R-09-03

Partitioning and transmutation

Annual report 2008

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Gunnar Skarnemark

Nuclear Chemistry, Department of Chemical and Biological
Engineering, Chalmers University of Technology

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Svensk Kärnbränslehantering AB
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This report concerns a study which was conducted for SKB. The conclusions and viewpoints presented in the report are those of the authors and do not necessarily coincide with those of the client.

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Abstract

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

Chalmers University of Technology is involved in research regarding the separation of actinides and lanthanides and between the actinides themselves as a partner in several European frame work programmes from NEWPART in the 4th framework via PARTNEW and EUROPART to ACSEPT in the present 7th programme. The aims of the projects have now shifted from basic understanding to more applied research with focus on process development. One process, the SANEX (Selective ActiNide EXtraction) is now considered to be working on a basic scale and focus has moved on to more process oriented areas. However, since further investigations on basic understanding of the chemical behaviour are required, we have our main focus on the chemical processes and understanding of how they work. Our work is now manly focussed on the so called GANEX (Group ActiNide EXtraction) process. Due to new recruitments we will now also work on ligand design and development. This will decrease the response time between synthesis of new ligands and their evaluation.

Sammanfattning

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

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

Contents

Introduction

The Partitioning and Transmutation (P&T) group at Nuclear Chemistry and Industrial Materials Recycling, Department of Chemical and Biological Engineering at Chalmers University of Technology investigates the separation of different chemical elements in 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 handle highly active aqueous and organic solutions already exists. Solvent extraction is also a good technique to use considering the high efficiency of separation that can be achieved.

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

The Chalmers group has been involved in the separation for transmutation research throughout three different European Union framework programmes*;* NEWPART (1996–1999), PARTNEW (2000–2003) and EUROPART (2004–2007). During this time the focus has changed slightly although the main content has remained the same. As time has passed the main effort has been more and more focussed on process development. In the early years there was a search for suitable extracting agents for separation of lanthanides from trivalent actinides following the CHON principle (only containing carbon, hydrogen, oxygen and nitrogen). This separation, the so called SANEX (selective Actinide EXtraction) is now considered to be working to a decent degree why the basic research is now redirected towards other, more sophisticated separation schemes, *e.g.* the GANEX (Group Actinide Extraction). The SANEX research has now continued in a different direction. Instead of improving the basic characteristics of the extracting ligand a further and closer collaboration with process expertise is made to make sure that the molecules not only have good separation capabilities but also work practically in a process. In addition, extra focus has been put on the whole organic system since by changing the diluent the hydrolytic and radiolytic stability can be increased as well as the separation factor enhanced. To further work towards an industrial process Chalmers is since 2008 a partner in the 7th European Union framework programme ACSEPT (2008–2012). The number of partners has now increased from 24 in EUROPART to 36 in ACSEPT. The research can be divided into originally five domains (the respective domain leaders and their organisations in parenthesis). However, due to cut backs from the commission the former DM4 which dealt with transmutation fuels was dropped:

- DM 1, Hydrometallurgical processes (Clèment Hill, CEA).
- DM 2, Pyrometallurgical processes (Concha Caravaca, CIEMAT)
- DM 3, Process development (Robin Taylor, UK-NNL)
- DM 4, Education and training (Christian Ekberg, Chalmers)

There was a similar attempt from the research community working with the fuel for transmutation but due to similar cut backs in the budget the partitioning domain was dropped also from that project, FAIRFUELS. However, in Sweden collaboration has started between KTH and Chalmers on the manufacturing of different fuel types.

The main experimental work at Chalmers concerns the extraction properties and other basic chemical characteristics of extraction ligands. We also now house the development and synthesis of new ligands in our newly built organic laboratory. Typical factors studied at Chalmers are among: the influence on extraction of pH, kinetics, ionic strength and media, absorbed dose and concentration of the involved species are studied in combination with modelling of the systems using *e.g.* solubility parameters. The role of the diluent used has been investigated in some detail and during 2009 a thesis dealing with this subject will be presented.

Research

During most part of 2008 five PhD students have worked in the project. Daniel Magnusson has finalised his studies on process development of the SANEX system using the setup at JRC-ITU (Joint Research Centrum – Institute for TransUranium elements) in Germany on genuine spent fuel. He has also spent the year writing his PhD thesis which was defended on the 18th of December 2008 and hence is available at Nuclear Chemistry, Chalmers. Teodora Retegan is now finalising her work on the effect of side groups of the extracting ligands and the diluent effects. She is working half time since June 2008 and plans to present her thesis in March 2009. Catharina Nästrén is back from her stay at JRC-ITU and is now finalising her work on the behaviour of transmutation fuels. She will present her thesis during April 2009. Anna Fermvik presented her licentiate thesis during 2008 and is studying the effects of radiolysis on the already selected extracting systems. In this light, the radiolysis products are one of the most interesting issues. As a part of this work she investigates how to inhibit this radiolysis. Also, different radiation doses seem to be responsible for different extraction behaviour. Collaboration in this area has been initiated between Chalmers and Zoltan Szabo at KTH. Emma Aneheim was mainly focussed on a new and novel extraction system which possibly may lead to a patent during 2009. She is also involved in the synthesis of new extraction ligands

Dr. Mark Foreman is working 50% within this project and 50% with other material recycling issues. The main part of his work this year has been the design and commissioning of an organic synthesis facility. The lab is up and running and some new molecules have been synthesised as well as work performed on the speciation in the organic phase of the extraction system.

A diploma worker, Karin Wald, started to work in the P&T group. She is studying the behaviour of a synergic mixture often used as a model system a decade ago, α-bromo decanoic acid and terpyridine in tributylbenzene (TBB). She has been on maternity leave for most of 2008

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

The ACSEPT project started in March 2008 and during the year there were two meetings. A kick off meeting in Nîmes, France and an information exchange meeting in Prague, Czech Republic in September. During this last meeting about half the time was dedicated to education and training by lectures on basic pyro- and hydro-processing organised by the Domain 4 group.

1 Definitions

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

1.1 Extraction

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

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

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

$$\mathrm{SF}_{\mathrm{A/B}} = \frac{D_A}{D_B}$$

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

1.1.1 Standard extraction experiment

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

Almost explicitly 3.5 mL glass vials are used for the extraction experiments. The volumes most commonly used are therefore 200–500 µL of organic phase and 200–500 µL of aqueous phase. Due to the mutual solubility of some of the solvents used (e.g. cyclohexanone) and the acidic water phases (e.g. water with 1M nitrate concentration), both phases used for extraction are pre-equilibrated with the corresponding aqueous and organic solution. In most extractions the metals are added in trace amounts by spiking with more concentrated stock solutions (often 10–20 µL are added). The phases are then often contacted by vigorously hand-shaking in an isolated canister in which the vials are placed. Sometimes a mechanical shaker is used (for systems requiring longer contact times). The contact time depends on how long time it takes for the extraction system to reach equilibrium. However, often 10 minutes of hand-shaking is sufficient. After contact, the phases are left to separate either by gravitation or by centrifuging. When the phases are completely separated samples of 100–200 µL from each phase are taken for analysis and prepared in different ways depending on the detection method used.

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

1.2 BTBP

BTBP is an abbreviation for *bis*-triazin-*bi*-pyridine, which refers to the nature of the central core common to all the molecules in the family. This is a group of molecules that can act as tetradentate ligands to metal ions and a high selectivity towards trivalent actinides over trivalent lanthanides has been observed /11, 6, 10/.

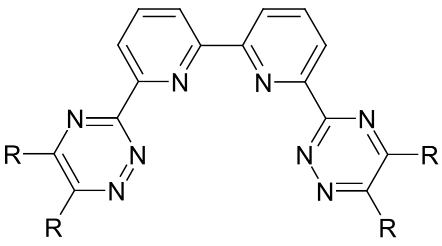


Figure 1-1. *The bis-triazin-bipyridine, or BTBP, core molecule.*

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

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

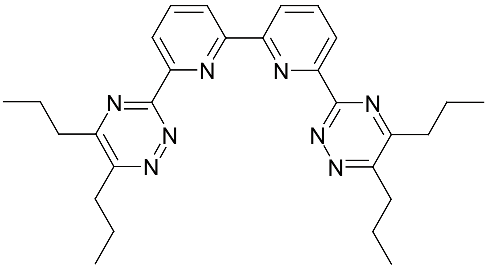


Figure 1-2. *Molecular structure of C3-BTBP.*

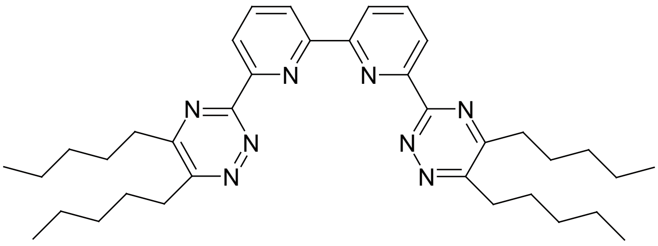


Figure 1-3. *Molecular structure of C5-BTBP.*

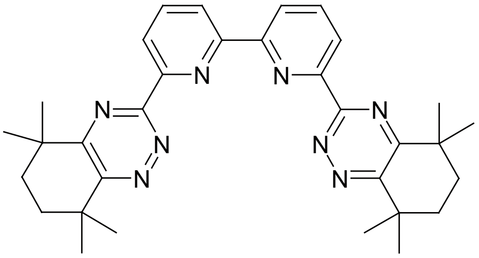


Figure 1-4. *Molecular structure of $CyMe_4$-BTBP.*

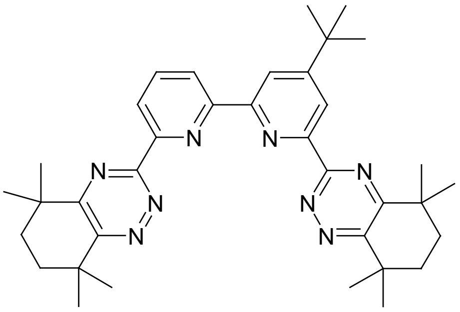


Figure 1-5. *Molecular structure of MF2-BTBP.*

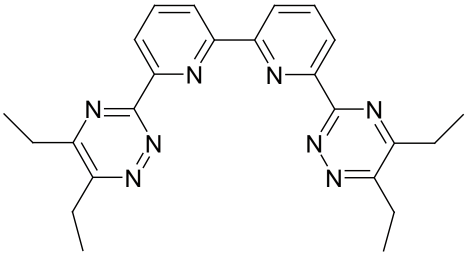


Figure 1-6. *Molecular structure of C2-BTBP.*

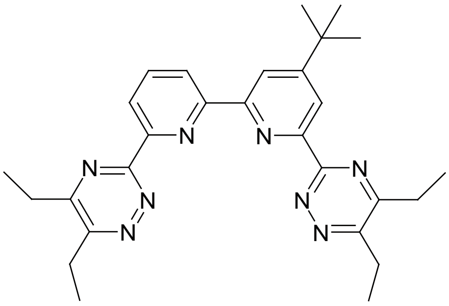


Figure 1-7. *Molecular structure of MF1-BTBP.*

1.3 Detection

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

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

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

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

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

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

ICP-MS: ELAN 6000 Inductively Coupled Plasma Mass Spectrometer

Spectrophotometer: Perkin Elmer Lambda 19 Uv/VIS/NIR spectrometer.

Irradiation source

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

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

The estimated dose given to samples put in the source is now approximately 12 Gy/h.

2 Radiolysis

Since the separation process using the BTBP molecules takes place in a high radiation flux the solvent, i.e. both the extractant and the diluent, must be resistant to radiation. A number of organic systems were irradiated and then studied in terms of degradation products and the effect on extraction. Most solvents were irradiated with the ^{60}Co-source at Chalmers if nothing else is stated. If the ageing of the solvent was unknown corresponding samples were placed in a flask outside the gamma source, at a remote distance, to act as a reference for investigation of the possible degradation over time of the molecule. Samples were taken from the solvents at the start of the experiments and then at different times during a longer time period.

2.1 Alpha- vs. gamma-radiolysis

This study investigated how the distribution ratio of americium changed when organic solvents were irradiated with low doses of alpha and gamma radiation, respectively. Both types of irradiation were given with a low dose rate and the total received dose was approximately 17 kGy. In addition, irradiation with alpha at a much higher dose rate was also done with one of the solvents, and the results were compared with the low dose rate experiment.

Two organic solvents were used: one contained 0.005 M CyMe$_4$-BTBP in cyclohexanone and one contained 0.005 M C5-BTBP in cyclohexanone. For the high dose rate alpha experiments with CyMe$_4$-BTBP, the ligand concentration was higher, 0.01 M.

Gamma irradiation experiments

Five sealed glass bottles were placed in the ^{60}Co source at Chalmers and removed at various times, i.e. after various doses up to a total received dose of almost 20 kGy. After removal from the source, the organic phase was contacted with an aqueous phase comprising 0.01 M HNO_3 and 0.99 M $NaNO_3$ and spiked with ^{241}Am and ^{152}Eu. The phases were pre-equilibrated prior to contact. A previous study has shown that pre-equilibration does not affect the distribution ratios /4/, thus the results can be compared with the results from alpha radiolysis (in which the phases were not pre-equilibrated). After 10 minutes of manual shaking the samples were centrifuged to ease phase separation and then aliquots were taken from each phase and analyzed in HPGe2. All experiments were made in duplicate and uncertainties were calculated using error propagation based on measurement statistics.

Alpha irradiation experiments – low dose rate

The alpha radiolysis experiment was done by extracting ^{241}Am from an aqueous phase into the organic phase and then performing extraction tests at various times, i.e. after various doses. The original aqueous solution contained ca 2.7 MBq/mL (0.09 mM) of ^{241}Am in 0.01 M HNO_3 + 0.99 M $NaNO_3$. Equal volumes of organic and aqueous phase were contacted during 10 minutes manual shaking and the allowed to separate. 5 µL samples were taken then taken from each phase and placed in a pre-weighed scintillation flask. 10 mL scintillation cocktail (Hionic-Fluor, Packard BioScience) was added and the samples were measured using Liquid Scintillator 2. After various times the procedure of shaking, allowing to separate and taking samples was repeated and a new distribution ratio could be calculated. These experiments were only made as single samples.

By knowing the distribution ratio for americium, the content in the organic phase could be determined and the dose rate given to the solvent could be calculated. (^{241}Am: $t_{1/2}$ = 432.2 a, E_α = 5.486 MeV). The glass vial was left untouched between the sampling points and the distribution between the phases was assumed to be unchanged during this time, thus the dose rate was constant between sampling points. After a certain dose, when a new extraction test (shaking, separation, sampling) was done, the distribution ratio changed, hence the dose rate also changed during the time of the experiment. At the start of the experiment, when the organic solvent had not been exposed to any radiation, the distribution ratio was around 5 for the CyMe4-BTBP solvent, resulting in a dose rate of ca 7 Gy/h, and around 30 for the C5-BTBP solvent, resulting in a dose rate of ca 8 Gy/h.

Alpha irradiation experiments – high dose rate

The high dose rate experiments were conducted in a similar manner as the low dose rate ones. Apart from the differences mentioned below, all other experimental details were the same. The initial aqueous phase contained a much higher concentration of ^{241}Am, 0.007 M. Also the concentration of $CyMe_4$-BTBP was higher in the high dose rate experiments, 0.01 M, resulting in a higher distribution ratio for Am and consequently higher dose rate to the organic phase. After one day the phases were diluted to a total volume of 1 mL each. At the start of the experiment the distribution ratio was around 90, but after receiving 40 kGy it had decreased to around 30. Before dilution of the phases, the dose rate was around 670 Gy/h, but the dilution caused a decrease to around 130 Gy/h.

Results $CyMe_4$-BTBP

$CyMe_4$-BTBP has been shown to be rather stable with time /12, 9/, i.e. it can be assumed that the change in distribution ratio is caused by the irradiation. Figure 2-1 illustrates how the distribution ratio of americium changed when the organic solvent was irradiated with low dose rate of both alpha and gamma radiation. The values are plotted as % of the start D, which were 5.1 for the alpha experiment and 4.4 for the gamma experiment. There is no clear difference between the two curves, possibly the gamma radiation affects the system a bit more than alpha does. Both types of irradiation cause an increase in distribution ratio. This behaviour is not the common behaviour for BTBP type molecules but it has been reported for $CyMe_4$-BTBP before /4/.

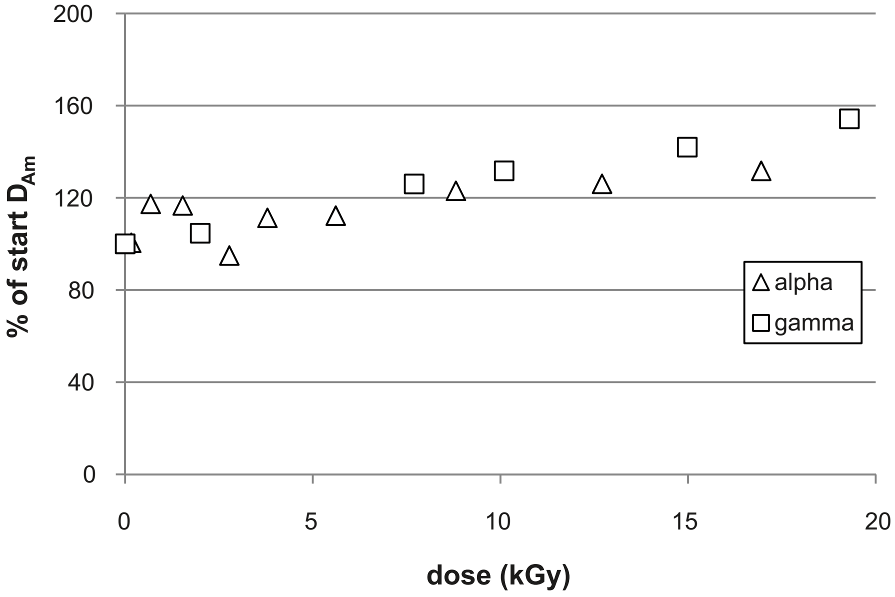


Figure 2-1. *Distribution ratio (Am) for a solvent containing 0.005 M $CyMe_4$-BTBP in cyclohexanone expressed as % of start D as a function of the received dose, for both alpha and gamma irradiation.*

Figure 2-2 shows the distribution ratio of Am for the two different dose rates of α irradiation. Both experiment series included only single samples hence the results are uncertain, but it is clearly indicated that the high dose rate severely degrades the molecule and decreases the extraction of Am, at least at doses exceeding 12 kGy. Values are plotted as % of the start D, which were 92 for the high dose rate experiment and 5.1 for the low dose rate experiment.

Results C5-BTBP

Unlike CyMe$_4$-BTBP, C5-BTBP is not stable over time /4/ and the distribution ratio of Am decreases as the solvent is ageing. This must be taken into account when evaluating data from radiolysis experiment, since the degradation of the solvent then is a combination of irradiation and ageing. During six months ageing of a solvent containing C5-BTBP in cyclohexanone the Am distribution ratio decreased with 50%. The same decrease was observed after around 600 hours of alpha irradiation and after around 300 hours of gamma irradiation. Thus, it can be concluded that the decrease in extraction is not just due to ageing, but the irradiation highly affects the degradation of the solvent. In Figure 2-3 the decrease in D_{Am} is plotted as a function of the dose for both alpha and gamma radiation. The D_{Am} start value was 30 for the alpha experiment and 38 for the gamma experiment. The solvent appears to be more affected by the alpha radiation than the gamma radiation, at least the distribution ratio decreases more when the solvent is exposed to alpha radiation. Thus, C5-BTBP seems to be more sensitive to alpha than gamma radiation, while CyMe$_4$-BTBP shows the same change for both types of radiation (see above). This is unexpected and needs further investigation.

