDOHEMA + octanol system is 222.

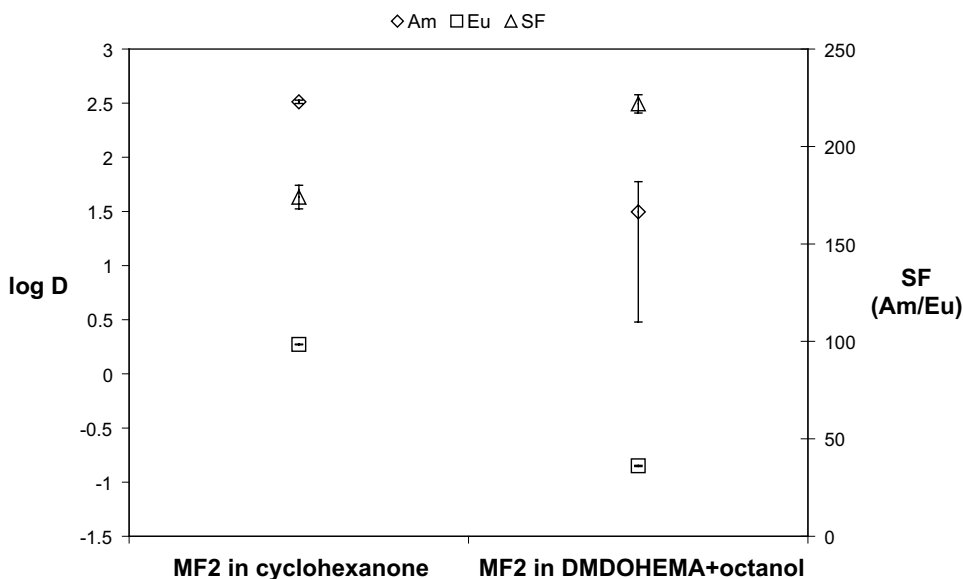
### Stripping

The organic phases from the extraction experiments were contacted with an aqueous solution containing 0.05 M glycolic acid. The pH of the solution was adjusted to 4 by adding  $\text{NH}_3$ . In the case of the solution containing cyclohexanone, the glycolic acid solution was pre-equilibrated with cyclohexanone. 300  $\mu\text{L}$  of each phase were contacted during 5 minutes shaking. Samples of 100  $\mu\text{L}$  from each phase were taken and measured in a HPGe detector of the same type as used above. 100  $\mu\text{L}$  aliquots were taken from the aqueous phase before and after contact for titration purposes. The reason for this titration is that the pH of the stripping solution will be lowered by nitric acid previously extracted together with the metals and now also stripped. With cyclohexanone and octanol, both contacted with 1 M  $\text{HNO}_3$  during extraction, the typical  $\text{HNO}_3$  concentration in the aqueous phase after stripping is 0.14 and 0.11 M respectively. The experiments were carried out with single samples.

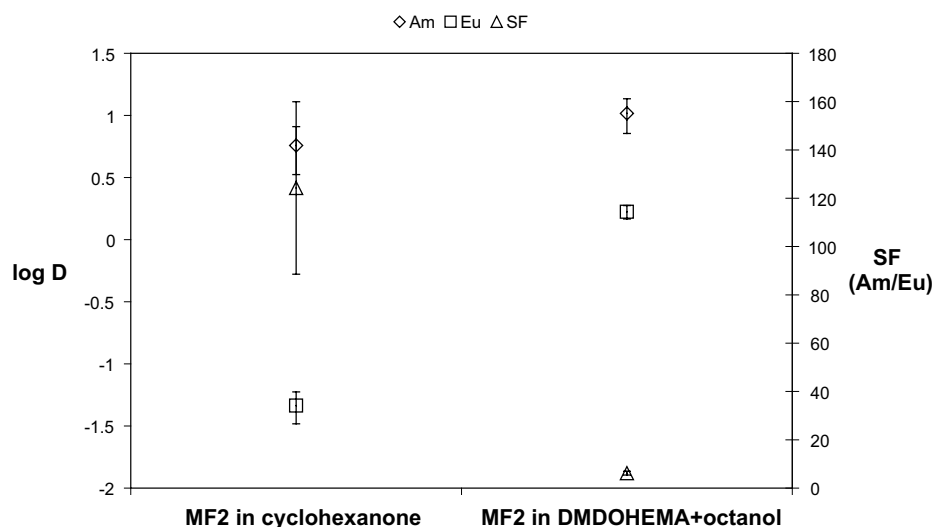
The result of the stripping is presented in Figure 1-6. The big difference between the two systems is the stripping of Eu, which is much poorer stripped in the DMDOHEMA+octanol system, while the Am stripping does not vary that much, resulting in separation factors of 124 and 6, respectively.

## 1.2 Detailed studies

During the development process several different side chains or groups were attached to the “core” molecule for different purposes *e.g.* increasing the solubility in the organic phase or decreasing the solubility in the aqueous phase, a better resistance towards radiolysis, etcetera. This section describes detailed studies on some BTBPs, the structures shown in Table 1-2.

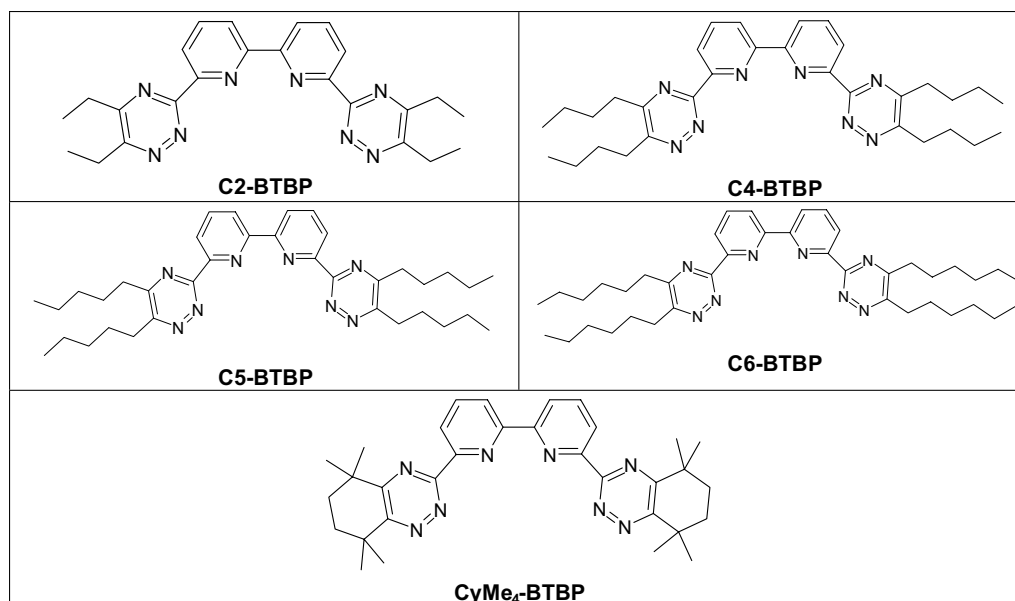


**Figure 1-5.** Extraction of Am and Eu for two systems containing 20mM MF2-BTBP in different solvents.



**Figure 1-6.** Results from stripping of two different organic phases with 0.05 M glycolic acid. The pH of the aqueous phase was set to 4 prior to contact.

**Table 1-2. Structure of the BTBPs used in the experiment.**



### 1.2.1 Extraction

Extraction experiments have been performed with various metals. Some experiments focussed on D and SF of different systems, and how they depend on the side group, while other looked at the kinetics of the systems.

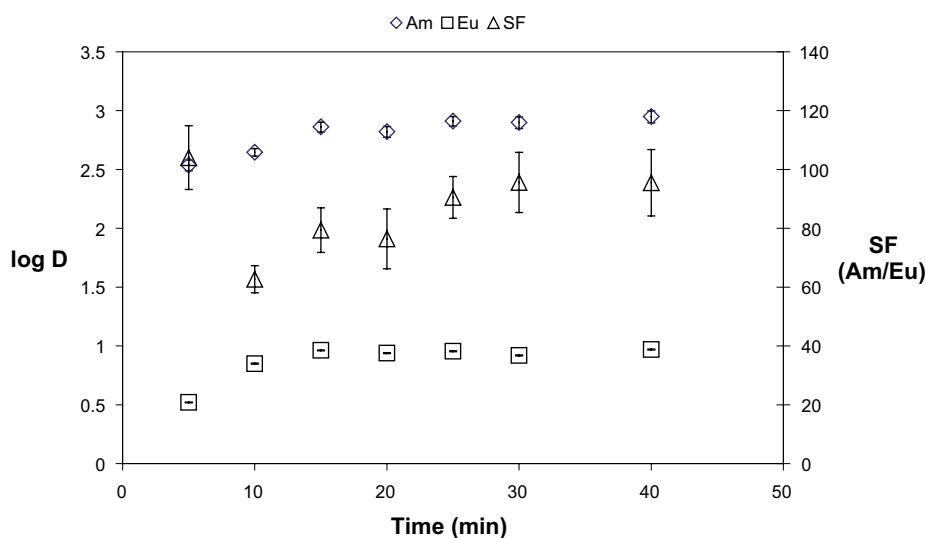
#### *Am and Eu*

##### **CyMe<sub>4</sub>-BTBP**

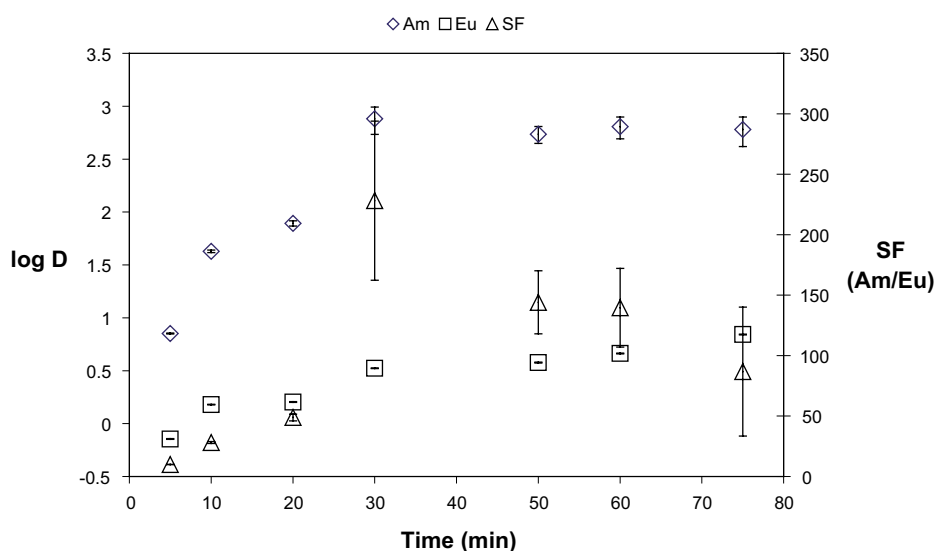
Three extraction kinetics experiments were carried out with similar systems in which only the diluent varied. The organic phase consisted of 0.01 M CyMe<sub>4</sub>-BTBP dissolved in nitrobenzene, p-anisaldehyde or cinnamaldehyde while the aqueous phase consisted of 0.01 M HNO<sub>3</sub> + 0.99 M NaNO<sub>3</sub> spiked with trace amounts of <sup>152</sup>Eu, <sup>241</sup>Am and <sup>244</sup>Cm (nitrobenzene and p-anisaldehyde system) or <sup>152</sup>Eu and <sup>241</sup>Am separately (cinnamaldehyde system). All experiments were carried

out in triplicates. 500  $\mu\text{L}$  of each phase was contacted for different periods of times by manual shaking. For the system containing nitrobenzene, the contact times were 5, 10, 15, 20, 25, 30 and 40 minutes, for the system containing p-anisaldehyde the contact times were 5, 10, 20, 30, 50, 60 and 75 minutes and for the system with cinnamaldehyde the contact times were 1, 3, 5, 10, 20 and 30 minutes. Aliquots of 200  $\mu\text{L}$  was taken from each phase and analyzed with a HPGe detector (Oretc, Gamma Analyst GEM 23195) (nitrobenzene and p-anisaldehyde system) or a NaI(Tl)-scintillation well detector (Intertechnique GC-4000) (cinnamaldehyde system). The results are shown in Figure 1-7 to 1-9.

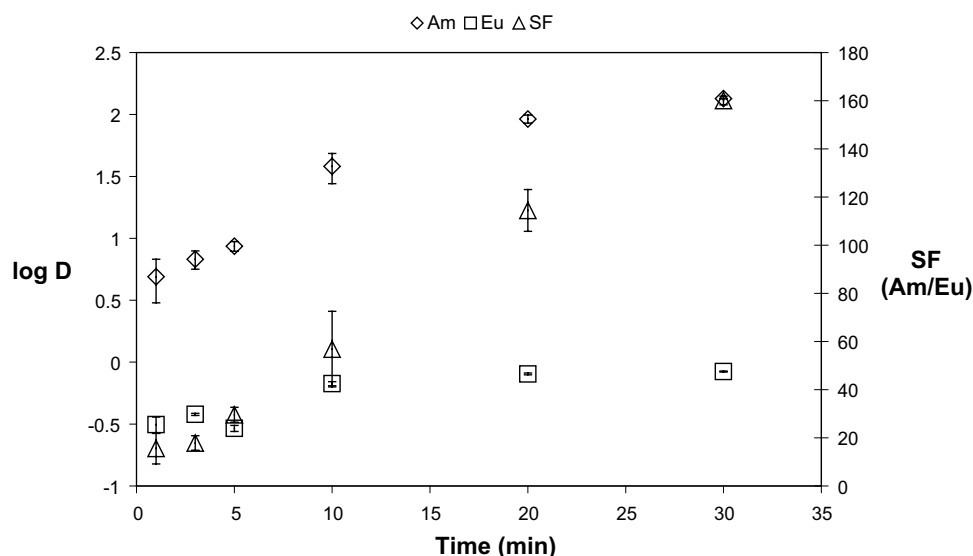
As can be seen in the figures above the three organic systems have different behaviour both kinetically and also with respect to the extraction efficiency. The nitrobenzene system, see Figure 1-7, reaches equilibrium after 15 minutes with a SF around 100. The system containing p-anisaldehyde behaves quite differently, Am reaching equilibrium after 30 minutes while Eu is still being slowly extracted, even after 75 minutes. The SF after 75 minutes is about 100. In the system containing cinnamaldehyde as diluent, it is the Eu that reaches equilibrium first, after just 10 minutes, while Am is still slowly extracted even after 30 minutes. SF at that point is about 160.



**Figure 1-7.** Kinetic experiment using 0.01 M CyMe<sub>4</sub>-BTBP in nitrobenzene. The aqueous phase contained 0.01 M HNO<sub>3</sub>, 0.99 M NaNO<sub>3</sub> and trace amounts of <sup>152</sup>Eu, <sup>241</sup>Am and <sup>244</sup>Cm.



**Figure 1-8.** Kinetic experiment using 0.01 M CyMe<sub>4</sub>-BTBP in p-anisaldehyde. The aqueous phase contained 0.01 M HNO<sub>3</sub>, 0.99 M NaNO<sub>3</sub> and trace amounts of <sup>152</sup>Eu, <sup>241</sup>Am and <sup>244</sup>Cm.



**Figure 1-9.** Kinetic experiment using 0.01 M CyMe<sub>4</sub>-BTBP in cinnamaldehyde. The aqueous phase contained 0.01 M HNO<sub>3</sub>, 0.99 M NaNO<sub>3</sub> and trace amounts of <sup>152</sup>Eu, <sup>241</sup>Am and <sup>244</sup>Cm.

These different behaviours cannot really be explained as chemical interactions between the diluent and the ligand. Also, even if we take into consideration the activity of the diluents, we still cannot explain the lower extraction of Eu in the organic systems containing p-anisaldehyde and cinnamaldehyde than the extraction achieved in the nitrobenzene containing system. Further investigations on the molecular level are needed.

### Th, U and Np

#### Different BTBPs

A study has been carried out in order to compare the influence of the side groups and the influence of the BTBP concentration on the extraction of actinides. For this purpose, three different oxidation states were chosen: Th (IV), Np (V) and U (VI). Five different BTBPs were used for the extraction: C2-, C4-, C5-, C6- and CyMe<sub>4</sub>-BTBP.

The aqueous phase consisted of 2 μM <sup>234</sup>Th, 2 μM natural U and 0.4 μM <sup>237</sup>Np in 1 M HNO<sub>3</sub>. The organic phase consisted of one of the BTBPs dissolved in cyclohexanone pre-equilibrated with aqueous phase without metals. The concentrations of the BTBPs used for each batch were: 0.00005 M, 0.0001 M, 0.0005 M, 0.001 M, 0.005 M and 0.01 M. The detection was performed with ICP-MS (Elan 6100 DRC, Perkin Elmer Sciex) and the internal standards used for the measurements were: Rh, In, Ho and Yb in 1 M ultrapure HNO<sub>3</sub>.

500 μL of each phase were contacted for 5 minutes. After contact, the samples were centrifuged at 800 g for 10 minutes and aliquots of 200 μL of the aqueous phase were taken and diluted 1:20 using the internal standard solution for the ICP-MS measurement. Aliquots were also taken from the aqueous phase before contact. The difference in metal concentration before and after contact was assigned the organic phase after contact and the distribution ratios could be calculated. All experiments were made in duplicates.

The results of the experiments are shown in Figure 1-10 to 1-14.

The conclusion of this experiment is clear: Np is the only metal extracted by all these systems, independent of the concentration used. The trend in Np extraction capability is clear: it increases with the increase of ligand concentration and the calculated log-log slope is about 0.7. In the case of C2-BTBP the D does not reach as high a value as for the molecules with longer carbon chain (C4-, C5- and C6-BTBP). CyMe<sub>4</sub>-BTBP on the other hand, show D's higher than all the other BTBPs, at all concentrations.

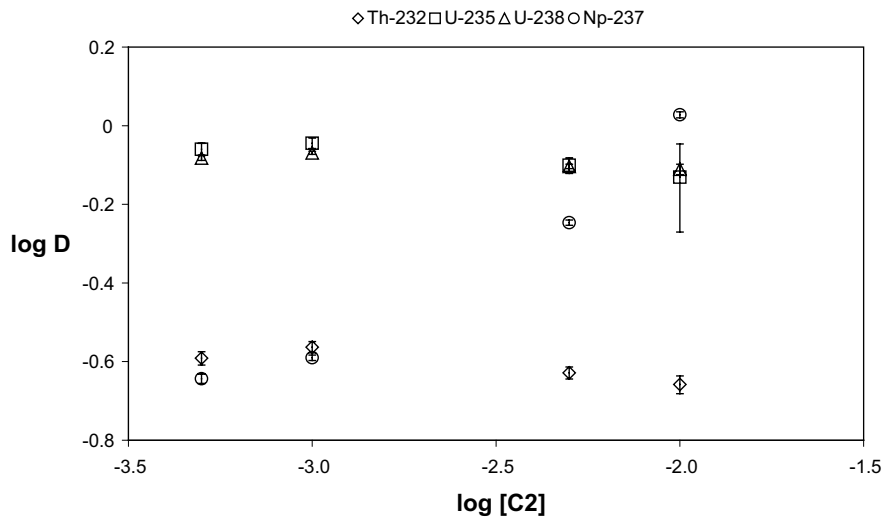


Figure 1-10. Extraction of actinides with varying concentration of C2-BTBP in cyclohexanone.

