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Annual Report 2004

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Nuclear Chemistry
Department of Materials and Surface Chemistry
Chalmers University of Technology

January 2005

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Abstract

The long-lived elements in the spent nuclear fuels are mostly actinides, some fission products (^{129}I, ^{99}Tc, ^{135}Cs, ^{93}Zr and ^{126}Sn) and activation products (^{14}C and ^{36}Cl) [OEC 99]. To be able to destroy the long-lived elements in a transmutation process they must be separated from the rest of the spent nuclear fuel. The most difficult separations to make are those between trivalent actinides and lanthanides, due to their relatively similar chemical properties, and those between different actinides themselves. This separation is necessary to obtain the desired efficiency in the transmutation process in order not to create any unnecessary waste thus rendering the process useless. Solvent extraction is an efficient and well-known method that makes it possible to have separation factors that fulfil the highly set demands on purity of the separated phases and on small losses.

Chalmers University of Technology is involved in research regarding the separation of actinides and lanthanides and between the actinides themselves as a partner in the European Union sixth framework program project EUROPART. This is a continuation of the projects we participated in within the fourth and fifth framework programmes NEWPART and PARTNEW respectively. The aims of the projects have now shifted from basic understanding to more applied research with focus on process development.

Sammanfattning

De långlivade ämnena i det använda kärnbränslet består till största delen av aktinider, en del fissionsprodukter (^{129}I, ^{99}Tc, ^{135}Cs, ^{93}Zr and ^{126}Sn) och aktiveringsprodukter (^{14}C and ^{36}Cl) [OEC 99]. För att kunna förstöra de långlivade ämnena i en transmutationsprocess måste de separeras från resten av det använda kärnbränslet. De svåraste separationerna att göra är de mellan trevärda aktinider och lantanider, på grund av deras relativt liknande kemi, samt dem mellan aktiniderna själva. Denna separation är nödvändig för att uppnå den önskade effektiviteten i transmutationsprocessen samt för att undvika extra avfall som skulle göra hela processen överflödig. Vätskeextraktion är en effektiv och välkänd metod som gör det möjligt att uppnå separationsfaktorer som uppfyller de högt ställda kraven på renhet i de separerade faserna och små förluster.

Chalmers tekniska högskola deltar i forskningen rörande separationen av aktinider och lantanider och mellan aktiniderna själva, genom att vara en partner i EUROPART, ett projekt inom EUs sjätte ramprogram. Detta projekt är en fortsättning på tidigare projekt vi deltagit i inom det fjärde och femte ramprogrammet, nämligen NEWPART och PARTNEW. Målet med arbetet har under denna tid flyttats från grundläggande forskning till mer tillämpad forskning och processberäkningar och verkliga experiment

Contents

1 Introduction

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

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

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

The Chalmers group has been involved in the separation and transmutation research throughout three different European Union framework programmes, i.e. NEWPART (1996–1999), PARTNEW (2000–2003) and EUROPART (2004–2007). During this time the focus has changed slightly although the main content is still the same. As time has passed the main efforts have been more and more focussed on process development. In the early years there was a search for suitable extracting agents following the CHON principle (only containing carbon, hydrogen, oxygen and nitrogen). This search has continued but now in more close collaboration with process expertise to make the molecules not only having good separation capabilities but also to survive practically and economically in a process. The research can be divided into three different areas:

- Co-extraction of actinides and lanthanides from acidic high active raffinate − DIAMEX process.
- Separation of actinides and lanthanides − SANEX process.
- Separation of Am and Cm.

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

The main laboratory work at Chalmers concerns the extractive properties and other basic chemical properties of the ligands synthesised in Reading, UK. The influence of pH, ionic strength and media, absorbed dose and concentration of the involved species are studied in combination with modelling of the systems using solubility parameters. However, we are also involved in process development and flow sheet calculations. Experiments with synthetic waste are in these cases the basis for our understanding. The heavy actinides, represented by berkelium and californium were also studied.

2 Research

During 2004 Sofie Andersson and Mikael Nilsson continued their work as PhD students. Both of them have spent time in laboratories abroad. Sofie spent five months in Berkeley to study the chemistry of berkelium and Mikael spent two months in Forschungszentrum Jülich to study a process based on one of the new extractants (C5-BTBP). The kick-off meeting for the EUROPART project was in Avignon in February and one additional meeting in Madrid in July. A French diploma worker, Francois Drouet worked in the P&T group studying some extraction behaviour and radiation stability of C5-BTP. Two new PhD students have started during 2004. Daniel Magnusson who is a joint student with the Institute for Transuranium Elements in Karlsruhe will work with modelling of processes and also process experiments on real high active raffinate. In December Teodora Retegan, a scholarship student from Romania, also joined the group. She will continue the work with the basic chemistry of new ligands.

2.1 Chemical behaviour of C5-BTBP

The chemical structure of C5-BTBP (C5) can not be given at the present stage due to confidentiality, hoverer it is a derivative of the BTBP molecule, see Figure 2.1.

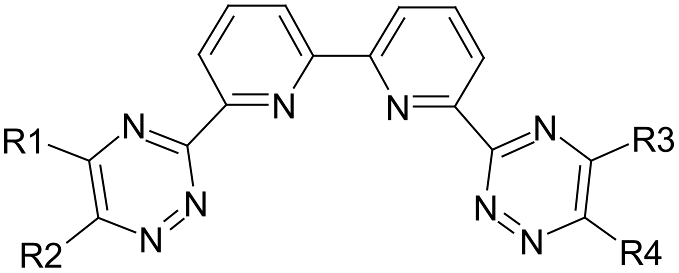


Figure 2.1. *Shematic picture of a BTBP.*

The different properties that have been studied are:

- Basic extraction studies with organic diluent tert-butylbenzene (TBB)
- Extraction studies with organic diluent 1,1,2,2-tetrachloroethane (TCl)
  - Basic extraction experiments
  - Temperature studies
  - Kinetics studies
  - Stripping of americium with oxalic acid
- Extraction studies with organic diluent cyclohexanone
  - Basic extraction experiments
  - Varying HNO_3-concentration
  - Temperature studies
  - Kinetics studies
  - PUREX-raffinate extraction

- Extraction with several other organic diluents
- Extraction with different 1-alcohols as organic diluent
- Extraction with different concentration of C5
- Radiolysis experiments, cf section 2.2

Basic extraction studies with organic diluent tert-butylbenzene

Initial tests were made using 0.005 M C5 dissolved in TBB and using an aqueous phase consisting of 0.01 M H^+ and 1 M ionic strength with either nitrate or perchlorate. Experiments were made in triplicates with both ^{241}Am and ^{152}Eu. The results are shown in Table 2.1.

Table 2.1. Extraction with C5 dissolved in TBB.

Nitrate		Stdev%	Perchlorate		Stdev%
D Am	1.36E–04	34.08	D Am	53.89	5.94
D Eu	1.78E–05	174.63	D Eu	1.44	3.24
SF Am/Eu	7.65	177.93	SF Am/Eu	37.44	6.77

2-bromodecanoic acid (HA) was added to the system in an attempt to increase extraction efficiency. The system consisted of 0.01 M C5 and 0.25 M HA. The aqueous phase was identical with the one used in the previous experiment with nitrate. Experiments were made in triplicates. The results are shown in Table 2.2.

Table 2.2. Extraction with C5 dissolved in TBB and HA.

		Stdev%
D Am	643.28	8.37
D Eu	4.81	4.73
SF Am/Eu	133.81	9.61

Thus, addition of 2-bromodecanoic acid increased both the distribution ratios and the separation efficiency.

One test to see if an increase of the nitrate ion concentration could yield higher distribution ratios (D) were made. The organic phase consisted of 0.005 M C5 dissolved in TBB. The aqueous phase contained 3 M NO_3^- and 0.01 M H^+ and the experiment were made in triplicates with both ^{241}Am and ^{152}Eu. The results are shown in Table 2.3.

Table 2.3. Extraction with 3 M NO_3^- in the aqueous phase.

3 M NO_3^-	D	Stdev%
Am	3.12E–03	7.19
Eu	8.93E–05	53.60
SF Am/Eu	34.92	54.08

The addition of nitrate ions seems to yield an increase in extraction. It is reasonable to assume that nitrate is the counter ion in the extracted complex, cf Table 2.1.

Tests were also made with different acid concentrations. Aqueous phases with 1, 2, 3 and 4 M HNO_3 were used together with an organic phase consisting of 0.01 M C5 and 0.25 M HA in TBB. Single samples were made and thus no uncertainties could be calculated. The results are shown in Table 2.4. No precipitation was observed in any case but at 3 and 4 M HNO_3 the organic phase changed colour from light yellow to darker yellow and after a day it was almost red.

Table 2.4. Extraction with different HNO_3 concentrations in the aqueous phase.

1 M HNO_3	**D**	**2 M HNO_3**	**D**
Am	0.52	Am	0.71
3 M HNO_3	**D**	**4 M HNO_3**	**D**
Am	1.04	Am	0.18

There seems to be an optimum with respect to hydrogen- and nitrate ions. The reason for this ought to be investigated further.

In comparison to the experiments above, a number of extractions was made using an organic phase consisting of 0.005 M C5 in cyclohexanone. In the aqueous phase the HNO_3-concentration was varied and although macro amounts of lanthanides was used only ^{241}Am and ^{152}Eu extraction were investigated. The results can be seen in Figure 2.2. For all HNO_3-concentrations below 1 M, $NaNO_3$ was added to have a NO_3^- concentration of 1 M. The distribution ratios are not significantly changed by the increase of HNO_3 concentration, except when using 3 M HNO_3 where the distribution ratio for americium drops. However, as can be seen in Figure 2.2 the decrease in Am-extraction for 3 M HNO_3 is quite small and the D for Eu actually shows a small increase, although perhaps not significant, which is the reason for the apparently big decrease in separation factor.

Tests to find the optimum system for an extraction process (D-values for Am and Eu should spread an equal distance from a log D value of 0) were made. Different concentrations of C5 and HA were tested but the ratio C5:HA was held constant at 1:20 in all cases. The aqueous phase was 1 M NO_3^- and 0.01 M H^+. All experiments were made in duplicates.

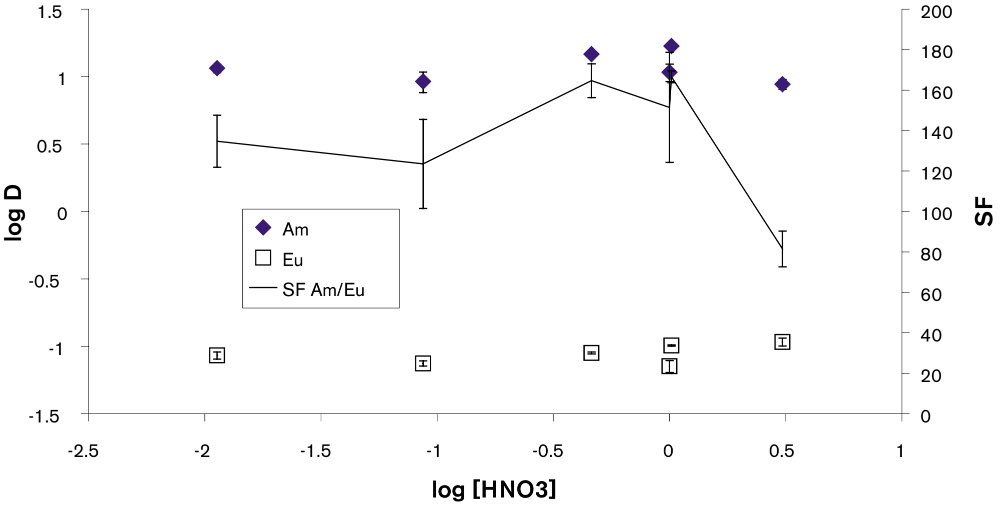


Figure 2.2. *Acidity behaviour of the extraction of ^{241}Am and ^{152}Eu using C5 in cyclohexanone.*

The results are shown in Table 2.5. The optimum system was found for an organic phase consisting of 0.004 M C5 and 0.08 M HA which gave D for Am of ~10 and Eu of ~0.12 and a separation factor of around 85.

Table 2.5. Extraction with different C5 and HA concentration at constant C5:HA ratio.

0.0025 M C5, 0.05 M HA		Stdev%	0.004 M C5, 0.08 M HA		Stdev%
D Am	1.75	0.98	D Am	10.20	6.87
D Eu	2.04E–02	1.74	D Eu	0.12	0.58
SF Am/Eu	85.63	2.00	SF Am/Eu	83.67	6.90

Extraction experiments with macro amounts of Ln in the aqueous phase were made. C5 was dissolved to 0.01 M in tert-butyl benzene together with 0.25 M 2-bromohexanoic acid. The reason for the increased concentrations of C5 and acid was that we used macro amounts of lanthanides and was trying to avoid loading. The C5:acid ratio was 1:25. 10 different experiments were performed, called M1–M10, details are accounted for in Table 2.6. The phases were contacted using vortex-shakers that were proven to be as effective in 10 minutes shaking as shaking by hand for 5 min, which is the usual procedure. After contact the shaking vials were centrifuged and aliquots were taken from both phases. All samples were analysed with gamma spectroscopy for ^{241}Am and ^{152}Eu analysis, alpha spectroscopy for ^{241}Am, ^{244}Cm and ^{252}Cf and finally ICP-MS analysis for inactive lanthanides (La, Ce, Pr, Nd, Sm, Eu, Gd) and Y.

Table 2.6. Composition of the different aqueous phases. Macro amounts of Ln mean 2.5x the concentration in a simulated back-extraction solution from the DIAMEX process.

Aq No.	HNO_3 [M]	Mixing time	Macro, Ln
M1	0.050	5 min	No
M2	0.52	5 min	No
M3	1.00	5 min	No
M4	0.046	5 min	Yes
M5	0.50	5 min	Yes
M6	1.00	5 min	Yes
M7	0.050	1 h	No
M8	0.046	1 h	Yes
M9	0.050	15 h	No
M10	0.046	15 h	Yes

Results from these experiments indicate that, except maybe for the M1-solution, 5 min of shaking is not enough for reaching equilibrium, see Figures 2.3, 2.4 and 2.5. This behaviour was not observed later when investigating the kinetics using only tracer amounts, see Figure 2.16. The concentration of HNO_3 seems of less importance than the contact time, see Figure 2.3. For a short contact time most lanthanides have higher distribution ratios but these decrease when equilibrium is reached, the opposite is true for the actinides, see Figure 2.6. This behaviour was observed later using C5 in cyclohexanone, see Figures 2.18 and 2.19.

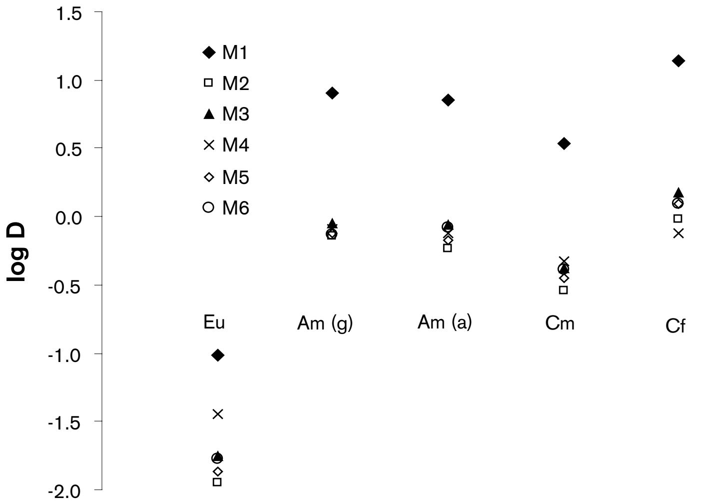


Figure 2.3. *Comparison between different concentrations of HNO_3 and lanthanides. Shaking time 5 min for all series. The data are from alpha (a) and gamma (g) spectrometry.*

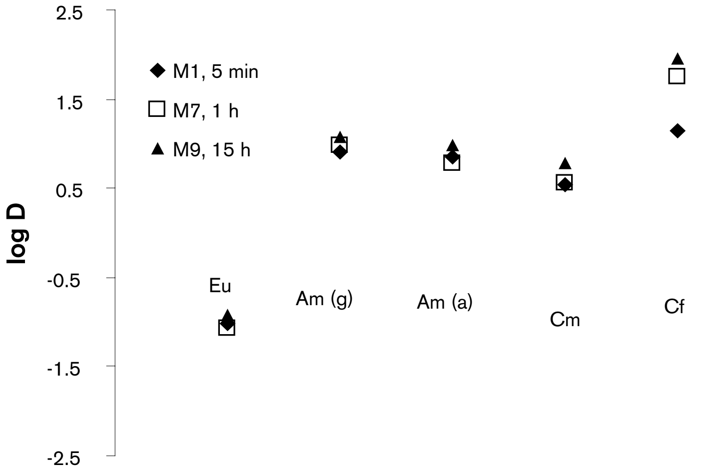


Figure 2.4. *Comparison between different shaking times when using 0.05 M HNO_3 and no macro amounts of lanthanides. The data are from alpha (a) and gamma (g) spectrometry.*

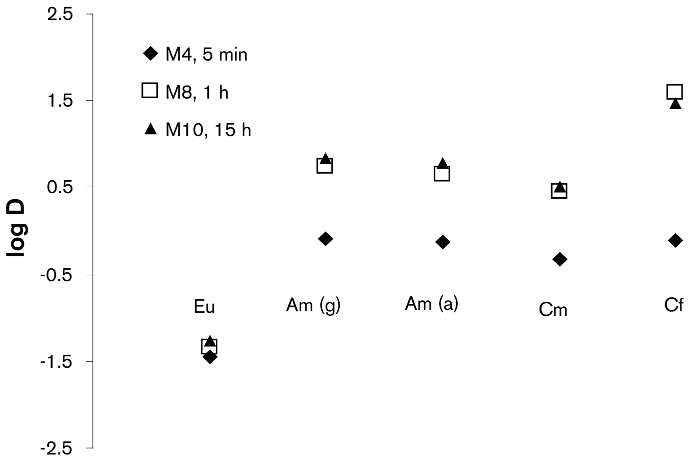


Figure 2.5. *Comparison between different shaking times when using 0.05 M HNO_3 and macro amounts of lanthanides. The data are from alpha (a) and gamma (g) spectrometry.*

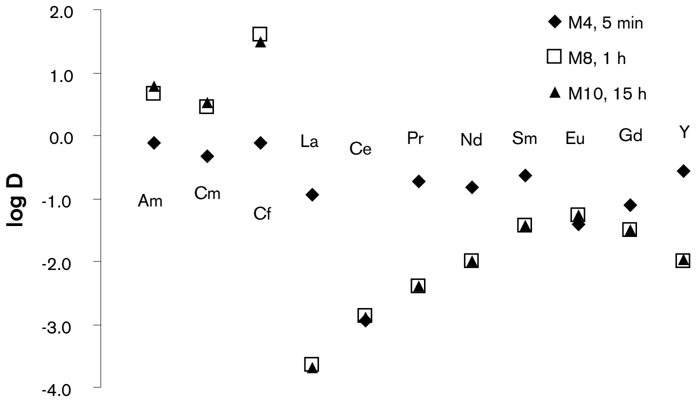


Figure 2.6. *Comparison between different shaking times when using 0.05 M* HNO_3 *and macro amounts of lanthanides. The data are from alpha spectrometry and ICP-MS measurements.*

In an attempt to get rid of the bromodecanoic acid (since it does not fulfil the CHON principle) organic phases consisting of 0.004, 0.01, 0.02 and 0.04 M C5 and also 0.5 M nonanoic acid dissolved in TBB were contacted with aqueous phases of 0.01 M H^+ and 1 M NO_3^-. All experiments were made in triplicates. The results are shown in Table 2.7. When plotting the logarithm of D against the logarithm of the C5 concentration the slope for Am-complexes is around 1.8 while the slope for Eu-complexes is around 1.6. Slopes with a value that is not an integer were also observed later when investigating the concentration behaviour, see Figures 2.20 and 2.21. One possible explanation could be dimerisation of the C5 in the organic phase.