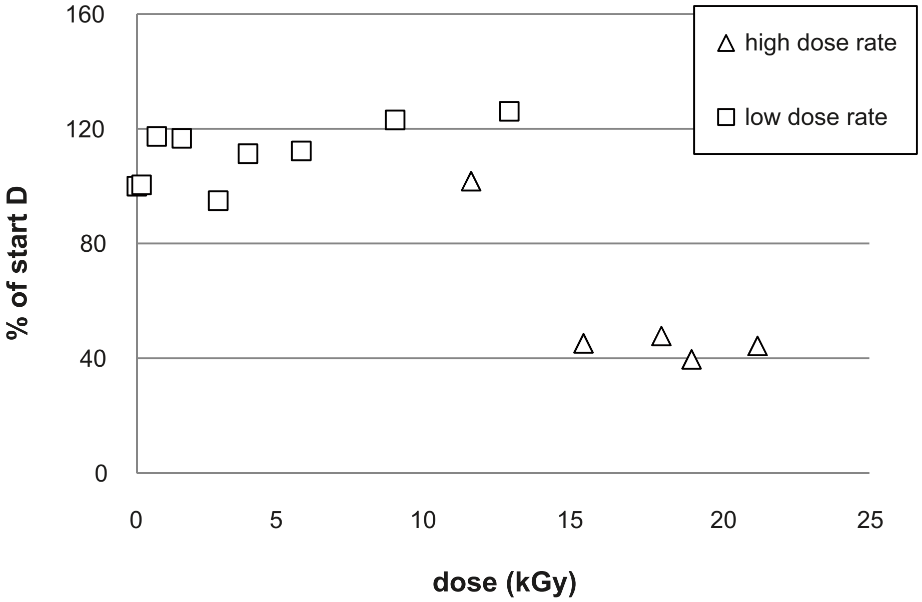


Figure 2-2. *Distribution ratio (Am) for a solvent containing CyMe$_4$-BTBP in cyclohexanone expressed as % of start D as a function of the received dose, for both high and low dose rate of alpha radiation. The concentration of the ligand was 0.01 M for the high dose rate experiments and 0.005 M for the low dose rate experiments.*

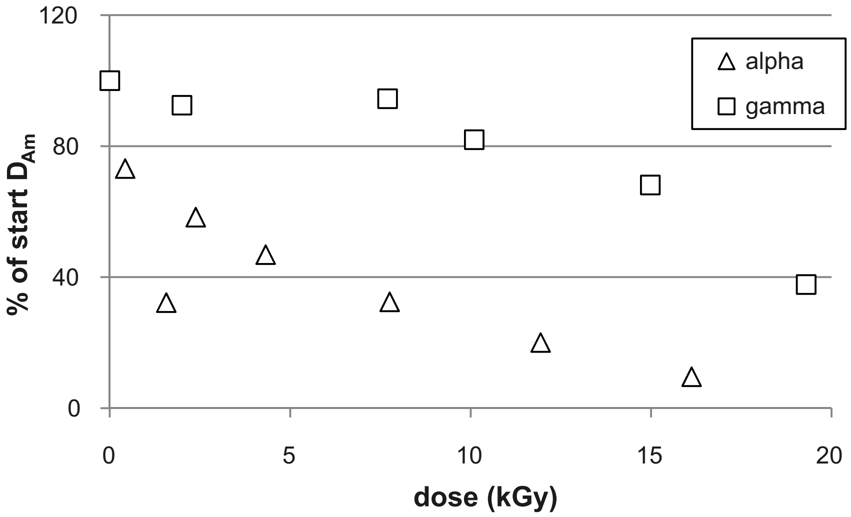


Figure 2-3. *Distribution ratio (Am) for a solvent containing 0.005 M C5-BTBP in cyclohexanone expressed as % of start D as a function of the received dose, for both alpha and gamma irradiation.*

2.2 Effect of the storage temperature between irradiation and extraction

A study was done to determine the effect of temperature during storage of irradiated samples between the irradiation and further experiments (e.g. extraction experiments). Four organic solvents were irradiated and then stored for a long time before extraction experiments were carried out. Two of the solvents contained 0.005 M C5-BTBP dissolved in either hexanol or cyclohexanone and two solvents contained 0.005 M $CyMe_4$-BTBP in the same diluents. The solvents were irradiated with γ-radiation using the Chalmers ^{60}Co-source.The solvents received a total dose of 20 kGy.

Samples were removed from the γ-source at five different times and 750 µL were stored in room temperature while 750 µL were stored in a freezer. The solutions were stored in 3.5 mL glass vials with a plastic lid. The room temperature was 21±1ºC and the temperature in the freezer was –25±1ºC. After a long period of time (4–5 months) extraction experiments with all solvents were carried out. The samples that were first removed from the irradiation source were consequently stored for the longest period of time; just over five months, while the samples removed at the last sampling point were stored for four months before the extraction experiments. The extraction experiments were carried out according to the general procedure described under *Standard extraction experiment* in the *Definitions* chapter.

Results

For C5-BTBP in hexanol, round white crystals were observed in four out of the five irradiated bottles that had been stored in room temperature. The solution that did not show any crystals was the one that had received the lowest dose, 5.1 kGy. No crystals were observed immediately when the bottles were taken out from the irradiation source, only later, nor were there any signs of crystals in the solutions stored in the freezer. C5-BTBP in hexanol has a yellowish colour, but the solution above the white crystals seemed to have lost some of its yellow colour. It was suggested that the crystals were *di*-cyano-*bi*-pyridine and an IR-spectra from the unknown crystals was compared to a spectra from a known sample of *di*-cyano-*bi*-pyridine. The distinctive “cyano peak”, between 2,000 and 2,500 cm^{-1}, was not observed for the unknown crystals; hence it could not be identified as *di*-cyano-*bi*-pyridine. Figure 2-4 shows the IR-spectra for the two samples. NMR measurements on the crystals are to be done.

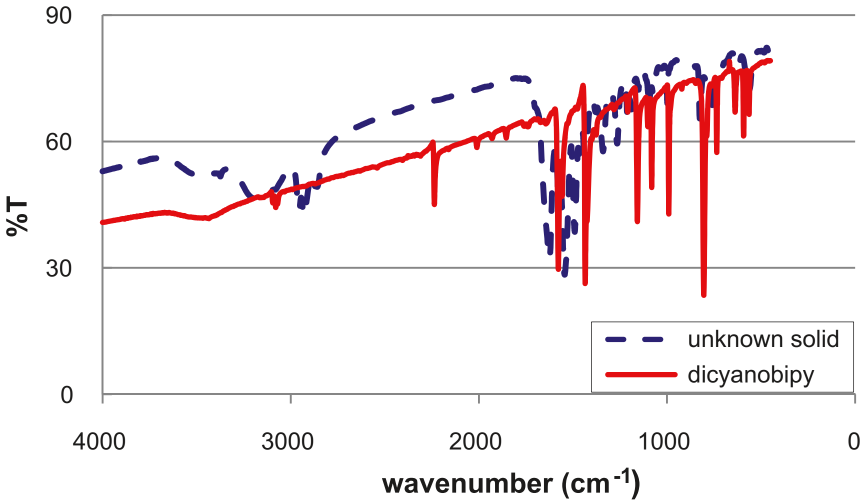


Figure 2-4. *IR-spectra from a known sample of di-cyano-bi-pyridine and the unknown white solid formed when a solvent containing 0.005 M C5-BTBP in hexanol was irradiated with doses above 5 kGy.*

No crystals were observed in the bottles containing C5-BTBP in the other diluent, cyclohexanone. Crystals have previously been observed in this solvent but at higher doses, above 80 kGy /4/. The crystals formed during that study did not resemble the ones formed in irradiated C5-BTBP in hexanol (above) but looked more like oblong yellowish straws. When these crystals were observed the solvent had dramatically lost its ability to effectively extract americium. The crystals are currently being studied using NMR by Dr Zoltan Szabo at KTH, Stockholm.

At the sampling of C5-BTBP in cyclohexanone there were some problems with cloudy aqueous phases. It was noted for which samples there had been problems and this was taken into account when evaluating the data from the HPGe measurements. No deviating distribution ratios occurred for the "problem samples". For the solvents containing $CyMe_4$-BTBP there were no problems with cloudy aqueous phases and no crystal observations.

It has previously been shown that irradiated solvents containing C5-BTBP gradually lose their ability to efficiently extract americium from the aqueous phase as the solvent receives more dose /10, 4/. The extraction of europium also decreases but not to the same extent as americium, resulting in a decreasing separation factor between americium and europium. This behaviour is valid both when the diluent is hexanol and when it is cyclohexanone. Solvents with hexanol as diluent show a larger decrease (in percent) than solvents containing cyclohexanone.

The solvents containing the other BTBP molecule, $CyMe_4$-BTBP, have previously shown an opposite behaviour in most aspects /4/. As the solvent receives higher doses the extraction of both metals increase, and the separation factor remains at a constant level. The change in extracting capacity is larger for the solvent with hexanol as diluent, a behaviour similar to that of the experiments with C5-BTBP. Figure 2-5 to 2-8 illustrates the extraction of americium as an effect of received dose when using different storing techniques for the four solvents. The uncertainties are small and "hidden" within the markers.

A summarizing comment is that the change in D_{Am} was larger for the solvents stored in room temperature compared to the solvents stored in the freezer, whether it is an increase or a decrease. When the solvent comprised C5-BTBP in hexanol the difference between the solutions stored in room temperature and freezer was larger than when the diluent was cyclohexanone. This behaviour is similar to the behaviour described above, where cyclohexanone seem to lessen the effect of irradiation of the solvent compared to hexanol. For $CyMe_4$-BTBP the trend is not as obvious. With hexanol as diluent the difference between D_{Am} for the solvent kept in the freezer and the D_{Am} for the solvent kept in room temperature is rather constant. If the diluent instead is cyclohexanone the difference between "freezer" and "room temperature" samples gets larger as the received dose increases.

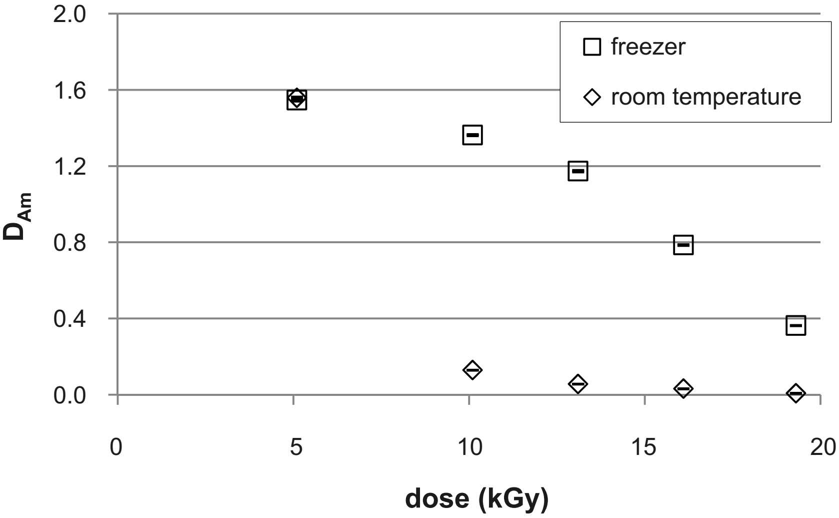


Figure 2-5. *Distribution ratio (Am) as a function of the dose received by the organic solvent before contact with the aqueous phase. The organic phase comprised 0.005 M C5-BTBP in hexanol and the aqueous phase comprised 0.01 M* HNO_3*, 0.99 M* $NaNO_3$ *and traces of* ^{241}*Am and* ^{152}*Eu. The two series refer to temperature during the storage between irradiation and extraction experiments (4–5 months). In the freezer the temperature was around –25ºC and the room temperature was around +21ºC.*

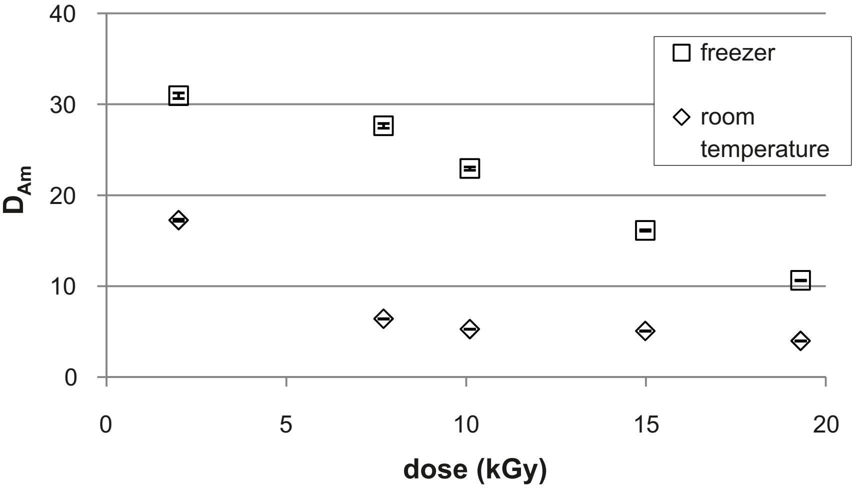


Figure 2-6. *Distribution ratio (Am) as a function of the dose received by the organic solvent before contact with the aqueous phase. The organic phase comprised 0.005 M C5-BTBP in cyclohexanone and the aqueous phase comprised 0.01 M* HNO_3*, 0.99 M* $NaNO_3$ *and traces of* ^{241}*Am and* ^{152}*Eu. The two series refer to temperature during the storage between irradiation and extraction experiments (4–5 months). In the freezer the temperature was around –25ºC and the room temperature was around +21ºC.*

Figure 2-7. *Distribution ratio (Am) as a function of the dose received by the organic solvent before contact with the aqueous phase. The organic phase comprised 0.005 M* $CyMe_4$*-BTBP in hexanol and the aqueous phase comprised 0.01 M* HNO_3*, 0.99 M* $NaNO_3$ *and traces of* ^{241}Am *and* ^{152}Eu*. The two series refer to temperature during the storage between irradiation and extraction experiments (4–5 months). In the freezer the temperature was around –25ºC and the room temperature was around +21ºC.*

Figure 2-8. *Distribution ratio (Am) as a function of the dose received by the organic solvent before contact with the aqueous phase. The organic phase comprised 0.005 M* $CyMe_4$*-BTBP in cyclohexanone and the aqueous phase comprised 0.01 M* HNO_3*, 0.99 M* $NaNO_3$ *and traces of* ^{241}Am *and* ^{152}Eu*. The two series refer to temperature during the storage between irradiation and extraction experiments (4–5 months). In the freezer the temperature was around –25ºC and the room temperature was around +21ºC.*

For all solvents, the D_{Eu} follows the same trend as D_{Am} of either decreasing or increasing when the received dose increases, but not always to the same extent (see the discussion about $SF_{Am/Eu}$ below).

As the solvents received a higher dose the $SF_{Am/Eu}$ decreased for the solvents containing C5-BTBP. As mentioned above, this behaviour is common when C5-BTBP is being irradiated. For the solvents stored in room temperature the SF decreased more than for corresponding solvents kept in the freezer. When the solvents contain $CyMe_4$-BTBP instead of C5-BTBP the SF remained at a constant level as the dose increased. Figure 2-9 and 2-10 illustrates the change in $SF_{Am/Eu}$ as a function of received dose for solvents containing C5-BTBP (Figure 2-9) and $CyMe_4$-BTBP (Figure 2-10).

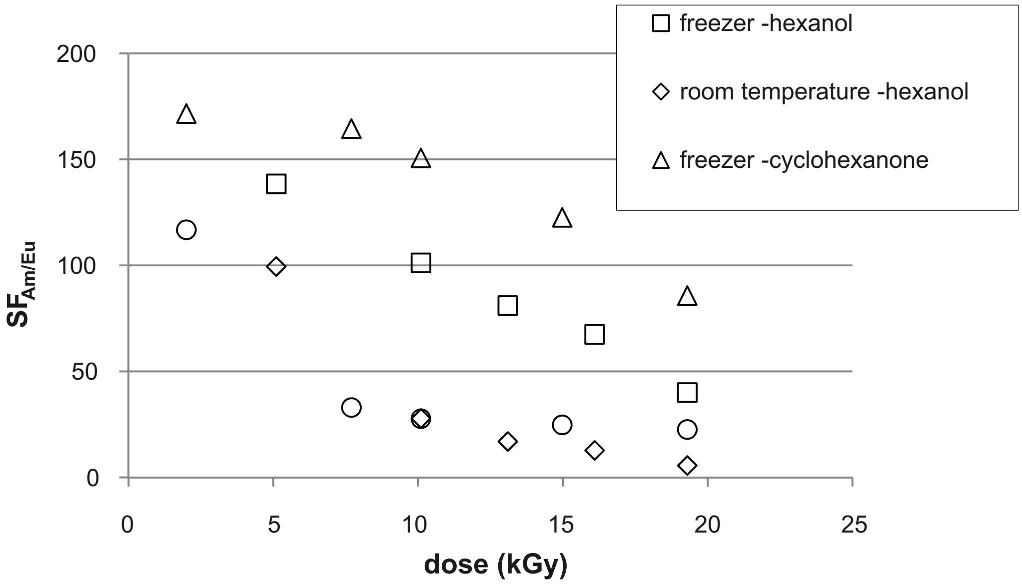


Figure 2-9. *$SF_{Am/Eu}$ as a function of the received dose for an irradiated organic phase containing C5-BTBP in either hexanol or cyclohexanone. The aqueous phase comprised 0.01 M HNO_3, 0.99 M $NaNO_3$ and traces of ^{241}Am and ^{152}Eu. The labels "freezer" and "room temperature" refer to temperature during the storage between irradiation and extraction experiments (4–5 months). In the freezer the temperature was around –25ºC and the room temperature was around +21ºC.*

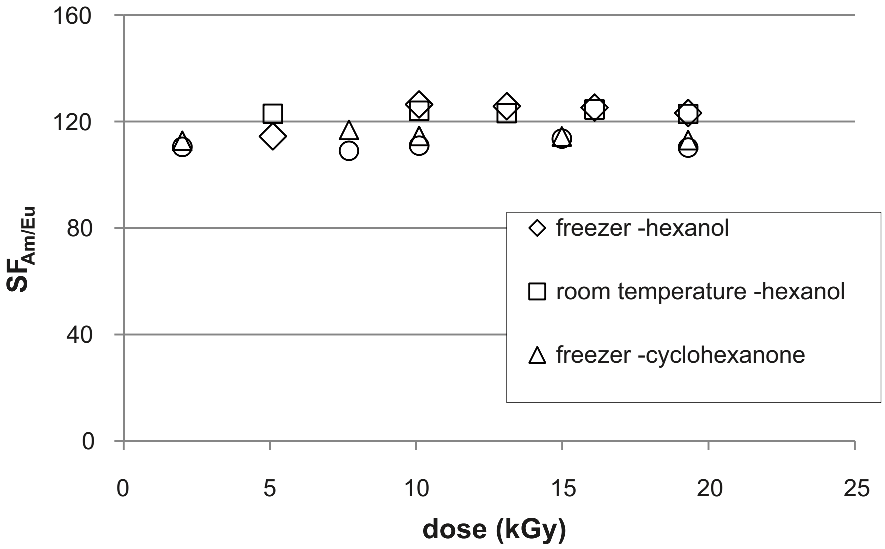


Figure 2-10. *$SF_{Am/Eu}$ as a function of the received dose for an irradiated organic phase containing $CyMe_4$-BTBP in either hexanol or cyclohexanone. The aqueous phase comprised 0.01 M HNO_3, 0.99 M $NaNO_3$ and traces of ^{241}Am and ^{152}Eu. The labels "freezer" and "room temperature" refer to temperature during the storage between irradiation and extraction experiments (4–5 months). In the freezer the temperature was around –25ºC and the room temperature was around +21ºC.*

When working with the solvent containing C5-BTBP in cyclohexanone it has to be taken into account that the solvent degrades to a certain extent with time (see discussions in "Alpha- vs. gamma-radiolysis" and "Degradation products and how they vary with dose"). C5-BTBP in hexanol has also shown signs of ageing, but not to same extent as in cyclohexanone. The solvents containing CyMe$_4$-BTBP have previously been shown to be stable with time.

It was shown above that the storage temperature affects the distribution ratios (Am and Eu) for irradiated organic solvents containing BTBP molecules in hexanol or cyclohexanone. In Figure 2-11 to 2-14 the curve showing the distribution ratio calculated from experiments made just after the removal from the irradiation source (within one hour) is also included. In this way it can be concluded which type of storage that gives a distribution ratio most accurately corresponding to the distribution ratio of the solvent at the end of irradiation. It is clear that for C5-BTBP the method of storing the solvents in the freezer gives distribution ratios more similar to the ones obtained just after irradiation, but the values are still deviating from the "direct" ones. With hexanol as diluent the deviation is larger at the low doses; that is for the samples that were kept in the freezer for the longer time period. On the other hand, when the diluent is cyclohexanone, the deviation from the distribution ratios obtained just after irradiation is more or less constant over the whole dose range. The distribution ratios for the stored solvents containing C5-BTBP are consistently lower than for corresponding solvent just after irradiation. This could be a result of degradation processes initialized by the radiation and continuing after the irradiation has stopped. These processes are possibly slowed down by the lower temperature in the freezer compared to room temperature.

When it comes to the solvents containing CyMe$_4$-BTBP the results are not unambiguous. The distribution ratios from the "direct" extractions are either higher than the distribution ratios for the stored solvents or a value in between. In contrast to the solvents containing C5-BTBP the CyMe$_4$-BTBP solvents stored in room temperature give distribution ratio more similar to the ratios from "direct" extraction compared to the solvents stored in the freezer.

The results from these experiments highlight the importance of being consistent when conducting extraction experiments following irradiation and to be attentive when comparing different radiolysis studies.

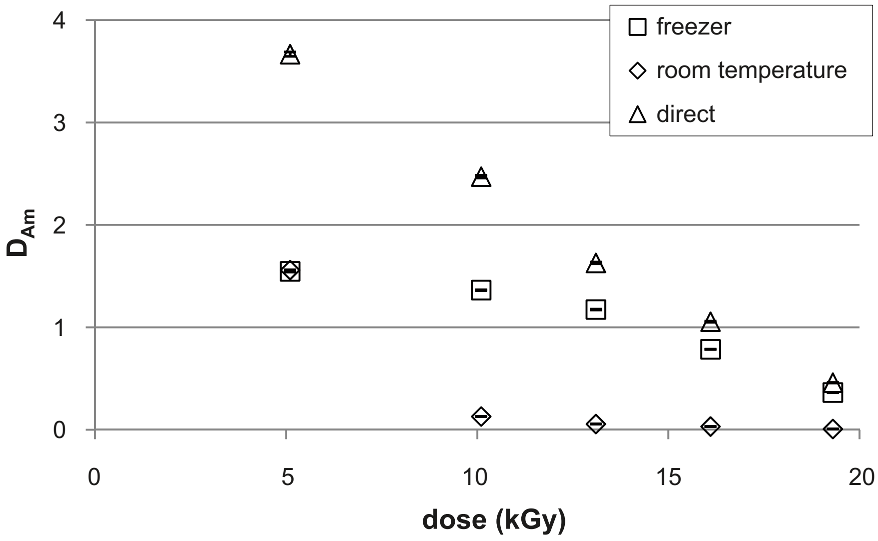


Figure 2-11. Same as Figure 2-5, but with the addition of the distribution ratios obtained from an extraction experiment just after end of the irradiation. The experimental conditions were the same as described for the stored solvents.