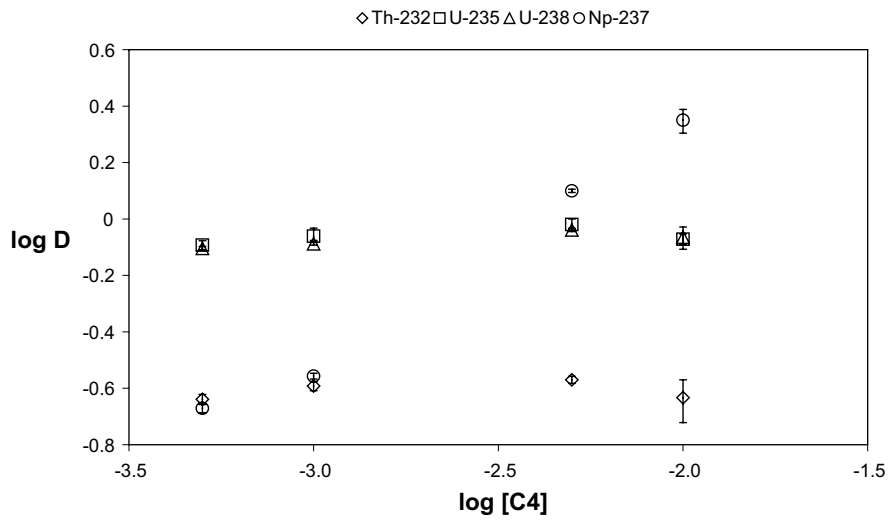


Figure 1-11. Extraction of actinides with varying concentration of C4-BTBP in cyclohexanone

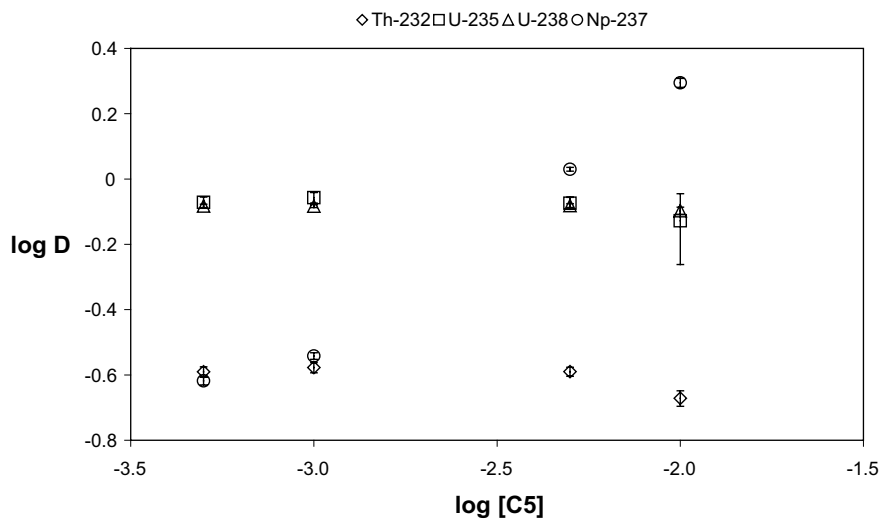


Figure 1-12. Extraction of actinides with varying concentration of C5-BTBP in cyclohexanone.



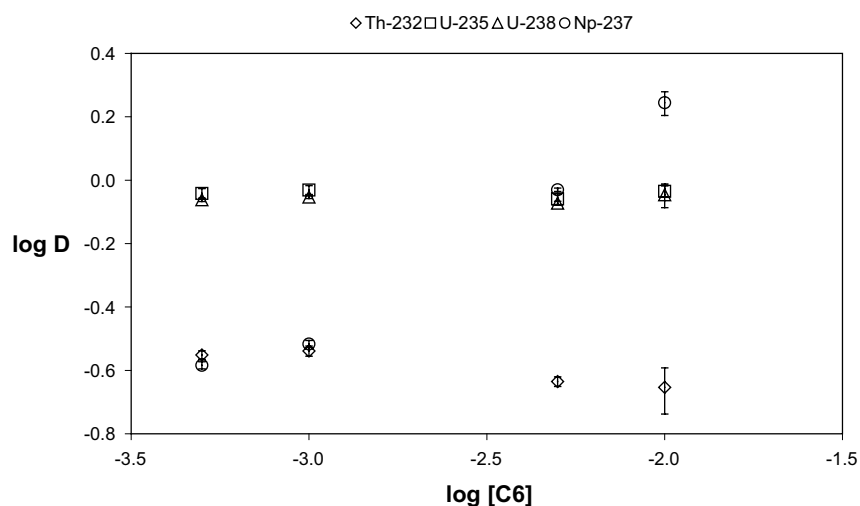


Figure 1-13. Extraction of actinides with varying concentration of C6-BTBP in cyclohexanone.

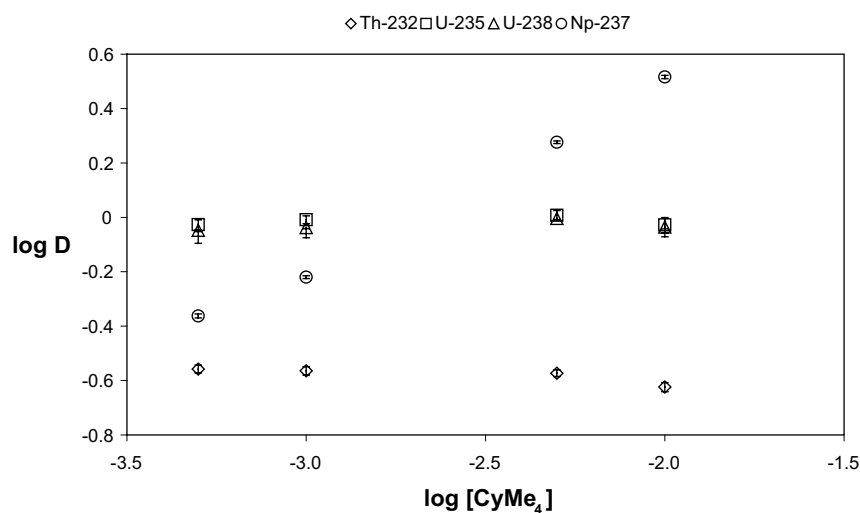
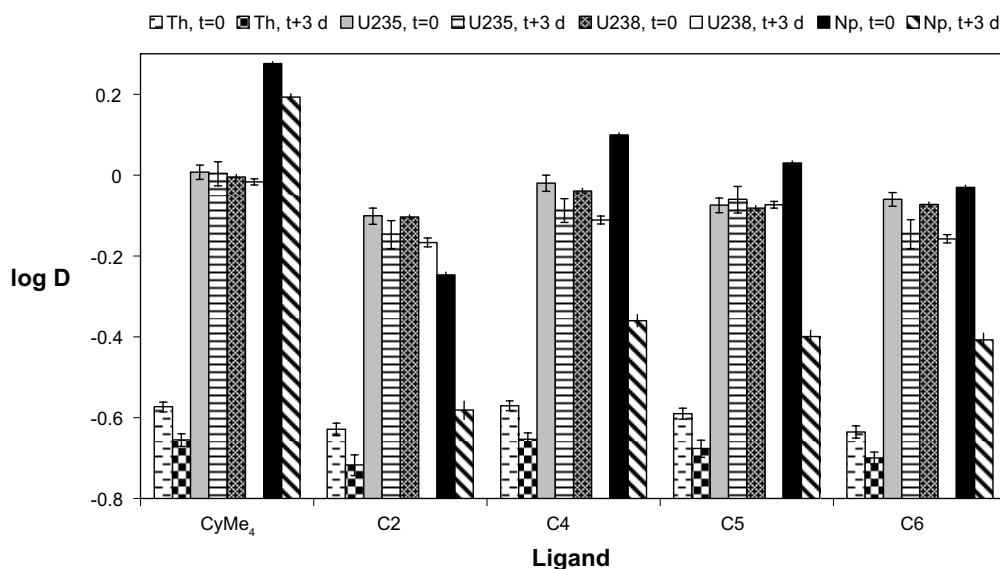


Figure 1-14. Extraction of actinides with varying concentration of CyMe<sub>4</sub>-BTBP in cyclohexanone.

### Ageing

During the experiments it was observed that the extraction properties of the molecules were changing over time, and from previous experience it is known that some of them are ageing. A series of experiments was carried out in order to check if the ageing products could extract other metals than Np. The conditions of the experiment remain as stated before, but only one ligand concentration was chosen; 0.005 M. A fresh solution was prepared and named  $t = 0$ . An old organic solution (3 days old) named  $t + 3$  d was used as comparison. The experiments were carried out in duplicates for the solution named  $t = 0$  and single samples for the solution named  $t + 3$  d. The measurements were carried out with ICP-MS, using the same condition as before. The results are shown in Figure 1-15.

It can be observed in the figure above that CyMe<sub>4</sub>-BTBP is little affected by ageing effect, but the same cannot be said about the other molecules. It might be possible to assume that it can be an effect of the degradation of the side group bound to the molecule, since this is the only difference between them. Probably the cyclic side group bound to the core molecule in CyMe<sub>4</sub>-BTBP is much more chemically resistant.



**Figure 1-15.** Result of ageing effect experiments with the five BTBP molecules. Distribution ratios for different metals at time zero and after three days of ageing are displayed.

## Ni

### C2- and C5-BTBP

Nickel is a corrosion product that inevitably will be present in an industrial extraction system. Due to high distribution ratios for nickel with some nitrogen donor ligands it may be feared that the extraction of the actinides may be hampered. In addition, nickel is a generally difficult element due to the combination of charge and valence, making it difficult to saturate and fear of formation of poly nuclear complexes may exist. Ni extraction experiments with two different ligands, C2-BTBP and C5-BTBP, have been performed. The choices of ligands were made due to the different complexes formed. In general the C2-BTBP forms a 1:1 complex while the C5-BTBP forms a 1:2 complex. The main aim was to study the distribution of these two major complexes.

The procedures were the same for both C2-BTBP and C5-BTBP experiments. The organic phases consisted of the BTBP (either C2- or C5-) dissolved in cyclohexanone. The solvent had previously been pre-equilibrated with the aqueous phase used in the experiments, 1 M HNO<sub>3</sub>. Thus both the aqueous and the organic phase were saturated with respect to the other.

500 µL of each phase were taken and mixed in a 3.5 mL vial. Before starting the contact, 10 µL of a <sup>63</sup>Ni spike solution was added. All experiments were made in triplicates. The samples were shaken 5 hours with a shaking device. As the two phases separated easily, the samples were just left for gravitational separation and then 200 µL of each phase were taken out and measured with a liquid scintillation counter (Wallac 1414 WinSpectral).

One problem that immediately arises when using <sup>63</sup>Ni as tracer is that the best method for detection in solution is liquid scintillation counting. Such measurements are encumbered with several difficulties with quenching being of major importance. Quenching in this context means that part of the light emitted by the scintillator is lost or loses intensity due to absorption processes in the sample. In our case we have both the cyclohexanone and the ligands, C2-BTBP and C5-BTBP that cause quenching. To correct this, quenching curves were made using known amounts of the radioactive element and varying the quenching molecule, see Figure 1-16 for a quench curve for the C5-BTBP system. The factor obtained from the quench curves is then used to correct the actual sample results by dividing the obtained count rate by the quench factor.

The extraction results seen in Figure 1-17 and 1-18 clearly show the differences between the extraction using C2-BTBP and C5-BTBP.

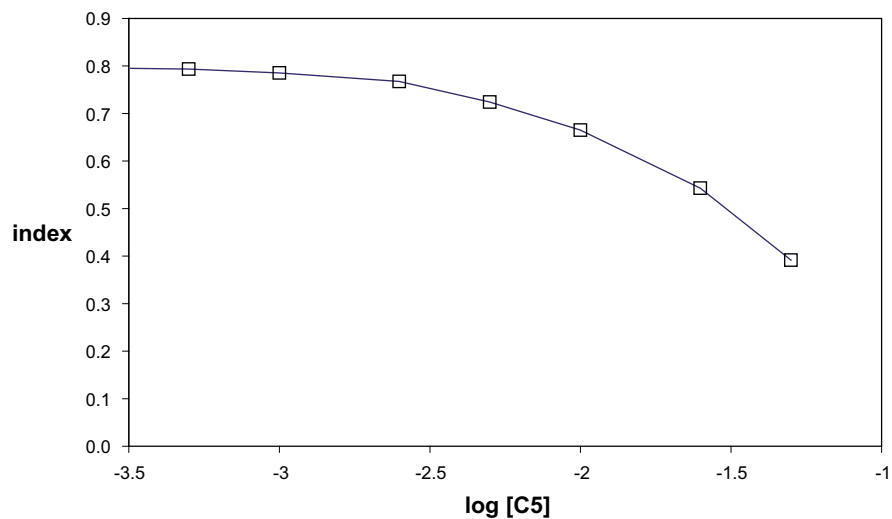


Figure 1-16. Quench curve for C5-BTBP in cyclohexanone.

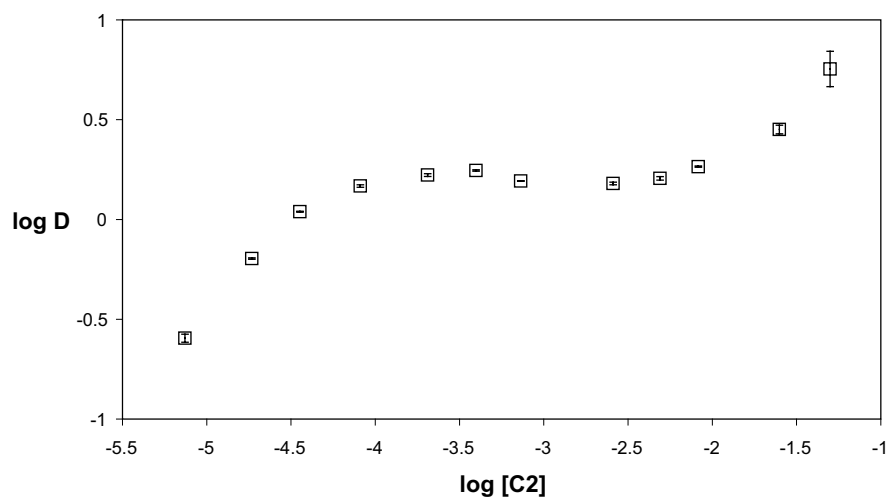


Figure 1-17. Extraction of  $^{63}\text{Ni}$  by C2-BTBP in cyclohexanone.

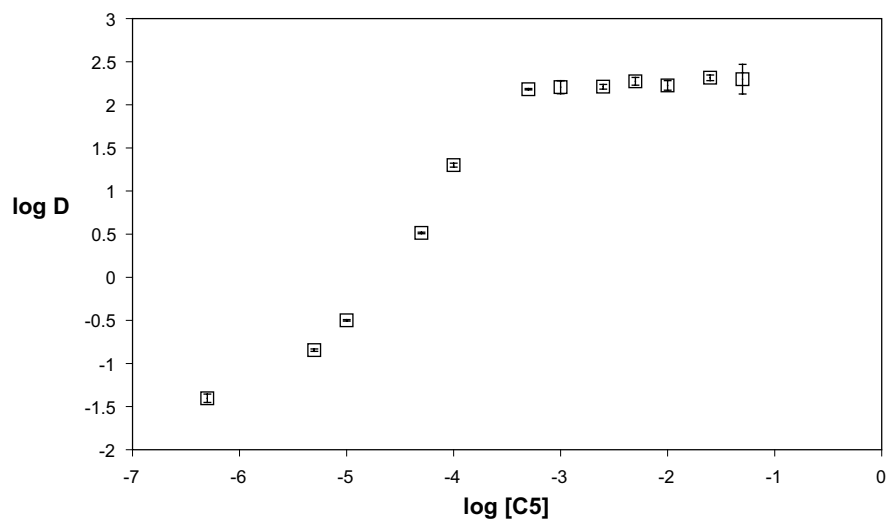


Figure 1-18. Extraction of  $^{63}\text{Ni}$  by C5-BTBP in cyclohexanone.

Both curves reach a plateau in the extraction where a further increase in the BTBP concentration causes little or no increase in the nickel distribution ratio. This appearance of a plateau can be explained by the hypothesis that at low concentrations ( $< 10^{-4}$  M) of the BTBPs the nickel distribution ratio is governed by the association of the nickel with the BTBP while at higher concentrations ( $> 10^{-3}$  M) the nickel distribution ratio is governed by the partitioning of the nickel/BTBP complex between the two liquid phases.

In the case of C5-BTBP the extraction curve shows a clear saturation and the reach of a distribution coefficient,  $k_d$ , of the extracted complex independent of the ligand concentration. This would be a normal case if the extracted complex could be assumed to dominate both in the aqueous and the organic phase. However, using spectrophotometric methods no C5-BTBP could be shown to exist in the aqueous phase. This is also in accordance with the findings of Nilsson et al. /5/. However, when investigating the material balances it is clear that a significant part of the nickel is not present in any of the phases and since sorption can be ruled out it is concluded that nickel is present in the phase boundary. This is supported by the extraction curve where the  $k_d$  observed is then not between the organic and aqueous phases but between the organic phase and phase boundary where the amount seems to increase with increasing ligand concentration while  $D$  remains constant. The slope on the straight part of the extraction curve is close to two why it is reasonable to assume that it is the (1:2) complex that dominates the extraction.

For the C2-BTBP the story seems similar except that the nickel extraction increases again at high concentrations which would be consistent with the formation of a 1:2 complex. This is because a 1:2 complex is likely to be more lipophilic and have a lower stability than the 1:1 complex. Due to the limit of solubility of C2-BTBP it was not possible to increase the BTBP concentration further to reveal the next plateau. A similar behaviour might be possible with higher concentrations of C5-BTBP, but this can not be observed because of the limited solubility of the C5-BTBP in cyclohexanone.

The observations for C2-BTBP and C5-BTBP are in accordance with crystal structures determined at Reading University /6/.