Table 2.7. Extraction with nonanoic acid.

0.004 M C5		**Stdev%**	**0.01 M C5**		**Stdev%**
D Am	1.90E–02	14.79	D Am	9.42E–02	2.35
D Eu	2.60E–04	8.11	D Eu	9.45E–04	4.39
SF Am/Eu	73.07	16.86	SF Am/Eu	99.72	4.98
0.02 M C5		**Stdev%**	**0.04 M C5**		**Stdev%**
D Am	3.32E–01	1.16	D Am	1.13E+00	1.05
D Eu	2.62E–03	0.42	D Eu	9.52E–03	2.07
SF Am/Eu	126.91	1.24	SF Am/Eu	118.27	2.32

Extraction with different organic diluents

A halogenated organic diluent was tested to see the impact of a more electronegative diluent and thus trying to avoid dimerisation of C5 in the organic phase. Two organic phases were prepared. The first one contained 0.005 M C5 dissolved in TCl and the other one contained 0.004 M C5 and ~0.08 M HA dissolved in TCl. These organic phases were contacted with an aqueous phase consisting of 0.01 M H^+ and 1 M NO_3^- with trace amounts of ^{241}Am or ^{152}Eu. All experiments were made in triplicates. The results are shown in Table 2.8.

Table 2.8. Extraction with TCl as organic diluent.

0.005 M C5		Stdev%	0.004 M C5, 0.08 M HA		Stdev%
D Am	1.82E+00	4.28	D Am	6.08E–01	4.43
D Eu	2.06E–02	3.32	D Eu	8.05E–02	1.86
SF Am/Eu	88.17	5.42	SF Am/Eu	7.55	4.81

The addition of 2-bromodecanoic acid to the TCl solution did not have the same effect as when the acid was added to the TBB solution. In this case, both the extraction and the separation was less with the acid present.

A range of different organic diluents were tested to see what influence the organic diluent would have on D-values and SF. 0.005 M C5 was dissolved in different diluents. The different diluents are displayed below. The organic phases were contacted with a standard aqueous phase, 0.01 M H^+ and 1 M NO_3^- with trace amounts of ^{241}Am or ^{152}Eu. All experiments were made in triplicates. The results are displayed in the Figure 2.7. Hexane, TPH and trichloroethylene was also tested but C5 could not be dissolved in the two first ones and no extraction ($D<10^{-4}$) was observed for neither americium nor europium with the third one.

Extraction with an organic phase composed of 0.005 M C5 dissolved in 1-alcohols was investigated to determine the effect of the chain length of the diluent. Linear alcohols from hexanol to decanol were used. The reason for the study was to find a diluent that follows the CHON principle. The organic phases were contacted with a standard aqueous phase, 0.01 M H^+ and 1 M NO_3^- with trace amounts of Am or Eu. The results are presented in Figure 2.8.

Clearly the longer chain the lower the extraction and the separation. This is not so good for processes where long chained hydrocarbons, such as kerosene, are often used as diluents.

It seems that the diluent not only affects the D-value but also the SF between actinides and lanthanides. This was not in accordance to earlier modelling using a different system [NIL 02] and the results obtained here will be used for further modelling efforts.

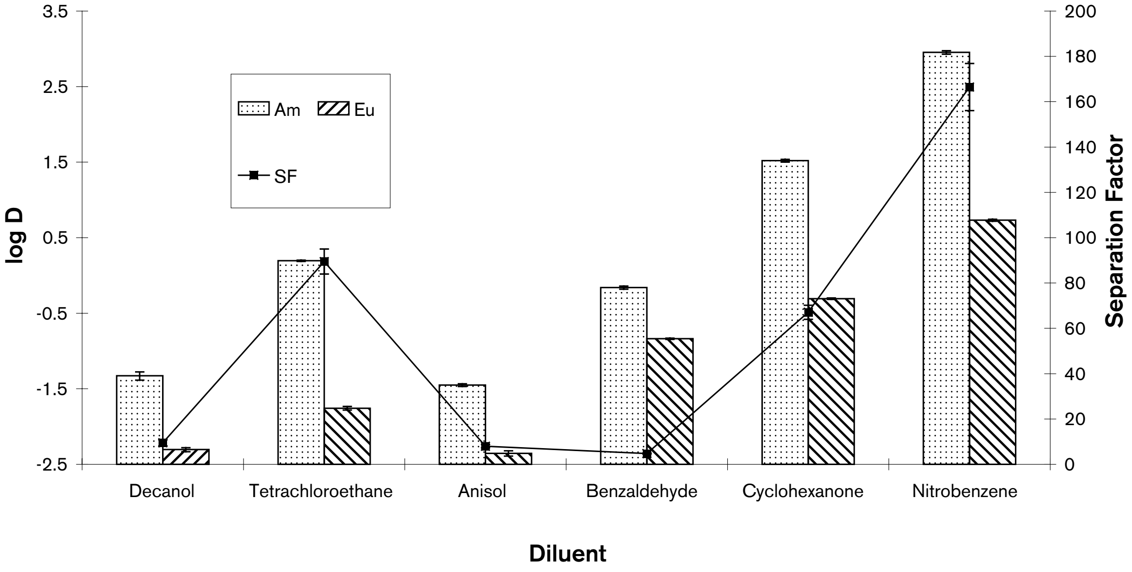


Figure 2.7. *Distribution ratios and separation factors for different diluents.*

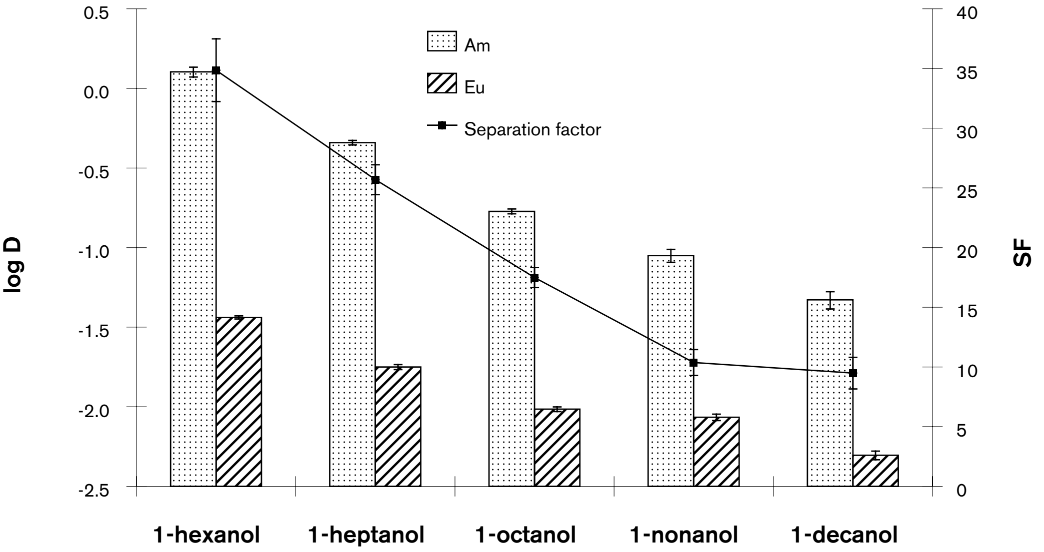


Figure 2.8. Extraction with different 1-alcohols.

Presence of C5 in aqueous phase when using cyclohexanone

Since cyclohexanone was proven to work quite well for the extraction a more thorough study of C5 in cyclohexanone was conducted. The use of cyclohexanone for solvent extraction gives a problem because of the mutual solubility of water in the organic phase and vice versa. For a process this problem can be reduced by pre-equilibrating both phases, i.e. saturating them with an organic or aqueous solution respectively. One major problem may of course arise if the extracting agent follows the organic phase into the aqueous, which, in a process, would result in a continuous loss of extracting agent.

To investigate the presence of C5 in the aqueous phase a UV-VIS spectrometer was used. Spectra were obtained for cyclohexanone and for a mixture of C5 in cyclohexanone, see Figure 2.9.

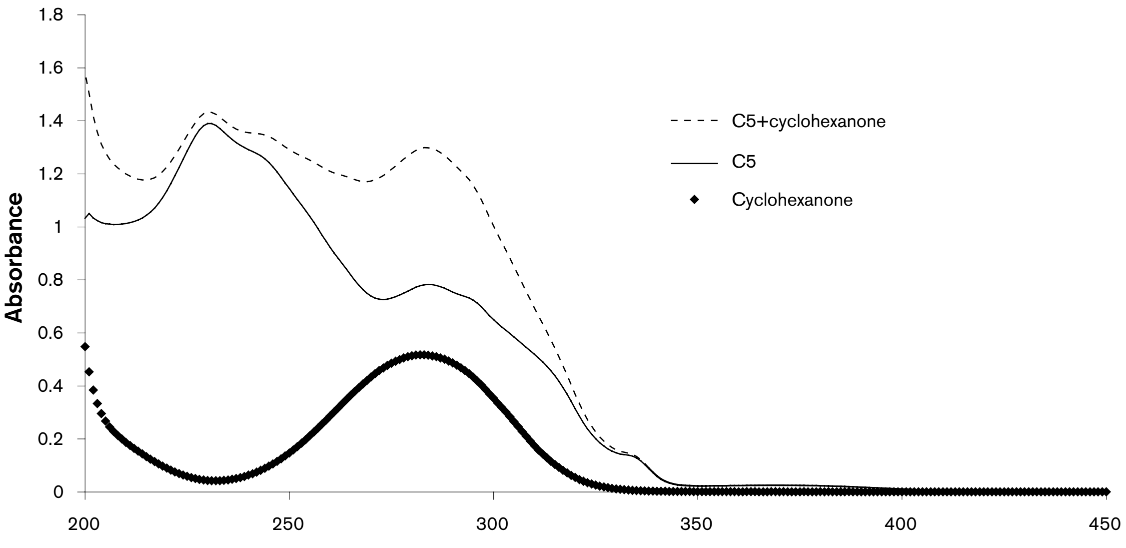


Figure 2.9. UV-VIS spectra of cyclohexanone and C5 in cyclohexanone. The calculated spectrum of C5 is also included.

By subtracting the spectrum of cyclohexanone from the mixed spectrum the spectrum of C5 was obtained, see Figure 2.9. C5 has a peak at 231 nm, which does not interfere much with the spectrum of cyclohexanone. A number of different concentrations of C5 in cyclohexanone was measured and a calibration curve was obtained by using Beer-Lamberts law, see Figure 2.10.

Organic solutions containing C5 dissolved in cyclohexanone were contacted with two different aqueous phases, one containing 1 M nitrate and the other ultra pure water (>18 MΩ). Spectra were obtained from both aqueous and organic samples before and after contact. No C5 was observed in the aqueous phase. This indicates that although some cyclohexanone is dissolved in the aqueous phase the character of that phase is not altered enough to dissolve any C5.

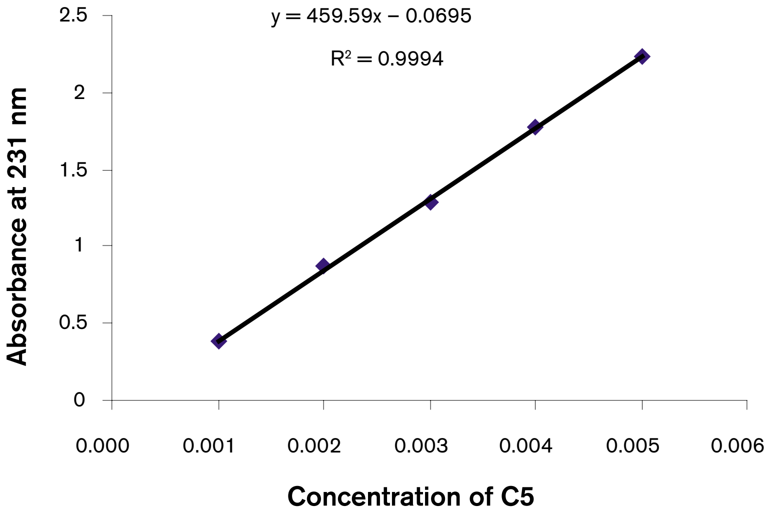


Figure 2.10. *Calibration curve for C5 using the absorbance peak at 231 nm.*

Temperature dependencies

The effect on the distribution ratios at different temperatures was investigated. An organic phase of 0.004 M C5 in TCl was contacted with an aqueous phase consisting of 0.01 M H^+ and 1 M NO_3^- with trace amounts of either ^{241}Am or ^{152}Eu. All experiments were made in triplicates at 10, 20 and 30 ºC. The results are shown in Figure 2.11. The extraction clearly decreases with temperature.

The temperature dependence of extracting using C5 and also $CyMe_4$-BTBP, another derivative of the BTBP family, in cyclohexanone was investigated. Aqueous phase was 0.5 M HNO_3 + 0.5 M $NaNO_3$ with 10^{-3} M lanthanides and spiked with trace amounts of ^{241}Am, ^{244}Cm, ^{252}Cf and ^{152}Eu. The contact time was 30 minutes in a thermo shaker device. The efficiency of the thermo shaker was investigated beforehand and it was found that 30 minutes contact time was enough to reach equilibrium. All phases were pre-equilibrated before extraction experiments were carried out.

The temperature ranged from ~29 to 45 ºC. The plot of log D versus 1/T indicates that for both C5 and $CyMe_4$-BTBP the extraction reaction is slightly exothermic, see Figures 2.12 and 2.13.

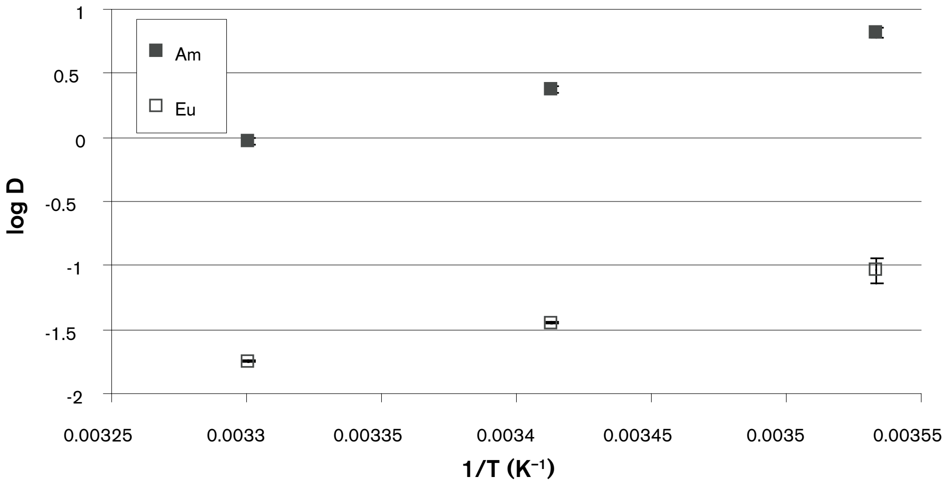


Figure 2.11. Temperature studies for extraction with C5 in TCl.

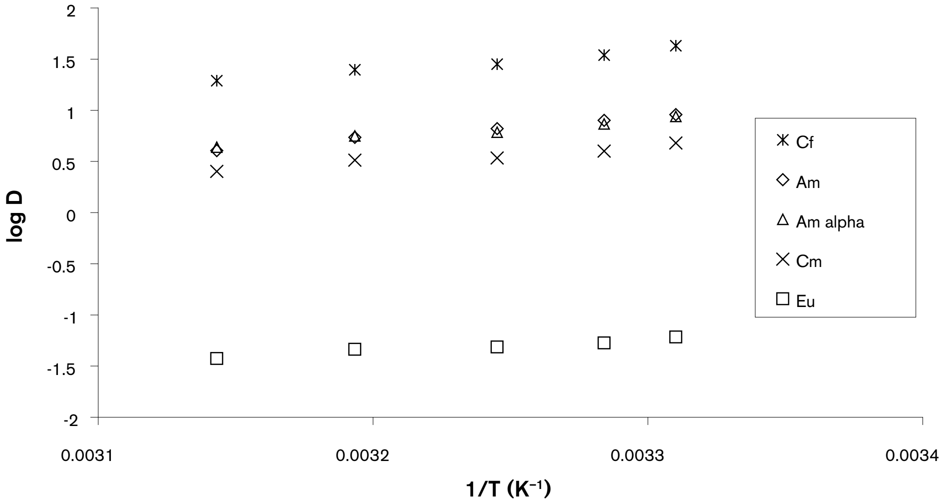


Figure 2.12. Temperature dependence of the extraction using C5 in cyclohexanone.

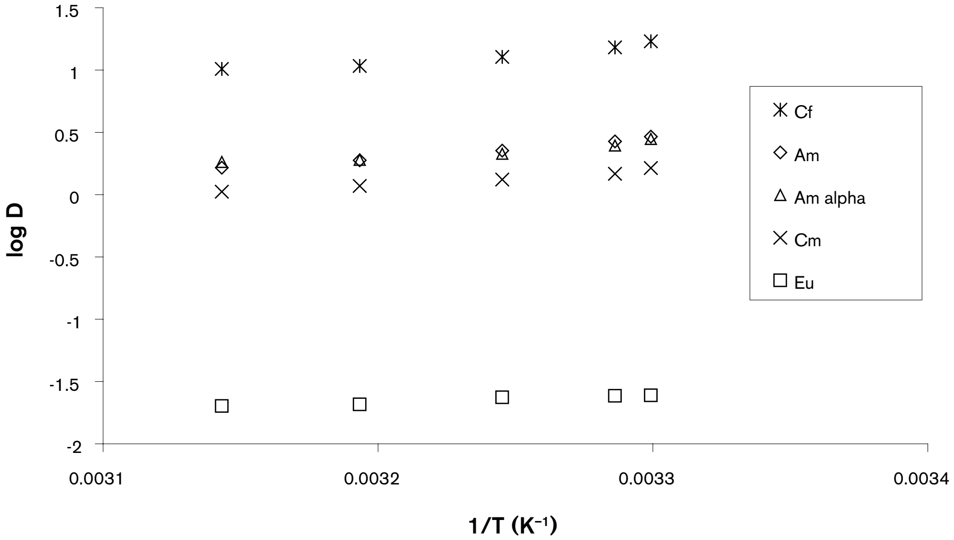


Figure 2.13. Temperature dependence of the extraction using CyMe$_4$-BTBP in cyclohexanone.

For the lanthanides the temperature dependence is less exclaimed and therefore no conclusions can be drawn from the results of the ICP-MS analysis except that the lanthanides follow a trend with higher extraction for the heaviest and gadolinium at a breaking point, see Figure 2.14. This behaviour is observed on several occasions when working with lanthanides and this behaviour including the tetrad effect is explained later, cf section 2.3.

