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Partitioning and transmutation
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PARTITIONING AND TRANSMUTATION ANNUAL REPORT 1997

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CONTENTS

APPENDICES

Articles/Reports

I   Enarsson, Å., Hagström, I., Liljenzin, J.O., Skålberg, M. and Spjuth, L.: *Second Semestrial Report on "Partitioning Experiments and Waste Minimisation", Contract NEWPART (FI41-CT-96-0010),* May (1997)

II   Landgren, A. and Liljenzin, J-O.: "Extraction Behaviour of Technetium and Actinides in the Aliquat-336/Nitric Acid System", *OECD Conference on "Long-Lived Radionuclide Chemistry in Nuclear Waste Treatment",* Villeneuve-lés-Avignon, France, June 20-21(1997)

III   Enarsson, Å., Liljenzin, J.O., Skålberg, M. and Spjuth, L.: *Third Semestrial Report on "Partitioning Experiments and Waste Minimisation", Contract NEWPART (FI41-CT-96-0010),* October (1997)

IV   Korp, U.: "The Influence of Degradation by Radiolysis of Two Nitrogen Containing Extractants", *Diploma Thesis, Department of Nuclear Chemistry, Chalmers University of Technology,* December (1997)

V   Johansson, M.: "Extraction Studies and Process Calculation for Separation of Trivalent Actinides and Lanthanides", *Diploma Thesis, Department of Nuclear Chemistry, Chalmers University of Technology,* December (1997)

Travelling Reports

VI   Visit to the University of Reading, Department of Chemistry, March 10-14 (1997)

VII   OECD Conference on "Long-Lived Radionuclide Chemistry in Nuclear Waste Treatment", June 20-21, Villeneuve-lés-Avignon, France (1997)

VIII   IVA's International Conference "Why Research on Accelerator-driven Transmutation Technology", October 24, Stockholm, Sweden (1997)

1. INTRODUCTION

The current research project on Partitioning and Transmutation (P&T) at the Department of Nuclear Chemistry, CTH, has the primary objective to investigate separation processes useful in connection with transmutation of long-lived radionuclides in high level nuclear waste. Partitioning is necessary in order to recover and purify the elements before and after each irradiation in a P&T treatment. In order to achieve a high transmutation efficiency the chemical separation process used must have small losses to various waste streams.

At present, only aqueous based separation processes are known to be able to achieve the high recovery and separation efficiencies necessary for a useful P&T process. The engineering and operation experience from wet separation processes by far exceed those of alternative processes based on melt refining, molten salt electrolysis, pyroprocessing, and volatility. It is realistic to believe that aqueous separation techniques will continue to be far ahead of the other possibilities for a long time to come. This belief is shared by our European project partners and is the main reason why research on separation processes at the department is concentrated on aqueous/organic liquid-liquid extraction systems.

2. Solvent extraction research

New extraction reagents should be selective, have a high loading capacity and be completely incinerable without solid residues. This limits the possible elements in the extractant molecules to carbon, hydrogen, oxygen and nitrogen, the so called CHON-principle. However, the CHON-principle has also a wider meaning. Addition of chemicals to the process solution should be limited to those already present in large amounts in high level waste from conventional PUREX reprocessing of spent fuel, i.e. water and nitric acid.

Long chained amines and quaternary ammonium salts constitute a group of possible CHON-reagents. Other useful reagent classes are derivatives of malonamides, of tri-pyridyl-triazines, of picolinamides, and various oligopyridines, e.g. terpyridine and its derivatives. In order to comply with the requirements of high loading capacity, reasonable viscosity and high solubility in suitable organic diluents, the molecular weight of the reagent must not be too high. Furthermore, part of the reagent structure should have some similarity to the diluent molecules in order to maximise solubility. On the other hand, the molecular weight of the reagent should be high enough to make the reagent little soluble in the aqueous phase.

Due to the similarity in chemical behaviour of lanthanides and the trivalent actinides (americium and curium) various routes can be envisaged, e.g. (i) coextraction of both element groups followed by stripping and separation of the element groups (or single elements) by a second reagent having sufficient separation power, (ii) extraction of trivalent actinides only by using a very selective reagent. The main strategy in our research follows route (i) above.

2.1 Long chain quaternary amines

Aliquat-336 (tricapryl-methylammonium nitrate) is a quaternary ammonium salt that extracts negatively charged species with an anion exchange mechanism. The diluent used is a dialkyl substituted aromatic compound, 1,3-diisopropylbenzene.

The extraction of metal cations with Aliquat-336 will depend on the charge and radius of the metal ion i.e. the ability to form complexes with the ligand, the ligand concentration and the extractant concentration. By varying the oxidation state of the metal and the ligand concentration it is possible to separate different elements from each other.

During 1997 the extraction of some actinides with Aliquat-336 has been investigated and modelling of their behaviour has been done [1]. In Figure 1 some distribution ratios for uranium and plutonium as a function of the initial nitric acid concentration are shown. The results are given at 0.20 M Aliquat-336 in the organic phase except for Pu(IV) which are given at 0.05 M. Data for thorium(IV) is given for comparison. Uranium(IV) was prepared by reduction of uranium(VI) with hydrogen gas bubbling through the solution in contact with a catalyst of platinum black. Plutonium(VI) was prepared by oxidation of plutonium(IV) with silver(II)oxide. As can be seen, uranium and plutonium in the tetravalent state behave like thorium. High distribution ratios are obtained for uranium(IV) and plutonium(IV) since complexation with nitrate is favoured with the highly charged M^{4+} ion.
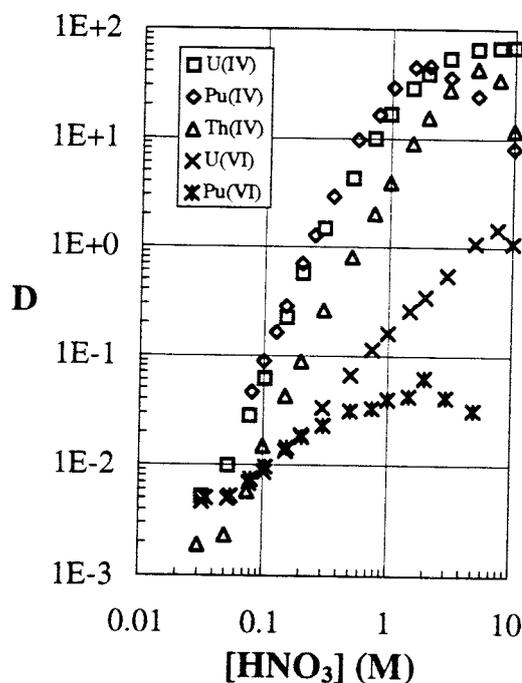
Figure 1. Distribution ratios for uranium and plutonium as a function of the initial nitric acid concentration.

2.2 Malonamides

An optimised malonamide molecule is considered to be used in the first part of the DIAMEX-process as a coextractant for trivalent actinides and lanthanides. To be able to understand the extraction mechanism careful investigations of the malonamides are necessary. Three different malonamides have been studied in this project, see Figure 2.

O H O
CH₃\N—C—C—C—N/CH₃
C₄H₉   C₁₈H₃₇   \C₄H₉

O H O
CH₃\N—C—C—C—N/CH₃
C₆H₁₁   C₁₄H₂₉   \C₆H₁₁

O H O
CH₃\N—C—C—C—N/CH₃
Φ   C₁₄H₂₉   \Φ
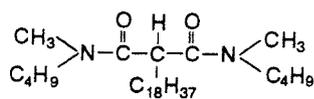
N,N′-dimethyl-N,N′-dibutyloctadecyl
malonamide (DMDBODMA)
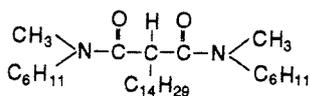
N,N′-dimethyl-N,N′-
dicyclohexyltetradecyl
malonamide (DMDCHTDMA)
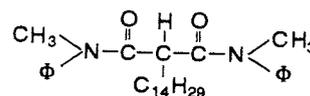
N,N′-dimethyl-N,N′-
diphenyltetradecyl malonamide
(DMDPHTDMA)

Figure 2. The different malonamide studied.

The extraction mechanism of the malonamides is still not fully understood and both an ion-pair mechanism and a solvation mechanism have been proposed [2]. A protonated and thus cationic malonamide is suggested to extract anionic metal complexes at high nitric acid concentration and solvation of neutral metal species is considered at low nitric acid concentration. The extraction of metals from $LiNO_3$ media, is just as high or higher than extraction from nitric acid. This suggests a solvation extraction mechanism since no protonated malonamide is present in the organic phase. One could assume that extracted lithium might form cationic species with the malonamide in the organic phase and could be the reason for the high metal extraction, but lithium was shown not to be extracted with the malonamides studied and thus no cationic malonamides ($MALi^+$ or MAH^+) are present in the organic phase. However, pertechnetate, TcO_4^-, which is an anion itself, behaves when extracted with the malonamides in the same way as when extracted by a liquid anion exchanger, Aliquat-336, see Figure 3. Modelling of the extraction mechanism has been initiated and might verify which mechanism is the most important.

Figure 3. Extraction graph: D vs [HNO₃]initial(M), with curves for —□— 0.2M Aliquat-336-dipb and —■— 0.1M DMDBOD-tbb; dD/[HNO₃]=-1
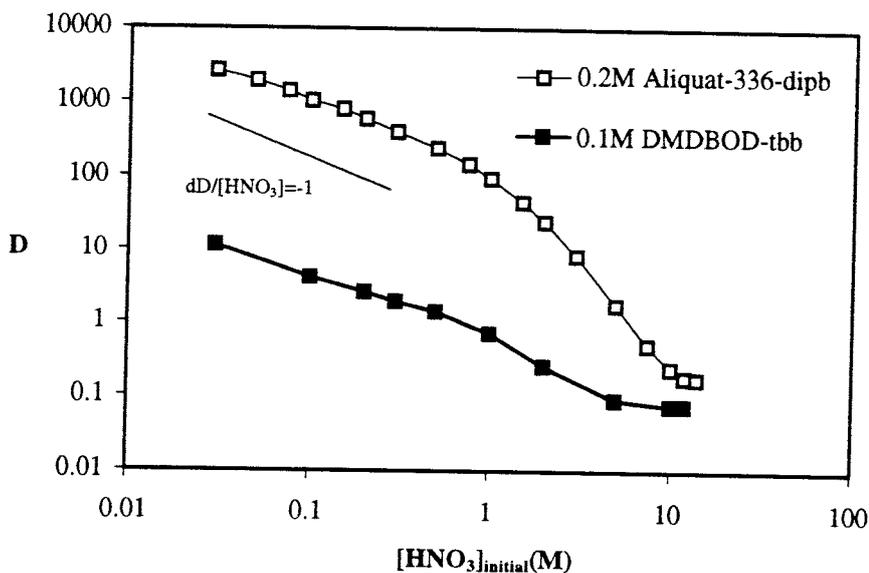
Figure 3. Extraction of pertechnetate (TcO_4^-) from different nitric acid concentrations with 0.1M DMDBODMA in tert-butylbenzene and 0.2M Aliquat-336 in 1,3-diisopropylbenzene.

To be able to understand the extraction system the extraction of water has been studied for the different malonamides at different nitric acid concentrations and at different malonamide concentrations [3]. This data is also planned to be used in the modelling of the extraction mechanism together with data for extraction of nitric acid [4].

5

One graduate student (Ulrika Korp) finished her diploma work concerning the radiolysis of one of the malonamides (DMDPHTDMA) and Aliquat-336. Extraction behaviour after intense γ-ray irradiation was investigated and degradation products were analysed with GC-MS [5].

2.3 Oligopyridines

Oligopyridines are nitrogen-donor reagents which are, in synergism with a lipophilic acid (2-bromodecanoic acid), able to separate trivalent actinides from lanthanides. This is probably due to the more covalent character of the nitrogen-actinide bond compared to the nitrogen-lanthanide bond.

The unsubstituted terpyridine (terpy) can separate trivalent actinides from lanthanides [7] but has the disadvantage of protonation at higher acidities. The higher hydrophilicity of the protonated terpy leads to very low concentrations of terpy in the organic phase making extraction at higher acidities almost impossible.

To enhance the extraction properties, new oligopyridines were synthesised at the University of Reading. Different substituents were added to the terpyridine to try to alter the electroconfiguration of the nitrogen in the central pyridine ring to fit the actinides better than the lanthanides and also to make the oligopyridine less basic and more lipophilic. Also oligopyridines with four and five pyridine rings were synthesised.

Four different terpyridines, one quaterpyridine and one quinquepyridine and their extraction behaviour have been studied during 1997 (Table 1). The substituted terpyridines examined show lower distribution ratios than the unsubstituted ones but the separation factors between americium and europium are the same. The type of substituent seems to have little effect on the extraction behaviour [3]. The quaterpyridine and the quinquepyridine show higher distribution ratios and higher separation factors than the terpyridines at low nitric acid concentrations, but at higher nitric acid concentrations the separation factor diminishes.

For all the oligopyridines the extraction conditions are limited due to solubility problems and protonation. The protonated terpy is highly soluble in the aqueous phase but the other oligopyridines form, when protonated, a third phase.

One graduate student (Marcus Johansson) finished his diploma work in December 1997. The work concerned extraction studies and process calculations for separation of trivalent actinides and lanthanides with the synergistic system terpyridine and 2-bromodecanoic acid [6].

Table 1. Overview of the oligopyridines investigated and comparison of the extraction and separation of americium and europium at 0.02M oligopyridine, 1M 2-bromodecanoic acid in *tert*-butylbenzene from 0.01M nitric acid.

Name	Structure	D_{Am}	Separation factor (D_{Am}/D_{Eu})
2,2':6',2''-terpyridine (Terpy) Aldrich		13	7
4'-tolyl-2,2':6'2''-terpyridine (Tolpy) Reading University		3	8
4'-(4-nitrophenyl)-2,2':6'2''-terpyridine (Nitroterpy) Reading University		4	8
4'-(4-dodecyloxyphenyl)-2,2':6'2''-terpyridine (Dodoxy) Reading University		3	9
(4',4'')-Ditolyl-2,2':6'2'':6''2'''-quaterpyridine (Quater) Reading University		390	19
(4',4''')-Di-(4-heptyloxyphenyl)-2,2':6'2'':6''2''':6'''2''''-quinquepyridine (Quinque) Reading University		12	22
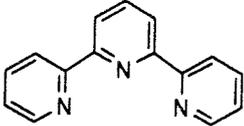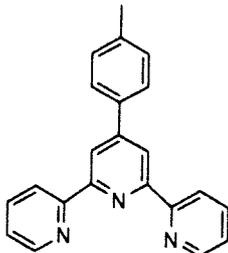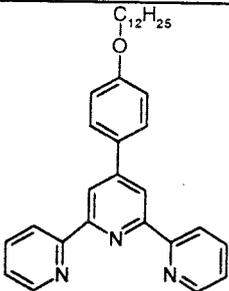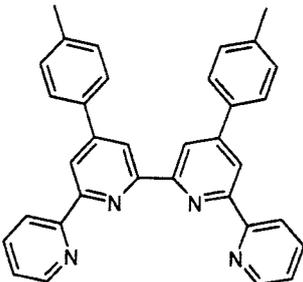
7
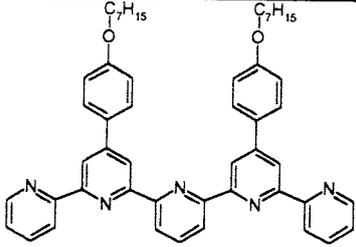
3. COLLABORATIONS

Sweden
The Swedish partitioning and transmutation co-ordination group, initiated in 1993, consists of representatives from universities and industries;

* Chalmers University of Technology, Göteborg
* Royal Institute of Technology, Stockholm
* Uppsala University and The Svedberg Laboratoriet, Uppsala
* Manne Siegbahn Laboratory, Stockholm
* Scanditronix Medical Systems AB, Uppsala
* Experts on reactor technology, Västerås
* The Industrial Group

Europe
On the 1st of May, 1996, a collaboration with France, United Kingdom, Germany, Italy and Sweden officially started and the project is funded by the EC (NEWPART CT FI4I-CT96-0010) within the Nuclear Fission Safety programme. The different participants are;
CEA (France), University of Reading (UK), Chalmers University of Technology (Sweden), Transuranium Institute (Germany), Forschungszentrum Karlsruhe (Germany), Forschungsanlage Jülich (Germany) and ENEA (Italy). Project meetings are held every 6 months. This year the Department of Nuclear Chemistry organised the first project meeting held in Marstrand on the 28-30th of May. The second meeting was held in Aix-en-Provence, France, November 4-7.

United Kingdom
Within the EC-contract there is a close collaboration between Chalmers and the University of Reading, UK, concerning synthesis and investigations of new nitrogen containing extractants. Several extractants synthesised in Reading were investigated at the Department of Nuclear Chemistry, CTH, during 1997. P.B. Iveson and M.L. Russell from the University of Reading spent a week at the department in May 1997. They took part in the radiochemical work concerning studies of new extractants for separation of trivalent actinides and lanthanides. Dr. M.J. Hudson, who is leading the Reading group, also visited the department for one week in August 1997 and gave a lecture on "the History of Macrocyclic Extractants". Discussions about future work were also held.

France
The close collaboration with CEA in France continued. Present and future work have been discussed with Charles Madic and co-workers at several occasions and there is a continuous exchange of research results.

U.S.A.
An informal collaboration was initiated in 1992 between the Los Alamos National Laboratory (LANL) and the Department of Nuclear Chemistry, CTH. The collaboration involves exchange of information and results within aqueous based partitioning processes.