### ***Fission products***

The high-level liquid waste (HLLW) solutions contain a mixture of fission products, corrosion products and actinides. The extraction ability of three different BTBPs towards some of these fission products was studied. All experiments were analyzed using ICP-OES (Optima 3000).

### **CyMe<sub>4</sub>-BTBP**

The extraction ability of CyMe<sub>4</sub>-BTBP towards some fission products has been studied before, but with ICP-MS (Elan 6100 DRC, Perkin Elmer Sciex) as analysis technique /6, 9/. For the experiments here, using ICP-OES, the metal concentration was lower than in previous studies (1  $\mu$ M compared to 50  $\mu$ M) but all other experimental conditions were the same:

Two concentrated (inactive) solutions containing  $10^{-4}$  M of each of the following elements in 1 M HNO<sub>3</sub> were used:

Solution 1: Se, Sr, Zr, Ru, Ag, In, Sb, La, Pr, Sm and Gd,

Solution 2: Rb, Y, Rh, Pd, Cd, Te, Ce, Nd and Eu.

The aqueous phases were diluted from these solutions and initially contained 1  $\mu$ M of each element in 1 M HNO<sub>3</sub>. The organic phase contained 0.01 M CyMe<sub>4</sub>-BTBP in octanol and 800  $\mu$ L of each phase were shaken manually. The contact time was 5 minutes and when the phases had separated samples were taken from the aqueous phase. Samples were also taken from the aqueous phase before contact and all samples were analysed using ICP-OES. 100  $\mu$ L of sample was diluted with 5 mL of ultrapure 1 M HNO<sub>3</sub> before analysis. The difference in metal concentration in the aqueous phase before and after contact was calculated and assigned to the organic phase after contact.

Table 1-3 and 1-4 present the distributions ratios for the different elements. The elements that are present in the solutions but not included in the tables showed results below the detection limit.

**Table 1-3. D of the light lanthanides and yttrium using 0.01 M CyMe<sub>4</sub>-BTBP in octanol.\* indicates that the result is based on a single sample.**

La	Pr*	Ce	Nd*	Sm	Eu	Gd	Y
1.2	2.2	2.5	0.4	47	2.4	0.06	0.04

**Table 1-4. D of various fission products using 0.01 M CyMe<sub>4</sub>-BTBP in octanol.**

Se	Zr	Pd	Ag	Cd	In	Sb	Te
2.5	0.5	2.3	16	9.4	1.7	0.6	2.6

Most of the elements show low D, only samarium (Sm), silver (Ag) and cadmium (Cd) have D close to or above 10. It should be noted that some of the values are based on single samples (denoted \* in the tables) since the other sample in that case showed unreasonable values, for example was below the detection limit.

When comparing these results to earlier experiments with the same synthetic solutions /6, 9/, the distribution ratios are generally higher, except for Ag and Cd that in the previous study showed ratios of 300 and 400, respectively. The lanthanides showed distribution ratios around 0.05 in the old experiment, while most of them now show values around 1 or 2.

### MF1-BTBP

The extraction ability of MF1-BTBP was performed using the same experimental conditions as in the CyMe<sub>4</sub>-BTBP experiments described above, but the diluent was pre equilibrated cyclohexanone instead of octanol. The sample preparation was made by diluting 200 µl aliquots from the aqueous phases with 12 mL ultrapure 1 M HNO<sub>3</sub>.

Table 1-5 and 1-6 list the distributions ratios for the different elements. The elements that are present in the solutions but not included in the tables showed results below the detection limit.

As can be seen, the D in the case of lanthanides is above one for lanthanum (La) and cerium (Ce), and 10<sup>-2</sup> for yttrium (Y). In the case of the other fission and corrosion products Ag show quite a high D, as previously seen in the case of CyMe<sub>4</sub>-BTBP /1/, closely followed by selenium (Se) and Cd.

### C2-BTBP

An extraction experiment was carried out for checking the extraction ability of C2-BTBP and for comparison with the experiments where extraction of Th, Np and U was tested (earlier in this chapter). The organic phase contained different concentrations of C2-BTBP dissolved in cyclohexanone, pre-equilibrated with 1 M HNO<sub>3</sub>. The concentrations used were 0.0025 M, 0.005 M and 0.01 M. The aqueous phase consisted of 1 M HNO<sub>3</sub>, pre-equilibrated with pure cyclohexanone, in which a multi standard solution was added for calibration purposes. The multi standard solution contained a series of metals; all listed in Table 1-7 and the concentration of each metal was 1 ppm.

**Table 1-5. D of the light lanthanides and yttrium using 0.01 M MF1-BTBP in cyclohexanone.**

La	Ce	Nd	Sm	Eu	Gd	Y
1.88	1.40	0.69	0.57	0.01	0.92	0.03

**Table 1-6. D of various fission and corrosion products using 0.01 M MF1-BTBP in cyclohexanone.**

Se	Zr	Ag	Cd	In	Ru
3.22	0.42	3.74	2.42	1.26	1.16

The rest of the experimental conditions were the same as for MF1-BTBP and the results are shown in Table 1-7.

Many of the distribution ratios are around one for the lower ligand concentration. In the cases with higher ligand concentration there were significant measurement problems and thus only few elements are properly analysed. The sign (-) denote the measurements problems. Similar to the extraction experiments with Th, U and Np, the uranium seems to give the highest D at low concentration.

**Table 1-7. Extraction of various metals with different concentrations of C2-BTBP in cyclohexanone.**

Metals	[C2-BTBP]		
	0.0025 M D	0.005 M	0.01 M
Li	0.79	-	-
Na	1.35	-	-
K	-	-	-
Be	1.27	-	-
Mg	0.51	-	-
Ca	2.97	0.11	-
Sr	1.05	-	-
Ba	1.42	-	-
B	3.28	0.54	0.03
Al	0.75	-	-
In	3.10	-	-
Tl	1.45	-	-
Sn	0.85	0.11	0.63
Pb	0.88	-	-
As	1.67	-	-
Sb	1.61	-	-
Bi	-	0.80	0.80
S	2.31	-	-
Se	1.30	-	-
Y	-	-	-
V	1.46	-	-
Cr	1.06	-	-
Mo	2.44	-	-
Mn	-	-	-
Fe	-	-	-
Co	-	1.16	-
Rh	0.16	-	-
Ni	-	0.14	-
Cu	6.25	5.59	4.01
Ag	1.66	0.05	-
Zn	-	-	-
Cd	1.92	2.56	3.23
La	1.08	-	-
Eu	2.80	-	-
Ho	1.25	-	-
Yb	1.02	-	-
Th	0.80	-	-
U	49.50	-	-

## 1.2.2 Stripping

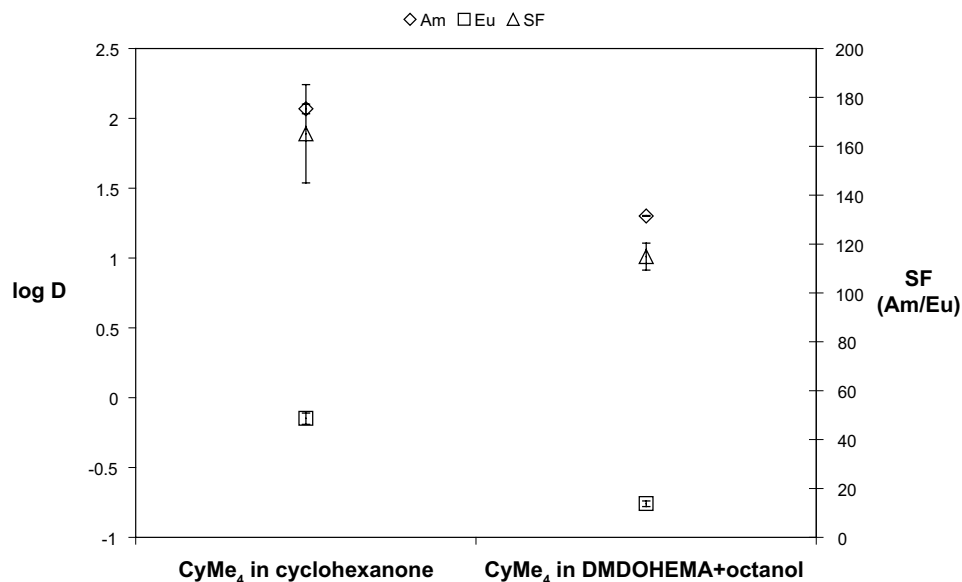
Stripping (back-extraction) experiments have been carried out with glycolic acid (hydroxyacetic acid) as the strip solution.

### CyMe<sub>4</sub>-BTBP

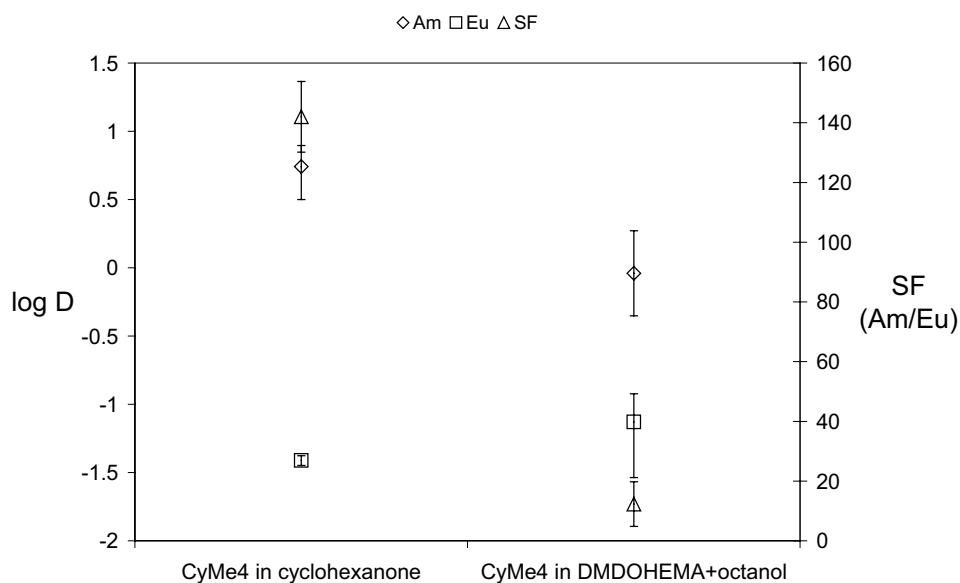
Two organic phases from an extraction experiment were each contacted with an aqueous solution containing 0.05 M glycolic acid. Prior to contact, the pH of the solution was adjusted to 4 by adding NH<sub>3</sub>. The organic phases contained 20 mM CyMe<sub>4</sub>-BTBP in either cyclohexanone pre-equilibrated with 1 M HNO<sub>3</sub> or octanol + 0.25 M DMDOHEMA and the radionuclides <sup>152</sup>Eu, <sup>241</sup>Am and <sup>244</sup>Cm extracted from an aqueous phase. The contact time during extraction was 10 minutes and the activity of the samples was measured with a HPGe detector (Ortec, Gamma Analyst GEM 23195). The results of the extraction, based on double samples, are illustrated in Figure 1-19.

Before stripping the cyclohexanone system, the glycolic acid solution was pre-equilibrated with cyclohexanone. 300 μL of each phase was contacted during 5 minutes manual shaking. Samples of 100 μL from each phase were taken and measured with the HPGe detector. 100 μL aliquots were taken from the aqueous phase before and after contact for titration purposes. Due to the stripping of the nitric acid previously extracted together with the metals the pH will be lowered. With cyclohexanone and octanol, both contacted with 1 M HNO<sub>3</sub> during extraction, the typical HNO<sub>3</sub> concentration in the aqueous phase after stripping is 0.14 and 0.11 M respectively. The experiments were carried out with single samples.

The result of the stripping is presented in Figure 1-20. As can be seen, Am is stripped to a higher extent in the DMDOHEMA+octanol system than in the cyclohexanone system, while Eu acts just the opposite. This gives a high SF for the cyclohexanone system and a low SF for the DMDOHEMA+octanol system.



**Figure 1-19.** Extraction of Am and Eu from an aqueous phase of 1 M HNO<sub>3</sub> and traces of radionuclides for two organic systems.



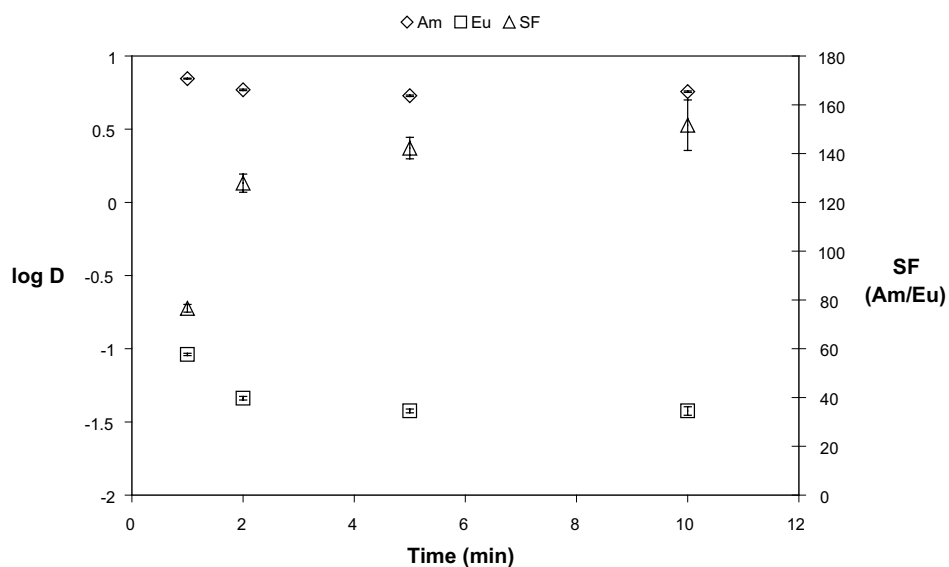
**Figure 1-20.** Stripping of Am and Eu with 0.05 M glycolic acid from two different organic systems containing 20 mM CyMe<sub>4</sub>-BTBP.

### Stripping kinetics

An experiment was carried out to establish the stripping kinetics of the two systems. The organic phases were exactly the same as the one used in the previous stripping experiment. Since the stripping was poor in the previous experiments, the glycolic acid concentration was increased to 0.2 M. The pH was adjusted to ~ 4 with NH<sub>3</sub>.

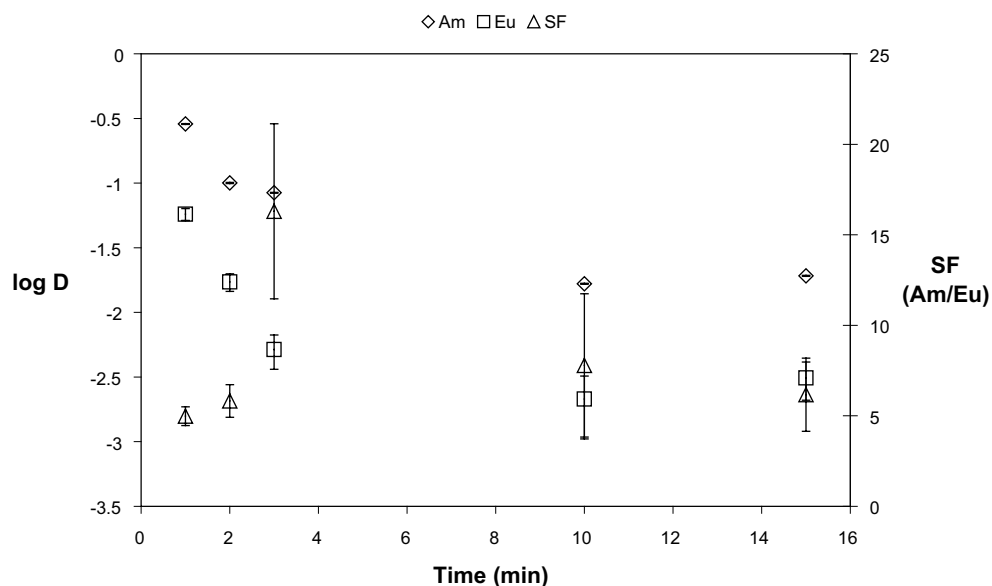
300 μL of each phase were contacted during 1, 2, 5 and 10 minutes for the cyclohexanone system and 1, 2, 3, 10 and 15 minutes for the octanol system. Aliquots of 100 μL of each phase were taken and measured with the HPGe detector. The experiments were carried out with single samples. Figure 1-21 shows the result for the cyclohexanone system. Both Am and Eu seem to have reached an equilibrium plateau after 5 minutes.

In Figure 1-22 the corresponding results for the octanol system are illustrated. The stripping of both nuclides seems to reach an equilibrium plateau after approximately 10 minutes.



**Figure 1-21.** Stripping kinetics of CyMe<sub>4</sub>-BTBP in cyclohexanone contacted with 0.2 M glycolic acid.



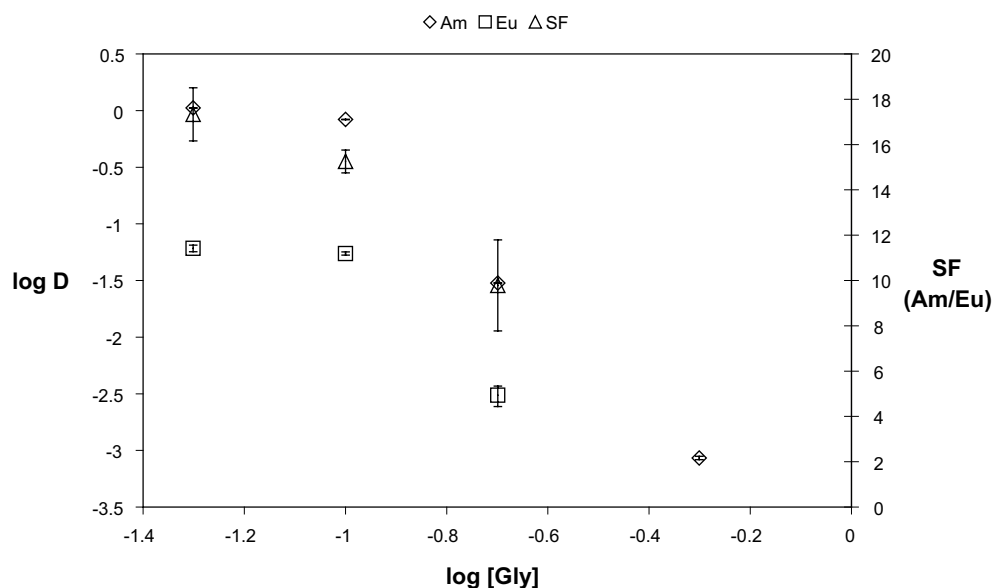


**Figure 1-22.** Stripping kinetics of  $CyMe_4$ -BTBP in octanol + 0.25 M DMDOHEMA contacted with 0.2 M glycolic acid.

### Concentration dependence

According to the kinetics experiments above, it was suggested that 5 minutes was enough to reasonably strip Am and Eu from the octanol system. A concentration dependence experiment was carried out with this system in order to find out which aqueous system is most suitable for stripping. 300  $\mu$ L of organic phase were contacted with 300  $\mu$ L of aqueous phase containing 0.05, 0.1, 0.2, 0.5 M glycolic acid, the pH of each of the aqueous solutions was adjusted to  $\sim 4$  with  $NH_3$ . Aliquots of 100  $\mu$ L were taken from each phase and measured with the HPGe detector. The experiments were carried out with double samples.