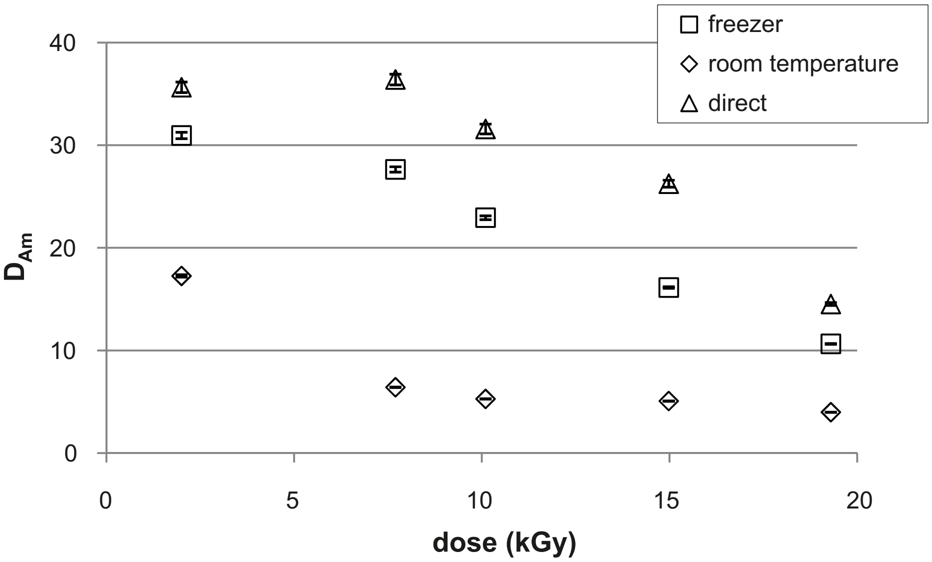


Figure 2-12. *Same as Figure 2-6, but with the addition of the distribution ratios obtained from an extraction experiment just after end of the irradiation. The experimental conditions were the same as described for the stored solvents.*

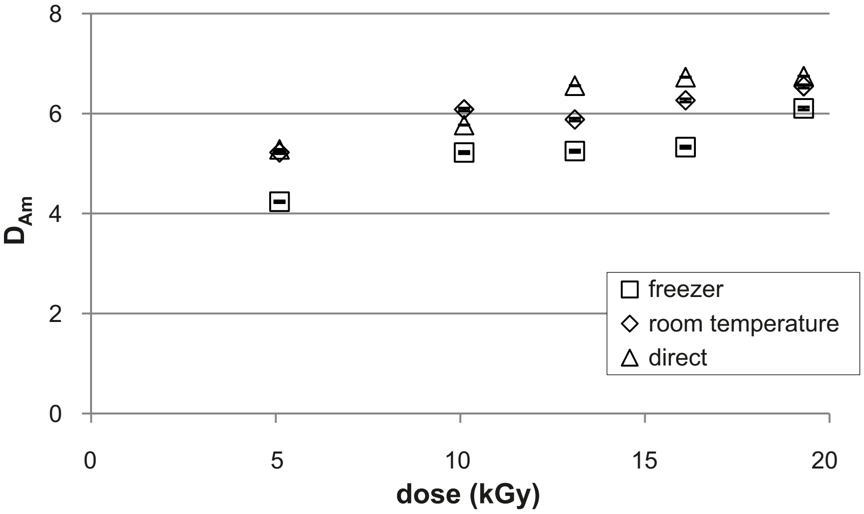


Figure 2-13. *Same as Figure 2-7, but with the addition of the distribution ratios obtained from an extraction experiment just after end of the irradiation. The experimental conditions were the same as described for the stored solvents.*

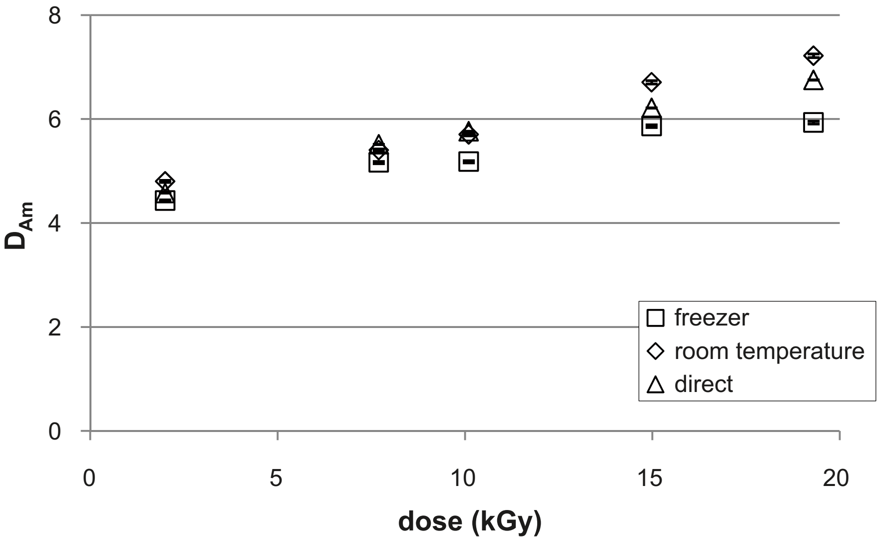


Figure 2-14. *Same as Figure 2-8, but with the addition of the distribution ratios obtained from an extraction experiment just after end of the irradiation. The experimental conditions were the same as described for the stored solvents.*

2.3 Effect of dose rate

Four organic solvents were irradiated with two γ sources with different dose rates. Two of the solvents contained 0.005 M C5-BTBP dissolved in either hexanol or cyclohexanone and two solvents contained 0.005 M $CyMe_4$-BTBP in the same diluents. One of the γ sources was the Chalmers ^{60}Co-cell with a dose rate of approximately 12.5 Gy/h. The other γ source was a ^{137}Cs source (IBL637, CISBio International) with a higher dose rate, varying from 900–1,650 Gy/h depending on where the sample was placed. Samples were taken at five different received doses, the highest dose being around 20 kGy. The solvents were stored in a freezer (see previous chapter) and occasionally, for short period of times, in room temperature while awaiting extraction experiments. All extraction experiments were done approximately at the same time, after the end of all irradiations.

Extraction experiments

The organic phase was contacted with an aqueous phase comprising 0.01 M HNO_3 and 0.99 M $NaNO_3$ and spiked with ^{241}Am and ^{152}Eu. When cyclohexanone was used as diluent the phases were pre-equilibrated before contact. The solvents with cyclohexanone as diluent have fast kinetics and ten minutes of manual shaking was enough to ensure that the system had reached equilibrium. For the solvents using hexanol as diluent a longer contact time was required and the samples were shaken for 6 h 15 min using a mechanical shaker.

After the required contact time the phases were allowed to separate and the vials were centrifuged to ease the phase separation. Aliquots were then taken from both phases and analyzed in a high purity germanium HPGe 2. All experiments were made in duplicate and uncertainties were calculated using error propagation based on measurement statistics.

Observations during extraction experiments

In some of the samples containing C5-BTBP in hexanol, a kind of precipitation was observed. It cannot really be described as crystals, more like finely grinded sediment that floats in the solvent and makes it a bit "cloudy" if it is moved to rapidly. No precipitation was observed in the solvent containing C5-BTBP in cyclohexanone or in the CyMe$_4$-BTBP solvents. Crystal formation has previously been observed in a solvent containing C5-BTBP in cyclohexanone and irradiated with 80 kGy with the low dose rate. The crystals are, as mentioned above, being studied using NMR in collaboration with Dr Zoltan Szabo at KTH, Stockholm.

Results – extraction

Figure 2-15 to 2-18 show how the distribution ratio for americium changes as the solvents receive higher doses by the two different dose rates. The extraction of Am increases for both solvents containing C5-BTBP while it decreases for the solvents containing CyMe$_4$-BTBP.

For C5-BTBP in hexanol (Figure 2-15), the decrease is larger when the higher dose rate is used. This is particularly visible at the low doses, around 5–10 kGy. As the dose gets higher the curves approach each other.

In Figure 2-16, where the diluent instead is cyclohexanone, the curves more or less follow each other up to 10 kGy, and then the curve representing the low dose rate continues to decrease quite rapidly, while the high dose rate curve seems to start to flatten out.

When looking at CyMe$_4$-BTBP in the two diluents, the largest increase in distribution ratio takes place when the diluent is hexanol (Figure 2-17). As opposed to the system with C5-BTBP in hexanol, the change is here larger for the low dose rate than the high dose rate.

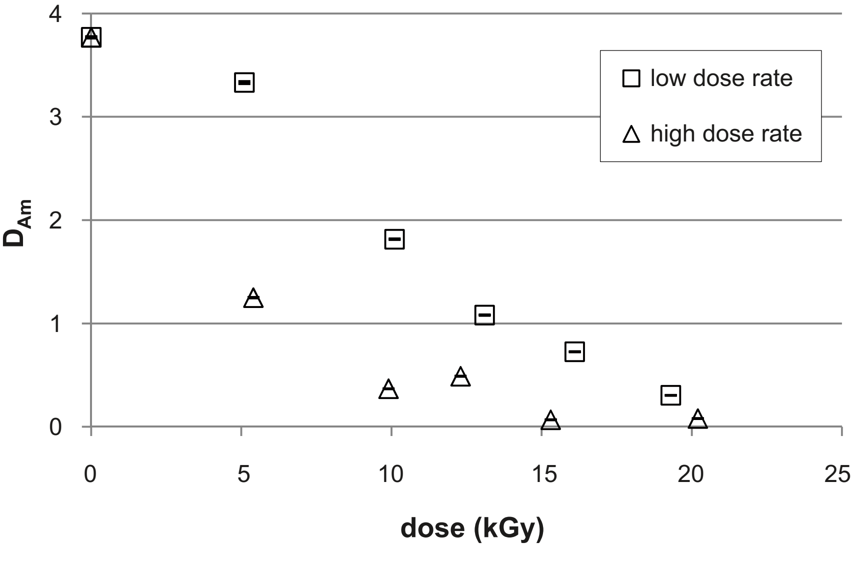


Figure 2-15. Distribution ratio (Am) for a solvent consisting of 0.005 M C5-BTBP in hexanol and irradiated to various doses with two different dose rates. The low dose rate was approximately 12.5 Gy/h and the high dose rate was approximately 1.6 kGy/h. The aqueous phase comprised 0.01 M HNO$_3$, 0.99 M NaNO$_3$ and trace amounts of ^{241}Am and ^{152}Eu.

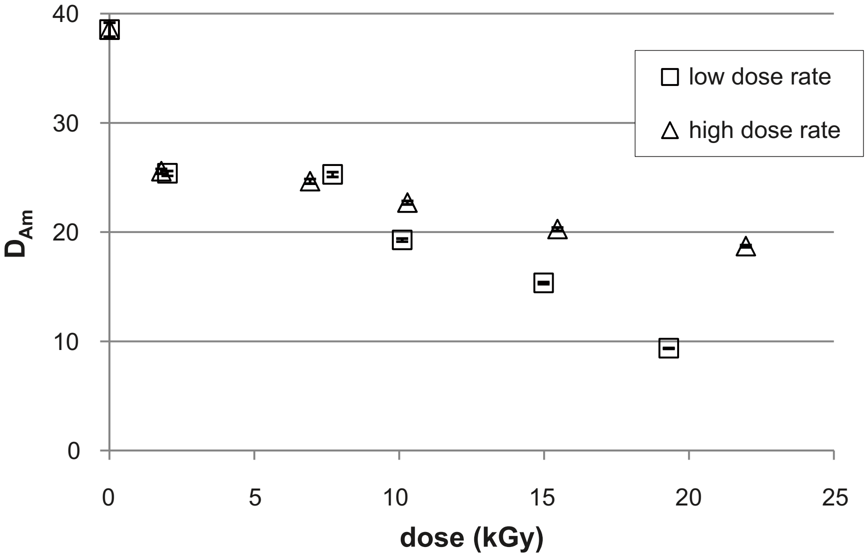


Figure 2-16. Distribution ratio (Am) for a solvent consisting of 0.005 M C5-BTBP in cyclohexanone and irradiated to various doses with two different dose rates. The low dose rate was approximately 12.5 Gy/h and the high dose rate was approximately 1.6 kGy/h. The aqueous phase comprised 0.01 M HNO_3*, 0.99 M* $NaNO_3$ *and trace amounts of* ^{241}Am *and* ^{152}Eu*.*

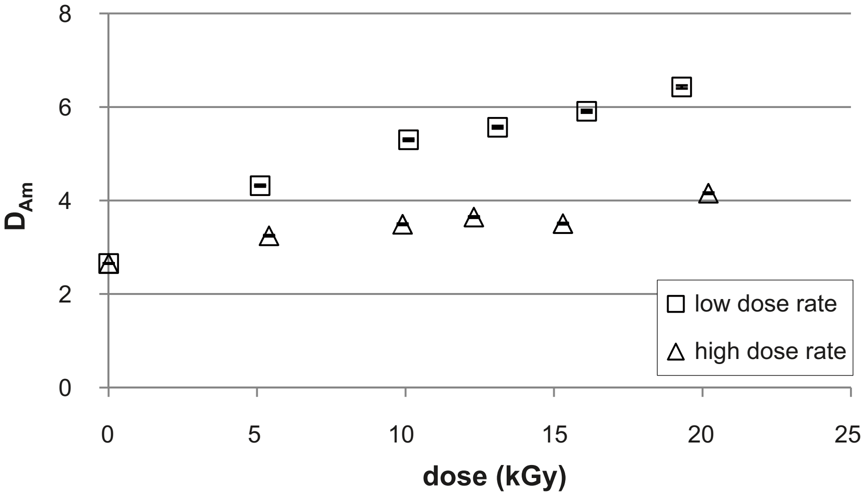


Figure 2-17. Distribution ratio (Am) for a solvent consisting of 0.005 M $CyMe_4$*-BTBP in hexanol and irradiated to various doses with two different dose rates. The low dose rate was approximately 12.5 Gy/h and the high dose rate was approximately between 0.9 and 1.1 kGy/h. The aqueous phase comprised 0.01 M* HNO_3*, 0.99 M* $NaNO_3$ *and trace amounts of* ^{241}Am *and* ^{152}Eu*.*

For CyMe$_4$-BTBP in cyclohexanone (Figure 2-18), the behaviour resembles the C5-BTBP in cyclohexanone case: the curves look similar up to 10 kGy from where the low dose rate curve starts to increase steeper.

The distribution ratios for europium changes similarly to the distribution ratios for americium for the CyMe$_4$-BTBP solvents, but for the C5-BTBP solvents the change in D_{Eu} is smaller than the change in D_{Am}, resulting in a decreasing separation factor ($SF_{Am/Eu}$). Figure 2-19 and 2-20 show the change in $SF_{Am/Eu}$ for C5-BTBP in hexanol and cyclohexanone, respectively. In hexanol, the change in $SF_{Am/Eu}$ is more or less the same for both dose rates, but in cyclohexanone the low dose rate curve decreases noticeably more than the high dose rate curve.

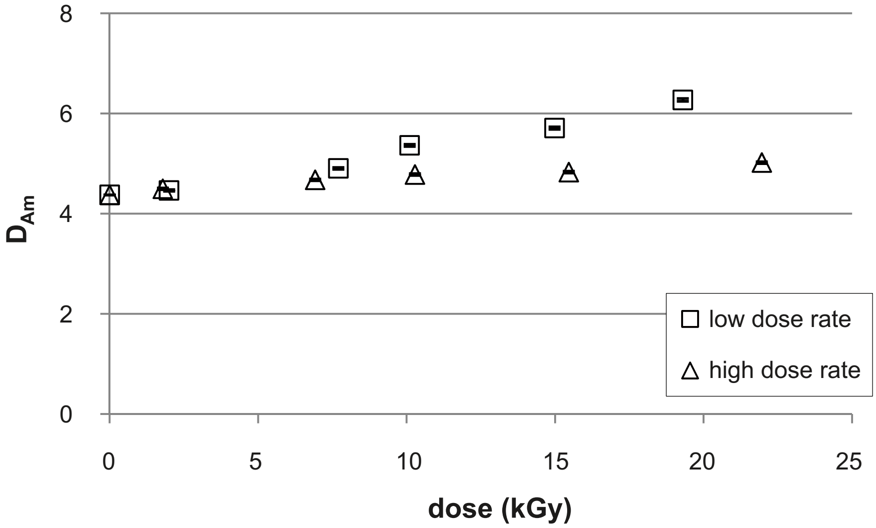


Figure 2-18. *Distribution ratio (Am) for a solvent consisting of 0.005 M CyMe$_4$-BTBP in cyclohexanone and irradiated to various doses with two different dose rates. The low dose rate was approximately 12.5 Gy/h and the high dose rate was approximately between 0.9 and 1.1 kGy/h. The aqueous phase comprised 0.01 M HNO$_3$, 0.99 M NaNO$_3$ and trace amounts of ^{241}Am and ^{152}Eu.*

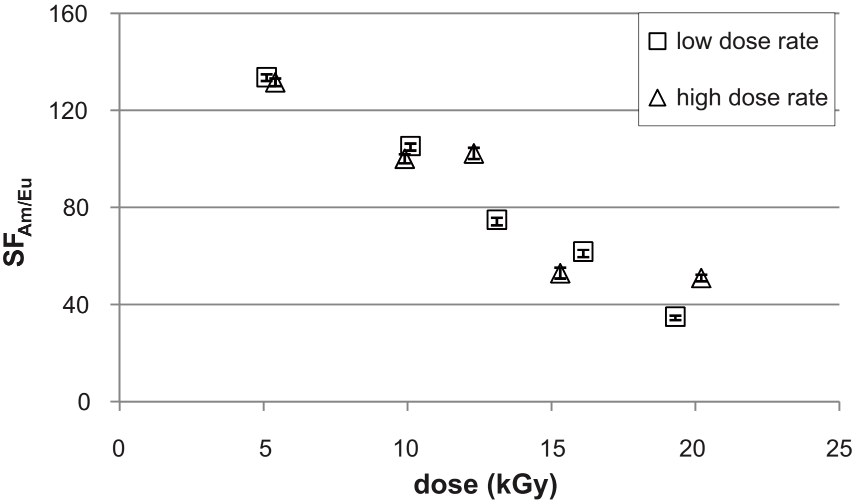


Figure 2-19. *Separation factor (Am/Eu) for a solvent consisting of 0.005 M C5-BTBP in hexanol, irradiated with two different dose rates. The low dose rate was approximately 12.5 Gy/h and the high dose rate was approximately 1.6 kGy/h. The aqueous phase comprised 0.01 M HNO$_3$, 0.99 M NaNO$_3$ and trace amounts of ^{241}Am and ^{152}Eu.*

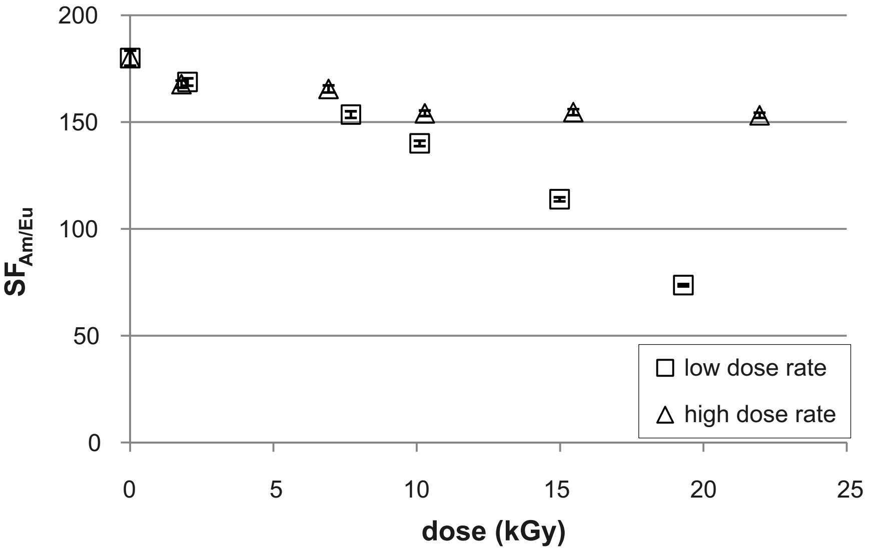


Figure 2-20. *Separation factor (Am/Eu) for a solvent consisting of 0.005 M C5-BTBP in cyclohexanone, irradiated with two different dose rates. The low dose rate was approximately 12.5 Gy/h and the high dose rate was approximately 1.6 kGy/h. The aqueous phase comprised 0.01 M* HNO_3*, 0.99 M* $NaNO_3$ *and trace amounts of* ^{241}*Am and* ^{152}*Eu.*

2.4 Degradation products and their variation with dose

The four irradiated organic solvents described in the previous section were analyzed using ESI-MS and APCI-MS. The samples were diluted either 1:50 or 1:100 with a mixture of CH_3CN/H_2O (1:1) and the measurements were recorded in positive ionization mode. Attempts were made to identify some of the degradation products and establish how their presence/abundance varies with the dose.

ESI- and APCI-MS are not quantitative methods and therefore no conclusions about the amounts produced of the degradation products can be reached by studying the total intensity of various peaks. Instead a ratio between the peak of interest and the original BTBP molecule is calculated. This ratio can thus be a combination of an increase of the oxidized species and a decrease of the original BTBP.