Kinetics

Kinetic studies were performed to see how long time it takes to reach equilibrium. An organic phase of 0.004 M C5 in TCl was contacted with an aqueous phase consisting of 0.01 M H^+ and 1 M NO_3^- with trace amounts of either Am or Eu. The samples were shaken 1, 3, 5, 10, 20, 30, 40 or 60 minutes by hand or for 1 or 24 hours with a shaking machine. All experiments were made in triplicates. The results are shown in Figure 2.15. The values for one hour are higher for the shaking machine. The reason is that these samples are shaken at room temperature (~20 ºC) while the other samples are shaken at elevated temperature due to the contact with the shakers hand, thereby decreasing the extraction according to Figure 2.11. From Figure 2.15 it is reasonable to draw the conclusion that shaking for 5 minutes is enough to reach equilibrium when working with tracer amounts.

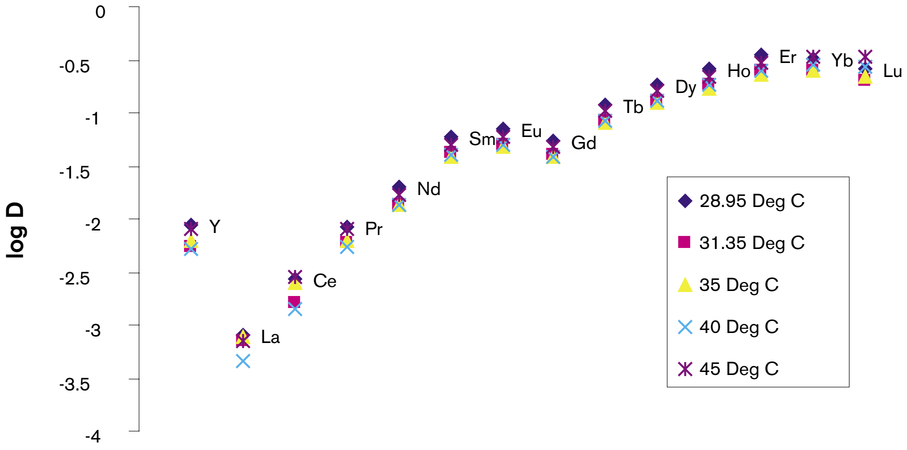


Figure 2.14. *Temperature dependence for the lanthanide series when using C5. The results for CyMe$_4$-BTBP are similar.*

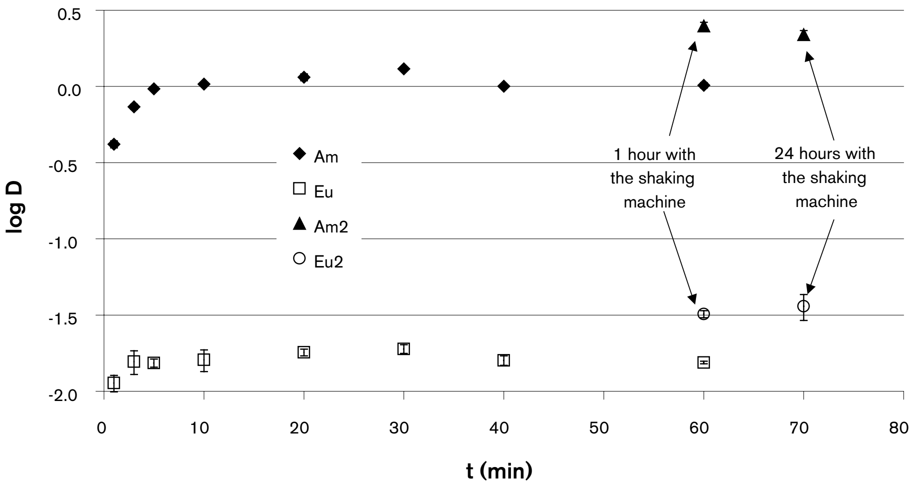


Figure 2.15. *D-values for different shaking times.*

The kinetics of the extraction was also investigated by using C5 in cyclohexanone. An organic solution of 0.01 M C5 in cyclohexanone was contacted with an aqueous phase of 0.5M HNO_3 + 0.5M $NaNO_3$ with 10^{-3} M lanthanides and spiked with ^{241}Am, ^{244}Cm, ^{252}Cf and ^{152}Eu. Both phases were pre-equilibrated before extraction experiments were carried out.

The phases were contacted for 1 up to 60 minutes in the vortex-shakers. Results, shown in Figure 2.16, indicate that 5 or 10 minutes contact is enough to reach equilibrium for the actinides. The distribution ratios decrease somewhat for the longest contact time, which may be due to increased temperature from prolonged running of the vortex-shakers. A possible explanation may also be that the optimal contact time is around 20 min for the actinides. For europium there seems to be a negative effect on D with increasing contact time, see also Figures 2.17 and 2.18.

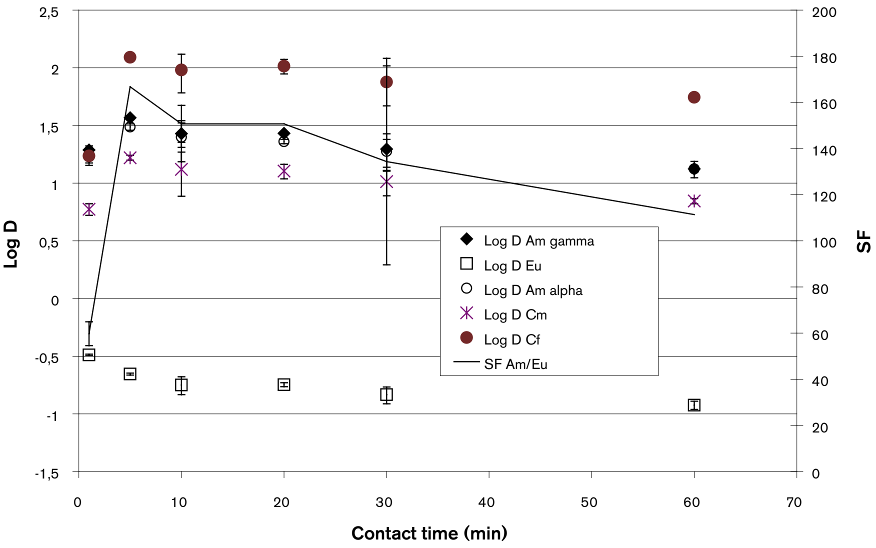


Figure 2.16. *Kinetic behaviour of ^{241}Am, ^{244}Cm, ^{252}Cf and ^{152}Eu.*

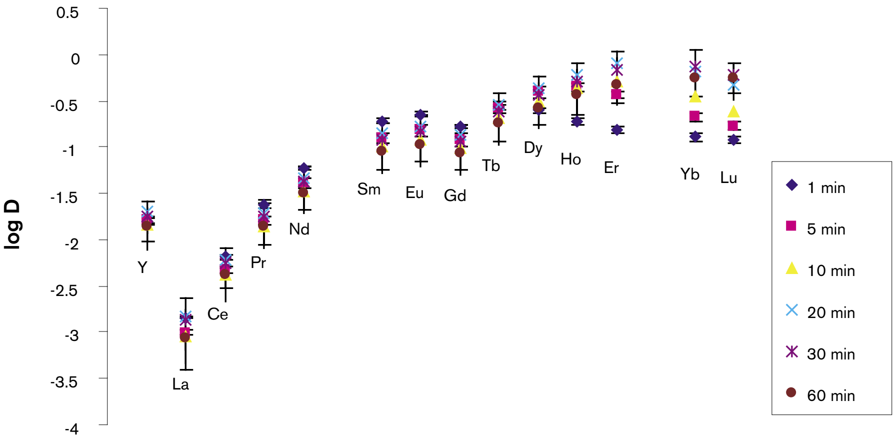


Figure 2.17. *Kinetic behaviour for the lanthanide serie.*

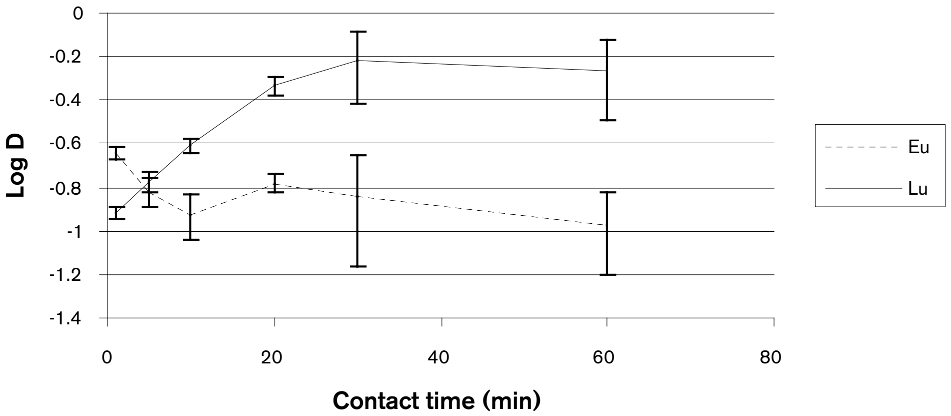


Figure 2.18. *The kinetic behaviour of two lanthanides.*

Although for the lanthanide series the kinetics is not so easily explained. For the lightest lanthanides the kinetics seem to be very fast and a prolonged contact time will decrease the amount of lanthanide extracted. For the heavier lanthanides the behaviour is the opposite, and the breaking point is somewhere around gadolinium, see Figures 2.14 and 2.17.

In figure 2.17 the tetrad effect can be seen, although promethium and thulium are missing. There is a pronounced breaking point at gadolinium.

The heaviest lanthanide, lutetium, shows an increase in extraction as the contact time increases while europium shows a decrease. The lanthanides lighter than europium all show the same trend as europium in figure 2.18.

Extraction with different concentration of C5

Experiments were made using different concentrations of C5 to study the influence of C5 concentration on the extraction. Two different organic diluents were used, tetrachloroethane and anisole. The reason for choosing these diluents was that the results from the earlier experiments indicated that they both gave good extraction but very different SF. The aqueous phase consisted of 1 M NO_3^- and 0.01 M H^+ as usual. All experiments were made in triplicates. The results, Figures 2.19 and 2.20, indicate that for tetrachloroethane the concentration behaviour of the extraction can be plotted as a straight line in a logarithmic scale. The slope is approximately 1.5 for both americium and europium. For anisole it is more difficult to see the concentration dependence. There may be a curve instead of a line, which could indicate that there is more than one species that is being extracted and that there is no species that have total dominance in the concentration range that was investigated. Dimerisation of the C5 in the organic phase could also explain the shape of the graphs.

Extraction experiments were also made with different amounts of C5 in cyclohexanone. The aqueous phase was 0.5M HNO_3 + 0.5M $NaNO_3$ with trace amounts of ^{241}Am, ^{244}Cm, ^{252}Cf and ^{152}Eu. Contact time was 10 minutes in the vortex shakers. Both phases were pre-equilibrated before extraction experiments were carried out.

From the slope analysis one can draw the conclusions that two C5 molecules bind to each metal ion, see Figure 2.21. The slope for Eu is somewhat lower than for the actinides and it may be possible that there exist metal complexes with only one C5 but that the complexes with two C5 molecules dominate. This is more pronounced for the actinides than for europium. These results differ somewhat from above results that did not yield any integer values for the slope analysis. The reason for using just trace amounts of metals is to avoid loading and also to be able to neglect the change in free ligand concentration when metals are complexed.

The dependency of changing C5 concentration was also investigated for berkelium, cf section 2.5.

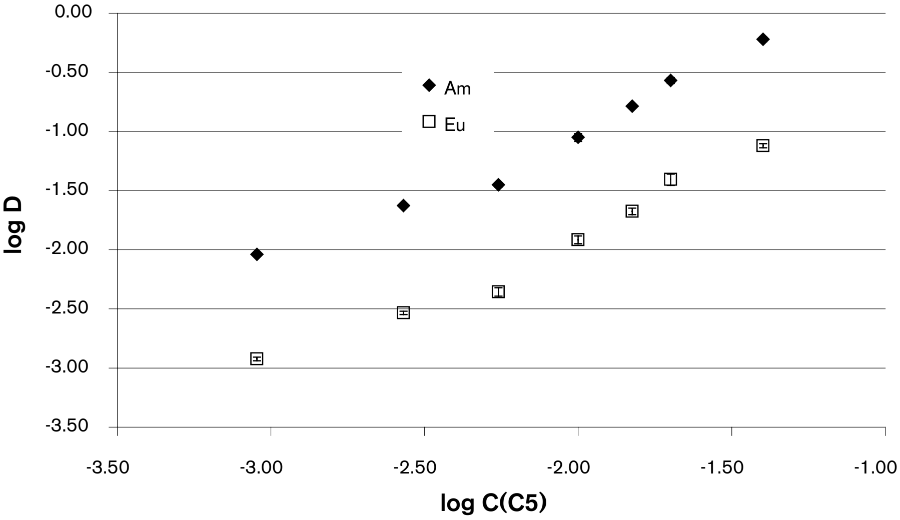


Figure 2.19. *D for different C5 concentrations in anisol.*

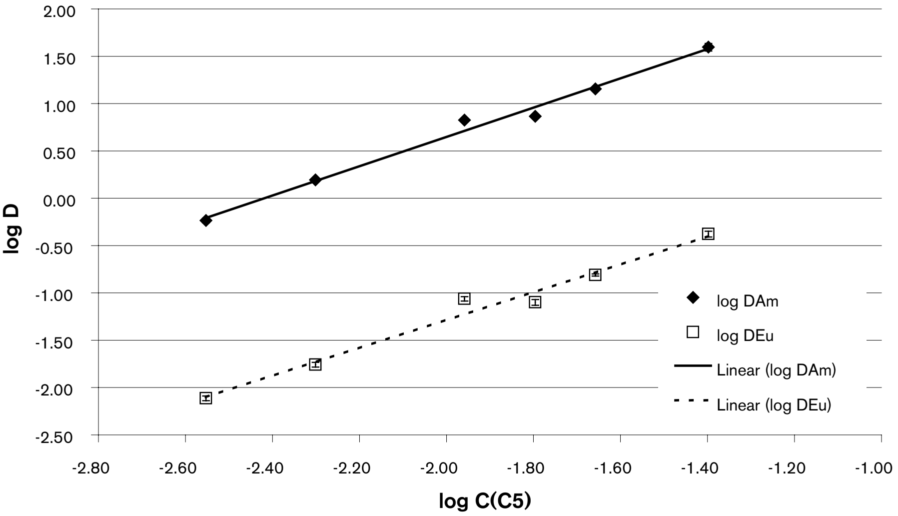


Figure 2.20. *D for different C5 concentrations in TCl.*

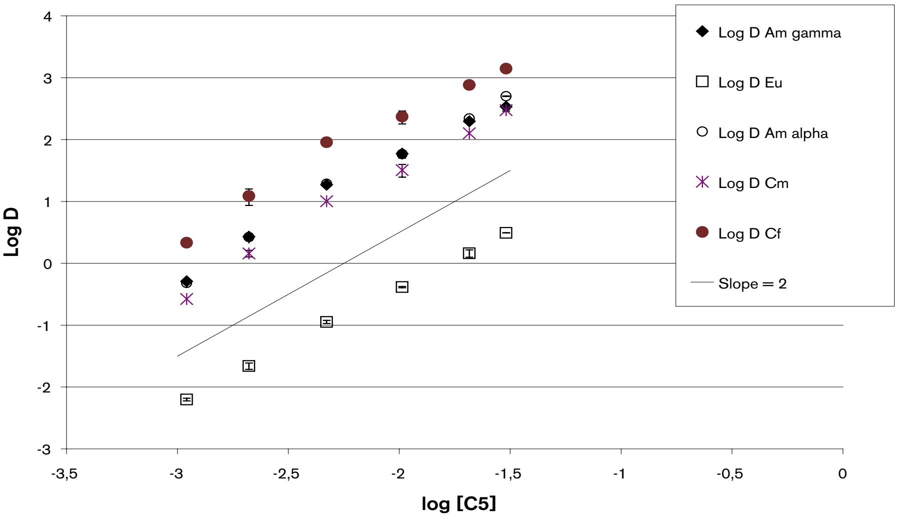


Figure 2.21. *Slope analysis for C5 in cyclohexanone.*

Extraction using simulated HAW

Experiments were made by contacting an organic phase of saturated C5 in cyclohexanone with simulated PUREX raffinate (HAW) of different HNO_3 concentrations, the aqueous phases were spiked with trace amounts of ^{241}Am, ^{244}Cm, ^{252}Cf and ^{152}Eu. All phases were pre-equilibrated before contact. 0.5, 1, 3 and 4 M HNO_3 HAW-solutions were used. Results are still under evaluation but so far the results indicate that the americium and europium separation is quite constant up to 3 M HNO_3 and drops as the americium extraction drops at the strongest HNO_3-concentration, see Figure 2.22. This is similar to previous experiments using high concentrations of HNO_3 that indicate only a slight decrease at 3 M and a considerably larger at 4 M, see Figure 2.22 and Table 2.23. Another problem with the highest HNO_3 concentration was that the mutual solubility of aqueous and organic phase seemed to increase with increasing HNO_3 concentration resulting in a notable difference in phase volumes.

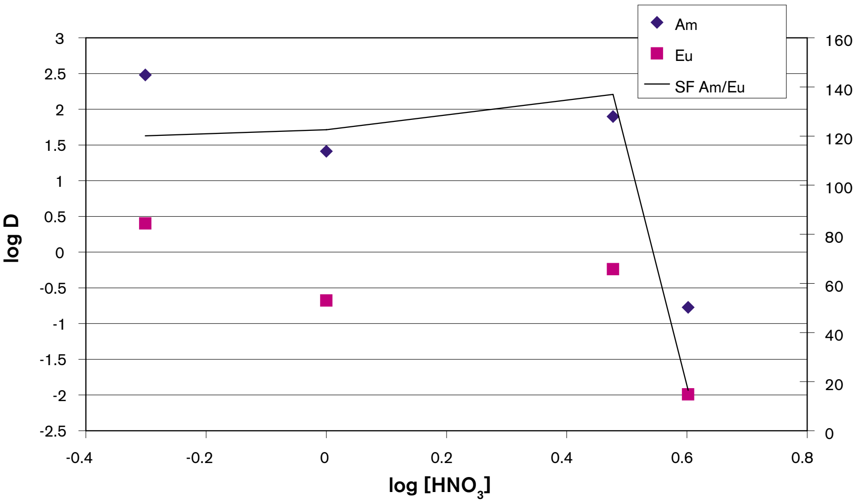


Figure 2.22. *Separation of americium and europium in HAW-solutions at different HNO_3 concentrations.*

The lanthanides seem to follow more or less the same trend as before although the results are quite uncertain since only a few samples have been analysed so far. However, it seems that is should be possible to selectively extract Am over the lanthanides in a HAW-solution of at least 1 M HNO_3, see Figure 2.23.

The values for the lanthanides in Figure 2.23 are the results from only one sample so far. This fact makes uncertainties impossible to calculate and the final results may differ. Also the heaviest lanthanides were present only in small amounts in the initial aqueous solutions, which makes the evaluation even more difficult.