The stripping of Am increases with increasing glycolic acid concentration. The log-log curve in Figure 1-23 gives a slope of about  $-4$  for the three highest concentrations (0.1, 0.2 and 0.5 M). This is surprising as a slope of  $-3$  was expected as each Am atom could react with three glycolate anions.



**Figure 1-23.** Log  $D$  for stripping with varying glycolic acid concentration.

## MF2-BTBP

Kinetics experiments have also been made with the new molecule MF2-BTBP dissolved in the same organic diluents as above, namely cyclohexanone and 0.25 M DMDOHEMA + octanol, respectively. The experimental conditions were the same as for the CyMe<sub>4</sub>-BTBP systems, except that the contact times were 1, 2, 5, 10 and 15 minutes. Figure 1-24 and 1-25 shows the results of the experiments, based on single samples only. The major difference between the systems, except the values of the distribution ratios, is the trend of the SFs. For the cyclohexanone system the SF increases with increased contact time, while the SF for the octanol system acts just the opposite. The error bars in Figure 1-24 and 1-25 are based on detection uncertainties.

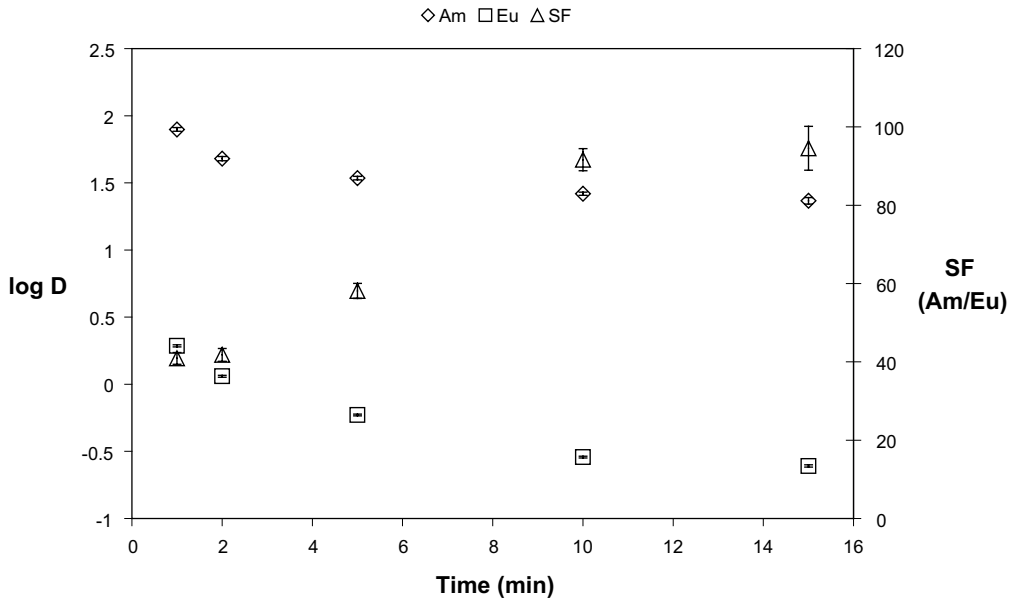


Figure 1-24. Stripping kinetics of MF2-BTBP in cyclohexanone contacted with 0.2 M glycolic acid.

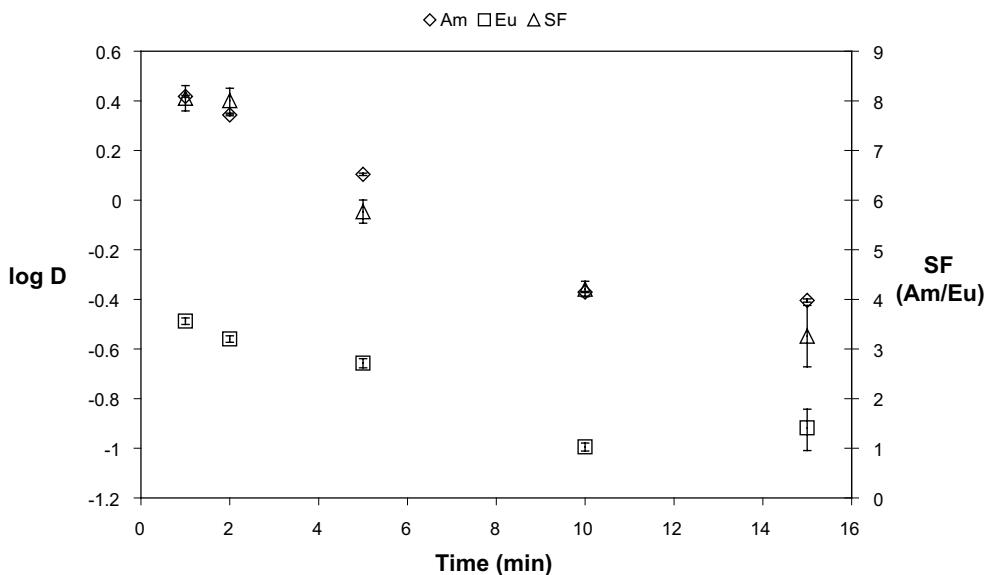


Figure 1-25. Stripping kinetics of MF2-BTBP in 0.25 M DMDOHEMA + octanol contacted with 0.2 M glycolic acid.

### 1.2.3 Radiolysis

Since separation process intended for the BTBP molecules takes place in a high radiation flux, both the extractant and the diluent must be resistant to radiation. A number of organic systems were irradiated and the effect on extraction was studied. Solutions were placed in glass bottles in a  $^{60}\text{Co}$ -source (Gamma cell 220 from Atomic Energy of Canada Ltd) with an estimated dose rate to water of  $\sim 20$  Gy/h. Corresponding samples were placed in a flask outside the gamma source, at a remote distance, to act as a reference and investigate the possible ageing of the molecule. Samples were taken from the organic systems at the start of the experiments and then at different times during a longer time period. 500  $\mu\text{L}$  of the sample was contacted with 500  $\mu\text{L}$  of an aqueous phase (varying for the different systems) spiked with  $^{152}\text{Eu}$ ,  $^{241}\text{Am}$  and  $^{244}\text{Cm}$ . After 5 minutes manual shaking, the samples were centrifuged for 10 minutes at 800 g. Aliquots of 200  $\mu\text{L}$  were taken from each phase and analyzed with two different HPGe detectors (Ortec, Gamma Analyst GEM 23195 and EG&G Ortec).

#### **C5-BTBP**

An earlier study indicated that the selectivity between Am and Eu for C5-BTBP in cyclohexanone changes after some degradation due to irradiation [7]. In the experiments in that study the organic phase was not pre-equilibrated with aqueous phase. This study includes irradiation of C5-BTBP in cyclohexanone, with pre-equilibration before contact with radionuclides, as well as irradiation of C5-BTBP in hexanol.

0.005 M C5-BTBP was dissolved in 50 mL of the two diluents. Three times 500  $\mu\text{L}$  were taken from the two solutions to determine the D at time zero. Samples were taken from each flask at different times during a total time period of 3,503 hours for the cyclohexanone system and 1,387 hours for the hexanol system (the irradiation of this system was then stopped due to crystal formation). This corresponds to a total dose for the irradiated samples of 70 and 28 kGy, respectively. Triple samples were taken from the irradiated solutions while single or double samples were taken from the reference solutions. Before the extraction experiments the cyclohexanone systems were pre-equilibrated with aqueous phase (0.99 M  $\text{NaNO}_3$  and 0.01 M  $\text{HNO}_3$ ) and the aqueous phase was pre-equilibrated with fresh cyclohexanone. Another option is to pre-equilibrate the aqueous phase with the irradiated and reference cyclohexanone solutions.

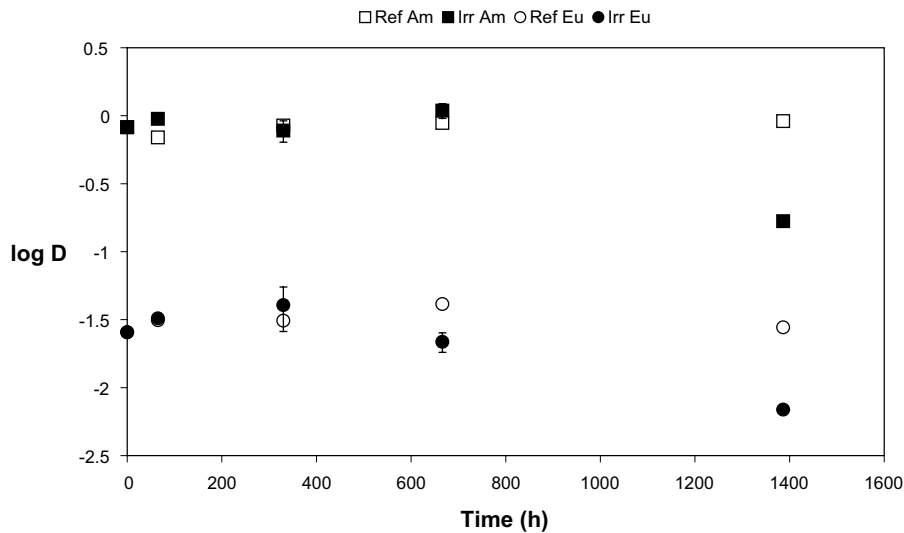
#### **Results hexanol**

At the sampling time 1,387 h (approx. two months) the hexanol solution had formed distinct white crystals at the bottom of the irradiated flask. Samples were taken anyway to see how the extraction was affected by the crystal formation. No crystals were observed in the reference solution. The hexanol solution was removed from the  $^{60}\text{Co}$  source and attempts to analyze the crystals have started. Figure 1-26 illustrates the distribution ratios of Am and Eu for the irradiated and reference solutions as a function of time. The extraction capacity of the C5-BTBP/hexanol system is constant until the crystal formation starts, somewhere in the time span 700–1,350 hours. Both the Am and the Eu extraction decreases when crystals have started to form. The SF between Am and Eu is around 25–30 at all sampling times.

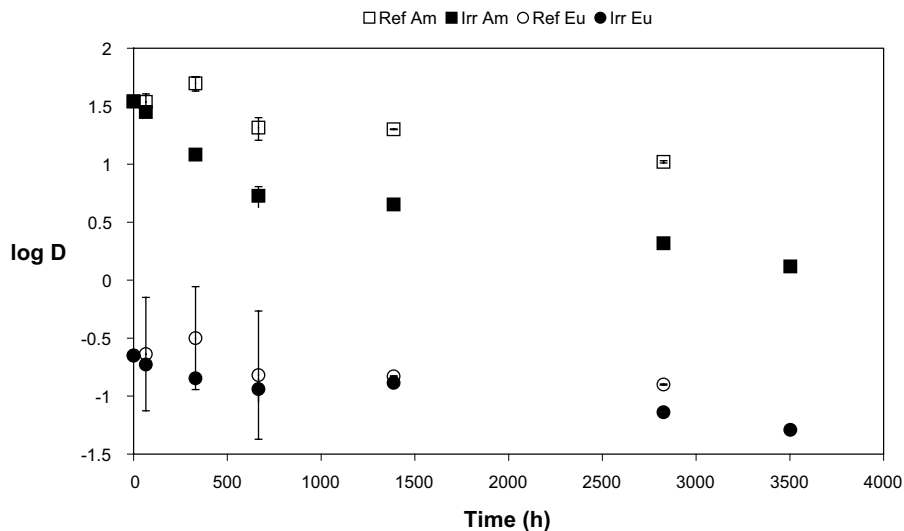
#### **Results cyclohexanone**

The extraction of Am by the cyclohexanone system is highly affected by the irradiation time, hence the received dose, see Figure 1-27. As can be seen, also the extracting capacity of the reference solution decreases with time. An interesting observation is that the difference between  $\log D$  Am for the reference solution and for the irradiated solution is approximately constant from 500 h and on. This indicates that the percentage decrease in distribution ratio of Am is the same for both solutions.

The changes in SF of the cyclohexanone solutions are illustrated in Figure 1-28. Both the irradiated and the reference solution lose their capacity of separating Am and Eu with time, but the decrease is more evident when the solution is exposed to radiation.



**Figure 1-26.** Log D for the reference and irradiated solutions containing C5-BTBP in hexanol at various times. The error bars for Eu, reference samples are large and excluded to make the figure more clear.

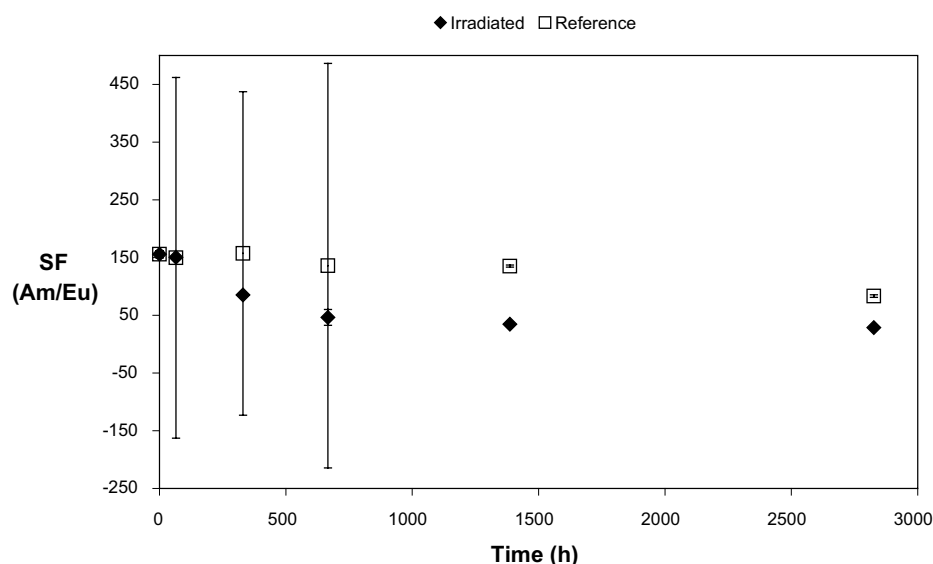


**Figure 1-27.** Log D for the reference and irradiated solutions containing C5-BTBP in cyclohexanone at various times. At the last sampling point, only the irradiated solution was measured.

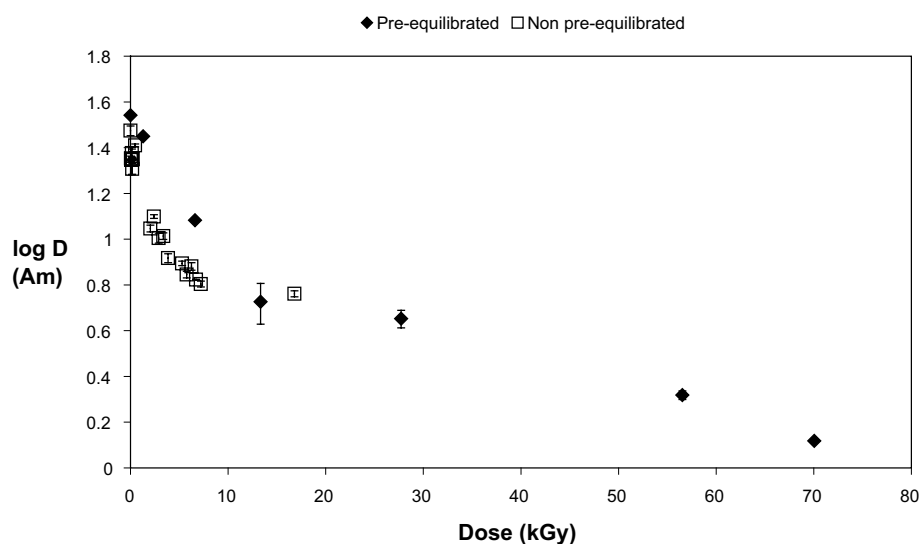
### Comparison with study without pre-equilibration

The results of the experiments with cyclohexanone were compared to the similar study by Nilsson et al. [7]. In this latest study both the organic and the aqueous phases were pre-equilibrated just before contact while in the old study no pre-equilibration was performed. Another difference is the irradiation and ageing time, with the latest study covering a longer time period than the old study. All other experimental conditions are the same. When comparing the results for the irradiated solution, it seems to be no apparent difference in extraction capacity between a pre-equilibrated and a non pre-equilibrated cyclohexanone solution. At least not up to a received dose of 17 kGy, this is where the old study ended. Both systems are losing their capacity to extract Am with increased received dose, see Figure 1-29, and the same behaviour is valid for the extraction of Eu.

In the earlier study no degradation of the reference solution was reported and when comparing the extracting capacity for the two reference solution it can be seen that the experimental data is concordant in the beginning of the experiments, see Figure 1-30. The degradation of the reference solution reported in this study is visible after a longer period of time, above all at the last sampling point, ~ 2,800 hours.