Japan
A collaboration was initiated in 1993 between the Department of Nuclear Chemistry, CTH and the Department of Fuel Cycle Safety Research at Japan Atomic Energy Institute (JAERI). It was agreed to exchange information, results and personnel between CTH and JAERI.

4. TRAVELLING

Several meetings and conferences were attended during 1997, see the travelling reports (appendix VI-VIII).

5. REFERENCES

[1] Landgren, A. and Liljenzin, J.O.: "Extraction Behaviour of Technetium and Actinides in the Aliquat-336/Nitric Acid System", *OECD Conference on "Long-Lived Radionuclide Chemistry in Nuclear Waste Treatment"*, Villeneuve-lés-Avignon, France, June 20-21 (1997)

[2] Chan, G.Y.S., Drew, M.G.B., Hudson, M.J., Iveson, P.B., Liljenzin, J.O., Skålberg, M., Spjuth, L., Madic, C.: "Solvent extraction of metal ions from nitric acid solution using N,N'-substituted malonamides. Experimental and crystallographic evidence for two mechanisms of extraction, metal complexation and ion-pair formation. *Accepted J. Chem. Soc. Dalton Trans* (1996)

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[6] Johansson, M.: "Extraction Studies and Process Calculations for Separation of Trivalent Actinides and", *Diploma Thesis, Department of Nuclear Chemistry, Chalmers University of Technology*, December (1997)

[7] Enarsson, Å., Hagström, I., Liljenzin, J.O., Skålberg, M. and Spjuth, L.: *Second Semestrial Report on "Partitioning Experiments and Waste Minimisation", Contract NEWPART (FI41-CT-96-0010)*, May (1997)

Appendix I

Contract FI41-CT-96-0010, Participant No. 3, Chalmers University of Technology, Progress Report from 1st November to 31st May

Å. Enarsson, I. Hagström, J.O. Liljenzin, M. Skålberg and L. Spjuth

Introduction

Further investigations of the oligopyridine 2,2'-6',2''-terpyridine have been performed at Chalmers during the last semester. The distribution of terpyridine between organic and aqueous phase has been investigated and the stoichiometry of the extracted europium complex has been determined in the synergistic system with terpyridine and 2-bromodecanoic acid. The two malonamides N,N'-dimethyl-N,N'-dicyclohexyltetradecyl malonamide (DMDCHTD) and N,N'-dimethyl-N,N'-diphenyltetradecyl malonamide (DMDPHTD) have also been used in synergy with 2-bromodecanoic acid and the stoichiometry of the extracted complex with DMDCHTD has been suggested. A new oligopyridine, 4'-tolyl-2,2'-6',2''-terpyridine, was synthesised at the University of Reading and extraction studies with this new extractant have been initiated. Its extraction capability and selectivity for trivalent actinides over lanthanides have been investigated in synergy with 2-bromodecanoic acid. *Tert*-butylbenzene has been used as diluent in these studies.
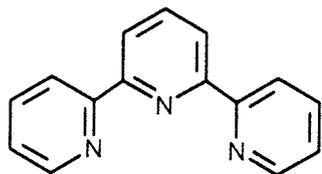
Figure 1.   2,2'-6',2''-terpyridine   4'-tolyl-2,2'-6'2''-terpyridine (tolpy)
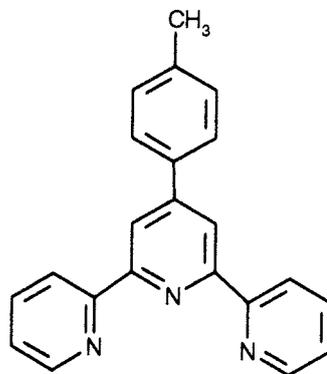
Results

As presented at the previous progress meeting [1], the metal extraction by 0.02M terpyridine in synergy with 1M 2-bromodecanoic acid in *tert*-butylbenzene decreases dramatically when the nitric acid concentration is increased. One reason for this decrease is the association of 2-bromodecanoic when the nitric acid concentration increases. The 2-bromodecanoic acid has to be dissociated to be able to form neutral complexes with the metal ions and the complexes are thereafter extracted by terpyridine.

It was observed that terpyridine was protonated quite readily even at reasonably low nitric acid concentrations and the protonated form of terpyridine was found in the aqueous phase. The protonation was measured by two-phase titration of 0.1M terpyridine in *tert*-butylbenzene in contact with an aqueous phase. There was a slower decrease in pH in the aqueous phase when nitric acid was added than expected if no protonation had occurred (Fig. 2).
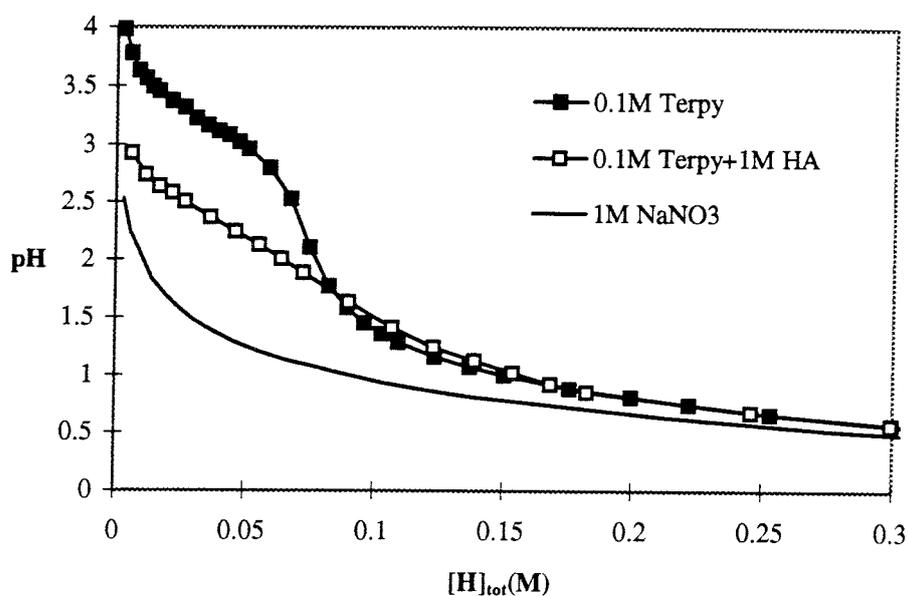
Figure 2. pH in the aqueous phase after addition of nitric acid when contacted with 0.1M terpyridine in *tert*-butylbenzene compared to the pH in an aqueous solution with the same addition of nitric acid. In both cases the ionic strength in the aqueous phase was kept constant at 1M (Na, H)NO$_3$. [H]$_{tot}$ is the added amount of nitric acid divided by the volume of the aqueous phase.

The transfer of protonated terpyridine from the organic phase to the aqueous phase was detected by titration of the organic phase dissolved in acetic acid anhydride by HClO$_4$ in acetic acid (Fig. 3) [2]. When 2-bromodecanoic acid was present in the organic phase a higher nitric acid concentration was needed to protonate the terpyridine and transfer it to the aqueous phase. This could be due to formation of adducts between terpyridine and 2-bromodecanoic acid. This transfer of extractant to the aqueous phase is contributing to the steep decrease in metal extraction when the nitric acid concentration is increased.
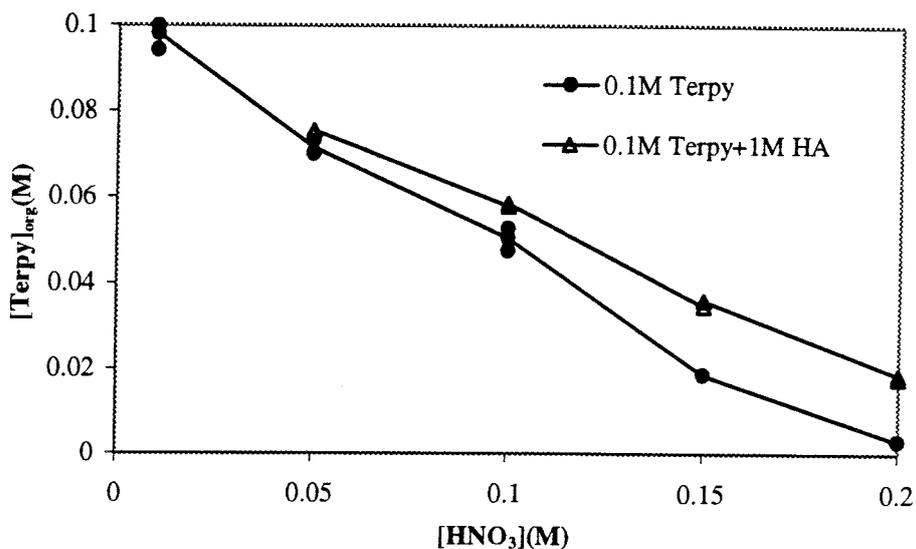
Figure 3. Concentration of terpyridine in the organic phase at different nitric acid concentrations after extraction by 0.1M terpyridine in *tert*-butylbenzene or 0.1M terpyridine + 1M 2-bromodecanoic acid (HA) in *tert*-butylbenzene.

If the method of continous variation is performed with a constant total concentration of 2-bromodecanoic acid and terpyridine and with a relatively high concentration of metal, than the maximum extraction is related to the stoichiometry of the extracted complex.
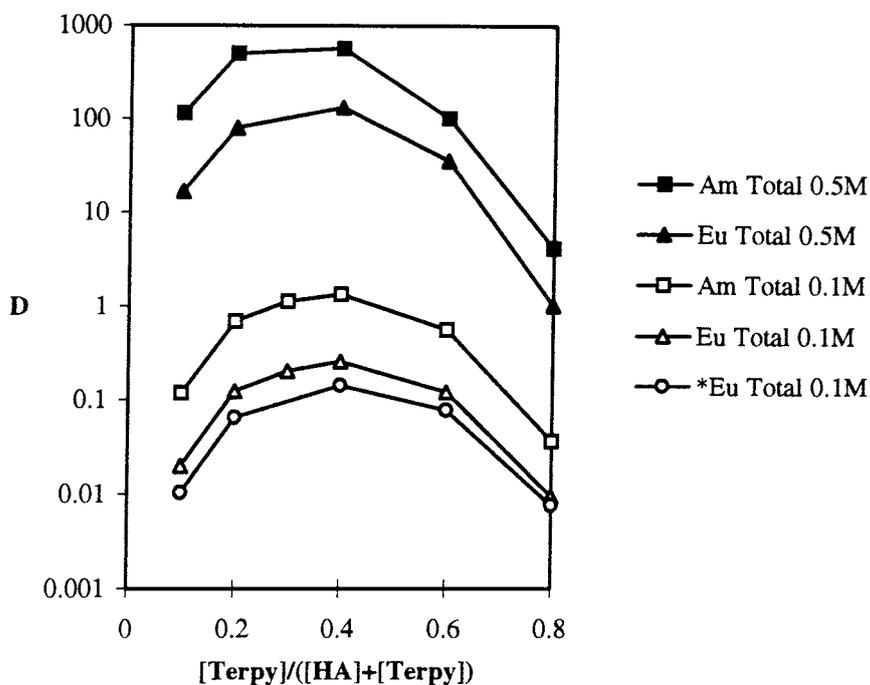
Figure 4. The extraction of tracer amounts of americium and europium (*=0.01M Eu) from 0.011M HNO_3 with a total concentration of 0.1M and 0.5M of terpyridine and 2-bromodecanoic acid in tbb.

As seen in Fig. 4, a maximum in extraction is observed at 40 percent terpyridine and 60 percent 2-bromodecanoic acid. This suggests that the optimum ligand:acid ratio is 2:3 and thus the stoichiometry of the extracted complex is EuA_3L_2.

Similar experiments with the malonamide - 2-bromodecanoic acid synergistic system suggested the extracted complex $EuA_3(HA)_3 \cdot L$. HA is 2-bromodecanoic acid and A is the anion of 2-bromodecanoic acid.
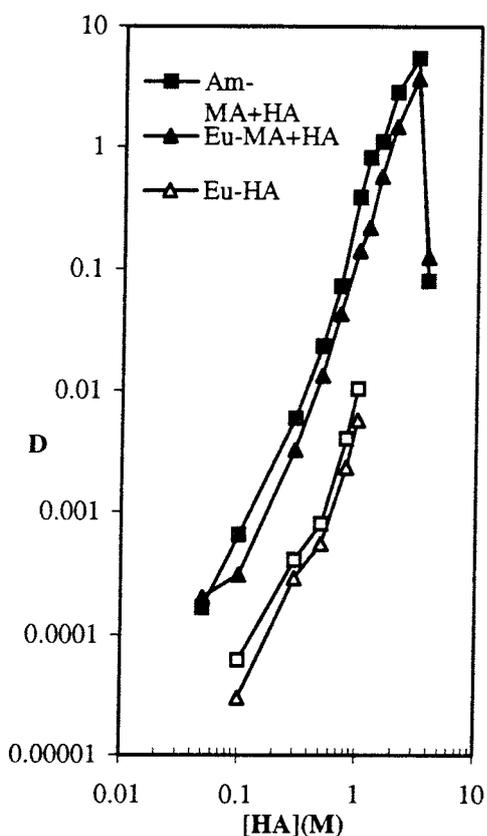
Figure 5. The extraction of europium and americium by 0.1M DMDCHTD and different concentrations of 2-bromodecanoic acid in tbb.

The extraction of europium and americium by 0.1M DMDCHTD and different concentrations of 2-bromodecanoic acid was determined, Fig.5. The separation factor is quite small compared to the terpyridine mixture and doesn't vary considerably with 2-bromodecanoic acid concentration.

The tolpy was found to be less soluble in tert-butylbenzene than terpyridine ([tolpy]<0.07M). In combination with 2-bromodecanoic acid the solubility was enhanced considerably.

Two-phase titration of 0.02M tolpy showed the same decrease in pH as expected when no protonation occurs. Contacts with nitric acid solutions higher than 0.015M, cause third phase formation. This third phase is probably protonated tolpy insoluble in the aqueous phase as well as in the organic phase. When 2-bromodecanoic acid was present the use of a higher concentration of nitric acid was possible without third phase formation.

Extraction experiments show that tolpy itself extracts Am and Eu rather poorly but does separate them. With mixtures of tolpy and 2-bromodecanoic acid the extraction is enhanced and the separation factor is around 8 (Fig. 6). The distribution ratios of Pm are similar to the ones of Eu. When the metal extraction in the synergistic system of tolpy and 2-bromodecanoic acid is plotted in a log-log plot versus the concentration of nitric acid the gradient is -3. This could indicate that 3 protons are released in the extraction, if so probably from the 2-bromodecanoic acid.
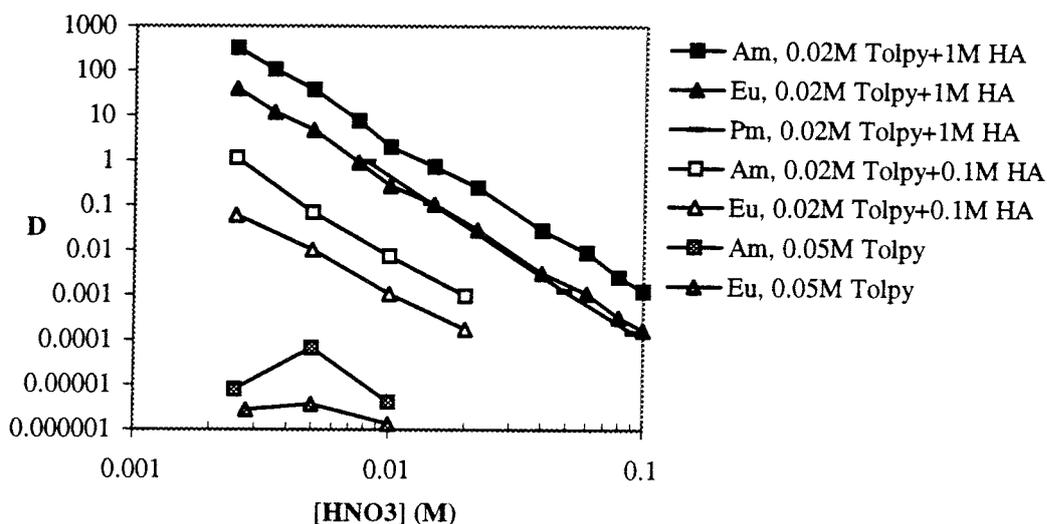
Figure 6. Extraction of Am and Eu by 0.02M tolpy in *tert*-butylbenzene and by 0.02M tolpy and two different concentrations of 2-bromodecanoic acid (HA) in *tert*-butylbenzene. Extraction of Pm by 0.02M tolpy and 1M 2-bromodecanoic acid (HA) in *tert*-butylbenzene.