Both MS techniques indicated that the presence of oxygen containing compounds was high in many of the solvents. The solvents irradiated with the lower dose rate, and consequently during a much longer time, had a much higher content of oxygen containing compounds. This coincides with the water content in the solvents, measured with Karl Fisher coulometer. The concentration of water was substantially higher in the solvents irradiated with the low dose rate.

Results C5-BTBP

Solvents containing C5-BTBP are ageing, i.e. they are to a certain extent degrading with time and the extraction is affected. Figure 2-21 shows how the D_{Am} changed when the solvents containing C5-BTBP were left to age for around 5 months. The extraction decreases for both solvents, but to a larger extent when cyclohexanone is used as diluent. No clear increase of any of the possible degradation products suggested below could be seen in the MS-spectra of the aged samples compared to the fresh solution. Therefore it is likely to assume that these molecules are in one way or the other an effect of the irradiation, or of the combination of irradiation and ageing.

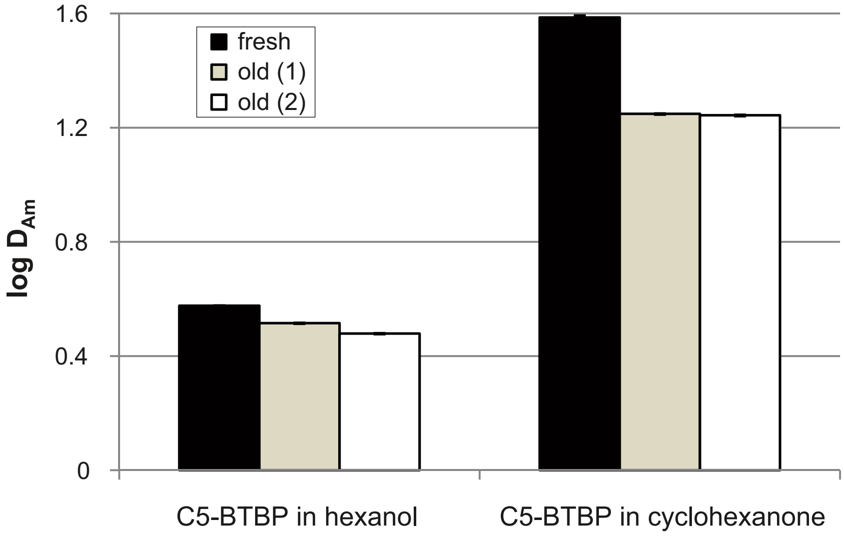
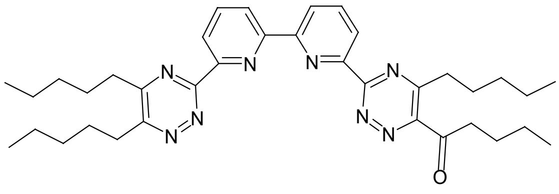
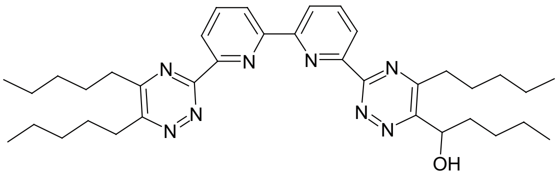
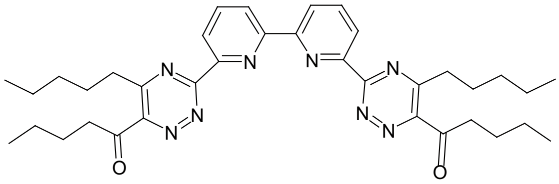
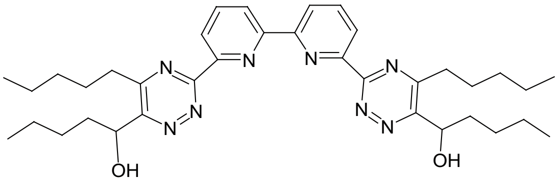


Figure 2-21. *Extraction of americium by two different solvents containing C5-BTBP.The label fresh refers to a newly prepared solution while old refers to solutions that had been left for around five months. The concentration of C5-BTBP was 0.005 M and the aqueous phase in the extraction experiments contained 0.01 M* HNO_3*, 0.99 M* $NaNO_3$ *and trace amounts of* ^{241}Am *and* ^{152}Eu*.*

The oxidized C5-BTBP molecules that were observed in the solvents (both hexanol and cyclohexanone as diluent) had the m/z ratios 609.5, 611.5, 623.5 and 627.5 and these probably correspond to the molecules listed in Table 2-1.

In Figure 2-22 and 2-23 the ratio between the oxygen containing molecules and the original molecule (C5-BTBP) is plotted against the dose received by the irradiated solvent consisting of 0.005 M C5-BTBP in hexanol. The top figure (2-22) shows the result when the low dose rate is used and the bottom figure (2-23) show the result with the high dose rate. With both dose rates the ratios are increasing with increasing dose, but the curves are much steeper and reach much higher values with the low dose rate.

Table 2-1. Suggested structure of four oxidized forms of the original molecule C5-BTBP.

 m/z = 609.5	 m/z = 611.5
 m/z = 623.5	 m/z = 627.5

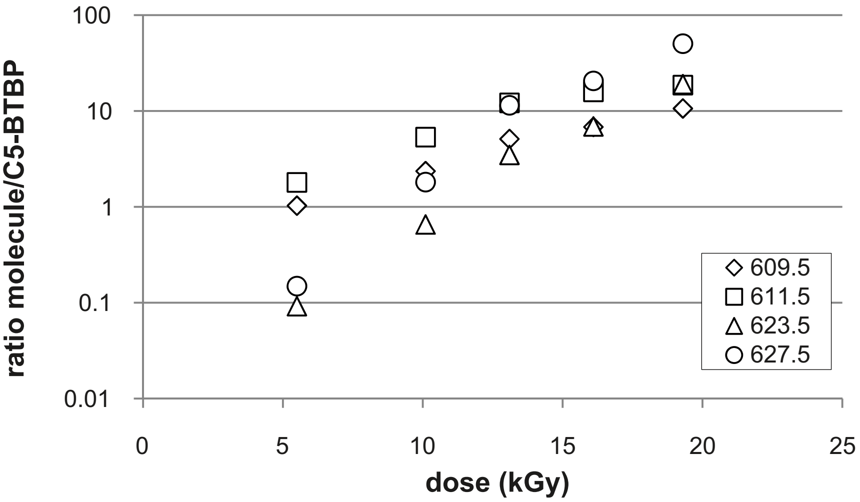


Figure 2-22. *APCI-MS measurements on solvents containing 0.005 M C5-BTBP in hexanol and irradiated with the low dose rate. The ratio is calculated by comparing the intensity of the molecule in question with the intensity of the original molecule, C5-BTBP (M). The label 609.5 m/z corresponds to M=O, 611.5 m/z corresponds to M-OH, 623.5 m/z corresponds to* $M(=O)_2$ *and 627.5 m/z corresponds to* $M(-OH)_2$.

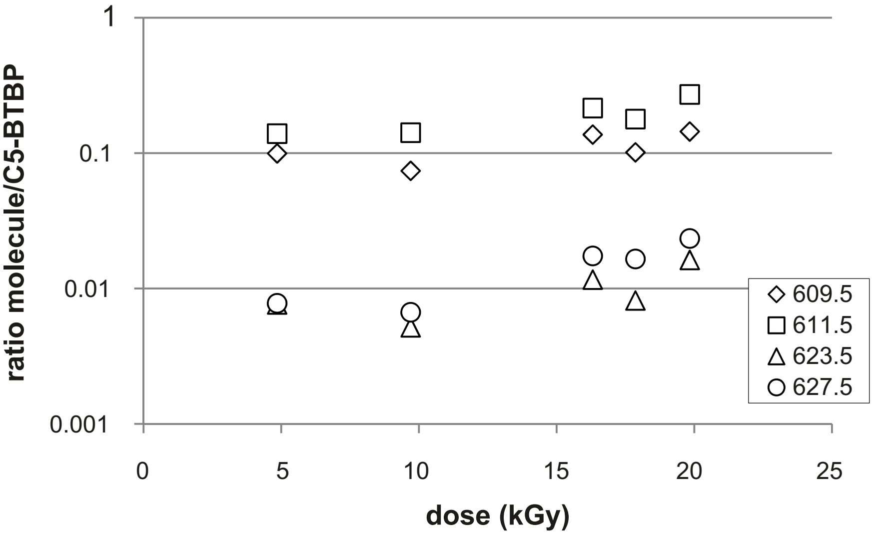


Figure 2-23. *APCI-MS measurements on solvents containing 0.005 M C5-BTBP in hexanol and irradiated with the high dose rate. The ratio is calculated by comparing the intensity of the molecule in question with the intensity of the original molecule, C5-BTBP (M). The label 609.5 m/z corresponds to M=O, 611.5 m/z corresponds to M-OH, 623.5 m/z corresponds to* $M(=O)_2$ *and 627.5 m/z corresponds to* $M(-OH)_2$.

It was reported above that when a solvent comprising C5-BTBP dissolved in cyclohexanone instead of hexanol, the extraction of americium does not decrease to the same extent. When it comes to the content of oxygen containing species in an irradiated solvent a similar behaviour regarding the difference between the two diluents was observed. Figure 2-17 shows the ratio between the oxygen containing molecules and the original molecule as a function of the received dose (low dose rate) for a solvent consisting of 0.005 M C5-BTBP in cyclohexanone. By comparing Figure 2-22 and Figure 2-24 it can be seen that the presence of oxygen containing compounds appears to be smaller when cyclohexanone is used as diluent instead of hexanol.

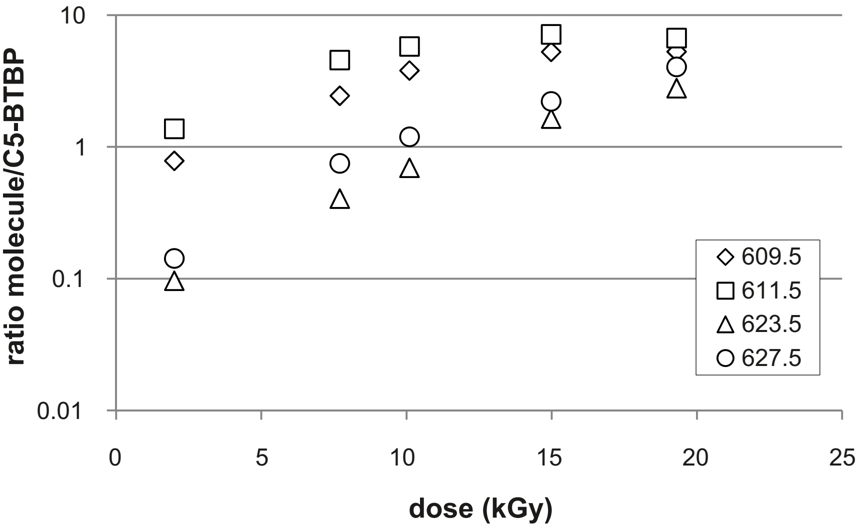


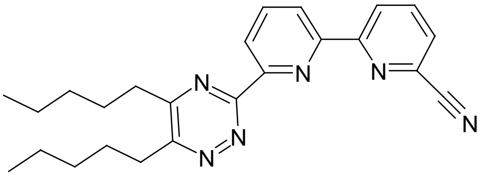
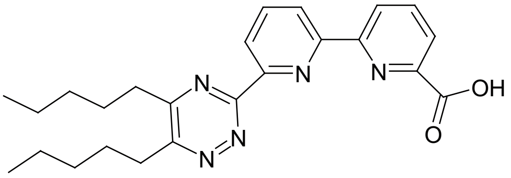
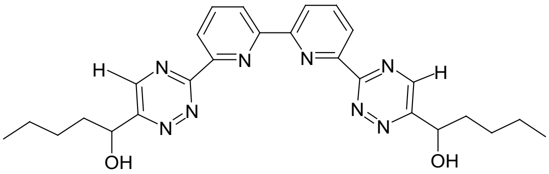
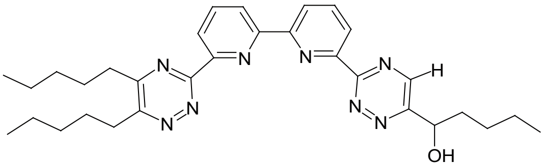
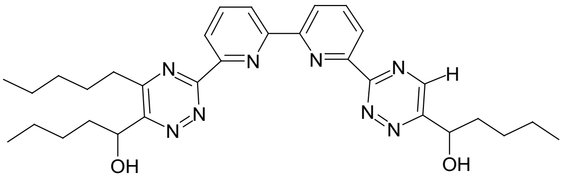
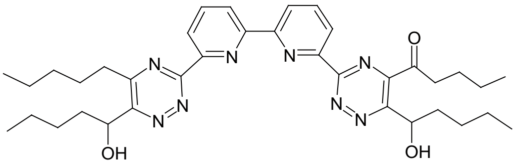
Figure 2-24. *APCI-MS measurements on solvents containing 0.005 M C5-BTBP in cyclohexanone and irradiated with the low dose rate. The ratio is calculated by comparing the intensity of the molecule in question with the intensity of the original molecule, C5-BTBP (M). The label 609.5 m/z corresponds to M=O, 611.5 m/z corresponds to M-OH, 623.5 m/z corresponds to* $M(=O)_2$ *and 627.5 m/z corresponds to* $M(-OH)_2$*.*

(The solubility of oxygen (solute mole fraction, χ) is 70.6 10^{-5} for 1-hexanol and 64.1 10^{-5} for cyclohexanone /7/.)The increase with increasing dose is still obvious but not the same extent as in Figure 2-22. APCI-MS data for C5-BTBP in cyclohexanone irradiated with the high dose rate was very limited, but a comparison of the solvents that received the highest dose with both dose rates clearly indicates the same pattern as above, i.e. the solvent irradiated with the low dose rate shows much higher ratios. The ratios at ca 20 kGy with the high dose rate were 0.96 (m/z = 609.5), 1.04 (m/z = 611.5), 0.26 (m/z = 623.5) and 0.13 (m/z = 627.5).

In addition to the species discussed above other potential degradation products were also observed. Possible chemical structures were suggested and they are presented in Table 2-2. Molecule 1 is probably formed by a break in one of the triazine rings, and number 2 results from oxidation of this molecule. If one C5-chain is cut off and oxygen is added to one of the other C5-chains, then molecule 4 can be formed. If yet another oxygen is added to a C5-chain the resulting molecule formed can be number 5. Molecule 3 can be formed if a C5-chainis cut off from molecule 5. Molecule 6 is formed if an oxidized C5-chain is added to molecule 5. One peak, a +1 charged molecule with the m/z ratio 579.4, was identified as a possible degradation product but the no structure has yet been proposed.

In C5-BTBP in hexanol irradiated with the low dose rate all suggested degradation products were observed and their ratio was clearly increasing with increased dose. This is illustrated in Figure 2-25 where the ratio molecule/C5-BTBP is plotted as a function of the received dose. The corresponding figure for C5-BTBP in cyclohexanone (Figure 2-26) shows that the ratios are much lower in this diluent, and the increase with dose is not as clear. As a matter of fact, the ratio for the molecule with m/z = 401.4 is decreasing with increased dose, opposite to the behaviour when hexanol is the diluent. The mutual order of the different molecules is more or less the same for the two diluents though. Molecules 4 and 5 show the highest ratios in both diluents. Both of them contain oxygen and are very similar to the oxidized molecules with m/z = 611.5 and 627.5 that was discussed above, just with the cut-off of a C5-chain. The suggestion above that the added oxygen contributes to the decrease in $SF_{Am/Eu}$ may thus apply on these potential degradation products as well.

Table 2-2. Additional possible degradation products from irradiated solvents comprising 0.005 M C5-BTBP in either hexanol or cyclohexanone. The irradiated solvents were diluted with CH_3CN/H_2O (1:1) and then measured with ESI- and/or APCI-MS. The measurements were recorded in positive ionization mode.

 1.m/z = 401.4	 2.m/z = 417.4
 3. m/z = 487.3	 4. m/z = 541.5
 5. m/z = 557.5	 6. m/z = 641.5

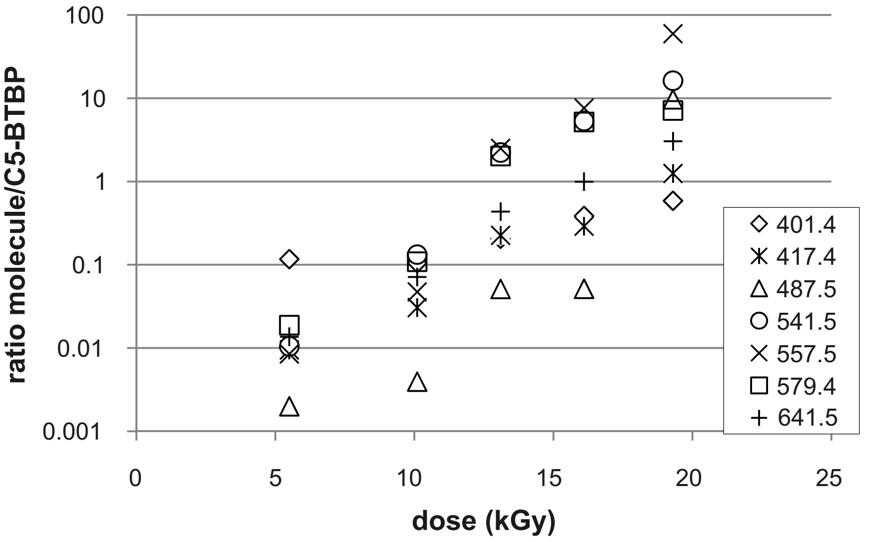


Figure 2-25. *APCI-MS measurements on solvents containing 0.005 M C5-BTBP in hexanol and irradiated with the low dose rate. The ratio is calculated by comparing the intensity of the molecule in question with the intensity of the original molecule, C5-BTBP (M). The potential degradation products, in the figure labelled with their m/z ratio, are illustrated in Table 2-2.*

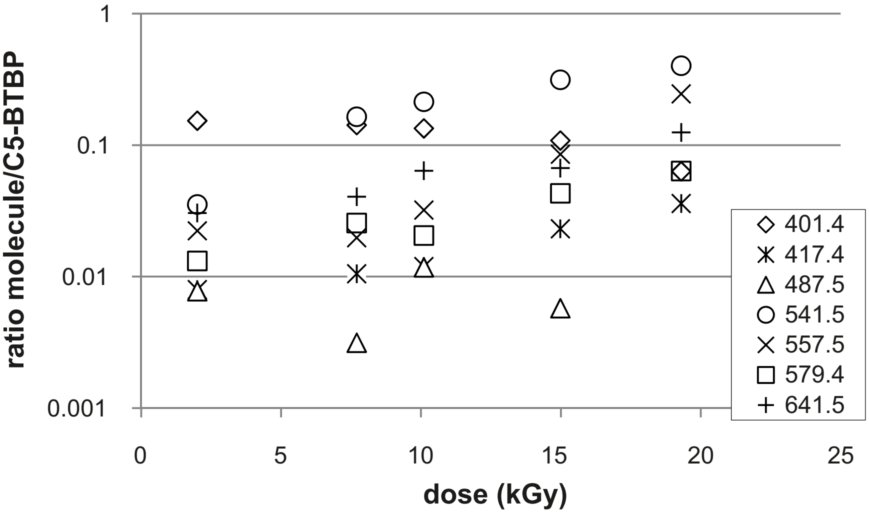


Figure 2-26. *APCI-MS measurements on solvents containing 0.005 M C5-BTBP in cyclohexanone and irradiated with the low dose rate. The ratio is calculated by comparing the intensity of the molecule in question with the intensity of the original molecule, C5-BTBP (M). The potential degradation products, in the figure labelled with their m/z ratio, are illustrated in Table 2-2.*

For the solvents irradiated with the high dose rate, MS-measurements were only available for the solutions with hexanol as diluent. Figure 2-27 shows the ratio of possible degradation products as a function of the dose (high dose rate) and the intensities are much lower than when the solvent was irradiated with the lower dose rate, and the increase with dose is not clear. The only ratios that clearly seem to be increasing are for the degradation products with m/z = 541.5 and 641.5.

C5-BTBP irradiated alone, i.e. not in a diluent, was dissolved in acetone and then diluted with CH_3CN/H_2O (1:1). The sample was measured with both ESI-MS and APCI-MS to see which, if any, of the molecules discussed above that was present in the pure irradiated C5-BTBP. It had received 20 kGy, same as the highest dose given to the solvents. Most of the peaks from the different molecules could be found in the spectra, but with very low intensities, indicating that the formation of degradation products was to the largest extent caused by the radiolysis of the diluent, and the species formed in these reactions.