**Figure 1-28.** *SF (Am/Eu) for the irradiated and reference solutions containing C5-BTBP in cyclohexanone. The high uncertainties for some of the reference samples are due to single samples.*

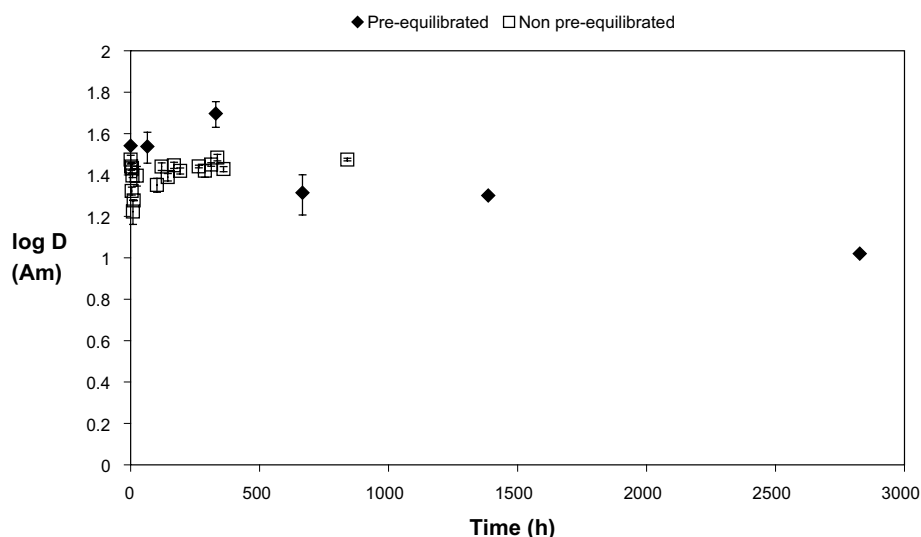


**Figure 1-29.** *Change in log D (Am) with received dose for two different systems: one system with pre-equilibration of both phases before contact and one with no pre-equilibration.*

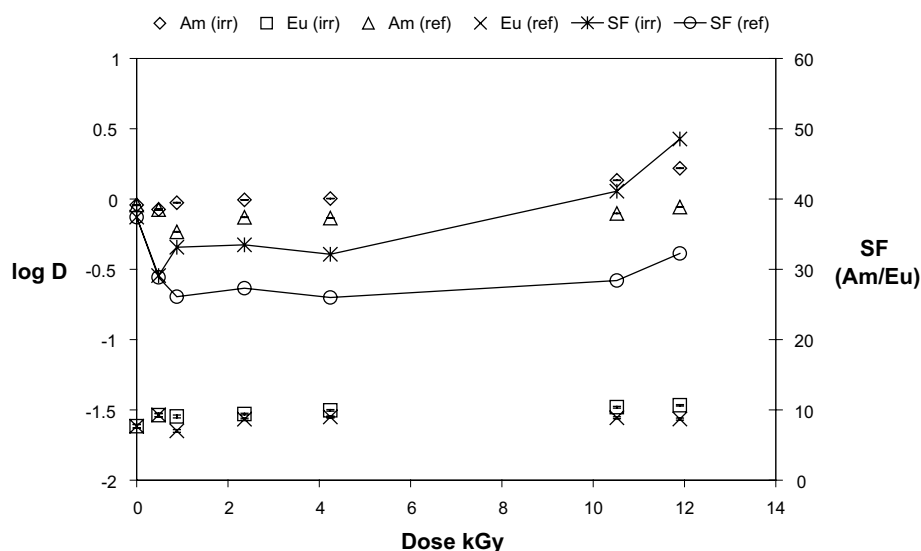
### CyMe<sub>4</sub>-BTBP

A radiolysis test was performed with an organic system containing 0.005 M CyMe<sub>4</sub>-BTBP dissolved in hexanol. The solution was placed in two 25 mL flasks and double samples were taken from the reference solution and triple samples were taken from the irradiated solution over a total period of time of 595 hours, corresponding to a total dose of 12 kGy. A slight fading of the yellow colour in the irradiated samples was observed. The aqueous phase consisted of 1 M HNO<sub>3</sub> spiked with radionuclides.

As can be seen in Figure 1-31, the extraction of Eu seems to be the same for both irradiated and reference solutions even after 12 kGy, while the extraction of Am begin to slowly increase after just a low dose (less than 2 kGy).



**Figure 1-30.** Change in  $\log D$  (Am) over time for two reference solutions. One includes pre-equilibration of both phases before contact while the other is not pre-equilibrated.



**Figure 1-31.** Extraction and separation of Am and Eu with a varying received dose when hexanol is used as diluent for  $CyMe_4$ -BTBP.

### MF1-BTBP

Radiolysis experiments of 0.005 M MF1-BTBP dissolved in cyclohexanone were done. After 4 kGy, samples were taken but no extraction experiments were carried out due to the fact that about half of the organic phase dissolved into the aqueous phase when pre-equilibration was attempted. This has not been observed before. Radiolysis experiments with other ligands dissolved in cyclohexanone have been performed before, but this kind of behaviour was not reported. Further irradiation experiments are planned, possibly with a different diluent (e.g. octanol).

### MF2-BTBP

The radiolysis of 0.01 M MF2-BTBP in two diluents, cyclohexanone and octanol, was investigated. Triplicate samples were taken from the irradiated solutions and triplicate or duplicate samples were taken from the reference. The cyclohexanone solutions were pre-equilibrated with 1 M  $HNO_3$ , which was the base for the aqueous solution. 1 M  $HNO_3$  was pre-equilibrated

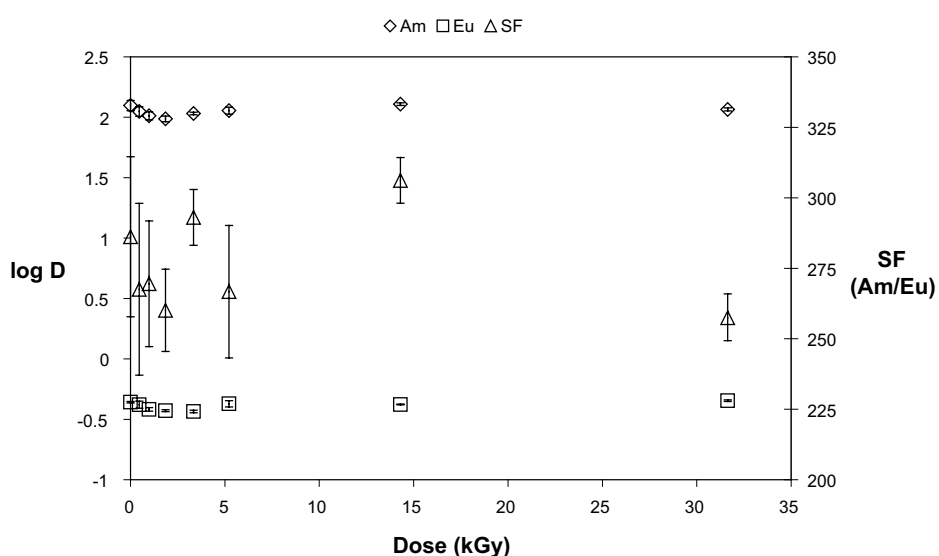
with pure unirradiated cyclohexanone. This is important to notice, since the cyclohexanone in the samples may have degraded and does not possess the same properties as pure, fresh cyclohexanone. An option could be to pre-equilibrate the acid with the irradiated solution and the reference solution respectively, but then the ligand will be present.

### Results cyclohexanone

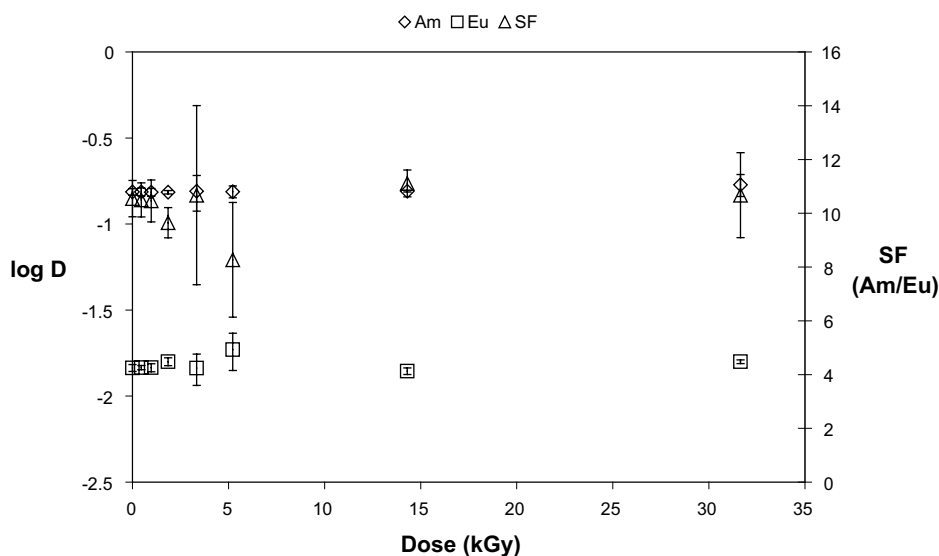
After a dose of 31.6 kGy (1,582 h) no effect of irradiation on extraction of Am and Eu was observed, see Figure 1-32. Nor the reference sample showed any change in distribution ratios.

### Results octanol

After a dose of 31.6 kGy (1,582 h) no effect of irradiation on extraction of Am and Eu was observed, see Figure 1-33. Nor the reference sample showed any significant change in distribution ratios.



**Figure 1-32.** Extraction and separation of Am and Eu with a varying received dose when cyclohexanone is used as diluent for MF2-BTBP.



**Figure 1-33.** Extraction and separation of Am and Eu with a varying received dose when octanol is used as diluent for MF2-BTBP.

## 2 BTP chemistry

One precursor to the BTBP family was the BTP family, also showing high D's for actinides. The idea of using them in a separation process was abandoned due to their too strong complex formation with actinides (problems with stripping) and their sensitivity towards radiolysis. The use of a BTP molecule in the following study was based on a previous study, and the wish to make reliable comparisons.

### 2.1 Radiolysis

#### C2-BTP

It has previously been shown that an addition of nitrobenzene to an organic phase containing 0.0018 M 2,6-di(5,6-diethyl-1,2,4-triazin-3-yl)pyridine (C2-BTP), see Figure 2-1a, in hexanol can inhibit the degradation of the BTP molecule /2/. The reason for this protection has been assigned the ability of nitrobenzene to remove solvated electrons and  $\alpha$ -hydroxy alkyl radicals, both products from radiolysis of alcohols. A similar experiment was performed with varying addition of cinnamaldehyde (see Figure 2-1b) to the organic phase. Similar to nitrobenzene, cinnamaldehyde contains an aromatic ring that generally has a relatively high resistance towards radiolysis.

C2-BTP was dissolved in pure hexanol, pure cinnamaldehyde and in hexanol with an addition of 1, 5, 10, and 20 vol % cinnamaldehyde. The solutions were placed in a  $^{60}\text{Co}$ -source (Gamma cell 220 from Atomic Energy of Canada Ltd.) with an estimated dose rate to water of  $\sim 20$  Gy/h. Solutions with the same composition were placed outside the gamma source to act as a reference and investigate the ageing of the molecule in the different solution compositions. Samples were taken from each flask at the start of the experiment and then at different times over a total time period of 1,250 hours. This corresponds to a total received dose for the irradiated samples of 25 kGy. The samples were contacted with an aqueous phase containing 0.99 M  $\text{NaClO}_4$ , 0.01 M  $\text{HClO}_4$  and trace amounts of  $^{241}\text{Am}$ . After vigorously shaking for 5 minutes the phases were separated by centrifugation for 15 minutes at 800 g. Aliquots from both phases were taken and measured in a  $\text{NaI}(\text{Tl})$  well type scintillation detector. Triple samples were taken from the irradiated solutions while double samples were taken from the reference solutions.

#### Ageing

The results from the experiment show that cinnamaldehyde is not stable over time and the D of Am starts to decrease instantly. The organic system with pure hexanol as diluent is also affected over time, which was not expected with regard to the similar experiment carried out with an addition of nitrobenzene /2/. Figure 2-2 illustrates the degradation of the reference samples. As can be seen, an addition of cinnamaldehyde increases the rate of degradation compared to the pure hexanol solution.

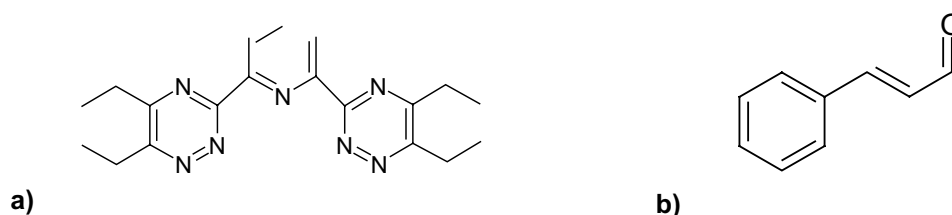


Figure 2-1. Schematic picture of C2-BTP(a) and cinnamaldehyde(b).



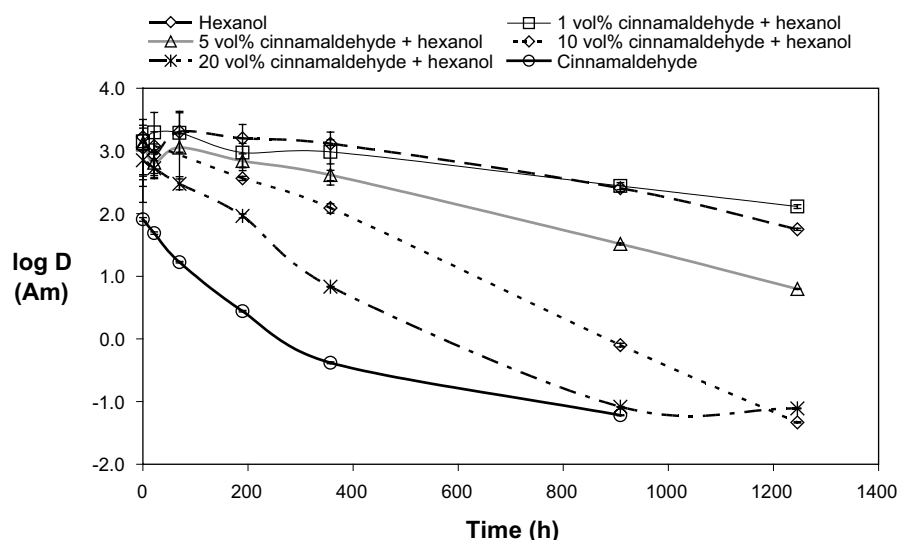


Figure 2-2. Change in log D for the reference samples left outside the irradiating source.

### Degradation due to irradiation

Due to the simultaneous ageing, the analysis of the radiolytic degradation is complicated. The system containing degradation products due to ageing may be more or less stable towards radiolysis compared to the original system. All solutions in the study show a dramatically decreased D after 25 kGy, either due to ageing or radiolytic degradation. The changes in D for the irradiated samples are presented in Figure 2-3.

As the dose became higher the colour of the irradiated solutions changed. The yellow colour given to the solutions by C2-BTP faded more and more for each sampling. The solution with cinnamaldehyde as diluent did not seem to lose colour to the same extent as the other samples. Cinnamaldehyde is itself light yellow; thus it was important not to compare the irradiated samples with each other but to compare them with the reference samples. Figure 2-4 shows one vial with reference solution and one with irradiated solution, illustrating the change in colour with increased dose.

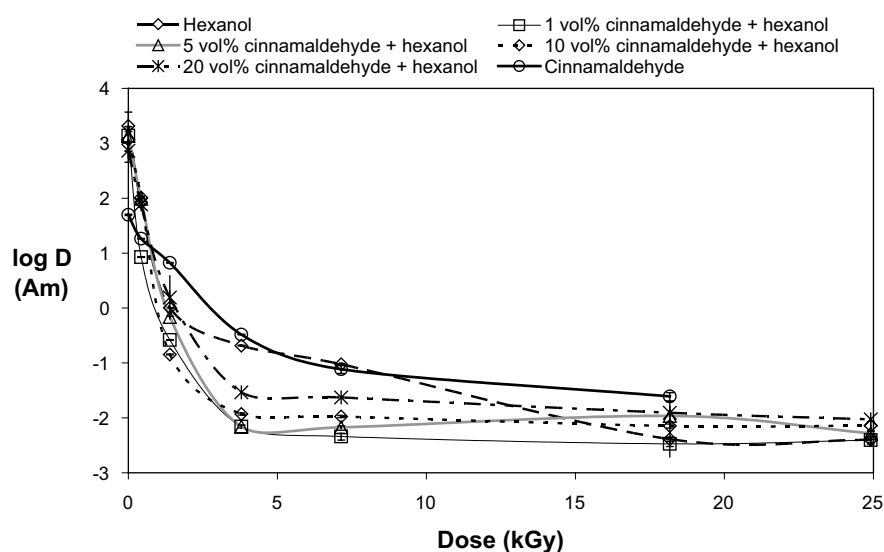
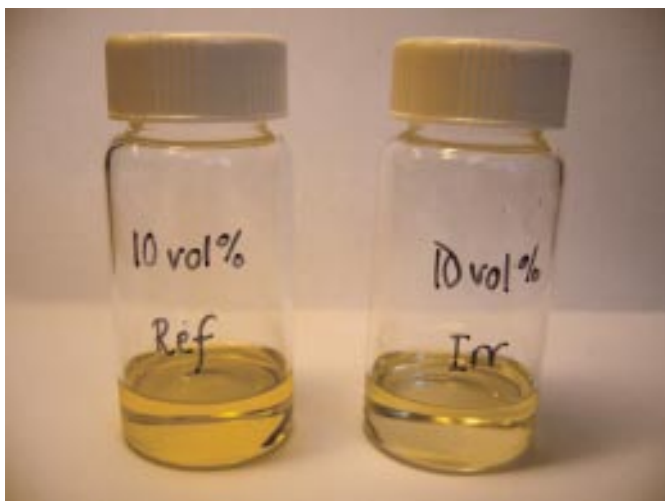


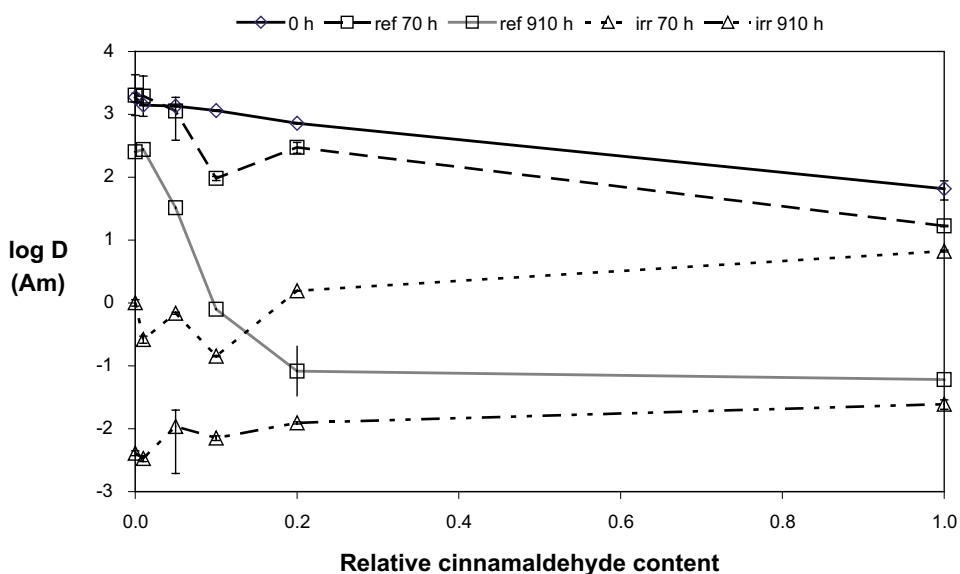
Figure 2-3. Change in log D for the irradiated samples. The solution containing C2-BTP in pure cinnamaldehyde was removed from the irradiating source after a total dose of 18 kGy due to the formation of crystals in the flask.