The distribution ratio is increased when the concentration of 2-bromodecanoic acid is increased (Fig. 7). The gradient in a log-log plot is about 3, indicating that there are three 2-bromodecanoic acid molecules in the extracted complex. At higher concentrations of 2-bromodecanoic acid the increase in extraction diminishes and at 3M 2-bromodecanoic acid a precipitate is formed. This might be explained by the small amount of diluent present at these high concentrations of 2-bromodecanoic acid.
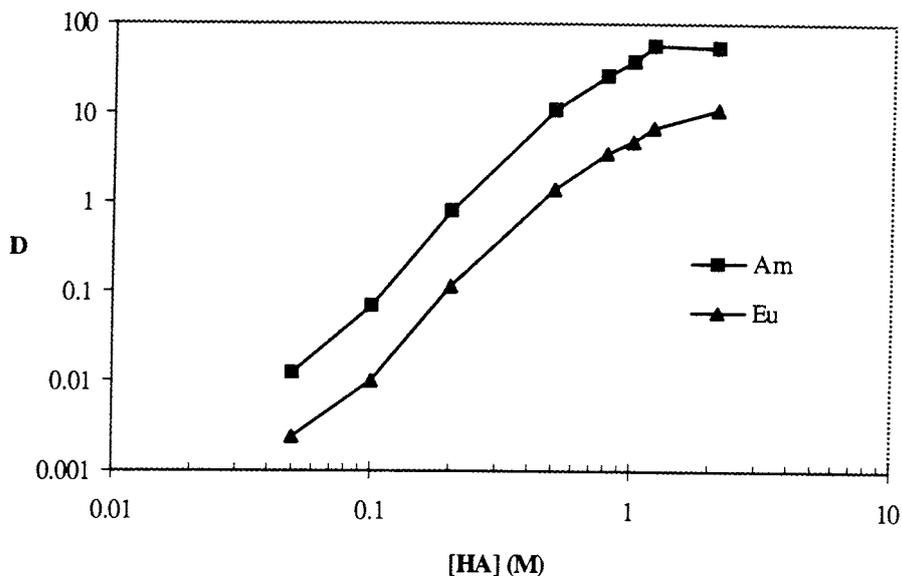
Figure 7. Extraction of Am and Eu by 0.02M tolpy and various concentrations of 2-bromodecanoic acid (HA) in *tert*-butylbenzene from 0.005M nitric acid.

Future Work

Studies to determine the stoichiometry of the complex extracted by tolpy and 2-bromodecanoic acid will be performed. Oligopyridines are promising extractants for trivalent actinide-lanthanide separation. The problem with tolpy is the low solubility in *tert*-butylbenzene and the insolubility of the protonated form. New oligopyridines, substituted with longer carbon chains, are expected to have a better solubility and are therefore interesting to study in order to determine the influence of structure on metal extraction. Extraction studies of multivalent actinides and di- and monovalent fission products with the oligopyridines will be performed. Further basic investigations, like water extraction, with the malonamides will also be initiated shortly.

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[2] D.C. Wimer, Analytical Chemistry, 30, 77 (1958)

Appendix II

EXTRACTION BEHAVIOUR OF TECHNETIUM AND ACTINIDES IN THE ALIQUAT-336/NITRIC ACID SYSTEM

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Abstract

The extraction behaviour of technetium, thorium, uranium, neptunium, plutonium, americium and curium in the Aliquat-336 (diluted with 1,3-diisopropyl benzene) - nitric acid system have been studied. Aliquat-336 (tricapryl-methylammonium nitrate) is a quaternary ammonium salt extracting different species with an anion exchange mechanism. Distribution data obtained are modeled by anion exchange (Tc) and ion-pair formation mechanisms (actinides) with the extraction of nitric acid included to account for the lowering of the free extractant concentration.

Introduction

Transmutation of long lived nuclear waste puts high demands on the partitioning process since a high quantitative yield as well as a good separation yield is needed.The extractants to be used in such a separation process must have a good selectivity for the elements to be separated, a high radiation stability and they should be completely incinerable i.e. they should obey the CHON-principle. One group of extractants that fulfils the above demands are the long-chained quaternary ammonium salts. At first the extraction of metals and acids with quaternary ammonium salts seems to be rather uncomplicated but when the system is formulated mathematically in order to calculate the parameters in the model, it is found that the system is not simple. Problems arise because it is necessary to take into account the formation of several metal ligand complexes in the aqueous phase, formation of different species in the organic phase, the extraction of acid and the formation of micelles in the organic phase. Furthermore, activities instead of concentrations must be considered since both high and low ionic strengths are necessary in a separation process. In this work, Aliquat-336 (tri-capryl methyl ammonium nitrate) has been studied which has three straight carbon chains containing eight to ten carbon atoms and a methyl group connected to the nitrogen atom and is denoted $R_3R'NNO_3$ in this text.

Theory

Aliquat-336 is known to form micelles in organic solutions which can be described as

$$q\overline{R_3R'NNO_3} \xrightleftharpoons{k_{mq}} \overline{(R_3R'NNO_3)_q} \tag{1}$$
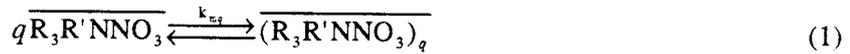
where q is an integer ≥ 0 and k_{mq} is the equilibrium constant. The bar above the molecule denotes the organic phase. The extraction of nitric acid with Aliquat-336 is assumed to take place in such a way that Aliquat-336 is able to extract nitric acid according to equations (2) and (3).

$$HNO_3 \xrightleftharpoons{\lambda_H} \overline{HNO_3} \tag{2}$$

$$\overline{(R_3R'NNO_3)_q} + l\overline{HNO_3} \xrightleftharpoons{k_{Hql}} \overline{(R_3R'NNO_3)_q(HNO_3)_l} \tag{3}$$

λ_H and k_{Hql} are the equilibrium constants for reaction (2) and (3) respectively and l is an integer ≥ 0. In the aqueous phase the nitric acid is dissociated to hydrogen and nitrate ions according to reaction (4) (here written as an association equilibria)

$$H^+ + NO_3^- \xrightleftharpoons{k_a} HNO_3 \tag{4}$$

where k_a is the association constant. The extraction of nitric acid can be described by the distribution ratio, D, taking into account all species containing nitric acid in both phases and activity factors (here denoted y).

$$D_{HNO_3} = \frac{\left[\overline{HNO_3}\right]_{tot}}{[HNO_3]_{tot}} = \frac{\displaystyle\sum_{l=0}^{L}\sum_{q=0}^{Q} l \cdot \left[\overline{(R_3R'NNO_3)_q(HNO_3)_l}\right]}{[HNO_3] + [NO_3^-]} =$$

$$\frac{\displaystyle\sum_{l=0}^{L}\sum_{q=0}^{Q} l \cdot k_{Hql} \cdot k_{mq} \cdot \lambda_{H}^{l} \cdot k_{a}^{l} \cdot \left[\overline{R_{3}R'NNO_{3}}\right]^{q} \cdot \left[NO_{3}^{-}\right]^{2l} \cdot \dfrac{y_{\overline{R_{3}R'NNO_{3}}}^{q} \cdot y_{H^{+}}^{l} \cdot y_{NO_{3}^{-}}^{l}}{y_{\overline{(R_{3}R'NNO_{3})_{q}(HNO_{3})_{l}}}}}{\left[NO_{3}^{-}\right] \cdot \left(1 + k_{a} \cdot \left[NO_{3}^{-}\right] \cdot \dfrac{y_{H^{+}} \cdot y_{NO_{3}^{-}}}{y_{HNO_{3}}}\right)} \tag{5}$$

In this work the metal concentration is negligible compared to the extractant concentration so the only species consuming a considerable amount of extractant molecules is nitric acid. The lowering of the free extractant concentration can be described by the equation for the total concentration of Aliquat-336,

$$\left[\overline{R_{3}R'NNO_{3}}\right]_{tot} = \sum_{l=0}^{L}\sum_{q=0}^{Q} q \cdot \left[\overline{(R_{3}R'NNO_{3})_{q}(HNO_{3})_{l}}\right] =$$

$$= \sum_{l=0}^{L}\sum_{q=0}^{Q} q \cdot k_{Hql} \cdot k_{mq} \cdot \lambda_{H}^{l} \cdot k_{a}^{l} \cdot \left[\overline{R_{3}R'NNO_{3}}\right]^{q} \cdot \left[NO_{3}^{-}\right]^{2l} \cdot \frac{y_{\overline{R_{3}R'NNO_{3}}}^{q} \cdot y_{H^{+}}^{l} \cdot y_{NO_{3}^{-}}^{l}}{y_{\overline{(R_{3}R'NNO_{3})_{q}(HNO_{3})_{l}}}} \tag{6}$$

If it is then assumed that only the monomer and dimer form of Aliquat-336 exist and that only one nitric acid molecule can be bound to Aliquat-336 [1] i.e. $Q = 2$ and $L = 1$ in equations (5) and (6), the free extractant concentration can be obtained by solving the resulting second order equation. This solution for the free extractant concentration, $[R_{3}R'NNO_{3}]$, used in equation (5) describes the extraction of nitric acid.

The extraction of anions, A^{z-}, by an anion exchange reaction can be described by equations (7) and (8) where z is the charge of the ion and ε_{z} is the equilibrium constant.

$$z\overline{R_{3}R'NNO_{3}} + A^{z-} \underset{\varepsilon_{z}}{\overset{}{\rightleftharpoons}} \overline{(R_{3}R'N)_{z}A} + zNO_{3}^{-} \tag{7}$$
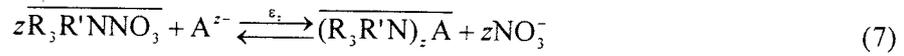
$$D_{A^{z-}} = \frac{\left[\overline{(R_{3}R'N)_{z}A}\right]}{\left[A^{z-}\right]} = \varepsilon_{z} \cdot \frac{\left[\overline{R_{3}R'NNO_{3}}\right]^{z}}{\left[NO_{3}^{-}\right]^{z}} \cdot \frac{y_{\overline{R_{3}R'NNO_{3}}}^{z} \cdot y_{A^{z-}}}{y_{\overline{(R_{3}R'N)_{z}A}} \cdot y_{NO_{3}^{-}}^{z}} \tag{8}$$

For the extraction of cations to take place, formation of neutral or negatively charged metal nitrate complexes in the aqueous phase must preceed the extraction to the organic phase. In the aqueous phase the complex formation is described by the use of stability constants according to

$$M^{z+} + nNO_{3}^{-} \underset{\beta_{n}}{\overset{}{\rightleftharpoons}} M(NO_{3})_{n}^{z-n} \tag{9}$$
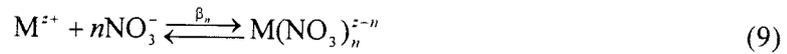
where β_{n} is the stability constant for reaction (9) and n is an integer ≥ 0. The extraction of cations can be described in two different ways but the end products will be the same in both cases. The difference between the two extraction mechanisms is whether the reaction with Aliquat-336 takes place in the bulk of the organic phase or at the interface between the two phases. When the number of nitrate ions that must co-ordinate to the cations for extraction to take place is considered, it seems to be more likely that the reaction with the extractant takes place in the organic phase. The extraction can then be described as

$$p\overline{R_3RNNO_3} + \overline{M(NO_3)_z} \xrightleftharpoons{\alpha_p} \overline{(R_3R'N)_p M(NO_3)_{z+p}} \tag{11}$$
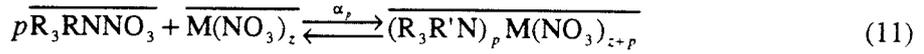
$$D_{M^{z+}} = \frac{\left[\overline{M}\right]_{tot}}{[M]_{tot}} = \frac{\sum_{p=0}^{P}\left[\overline{(R_3R'N)_p M(NO_3)_{z+p}}\right]}{\sum_{n=0}^{N}\left[M(NO_3)_n^{z-n}\right]} = \frac{\sum_{p=0}^{P}\alpha_p \cdot \left[\overline{R_3R'NNO_3}\right]^p \cdot \dfrac{y^p_{\overline{R_3R'NNO_3}}}{y_{\overline{(R_3R'N)_p M(NO_3)_{z+p}}}}}{\dfrac{1}{\lambda_z\beta_z} \cdot \sum_{n=0}^{N}\beta_n \cdot \left[NO_3^-\right]^{n-z} \cdot \dfrac{y^{n-z}_{NO_3^-}}{y_{M(NO_3)_n^{z-n}}}} \tag{12}$$

where λ_z and α_p are equilibrium constants and p is an integer ≥ 0. If the extraction reaction takes place at the interface between the two phases, negatively charged metal nitrate complexes must be formed in the aqueous phase before extraction can take place which is shown in equations (13) and (14)

$$p\overline{R_3R'NNO_3} + M(NO_3)_{z+p}^{p-} \xrightleftharpoons{\delta_p} \overline{(R_3R'N)_p M(NO_3)_{z+p}} + pNO_3^- \tag{13}$$
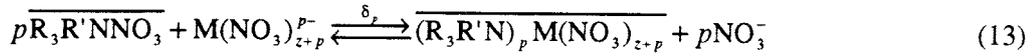
$$D_{M^{z+}} = \frac{\left[\overline{M}\right]_{tot}}{[M]_{tot}} = \frac{\sum_{p=0}^{P}\left[\overline{(R_3R'N)_p M(NO_3)_{z+p}}\right]}{\sum_{n=0}^{N}\left[M(NO_3)_n^{z-n}\right]} = \frac{\sum_{p=0}^{P}\delta_p \cdot \beta_{z+p} \cdot \left[\overline{R_3R'NNO_3}\right]^p \cdot \dfrac{y^p_{\overline{R_3R'NNO_3}}}{y_{\overline{(R_3R'N)_p M(NO_3)_{z+p}}}}}{\sum_{n=0}^{N}\beta_n \cdot \left[NO_3^-\right]^{n-z} \cdot \dfrac{y^{n-z}_{NO_3^-}}{y_{M(NO_3)_n^{z-n}}}} \tag{14}$$

where δ_p is the equilibrium constant. The above equations (5), (8) and (12) describing the distribution of nitric acid, anions and cations respectively are all functions of the nitrate concentration and the Aliquat-336 concentration. Varying the total extractant concentration and the nitric acid concentration should give data from which the model parameters can be determined. The dissociation and activity factors for nitric acid are investigated by Davis and de Bruin [2] and are used in the determination of the model parameters. These results [2] are used to calculate the nitrate ion concentration from the total concentration of nitric acid by assuming a polynomial expression for the degree of dissociation, α, and thereafter determine the parameters, k_i, in that polynom.

$$\alpha = \sum_{i=0}^{6} k_i \cdot [HNO_3]_{tot}^i \tag{15}$$

The mean ionic activity coefficient and the activity coefficient for undissociated nitric acid are then expressed as a function of the equilibrium concentration of nitrate ions in equations (16) and (17).

$$y_\pm = \sqrt{y_{H^+} \cdot y_{NO_3^-}} = \frac{\sum_{i=0}^{4} a_i \cdot \left[NO_3^-\right]^i}{1 + \sum_{i=5}^{7} a_i \cdot \left[NO_3^-\right]^{i-4}} \tag{16}$$

$$y_{HNO_3} = \frac{\sum_{i=0}^{4} b_i \cdot \left[NO_3^-\right]^i}{1 + \sum_{i=5}^{7} b_i \cdot \left[NO_3^-\right]^{i-4}} \tag{17}$$

The activity coefficients for the charged metal nitrate complexes are approximated using equations (18) and (19)

$$\log y_i = -\frac{1}{2} \cdot z_i^2 \cdot \frac{\sqrt{I}}{1+\sqrt{I}}; \quad I \leq 0.25 \tag{18}$$

$$\log y_i = -\frac{z_i^2}{6}; \quad I \geq 0.25 \tag{19}$$

where I is the ionic strength in the aqueous phase. The above equations only describe the activity coefficients for charged species. To estimate the activity coefficients for neutral species the *Setchenov equation* (20) is used

$$\log y_N = \log y_N^0 + k_{N,CA} \cdot c_{CA} \tag{20}$$

where y_N^0 is the activity coefficient for the neutral species N in absence of the electrolyte CA. $k_{N,CA}$ is a constant called the salting-out constant if its value is positive or the salting-in constant if its value is negative. Its sign depends on the combination of electrolytes in the system and it is therefore impossible to predict a priori if salting-in or salting-out occurs [3], [4]. c_{CA} is the electrolyte concentration. The activity coefficients quotients for the organic species are unknown and are therefore set to unity in this calculation.

Experimental

Nitric acid solutions were prepared from concentrated nitric acid of analytical grade (J.T. Baker). The organic phase was prepared by dissolving Aliquat-336 in the nitrate form (Fluka) in 96 % 1,3-diisopropyl benzene (Acros) to which 5 vol-% 1-dodecanol (Fluka, $\geq$ 99.5 %) was added as a third phase inhibitor. [238]Pu, and [244]Cm were commercially available from AEA Technology, Harwell, [235]U from Eurochemic, [241]Am from Amersham and ^{99m}Tc from Ultra-Technekow FM, Mallinckrodt Medical. The [239]Np stock solution was prepared by neutron activation of [238]UO$_2$(NO$_3$)$_2$·6H$_2$O. The irradiated target was dissolved in concentrated nitric acid and purified with thenoyltrifluoroacetylacetone [5]. [239]Np^{4+} was then prepared by reduction with hydrogen and a catalyst of platinum black.

Tetravalent plutonium was prepared by a method described by Stary [5]. [234]Th was obtained by contacting an ether solution containing [238]UO$_2$(NO$_3$)$_2$ in radioactive equilibrium with [234]Th with a small volume of 0.1 M nitric acid. This aqueous solution was then purified on an ion exchange resin according to Murase et al [6].

The distribution experiments started by adding 3.98 ml nitric acid to a test tube. 20 µl of the radionuclide stock solution was added to the tube whereafter 4.0 ml organic phase was added. After shaking the tube vigorously for five minutes the phases were separated in a centrifuge at about 4000 rpm. A sample of suitable volume was withdrawn from each phase and transferred to a measuring vial. [235]U was determined by γ-spectrometry using a HPGe-detector, [234]Th, [238]Pu, [241]Am and [244]Cm were measured by liquid scintillation counting using a LKB WALLAC 1219 RACKBETA and ^{99m}Tc and [239]Np by a NaI(Tl) scintillation detector, Intertechnique model CG-4000. The extraction of nitric acid was investigated by potentiometric titration of hydrogen ions in both the aqueous and organic phases with sodium hydroxide (Riedel-de-Haën) using Mettler DL20 titration equipment. The organic phase was titrated in 95 % ethanol (Kemetyl).