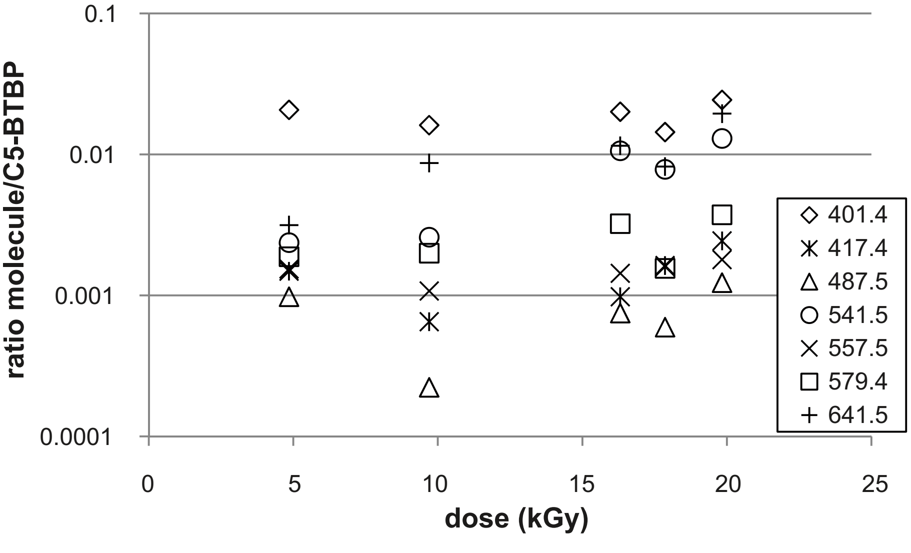


Figure 2-27. *APCI-MS measurements on solvents containing 0.005 M C5-BTBP in hexanol and irradiated with the high dose rate. The ratio is calculated by comparing the intensity of the molecule in question with the intensity of the original molecule, C5-BTBP (M). The potential degradation products, in the figure labelled with their m/z ratio, are illustrated in Table 2-2.*

Results CyMe$_4$-BTBP

Contrary to solvents containing C5-BTBP, solvents with CyMe$_4$-BTBP show an increase in distribution ratio of Am and Eu with increased dose. This behaviour makes the identification of degradation products even more interesting and useful, since information about molecules that extract metals efficiently may be very useful for future synthesis of new extracting molecules. However, the data from ESI-MS and APCI-MS measurements did not give as much information as it did for C5-BTBP. The cyclic structure of the side groups in CyMe$_4$-BTBP prevents the formation of oxygen containing molecules corresponding to the ones described above for C5-BTBP. Another factor that differentiates from C5-BTBP is that solvents containing CyMe$_4$-BTBP are much more stable in time. No change in extracting capacity has been observed for CyMe$_4$-BTBP in hexanol and in cyclohexanone even after six months.

Two possible degradation products were identified using APCI-MS and their suggested structural formulas are illustrated in Table 2-3. If the trap drive was lowered from 50 to 30 these molecules could also be observed in the ESI-MS spectra. A lower trap drive means that the intensities of molecules with low *m/z* ratio are strengthened. With the lower trap drive an additional molecule could be observed in all solutions, with an *m/z* ratio of 346.35. It was not seen in irradiated pure cyclohexanone, thus it probably derives from the CyMe$_4$-BTBP.

APCI-MS measurements indicate that the presence of the two molecules above increases somewhat with increased dose in both diluents. Table 2-4 gives the ratio between the intensity of the possible degradation product and the intensity of the original CyMe$_4$-BTBP molecule for both non irradiated solvents and for the most irradiated ones (with both low and high dose rate).

MS-measurements on CyMe$_4$-BTBP irradiated in its solid form, i.e. not dissolved in a diluent were also done. A sample that had received 19.9 kGy was dissolved in acetone and then diluted with CH_3CN/H_2O (1:1). APCI-MS indicated a small presence of 371- and 389-molecules, but at ratio levels comparable to the non irradiated solutions in Table 2-4. Thus, the degradation of the molecule is higher if it is dissolved in a diluent during irradiation. This behaviour seems to be the same for C5-BTBP and CyMe$_4$-BTBP.

Table 2-3. Possible degradation products formed from CyMe$_4$-BTBP.

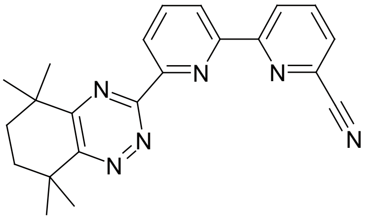
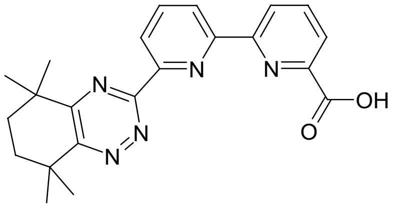
 m/z = 371	 m/z = 389

Table 2-4. Intensity ratio between possible degradation product and CyMe$_4$-BTBP in two different diluents and either non irradiated or exposed to ca 20 kGy. Intensities from APCI-MS measurements.

	Dose (kGy)	371/CyMe$_4$-ratio	389/CyMe$_4$-ratio
CyMe$_4$-BTBP in hexanol	0	0.0077	0.0064
CyMe$_4$-BTBP in hexanol	19.3 (low rate)	0.0165	0.0157
CyMe$_4$-BTBP in hexanol	20.2 (high rate)	0.0125	0.0130
CyMe$_4$-BTBP in cyclohexanone	0	0.0078	0.0059
CyMe$_4$-BTBP in cyclohexanone	19.3 (low rate)	0.0171	0.0199
CyMe$_4$-BTBP in cyclohexanone	22.0 (high rate)	0.0208	0.0213

2.4.1 Water content

Since many of the degradation products contain oxygen it was of interest to establish the water concentration in the different organic phases and this was done using Karl Fisher Coulometer measurements. Three measurements per sample were done. The syringe was weighed before and after each addition of sample to the solution. This way the exact mass of the measured sample could be calculated. It worked smoothly for the solutions in which hexanol was used as diluent, but for samples with cyclohexanone the device could not measure, probably because too high water solubility in cyclohexanone. The cyclohexanone samples were then diluted with hexanol to enable analysis. The dilution gave rise to large uncertainties; hence the data for the solvents with cyclohexanone as diluent are not very reliable.

The coulometer gives the water content as µg (µg/sample), and by knowing the weight of the sample a value of µg water/mg sample could be calculated. To get the molar concentration the density of the solutions was determined. The concentration of water in pure hexanol was 0.05 M and in cyclohexanone 0.265 M.

Figure 2-28 to 2-31 illustrates the change in water content with increased dose for the two dose rates for each of the four solvents.

For all four solvents the trend is similar: the water content is increasing with increased dose (and increased time of irradiation) and the content in the low dose rate samples is much higher than in the high dose rate samples. When the solvents are being irradiated they are kept in a glass bottle with a plastic lid that is just loosely screwed on, in order to allow for equalization of potential over pressure. This is theoretically a source of fresh air/oxygen and whether or not this “exposure” to air affects the water content in the organic solvents is being investigated. 10 glass bottles containing pure cyclohexanone and 10 bottles containing pure hexanol are left with the lid loosely on. After various periods of time the lids are screwed on tightly and the water content in the different samples will be measured.

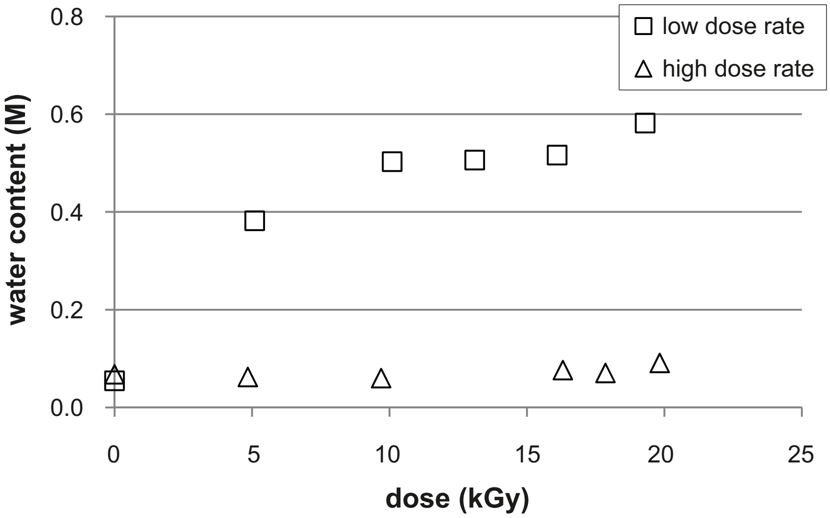


Figure 2-28. *Water content as a function of the dose in a solvent containing 0.005 M C5-BTBP in hexanol, irradiated with two different dose rates.*

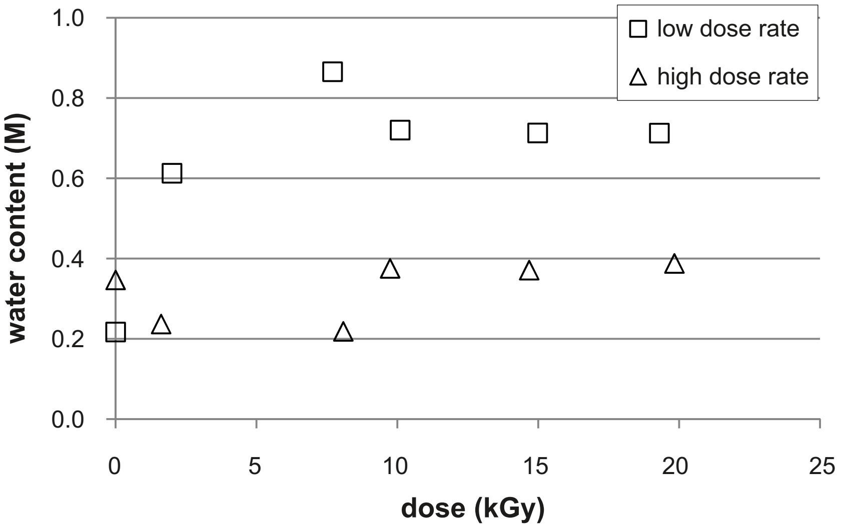


Figure 2-29. *Water content as a function of the dose in a solvent containing 0.005 M C5-BTBP in cyclohexanone, irradiated with two different dose rates.*

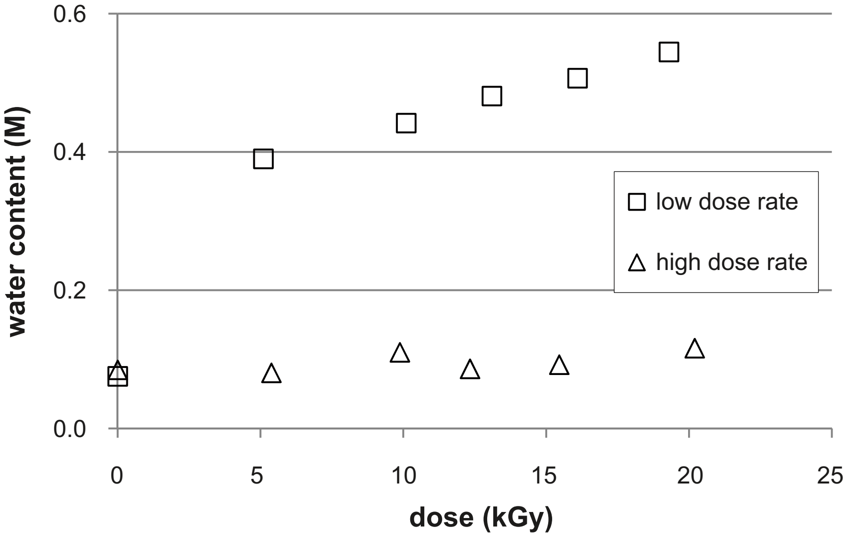


Figure 2-30. *Water content as a function of the dose in a solvent containing 0.005 M CyMe$_4$-BTBP in hexanol, irradiated with two different dose rates.*

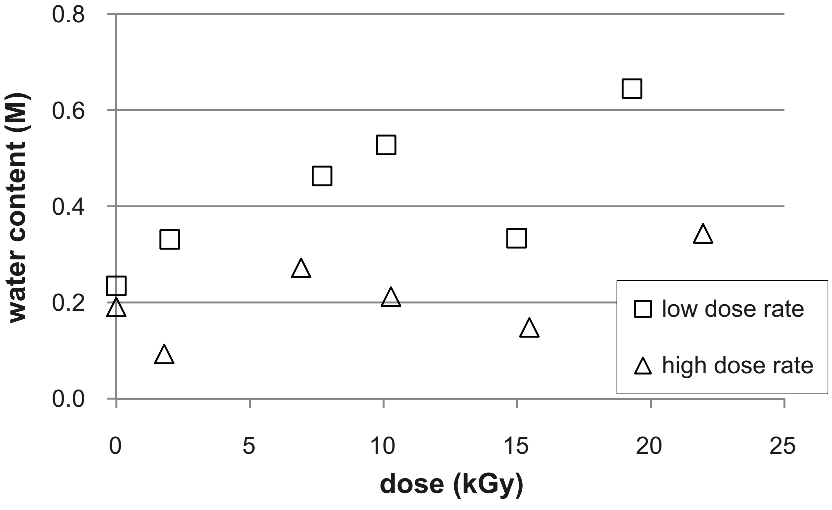


Figure 2-31. *Water content as a function of the dose in a solvent containing 0.005 M CyMe$_4$-BTBP in cyclohexanone, irradiated with two different dose rates.*

Conclusion

Many oxidized molecules and other possible degradation products were observed for C5-BTBP solutions and many of them show a clear increase with increasing dose. The effect was most obvious when the diluent was hexanol and the solvent was irradiated with the low dose rate.
It was clear that the presence of oxygen containing species was high, especially in the samples irradiated with the low dose rate, hence during a much longer time than corresponding samples irradiated with the high dose rate. Thus, it appears that the total time of irradiation has a decisive influence on the degree of degradation and change in extracting capacity.

For CyMe$_4$-BTBP the oxidized forms of the molecule were not observed, probably due to the ring structure of the side groups. The number of other degradation products observed was much lower for CyMe$_4$-BTBP than for C5-BTBP, and the intensity of the few species observed was much weaker. But considering that solvents containing CyMe$_4$-BTBP do not loose/decrease their extracting capacity when they are being irradiated, this was expected.

For both the BTBP-molecules, there is no apparent difference in the structure of potential degradation products when altering the diluent (this study only includes hexanol and cyclohexanone). But there is a difference if the molecule is irradiated in its dissolved form or in its solid form. The presence of various degradation products is higher if the BTBP is dissolved before irradiation.

3 Investigations of a novel GANEX system

A novel GANEX system for liquid-liquid extraction in connection to separation for transmutation is being investigated but due to a pending patent nothing can yet be published regarding the work.

4 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.

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.

4.1 A comparative study of C2-BTBP and MF1-BTBP

C2-BTBP and MF1-BTBP are two similar molecules (see Figure 1-6 and 1-7) where the only difference is the addition of a tert-butyl attached to the initial C2-BTBP molecule to achieve MF1-BTBP. The addition has been meant to increase the solubility of the initial molecule in the organic phase. A series of experiments have been carried out in order to assess the properties of the new molecule in comparison with the initial one, like dissolution and extraction experiments with different diluents, kinetics and ligand concentration dependence in order to establish the stoechiometry of the new system.

The experiments were carried out in duplicate samples according to the standard extraction experiment procedure. All phases were pre-equilibrated and the samples were analyzed with HPGe2.

4.1.1 Different diluents

As mentioned above the addition of a tert-butyl group in MF1-BTBP increases the lipophilicity compared to C2-BTBP and hence the dissolution in organic diluents is facilitated. Seven diluents were tested in terms of dissolution capability: cyclohexanone, alcohols (hexanol to decanol) and also hexanol with an addition of 10 vol% nitrobenzene. MF1-BTBP dissolved in all diluents (0.01 M) but required some heat and ultrasound. The dissolution was much faster in cyclohexanone and the hexanol/nitrobenzene mixture than in the alcohols. C2-BTBP dissolved in cyclohexanone (0.01 M) but not good enough in the alcohols (< 0.005 M). When 10 vol% nitrobenzene was added to the hexanol it was possible to dissolve also this ligand (0.01 M).

The extraction of Am(III) and Eu(III) by MF1-BTBP in the different long chain alcohols (C6–C10) showed an increase in $SF_{Am/Eu}$ with the length of the carbon chain. The result is shown in Figure 4-1 where D_{Am}, D_{Eu} and $SF_{Am/Eu}$ are plotted for the five different alcohols, (C6: hexanol, C7: heptanol, C8: octanol, C9: nonanol and C10: decanol). It looks as if the extraction of Am is increasing with chain length while the extraction of Eu seems to slightly decrease.

4.1.2 Kinetics

Extraction kinetics experiments were performed for four of the solvents (cyclohexanone, octanol, hexanol and hexanol + 10 vol% nitrobenzene) containing MF1-BTBP and two of the solvents (cyclohexanone and hexanol + 10 vol% nitrobenzene) containing C2-BTBP. The aqueous phase contained 1 M HNO_3 and traces of ^{241}Am or ^{152}Eu. Double samples were used in all experiments.

Figure 4-2 illustrates that both ligands showed fast kinetics for Am and Eu extraction when the diluent was cyclohexanone and equilibrium was reached in about 2 minutes for MF1-BTBP and after 5 minutes for C2-BTBP (manual shaking). The ligand concentration in these experiments was 0.01 M. D_{Am} was 80 for MF1-BTBP and 12 for C2-BTBP and the corresponding D_{Eu} values were 0.6 and 0.15.

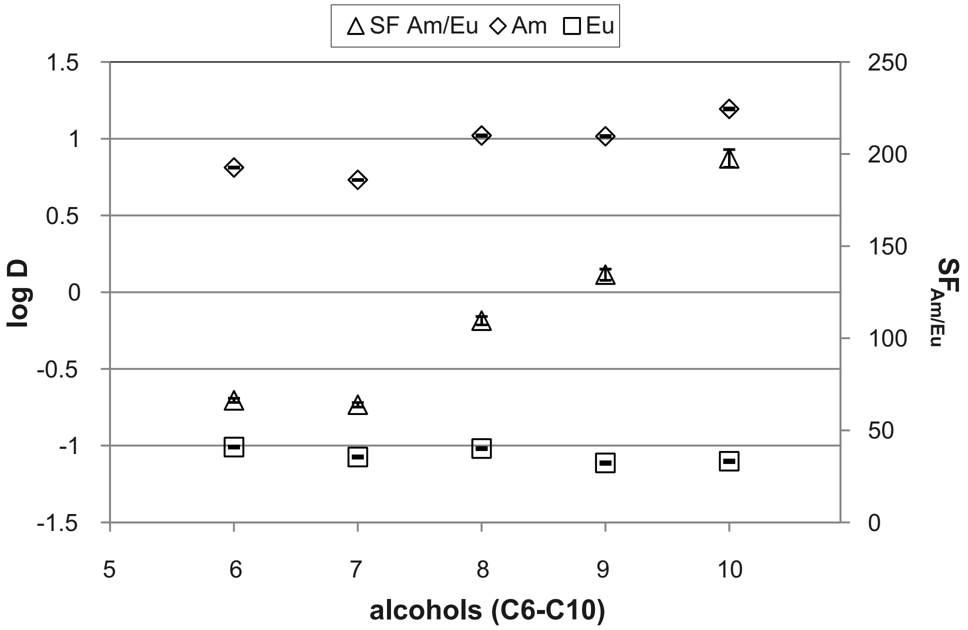


Figure 4-1. Extraction of Am(III) and Eu(III) by MF1-BTBP in different long chain alcohols (C6–C10), distribution ratios as a function of length of the carbon chain of the alcohol. Organic phase, 0.01 M MF1-BTBP in the alcohol. Aqueous phase1 M HNO_3 spiked with trace amounts of ^{152}Eu and ^{241}Am. T = (20 ± 1) °C.

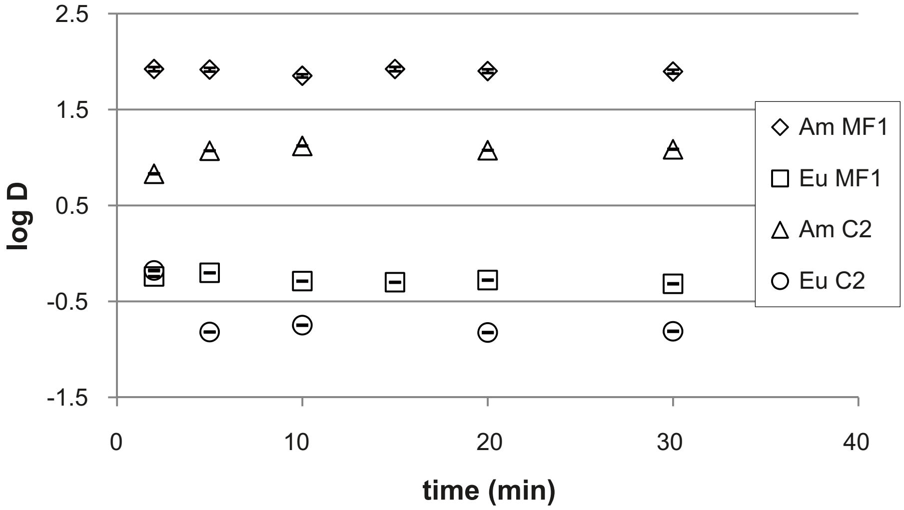


Figure 4-2. Extraction of Am(III) and Eu(III) by C2-BTBP and MF1-BTBP in cyclohexanone, distribution ratios as a function of contacting time. Organic phase, 0.01 M ligand in cyclohexanone. Aqueous phase, 1 M HNO_3 spiked with trace amounts of ^{152}Eu and ^{241}Am. T = (20 ± 1) °C.

MF1-BTBP was the only ligand that was soluble in the alcohols. The extraction kinetics was much slower in alcohols compared to in cyclohexanone. In both octanol and hexanol, the equilibrium for americium had not been reached after 15 minutes of manual shaking (see Figure 4-3).