**Figure 2-4.** C2-BTP in 10 vol% cinnamaldehyde + hexanol after ~ 900 hours. Reference solution to the left and irradiated solution to the right.

Figure 2-5 illustrates how the log D for irradiated and reference solutions at various times depend on the cinnamaldehyde content. The irradiated samples with pure hexanol as diluent (left hand axis) show much lower D's than corresponding reference values at all times, indicating that the hexanol system is highly affected by irradiation. The more cinnamaldehyde that is added, the smaller is the difference between reference and irradiated sample and for pure cinnamaldehyde as diluent (right hand axis) it is clear that most of the decrease in D is due to ageing. Thus an addition of cinnamaldehyde inhibits the effect of irradiation to a certain extent, but compared to the study with nitrobenzene as additive /2/ a much larger volume of cinnamaldehyde is required to inhibit the radiolysis to the same extent as the nitrobenzene did. When taking both ageing and radiolysis into account, none of the solutions is able to inhibit the degradation of the molecule.

After a dose of 18 kGy the solution containing C2-BTP in cinnamaldehyde was removed from the irradiating source due to crystal formation (probably an insoluble acid). The same type of formation could be seen in the reference sample but to a lesser extent. None of the other solutions showed any sign of crystal formation. The crystals have not yet been analyzed.



**Figure 2-5.** Log D at different times for reference and irradiated solutions of hexanol with different cinnamaldehyde contents, ranging from zero (pure hexanol) to one (pure cinnamaldehyde).

### 3 Calixarenes

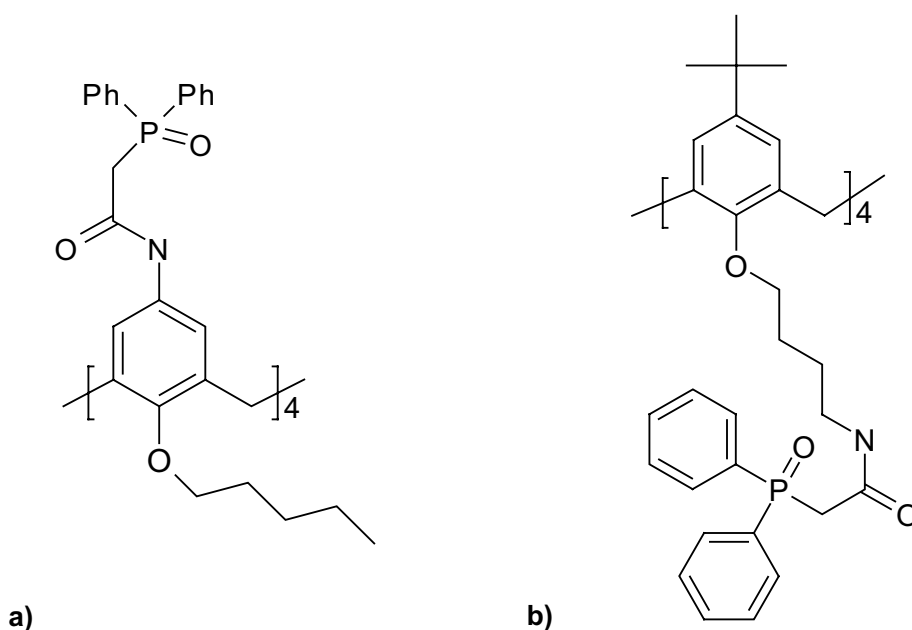
Calixarenes are a type of molecules primarily designed for separating cesium from high-level waste, but the possibility to use them for other types of separation has also been investigated.

In the last annual report an initial extraction experiment and a radiolysis experiment were reported for two calixarenes; wide rim tetra-CMPO calix[4]arene (JMA4) and narrow rim tetra-CMPO calix[4]arene (JMB3) /8/. Further extraction experiments have been performed with both of them. The ligands were synthesised by the Johannes Gutenberg Universität, Mainz, and the structures are presented in Figure 3-1.

#### 3.1 Wide rim tetra-CMPO calix[4]arene

We have received a number of batches of the wide rim tetra-CMPO calix[4]arene and in this report the code name JMA4 refers to the molecule, irrespective of which batch it originates from.

After analyzing all results it was seen that the extraction capacity of the calixarene varied a lot for the different experiments. Some of them were made with different batches and at different times. The investigations of  $[H^+]$  and  $[NO_3^-]$  dependence were performed several weeks after the ligand and  $HNO_3$  concentration dependence experiments and they both show much lower D. This was investigated further by looking at earlier experiments made with the same batches and also completed with new comparisons of the different batches. The most recently received batch had not been used before and was now compared with small remains of the two batches used for the experiments. Since only small amounts of the two old batches were available, double samples using a low concentration, 0.006 M, were made. The results showed that the oldest batch gave the poorest extraction, while the newest batch, so far not used in any other experiments, gave the highest value, indicating a degradation of the molecule. This theory was confirmed by going through and evaluating old experiments made with the two old batches and comparing these values with the more recent ones. It was also noted that the solution containing



**Figure 3-1.** Chemical structure of wide rim tetra-CMPO calix[4]arene (a) and narrow rim tetra-CMPO calix[4]arene (b).

the most recent received batch had a much darker color than the other two. This is the batch used for the experiments with fission and corrosion products. Taking all old results into account, the SF between Am and Eu does not seem to be affected with time.

*Due to these uncertainties the results presented in the following sections cannot be seen as absolute values, if anything just to show relations and trends.*

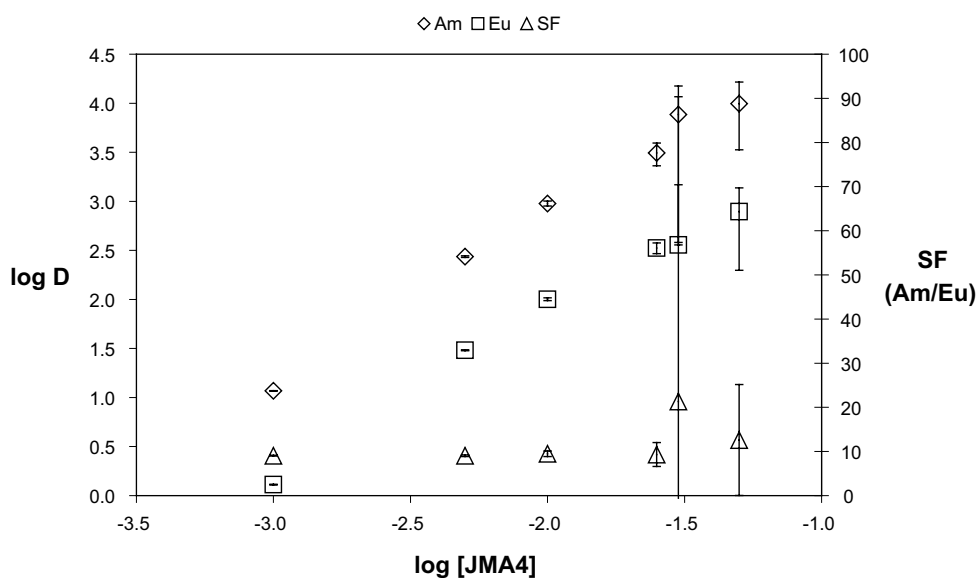
During all experiments 500  $\mu\text{L}$  of organic phase was contacted with 500  $\mu\text{L}$  aqueous phase and 10  $\mu\text{L}$  spike solution containing  $^{152}\text{Eu}$ ,  $^{241}\text{Am}$  and  $^{244}\text{Cm}$ . The contact time was 5 minutes and the shaking was made by hand. After centrifuging for 10 minutes at 800 g, 200  $\mu\text{L}$  aliquots were taken from each phase and analyzed with a HPGc detector (EG&G Ortec). For the ligand concentration experiments, the samples were also analyzed with  $\alpha$ -spectroscopy (EG&G Ortec). The organic diluent used in all experiments was tetrachloroethane.

### Influence of ligand concentration on the extraction

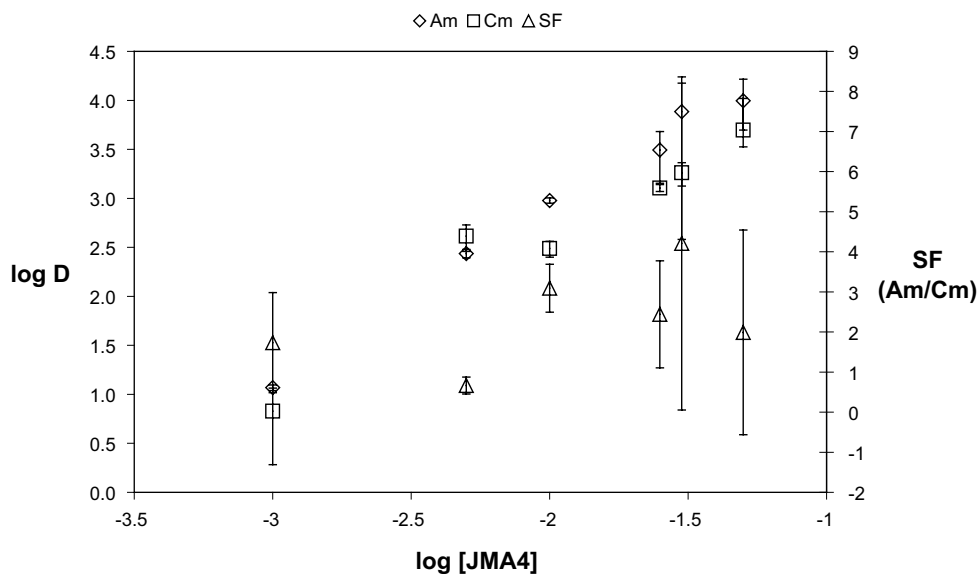
A short test of the  $\text{HNO}_3$  concentration dependence was made in order to establish a suitable  $\text{HNO}_3$  concentration for the aqueous phase in the ligand concentration dependence experiment. The concentration chosen was 2 M, since this showed high extraction and a high SF between Am and Eu. The ligand concentration was varied between 0.001 M and 0.05 M and the results are shown in Figure 3-2.

The extraction of both Am and Eu was increasing with increasing ligand concentration; with  $\log D$  vs  $\log [\text{JMA4}]$  slopes of 1.75 and 1.62, respectively, but the SF between the two remained at a constant level. It was decided not to increase the ligand concentration even further, even though a maximum in extraction had not been reached yet. For the further experiments a ligand concentration of 0.03 M was used, since the extraction at this concentration was high, almost as high as for 0.05 M.

In Figure 3-3, the extraction of Am and Cm are illustrated. The Cm data originates from  $\alpha$ -spectroscopy while the Am data comes from HPGc measurements, since the  $\alpha$ -spectroscopy could not provide reliable Am data points. The extraction of Am was generally a bit higher than the extraction of Cm and Am also showed a steeper slope, approximately 1.75 ( $R^2 = 0.989$ ) compared to approximately 1.55 ( $R^2 = 0.938$ ) for Cm. The SF (Am/Cm) varied a bit but seemed to be around 3. It should be noted that in these experiments, the activity of Am was at least twice as high as the activity of Cm.



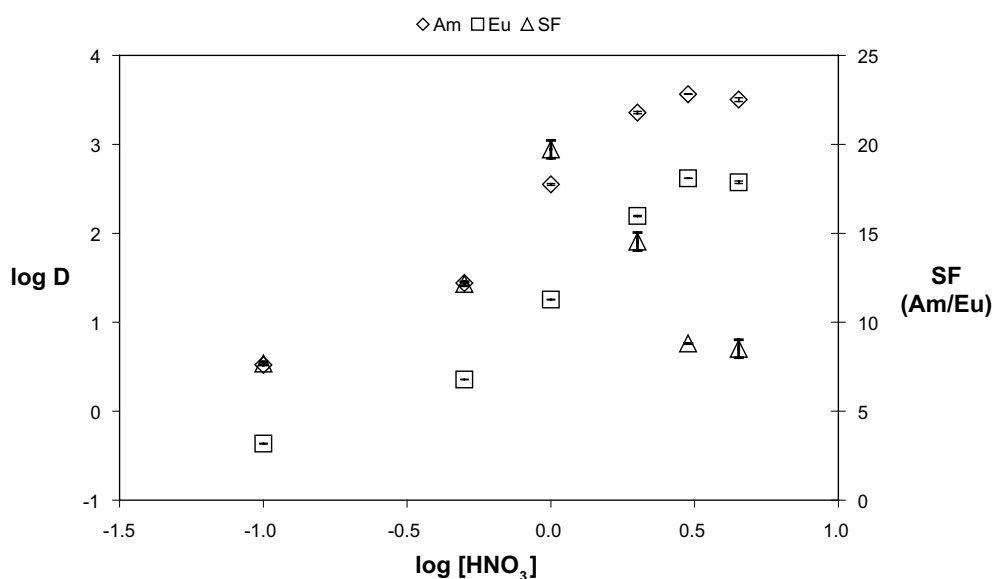
**Figure 3-2.** Extraction results (Am and Eu) using different concentrations of the ligand (JMA4) in tetrachloroethane.



**Figure 3-3.** Extraction results (Am and Cm) using different concentrations of the ligand (JMA4) in tetrachloroethane.

### Influence of HNO<sub>3</sub> concentration

To determine the dependence of nitric acid concentration, the aqueous phase was varied from 0.1 M to 4.5 M HNO<sub>3</sub>. The organic phase contained 0.03 M JMA4, established as suitable concentration in the previous experiment. The results show (Figure 3-4) that there is a maximum in SF (Am/Eu) at a nitric acid concentration of 1 M, but the extraction of both Am and Eu was continuing to increase a bit more after that. Where the Am and Eu curves are straight, for the four middle concentrations, the slopes are approximately 3, indicating that three anions are involved in the extracted complex. The extraction seemed to reach a maximum value, or at least a plateau, at around 3 M but at this point the SF has halved compared to the highest value. For the following experiments an HNO<sub>3</sub> concentration of 2 M is used. This concentration gave an extraction almost as high as the assumed maxima, and the SF is still rather high.



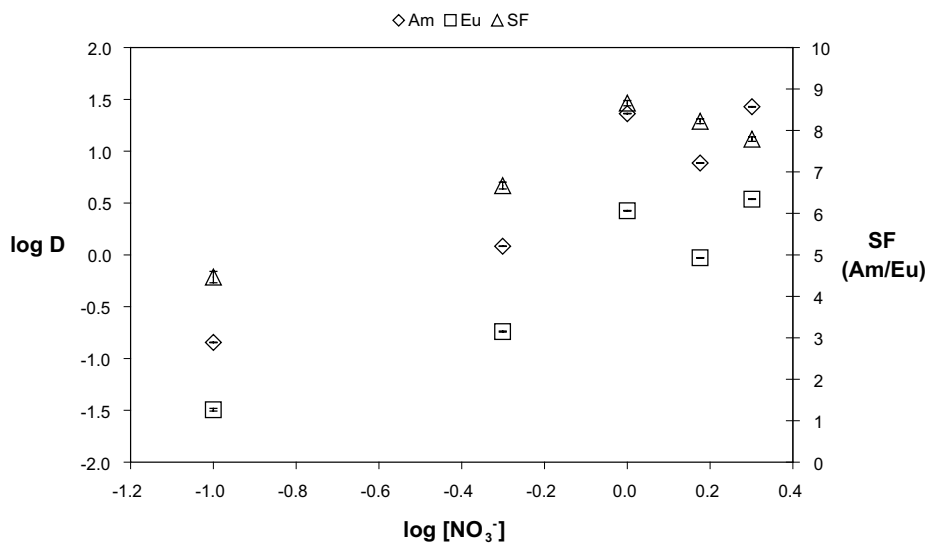
**Figure 3-4.** Extraction results (Am and Eu) from experiments using different concentrations of HNO<sub>3</sub> in the aqueous phase. The ionic strength was kept constant.

### Influence of ionic media

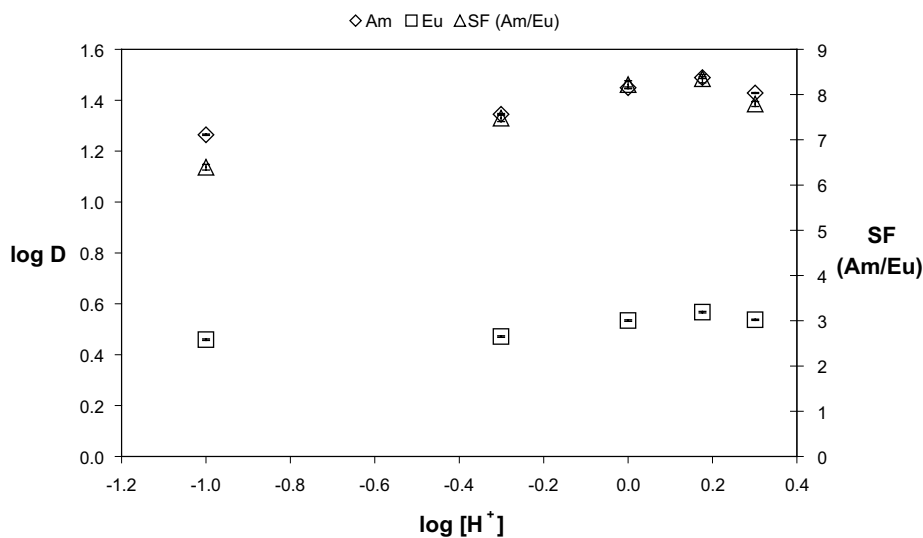
Experiments were performed to study the influence of nitrate concentration on the extraction. The concentration of  $\text{NO}_3^-$  was varied between 0.1 and 2 M while the hydrogen ion concentration was kept constant at 2 M. To keep the total anion concentration constant chloride ions were also used as counter ion and added so that  $[\text{NO}_3^-] + [\text{Cl}^-] = 2 \text{ M}$ . The experiments showed that the SF increases up to 1 M and thereafter it is almost constant, decreasing a bit as the  $\text{NO}_3^-$  concentration increases, see Figure 3-5. The slope of the straight part of the extraction curve (three lowest  $[\text{NO}_3^-]$ ) is 2 for Am and 1.8 for Eu. This suggests that two nitrate ions bind to each metal complex.

### Influence of $\text{H}^+$ concentration

In order to establish the hydrogen ion dependence, this was varied between 0.1 and 2 M. The  $\text{NO}_3^-$  concentration was kept constant at 2 M, hence  $\text{NaNO}_3$  was added to reach this concentration. According to the results presented in Figure 3-6 there seem to be little influence of the  $\text{H}^+$  concentration.



**Figure 3-5.** Extraction results (Am and Eu) from experiments using different concentrations of  $\text{NO}_3^-$  but keeping the hydrogen ion concentration and total anion concentration constant.



**Figure 3-6.** Extraction results (Am and Eu) from experiments using different  $\text{H}^+$  concentrations. The concentration of nitrate was kept constant and Na was used as counter ion to keep the total cation concentration constant.