Determination of model parameters

First, the parameters in the model for extraction of nitric acid were calculated. The experimentally determined distribution ratios for nitric acid were used to calculate the total nitric acid concentration in the aqueous phase at equilibrium. By using the degree of dissociation for nitric acid determined by Davies and de Bruin [2] the nitrate concentration was calculated. The mean ionic activity coefficient, $y_\pm = \sqrt{y_{H^+} \cdot y_{NO_3^-}}$, and the activity coefficient for undissociated nitric acid, y_{HNO_3}, were used in the model in the form of equations (16) and (17) respectively. Equation (6) in (5) with $L = 1$, $Q = 2$ and $k_a = 0.0645$ M^{-1} [2] then gives the distribution ratio for nitric acid as a function of the nitrate concentration in the aqueous phase. The parameters in the model were then calculated by seeking the minimum of the function, U, in equation (21).

$$U = \sum_{j=1}^{J} w_j \cdot (D_{j,\,calc} - D_{j,\,exp})^2 \tag{21}$$

Here $D_{j,\,calc}$ and $D_{j,\,exp}$ are the j:th estimated and experimental distribution ratios respectively. J is the number of data points and w_j is the weight factor for the j:th point. In this calculation $w_j = 1/D_{j,\,exp}^2$. The determined parameters were then used in equation (6) to obtain the free extractant concentration by solving the resulting second order equation. This solution was then used in equations (8) and (12) to calculate the parameters in the metal extraction model. In equation (12) the activity coefficient for the nitrate ions, $y_{NO_3^-}$, was approximated with the mean ionic activity coefficient, $y_\pm$, determined by Davies and de Bruin [2] and the activity coefficient for the metal nitrate complex, $y_{M(NO_3)_n^{z-n}}$, was estimated with equations (18) and (19) if $n \neq z$ and with the Setchenov equation (20) if $n = z$.

Results

The results from the calculation of the parameters in equations (15), (16) and (17) are given in table 1.

Table 1 Calculated values of parameters in equations (15), (16) and (17).

i	0	1	2	3	4	5	6	7
k_i	1.00	-0.0349	0.0131	-0.00573	0.000837	-0.00005	0.000001	-
a_i	1.07	363	-137	57.7	-8.29	441	-78.4	-1.35
b_i	0.998	12.6	0.393	0.575	-0.185	12.0	-2.51	0.0308

The parameters determined in the model for the extraction of nitric acid are given in table 2.

Table 2 Determined parameters in the model for extraction of nitric acid.

$\log k_{m2}$	$\log \lambda_H$	$\log k_{H11}$	$\log k_{H21}$
-3.6	-1.0	1.9	6.2

The parameters in the model for metal extraction were also determined and are given in table 3.

Table 3 Determined parameters in the model for extraction of metals. Literature data are given in parenthesis.

	$\log \varepsilon$	$\log \alpha_2$	$\log \beta_1$	$\log \beta_2$	$\log \beta_3$	$\log \beta_4$	$\log \lambda_z$	$-k_{N,CA}$
TcO_4^-	2.81	-	-	-	-	-	-	-
[10] Th^{4+}	-	3.0	-0.2 (1.22)	-2.8 (1.53)	-6.3 (1.1)	-2.7	3.9	0.55
[11] UO_2^{2+}	-	-4.7	1.8 (0.47)	0.6 (-1.5)	-	-	0.7	0.078
[12] Pu^{4+}	-	5.0	-0.7 (0.70)	0.6 (1.1)	-7.7 (1.1)	-3.8 (0.6)	4.7	0.78
[11] Np^{4+}	-	2.0	-0.7 (-1.52)	1.3 (-0.17)	-7.8 (-0.82)	-1.8 (-0.89)	5.3	0.67
[11,13] Am^{3+}	-	4.5	2.2 (0.23)	-1.3 (0.13)	-8.2 (-1.40)	-	6.2	2.0
[14] Cm^{3+}	-	4.2	2.5 (0.34)	-2.6 (0.10)	-4.4	-	2.5	1.2

The experimental distribution ratios are plotted against the equilibrium concentration of nitrate ions in the aqueous phase together with the fitted values in Figure 1a, 1b and 2.
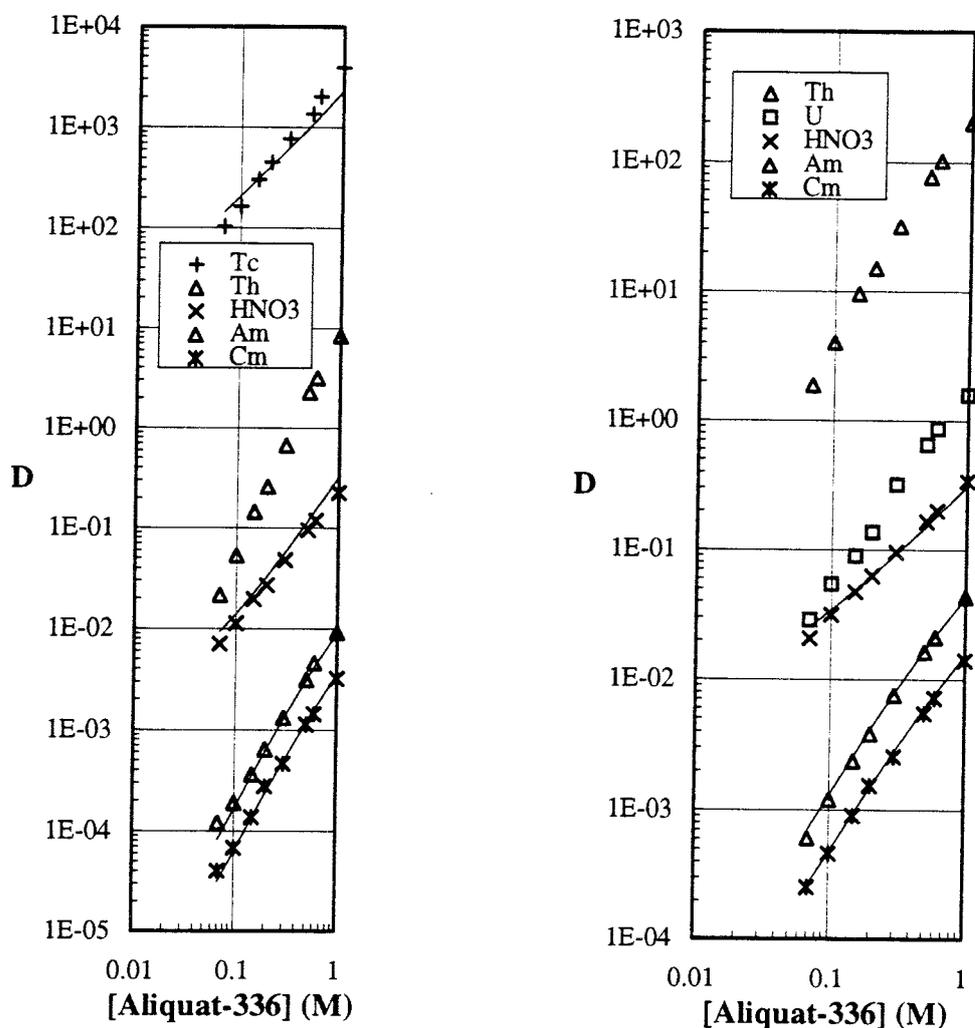
Figure 1a, b Experimental and calculated distribution ratios for some elements as a function of the total Aliquat-336 concentration at a total nitric acid concentration of a: 0.30 M, b: 2.0 M (U given at 1.0 M).
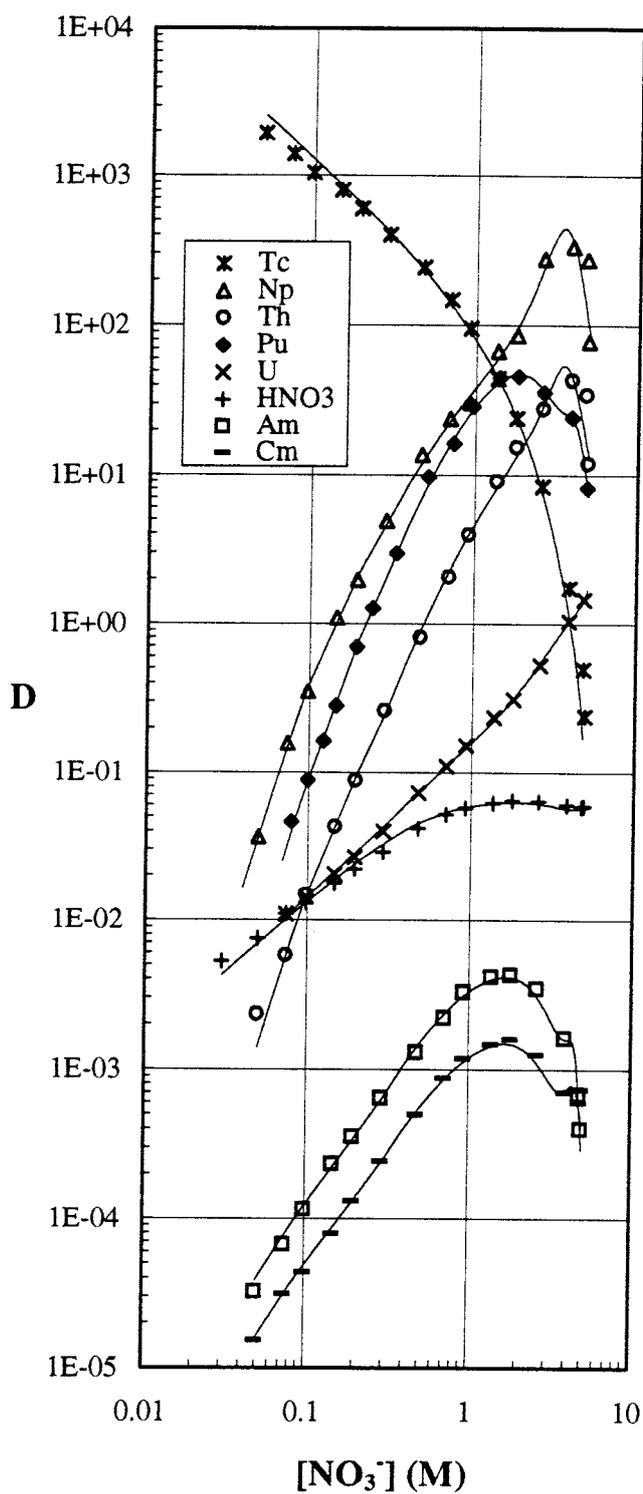
Figure 2 The distribution ratios for nitric acid, technetium and some actinides as a function of the equilibrium nitrate ion concentration in the aqueous phase. The distribution ratios calculated from the model are also shown. Note that the plutonium data are given at a total extractant concentration of 0.05 M while the other are given at 0.20 M.

Discussion

From the calculated parameters in table 2 it is seen that the dimer formation constant, k_{m2} is very low which means that Aliquat-336 mainly exists in the monomer form. This can be explained by the fact that 1,3-diisopropylbenzene is used as diluent in combination with the added third phase inhibitor, 1-dodecanol. According to Rydberg et al [1] the micelle formation in inert diluents can be reduced by using an aromatic diluent and by adding a modifier usually a strong Lewis base for example a long chained alcohol or TBP. Furthermore, the micelles seem to behave as monofunctional species extracting only one metal nitrate complex and therefore L was set to one in equations (5) and (6). The distribution constant, λ_H, has a low value since the polar nitric acid molecules prefer the polar aqueous phase to the organic phase. These parameters are then used in the model to calculate distribution ratios at a constant total nitric acid concentration while the total extractant concentration is varied. The results are shown in Figure 1a and 1b together with the experimentally determined distribution ratios. As can be seen, the calculated values are in good agreement with the experimental values.

The experimental and calculated distribution ratios for technetium are shown in Figure 1a and 2. High values are obtained because technetium exists as pertechnetate ions. In this case the extraction must take place at the interface between the two phases since no neutral complex is formed in the aqueous phase. The distribution ratio decreases as the nitrate concentration is increased due to increased competition of nitrate ions for extractant molecules. Initially, the slope is -1 as predicted by equation (8) but then the gradient decreases. This can be explained by the fact that the free extractant concentration is decreased due to extraction of nitric acid.

For the extraction of the actinide cations the salting-in of the neutral metal nitrate complex plays an important role at high nitric acid concentrations. It means that the activity coefficient of the neutral metal nitrate complex is smaller in the electrolyte solution than in pure water. To compensate for the lowering of the activity coefficient the concentration of the metal nitrate complex must increase which implies that the distribution ratio decreases. The negative sign of the constant, $k_{N,CA}$, in equation (20) indicates that salting-in rather than salting-out occurs.

As can be seen from Figure 1a, 1b and 2 the extraction of the trivalent actinides, americium and curium, is very low which is also true for the trivalent lanthanides [7]. Initially the slope is about two which means that the first nitrate complex dominates in the aqueous phase whereafter the slope is decreasing to a negative value due to decreased free extractant concentration and salting-in. From Figure 1a and 1b it should be noted that the the slope is nearly two which means that P in equation (12) must be at least two. The extraction of americium and curium is therefore assumed to involve two extractant molecules for each americium or curium atom.

Uranium in its hexavalent state is extracted better than americium and curium. According to Shabana and Ruf [8] only one extractant molecule is needed for each uranium atom but in Figure 1b it can be observed that the slope is about 1.5. Note that these values are given at a total nitric acid concentration of 1.0 M. This indicates that the extraction also might involve two extractant molecules From the stability constants in table 3 it can be concluded that the first nitrate complex dominates in the aqueous phase. This can also be observed in Figure 2 where the initial slope is about one.

For the tetravalent elements the activity factor for the metal ion has been set to unity in order to obtain a good curve fit, otherwise a curve form different from the experimental is obtained. For all the tetravalent elements high distribution ratios are obtained. The relative amount of neutral metal nitrate complex is higher for the tetravalent metals than for the trivalent, which is seen in table 3. From the stability constants for thorium, neptunium and plutonium given in table 3 it is seen that the third nitrate complex is present at a very low concentration. This is in agreement with the results for plutonium reported by Allen et al [9] where the di-, tetra- and hexanitrato complexes where found to dominate in nitric acid. The hexanitrato complex was found at 13 M nitric acid ie at a higher nitric acid concentration than was used in this work.

It should be pointed out that this is not a method for the determination of stability constants but one way of describing the extraction system with Aliquat-336 and nitric acid in the range 0.07-1 M Aliquat-336 (HNO_3, Tc, Am and Cm) and 0.05-10 M HNO_3. The obtained values of the parameters in the model must be used with extreme care since there are several assumptions made within the calculation. The obtained values of the stability constants differ from other values reported as can be seen in table 3. Some possible explanations are that the ionic strength is not kept at a constant level as in the case with the reported values. The activity coefficient quotients for species in the organic phase are set to unity in the calculation and the activity coefficients for the metal nitrate complexes are estimated with an equation which is valid only at lower ionic strengths and at lower ionic charges. The complexity of the quaternary amine nitric acid system implies that the model must contain a large number of parameters which makes the determination of them more uncertain especially in the case of tetravalent elements. Nevertheless, the model can be used to predict unknown distribution ratios and may be useful in calculations for process design.

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Appendix III

Contract FI41-CT-96-0010, Participant No. 3, Chalmers University of Technology, Progress Report from 1st June to 31st October

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Introduction

The NEWPART-work at the Department of Nuclear Chemistry, Chalmers, is concentrated on the extraction by malonamides and new oligopyridines provided by the Reading group. The malonamides are considered to be used as coextractants for trivalent actinides and lanthanides in the first part in the DIAMEX process and the oligopyridines have showed potential to separate trivalent actinides from lanthanides in the second part of the process. New metal extraction data, mechanism studies and basic chemistry of the different extractants have been performed.

Results

Oligopyridines

Complementary extraction data with the simple terpyridine (2,2'-6',2''-terpyridine) in synergy with 2-bromodecanoic acid have been performed for several different lanthanides and Cm with *tert*-butylbenzene as diluent, Fig. 1. There is a slight correlation of ionic radius on the metal extraction; the smaller the ion the better the metal extraction. A parameterisation of the D-values for the different lanthanides, Am and Cm has been initiated and are planned to be used in process calculations with this synergistic mixture.
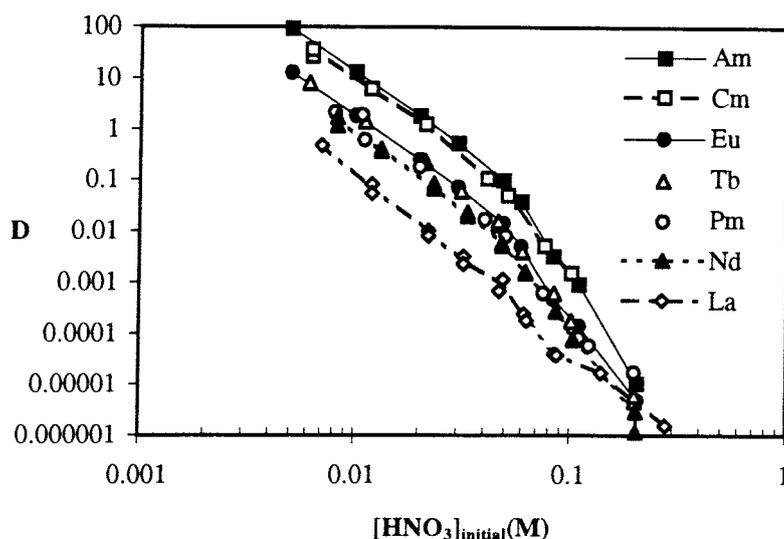
Figure 1. Extraction of some trivalent actinides and lanthanides with 0.02M terpyridine and 1M 2-bromodecanoic acid in *tert*-butylbenzene.