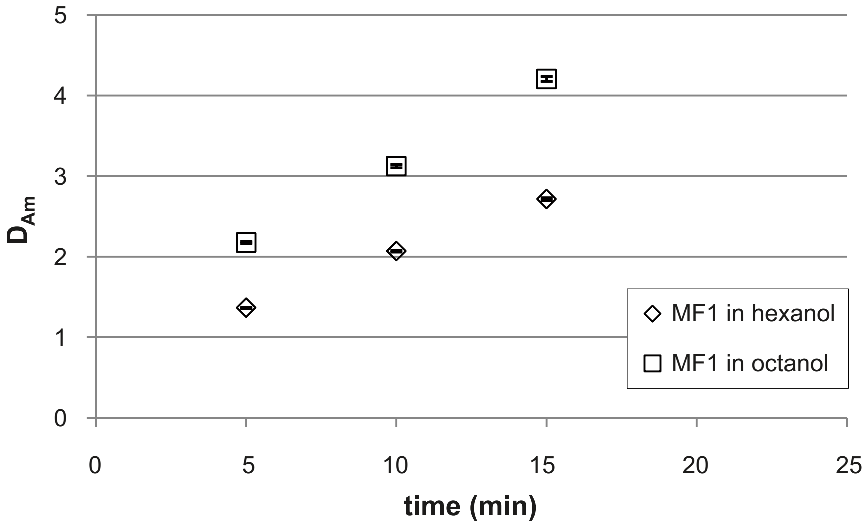


Figure 4-3. *Extraction of americium as a function of contact time for two different solvents containing 0.005 M MF1-BTBP in octanol and hexanol, respectively. The aqueous phase contained 1 M* HNO_3 *and traces of* ^{241}*Am. Samples measured in NaI(Tl) detector. Uncertainties were calculated using error propagation based on measurement statistics.*

When 10 vol% nitrobenzene was added to hexanol both ligands were soluble (up to 0.01 M of BTBP was tested) but the kinetic behavior differed between them in the case of Am. The kinetics for Eu was however the same. The solvent containing C2-BTBP had reached equilibrium after 5 minutes for both Am and Eu. MF1-BTBP on the other hand, seemed to have a slow kinetics regarding the Am extraction. Equilibrium was reached after 5 minutes for Eu but the extraction of Am was still increasing after 20 minutes. Figure 4-4 shows the extraction of Am and Eu by the two ligands as a function of contact time when hexanol/nitrobenzene is used as diluent. A difference in extraction kinetics for Am and Eu has been observed before /4/ but the reason for this has not yet been established.

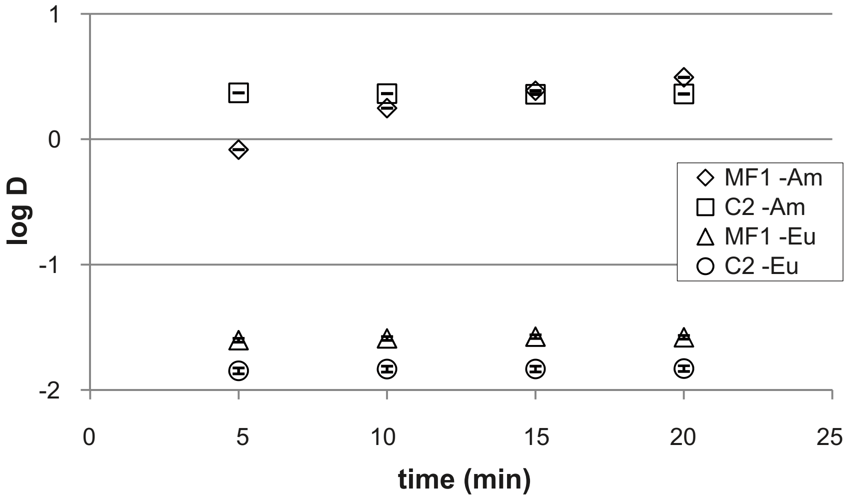


Figure 4-4. *Extraction of americium and europium (log D) as a function of contact time for two different solvents containing 0.005 M MF1-BTBP or C2-BTBP in hexanol/nitrobenzene (10 vol%). The aqueous phase contained 1 M* HNO_3 *and traces of* ^{241}*Am or* ^{152}*Eu. Samples measured in NaI(Tl) detector. Uncertainties were calculated using error propagation based on measurement statistics.*

4.1.3 Concentration dependence

The extraction of Am(III) and Eu(III) as a function of concentration of the two ligands in cyclohexanone showed slightly different trends than expected. Figure 4-5 shows the log D vs. log [ligand] for C2-BTBP and MF1-BTBP in cyclohexanone.

Two important differences between the C2-BTBP and MF1-BTBP molecule were noticed, one connected to the slope analysis and another one connected to the $SF_{Am/Eu}$ for the systems. The slope analysis for C2-BTBP gave a value of 1.53 for Am(III) while for MF1-BTBP it was 1.98. The slope for Eu(III) was 1.29 for C2-BTBP and 1.74 for MF1-BTBP.

The separation factor for C2-BTBP was almost twice as high as the separation factor for MF1-BTBP: around 160 and 80, respectively.

4.2 A comparative study of $CyMe_4$-BTBP and MF2-BTBP

As previously presented in the case of C2-BTBP and MF1-BTBP, $CyMe_4$-BTBP and MF2-BTBP are two molecules with similar structures (see Figure 1-4 and 1-5) where the only difference is the addition of a tert-butyl attached to the initial $CyMe_4$-BTBP molecule to achieve MF2-BTBP. This is done for the same reason as with MF1, to increase the lipophilicity.

4.2.1 Different diluents

The extraction of Am(III) and Eu(III) with organic systems containing $CyMe_4$-BTBP and MF2-BTBP dissolved in different long chain alcohols (C6-C10) is presented in Figure 4-6. As opposed to the problems described above when trying to dissolve C2-BTBP in various alcohols, both $CyMe_4$- and MF2-BTBP were dissolved in all diluents tested (cyclohexanone and alcohols (C6-C10)). Both D_{Am} and D_{Eu} are higher for $CyMe_4$-BTBP than for MF2-BTBP and the extraction seems to be decreasing with the number of carbons in the alcohol, except for the Am extraction by MF2-BTBP, which appears to have a minimum extraction for octanol. This can be compared to the behaviour observed for MF1-BTBP above, where the extraction of Am increased and the extraction of Eu decreased with alcohol chain length.

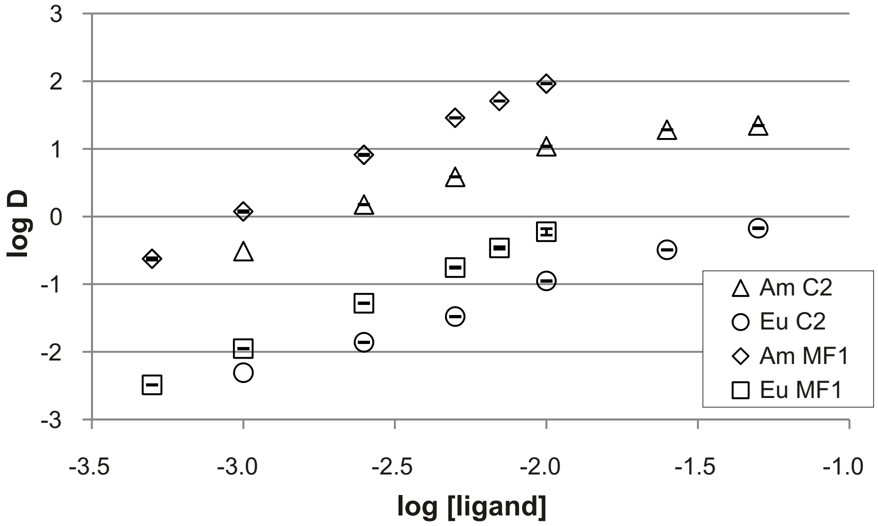


Figure 4-5. Extraction of Am (III) and Eu(III) by C2-BTBP and MF1-BTBP in cyclohexanone, distribution ratios as a function of different concentrations of the respective ligand. Organic phase, 0.01 M ligands in cyclohexanone. Aqueous phase 1 M HNO_3 *spiked with trace amounts of* ^{152}Eu *and* ^{241}Am. *T = (20 ± 1) °C.*

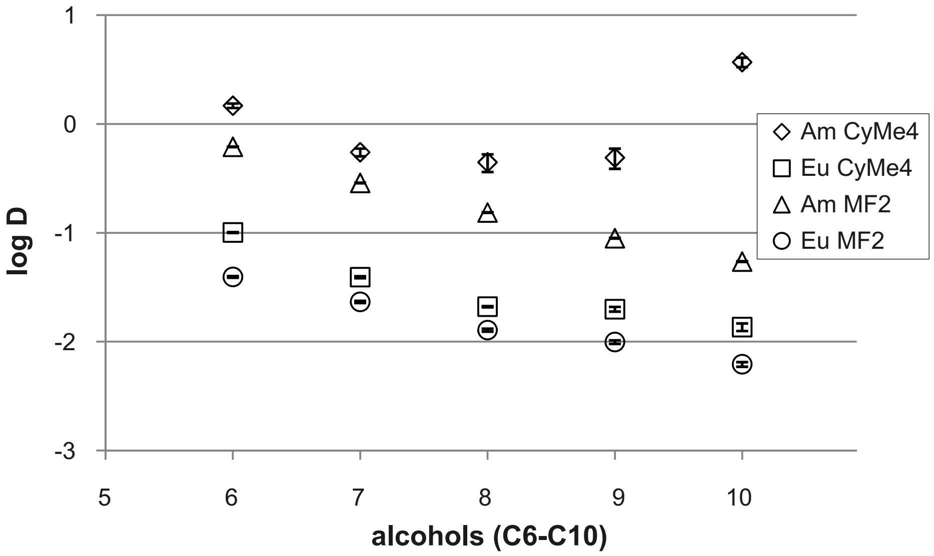


Figure 4-6. *Extraction of Am (III) and Eu(III) by CyMe$_4$-BTBP and MF2-BTBP in different long chain alcohols (C6: hexanol, C7: heptanol, C8: octanol, C9: nonanol, C10: decanol). Distribution ratios are plotted as a function of the number of carbons of the respective alcohol. Organic phase, 0.01 M ligands in the alcohol. Aqueous phase 1 M HNO$_3$ spiked with trace amounts of ^{152}Eu and ^{241}Am. T = (20 ± 1) °C.*

4.2.2 Kinetics

The kinetics of the system containing the MF2-BTBP in cyclohexanone showed to be slower than the corresponding system containing CyMe$_4$-BTBP. CyMe$_4$-BTBP had reached equilibrium already after 5 minutes while the extraction of both Am and Eu was still increasing after 20 minutes for MF2-BTBP.

In addition, both D_{Am} and D_{Eu} are higher for the system containing MF2-BTBP than for the system containing CyMe$_4$-BTBP. It can be observed that $SF_{Am/Eu}$ for the system containing MF2-BTBP is smaller than for the CyMe$_4$-BTBP containing system. The $SF_{Am/Eu}$ is around 130 for CyMe$_4$-BTBP while it is varying between 10 and 40 for MF2-BTBP.

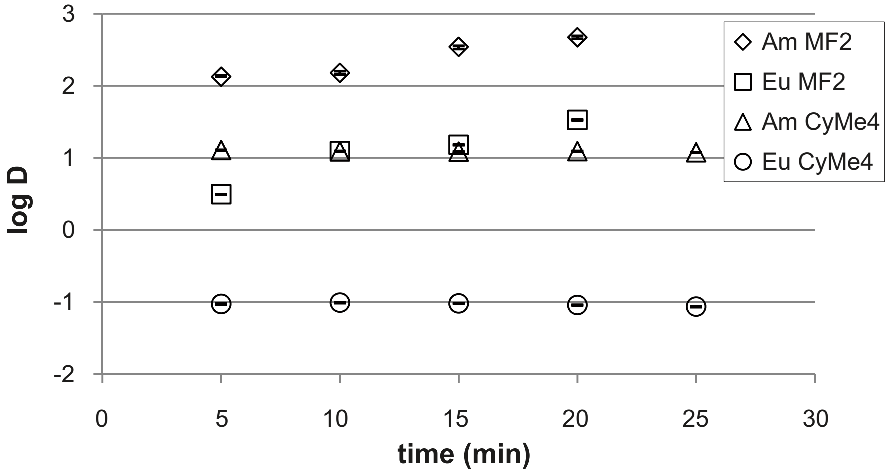


Figure 4-7. *Extraction of Am (III) and Eu(III) by CyMe$_4$-BTBP and MF2-BTBP in cyclohexanone, distribution ratios as a function of contacting time. Organic phase, 0.01 M ligands in cyclohexanone. Aqueous phase, 1 M HNO$_3$ spiked with trace amounts of ^{152}Eu and ^{241}Am. T = (20 ± 1) °C.*

4.2.3 Concentration dependence

Figure 4-8 shows log D vs. log [ligand] for $CyMe_4$- and MF2-BTBP in cyclohexanone. Due to the slow kinetics, the contact time for the MF2-BTBP experiments were 25 minutes For $CyMe_4$-BTBP the slope is 2.4 for Am and 1.75 for Eu, while for MF2-BTBP the corresponding values are 1.72 and 1.58.

The $SF_{Am/Eu}$ for $CyMe_4$-BTBP was higher than $SF_{Am/Eu}$ for MF2-BTBP at low ligand concentration and the opposite at higher ligand concentrations.

4.2.4 Conclusion

There are no simple explanations for the relatively big differences observed in the above described systems. The slight change in the molecular geometry seems to influence the extraction much more than expected. Further analysis and calculations are needed.

4.3 Solubility

As part of an ongoing investigation into the thermodynamics of the extraction of metals by BTBP reagents the thermodynamics of dissolution of $CyMe_4$-BTBP (and related compounds) in cyclohexanone was investigated. The solubility at a series of different temperatures was measured to permit the ΔH and ΔS of dissolution to be estimated. In this study we neglect the effect of the enthalpy and entropy of dilution. During the experiment the cyclohexanone/$CyMe_4$-BTBP system required an exceedingly long time to reach equilibrium and also the yellow crystals of the $CyMe_4$-BTBP fragmented. This fragmentation of the crystals suggested that some change to the crystal lattice was occurring. To investigate this, crystals of $CyMe_4$-BTBP was grown by slowly cooling a hot cyclohexanone solution and these crystals were supplied to Dr. Alex Slawin (St-Andrews, Scotland) for examination by single crystal X-ray diffraction. It was found that the crystals were of a cyclohexanone solvate. The crystal structure is similar to that of the methanol solvate determined by prof. M.G.B. Drew at Reading /5/, it is clear that the solid contains a series of one dimensional holes which can be filled with solvate molecules. In Figure 4-9 is shown a view of a unit cell (fragments which overlap between unit cells are shown in full) both with and without the cyclohexanone molecules present.

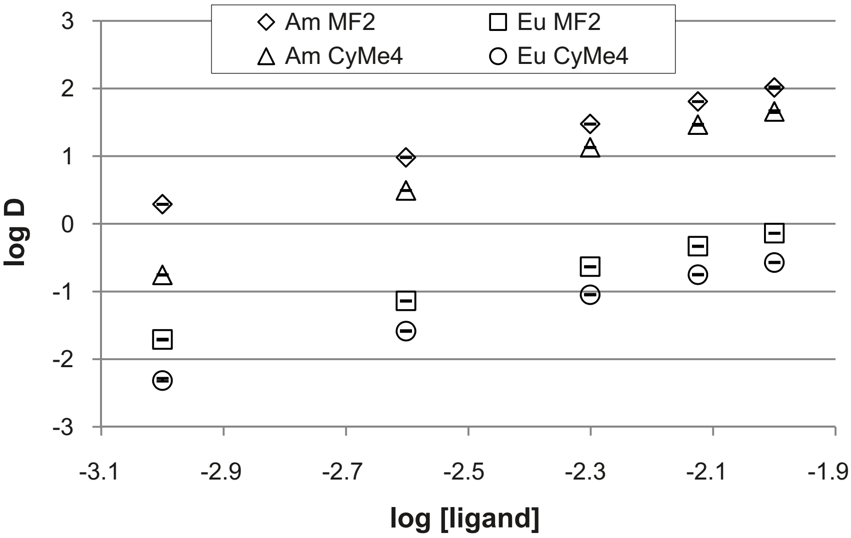


Figure 4-8. *Extraction of Am (III) and Eu(III) by $CyMe_4$-BTBP and MF2-BTBP in cyclohexanone, distribution ratios as a function of different concentrations of the respective ligand. Organic phase, 0.01 M ligands in cyclohexanone. Aqueous phase1 M HNO_3 spiked with trace amounts of ^{152}Eu and ^{241}Am. T = (20 ± 1) °C.*

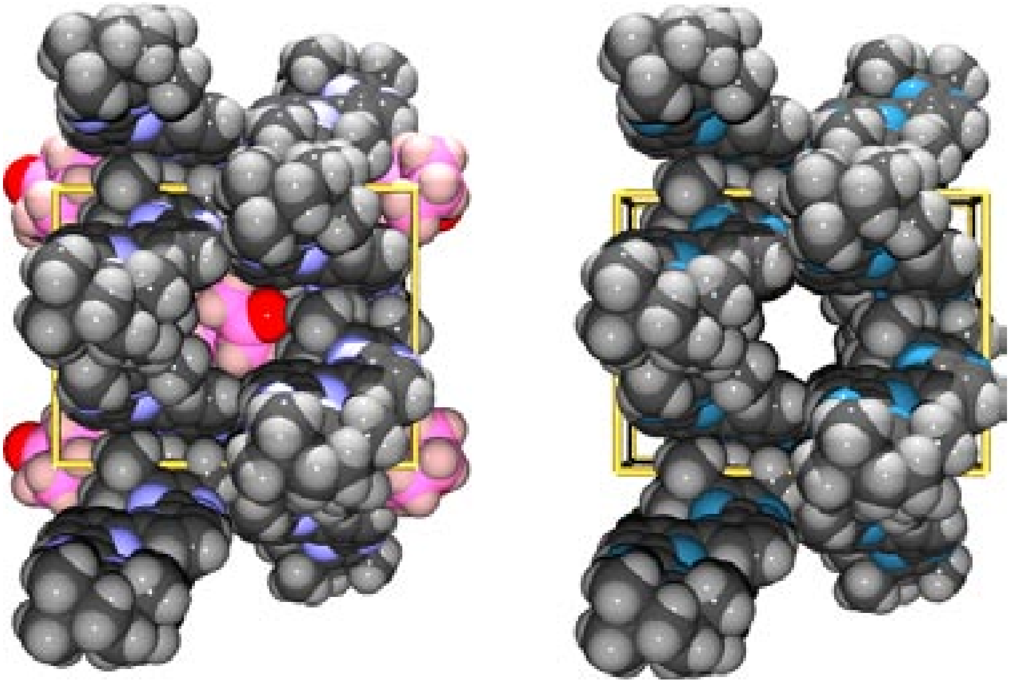


Figure 4-9. Crystallographic pictures of a unit cell of CyMe$_4$-BTBP, on the left the cyclohexanone molecules are shown in pink/red while on the right they are excluded to show the voids (fragments which overlap between unit cells are shown in full).

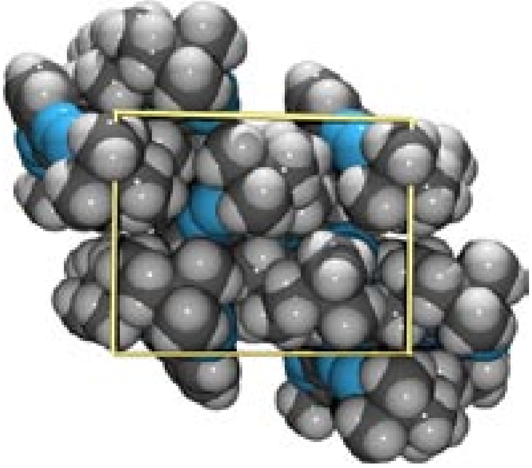


Figure 4-10. A view of a unit cell of CyMe$_4$-BTP (fragments which overlap between unit cells are shown in full).

The crystal structures of CyMe$_4$-BTP (see Figure 4-11 for molecular structure) and C2-BTBP were examined as well and no large voids were found in these structures, suggesting that of the three extractants considered (CyMe$_4$-BTP, C2-BTBP and CyMe$_4$-BTBP) only CyMe$_4$-BTBP is able to form solid crystalline solvates.

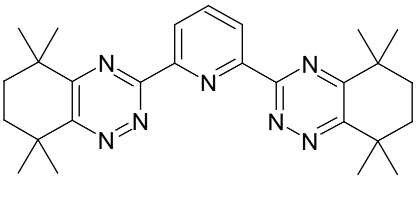


Figure 4-11. Molecular structure of CyMe$_4$-BTP.

4.4 Palladium

Spent nuclear fuel contains a large amount of palladium because it is a major fission product. While some of the palladium fails to dissolve when uranium dioxide fuel is treated with nitric acid the PUREX first cycle raffinate contains a substantial amount of palladium. Because Constable has reported that oligopyridines bind to palladium /1/ the binding of palladium to the BTBPs were considered.