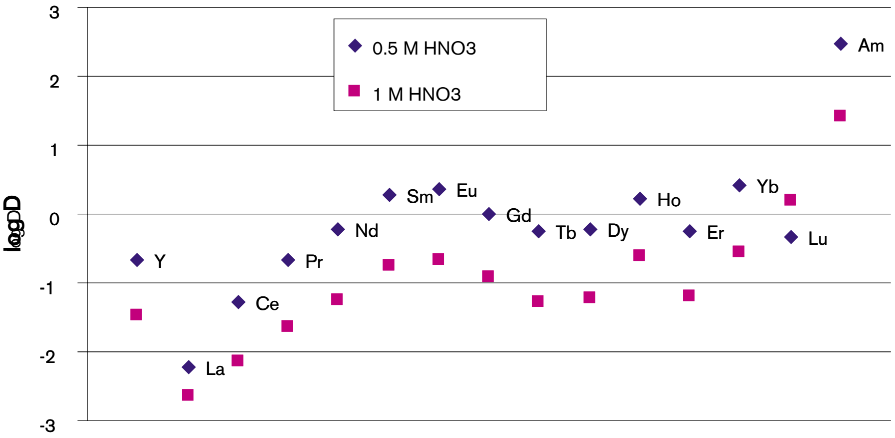


Figure 2.23. *Distribution ratios for the lanthanides. D for americium have been included for comparison.*

Stripping experiment

Stripping has been tested for the system with organic phase consisting of 0.004 M C5 in TCl. After contacting the organic phase with the aqueous phase, 0.01 M H^+ and 1 M NO_3^- with trace amounts of Am, the organic phase was scrubbed with an aqueous phase consisting of 0.01 M H^+ and 1 M NO_3^-. The stripping was then performed by contacting the organic phase with ~1 M oxalic acid. The results are shown in Table 2.9.

Table 2.9. Stripping test with oxalic acid.

	D Am	Stdev %
Extraction	2.60	2
Scrubbing	3.22	3
Stripping	$< 10^{-4}$	/

Another series was made with different concentration of the oxalic acid but otherwise the same conditions. The concentrations used were 0.5, 0.1, 0.05 and 0.01 M oxalic acid. The results are shown in Table 2.10.

Table 2.10. Variation in D-value with different oxalic acid concentrations.

	D Am	Stdev %
Extraction	2.28	/
Scrubbing	3.39	/
0,5M ox. acid	3.58E–04	8
0,1M ox. acid	4.00E–04	9
0,05M ox. acid	5.00E–04	4
0,01M ox. acid	5.93E–04	9

As expected the concentration of the oxalic acid is not important in this case since we are dealing with trace quantities of metals. In a system with macro amounts the situation might be rather different.

Extraction was also tested with the organic phase after stripping to see if the D-value was the same as before. No change could be seen.

2.2 Radiolysis of CyMe$_4$-BTP, CyMe$_4$-BTBP and C5-BTBP

Radiolysis of CyMe$_4$-BTP, CyMe$_4$-BTBP and C5 in cyclohexanol was studied. Cyclohexanone was used as diluent because it yields good distribution ratios and it should not protect the ligands from the radiolysis products. Two samples with 0.005 M CyMe$_4$-BTP, two samples with 0.005 M CyMe$_4$-BTBP and two samples with 0.005 M C5 in cyclohexanone was prepared. One sample of each molecule was placed in a gamma-irradiating cobalt source (Gamma cell 220 from Atomic Energy of Canada ltd) with an activity of 0.78 TBq ^{60}Co and an estimated dose rate to water of ~20 Gy/h at the time of the irradiation. The flasks were connected via tubes to a bubble flask to avoid any pressure build up. The three other samples were placed outside the gamma source during the irradiation time to serve as references. Samples were taken during a time period of ~850 h (35 days). At each sampling three samples of 0.5 ml were taken from each flask, both reference and irradiated. For the CyMe$_4$-BTP and CyMe$_4$-BTBP solutions, every second sampling an addition of three times 0.5 ml was taken from each flask.

The samples were contacted with 0.5 ml of an aqueous phase containing trace amounts of ^{241}Am, 1 M NO_3^- and 0.01 M H^+. The extra samples, taken every second time, were contacted with an aqueous phase containing trace amounts of ^{152}Eu, 1 M NO_3^- and 0.01 M H^+. For C5 both ^{241}Am and ^{152}Eu was added to all samples. The contact time was 5 min, shaking vigorously by hand. After contact the phases were separated by centrifugation for 15 min at 2000 g and aliquots of 100 µl were taken from each phase for gamma measurements in a NaI(Tl) detector (Intertechnique Gamma Counter 4000).

For the CyMe$_4$-BTP and CyMe$_4$-BTBP, the distribution ratios show no decrease due to radiolysis in any sample, see Figures 2.24 and 2.25. The D-values seems to rise during time but this could be explained by evaporation effects.

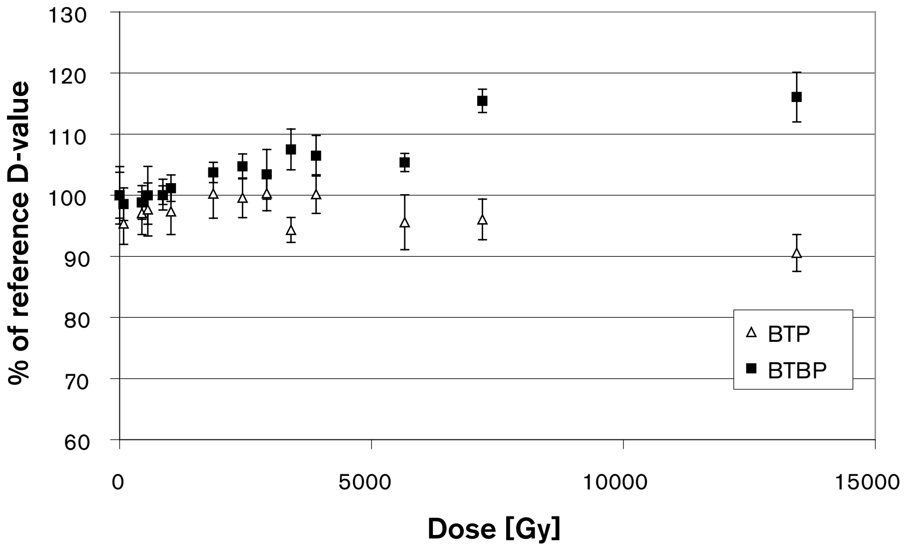


Figure 2.24. Distribution ratios of americium as percent of reference D-value plotted against the dose to the irradiated samples of CyMe$_4$-BTP and CyMe$_4$-BTBP.

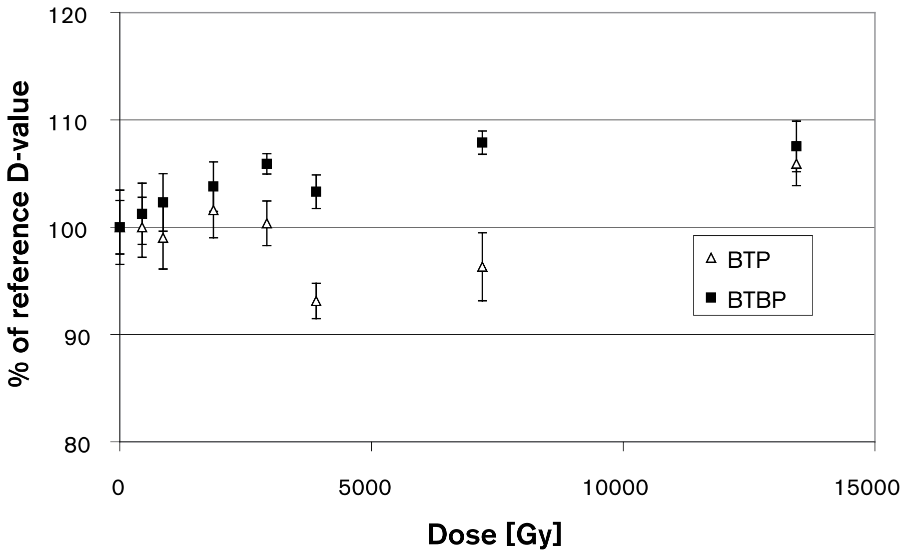


Figure 2.25. Distribution ratios of americium as percent of reference D-value plotted against the dose to the irradiated samples of CyMe$_4$-BTP and CyMe$_4$-BTBP.

For C5 the D-values for Am dropped to around 20% of the reference value after 35 days while the Eu stayed at around 80% of the reference, see Figure 2.26. The separation factor dropped from around 150 to 30 after 35 days in the gamma source. After irradiation the organic phase went clearer while the reference stayed at the same colour. It is noteworthy that the extraction capability for europium is nearly unchanged as the dose is increased while the extraction of americium is significantly decreased.

These results indicate that the extra ring structure of CyMe$_4$-BTBP as compared to C5 results in increased stability towards radiolysis.

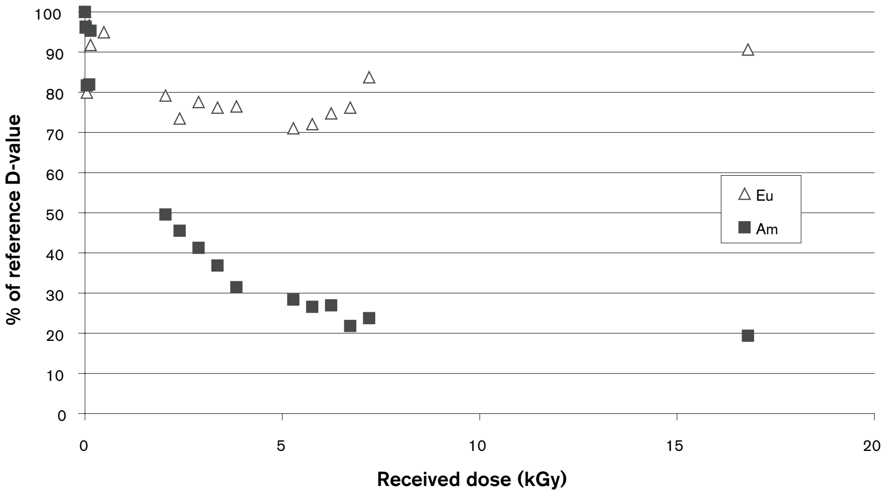


Figure 2.26. The decrease in D-values for irradiated samples as % of the reference D-values.

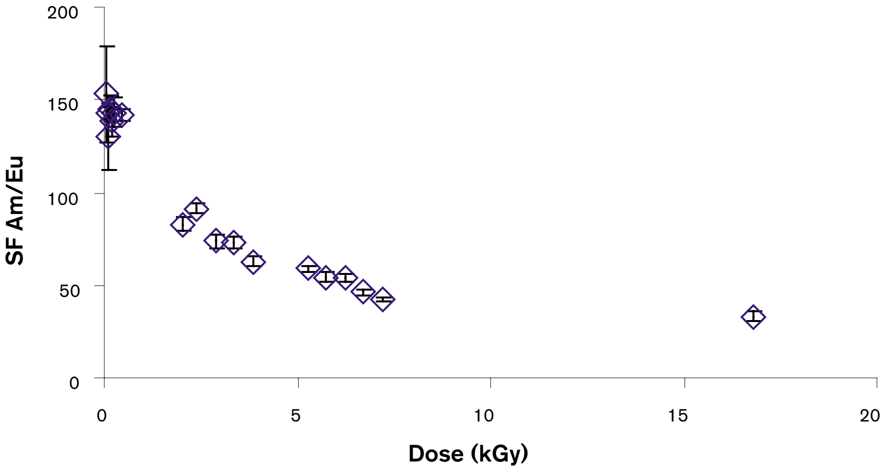


Figure 2.27. The separation between Am and Eu as a function of received dose.

2.3 Basic lanthanide chemistry

The basic extraction behaviour of lanthanides was investigated. This is an important field since generally all the lanthanides are represented by europium. In many cases this is not a representative lanthanide as will be seen in this chapter. There is a large difference in extraction behaviour within the lanthanide series.

Basic extraction

Some radionuclides mentioned in this report have short half-lives compared to the total measurement time, which demands correction calculations. Assuming that the dead-time of the detector is negligible gives the following expression for the experimental distribution ratio:

$$D = \frac{N_{org}^{zero}}{N_{aq}^{zero}} = \left(\frac{counts_{org} e^{\lambda \Delta t_{org}}}{(1 - e^{-\lambda t_{org}})} \right) \Bigg/ \left(\frac{counts_{aq} e^{\lambda \Delta t_{aq}}}{(1 - e^{-\lambda t_{aq}})} \right) \qquad (2.3.1)$$

where N is the number of atoms at time zero, counts is the sum of all counts in the peaks that have been used in the spectra evaluation (which is proportional to the amount or concentration of the studied species in the specific phase), Δt is the time difference between time zero and the start of the measurement, and t is the time of the actual measurement.

The uncertainty in distribution ratios comes from several sources: phase volumes, concentrations of different species in both phases, temperature, purities of stock solutions, pipetting, detector efficiencies etcetera. The factor that is believed to contribute most to the uncertainty in this case however is the spectra evaluation. The Genie 2000 program was used, importing spectra from an Intertechnique multi-channel analyzer system for the lanthanides evaluated in Germany and from Gamma Vision (Ortec) for the more long-lived radionuclides.

The uncertainty in D using i different peaks in the spectrum can be expressed as:

$$\sigma_D = D\sqrt{\left.\left(\frac{\sum_i \sigma_{xi}^2}{\sum_i x_i}\right)\right|_{aq} + \left.\left(\frac{\sum_i \sigma_{xi}^2}{\sum_i x_i}\right)\right|_{org}} \qquad (2.3.2)$$

where x_i is the total number of counts in peak i and σ_{xi} corresponding standard deviations (1 sigma).

Experimental

Trace activities of ^{140}La, ^{142}Pr, ^{149}Nd, ^{153}Sm, ^{159}Gd, ^{165}Dy, ^{166}Ho, ^{171}Er and ^{176m}Lu were produced at the TRIGA Mainz research reactor by thermal neutron activation. ^{141}Ce, ^{152}Eu, ^{160}Tb, ^{170}Tm and ^{175}Yb were produced at the Institutt for Energiteknikk in Kjeller, Norway (JEEP II reactor). Results for Pm and Eu have already been reported [AND 04B], but are included here to make the lanthanide series complete.

The organic phase consisted of 0.01 M BODO (see Figure 2.28), 1 M 2-bromodecanoic acid (HA) in tert-butyl benzene (TBB). The aqueous phase consisted of either 1 M perchlorate ion concentration (0.01 M H^+) or 5 M total ionic strength (0.01 M nitrate, 0.01 M H^+ the rest perchlorate). The results for the higher ionic strength were obtained from the experiments to determine the nitrate complex formation constants, described in section 2.4 in this report.

0.4 ml of each phase was contacted by vigorous shaking for 5 minutes. The phases were allowed to settle for a few minutes. Samples were taken from both the organic and aqueous phases for gamma analysis using HPGe detectors with efficiencies of between 17.7 and 29.2 % and resolutions of 1.69–1.8 keV (at ^{60}Co, 1332 keV), respectively. The organic and aqueous phases from the same shaking vial were always measured using the same detector. The measurement times were adjusted to optimise the influence of statistical uncertainties.

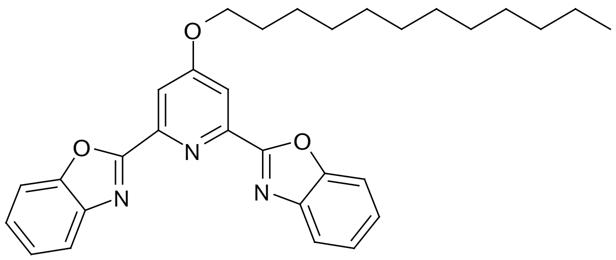


Figure 2.28. *2,6-bis-(benzoxazolyl)-4-dodecyloxylpyridine (BODO).*

All experiments were done in duplicate. A constant temperature was used (295 K) because the stability constants are temperature dependent, see e.g. [SIL 86]. Eu was measured in a NaI(Tl) scintillation well detector connected to an Intertechnique model CG-4000 with automatic sample changing and Pm in a LKB Wallac 1219 Rackbeta liquid scintillation detector.

The results for 1 and 5 M are shown in Figures 2.29 and 2.30.

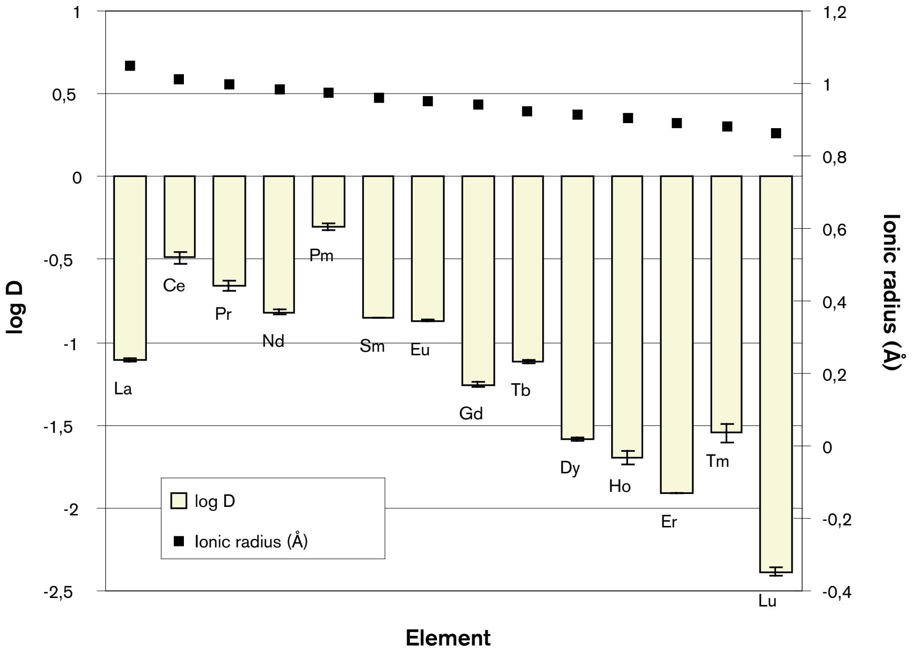


Figure 2.29. *Distribution ratios for the lanthanides at 1 M ionic strength (perchlorate ions, 0.01 M H^+, 295 K). Left axis: log D, right axis: ionic radius (coordination number 6). Uncertainties are included in the figure and are based on the standard deviation of the duplicate/triplicate samples.*

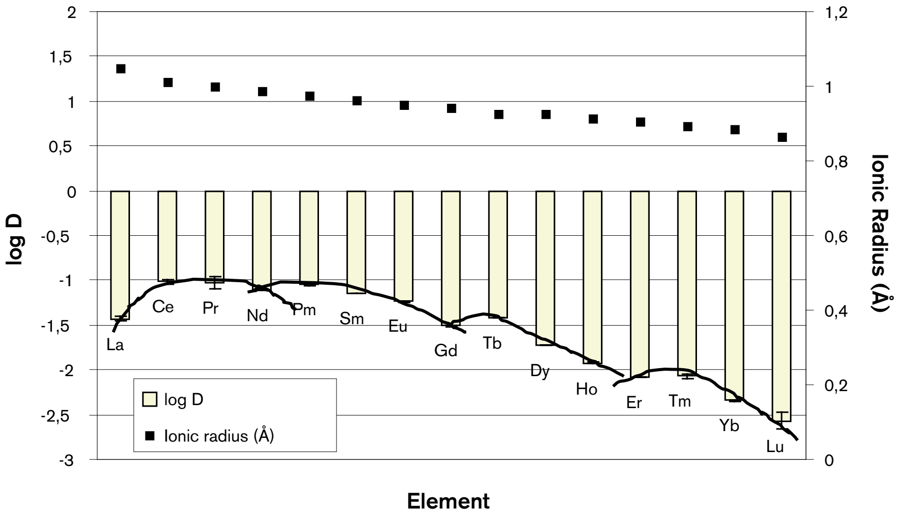


Figure 2.30. *Distribution ratios for the lanthanides at 5 M ionic strength (perchlorate ions, 0.01 M H^+, 295 K). Left axis: log D, right axis: ionic radius (coordination number 6). Uncertainties are included in the figure and are based on the standard deviation of the duplicate/triplicate samples.*

There is a clear trend with decreasing distribution ratios with increasing atomic number. The tetrad effect (or the double-double effect) has previously been described in the literature [FID 71, JOR 70, LIM 90, LIM 91, NUG 70, PEP 69, PEP 70]. It states that it is possible to group the lanthanide elements into four tetrads when plotting the logarithm of a certain parameter versus Z through the use of four smooth curves. The effect is explained by the stabilisation energy related to inter-electron repulsion energy for the 4f electrons. The gadolinium point is common to the second and third tetrad and can be explained by the extra stability in the $4f^7$ electron configuration. The two other break-points are located at $4f^3$–$4f^4$ and $4f^{10}$–$4f^{11}$, which is also the case here (neodymium and erbium). Here the tetrad effect is more pronounced at higher ionic strength and is indicated in Figure 2.30 by lines.