The dependence on terpyridine concentration of the extraction of americium and europium has been reproduced at a higher nitric acid concentration to decrease the D-values and thereby decrease the risk of contamination of organic phase in the aqueous sample. As reported at the last meeting [1] the separation factor decreased at higher 2-bromodecanoic acid concentrations which was probably due to difficulties in the measurement of high D-values. At the higher acidity now used, the separation factor is constant at all 2-bromodecanoic concentrations studied, Fig. 2.
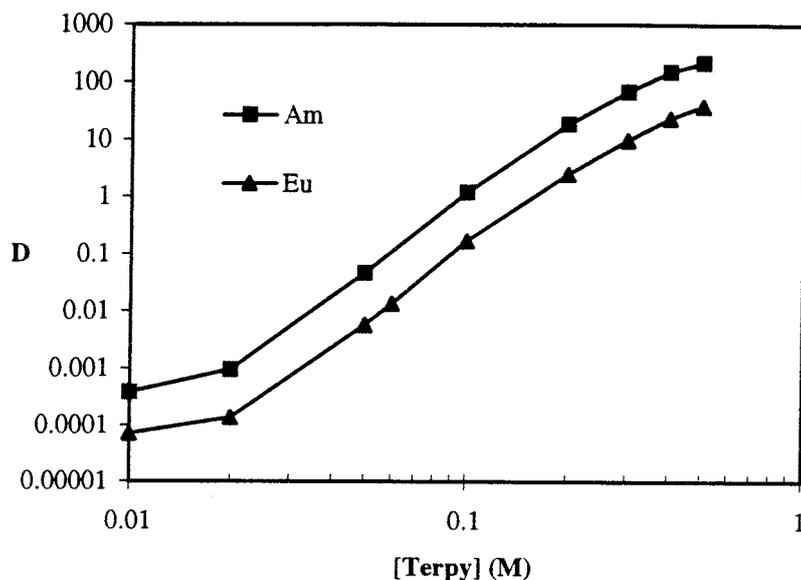
Figure 2. Extraction of americium and europium by different concentrations of terpyridine with 1M 2-bromodecanoic acid in *tert*-butylbenzene from 0.1M nitric acid.

The ionic strength has been shown to influence the terpyridine protonation and the metal extraction by terpyridine, 2-bromodecanoic acid in *tert*-butylbenzene.
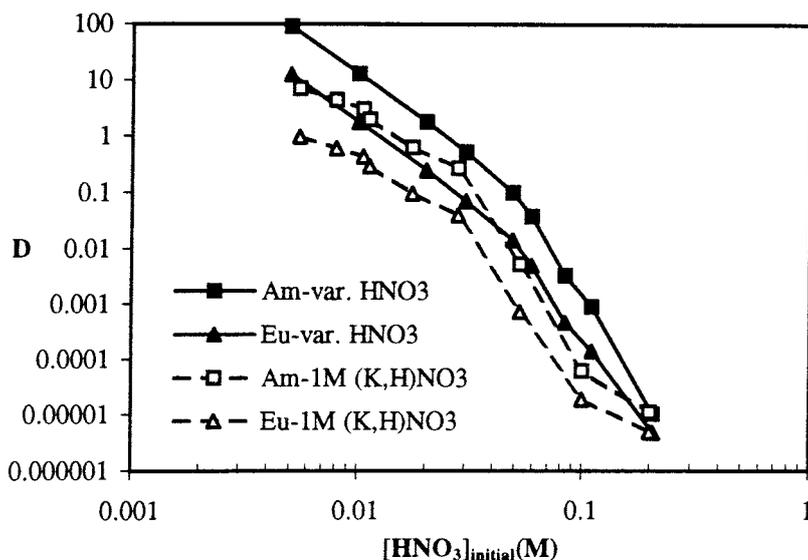
Figure 3. Extraction of americium and europium by 0.02M terpyridine, 1M 2-bromodecanoic acid in *tert*-butylbenzene at varying ionic strength (0.005M- 0.2M) and at constant ionic strength 1M (K,H)NO$_3$.
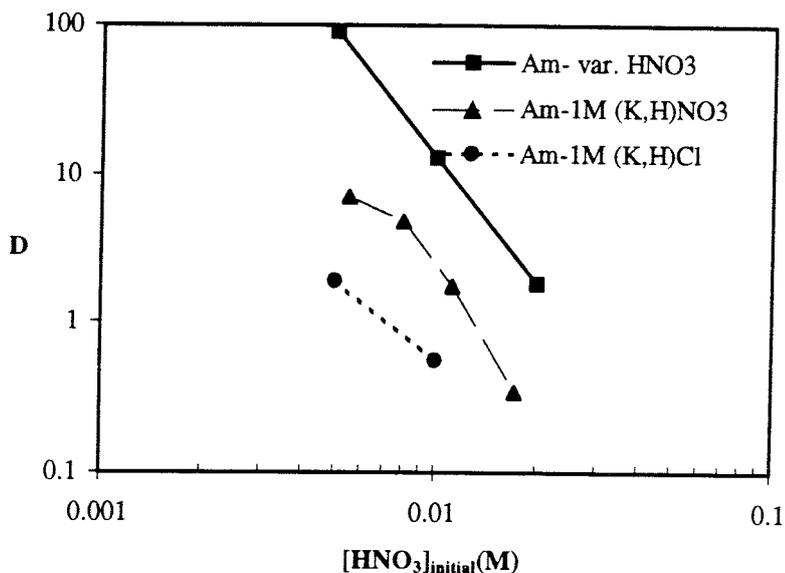
Figure 4. Extraction of americium and europium with 0.02M terpyridine and 1M 2-bromodecanoic acid in *tert*-butylbenzene from different ionic media.

The D-values for americium and europium decrease when the aqueous phase has a constant ionic strength of 1 M (K,H)NO₃ or 1 M (K,H)Cl compared to an aqueous phase where the ionic strength is only given by HNO₃ at each nitric acid concentration, Fig. 3-4. This might be partly due to formation of nitrate or chloride complexes and retention of the metal in the aqueous phase, but the effect of ionic strength is also seen when terpyridine itself is protonated, Fig. 5.
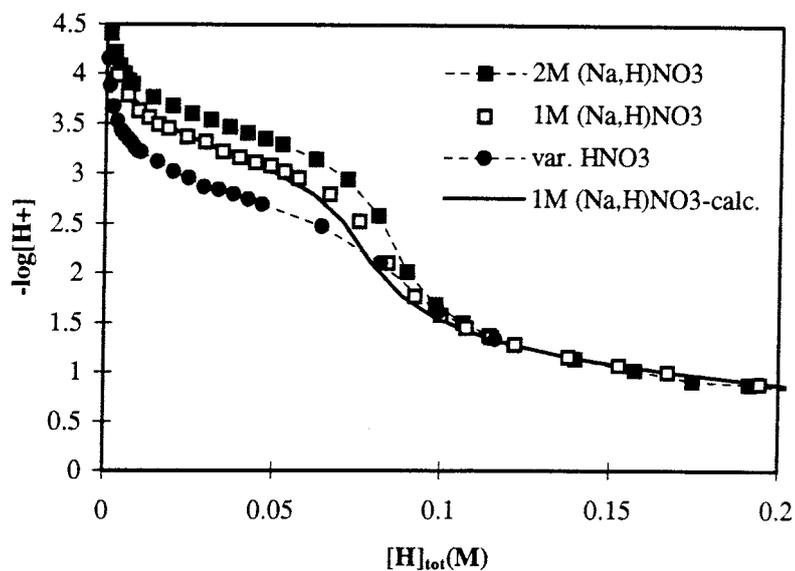
Figure 5. Two-phase titrations with 0.1M terpyridine in *tert*-butylbenzene at different ionic strength and calculated values at 1M (Na,H)NO₃.

When terpyridine in *tert*-butylbenzene is in contact with an aqueous phase of different ionic strength, the pH in the aqueous phase is higher at higher ionic strength at the same addition of nitric acid to the system, see Fig. 5. If terpyridine is supposed to be mono- or diprotonated and the protonated species are assumed to be present only in the aqueous phase, then modelling of the experimental data at 1 M $(K,H)NO_3$ fit the proposed mechanism, Fig. 5. To be able to fit the experimental data at 2 M $(K,H)NO_3$ some other effect has to be considered. The interaction between terpyridine and the potassium cation was included in the model at 2 M $(K,H)NO_3$ but this did not effect the result.

Extraction studies have been carried out on a number of oligopyridines in synergy with 2 -bromodecanoic acid in *tert*-butylbenzene, Table 1. With all these ligands, insolubility, third phase formation and protonation limit the concentration range for ligand, 2-bromodecanoic acid and nitric acid in the extraction experiments. The solubility of the oligopyridines is increased with increase in concentration of 2-bromodecanoic acid, probably caused by adduct formation.
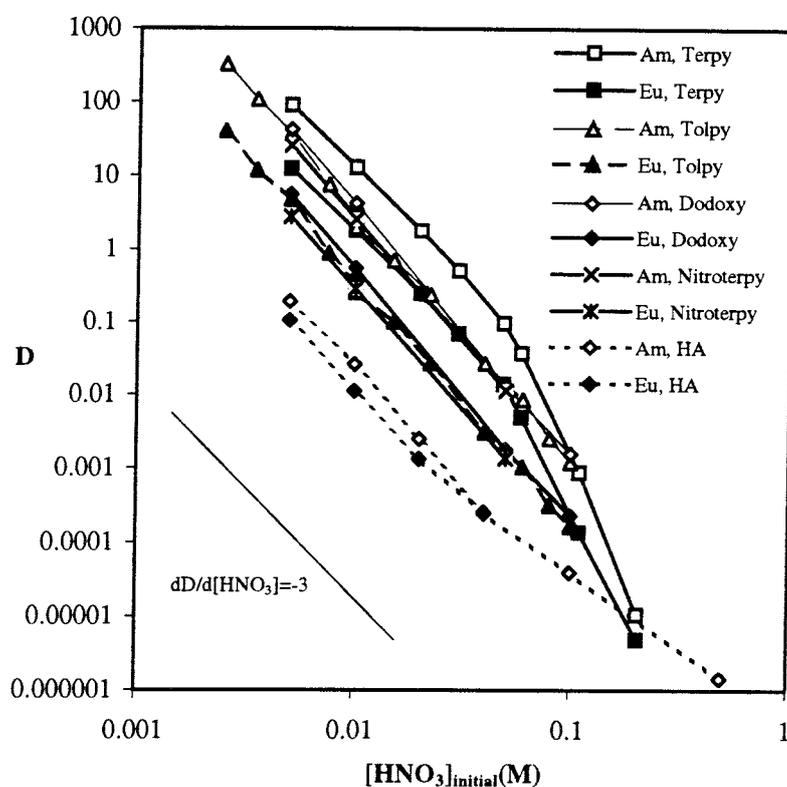
Figure 6. Extraction of americium and europium with 0.02M oligopyridine and 1M 2-bromodecanoic acid (HA) in *tert*-butylbenzene.

The substituted terpyridines in table 1, i.e. tolpy, dodoxy and nitroterpy, show similar nitric acid dependency, distribution ratios and separation factors for americium and europium, Fig. 6. The distribution ratios for the substituted terpyridines are lower than for terpy. In all cases the gradient is -3 in the log-log plot of distribution ratio versus nitric acid concentration, indicating a release of three H^+-ions in the extraction.

Table 1. Overview of the oligopyridines investigated and comparison of the extraction and separation of americium and europium at 0.02M oligopyridine 1M 2-bromodecanoic acid in *tert*-butylbenzene from 0.01M nitric acid.

Name	Structure	D_{Am}	Separation factor Am/Eu
2,2':6',2''-terpyridine (Terpy) Aldrich		13	7
4'-tolyl-2,2':6'2''-terpyridine (Tolpy) Reading University		3	8
4'-(4-nitrophenyl)-2,2':6'2''-terpyridine (Nitroterpy) Reading University	NO_2	4	8
4'-(4-dodecyloxyphenyl)-2,2':6'2''-terpyridine (Dodoxy) Reading University	$C_{12}H_{25}$ O	3	9
(4',4''')-Ditolyl-2,2':6'2'':6''2'''-quaterpyridine (Quater) Reading University		390	19
(4',4''')-Di-(4-heptyloxyphenyl)-2,2':6'2'':6''2''':6'''2''''-quinquepyridine (Quinque) Reading University	C_7H_{15} O C_7H_{15} O	12	22

Quaterpyridine and quinquepyridine both show larger selectivity for americium over europium than the terpyridines at low nitric acid concentration, Fig. 7. However, when the nitric acid concentration is increased the separation factor decreases to a value below the separation factor for the terpyridines. This extraction behaviour needs to be studied further.
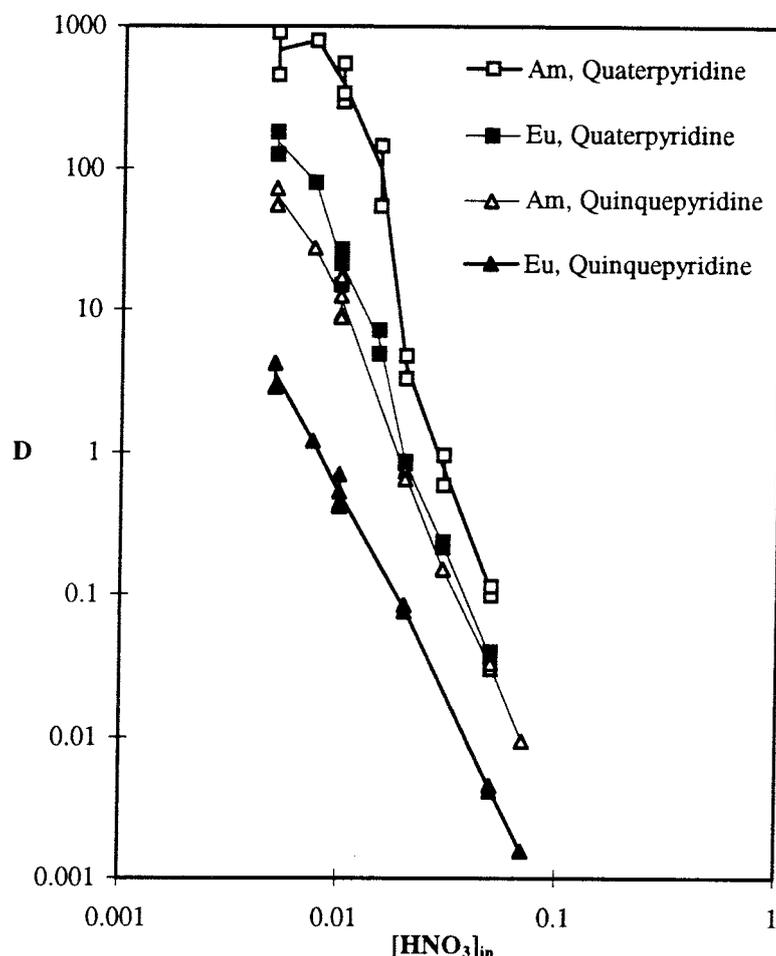
Figure 7. Extraction of americium and europium with 0.02M quater-/quinquepyridine and 1M 2-bromodecanoic acid in *tert*-butylbenzene from nitric acid.

The 2-bromodecanoic acid (HA) dependence has been studied, Fig 8, and slope analysis might indicate that there are three HA in the extracted complex for 2-bromodecanoic acid concentrations under 1M and two HA for concentrations above 1M. Due to solubility difficulties the concentration range is limited to the extent shown in Fig. 8.

10000

—△— Am, Nitroterpy

—▲— Eu, Nitroterpy

—□— Am, Quater

—■— Eu, Quater

—◇— Am, Quinque

—◆— Eu, Quinque

1000

100

D

10

dD/d[HA]=2

1

0.1

0.01   0.1   1   10

[HA] (M)

100

--◇-- Am, Dodoxy

--◆-- Eu, Dodoxy

—△— Am, Tolpy

—▲— Eu, Tolpy

10

1

D 0.1

0.01

0.001

dD/d[HA]=3

0.0001

0.01   0.1   1   10

[HA] (M)
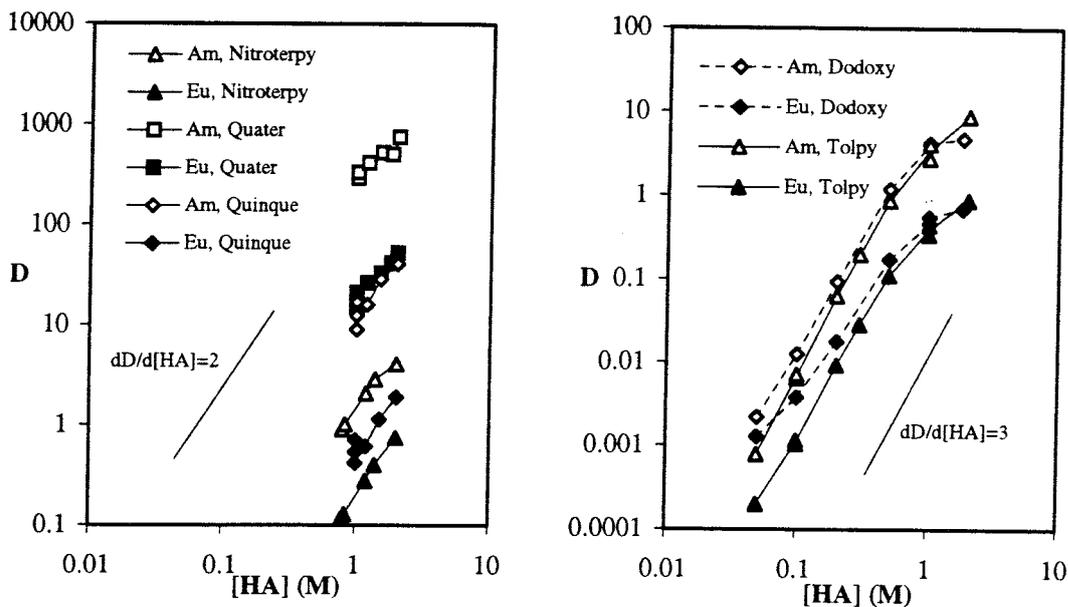
Figure 8. Extraction of americium and europium with 0.02M oligopyridine and different concentrations of 2-bromodecanoic acid in *tert*-butylbenzene from 0.01M HNO$_3$.