During attempts to investigate the bonding of BTBP to palladium(II) in chloride free media it was noticed that cyclohexanone and octanol are both able to reduce the palladium to metallic palladium. It is likely that the octanol reacts with the palladium as a reducing agent since it is well known in platinum group chemistry that alcohols are able to reduce these metals (Ru, Rh, Pd, Os, Ir and Pt). As such reactions are promoted by the addition of a base, for example $[RuHCl(CO)(PPh_3)_3]$ it is stable in boiling methoxyethanol but when it is boiled in alcoholic sodium hydroxide it forms $[RuH_2(CO)(PPh_3)_3]$. Octanol and cyclohexanone were shaken with a solution of palladium nitrate in 1M nitric acid. The formation of black precipitates of metals in both cases indicates clearly that the mere presence of nitric acid is unable to inhibit these reactions.

The formation of the palladium black in the case of the ketone (cyclohexanone) was initially explained by the hypothesis that a chemical process related to the famous ethylene to ethanal conversion process (Wacker process /19/) was in operation. It was postulated that the enol form of cyclohexanone forms a complex with the palladium, which contains a π-bonded olefin similar to that present in Zeise's salt ($K[PtCl_3(C_2H_4)]$). The π-bonded cyclohexanone ligand in the complex would then undergo either nucleophilic attack at an olefin carbon to form a σ-bonded alkyl ligand or would rearrange into a σ-bonded enolate. Either reaction pathway would form a species able to rapidly undergo a β-hydride elimination. This β-hydride elimination will form zerovalent palladium, and this palladium is likely to form palladium nanoparticles, palladium colloids or macroscopic metallic particles. As a test of this hypothesis a solution of palladium nitrate in dilute nitric acid was shaken with fenchone, this ketone was chosen because it is unable to assume an enol form. While initially the ketone appeared to be inert to the palladium nitrate solution, when left to stand palladium metal was seen to slowly form. Because of this observation we concluded that both enolisable and non-enoliseable aliphatic ketones were formed under conditions similar to those found in a nitrate based aqueous nuclear fuel reprocessing process. The reaction of fenchone with palladium nitrate has been rationalized by the fact that platinum group metals are able to activate alkyl C-H bonds, for example rhodium can react with 6-*tert*-butyl-2,2'-bipyridine to form a rhodium alkyl /22/.

4.4.1 Suppression by methionine

A key step in the rapid formation of the palladium metal using octanol or cyclohexanone is likely to be a β-hydride elimination. This reaction requires the availability of a vacant coordination site on the palladium. Thus, the addition of ligands which would inhibit this reaction (and the extraction of palladium by cyclohexanone) by preventing the appearance of a vacant site on the palladium was considered. The blocking of coordination sites with a ligand is also likely to prevent activation of C-H bonds which is likely to occur by oxidative addition (increases both the coordination number and the valence electron number for the metal centre).

The use of thiourea, as this is known to bind to the platinum group metals, was initially considered but when a solution of palladium nitrate in nitric acid is left in contact with an aqueous solution of thiourea a red crystalline solid is formed. Such a solid might have the potential to disturb an industrial process. From the work on platinum based cancer chemotherapy it is well known that *cis*-platin (*cis*-$[PtCl_2(NH_3)_2]$) reacts with methionine to form water soluble complexes which have been found in the urine of humans being treated with this drug /2/. Because a great deal of palladium chemistry can be reproduced with platinum (and *vice versa*) the knowledge from cancer chemotherapy was applied to the palladium problem. Therefore thiourea was rejected in favor of the amino acid methionine.

In an initial test it was found that acidic palladium nitrate solution on treatment with methionine forms a pale yellow solution which appears to be less able to form a precipitate. Without methionine mixtures of dilute nitric acid, palladium nitrate and cyclohexanone formed palladium metal within minutes. Both homogenous and biphasic systems were tested. It was found that within less than 24 hours a solution of cyclohexanone in water was able to precipitate more than 99% of the palladium. However, if methionine was present then all the palladium remained in the aqueous solution. Likewise when a biphasic mixture of dilute nitric acid and cyclohexanone was left for 20 hours the majority (>99.5%) of the palladium was precipitated as palladium black while if methionine was added the palladium remained in solution. The analyses were made with ICP-OES.

As stated earlier it can clearly be seen in Figure 4-12 that without the presence of methionine, palladium precipitates rather quickly in the presence of cyclohexanone. With a small addition of methionine a slight decrease in precipitation can be observed and with a large addition of methionine the system is kept stable (observed for more than one week).

4.4.2 Pre extraction with dioctyl sulfide

Another way to try to solve the problem with formation of metallic palladium and the extraction of the same with BTBPs is to extract palladium in another extraction cycle. This other cycle will precede the extraction that aims to partition the radioactive waste, using an organic solvent and/or extractant that does not initiate the formation of palladium black.

There are some reported extraction experiments of palladium with sulfur containing hydrocarbons /20/. In order to test if this could be a way to separate palladium from the rest of the spent nuclear fuel before final partitioning a solution containing different non radioactive metals was created. The approximate metal concentrations can be seen in Table 4-1.

A stability test was made with the usage of cyclohexanone as the diluent and dioctyl sulfide (=0.5 M) as the extractant. When leaving the organic phase in contact with a palladium containing aqueous solution the system first seemed to be stable but after several hours a slight darkening of the aqueous phase was observed suggesting precipitation of solid palladium, see Figure 4-13. This system is however much more stable than with pure cyclohexanone and quite stable enough to be able to perform the extraction experiments.

Figure 4-12. *An organic phase consisting of cyclohexanone is left in contact with three different palladium containing aqueous phases (Left: 4.95 mM Pd, 0.81 M NO_3^-. Middle: 4.95 mM Pd, 3.3 mM D,L-methionine, 0.81 M NO_3^- . Right: 4.95 mM Pd, 60 mM D,L-methionine, 2M NO_3^-) for 40 minutes.*

Figure 4-13. *Cyclohexanone with 0.5 M of dioctyl sulfide is left in contact with 4.95 mM Pd in a solution with 0.81M nitrate concentration for 40 minutes (Left) and 67 hours (right).*

Table 4-1. Approximate metal concentrations in the prepared solution which has a total nitrate concentration of 2M (due to the usage of metals in form of nitrate salts and the addition of conc. nitric acid).

Metal	concentration (g/dm³)	Metal	concentration (g/dm³)
Rb	0.12	Cs	1.26
Sr	0.28	Ba	0.59
Y	0.15	Nd	1.42
Zr	1.24 *	Pd	0.52
Mo	1.18	Ag	0.03
Ru	0.40	Cd	0.035

* Uncertain concentration due to incomplete dissolution of the salt, possibly caused by the wrong molecular formula.

The metal solution was extracted with the organic phase consisting of 0.5 M dioctyl sulfide in cyclohexanone according to the standard extraction experiment with pre-equilibration. After separation the aqueous phases were diluted to appropriate concentrations with an internal standard consisting of 2 ppb In and Pt in 1 M nitric acid for analysis with ICP-MS. The aqueous phases after extraction were compared with the aqueous phase before extraction since there was no possibility to analyze the organic phases. The resulting values of D for several of the metals were small negative numbers which of course is impossible and hence this result was just taken as an indication that almost nothing of these metals was extracted. The metals that this concerns are Rb, Sr, Y, Zr, Mo, Cs, Nd, Cd and they are therefore left out of Figure 4-14.

As can be seen from Figure 4-14 both palladium and silver are extracted to a great extent which is expected. To see how this extraction affects the nuclides that is of interest for the partitioning and transmutation process, three new extractions were performed with the same organic phase but with different aqueous phases. The first aqueous phase consisted of pre-equilibrated 2 M nitric acid spiked with traces of ^{241}Am, ^{152}Eu and ^{238}Pu and the second one of the same pre-equilibrated 2 M nitric acid spiked with ^{237}Np while the last aqueous phase consisted of 0.1 M natural uranium in an aqueous solution with 2 M nitrate concentration. The extraction experiment was performed according to standard procedure and the Am, Eu and Pu were detected with HPGe 1 while the Np and U were detected using liquid scintillator 1.

As can be seen from Figure 4-15 neither americium, neptunium or europium is extracted to any great extent but the fact that more than half of the uranium present is extracted is not a good sign since the amount of uranium present in the spent nuclear fuel is vastly larger than all other elements together.

The large extracted amount of uranium extracted is however found to be caused by the use of cyclohexanone as a diluent and hence experiments with other diluents have to follow.

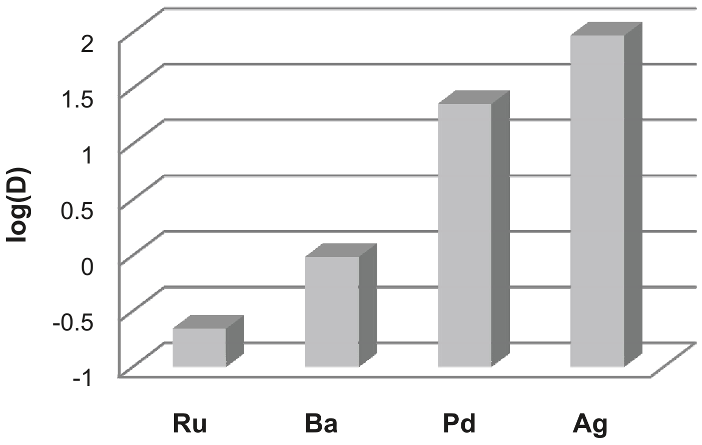


Figure 4-14. Extraction of a metal containing solution (see Table 4-1) with 0.5 M dioctyl sulfide in cyclohexanone.

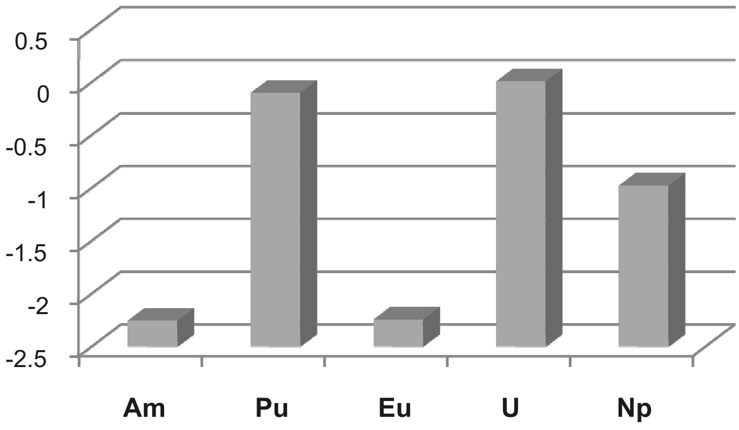


Figure 4-15. Extraction with 0.5 M dioctyl sulfide in cyclohexanone from 2 M nitric acid (Am, Eu, Pu and Np) and from 0.1 M Uranium solution with 2 M nitrate concentration.

4.5 Synthesis of new BTBPs

One of the stumbling blocks of the synthesis of the reference BTBP ($CyMe_4$-BTBP) is the production of the α-diketone (Figure 4-16).

The synthesis of this compound starts with a low yielding radical-radical coupling of 2-methyl-2-carboxyethyl radicals which are generated by the action of hydroxyl radicals upon 2,2-dimethylpropionic acid and later in the synthesis an acyloin condensation using Rühlmann's modification (addition of Me_3SiCl) is required /14/. The acyloin condensation has been identified as an expensive step in the synthesis and requires a large amount of powdered alkali metal (sodium or potassium) and the risk of fire is known to be relatively high for this type of reaction.

In addition it is possible that the sluggish extraction of metals by the $CyMe_4$ bearing triazine extractants may be due to the large alkyl group, as an alternative it was desired to create a new smaller alkyl side group which like $CyMe_4$ is devoid of benzylic hydrogens.

As a synthetically convenient alternative the production of 3,3,5,5-tetramethylcyclopentane-1,2-dione (Figure 4-17) has been explored in part.

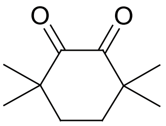


Figure 4-16. *The molecular structure of the α-diketone (3,3,6,6-tetramethylcyclohexane-1,2-dione).*

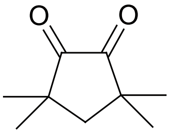


Figure 4-17. *The molecular structure of 3,3,5,5-tetramethylcyclopentane-1,2-dione.*

This compound has been reported to be accessible from 2,2,4,4-tetramethylcyclopentanone by a selenium dioxide oxidation. So far the efforts have been towards the synthesis of 3,3,5,5-tetramethylcyclopentanone. Copper catalysed addition of methyl magnesium iodide to 3,5,5-trimethylcyclohex-2-enone was used to form 3,3,5,5-tetramethylcyclohexanone. It was found that it is possible to oxidize this using nitric acid (with a vanadium catalyst) to form 2,2,4,4-tetramethylhexane-1,6-dioic acid. While the literature claimed that at 250°C, using a combination of barium hydroxide and manganese(II) carbonate, 2,2,4,4-tetramethylcyclopentanone would form by a Ruzicka cyclization, it was now found that only a simple dehydration occured at 250°C. It was found that a higher temperature (able to soften borosilicate glass) is required for the production of a semi-volatile organic compound.

An attempt was made to form the diethyl ester from 2,2,4,4-tetramethylhexane-1,6-dioic acid by means of a triethyl orthoformate assisted Fisher esterification. This reaction however formed a complex mixture of products which in contrast to the products of reacting 2,2,5,5-tetramethylhexane-1,6-dioic acid were more complex and difficult to separate by vacuum distillation. Despite this it has been possible to obtain a small amount of pure diester through repeated vacuum distillations. It is our intention to employ a intramolecular Dieckmann condensation followed by decarboxylation to form the required 3,3,5,5-tetramethylcyclopentanone.

4.6 Nickel extraction

Nickel is a corrosion product from stainless steel that will be present in almost any industrial liquid-liquid extraction system. Nickel is a generally difficult element to deal with due to the combination of charge and valence, making it difficult to saturate and therefore a formation of unwanted poly nuclear complexes could occur. Nickel is known to have high distribution ratios with some nitrogen donor ligands and hence it is interesting to further investigate its extraction properties with BTBP-type molecules. A comparison study of C5-BTBP and C2-BTBP was reported in the SKB-report of 2006 /3/ and now another extraction experiment of nickel with the two different BTBP's, MF1- and C3-, was performed.

This was done to investigate if the extraction possibility of the extractants is connected to the molecular weight since the two molecules MF1- and C3-BTBP have the exact same molecular weight (M=482.64 g/mol) and complex formation sites but otherwise quite different structures (see Figure 1-2 and 1-7).

4.6.1 Kinetics

First the kinetics of the systems had to be investigated to see for how long the different samples had to be shaken to reach equilibrium. This was done according to the standard extraction experimental procedure. The two phases consisted of a low concentration of pre-equilibrated organic extractant (10^{-5} M) in cyclohexanone and pre-equilibrated 1 M nitric acid. 10 µL of ^{63}Ni stock solution was used for spiking. The phases were then contacted using a shaking machine for different periods of times. Only single samples were used in this experiment. After extraction the phases were separated and transferred to 20 mL scintillation vials containing 10 mL of scintillation cocktail (Emulsifier Safe) for analysis with liquid scintillator 1.

The results can be seen below, Figure 4-18, and with this as a base the shaking time was chosen to 18 hours (1,080 minutes) for the MF1-BTBP samples and 15 hours (900 minutes) for the C3-BTBP samples.

4.6.2 Extraction

To determine the difference in extraction ability already indicated in the shaking time experiment, triple samples with different extractant-concentrations (10, 5, 1, 0.1, 0.01 and 0.001 mM) were prepared and pre-equilibrated together with the aqueous phase in the same way as earlier. The MF1-samples were then left on the shaking machine for 18 hours (1,080 minutes) and the C3-samples were left for 15 hours (900 minutes). After contact the phases were separated and transferred to scintillation vials.

The results from the liquid scintillation analysis can be seen in Figure 4-19. This gives proof that the extraction ability of the extractants is not correlated to the molecular mass but rather to its overall structure. Compared to the results obtained for C5-BTBP and C2-BTBP (Figure 4-20) one can also conclude that the extraction ability and behavior of C3-BTBP as well as MF1-BTBP are more similar to that of C5-BTBP than that of C2-BTBP with the exception that they reach the same D-values at higher BTBP-concentrations (a comparison between all four BTBPs is given in Figure 4-21). This indicates that both C3-BTBP and MF1-BTBP form 1:2 complexes with Ni just like C5-BTBP and hence differs from C2-BTBP which forms 1:1 complexes.

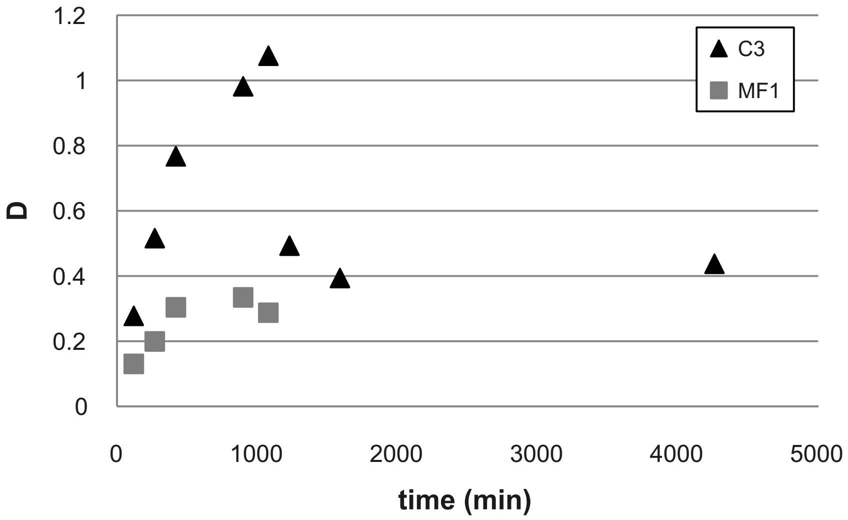


Figure 4-18. *Extraction of ^{63}Ni with 10^{-5} M of C3-BTBP in cyclohexanone and 10^{-5} M MF1-BTBP in cyclohexanone from 1 M nitric acid after different contact times.*

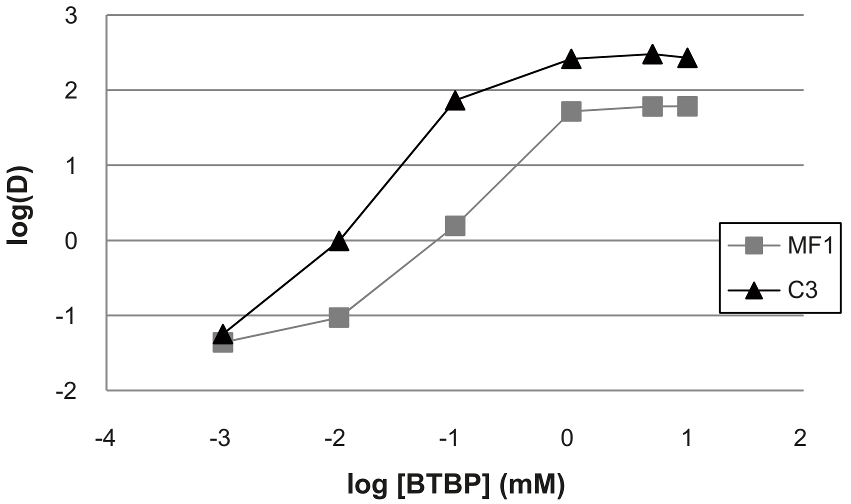


Figure 4-19. *Extraction of* ^{63}*Ni with different concentrations of C3-BTBP in cyclohexanone and different concentrations of MF1-BTBP in cyclohexanone from 1 M nitric acid.*

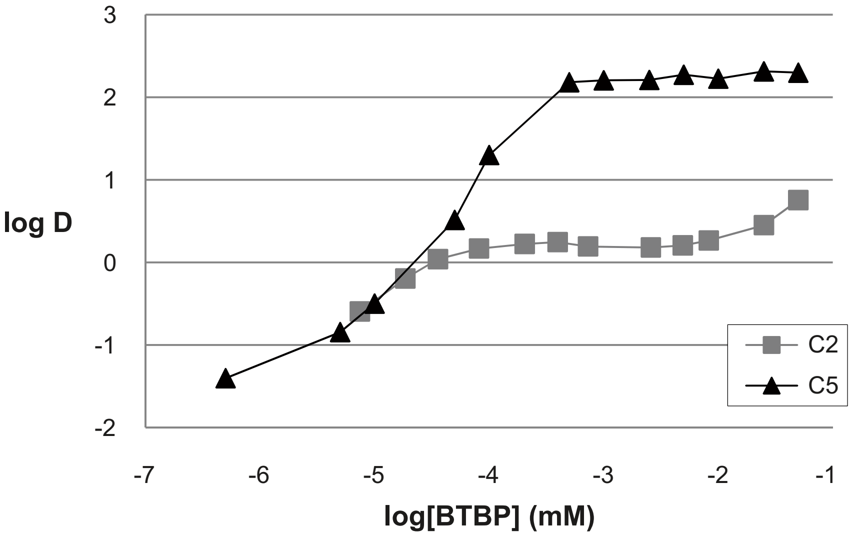


Figure 4-20. *Extraction of* ^{63}*Ni with different concentrations of C2-BTBP in cyclohexanone and different concentrations of C5-BTBP in cyclohexanone from 1 M nitric acid /3/.*

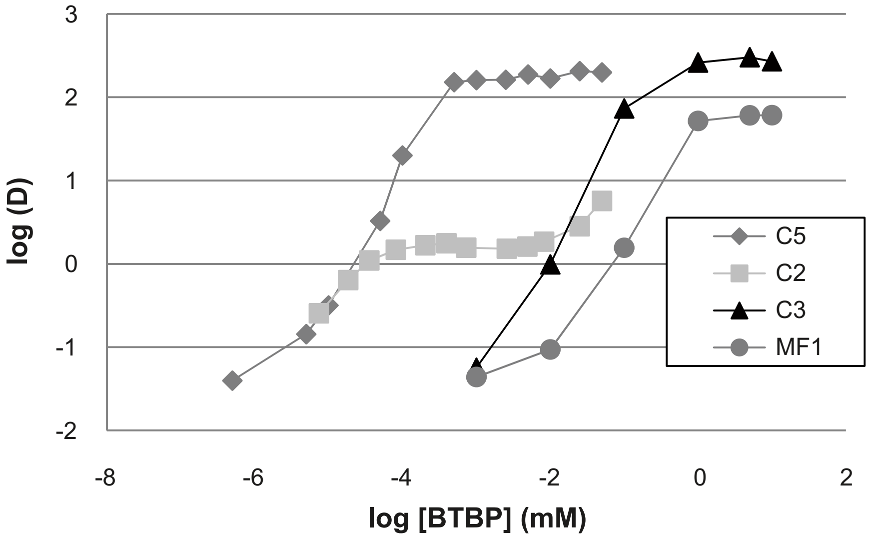


Figure 4-21. *Figure 4-19 and 4-20 put together into one graph for easier comparison.*

4.7 Diluent studies

A high solubility of a good extracting molecule in desired diluents is always a priority. Effort and knowledge is directed into this process. When a number of diluents were tested together with the BTBP-type molecules for assessing the solvent extraction capabilities, the results showed an interesting extraction variation of each organic system, like difference in extraction capability, kinetics, solubility, and function of these diluents /10, 12, 13/. It has become obvious that by changing the diluent, this promising ligand family can successfully be used in a real life process. Due to various kinetics showed by different diluents, different type of equipment can be selected, like e.g. centrifugal contactors, with a short residence time; or mixer-settlers, with longer residence time.