### Extraction of fission products

The extraction property of JMA4 towards a number of fission products was investigated. For this experiment the most recently received batch of calixarene was used. Two solutions containing  $10^{-6}$  M of each of the following elements in 1 M HNO<sub>3</sub> were used:

Solution 1: Se, Sr, Zr, Ru, Ag, In, Sb, La, Pr, Sm and Gd.

Solution 2: Rb, Y, Rh, Pd, Cd, Te, Ce, Nd and Eu.

800  $\mu$ L of organic phase was contacted with 800  $\mu$ L aqueous phase during 5 minutes, vigorously shaken by hand. After allowing the phases to separate gravimetrically a 100  $\mu$ L sample was taken from the aqueous phase, diluted with 6 mL ultrapure HNO<sub>3</sub> and analyzed using ICP-OES (Optima 3000). Samples were also taken from the aqueous phase before contact and the difference in metal content before and after was assigned the organic phase after contact. The distribution ratios for the different elements are presented in Table 3-1 to 3-3. Some elements are not presented in the tables since the measured values were below the detection limit.

There is a large difference in extraction of the different elements. Zirconium shows the highest D, 147, while some elements e.g. cadmium and praseodymium hardly are extracted at all ( $D \sim 0.1$ ).

### 3.2 Narrow rim tetra-CMPO calix[4]arene + COSAN

The extracting properties of a mixture of COSAN and narrow rim tetra-CMPO calix[4]arene and similar mixtures of chloroprotected COSAN and the calixarene were studied. The narrow rim tetra-CMPO derivative will in the following section be called RV142, referring to the name of the specific batch used. Both the COSAN ( $[(C_2B_9H_{11})_2Co]Cs$ ) and the chloroprotected COSAN ( $[(C_2B_9H_8Cl_3)_2Co]Cs$ ) were received from Katchem spol S.r.o., Czech Republic.

The molecules were dissolved in nitrobenzene and the aqueous phase used contained 4.5 M HNO<sub>3</sub> with traces of <sup>232</sup>Th, <sup>237</sup>Np, <sup>238</sup>U and <sup>241</sup>Am. Hence four oxidation states were represented: III (Am), IV (Th), V (Np) and VI (U). Different concentrations of the calixarene were investigated; 0.0001, 0.0005, 0.001 and 0.002 M and for each concentration the calixarene: COSAN ratio was varied between 1:1, 1:2 and 1:3. The reason for the rather low concentration of RV142 is the difficulty in dissolving higher concentrations of both calixarene and COSAN in the same solution. The same concentrations and ratios were used for the parallel experiments with chloroprotected COSAN.

**Table 3-1. D of the light lanthanides using 0.03 M JMA4 in tetrachloroethane.**

Ce	Pr	Nd	Eu	Gd
12	0.1	0.8	6.9	36

**Table 3-2. D of various fission products using 0.03 M JMA4 in tetrachloroethane.**

Se	Y	Zr	Ru	Rh
12	5.6	147	0.4	0.5

**Table 3-3. D of various fission products using 0.03 M JMA4 in tetrachloroethane.**

Pd	Ag	Cd	In	Sb
25	8.9	0.1	2.4	5.8

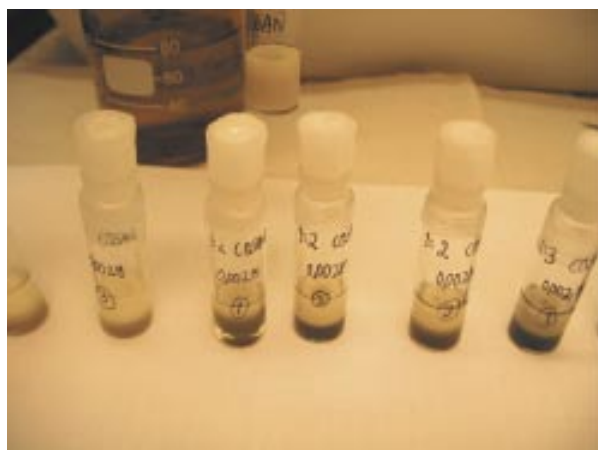
The distributions of Th, Np and U were measured using ICP-MS (Elan 6100 DRC, Perkin Elmer Sciex) while a NaI(Tl) scintillation well detector (Intertechnique GC-4000) was used for measuring Am. The interference of Np on the Am measurements could be controlled since the Am activity in the aqueous phase is about 1,000 times higher than the Np activity. Samples of aqueous phase without Am were measured both with the NaI(Tl) detector and with ICP-MS to establish the Np contribution of counts to the Am energy window in the scintillation detector. The number of counts was negligible. For both detection methods, a sample of 150  $\mu$ L was measured.

The first shake was made with the highest concentration of RV142 since the following concentrations were diluted from this one. All experiments were performed at room temperature without any additional heating due to hand contact. After less than two minutes of contact the samples changed colour and it looked like an emulsion forming. For the samples containing COSAN, the colour changed from orange to grey or dark greenish. The natural separation (without centrifuge) was extremely slow. An additional shaking was made with pure aqueous phase, without the metals present, and the same thing occurred. Possibly, some kind of reaction takes place between the COSAN and the nitric acid. Figure 3-7 shows a COSAN sample shaken without metals (in the top of the picture) and a number of samples including metals. The sample without metal is less separated since it was shaken after the others. The colour change and the emulsion-like formation indicate that some kind of reaction occurs between COSAN and nitric acid even without metals present. There is a slight difference in the shades of grey between the samples with different ratios but this difference decreased with time and was after centrifugation almost negligible.

As can be seen in Figure 3-8 the difference in colour between samples with COSAN and samples with chloroprotected COSAN was large. The picture shows one sample containing COSAN (left) and a corresponding sample containing chloroprotected COSAN (right). The samples with chloroprotected COSAN also seemed to form an emulsion but there were almost no change in colour. The phases also separated faster than the COSAN samples when left standing. But there still seems to be some kind of reaction with the nitric acid.

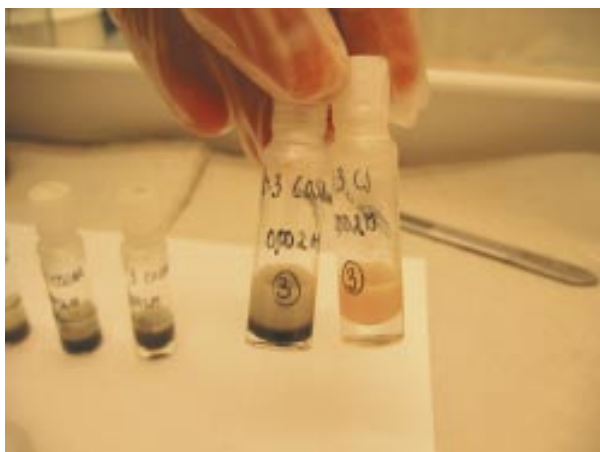
After centrifugation the phases had separated for all samples and the colour had somewhat changed. Figure 3-9 shows the samples containing RV142 and COSAN in ratio 1:3 and 1:2 after centrifugation. No precipitation or emulsion could be seen.

The samples with lower concentration of calixarene and COSAN's also show the same tendency during contact, but the change in colour decreases with decreasing concentration. Figure 3-10 shows one sample containing 0.001 M RV142 and COSAN and one sample containing 0.001 M RV142 and chloroprotected COSAN just after shaking.



**Figure 3-7.** COSAN sample shaken without metals (top of the picture) compared with samples shaken with metals present in the aqueous phase (bottom row).

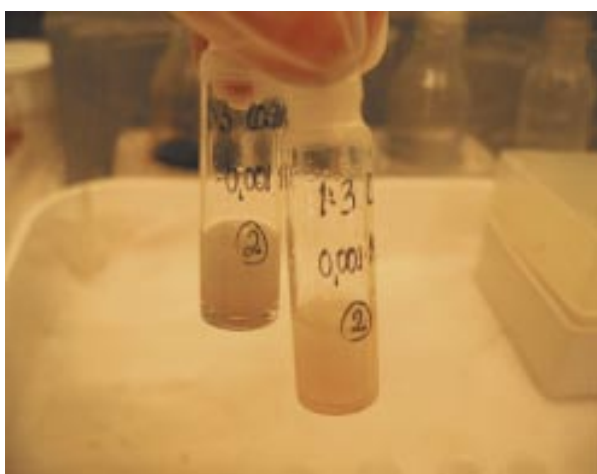




**Figure 3-8.** Sample with COSAN (left) and chloroprotected COSAN (right).



**Figure 3-9.** Samples containing different ratios of calixarene and COSAN. Ratio 1:3 to the left and ratio 1:2 to the right.

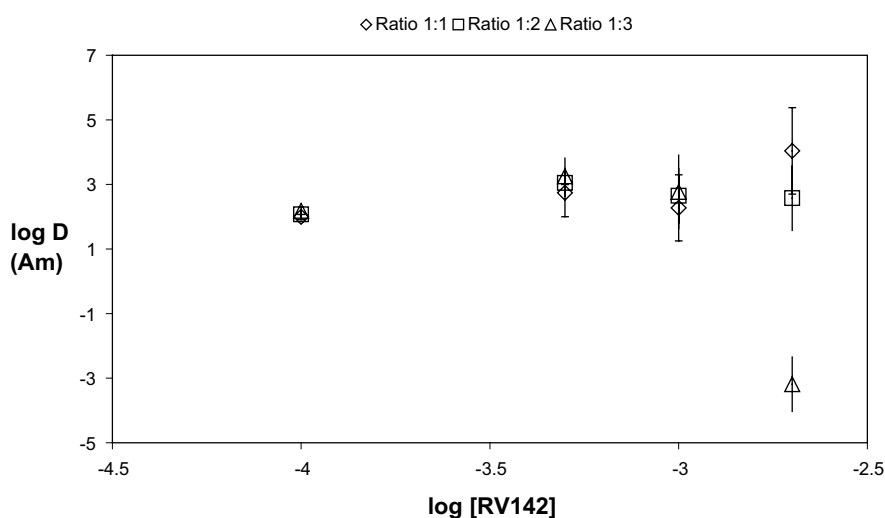


**Figure 3-10.** Samples just after shaking, containing calixarene and COSAN (left) and calixarene and chloroprotected COSAN (right) at low calixarene concentration.

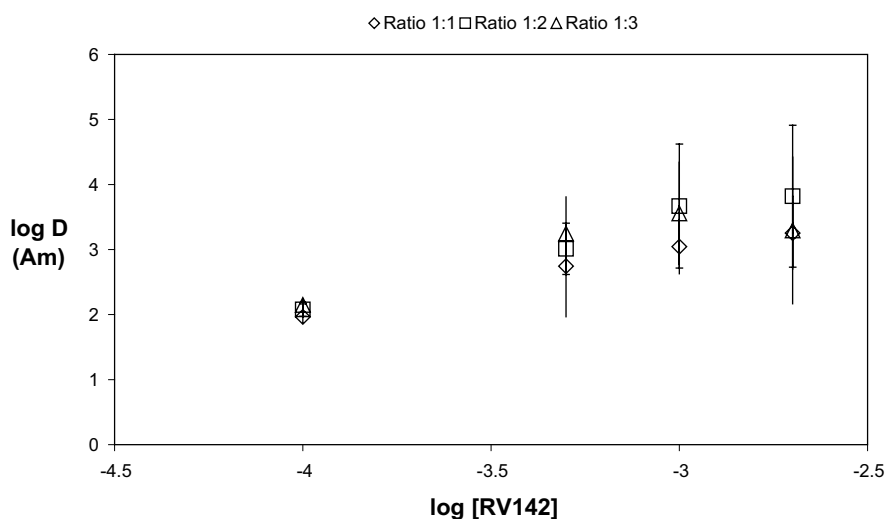
The data from ICP-MS measurements has very large uncertainties since so much is extracting that the content in the aqueous phase after contact is close to the background values and hence close to the detection limit. In this study  $D$  up to  $\sim 100$  can be considered trustworthy while higher  $D$  can only be used for comparisons and trends. Also the results from the  $\text{NaI(Tl)}$  measurements show quite high uncertainties.

As can be seen in Figure 3-11 there is a difference in extraction behaviour towards americium between the COSAN and chloroprotected COSAN system only at the two highest concentrations. These are also the concentrations where the samples containing COSAN changed into a greenish colour during shaking. For the chloroprotected COSAN the  $D$  increases with increasing calixarene concentration. The COSAN shows the same tendency at lower concentrations but then the value of  $D$  decreases again, most likely due to the reaction with nitric acid that probably took place during shaking.

Figure 3-12 shows that the  $D$  of Am increases with increasing concentration of calixarene and at the lower concentrations also a bit with increasing ratio of calixarene:chloroprotected COSAN. At higher concentrations the 1:2 ratio shows the highest  $D$  but here the uncertainties are too high to draw any valid conclusions.



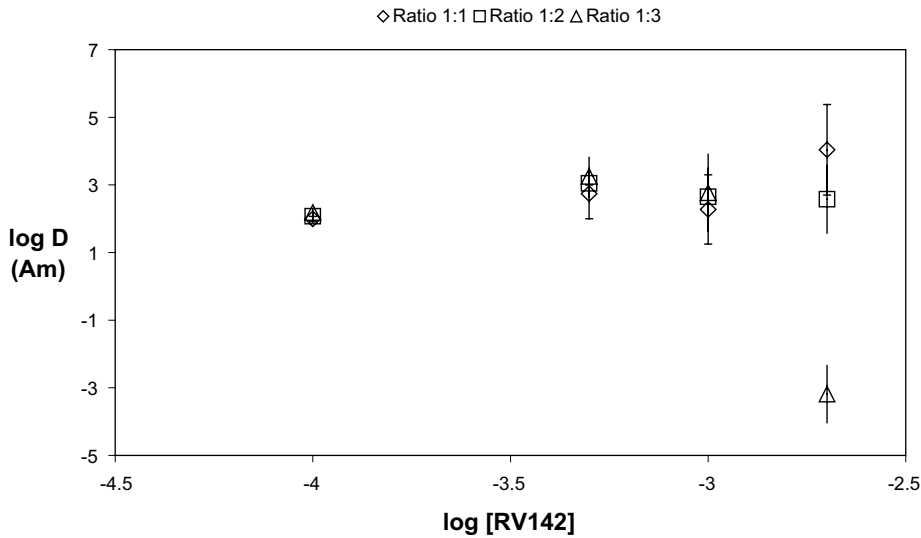
**Figure 3-11.** Log  $D$  for varying concentrations of calixarene + COSAN or chloroprotected COSAN in the ratio 1:2. (Data from  $\text{NaI(Tl)}$  measurements)



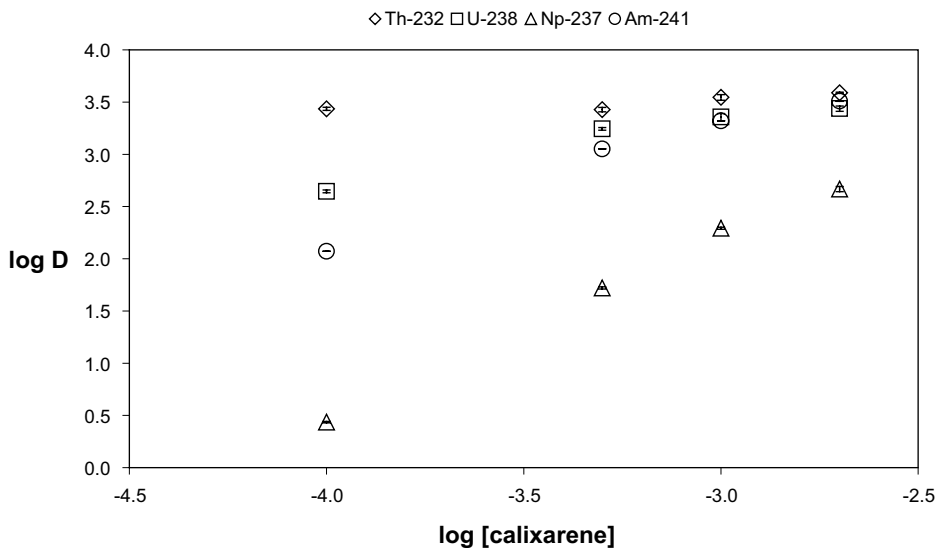
**Figure 3-12.** Extraction of Am with varying calixarene concentration and varying content of chloroprotected COSAN. (Data from  $\text{NaI(Tl)}$  measurements)

For the solutions containing pure COSAN the change in D with changing calixarene concentration shows the same trend as for the solutions containing chloroprotected COSAN, see Figure 3-13. But as mentioned before, for the solutions containing higher concentrations it was likely that a reaction with nitric acid took place during shaking and this may affect the results.

The values from ICP-MS measurements were among other things used to illustrate the selectivity of the system. As can be seen in Figure 3-14 neptunium is the least extracted metal and the metal extraction, particularly the extraction of Np, is rapidly increasing with increasing calixarene concentration. The figure shows the results of the experiments made with a 1:2 ratio between calixarene and COSAN, but the same pattern is valid for the other ratios as well.



**Figure 3-13.** Extraction of Am with varying calixarene concentration and varying content of COSAN. The reason for the obscure value at 0.002 M and ratio 1:3 is that the measured values for the organic phase were close to or below background values. (Data from NaI(Tl) measurements)



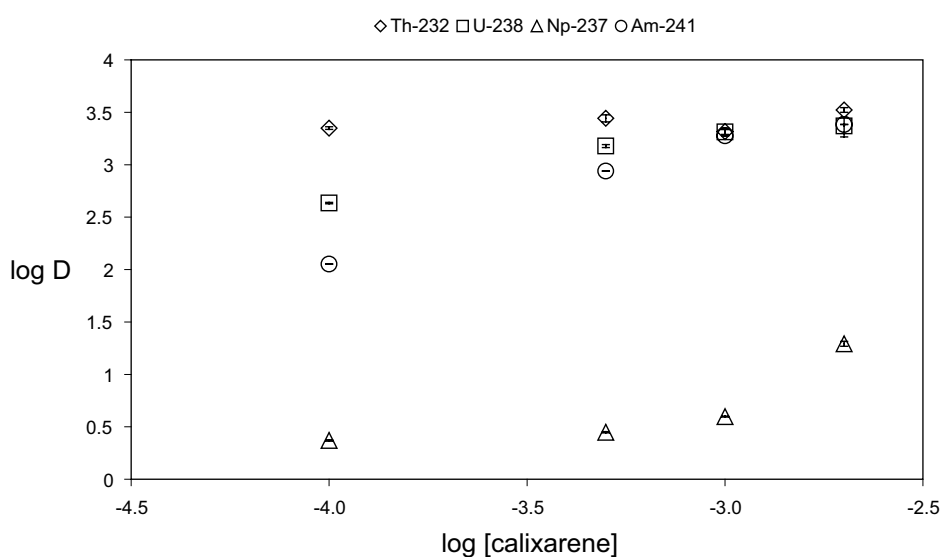
**Figure 3-14.** System with COSAN. Log D of the different metals present in the aqueous phase for varying concentration of calixarene are illustrated. The ratio of calixarene: COSAN is 1:2. (Data from ICP-MS measurements)

Figure 3-15 shows the concentration dependence of metal extraction for the system calixarene: chloroprotected COSAN in the ratio 1:2. When comparing this figure with the corresponding figure for the COSAN system (Figure 3-14) many similarities can be observed; the D's are approximately the same at the lower concentration, the extraction increases with increasing calixarene concentration and Th, U and Am have the same D at higher concentrations. The only difference is the behaviour of neptunium. The chloroprotected system reaches a log D of 1.3 to be compared with a value of 2.7 for the COSAN system. This is valid for all calixarene: chloroprotected COSAN ratios.