The decrease in extraction along the series may also be explained with lanthanide contraction in ionic radius. The ionic radii for coordination number 6 are shown in the figures. When the charge-to-radius ratio increases it will increase the reaction with the negatively charged 2-bromodecanoic acid anion, but at the same time decrease the BODO-metal interaction since the degree of covalency in the bonding decreases. This shows that the BODO-metal interaction is decisive for the distribution ratio. Another factor that may affect the trend in distribution ratio is the increase in hydration enthalpy along the series [BUR 78]. The decrease in extraction with increasing atomic number along the lanthanide series has been shown earlier with e.g. di(2-ethyl hexyl)orthophosphoric acid [PEP 57] and dihexyl-N,N-diehtyl-carbamoylphosphonate [HOR 81].

When plotting the logarithm of the distribution ratio versus the ionic radius there is a change in slopes between the light and heavy lanthanides, see Figure 2.31. This has been seen before [PEP 57] and the break-point is often set to gadolinium with its half-filled shell in reference to the electronic structure. This half-filled effect has also been mentioned by e.g. Bommer [BOM 37].

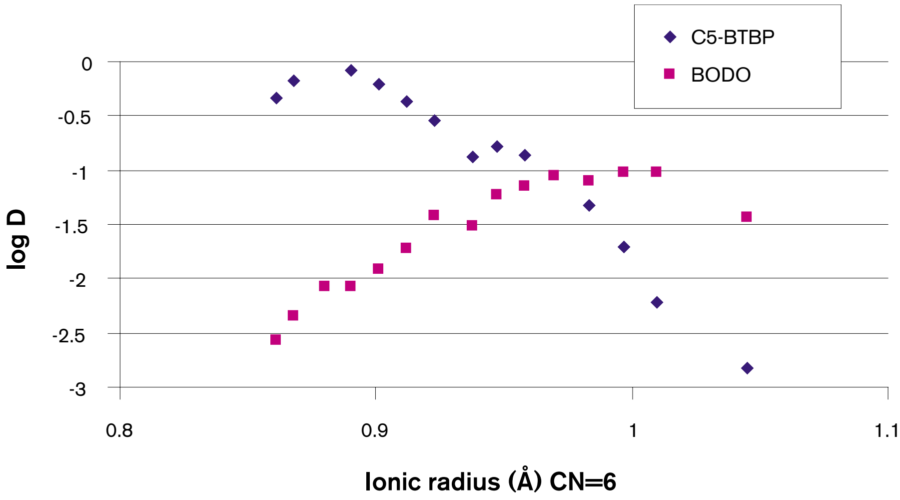


Figure 2.31. *Effect on ionic radius on the logarithm of the distribution ratio. For BODO (5 M total ionic strength, 0.01 M nitrate ion concentration). Tb (highest in the middle) and La (on the right side) exhibit abnormal behaviour compared to the rest of the elements. For C5 (1 M total ionic strength, only nitrate), the results are taken from the kinetic experiments, cf Figure 2.17.*

2.4 Nitrate complex formation (stability) constants

Theory

The nitrate complex formation reaction of a metal ion M^{3+} can be described as follows:

$$M^{3+} + iNO_3^- \rightleftharpoons M(NO_3^-)_i^{(3-i)+} \qquad (2.4.1)$$

Here the metal ion is assumed to be trivalent, which is the case for all lanthanides and studied actinides. The stability constants of these reactions can be expressed as:

$$\beta_i^* = \frac{\left[M(NO_3)_i^{(3-i)+}\right]}{\left[M^{3+}\right]\left[NO_3^-\right]} \qquad (2.4.2)$$

The modified stability constants are used (indicated by *) because the activity coefficients have been included in the constants themselves.

It is possible to study the nitrate complex formation using the BODO-HA synergic solvent extraction system. If the nitrate ion concentration in the aqueous phase is increased (still having a constant ionic strength, compensating with perchlorate ions) the nitrate complex formation will be more pronounced and will start competing with the extraction of metal ions into the organic phase. The distribution ratio will thus decrease and this gives a possibility to model the nitrate complex formation constants for the metal ion(s) studied. The distribution ratio in a system with nitrate complex formation as competing mechanism can be written as:

$$D_M = \frac{[M]_{org}^{tot}}{[M]_{aq}^{tot}} = \frac{D_0}{1 + \sum\limits_{i=1,2\ldots n} \beta_i^* \left[NO_3^-\right]^i} \qquad (2.4.3)$$

where D_0 is the metal distribution in the absence of nitrate ions in the system. It can be considered as a constant in the system studied: constant amount of BODO and no variation in the hydrogen ion concentration. Trace amounts of the metal ions is a requirement for this assumption to be valid.

Using a minimizing routing to fit Equation 2.4.3 to experimental data (distribution ratios) will determine the unknowns: D_0 and β_i.

Experimental

The organic phase consisted of 0.01 M BODO and 1 M HA in TBB. In the aqueous phase a constant ionic strength of 5 M was used, nitrate and perchlorate, to be able to include the activity coefficients of the reactions in the stability constants. The same experimental method as described in section 2.3 was used.

Results

The experimental results for the rest of the lanthanides are shown in Figures 2.32–2.35 and the modelled stability constants are given in Table 2.11.

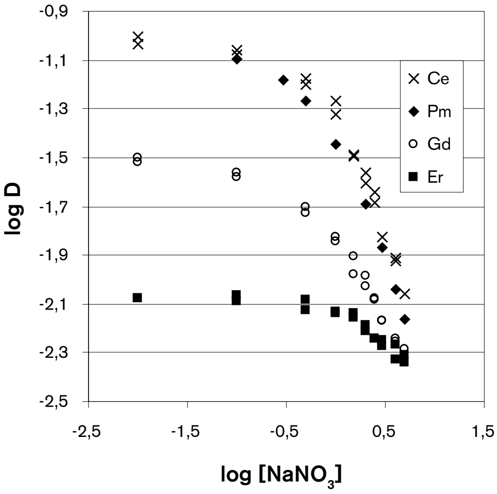


Figure 2.32. *Experimental distribution ratios for Ce, Pm, Gd and Er (0.01 M BODO, 1 M HA, 5 M total ionic strength).*

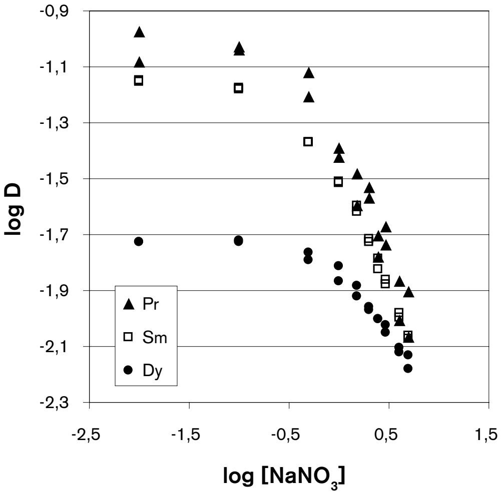


Figure 2.33. *Experimental distribution ratios for Pr, Sm and Dy (0.01 M BODO, 1 M HA, 5 M total ionic strength).*

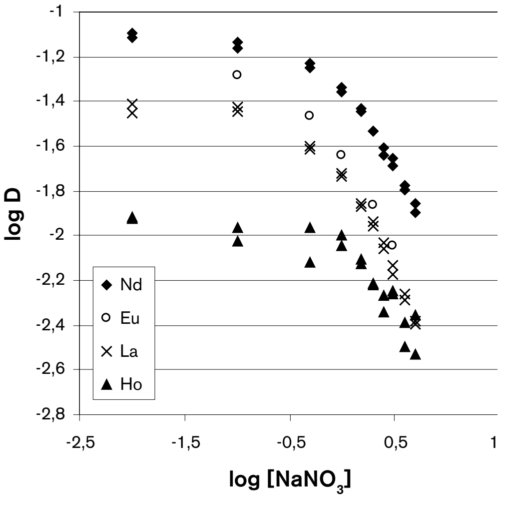


Figure 2.34. *Experimental distribution ratios for Nd, Eu, La and Ho (0.01 M BODO, 1 M HA, 5 M total ionic strength).*

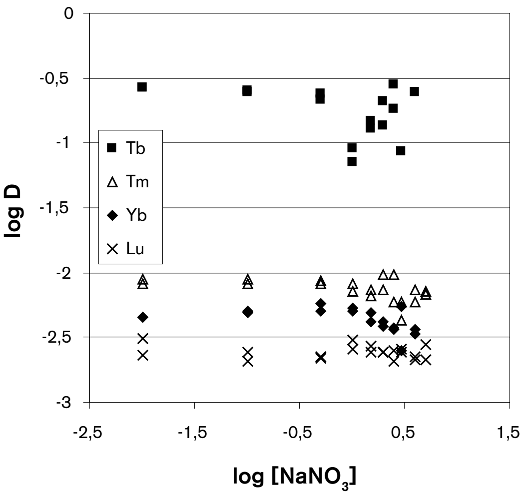


Figure 2.35. *Experimental distribution ratios for Tb, Tm, Yb and Lu (0.01 M BODO, 1 M HA, 5 M total ionic strength).*

Terbium, thulium, ytterbium and lutetium could not be evaluated because of either low distribution ratios and/or inherent difficulties in the spectra evaluation. The values for terbium in Figure 2.35 are too high and should be adjusted to the rest of the elements in that group. This was tested in an extra experiment and measurement in a NaI(Tl) scintillation well detector connected to an Intertechnique model CG-4000 with automatic sample changing instead of the HPGe that was used originally.

Table 2.11. Stability constants for nitrate complex formation of lanthanides, americium and curium.

Element	Beta 1	+/–	Beta 2	+/–
La	0.92	0,17/0,15	0.17	0,08/0,11
Ce	0.77	0,19/0,16	0.24	0,14/0,10
Pr	0.97	0,54/0,37	0.24	0,43/0,21
Nd	0.68	0,08/0,07	0.07	0,04/0,03
Pm	1.9	0,08/0,08	0.6	0,04/0,04
Sm	1.3	0,11/0,17	0.05	0,06/–
Eu	2.1	0,07/0,07	0.32	0,1/0,1
Gd	1.1	0,13/0,11	N/A	0,05/–
Dy	0.35	0,04/0,04	0.01	0,02/–
Ho	0.28	0,19/0,13	0.04	0,08/–
Er	0.17	0,03/0,03	N/A	0,09/–
Am	1.0	0,03/0,03	0.29	0,03/0,03
Cm	1.4	0,06/0,06	0.22	0,02/0,02

Evaluation of the stability constants is still not finished. The values above are still preliminary since here it is assumed that all sodium nitrate and sodium perchlorate are dissociated in the aqueous phase, which is not the case at 5 M total ionic strength. The results will be finished early next year.

The stability constants are also plotted in Figure 2.36 below. The clear tetrad effect that was seen for 5 M ionic strength (see Figure 2.30) is not that obvious when it comes to stability constants due to several factors: changes in coordination number [HAB 80] and variation in the free energy between hydration and ligation [SIE 92] among others.

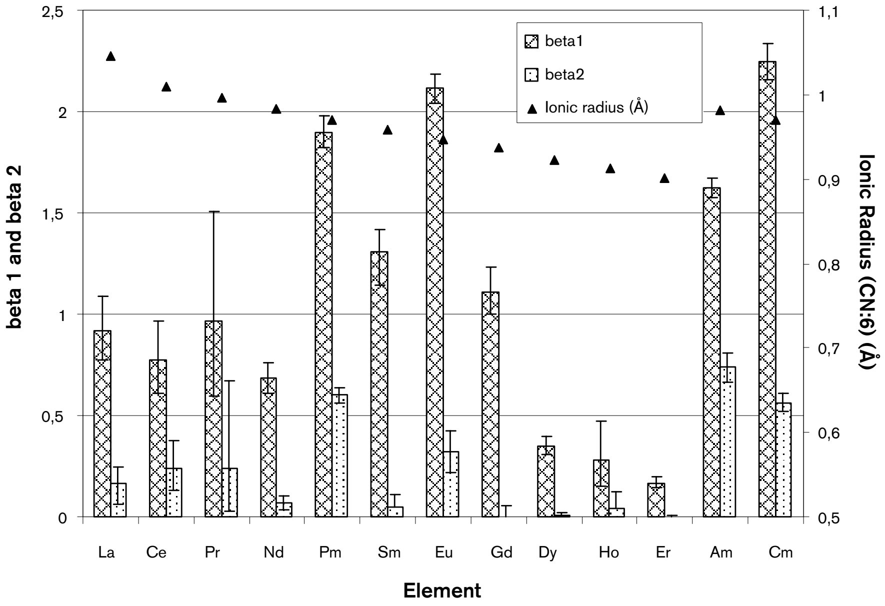


Figure 2.36. *Stability constants for the lanthanides and americium and curium.*

A comparison between actinides and lanthanides shows higher first stability constant for actinides than lanthanides of the same size, something that has been shown earlier too [ENS 84]. This means that there are other factors than the charge to ionic radius ratio that affect the distribution ratios.

2.5 Berkelium chemistry

The berkelium chemistry was done at Lawrence Berkeley National Laboratory in Berkeley, USA. The berkelium was provided by Oak Ridge National Laboratory. It was trivalent under the chosen experimental conditions [BAR 85].

The experiments can be divided in two groups: general extraction properties of some nitrogen containing extractants and determination of stability constants for nitrate complex formation.

The extractants that were investigated were, except 2,2':6',2-terpyridine (TERPY) and BODO, C5 and CyMe$_4$-BTP.

Initial experiments were made with TBB and HA, but the results were not very good considering huge uncertainties between distribution ratios of the samples. Indications however showed high distribution ratios for mixtures of the extractants in Figure 2.39 and HA in both nitrate and perchlorate media. The extractants also showed good extraction without HA in perchlorate media.

Experiments were done with cyclohexanone as organic diluent and with 0.001–0.005 M extractant concentration (C5 and CyMe$_4$-BTP). The aqueous phase was 0.1–5 M sodium nitrate with a constant hydrogen ion concentration of 0.01 M.

The phase volumes were 0.4 mL and the contact time was five minutes, which has been shown earlier (see e.g. Figure 2.15) is enough for actinides. The samples were centrifuged in 15 minutes to facilitate phase separation. Double aliquots were taken from each phase (to minimize statistical fluctuations) and mixed with 5 ml scintillation cocktail (Universol ES™, MP Biomedicals, Inc.). The measurements were made using an LKB Wallac 1219 Rackbeta liquid scintillation detector.

The results for C5 and CyMe$_4$-BTP are shown in Figures 2.37 and 2.38. The results of varying extractant concentration in the organic phase and its influence on the distribution ratio for berkelium are given. It is possible to say that a higher number of extractants are coordinated around the metal ions in the case of CyMe$_4$-BTP than with C5, but none of them have integers as slope when plotting log D versus log [extractant], which implies that several complexes can be formed.

The influence of nitrate ion concentration on the extraction was also tested (not constant ionic strength). The extraction increases when the nitrate ion concentration is increased. Here the ionic strength has not been kept constant, however. Only four of the data points were made during the same day (not the one at 1 M nitrate ion concentration), which might explain the somewhat too high distribution ratio in Figure 2.38. The C5 show a linear relationship with a slope close to 1.7, which is strange since three nitrates should be included in each extracted complex to neutralize the charge of the berkelium ion. The formation of nitrate complexes may affect the result. The experimental fluctuations for CyMe$_4$-BTP are also unexplainably high and no attempt was made to investigate the number of nitrate ions in the extracted complexes here.

When it comes to TERPY the results of varying nitrate ion concentration are shown in Figure 2.39. TERPY has not earlier shown an increase in extraction at increased nitrate ion concentration, mainly because no nitrate ions are believed to participate in the extraction according to the extraction mechanism. This is discussed e.g. in [SPJ 99].

The same experimental techniques and composition of organic and aqueous phases were used when investigating the nitrate complex formation for berkelium as for the earlier mentioned lanthanides.

The results for the tests with varying nitrate ion concentration (but constant ionic strength) are shown in Figure 2.40. It is possible to model the nitrate complex formation stability constants using the same method as described before, but this has not yet been done.

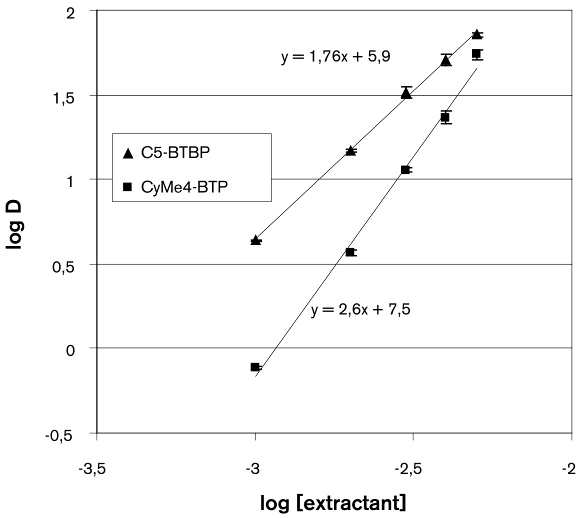


Figure 2.37. *Influence of varying extractant concentration on the distribution ratios (1 M (Na,H)NO$_3$, 0.01 M H$^+$). Organic diluent is cyclohexanone.*

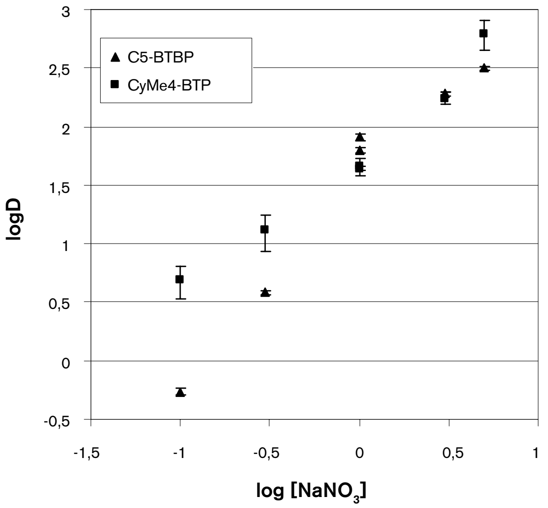


Figure 2.38. *Influence of nitrate ion concentration in the aqueous phase on the distribution ratios (0.005 M extractant concentration, 0.01 M H$^+$). Organic diluent is cyclohexanone.*

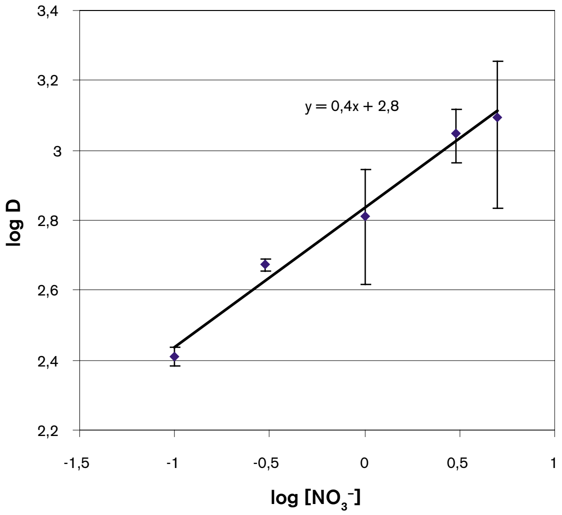


Figure 2.39. *Results for TERPY (0.1 M TERPY, 1 M HA in TBB) and varying nitrate ion concentration in the aqueous phase.*

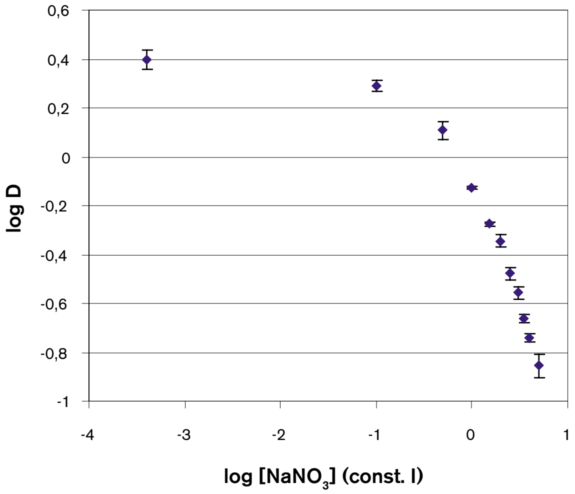


Figure 2.40. *Experimental distribution ratio at various nitrate ion concentrations in the aqueous phase (constant ionic strength (nitrate and perchlorate); 0.01 M BODO, 1 M HA in TBB; 295 K).*

2.6 Improved apparatus for automated vapour pressure measurements

The apparatus developed earlier [STR 94, ÖST 02] has been fitted with additional instruments for easier handling and evaluation and the PC control code has been improved. A thermostated vessel large enough to immerse the sample chamber has been built. This vessel keeps the temperature ± 0.02 ºC of the set value. The vessel also has an integrated electric motor for magnetic stirring inside the sample chamber. The setup of the system is described in Figure 2.41 and the thermo vessel and low-pressure sample chamber are described in Figure 2.42.