4.7.1 Fenchone

The diluents that are used for separation of actinides and lanthanides must possess certain properties. Since uranium is present in very large concentrations in the spent nuclear fuel compared to the other elements, it is not desirable that the diluents used interact with uranium. When cyclohexanone is used as solvent, uranium is extracted into the organic phase in small amounts. This is undesired since it could cause problems during the stripping process later on. The complex that forms is believed to involve the enolate form of cyclohexanone.

One solution to this problem could be to choose a solvent which cannot form enolates, like fenchone (see Figure 4-23). The fenchone molecule is also more sterically hindered than the cyclohexanone which would be beneficial for not forming complexes with uranium.

To see if this diluent could be used in a separation for transmutation process an extraction of Am and Eu with two common extraction agents was performed. This was done by hand shaking according to the standard extraction experiment for 5, 10 and 15 minutes respectively. The analysis was made with HPGe1 and the D for americium in fenchone was found to be very low. Therefore this diluent is not interesting for P&T applications.

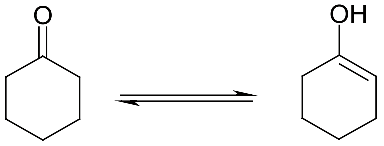


Figure 4-22. *Reversible enolate formation of cyclohexanone.*

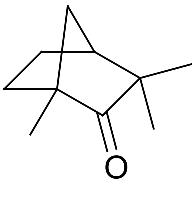


Figure 4-23. *Fenchone (a terpene).*

4.7.2 Colour chemistry

Many substances exhibit reversible variations of colour under differing physical or chemical conditions such as temperature, pressure, light and diluents /18/. Such reversible colour changes are known as "chromotropism". Sometimes metal complexes are used as chromophores, for example $[M(dike)(diam)]^{+}$ (where $M^{+}= Cu^{2+}$, Ni^{2+}, (dike)= β-diketonates and (diam)=diamines).

In the case of diluents, the colour is connected with the solvation of the complex associated with the transformation of the geometry of the complex, for example from square-planar structure to octahedral structure. This property has been used in many studies in the last decades, mainly for assessing the donor-acceptor properties of the diluents in simple or binary solutions /18, 16, 8/.

Basically, the diluents are seen as σ-donors (nucleophilic, basic, cation-solvating) or σ-acceptor (electrophilic, acidic, anion-solvating) entities which participate to nonprotic Lewis acid-base reactions accompanied by colour changes /16/.

There is a number of different equations derived from spectrophotometric measurements /16, 15, 8/ which can be applied to calculate donor number (DN) or acceptor number (AN). In this particular study, no attempt has been made to calculate an own equation but the ones existent in literature has been used /16/, selected to fit the diluents of interest (equation 1 and 2):

$$DN = 195.5 - 0.0102 \cdot v_{\text{max}} \qquad r = 0.990, \quad s = 1.37 \tag{1}$$

$$AN = -133.8 + 0.00933 \cdot v_{\text{max}} \qquad r = 0.980, \quad s = 4.58 \tag{2}$$

A least-squares linear regression analysis comprising diluents from both ends of a diluents scale (low DN to high DN and low AN to high AN respectively) has been calculated /16/. v_{max} denotes the maximum wave number (in cm^{-1}), r the correlation coefficient and s the mean deviation between experimental and calculated values in the respective reference.

Experimental

Four different diluents were used: hexanol, octanol, cyclohexanone and nitrobenzene. All of them were of analytical grade and none of them has been further purified.

The dicyano-*bis*-(1,10-phenantholine)-iron complexe, Figure 4-24, was obtained from ferrous sulfate, potassium cyanide and 1,10-phenantholine /17/.

The synthesis of acetylacetonato-copper(II)-tetramethylethylene diamine perchlorate, Figure 4-25, was based upon a literature method /21/.

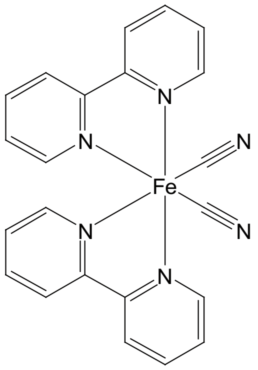


Figure 4-24. *The dicyano-bis-(1,10-phenantholine)-iron complex.*

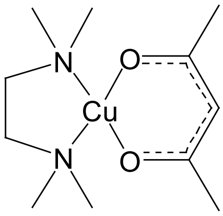


Figure 4-25. The cation present in acetylacetonato-copper(II)-tetramethylethylene diamine perchlorate.

Four diluents were selected, since the solvent extraction experiments with the BTBP type molecules are focussed on certain diluents, among which some just for experimental reasons (nitrobenzene) and not for further application in a process.

Each metal complex, illustrated in Figure 4-24 and 4-25, was dissolved in 15 mL of diluent. After complete dissolution, 1 mL of each solution was measured with a spectrophotometer and all UV/visible spectra were recorded using 1 cm quartz cells. The photo spectrometer was used to scan from 800 to 450 nm. All diluents used were of standard laboratory grade.

Results

DN and AN were calculated according to the previous equations and are displayed in Table 4-2 below.

Table 4-2. DN and AN of different diluents calculated as function of maximum wave number (in cm^{-1}) spectrophotometrically measured with the help of equation (1) and (2) /16/.

Diluents	DN	AN
Hexanol	24.07143	29.02723
Octanol	22.03061	29.02723
Cyclohexanone	18.1087	13.82658
Nitrobenzene	2.683365	20.1604
Fenchone	17.79965	n.a.

5 Dissolution and recovery of molybdenum CERMETS

Advanced fuels for transmutation of minor actinides and plutonium are presently under investigation. One potential fuel type is a CERMET (CERamic-METallic composite) where the actinide bearing phase is distributed in a molybdenum matrix. Mo is chosen due to its neutronic and thermal properties e.g. high thermal conductivity and relatively low neutron capture cross section. Investigations have shown that to minimize the buildup of ^{99}Tc during irradiation, the Mo matrix should contain highly enriched ^{92}Mo. To overcome the high enrichment costs recovery of the Mo is proposed. In damaged fuel pellets and fabrication scraps both the Mo matrix and the actinide phase could be recovered and re-introduced in fresh fuels. In a first step the Mo should be dissolved and separated from the actinide phase and thereafter an appropriate method for Mo metal conversion should be applied.

The investigations are ongoing and the aim is first to find a proper solvent which dissolves the Mo meanwhile the actinide phase is kept intact. It is also requested that the amount of steps in the procedure should be minimized and that the final process can be applied in industrial scale.

Experiments have been initiated on leaching and dissolution of the above mentioned fuel type. The samples were prepared by the sol-gel and infiltration route e.g. porous Pu particles (beads) were fabricated by sol-gel and were thereafter infiltrated by an Am-nitrate solution with a concentration which results in the requested Pu-Am composition. Two different Am concentrations were used e.g. ca 6 and 25 mol %. Conversion from nitrate to oxide was performed before mixing the actinide phase with molybdenum. Two different fractions of actinide phase was used, 20 and 40 volume %. Pellets (or discs) were compacted at 500 MPa followed by sintering in a reducing atmosphere. After sintering the actinide phase containing ^{239}Pu and ^{241}Am oxides forms a solid solution meanwhile the Mo remains as metal. The final material was inspected visually and geometrically before starting the dissolution experiments.

Various solutions should be tested but as a start, two different HNO_3 concentrations were chosen e.g. 7 and 9 M. The 7 M was chosen due to the similarity with PUREX conditions and the 9 M because it is close to the value, stated in literature, to give the highest dissolution rate of Mo.

Experimental

Two parallel experiments were initiated. Leaching of the pure actinide phase is a several month experiment meanwhile the $(PuAm)O_{2-x}$-Mo experiments were lasting around 7–10 days depending on the rate of Mo dissolution for each sample composition. Samples were taken in intervals of at least 1 h in the beginning of each experiment and more seldom at the end. The samples were measured on an ICP-MS and Mo, Pu and Am were the elements for determination.

5.1 Results and discussion

In the samples with pure actinide phase no color change in the solution was noticed and there was no vigorous dissolution observed. In the solutions with $(PuAm)O_{2-x}$-Mo pellets the Mo dissolution was relatively fast. In pellets with lower content actinide phase, the Mo was dissolving slightly slower. By observing the various colors of the solutions it was seen that some of the Am and Pu was dissolving as well. In Figure 5-1 and 5-2 the ICP-MS results from samples containing $(Pu_{0.76}Am_{0.24})O_{2-x}$-Mo (80 vol%) dissolved in 7 or 9 M HNO_3 are shown. The impact of HNO_3 concentration does not seem to have any visible effect on the dissolution rate of Mo and for both experiments the Mo is completely dissolved within the first two days. The dissolution of Pu and Am is very low, <1% Pu and ca 5% Am when the Mo is completely dissolved, and is not affected by increase in acid concentration. More details on the dissolution behavior of pure actinide phase and on other composite compositions are under investigation. The results are promising but further investigations needs to be performed in order to minimize the leaching of Pu/Am.

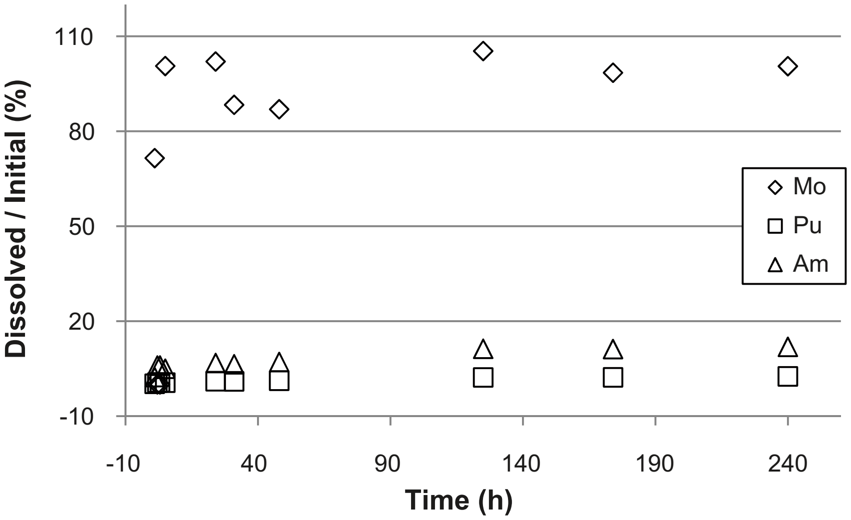


Figure 5-1. *(PuAm)O_{2-x}-Mo (80 vol%) dissolved in 7 M HNO_3*

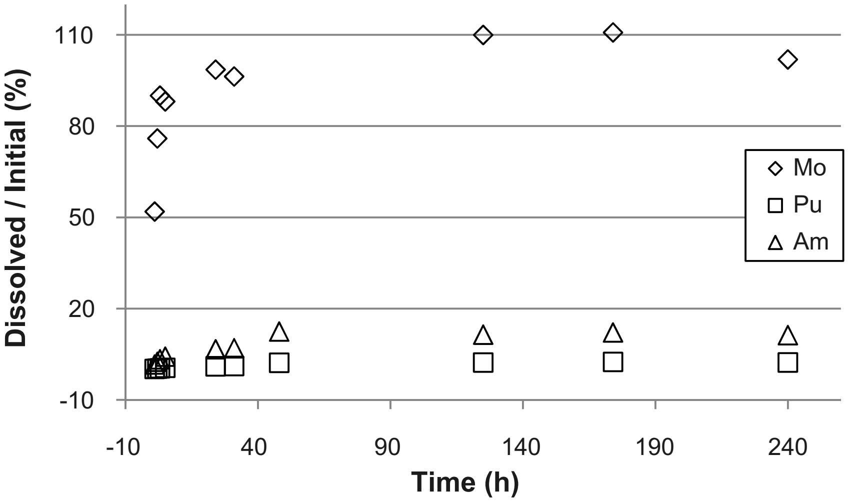


Figure 5-2. *(PuAm)O_{2-x}-Mo (80 vol%) dissolved in 9 M HNO_3*

Collaborations

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

A more intense collaboration with Chalmers exists with:
- Forschungszentrum Jülich, Germany
- University of Reading, UK
- Institut für Michrotechnik Mainz, Germany
- Kernchemie, Johannes Gutenberg-Universität, Germany
- CEA, France
- National Institute of Cryogenics and Isotopic Separation, Romania
- Institute of inorganic chemistry, Academy of sciences, Czech Republic

International scientific exchange

31/3–2/4 2008, ACSEPT kick off meeting in Nîmes, France.
Participants: E Aneheim, C Ekberg, A Fermvik, M Foreman.

13–18/4 2008, 2nd International Nuclear Chemistry Congress in Cancun, Mexico.
Participants: C Ekberg, T Retegan, G Skarnemark.
Poster presentation entitled **:** *CHON-Principle, a Viable Alternative for Separating the Actinides from Lanthanides for Further Transmutation?,* Teodora V Retegan, Christian Ekberg, Gunnar Skarnemark, Anna Fermvik, Mark St J Foreman (Abstract of papers).

3–5/9 2008, ACSEPT 1st half yearly meeting in Prague, Czech Republic.
Participants: E Aneheim, C Ekberg, A Fermvik, M Foreman, J-O Liljenzin.

15–19/9 2008, International Solvent Extraction Conference in Tuscon Arizona, USA.
Participants: A Fermvik, T Retegan, G Skarnemark.
Oral presentation entitled: *A Comparative Study of Some BTP and BTBP Class Ligands*, T Retegan, C Ekberg, A Fermvik, M R St J Foreman, and G Skarnemark.

6–10/10 2008, The 10th OECD/NEA Information Exchange Meeting on Actinide and Fission Product Partitioning and Transmutation in Mito, Japan.
Participants: E Aneheim, A Fermvik, J-O Liljenzin, T Retegan.
Two Poster presentations entitled: *Partitioning and Transmutation in Scandinavia – Chalmers Group*, E Aneheim, C Ekberg, A Fermvik, M St J Foreman, T Retegan, G Skarnemark, and *Development of Equipment for Pilot Scale Tests of Processes for Partitioning and Transmutation,* E Aneheim, C Ekberg, A Fermvik, M St J Foreman, T Retegan, G Skarnemark.

Articles and publications

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

Published

Ekberg C, Fermvik A, Retegan T, Skarnemark G, Foreman M R S, Hudson M J, Englund S, Nilsson M: An Overview and Historic Look Back at the Solvent Extraction Using Nitrogen Donor Ligands to Extract and Separate An(III) from Ln(III). Radiochimica Acta, 96(4-5), 225–233 (2008).

Fermvik A, Ekberg C, Foreman M R S, Retegan T, Skarnemark G: The effect of irradiation on extraction of various metals by C5-BTBP, Solvent Extraction: Fundamentals to Industrial Applications, Proceedings of ISEC 2008, Tucson, Arizona, US, Sept. 15–19, 2008, Vol 1, 551–556.

Fermvik A, Ekberg C, Englund S, Foreman M R S, Modolo G, Retegan T, Skarnemark G: Influence of dose rate on the radiolytic stability of a BTPB solvent for actinide(III)/lanthanide(III) separation, Accepted for publication in Radiochimica Acta, (2008).

Fermvik A: The effect of radiolysis of BTBP type molecules on distribution ratios. Licentiate Thesis, Chalmers University of Technology, Göteborg (2008), ISSN: 1652-943X.

Magnusson D: Recovery Process of Actinides from Genuine Spent Nuclear Fuel using TODGA and BTBP Extractants. Ph.D. thesis, Chalmers University of Technology, Göteborg (2008), ISBN: 978-91-7385-203-6.

Magnusson D, Christiansen B, Glatz J-P, Malmbeck R, Modolo G, Serrano-Purroy D, Sorel C: Demonstration of a TODGA based Extraction Process for the Partitioning of Minor Actinides from a PUREX Raffinate, Part III: Centrifugal Contactor Run using Genuine Fuel Solution, Accepted for publication in Solvent Extraction and Ion Exchange (2008).

Magnusson D, Christiansen B, Glatz J-P, Malmbeck R, Modolo G, Serrano-Purroy D, Sorel C: Towards an optimized flow sheet for a SANEX demonstration process using centrifugal contactors, Accepted for publication in Radiochimica Acta (2008).

Magnusson D, Christiansen B, Foreman M R S, Geist A, Glatz J-P, Malmbeck R, Modolo G, Serrano-Purroy D, Sorel C: Demonstration of a SANEX process in centrifugal contactors using the $CyMe_4$-BTBP molecule on a genuine fuel solution, Accepted for publication in Solvent Extraction and Ion Exchange (2008).

Retegan T, Ekberg C, Fermvik A, Foreman M R S, Skarnemark G: A comparative study of some BTP and BTBP class ligands, Solvent Extraction: Fundamentals to Industrial Applications, Proceedings of ISEC 2008, Tucson, Arizona, US, Sept. 15–19, 2008, Vol 1, 545–550.

Submitted

Magnusson D, Christiansen B, Glatz J-P, Malmbeck R: Investigation of the radiolytic stability of a $CyMe_4$-BTBP based SANEX solvent, Submitted to Radiochimica Acta (2008).

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

Under preparation

Retegan T, Aneheim E, Ekberg C, Fermvik A, Foreman M R S, Skarnemark G: The relationship between the properties of diluents and the extraction of trivalent f-block metals from nitrate media by BTBP reagents.

Retegan T, et al.: A study of the influence of diluents and side groups of the ligands on complex formation of actinides and lanthanides with BTBPs using Electrospray Ionization Mass Spectrometry (ESI-MS) technique; Financed by ACTINET.

Retegan T, Ekberg C, Fermvik A, Foreman M R S, Skarnemark G: A comparative study between x-BTBP and modified x-BTBP type ligands (where x = C2-; CyMe$_4$-; MF1-; MF2-).
Note: The title is just a provisory one and does not reflect the final version of this paper.

Retegan T: Investigations of solvent systems based on bis-triazine-bipyridine (BTBP) – class ligands for the separation of actinides from lanthanides, Ph.D. Thesis.
Note: The dissertation to be held on the 13 of March 2009.

Fermvik A, et al.: Radiolysis of solvents containing C5-BTBP – identification of degradation products and their dependence on absorbed dose and dose rate, Financed by ACTINET.

Fermvik A, et al.: Extraction with irradiated organic solvents containing BTBP molecules – the effect of dose rate, Financed by ACTINET.

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

Future work

The future work will continue along the suggested path of the ACSEPT project. However, we will do as previous years and use the complementary funding from the SKB to focus more on the basic scientific issues arising from the more process oriented studies. This building of knowledge is also the role of a University.

- Partitioning of actinides (different oxidation states, Th-Cm) for advanced dedicated future fuel cycles, like for example ADS nuclear systems. The co-extraction of actinides of different oxidation states will be studied. Mixtures of ligands, bitopic extractants and chromatographic techniques will be used.
- Studies on the radiolytic and hydrolytic stability and investigations of the decay products and their effects.
- Investigation of the effect of the diluents on the extraction, stripping and selectivity.
- Optimised selective stripping from a possible GANEX (Grouped ActiNide EXtraction) process.
- 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 continue in the group part time as a co-project leader.

Teodora Retegan will present her thesis in March dealing with 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. Attempts will be made to correlate the extraction behaviour to some more easily measured chemical property such as heat of dissolution.

Anna Fermvik will continue her studies on the effect of radiation on the extractant molecules used and what effect the products of radiolysis will have on the extraction. Identification of degradation products and routes will be studies together with Dr. Zoltan Szabo at KTH and Dr. Bohomir Gruner at Academy of Sciences of the Czech Republic.

Emma Aneheim will study development of new extracting ligands and ligands for selective stripping of actinides and lanthanides. In addition she will design a new GANEX process.

Catharina Nästren will present her thesis on the investigation of the chemical behaviour of different new fuel types in April 2009.

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

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