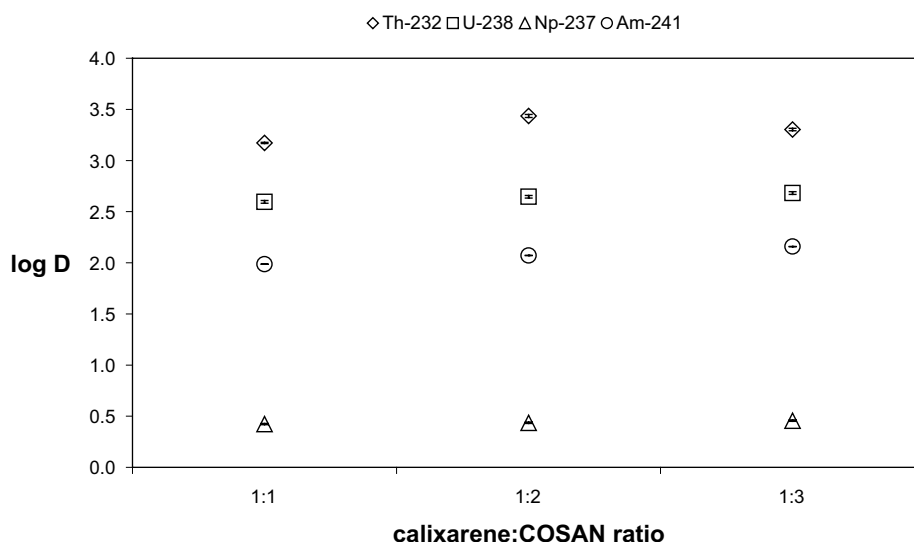
Both systems give a log-log slope value of 0.6 for U and 1.1 for Am, with good fittings ( $R^2$  between 0.945 and 0.974). The fitting for Th is poor for both systems, since the extraction of Th hardly changes with changing concentration. For Np, the chloroprotected COSAN systems shows a poor fitting while the COSAN system gives a slope of 1.75 with a very good fitting ( $R^2 = 0.995$ ).

Figure 3-16 shows the extraction of the different elements with varying calixarene: COSAN ratio. The calixarene concentration is 0.0001 M for all ratios and at that concentration a change in COSAN content seems to have little effect on the extraction. The log D's are relatively even spread between 0.5 up to 3.5, in the order Np, Am, U and Th in the top. But when the calixarene and hence the COSAN concentrations are increased the D's approach each other. Figure 3-17 illustrates the dependence of ratio for a higher calixarene concentration, 0.001 M. Neptunium is still poorest extracted but the other metals all show log D within a narrow span, approaching each other more as the calixarene: COSAN ratio is increased. So, at low calixarene concentrations the system is independent of the COSAN concentration, while at higher calixarene concentrations an addition of COSAN enhances the extraction. The system containing chloroprotected COSAN shows the same pattern.

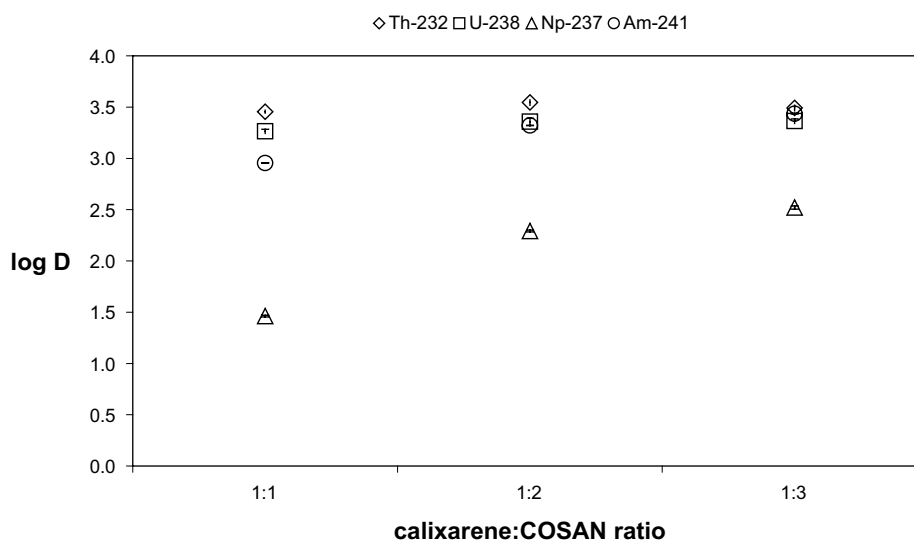
The only feature that clearly differs between the two systems is the extraction of neptunium. COSAN extracts neptunium to a higher extent than chloroprotected COSAN does, illustrated in Figure 3-18. The log D for the other three metals only differs with maximum  $\pm 0.2$  between the two systems. Figure 3-18 illustrates the comparison of the systems with a calixarene to COSAN/chloroprotected COSAN ratio of 1:2 but the other ratios shows the same trends. The slope of the curve has a value of 1.75 for the COSAN system (as mentioned previously) and at the higher concentrations, where the extraction starts to increase substantially for the chloroprotected system too, this system appears to have a similar value of the slope.



**Figure 3-15.** System with chloroprotected COSAN. Log D of the different metals present in the aqueous phase for varying concentration of calixarene are illustrated. The ratio of calixarene: chloroprotected COSAN is 1:2. (Data from ICP-MS measurements)



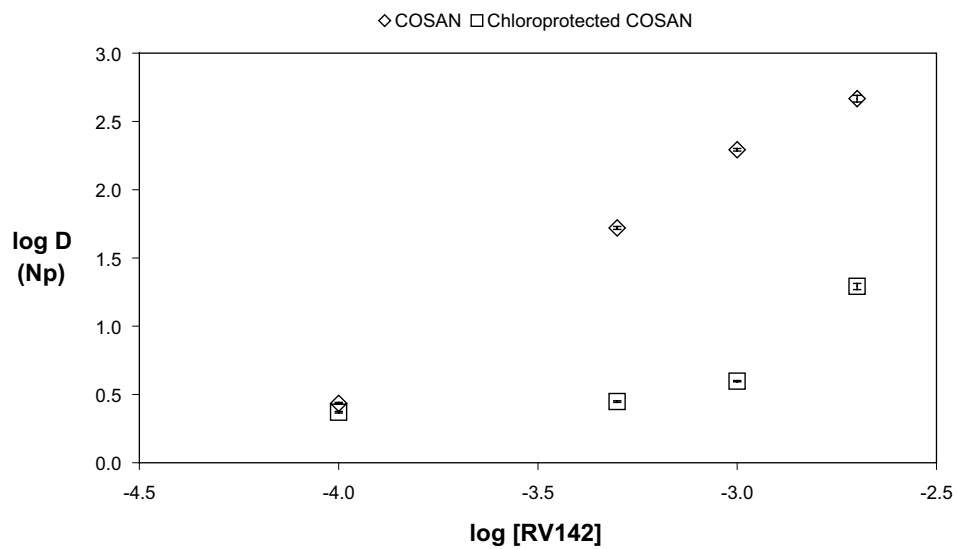
**Figure 3-16.** Extraction of Th, U, Np and Am for different ratios of calixarene: COSAN. The calixarene concentration is 0.0001 M in nitrobenzene. (Data from ICP-MS measurements)



**Figure 3-17.** Extraction of Th, U, Np and Am for different ratios of calixarene: COSAN. The calixarene concentration is 0.001 M in nitrobenzene. (Data from ICP-MS measurements)

The conclusion is that a system containing narrow rim tetra-CMPO calix[4]arene and COSAN or chloroprotected COSAN prefers the extraction of Am(III), Th(IV) and U(VI) over Np(V) as opposed to some of the systems in Section 1.2.1. In that study, the different BTBP's all prefer Np over Th and U. At lower calixarene concentrations the addition of more COSAN/chloroprotected COSAN barely affects the extraction but at higher concentrations a larger addition of COSAN/chloroprotected COSAN increases the extraction of all metals. It is a common behaviour of synergic systems to have a maximum extraction at a certain ratio between two substances /3/.

An important observation regarding the two systems is the reaction taking place between the two phases during time of contact. The reaction is most visible in the COSAN system and the indications of an undesired reaction decrease with decreasing calixarene concentration.



**Figure 3-18.** Extraction of  $N_p$  for systems containing COSAN or chloroprotected COSAN. The ratio between calixarene and COSAN/chloroprotected COSAN is kept at 1:2 while the concentration of calixarene is varied. (Data from ICP-MS measurements)

## Collaborations

The following laboratories are involved in EUROPART:

- Commissariat à l'énergie atomique (France)
- British Nuclear Fuels (United Kingdom)
- Chalmers University of Technology (Sweden)
- Centro de Investigaciones Energeticas MedioAmbientales y Tecnologicas (Spain)
- Czech Technical University in Prague (Czech Republic)
- Centre National de la Recherche Scientifique (France)
- Electricité de France (France)
- Ente per le Nuove Tecnologie, l'Energia, l'Ambiente (Italy)
- Forschungszentrum Jülich (Germany)
- Consejo Superior de Investigaciones Cientificas (Spain)
- Institute of Inorganic Chemistry, Academy of Sciences of the Czech Republic (Czech Republic)
- Forschungszentrum Karlsruhe (Germany)
- European Commission, Joint Research Centre, Institute of Transuranium Elements (Germany)
- Johannes Gutenberg-Universität (Germany)
- Katchem spol. S.r.o. (Czech Republic)
- Nuclear Research Institute Rez plc (Czech Republic)
- Politecnico di Milano (Italy)
- Universidad Autonoma de Madrid (Spain)
- Université de Liège (Belgium)
- Université Louis Pasteur I (France)
- Università degli studi de Parma (Italy)
- University of Reading (United Kingdom)
- University of Twente (The Netherlands)
- Instytut Chemii i Techniki Jądrowej (Poland)

A more intense collaboration with Chalmers exists with:

- Forschungszentrum Jülich, Germany
- University of Reading, UK
- Institut für Mikroelektronik Mainz, Germany
- Kernchemie, Johannes Gutenberg-Universität, Germany
- NEXIA, UK
- CEA, France
- National Institute of Cryogenics and Isotopic Separation, Romania

## International and national scientific exchange

January 2006, EUROPART 4th half year meeting in Aachen. C. Ekberg, A Fermvik, M. Nilsson and T. Retegan.

Every year a study tour for the students taking our basic Nuclear Chemistry course is arranged. This year they visited e.g. Helsinki, Lovisa, Ignalina and Warsaw. C. Ekberg and G. Skarnemark went along.

May 2006, poster exhibition of research projects at the Institution of Chemical and Biological Engineering at Chalmers University of Technology. A. Fermvik and T. Retegan.

June 2006, IYNC, International Youth Nuclear Congress in Stockholm and Olkiluoto. A. Fermvik and T. Retegan (chairmen and poster).

June 2006, EUROPART 5th half year meeting in Rome. C. Ekberg, A. Fermvik and T. Retegan.

July 2006, ACTINET Summer School, Saclay, France. Actinide behaviour in Natural Environment. A. Fermvik and T. Retegan.

Christian Ekberg was invited speaker and chairman at the 13th International Conference on Cryogenics and Isotopic Separation, Oct. 25–27 2006, Rm-Valcea, Romania. A. Fermvik and T. Retegan participated with a poster.

Nov–Dec 2006, MRS Fall Meeting, Boston MA, U.S. T. Retegan participated with a presentation and A. Fermvik with a poster.



## Articles and publications

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

### **Published**

M. Nilsson, S. Andersson, C. Ekberg, M. R. S. Foreman, M J. Hudson, G. Skarnemark, Inhibiting radiolysis of BTP molecules by addition of nitrobenzene, *Radiochimica Acta* 94(2), 103–106, 2006.

M. Nilsson, S. Andersson, C. Ekberg, J-O. Liljenzin, G. Skarnemark, Chemical properties of 2-bromodecanoic acid, *Solvent Extraction and Ion Exchange* 24(3), 407–418, 2006.

S. Andersson, H. Nitsche, R. Sudowe, Berkelium nitrate complex formation using a solvent extraction technique, *Radiochimica Acta* 94(1), 59–61, 2006.

M. Nilsson, C. Ekberg, M. Foreman, M. Hudson, J-O. Liljenzin, G. Modolo, G. Skarnemark, Separation of actinides(III) from lanthanides(III) in simulated nuclear waste streams using 6,6'-bis-(5,6-dipentyl[1,2,4]triazin-3-yl)[2,2']bipyridinyl (C5-BTBP) in cyclohexanone. *Solvent Extraction and Ion Exchange* 24(6), 823–843, 2006.

S. Andersson, K. Eberhardt, C. Ekberg, J.-O. Liljenzin, M. Nilsson, G. Skarnemark, Determination of stability constants of lanthanide nitrate complex formation using a solvent extraction technique. *Radiochimica Acta* 94(8), 469–474, 2006.

### **Submitted**

A. Fermvik, C. Ekberg, T. Retegan, G. Skarnemark Radiolysis and ageing of 2,6-di(5,6-diethyl-1,2,4-triazin-3-yl)pyridine in cinnamaldehyde/hexanol mixtures, submitted to MRS Fall Meeting Proceedings, 2006.

T. Retegan, A. Fermvik, C. Ekberg, G. Skarnemark, The effect of diluents on extraction of actinides and lanthanides, submitted to MRS Fall Meeting Proceedings, 2006.

### **Under preparation**

T. Retegan, A. Fermvik, C. Ekberg, D. Magnusson, G. Skarnemark, The behavior of organic systems containing C5-BTBP and CyMe<sub>4</sub>-BTBP at low irradiation doses, submitted to *Solvent Extraction and Ion Exchange*, 2006.

T. Retegan, I. Dubois, A. Fermvik, C. Ekberg, G. Skarnemark, Extraction of actinides with different 6,6'-bis-(5,6-R-1,2,4-triazin-3-yl)-2,2'-bipyridines (BTBPs), submitted to *Solvent Extraction and Ion Exchange*, 2006.

We have also written half-yearly reports to the EUROPART project.

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

## Future work

The future work will continue along the suggested path of the EUROPART project. However, as we are approaching the 7th framework programme the aim for building a process will become clearer.

- Partitioning of actinides (Am to Cf) from High Active Raffinates and High Active Concentrates issued from the reprocessing of UOX and MOX spent fuels using extracting agents belonging to the families of polyamides and polydentate bearing molecules and COSAN.
- 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.
- The effect of correlated data will be investigated further and included in a computer program for speciation calculations.
- Studies on the radiolytic and hydrolytic stability and investigations of the decay products and their effect.
- Investigation of the effect of the diluents on the extraction, stripping and selectivity.
- Hopefully we will be able to get a new irradiation source for basic stability testing of ligands.

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

Daniel Magnusson will continue his work on process development and verify the theoretical calculations with some experiments on real high active raffinate in Karlsruhe in Germany

Teodora Retegan will continue the existing work on basic chemical understanding of nitrogen donor ligands both for the DIAMEX and SANEX processes. The main focus will be on ligand-diluent interaction for understanding of the selectivity of the ligands.

Anna Fermvik, will study the effect of radiation on the extractant molecules used and what effect the products of radiolysis will have on the extraction.

Hopefully the participation within the 7th framework programme will be finalized during the year and we can then find a replacement for M. Nilsson, i.e. a new student.

We plan to increase the group with an organic chemist from Reading and thus start fabrication of ligand for the EU programme in Sweden. Thus we will have very short response times from synthesis and experiment.

We will probably also have some French diploma workers in our group. They will mainly work on EUROPART related screening investigation of new ligands.

## References

- /1/ **Andersson S, Ekberg C, Fermvik A, Hervieux N, Liljenzin J-O, Magnusson D, Meridiano Y, Nilsson M, Retegan T, Skarnemark G, 2005.** EUROpean research program for the PARTitioning of minor actinides from high active wastes issuing the reprocessing of spent nuclear fuels, Fourth Half-Yearly Report 2005, Contract EUROPART (FI6W-CT-2003-508854).
- /2/ **Nilsson M, Andersson S, Ekberg C, Foreman M R S, Hudson M J, Liljenzin J-O, Magnusson, Skarnemark G, 2006.** Inhibiting Radilolysis of BTP molecules by Addition of Nitrobenzene“, Radiochim. Acta, 94(1), 1–4.
- /3/ **Andersson S, Ekberg C, Hervieux N, Liljenzin J-O, Magnusson D, Meridiano Y, Nilsson M, Retegan T, Skarnemark G, 2005.** Chalmers University of Technology: Contribution to the third half-yearly report, Europart.
- /4/ **Andersson S, Ekberg C, Liljenzin J-O, Magnusson D, Nilsson M, Retegan T, Skarnemark G, 2004.** Chalmers University of Technology Contribution to the second half-yearly report, Europart.
- /5/ **Nilsson M, Ekberg C, Foreman M R S, Hudson M J, Liljenzin J-O, Modolo G, Skarnemark G, 2006.** Separation of Actinides(III) from Lanthanides(III) in Simulated Nuclear Waste Streams using 6,6'-Bis-(5,6-dipentyl-[1,2,4]triazin-3-yl)-[2,2']bipyridinyl (C5-BTBP) in Cyclohexanone, Solvent Extraction and Ion Exchange 24(6), 823–843.
- /6/ **Foreman M, 2006.** Personal communication.
- /7/ **Nilsson M, 2005.** Screening Investigations of Novel Nitrogen Donor Ligands for Solvent Extraction, PhD Thesis, Chalmers University of Technology, Department of Chemical and Biological Engineering.
- /8/ **Andersson S, Ekberg C, Fermvik A, Liljenzin J-O, Magnusson D, Meridiano Y, Nilsson M, Retegan T, Skarnemark G, 2005.** Partitioning and Transmutation Annual Report 2005. SKB R-06-45, Svensk Kärnbränslehantering AB.