1000

—◇— Am, Quater

—◆— Eu, Quater

--□-- Am, Quinque

--■-- Eu, Quinque

—△— Am, Dodoxy

—▲— Eu, Dodoxy

—✕— Am, Tolpy

—✱— Eu, Tolpy

—•— Am, Nitroterpy

—•— Eu, Nitroterpy

100

D

10

1

0.1

0.01

0.001   0.01   **[Ligand](M)**   0.1   1
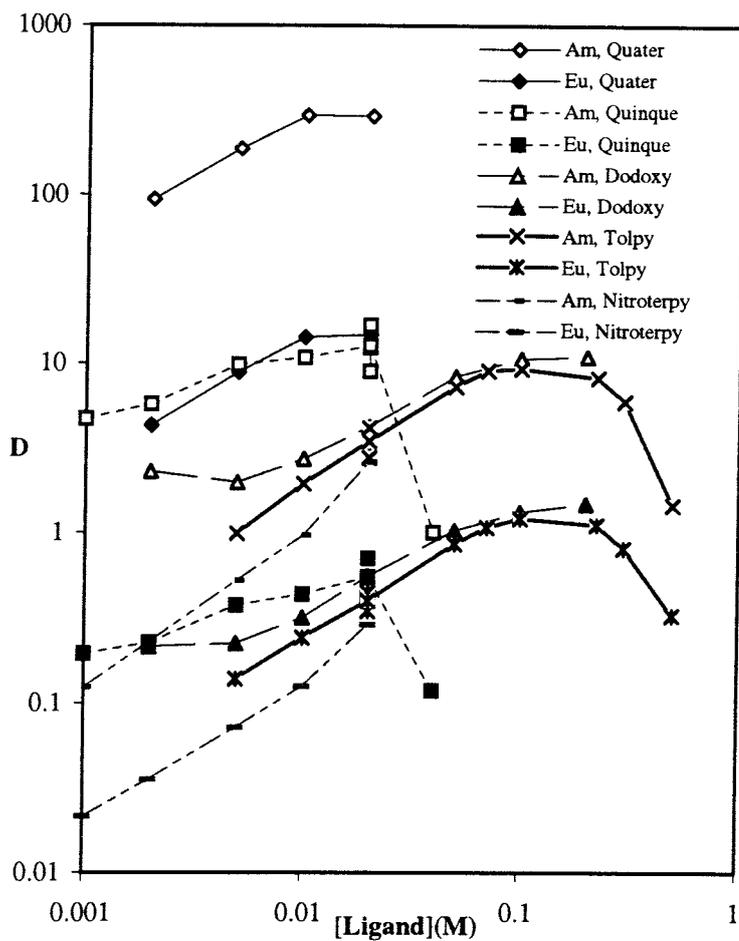
Figure 9. Extraction of americium and europium with different concentrations of oligopyridines and 1M 2-bromodecanoic acid in *tert*-butylbenzene from 0.01M nitric acid.

The distribution ratio increases with increased ligand concentration with a gradient, in a log-log plot, below 1 for all the oligopyridines, Fig. 9. At higher ligand concentrations the gradient diminishes and for tolpy and quinque even a decrease in extraction was observed.

Malonamides

Two different extraction mechanisms with the malonamides has earlier been proposed [2]. An ionpair extraction mechanism at high nitric acid concentration and a co-ordination mechanism at lower nitric acid concentrations. An ionpair mechanism is based on the fact that the malonamide is cationic and thus can extract anionic metal-nitrate species. Extraction of nitric acid show that a lot of nitric acid is present in the organic phase and the malonamide could therefore be protonated. There is also crystallographic evidence for a protonated malonamide [2].

Table 2. Malonamides used in this work.

Name	Structure
N,N′-dimethyl-N,N′-dicyclohexyltetradecyl malonamide (DMDCHTDMA) Reading University	
N,N′-dimethyl-N,N′-diphenyltetradecyl malonamide (DMDPHTDMA) Reading University	
N,N′-dimethyl-N,N′-dibutyloctadecyl malonamide (DMDBODMA). Synthelec AB	
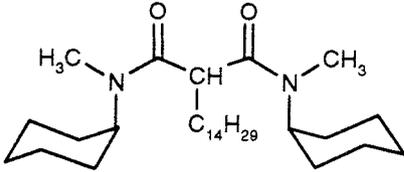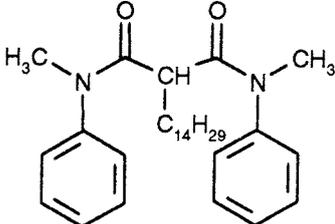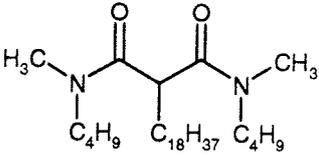
The metal extraction showed a steady increase when $LiNO_3$ or $NaNO_3$ concentrations were increased even though almost no protons were available. Li^+ or Na^+ are not extracted significantly in these systems, Table 3-4, and thus very little cationic malonamide ($L \cdot H^+$, $L \cdot Na^+$ or $L \cdot Li^+$) is present in the organic phase. As a comparison, when HNO_3 is extracted from 10 M nitric acid solution by 0.1M DMDPHTDMA in tbb, 210 mM HNO_3 is found in the organic phase (D_{HNO3}=0.021) but only 1.8 mM lithium is extracted to the organic phase from 10M $LiNO_3$ (D_{Li}=1.8·10⁻⁴) for the same extractant concentration. Even though less cationic malonamide is present in the

organic phase when extracted from $LiNO_3$ media, the distribution ratio for europium is surprisingly high ($D_{Eu}=13$ at 10 M $LiNO_3$ and $D_{Eu}=0.8$ at 10 M HNO_3). The reason for this high metal extraction is still under investigation, maybe another extraction mechanism or salting out.

Table 3. Distribution ratios for lithium by two different malonamides (lithium measured by AES).

Malonamide	[LiNO$_3$] (M)	D
0.1M DMDPHTDMA	10	$1.8 \cdot 10^{-4}$
0.3M DMDCHTDMA	10	$3.1 \cdot 10^{-4}$

Table 4. Distribution ratios for sodium by two different malonamides (^{22}Na measured with HPGe).

Malonamide	[NaNO$_3$] (M)	D	$D_{error}(\%)$
0.1M DMDPHTDMA	5	$1.3 \cdot 10^{-5}$	1.2
0.1M DMDPHTDMA	7.5	$1.4 \cdot 10^{-5}$	1.5
0.1M DMDCHTDMA	5	$3.9 \cdot 10^{-7}$	10.2
0.1M DMDCHTDMA	7.50	$5.4 \cdot 10^{-7}$	5.3

Extraction of technetium (TcO_4^-) shows the typical behaviour of an ionpair mechanism. The decrease in metal extraction at increased HNO_3 concentration might be due to competition between TcO_4^- and NO_3^- for the protonated malonamide. Extraction data for an ionpair extractant (Aliquat-336) is added in Fig. 10 for comparison.
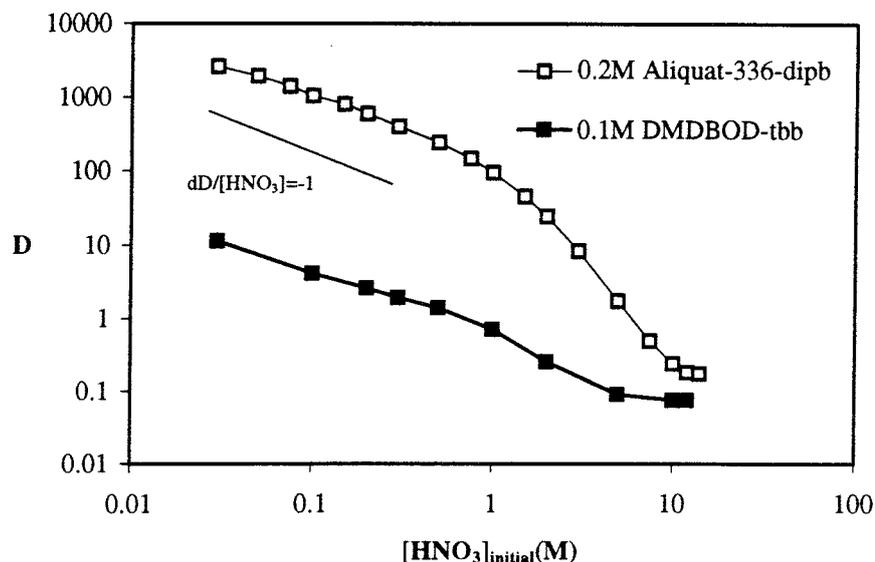
Figure 10. Extraction of pertechnetate (TcO_4^-) from different nitric acid concentrations with 0.1M DMDBODMA in *tert*-butylbenzene and 0.2M Aliquat-336 in 1,3-diisopropylbenzene.

Radiolysis of the malonamide DMDPHTDMA has been investigated during the last semester. The extractant was exposed to radiation doses up to 50 kGy. The D-values for americium and europium did not change significantly, but problems with evaporation of the diluent caused the concentration of malonamide to increase and thus a decrease in D-value due to degradation might have been compensated by the increase in extractant concentration. The degradation products are now being analysed by GC-MS.

The extraction of water by DMDCHTDMA and DMDPHTDMA has been investigated by the Karl-Fischer method. When the nitric acid concentration is increased, more water is extracted to the organic phase, Fig. 11-12.
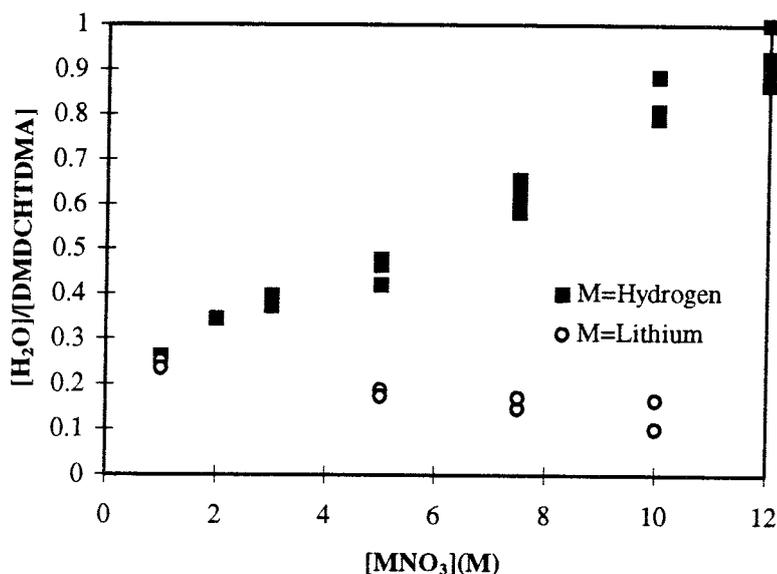
Figure 11. Average number of water molecules per malonamide molecule in the organic phase after extraction from different nitric acid concentrations with 0.3 M DMDCHTDMA in *tert*-butylbenzene.
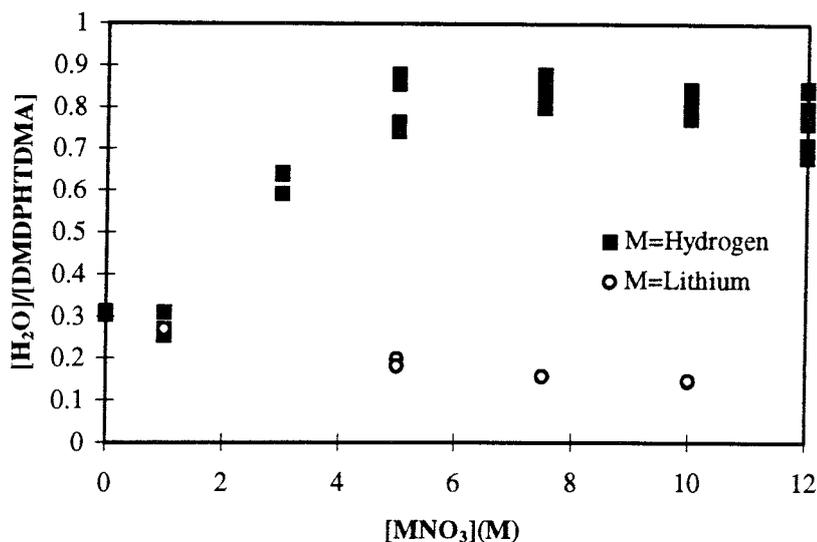
Figure 12. Average number of water molecules per malonamide molecule in the organic phase after extraction from different nitric acid concentrations with 0.3 M DMDPHTDMA in *tert*-butylbenzene.

The water extraction by DMDPHTDMA seems to reach a constant value at about 5 M HNO₃ but for DMDCHTDMA the extraction increases slowly at all nitric acid concentrations studied. At 10 M HNO₃ there are in average 0.8-0.9 water molecule per malonamide in the organic phase and this is almost independent of extractant concentration, Fig. 13.
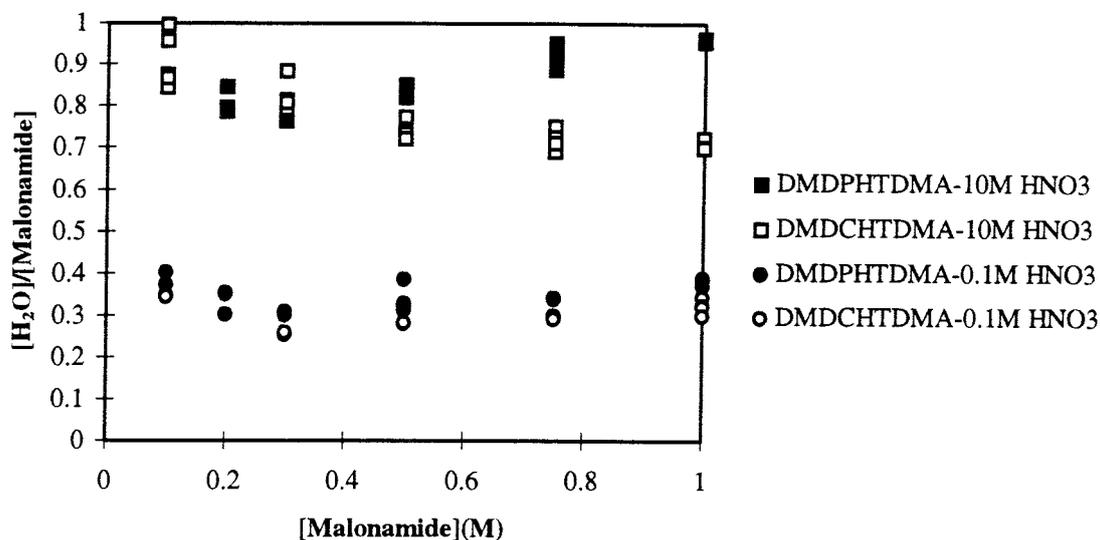
Figure 13. Average number of water molecules per malonamide molecule in the organic phase after extraction from 10 M HNO₃ with different malonamide concentrations in *tert*-butylbenzene.

Future Work

- Basicity evaluations of the oligopyridines, by titration in acetic anhydride, are being conducted.

- To find the extracted complexes for the oligopyridines, extraction experiments continue and the decrease in separation factor for quaterpyridine and quinquepyridine at higher acidity will be investigated further.

- Since the solubility and third phase formation are influenced by the adduct formation between oligopyridine and 2-bromodecanoic acid in the organic phase, spectrophotometric studies will be performed to evaluate the adduct formation.

- Studies of nitric acid extraction by malonamides at higher metal concentration have been initiated.

- Process calculations for the separation of trivalent actinides and lanthanides with the synergistic mixture of terpyridine and 2-bromodecanoic acid in *tert*-butylbenzene will be performed.