The samples are boiled to remove any gases. If the boiling point is too high there is a possibility to connect the vacuum pump to the preparation vessel to lower the pressure over the sample, thereby lowering the boiling point. The degassed sample is transported by the sample feeder (HPLC-pumps) to the rotating valve, where the sample is pre-heated before it is flushed into the low-pressure sample chamber. The pressure in the sample chamber and the temperature of the water surrounding it is constantly monitored and the values are sent to a PC. Some time after a sample has been introduced into the sample chamber the pressure and temperature will stabilise and the PC will then send a signal to the rotating valve to make another addition.

The apparatus is able to produce P,T,x-tables that can be used to calculate activity coefficients. The apparatus is highly sensitive to leaks and is still need some work until it can produce reliable data. A small leak could mean that the pressure increases slowly over time or that the pressure increases a constant amount at each addition, depending on where the leak is located. A graph showing the vapour pressure of a mix of water and sodium perchlorate is shown in Figure 2.43. When the molar ratio of a substance is approaching 1, the pressure will follow Raoults law. The test with sodium perchlorate was made in an attempt to find the dissociations constants for sodium perchlorate in water, needed for evaluation of the lanthanide nitrate complexation, cf section 2.3.

For the moment the code for calculating the activity coefficients is working but it needs to be developed further. Vapour-liquid equilibrium data was extracted from the literature [MAH 79] and the P,T,x-dataset was fed into the calculation code. The activity coefficients was found, see Figure 2.44, but there seems to some type of systematic error when looking at the difference between theoretical and experimental pressure, see Figure 2.45.

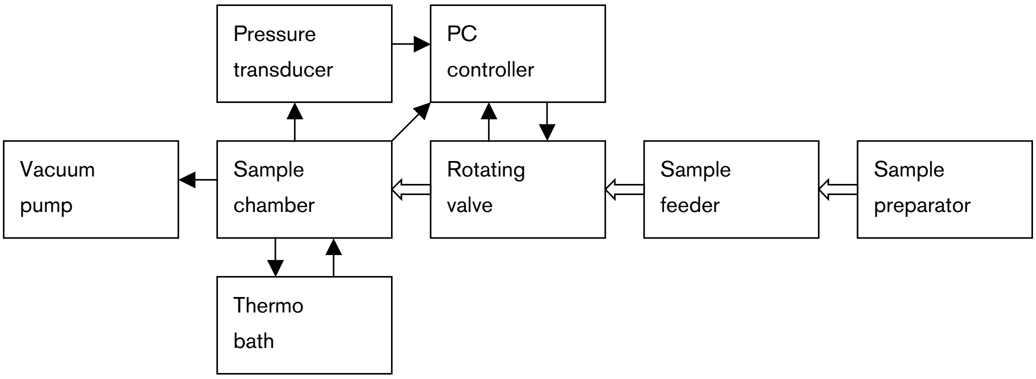


Figure 2.41. *Flow-sheet of the vapour pressure equipment.*

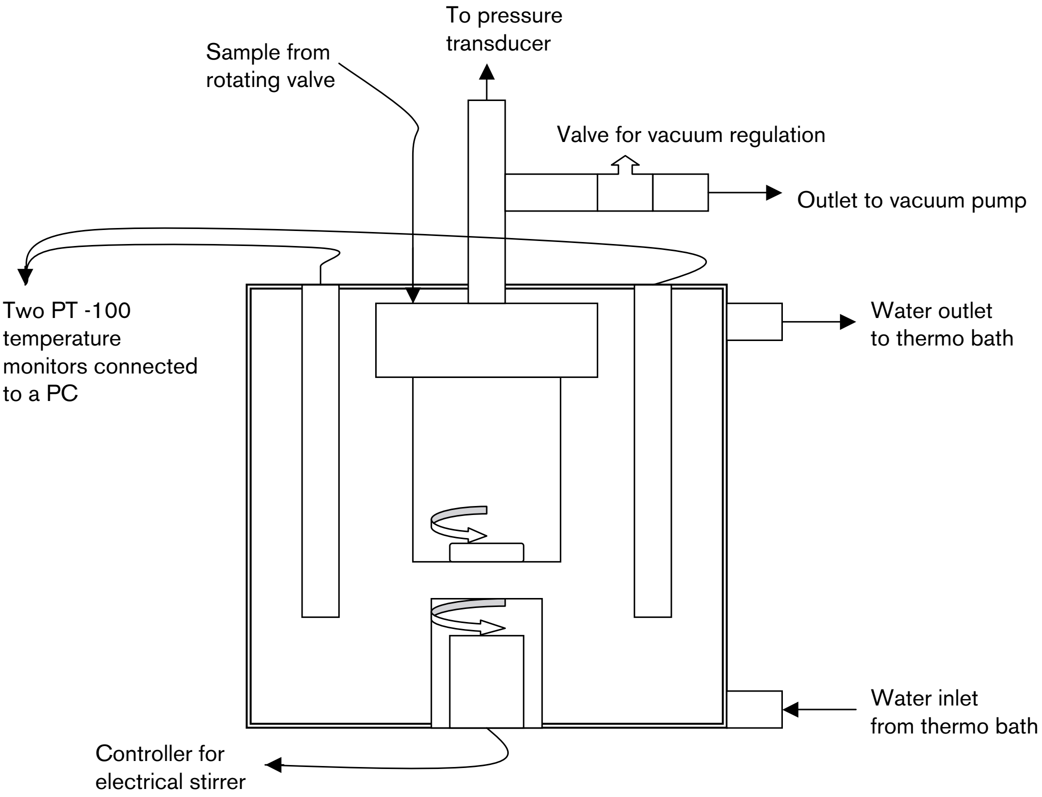


__Figure 2.42.__ Schematic picture of the thermo vessel and sample chamber.

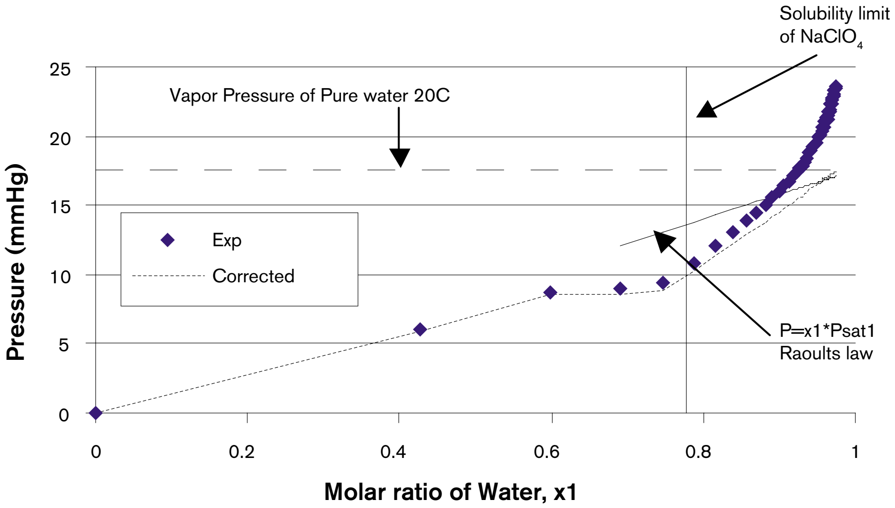


__Figure 2.43.__ Vapour pressure over a mixture of water and sodium perchlorate. The corrected curve is found by subtracting a constant factor from the total pressure by each addition of water.

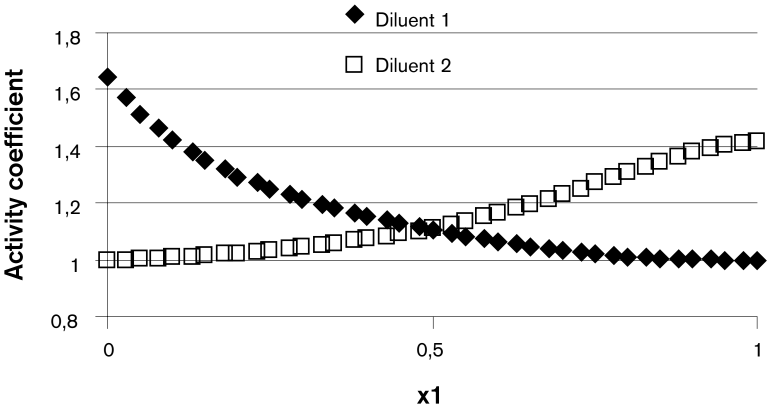


Figure 2.44. Activity coeffinients in a two-component system as a function of the molar ratio of one of the components. P,T,x-data taken from literature [MAH 79].

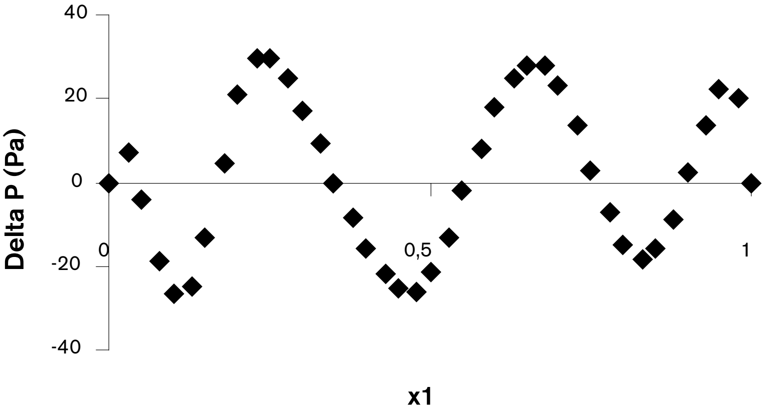


Figure 2.45. The difference in calculated and experimental pressure as a function of molar ratio. This graph shows clear signs of some systematic error. P,T,x-data taken from literature [MAH 79].

2.7 Experiments with a synthetic waste solution

As described in [AND 04] 1 M DMDOHEMA (DiMethylDiOctylHexaEthoxy-MAlonamide) in TPH (an aliphatic diluent) has been used to extract corrosion products, fission products and actinides from a synthetic HLLW solution. During 2004 the results have been thoroughly evaluated and also presented [SKA 04]. The waste solution had the same composition as the one used for cold tests of the CTH-process, and it was prepared according to Svantesson et al. [SVA 80], i.e. it consisted of about 30 stable elements. In addition to these elements it contained ^{59}Fe, ^{51}Cr, ^{63}Ni, ^{239}Np, ^{238}Pu or ^{241}Am.

Four series of batch extraction experiments were performed. The contact time was 1 h in all experiments. All extractions were performed in triplicate. After extraction, the phases were separated by centrifugation for 15 min at 2000 g. After phase separation aliquots were taken and analyzed by ICP-MS or radiometrical methods. Below three examples of the obtained results are shown.

A general conclusion from the experiments is that DMDOHEMA extracts actinides and lanthanides very well, especially at higher nitric acid concentrations. Trivalent actinides and lanthanides show a similar extraction (no significant separation factor) while actinides with higher oxidation states (U, Pu) are extracted with much higher distribution ratios.

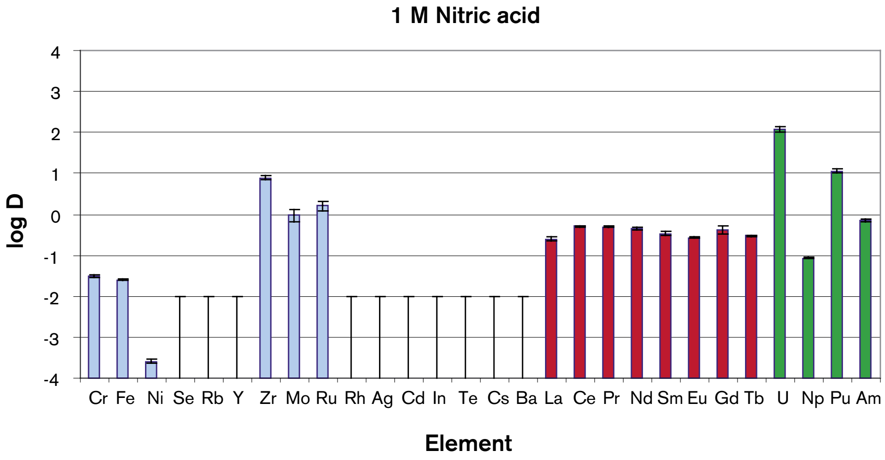


Figure 2.46. Extraction from 1 M HNO_3 into 1 M DMDOHEMA in TPH.

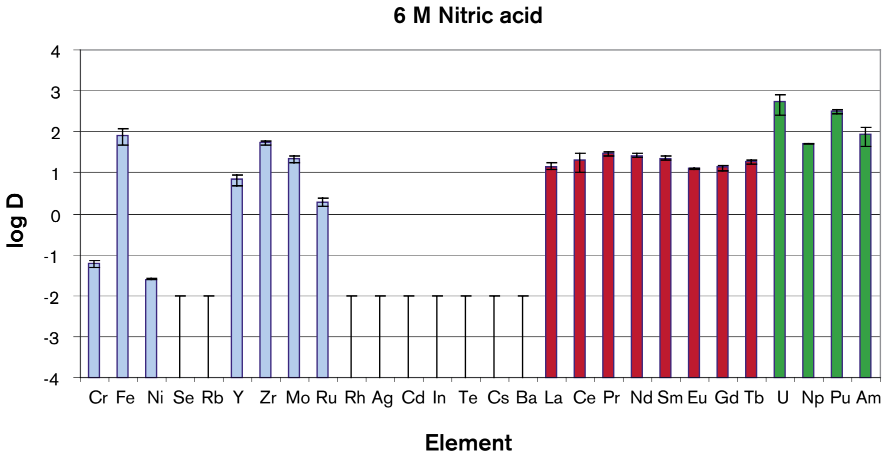


Figure 2.47. Extraction from 6 M HNO_3 into 1 M DMDOHEMA in TPH.

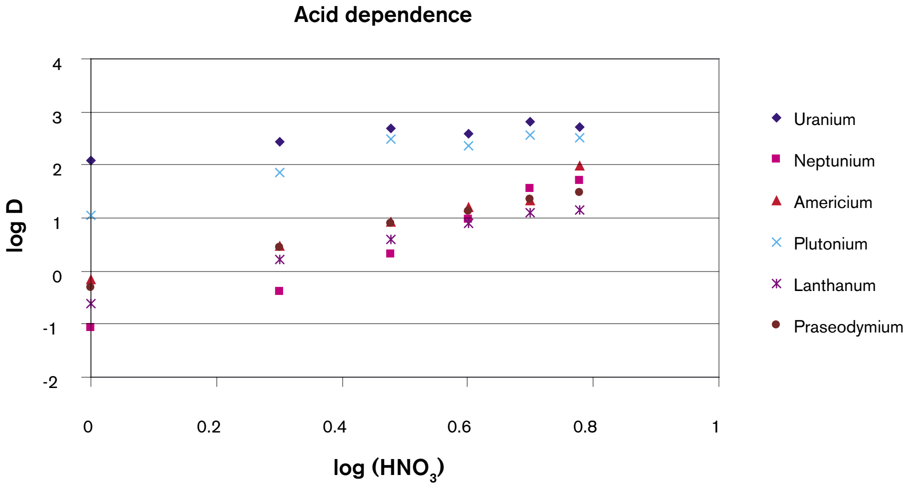


Figure 2.48. Acid dependence of the extraction of some actinides and lanthanides.

The separation of actinides and lanthanides from major fission products like Sr and Cs is good, with separation factors >1000 at >4 M HNO_3. DMDOHEMA does, however, extract Fe, Zr and Mo.

Another conclusion is that it is possible to use an ICP-MS instrument with moderate mass separation for analysis of the complex HLLW solution. The analysis is, however, not straight-forward. The standard analysis programs yield large errors for several elements. These uncertainties can be reduced by a thorough analysis of possible interferences. In this work the influence of interferences were taken care of by analysis of synthetic HLLW solutions that were lacking one element at the time. Analysis of the lacking elements gave a useful quantification of the interferences from other elements.

2.8 Process calculation program

A program for simulation of extraction in mixer-settlers has been developed. The program has the ability to simulate several mixer-settler batteries connected to a larger process. Concentrations in the in- and out flows can be simulated for up to 20 different solutes in one single run. The most powerful advantage with the program is the possibility to acquire data of the concentrations continuously and not necessarily at equilibrium. This makes it possible to study the kinetics of the system. Changes in flow rates towards equilibrium can also be investigated. The program is user friendly and easy to work with.

The basic idea of the program is that small volume elements are moved through the system in small time steps. After a volume is moved into a new part of the system, new concentrations and flows are calculated and data collected. This continues until a user decided stop time is reached.

Example

The following example shows calculations for a SANEX (Selective ActiNide EXtraction) process. SANEXs purpose is to separate actinides from lanthanides in the chain of separations previous to transmutation. The following process is simulated:

All solutes enter the system in the aqueous feed. In the SANEX battery the solutes are extracted according to the distribution ratios and then the organic phase is washed in the scrub battery. In this example the extracting battery consists of 10 mixer-settlers and the scrubbing battery of 7.

The “Battery” tab shows the properties of the SANEX battery (Figure 2.52). The solutes are some of the elements that could be of interest in a SANEX process and the concentrations are of expected size. The distribution ratios are those for a system with BODO (Figure 2.28) and HA (see section 2.3).