References

[1]   Contract NEWPART (FI41-CT-96-0010), Second Semestrial Report, 1ˢᵗ November 1996-30ᵗʰ April 1997

[2]   Chan, G.Y.S., Drew, M.G.B., Hudson, M.J., Iveson, P.B., Liljenzin, J.O., Skålberg, M., Spjuth, L. and Madic, C., *J. Chem. Soc., Dalton Trans., 1997,* *649-660.*

Appendix IV

The influence of degradation by
radiolysis of two nitrogen containing
extractants

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1997

EXAMENSARBETE 20P

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Sammanfattning

Effekten av bestrålning av två kväve innehållande extraktionsreagens Aliquat-336 och N,N'-dimethyl-N,N'-diphenyl-tetradecylmalonamide, DMDPHTDMA, har studerats. Bestrålningens påverkan på extraktionsegenskaperna för Am och Eu i salpetersyra har mätts och analys av vilka nedbrytningsprodukter som har bildats har utförts med GC-MS.

Metallextraktionen för Am och Eu minskade något för i/ bestrålad Aliquat-336 och ii/ obestrålad Aliquat-336 i kontakt med salpetersyra. Men för iii/ bestrålad Aliquat-336 i kontakt med salpetersyrara har metallextraktionen ökat något.

Metall extraktionen har inte ändrats för i/ bestrålad DMDPHTDMA och ii/ obestrålad DMDPHTDMA i kontakt med salpetersyra i ett mindre ventilerat system, men för iii/ obestrålad DMDPHTDMA i kontakt med salpetersyra i ett välventilerat system och iv/ bestrålat DMDPHTDMA i kontakt med salpetersyra ökade metallextraktionen men det beror troligen på att lösningdmedlet avdunstat och konsentrationen av DMDPHTDMA har ökat. Det var problem med att lösningsdmedlet avdunstade både för Aliquat-336 och DMDPHTDMA.

Summary

The effect of irradiation of two nitrogen containing extractants, Aliquat-336 and N,N'-dimethyl-N,N'-diphenyl-tetradecylmalonamide, DMDPHTDMA, has been studied. The extraction behavior for Am and Eu from nitric acid solution have been measured and analysis of degradation products by GC-MS has been performed.

The metal extraction of Am and Eu have slightly decreased for i/ irradiated Aliquat-336 and ii/ unirradiated Aliquat-336 in contact with nitric acid. However with iii/ irradiated Aliquat-336 in contact with nitric acid the metal extraction is increased.

The metal extraction for Am and Eu did not change for i/ irradiated DMDPHTDMA and ii/ unirradiated DMDPHTDMA in contact with nitric acid in a less closed system, but for iii/ irradiated DMDPHTDMA in contact with nitric acid and iv/ unirradiated DMDPHTDMA in contact with nitric acid in a well ventilated system the metal extraction increased probably due to that the diluent evaporated and the concentration of DMDPHTDMA subsubsequetly increased.

There were problems with evaporation of diluent for both the Aliquat-336 and the DMDPHTDMA system.

Table of contents

Introduction

The nuclear power industry is today faced with the problem of managing the nuclear waste. The high level waste includes both short-lived and long-lived radionuclides and can be divided into fission products, actinides and activation products. Radionuclides with a half-life shorter than thirty years are generally called short-lived and radionuclides with longer half-life are called long-lived. After three centuries, the radionuclides that are left in the stored high level waste, will be long-lived radionuclides. The potential hazard of long-lived radionuclides is chiefly due to the actinides [1].

Today, two alternatives are available to treat the nuclear waste: spent fuel disposal without any recovery of fissile material, or spent fuel reprocessing to recover uranium and plutonium in the PUREX process, followed by vitrification of the remaining high activity waste [2]. In recent years, a new idea has reemerge that consist of advanced reprocessing and transmutation. In this case all actinides are separated, not only U and Pu but also Am, Cm and Np, and then burned in special reactors or accelerator driven systems [3].

An optimised management of waste needs the separation of the α-emitters such as Pu, Am, Np and Cm and some fission products such as Tc from the bulk fission and corrosion products. Solvent extraction is a good separation method for this purpose provided that the process does not create a large quantity of secondary wastes. Many organophosphorus extractants have been studied, but degradation products due to hydrolysis (when an organic phase is in contact with an acid) and radiolysis (when an organic phase is irradiated, usually in contact with an acid) lead to the formation of precipitates or retention of actinides in the solvent. Moreover, the cleanup of the solvent for recycling often uses inorganic salt solutions, creating secondary wastes, and incineration of the degraded molecules produces P_2O_5. A new concept for extractants is to make them totally incinerable, which minimises production of

1

secondary wastes [3]. These new extractants ought to fulfil the CHON- principle, i.e. contain only C-, H-, O- and N- atoms, which makes them totally incinerable.

The organic extractant is heavily irradiated during the advanced reprocessing process. The estimated dose is 5 kGy/cycle [4]. It is therefore important to know the radiation stability of the reagent and to know what kind of degradation products that are formed. The extraction ability of these degradation products is also important to know.

This project has investigated how hydrolysis and radiolysis change the metal extraction properties of ^{241}Am and ^{152}Eu, by two nitrogen containing extractants, see figure 1-2.

$$R1 = C_{14}H_{29}$$
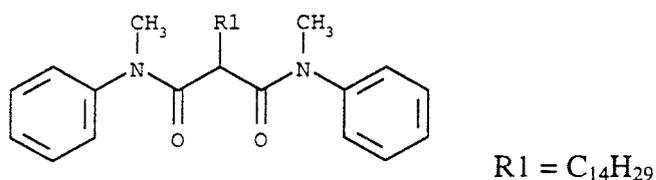
Figure 1. N,N'-dimethyl-N,N'-diphenyl-tetradecylmalonamide DMDPHTDMA
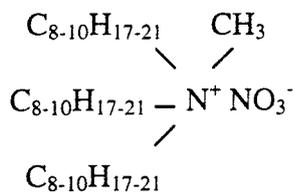
Figure 2. Aliquat-336, a quaternary ammoniumsalt

2

Theory

Distribution ratio

The extraction of a certain element from an aqueous phase to an organic phase is described by the distribution ratio, D_M.

$$D_M = \frac{\text{Total concentration of M in organic phase}}{\text{Total concentration of M in aqueous phase}} = \frac{[M]_{tot,org}}{[M]_{tot,aq}}$$

where M is the total concentration of a species M.

Errors in distribution ratio

The error in distribution ratio $\sigma D_{tot,M}$ consist mainly of a statistical error during measurement and a pipetting error.

Statistical error

D_M distribution ratio

N   measured pulses in the peak

dN   statistical variation of N

$$\sigma D_{statistical} = \sqrt{dN^2_{org}/N^2_{org} + dN^2_{aq}/N^2_{aq}} \, *D$$

Pipetting error

The pipetting error were measured by pipetting 0.9 ml of Aliquat-336 and DMDPHTDMA and 0.1 ml nitric acid to see how the volume variate. The pipetting error was 2.7% for nitric acid, 1.5 % for Aliquat-336 and 2.5% for DMDPHTDMA.

D   distribution ratio

N   measured pulses in the peak

t   measuring time

V   volume

$$D = N_{org}*t_{Aq}*V_{Aq}/ N_{Aq}/t_{org}/V_{org}$$

$$\sigma D_{pipette,Aliquat-336} = D*4.2\%$$

$$\sigma D_{pipette, DMDPHTDMA} = D*5.3\%$$

Experimental

Chemicals

The chemicals used in theses experiments are: N,N'-dimethyl-N,N'-diphenyl-tetradecylmalonamide, DMDPHTDMA, which is not commercially available and was thus synthesised by the University of Reading. The purity is over 99%. Aliquat-336 is bought from Fluka and has a purity over 90 %. Tert-butylbenzene, TBB, 99% and 1,-3-diisopropylbenzene, DIPB, 96% were bought from ACROS. 1-dodecanol was bought from Merck and has a purity between 90 to 95 %. Stock solutions of ^{241}Am and ^{152}Eu at 0.5 M HNO$_3$, were provided by the department, their purity were controlled by γ-spectrometry.

Methods and analysis

Experiments

The following sequence of experimental conditions were studied by examine the extraction of Am and Eu and what degradation products are formed.

• Irradiation of 0.1 M DMDPHTDMA in TBB.

• Irradiation of 0.1 M DMDPHTDMA in DIPB.

• Irradiation of 0.1 M Aliquat-336 in DIPB and with 5 vol% 1-dodecanol as a third phase inhibitor.

• Irradiation of 0.1 M DMDPHTDMA in DIPB as organic phase in contact with an aqueous phase of 3M HNO$_3$

• Irradiation of 0.1 M Aliquat-336 in DIPB and with 5 vol% 1-dodecanol as organic phase in contact with an aqueous phase of 3M HNO$_3$

- Hydrolysis A of 0.1 M DMDPHTDMA in DIPB as organic phase in contact with an aqueous phase of 3M HNO_3

- Hydrolysis B of 0.1 M DMDPHTDMA in DIPB as organic phase, in contact with an aqueous phase of 3M HNO_3. Hydrolysis B had less contact with air than hydrolysis A

- Hydrolysis of 0.1 M Aliquat-336 in DIPB and with 5 vol% 1-dodecanol as organic phase in contact with an aqueous phase of 3M HNO_3.

The samples were irradiated in a ^{60}Co source with a dose rate of 50 Gy/h. The ^{60}Co-source was ventilated during irradiation and a small motor-driven stirrer was installed to improve the phase contact, when the samples contained more than one phase. The hydrolysed samples were stirred by a magnetic stirrer outside the ^{60}Co-source. All experiments were performed at room temperature.

Distribution ratio

Distribution ratios were determined by contacting 1 ml organic phase, with 1 ml aqueous phase. The aqueous phase consisted of 0.98 ml 0.5 **M**, 3 **M** or 7.5 **M** HNO_3 and 10 µl of each stock solution containing ^{241}Am and ^{152}Eu respectivily. The aqueous solutions rest at least 1 hour to equilibrate. When irradiation or hydrolysis were performed in contact with nitric acid, the same acid was used in the extraction experiments. After addition of the organic phase, the test tubes were shaken for 2 minutes and then centrifuged for 10 min at 5000 rpm. 0.9 ml of the organic phase was diluted to 2 ml with DIPB and 0.1 ml of the aqueous phase was diluted to 2 ml with nitric acid before the samples were analysed with a HPGe detector. The phases were diluted to ensure that the samples had the same geometry in the detector.

Spectrophotometry

Spectrophotometry was used to study the colour change of the organic phase. The samples were scanned from 200 nm to 999 nm with a Perkin Elmer spectrophotometer 551 with a deuterium lamp.

GC-MS

To analyse what kind of degradation products that had been formed, Gas Cromatoghraphy-Mass Spectronetry, GC-MS, was used. The column was a GS2 and the carrier fluid was OV1. The temperature program started at 70°C and increased with 10°C /minute until 300°C, where the temperature was kept constant 10 minutes for the samples containing Aliquat-336 and 20 minutes for the ones with DMDPHTDMA.