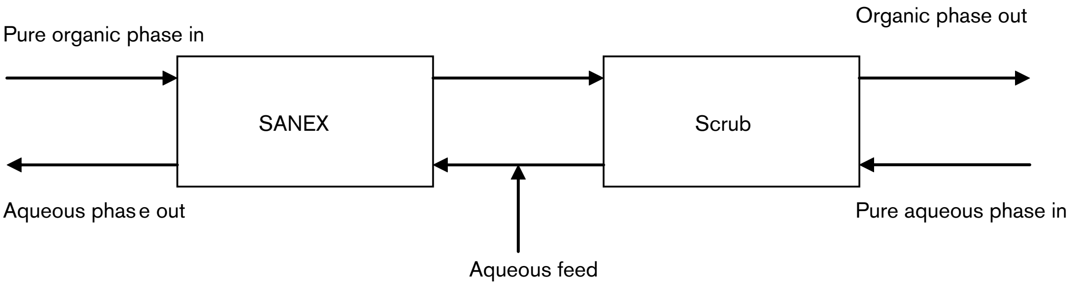
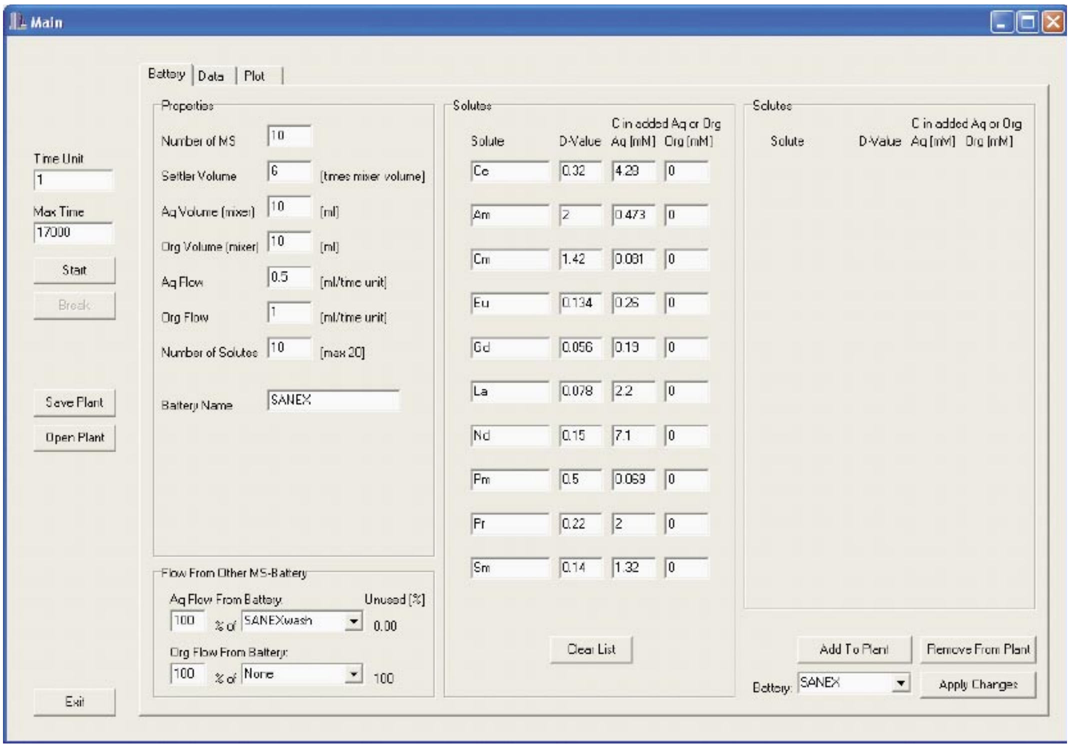


Figure 2.49. *Example process scheme.*



Time Unit: 1
Max Time: 17000

Properties

Number of MS: 10
Settler Volume: 6 [times mixer volume]
Aq Volume (mixer): 10 [ml]
Org Volume (mixer): 10 [ml]
Aq Flow: 0.5 [ml/time unit]
Org Flow: 1 [ml/time unit]
Number of Solutes: 10 [max 20]
Battery Name: SANEX

Flow From Other MS-Battery

Aq Flow From Battery: 100 % of SANEXwash; Unused [%] 0.00
Org Flow From Battery: 100 % of None; 100

Solutes

Solute	D-Value	C in added Aq or Org Aq [mM]	Org [mM]
Ce	0.32	4.29	0
Am	2	0.473	0
Cm	1.42	0.081	0
Eu	0.134	0.26	0
Gd	0.056	0.19	0
La	0.078	2.2	0
Nd	0.15	7.1	0
Pm	0.5	0.069	0
Pr	0.22	2	0
Sm	0.14	1.32	0

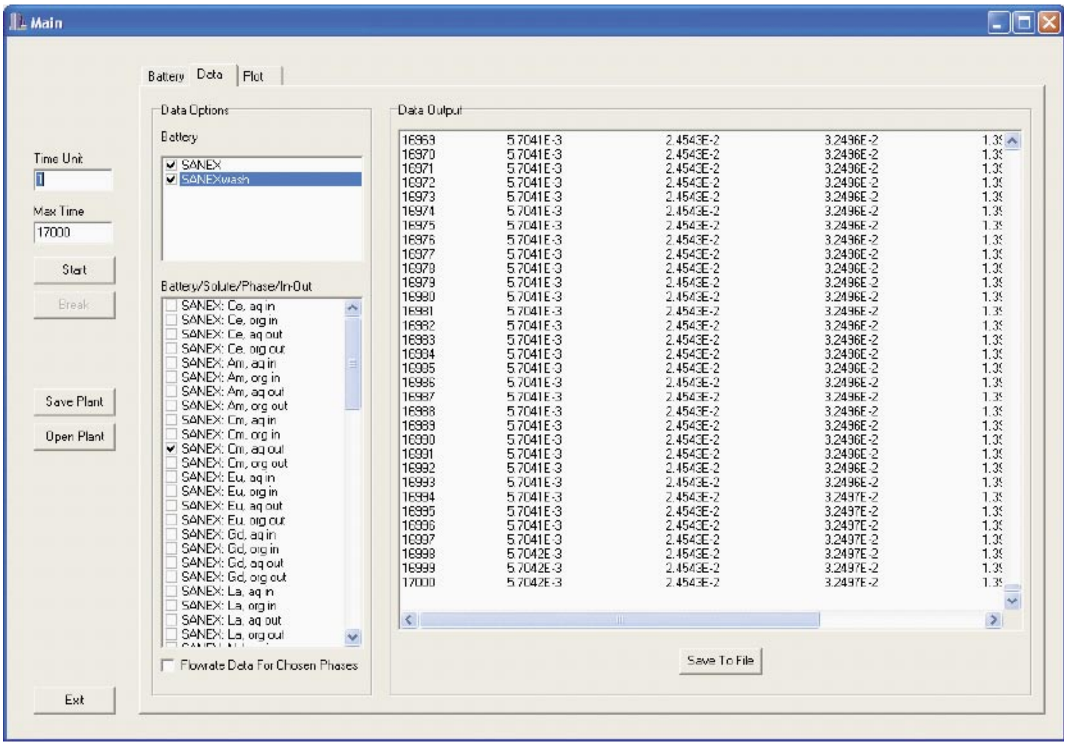
Solutes

Solute	D-Value	C in added Aq or Org Aq [mM]	Org [mM]

Battery: SANEX

Figure 2.50. *Program setup for the SANEX battery.*

Below data for Cm and Pm in the aqueous- and organic out flows (aqueous from the SANEX battery and organic from the scrub battery) has been collected (Figure 2.51). The data can be saved and imported to other programs, such as excel (Figure 2.52), for further evaluation. The result is also possible to view in a schematic plot in the "Plot" tab.



Time Unit: 1
Max Time: 17000

Data Options

Battery
☑ SANEX
☑ SANEXwash

Battery/Solute/Phase/In-Out
☐ SANEX: Ce, aq in
☐ SANEX: Ce, org in
☐ SANEX: Ce, aq out
☐ SANEX: Ce, org out
☐ SANEX: Am, aq in
☐ SANEX: Am, org in
☐ SANEX: Am, aq out
☐ SANEX: Am, org out
☐ SANEX: Cm, aq in
☐ SANEX: Cm, org in
☑ SANEX: Cm, aq out
☐ SANEX: Cm, org out
☐ SANEX: Eu, aq in
☐ SANEX: Eu, org in
☐ SANEX: Eu, aq out
☐ SANEX: Eu, org out
☐ SANEX: Gd, aq in
☐ SANEX: Gd, org in
☐ SANEX: Gd, aq out
☐ SANEX: Gd, org out
☐ SANEX: La, aq in
☐ SANEX: La, org in
☐ SANEX: La, aq out
☐ SANEX: La, org out

☐ Flowrate Data For Chosen Phases

Data Output

```
16969        5.7041E-3          2.4543E-2          3.2496E-2          1.3
16970        5.7041E-3          2.4543E-2          3.2496E-2          1.3
16971        5.7041E-3          2.4543E-2          3.2496E-2          1.3
16972        5.7041E-3          2.4543E-2          3.2496E-2          1.3
16973        5.7041E-3          2.4543E-2          3.2496E-2          1.3
16974        5.7041E-3          2.4543E-2          3.2496E-2          1.3
16975        5.7041E-3          2.4543E-2          3.2496E-2          1.3
16976        5.7041E-3          2.4543E-2          3.2496E-2          1.3
16977        5.7041E-3          2.4543E-2          3.2496E-2          1.3
16978        5.7041E-3          2.4543E-2          3.2496E-2          1.3
16979        5.7041E-3          2.4543E-2          3.2496E-2          1.3
16980        5.7041E-3          2.4543E-2          3.2496E-2          1.3
16981        5.7041E-3          2.4543E-2          3.2496E-2          1.3
16982        5.7041E-3          2.4543E-2          3.2496E-2          1.3
16983        5.7041E-3          2.4543E-2          3.2496E-2          1.3
16984        5.7041E-3          2.4543E-2          3.2496E-2          1.3
16985        5.7041E-3          2.4543E-2          3.2496E-2          1.3
16986        5.7041E-3          2.4543E-2          3.2496E-2          1.3
16987        5.7041E-3          2.4543E-2          3.2496E-2          1.3
16988        5.7041E-3          2.4543E-2          3.2496E-2          1.3
16989        5.7041E-3          2.4543E-2          3.2496E-2          1.3
16990        5.7041E-3          2.4543E-2          3.2496E-2          1.3
16991        5.7041E-3          2.4543E-2          3.2496E-2          1.3
16992        5.7041E-3          2.4543E-2          3.2496E-2          1.3
16993        5.7041E-3          2.4543E-2          3.2496E-2          1.3
16994        5.7041E-3          2.4543E-2          3.2497E-2          1.3
16995        5.7041E-3          2.4543E-2          3.2497E-2          1.3
16996        5.7041E-3          2.4543E-2          3.2497E-2          1.3
16997        5.7041E-3          2.4543E-2          3.2497E-2          1.3
16998        5.7042E-3          2.4543E-2          3.2497E-2          1.3
16999        5.7042E-3          2.4543E-2          3.2497E-2          1.3
17000        5.7042E-3          2.4543E-2          3.2497E-2          1.3
```

Figure 2.51. *Data output from the program.*

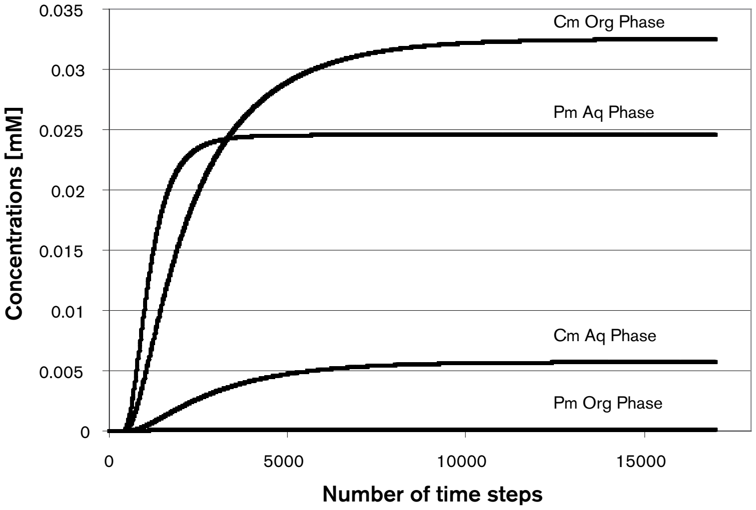


Figure 2.52. *Concentrations for Cm and Pm plotted in excel.*

Equilibrium values can be achieved from the data collected (Table 2.12).

Table 2.12. Equlibrium concentrations for Cm and Pm.

	Aqueous Phase (1.4 ml/time unit)		**Organic Phase (1 ml/time unit)**	
	Cm	**Pm**	**Cm**	**Pm**
Concentration [mM]	5.70E–3	2.45E–2	3.25E–2	1.40E–4

These data show that 80.3% of the Cm is extracted to the organic phase while 99.6% of the Pm will be in aqueous phase. For the SANEX process the demands on purity of the to phases are very high (>99 %) [LAN 99]. Here these goals are not reached but the supplied scheme has not been optimised and is just serving as an example.

2.9 Micro extraction device

A miniaturized system has been developed for performing fast and continuous liquid–liquid extraction. The apparatus consists of a micro mixer with interdigital channels for intense mixing of the phases. The emulsion is subsequently fed into one to three filter units (teflon membranes with 0.5 µm pore size) for phase separation. The extraction device has an inner volume of about 20 µL and a hold-up time of about 1 s at a flow-rate of 60 ml/h. It is intended to be used e.g. for process studies with new types of extractants that are available only in very small amounts. This development has not been funded by SKB, but by the European Union (EMERGE HPRI-CT-2002-00196) in a project involving our group, the Institut für Kernchemie of the University of Mainz (Germany) and the Institut für Mikrotechnik Mainz (Germany). The first results will be presented in [SKA 05].

The micro extraction apparatus uses the ability of a filter membrane to separate an organic and an aqueous phase. This has been known for a long time but it was not until Eberhardt et al. started testing different types of filters that it was realized that the separation can be fast and efficient [EBE 04, DIE 02].

Equipment for micro scale liquid-liquid extraction separations is of interest for basic science as well as for industrial applications. Some possible applications related to partitioning and transmutation are:

Development and pilot scale test of solvent extraction processes where the extractant is available only in very small amounts. An example is the investigation of new extractants that are usually synthesized in less than gram amounts.

Production of rare chemicals.

Use as a micro "AKUFVE" unit for studies of the distribution of an element between two immiscible phases. In this way thermodynamic properties can be determined. A micro extraction device will make it possible to study elements (e.g. actinides) as well as extractants or diluents that are available only in small amounts.

The apparatus is shown schematically in Figure 2.53. The mixer is based on the multi-lamination principle since micro-mixers based on this principle have been constructed and successfully applied by the Institut für Mikrotechnik Mainz. It has a volume of about 14 µL. The two main streams are split into 30 or more sub-streams and combined in a small slit in which the actual mixing by diffusion is executed. The mixture of the two phases is then fed into the membrane separator that can be described as two chambers separated by a hydrophobic membrane made of PTFE (poly tetra fluoro ethylene). The membrane separator needs a differential pressure to force the extract through the membrane. To adjust this pressure a valve is connected to the exit of the aqueous phase. For a water/organic phase system a differential pressure of 30–40 mbar is sufficient to transport the organic extract phase through the membrane. The channel on both sides of the membrane has rounded channel edges next to the membrane. The volume is approximately 2.5 µL per phase.

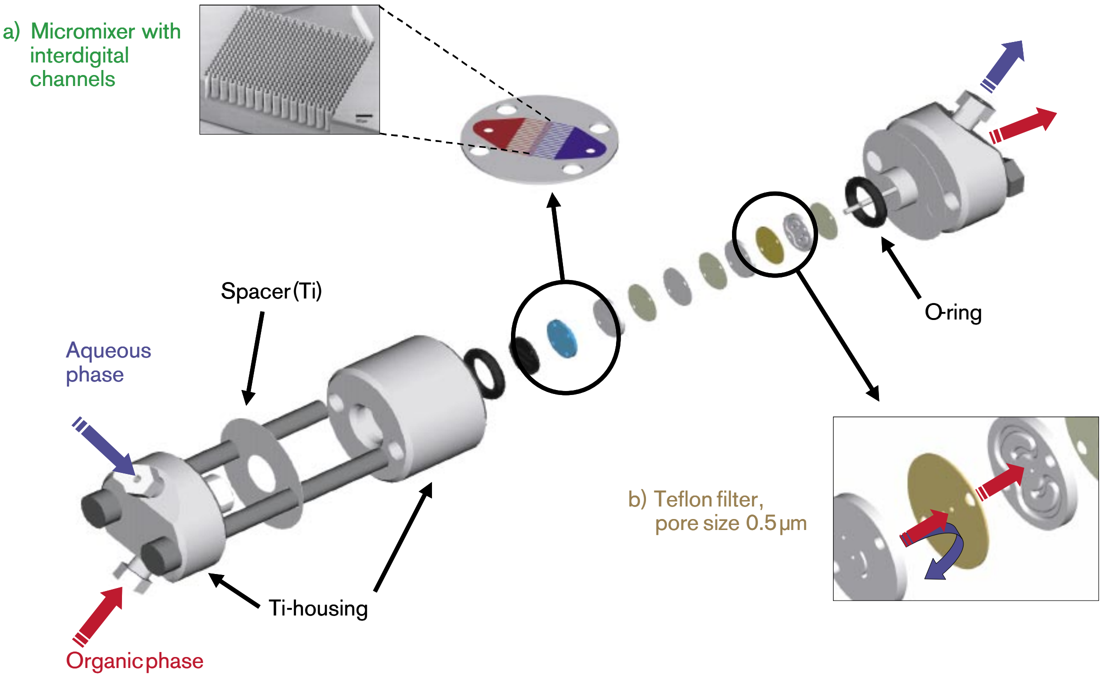


Figure 2.53. *The micro extraction device. The diameter of the housing is about 25 mm.*

To summarize the mixer inlays are made of stainless steel (laser-cut) or titanium. The porous membrane is made of PTFE with pore size 0.5 or 1.0 µm. The housing of the extraction device is made of titanium. The external sealings comprise Chemraz® O-rings and the internal sealings Chemraz® foil seals. The device is mounted by compression (seal force) pre-adjusted by spacers. Only two screws are needed to mount the device. All peripheral connections for fluids are Swagelok® compression type fitting 1/16”. The residence time can be increased by adding more membrane stages.

Tests have been performed to quantify i) the amount of aqueous phase in the organic phase, ii) the amount of organic phase in the aqueous phase and iii) the extraction efficiency, i.e. measured distribution ratios compared to known equilibrium distribution ratios.

The results show that it is possible to obtain an organic phase with no measurable phase entrainment in the flow-rate region from 5 ml/h per phase to 30 ml/h per phase. Above 30 ml/h the phase entrainment will be a few percent with the present version of the equipment.

Investigations of the amount of organic phase in the aqueous one showed that it was possible to keep the entrainment below 4% for flow-rates up to 60 ml/h per phase. As expected it was more difficult to keep the aqueous phase free from entrainment. There is, however, a possibility to couple three (or five) filters in series and this measure seems to improve the purity of the aqueous phase. The purity of the organic phase is not affected.

To determine the extraction efficiency three well known solvent extraction systems were used: i) the extraction of Gd from 0.01 M HNO_3 into 0.1 M HDEHP (bis-2-ethylhexyl orthophosphoric acid) in toluene occurs with a high distribution coefficient but with some kinetics, ii) the extraction of Hf from 6 M HNO_3 into 0.1 M HDBP (dibutyl phosphoric acid) in toluene also occurs with a high distribution coefficient and a faster kinetics than the Gd-HDEHP system and iii) the extraction of Tc (as TcO_4^-) from 0.01 M HNO_3 into 10^{-4} M TPAC (tetraphenyl arsonium chloride) in chloroform shows a high distribution coefficient and it is also extremely fast [ALT 90]. These experiments showed that the mixing has to be improved to obtain an acceptable extraction efficiency.

Conclusions

It is possible to obtain a pure organic phase at most running conditions and it is also possible to get both phases pure under certain conditions. A counter pressure is required on the outgoing aqueous phase. It was also found that three filters may give a better phase separation than just one filter. Filters with 0.5 µm pore size give more impurities in the aqueous phase than filters with 1 µm pores. The purity of the organic phase is, however, not affected very much by the filter chosen. Another conclusion is that the mixing is not optimal, since the distribution ratios are low even in systems where the extraction kinetics is known to be fast. Thus the mixing has to be improved. It was also found that the device is very sensitive for pulsating liquid flows, i.e. to get pure outgoing phases the feed solutions have to be delivered by pumps with a very constant flow-rate.

2.10 Handling of correlated data

When estimating different parameters from experimental data it is common to use some form of fitting the data to a theoretical function. The resulting parameters are often stated without any uncertainties although they are uncertain indeed. Several contributors to these uncertainties exist. The most obvious one is the uncertainty in the experimental results originating from various sources [AND 04B]. Now we are working on estimation of the correlations of the obtained parameters. This is a most important field but has not bee thoroughly investigated previously. Theoretical work is made and the applications to for example stability constants will be made. This work is ongoing and will be reported when in a more finished state.

3 Collaborations

The following laboratories are involved in EUROPART.

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

A more intense collaboration exist with:

Forschungszentrum Julich, Germany

Institut fur Michroteknik Mainz, Germany

Kernkemie, Johannes Gutenberg-Universität, Germany

- Lawrence Berkely National Laboratory, USA
- Forschungszentrum Jülich, Germany
- University of Reading, UK
- Institut fur Michroteknik Mainz, Germany
- Kernkemie, Johannes Gutenberg-Universität, Germany
- BNFL, UK
- National Institure of Cryogenics and Isotopic Separation, Romania

4 International and national scientific exchange

EUROPART kick-off meeting on Partitioning and Transmutation, Avignon, Januari 24–30
S. Andersson and C. Ekberg.

Visit to and presentation of our work at the nuclear chemistry group in Berkeley, USA, June 05–10.
C. Ekberg

Visit to Los Alamos National Laboratory, USA, June 7–9.
C. Ekberg and S. Andersson

Every year a study tour for the students taking our basic nuclear chemistry course is arranged. This year they visited e.g. la Haue, Mol (Belgium), Forshungszentrum Julich and Forschungszentrym Karlsruhe and their facilities dealing with the separation of the elements in the spent nuclear fuel.
G. Skarnemark.

Institut für Kernchemie , Johannes Gutenberg-Universität Mainz. Activation analysis of bromine as a part of the study of bromodecanoic acid.
G. Skarnemark

ACTINET summer school 2004, Avignon, June 17–19, 2004.
Daniel Magnusson and Mikael Nilsson

ATALANTE conference 2004, Advances for Future Nuclear Fuel Cycles, Nimes, June 21–24, 2004
Mikael Nilsson and Gunnar Skarnemark

EUROPART half year meeting on Partitioning and Transmutation, Madrid, July 19–22
S. Andersson, C. Ekberg, M. Nilsson and D. Magnusson

Nuclear and Radiochemistry conference NRC-6, Aachen, August 30–September 3
C. Ekberg, M. Nilsson, D. Magnusson and G. Skarnemark attended and presented 5 posters.

Lecture given on separation processes at KTH, Stockholm
C. Ekberg

Christian Ekberg was invited speaker and chairman at the 11th International Conference on Cryogenics and Isotopic Separation, Oct. 14-15 2004, Rm-Valcea, Romania

5 Articles and publications

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

Published

P-E. Ahlström (edt.), S. Andersson, C. Ekberg, J-O. Liljenzin, M. Nilsson, G. Skarnemark, J. Blomgren, M. Eriksson, P. Seltborg, B. R. Sehgal, Partitioning and Transmutation Current Development – 2004. A Report from the Swedish Reference Group on P&T-research, Svensk kärnbränslehantering AB, TR-04-15, 2004

S. Andersson, C. Ekberg, J-O. Liljenzin, M. Nilsson, G. Skarnemark, Study of Nitrate Complex Formation with Pm, Eu, Am and Cm Using a Solvent Extraction Technique, Radiochimica Acta 92, 863–867 (2004). **Abstract in APPENDIX I.**

K. Eberhardt, S. Andersson, C. Ekberg, B. Horn, J. V. Kratz, A. Müller, M. Nilsson, G. Skarnemark, N. Trautmann, MicroSISAK – A New Device for Fast and Continuous Liquid-liquid Extraction on a Microliter Scale, GSI Scientific Report 2004-1 (ISSN 0174-0814), 201 (2004).

C. Ekberg, G. Skarnemark, Uncertainty Evaluation for One-atom-at-a-time Studies of Transactinide Elements, Journal of Radioanalytical and Nuclear Chemistry 263(1), 71–74 (2005). **Abstract in APPENDIX II.**

Submitted

S. Andersson, K. Eberhardt, C. Ekberg, D. Magnusson, M. Nilsson, H. Nitsche, G. Skarnemark and R. Sudowe, Synergic Extraction of Lanthanides and Selected Actinides using 2,6-bis-(benzoxazolyl)-4-dodecyloxylpyridine and 2-bromodecanoic acid, submitted to the International Solvent Extraction Conference 2005 (2004). **Abstract in APPENDIX III.**

C. Ekberg, H. Persson, A. Ødegaard-Jensen, Y. Albinsson, S. Andersson, Redox control in solvent extraction studies using a PEEK AKUFVE unit, submitted to Applied Radiation and Isotopes (2004). Abstract in APPENDIX IV.

G. Skarnemark, S. Andersson, K. Eberhardt, C. Ekberg, V. Hessel, B. Horn, J. V. Kratz, P. Löb, A. Müller, M. Nilsson, A. Ødegaard-Jensen A Micro Reactor for Continuous Multistage Solvent Extraction, submitted to the International Solvent Extraction Conference 2005 (2004). **Abstract in APPENDIX V.**

In preparation (in principle ready for submission)

S. Andersson, K. Eberhardt, C. Ekberg, J-O. Liljenzin, M. Nilsson, G. Skarnemark, Determination of Stability Constants of Lanthanide Nitrate Complex Formation Using a Solvent Extraction Technique, in preparation (2004). **Abstract in APPENDIX VI.**

S. Andersson, C. Ekberg, J-O. Liljenzin, Uncertainty analysis of correlated stability constants, in preparation (2004).

S. Andersson, H. Nitsche, R. Sudowe, Bk nitrate complex formation using a solvent extraction technique, in preparation (2004).

S. Andersson, M. G. B. Drew, C. Ekberg, M. R. J. Foreman, M. J. Hudson, F. Marken, M. Nilsson, V, D-block metal complexes of 1,2,4-triazin-3-yl ligands, implications for the partioning of trivalent minor actinides and the radiation chemistry of the 1,2,4-triazines, in preparation (2004)

S. Andersson, C. Ekberg, M. R. S. Foreman, M. J. Hudson, M. Nilsson, H. Nitsche, G. Skarnemark, R. Sudowe, A Comparison of the Europium and Actinide Extraction Properties of a Bis-triazin-3-yl-[2,2']bipyridinyl (BTBP)., in preparation (2004).

M. Nilsson, S. Andersson, C. Ekberg, M. R. S. Foreman, G. Skarnemark, Inhibiting the Radiolysis of BTP-molecules by Addition of Nitrobenzene, in preparation (2004). **Abstract in APPENDIX VII.**

M. Nilsson, S. Andersson, C. Ekberg, J-O. Liljenzin, G. Skarnemark, The Chemical Properties of 2-Bromodecanoic Acid. In preparation (2004). **Abstract in APPENDIX VIII.**

G. Skarnemark, S. Andersson, C. Ekberg, M. Nilsson, A. Ødegaard-Jensen, Extraction of Actinides, Fission Products and Corrosion Products from Synthetic High Level Liquid Waste with Dimethyl-dioctyl-hexaethoxy-malonamide (DMDOHEMA), in preparation (2004). **Abstract in APPENDIX IX.**

We have also written half-yearly reports to the EUROPART project and participated in the preparation of the final report. This has not yet been published.

The abstract of the diploma work by F. Drouet is available at Chalmers University of Technology.

6 Future work

The future work will continue along the suggested path of the EUROPART project.

- Partitioning of actinides (Am to Cf) from High Active Raffinates and High Active Concentrates issued from the reprocessing of UOX and MOX spent fuels using extracting agents belonging to the families of polyamides and polydendate N or S- bearing molecules and cosan
- Partitioning of actinides 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.
- A more thorough investigation of uncertainties in these systems have been started. The main output will be effects of correlated parameters.

Mikael Nilsson will probably visit Forschungszentrum Jülich once more to work with process development of some promising ligands. Then he will finish his PhD studies at t he end of the year.

Sofie Andersson will finish her PhD studies in April but we hope to keep her to at least some part within the group.

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

The new PhD student, Teodora Retegan will continue the existing work on basic chemical understanding of nitrogen donor ligands both for the DIAMEX and SANEX processes.

Hopefully we will have the possibility of hiring another student to replace Sofie Andersson. This is important for the continuation of the knowledge within the group.

We will also have two new French diploma workers in our group, Nadege Hervieux and Yannick Meridiano. They will probably work with a new type of solid extractant synthesised within the EUROPART group.

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Appendix I

Study of Nitrate Complex Formation with Trivalent Pm, Eu, Am and Cm Using a Solvent Extraction Technique

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Summary

The separation of actinides and lanthanides is an important question in the treatment of spent nuclear fuel in the transmutation concept. To find an efficient and well functioning separation process it is necessary to study the chemistry of the elements in the two groups in different aqueous media. The stability constants of the nitrate complex formation with Pm, Eu, Am and Cm were determined using solvent extraction. The extraction was studied using the synergistic system of 2,6-bis-(benzoxazolyl)-4-dodecyloxylpyridine and 2-bromodecanoic acid in tert-butyl benzene. As the nitrate ion concentration in the aqueous phase was increased, a decrease in separation between actinides and lanthanides was seen owing to complex formation between the different elements and the nitrate ions.

Keywords: Nitrate complexation, Stability constants, Pm, Eu, Am, Cm

Appendix II

Uncertainty evaluation for one-atom-at-a-time studies of transactinides

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Liquid-liquid extraction is one of the methods that is used for one-atom-at-a-time separations of transactinide elements from heavy-ion reaction product mixtures. It is suitable for this purpose because it is fast, provided that a chemical system with negligible kinetics is used, and it can be used for continuous separations. It is, however, not quite easy to determine the uncertainties of the measured distribution coefficients or complex formation constants. In this paper methods for such estimates will be discussed.

Appendix III

Synergic extraction of lanthanides and selected actinides using 2,6-bis-(benzoxazolyl)-4-dodecyloxylpyridine and 2-bromodecanoic acid

Sofie Andersson, Klaus Eberhardt*, Christian Ekberg, Daniel Magnusson, Mikael Nilsson, Heino Nitsche**,***, Gunnar Skarnemark and Ralf Sudowe***

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**Department of Chemistry, University of California Berkeley, Berkeley, USA
***Lawrence Berkeley National Laboratory, Berkeley, USA

The separation of actinides and lanthanides is an important factor in the design of novel extraction systems for alternative methods to treat spent nuclear fuel (e.g. partitioning and transmutation or conditioning). In this work the extraction behaviour of several lanthanides was studied to explore differences within the lanthanide group and in comparison with actinides (Am and Bk). The synergic extraction system used was 2-bromodecanoic acid and 2,6-bis-(benzoxazolyl)-4-dodecyloxylpyridine in tert-butyl benzene. The aqueous phase consisted of trace amounts of metal ions and 1 or 5 M perchlorate ion concentration. Results indicate a decrease in extraction along the lanthanide series and a tetrad effect. The actinides (Am and Bk) show higher distribution ratios.

Appendix IV

Redox control in solvent extraction studies using a PEEK AKUFVE unit

by C. Ekberg*, H. Persson, A. Ödegaard-Jensen, Y. Albinsson and S. Andersson

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Abstract

When studying actinides or other elements with different oxidation states it is important to control which state is present in solution. Earlier this has been done by adding some other element to the solution but this approach incude a lot of uncertainties. Since the 60ies the AKUFVE apparatus has been used for precice solvent extraction studies. Now this equipment has been improved with redox contol facilities, additional thermal control and all parts in contact with the liquids are made of polyethyl ether ketone (PEEK) to minimise sorption.

Keywords: AKUFVE, solvent extraction, Redox control, Reducing conditions, Tetravalent metals, PEEK.

Appendix V

A micro reactor for continuous multistage solvent extraction

Gunnar Skarnemark, Sofie Andersson, Klaus Eberhardt*, Christian Ekberg,
Volker Hessel**, Benjamin Horn**, Jens V. Kratz*, Patrick Löb**, Andreas Müller**,
Mikael Nilsson and Arvid Ødegaard-Jensen

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** Institut für Mikrotechnik Mainz, Mainz, Germany

A miniaturized system has been developed for performing fast and continuous liquid-liquid extraction. The apparatus consists of a micro mixer with interdigital channels for intense mixing of the phases. The emulsion is subsequently fed into up to three filter units (teflon membranes with 0.5 µm pore size) for phase separation. The extraction device has an inner volume of about 20 µL and a hold-up time of about 1 s at a flow-rate of 60 mL/h. It is intended to be used e.g. for process studies with new types of extractants that are available only in very small amounts and for chemical studies of the heaviest elements.

Appendix VI

Determination of stability constants of lanthanide nitrate complex formation using a solvent extraction technique

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Summary

For lanthanides and actinides, nitrate complex formation is an important factor with respect to the reprocessing of nuclear fuels and in studies that treat partitioning and transmutation/conditioning. Different techniques, including microcalorimetry, various kinds of spectroscopy, ion exchange and solvent extraction, can be used to determine stability constants of nitrate complex formation. However, it is uncommon that all lanthanides are studied at the same time, using the same experimental conditions and technique. The strengths of the complexes are different for lanthanides and actinides, a feature that may assist in the separation of the two groups. This paper deals with nitrate complex formation of lanthanides using a solvent extraction technique. Trace amounts of radioactive isotopes of lanthanides were produced at the TRIGA Mainz research reactor and at the Institutt for Energiteknikk in Kjeller, Norway (JEEP II reactor).

The extraction of lanthanide ions into an organic phase consisting of 2,6-bis-(benzoxazolyl)-4-dodecyloxylpyridine, 2-bromodecanoic acid and tert-butyl benzene as a function of nitrate ion concentration in the aqueous phase was studied in order to estimate the stability constants of nitrate complex formation. When the nitrate ion concentration is increased in the aqueous phase, the nitrate complex formation starts to compete with the extraction of metal ions. Thus the stability constants of nitrate complex formation can be estimated by measuring the decrease in extraction and successive fitting of an appropriate model.

Extraction curves for La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Dy, Ho and Er were obtained and stability constants for their nitrate complex formation were estimated. Tb, Tm, Yb and Lu were also investigated, but no stability constants could be determined. The distribution ratios for the metal ions at low nitrate ion concentration were obtained at the same time, showing the effect of lanthanide contraction resulting in decreasing extraction along the series. A clear tetrad effect in the lanthanide group was also found.

Keywords: Nitrate complex formation, Lanthanides, Solvent extraction, Tetrad effect.

Appendix VII

Inhibiting radiolysis of btp molecules by addition of nitrobenzene

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Summary

Autoradiolysis of extraction systems sometimes occurs during reprocessing, which may result in a change in the extraction behaviour of the system. In the work reported here, an aromatic heterocyclic nitrogen bearing tridentate extraction agent, 2,6-di(5,6-diethyl-1,2,4-triazin-3-yl)pyridine (a BTP), was irradiated using a ^{60}Co source. The investigation focused on the effect of changing the organic diluent in the extraction system in order to protect the extracting agent from degradation.

A relationship between the distribution ratio and extracting agent concentration was determined, and it was found that the extraction efficiency decreased with increasing dose.

The effect on extraction of the degradation products from the organic diluents was also considered.

Keywords: Solvent extraction, Radiolysis, Americium, Nitrogen heterocycles, Triazines, BTP.

Appendix VIII

The chemical properties of 2-bromodecanoic acid

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Abstract

The equilibrium constants for 2-bromodecanoic acid were investigated. First the dimerisation constant of 2-bromodecanoic acid, k_2, in tert-butyl benzene was derived from IR-spectroscopy measurements. Secondly, the distribution coefficient, k_d, was found by combining the value of k_2 with distribution data obtained from solvent extraction experiments evaluated with the aid of neutron activation analysis. Finally the dissociation constant, k_a was estimated from two-phase titrations.

Appendix IX

Extraction of actinides, fission products and corrosion products from synthetic high level liquid waste with dimethyl-dioctyl-hexaethoxy-malonamide (DMDOHEMA)

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One of the processes that is evaluated for possible use to separate minor actinides from fission products in HLLW is the DIAMEX process. It is based on extraction of actinides and lanthanides using malonamides as extractants. In this investigation, 1 M DMDOHEMA (DiMethylDiOctylHexaEthoxyMAlonamide) in TPH (an aliphatic diluent) has been used to extract corrosion products, fission products and actinides from a synthetic HLLW solution. The waste solution has the same composition as the one used for cold tests of the CTH-process, and it was prepared according to Svantesson et al. [1]. It consists of about 30 elements dissolved in 6 M nitric acid. This solution was used to prepare solutions with 1, 2, 3, 4 and 5 M HNO_3 by dilution with water. To make the determination of Fe, Cr and Ni easier, ^{59}Fe, ^{51}Cr and ^{63}Ni tracers were added in the same chemical form as the macro amounts of these elements. In addition, trace amounts of ^{239}Np, ^{238}Pu or ^{241}Am were added to some samples to gain additional information about actinide extraction. These elements were added as Np(V), Pu(IV) and Am(III). To simulate process conditions no redox control was applied.

The contact time was 1 h in all experiments. All extractions were performed in triplicate. After extraction, the phases were separated by centrifugation for 15 min at 2000 g. After phase separation aliquots were taken and analyzed by ICP-MS or radiometrical methods.

The 31 solutes present in the samples make them a very complicated matrix. In order to study possible interferences between mass numbers another 31 samples were prepared. These samples contained either 6 M or 1 M HNO_3 and each sample lacks one solute. In this way it is possible to estimate interferences at the mass of the missing solute. These samples were diluted in the same way as the real samples.

A general conclusion from the experiments is that actinides, Zr, Mo and Fe are well extracted at the higher nitric acid concentrations (distribution ratios in the range 10–100), while the other elements are not extracted to any significant extent. Another conclusion is that it is possible to use ICP-MS to analyze such a complex mixture, although it is not a straight-forward method. It is necessary to keep good track of all possible mass interferences.

1. Svantesson, I., Persson G., Hagström, I., Liljenzin J-O.: J. inorg. nucl. Chem. 42, 1037 (1980).