Results

Aliquat-336

Distribution ratio

The D-values for Am and Eu decreased after irradiation and hydrolysis, figure 3-5 and 9. When Aliquat-336, in contact with nitric acid, was irradiated the D-values for Am and Eu first increased and thereafter slightly decreased, figure 8.
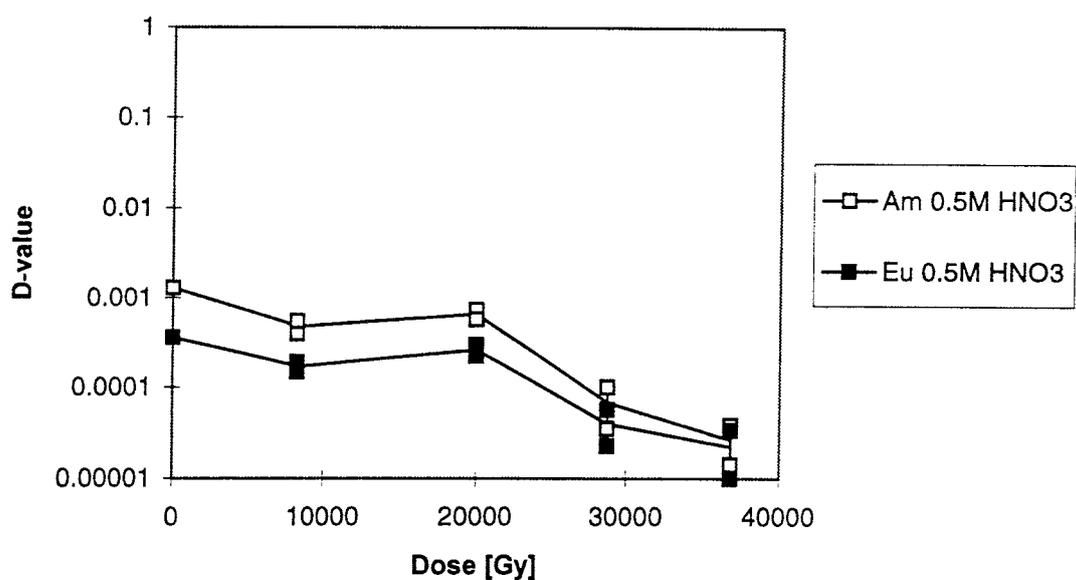
Figure 3. Am and Eu extracted from 0.5 M HNO_3 with irradiated 0.1 M Aliquat-336 in DIPB and 5 vol% dodecanol (Appendix 1, table 1)
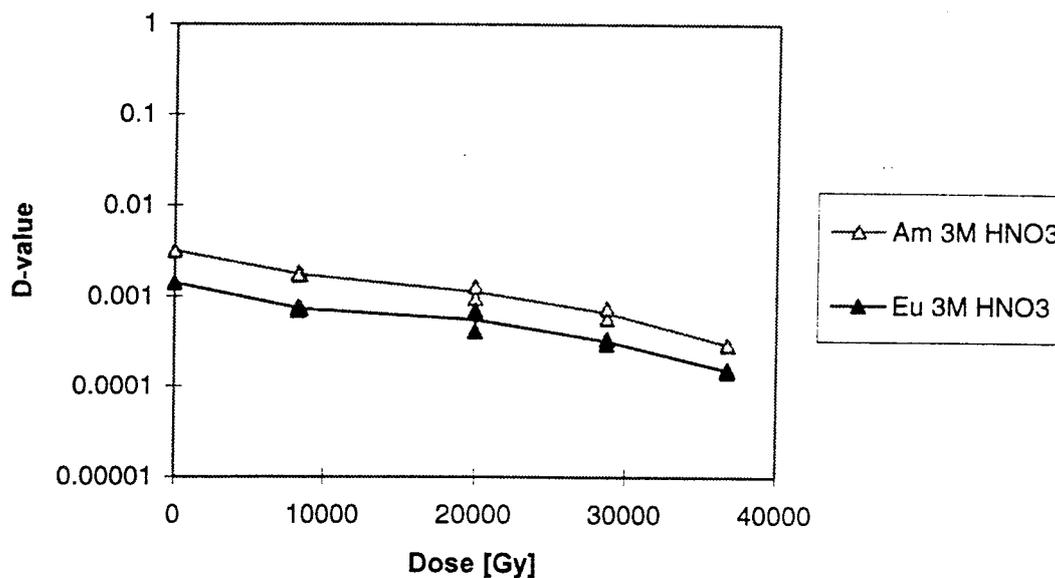
Figure 4. Am and Eu extracted from 3 M HNO_3 with irradiated 0.1 M Aliquat-336 in DIPB and 5 vol% dodecanol (Appendix 1, table 2)
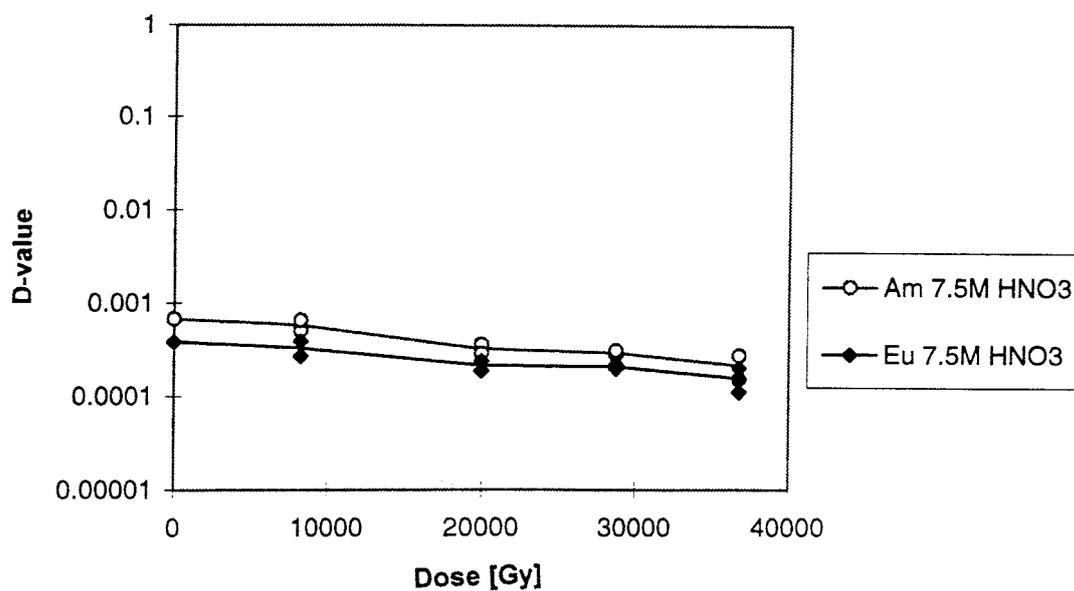
Figure 5. Am and Eu extracted from 7.5 M HNO_3 with irradiated 0.1 M Aliquat-336 in DIPB and 5 vol% dodecanol (Appendix 1, table 3)
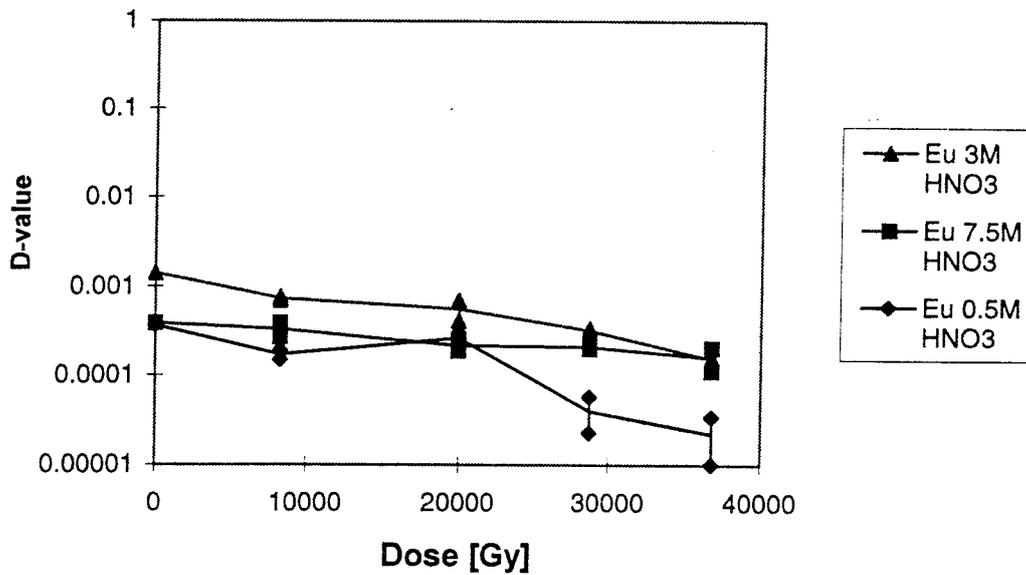
Figure 6. Eu extracted from 0.5M, 3M and 7.5M HNO$_3$ with irradiated 0.1 M Aliquat-336 in DIPB and 5 vol% dodecanol (Appendix 1, table 1-3)
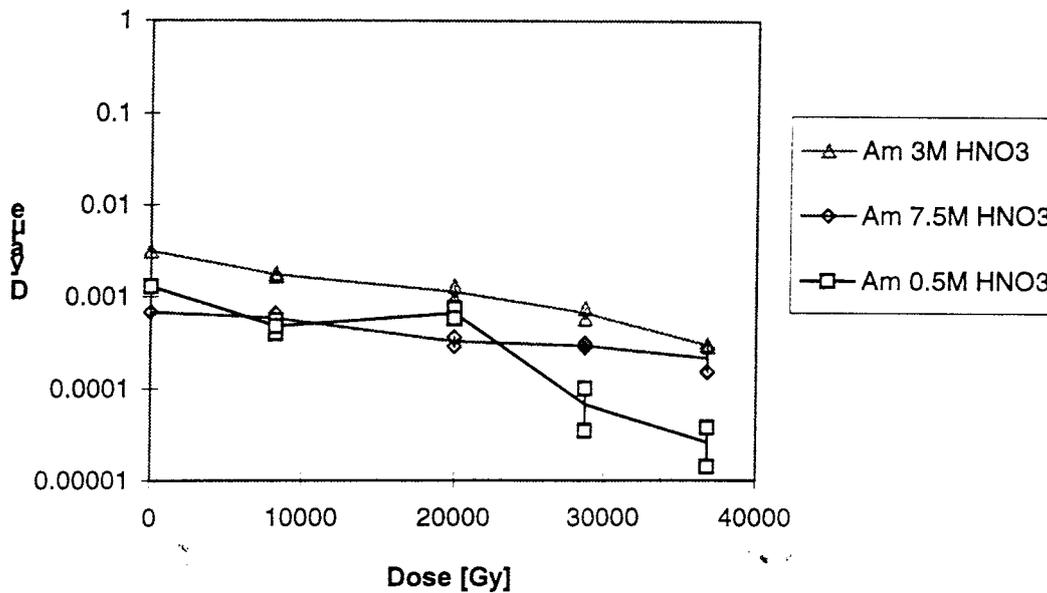
Figure 7. Am extracted from 0.5M, 3M and 7.5M HNO$_3$ with irradiated 0.1 M Aliquat-336 in DIPB and 5 vol% dodecanol (Appendix 1, table 1-3).
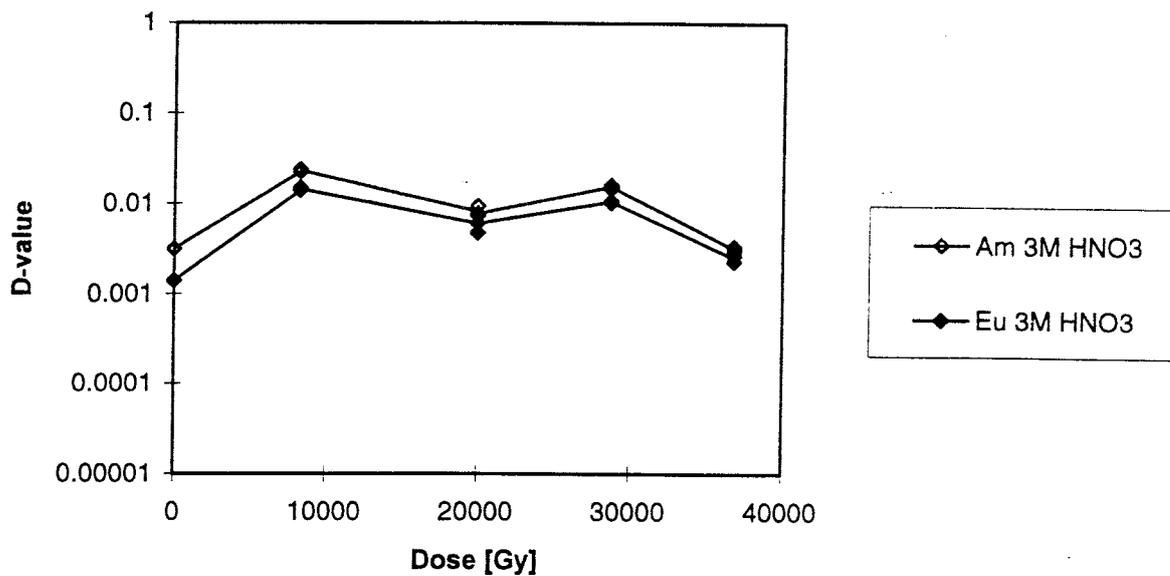
Figure 8. Am and Eu extracted from 3 M HNO₃ with irradiated 0.1 M Aliquat-336 in DIPB and 5 vol% dodecanol. Extractants were in contact with 3 M HNO₃ during irradiation (Appendix 1, table 4).
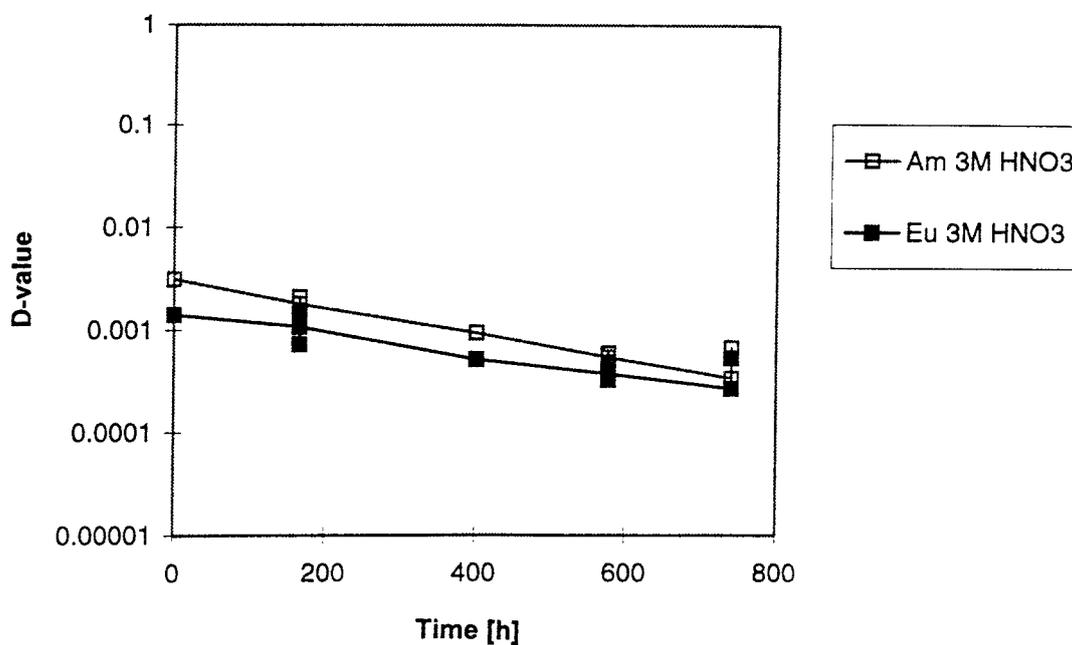
Figure 9. Am and Eu extracted from 3 M HNO₃ with hydrolysed 0.1 M Aliquat-336 in DIPB and 5 vol% dodecanol. Extractants in contact with 3 M HNO₃ during hydrolysis (Appendix 1, table 5).
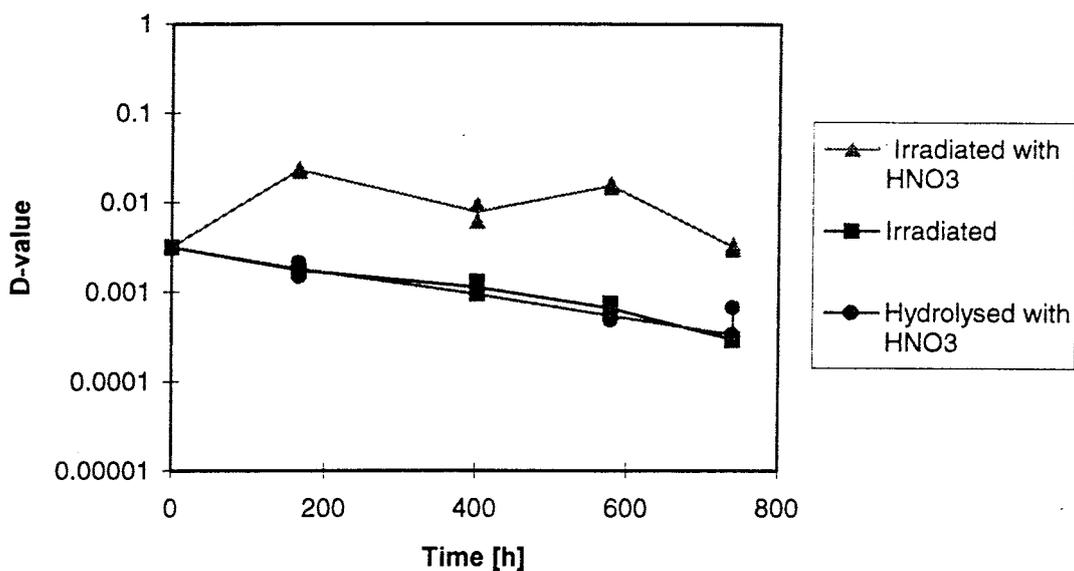
Figure 10. Am extracted from 3M HNO₃ with 0.1 M Aliquat-336 in DIPB and

5 vol% dodecanol, treated in different ways (Appendix 1, table 2, 4 and 5).
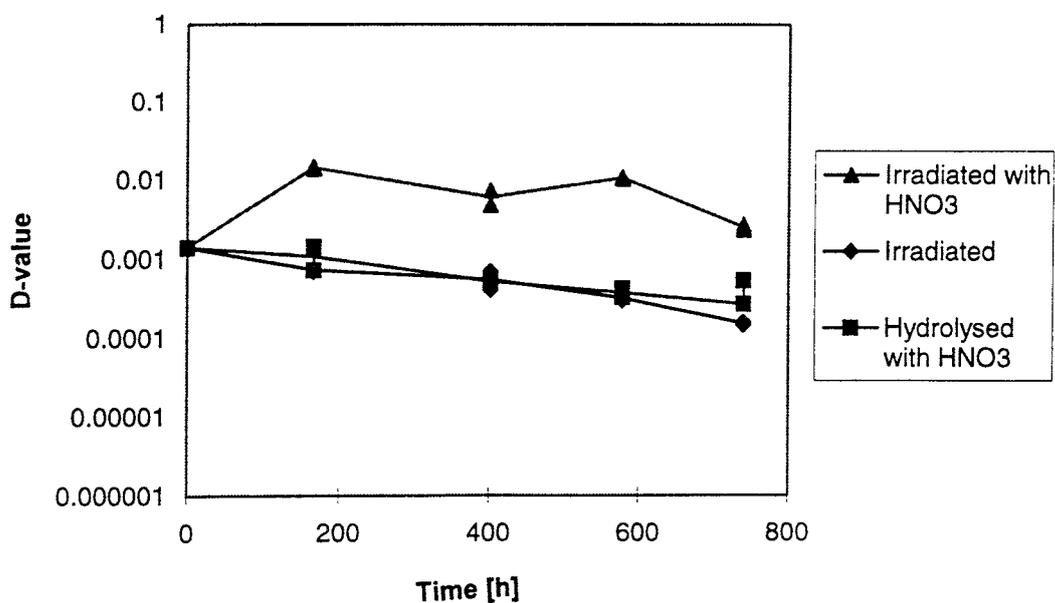
Figure 11. Am extracted from 3M HNO₃ with 0.1 M Aliquat-336 in DIPB and

5 vol% dodecanol, treated in different ways (Appendix 1 table 2, 4 and 5).

Degradation products

Aliquat-336 has the following structure $(C_{8-10}H_{17-21})_3CH_3N^+NO_3^-$. GC-MS analysis showed that the Aliquat-336 molecule either lost one $C_{8-10}H_{17-21}$ -group or the CH_3-group during irradiation. The same thing happened when Aliquat-336 was hydrolysed. When Aliquat-336 was irradiated in contact with nitric acid the molecule either loose one $C_{8-10}H_{17-21}$ -group, the CH_3-group or both one $C_{8-10}H_{17-21}$ -group and the CH_3-group. [Appendix 2]

Stability of Aliquat-336

Irradiated Aliquat-336, 37 kGy, was degraded 21 %, irradiated Aliquat-336, 37 kGy, in contact with nitric acid was degraded 55 % and unirradiated Aliquat-336 in contact with nitric acid was degraded 47 % [Appendix 3].

Spectrophotometry

The samples from different tests had changed colour after irradiation and hydrolysis. The spectroscopic curves follow each other and show that the coloured compound exists in all of them, as a blank sample unirradiated DIPB was used. Only DIPB and its degradation products exist in all samples so it is probably one of the degradation products from DIPB that causes the observed colour change, see figure 12.
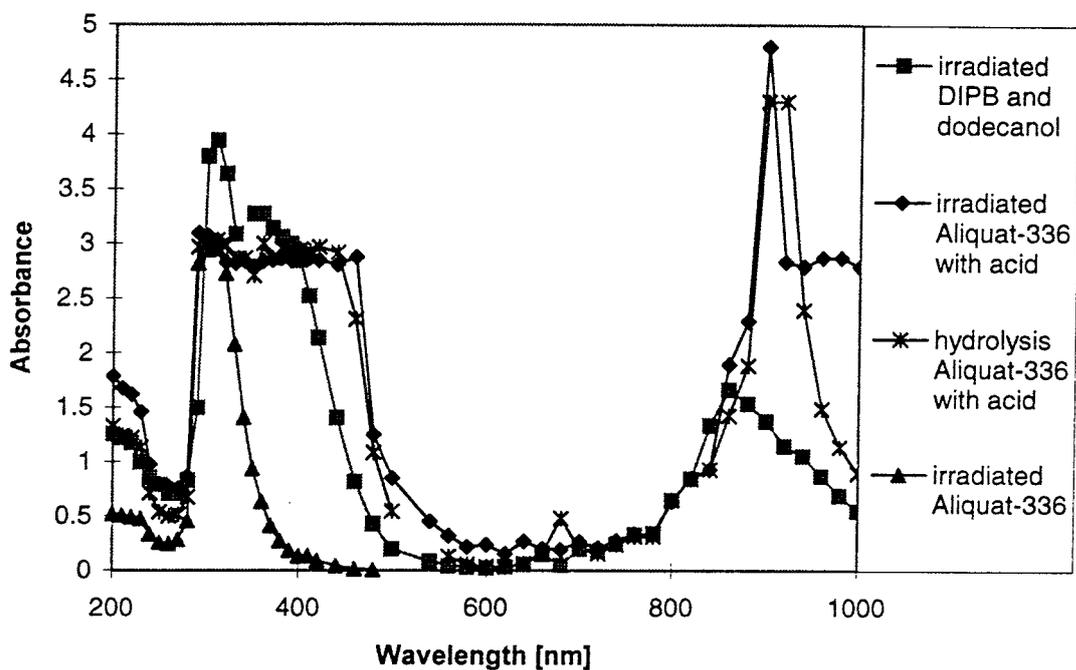
Figure 12 Spectrophotometric scan of colour changes in irradiated or hydrolysed samples.

DMDPHTDMA

Distribution ratio

The D-value did not change during irradiation or hydrolysis B, when less air is available, this might indicate that the degradation is not a severe problem, figure 13-15, but problems with evaporation of the diluent might have compensated for an actual decrease in the D-values. For the irradiated sample in contact with acid or the hydrolysed A samples the D-value increase 10-100 times, which probably is due to evaporation of the diluent, which cause an increace in concentration.
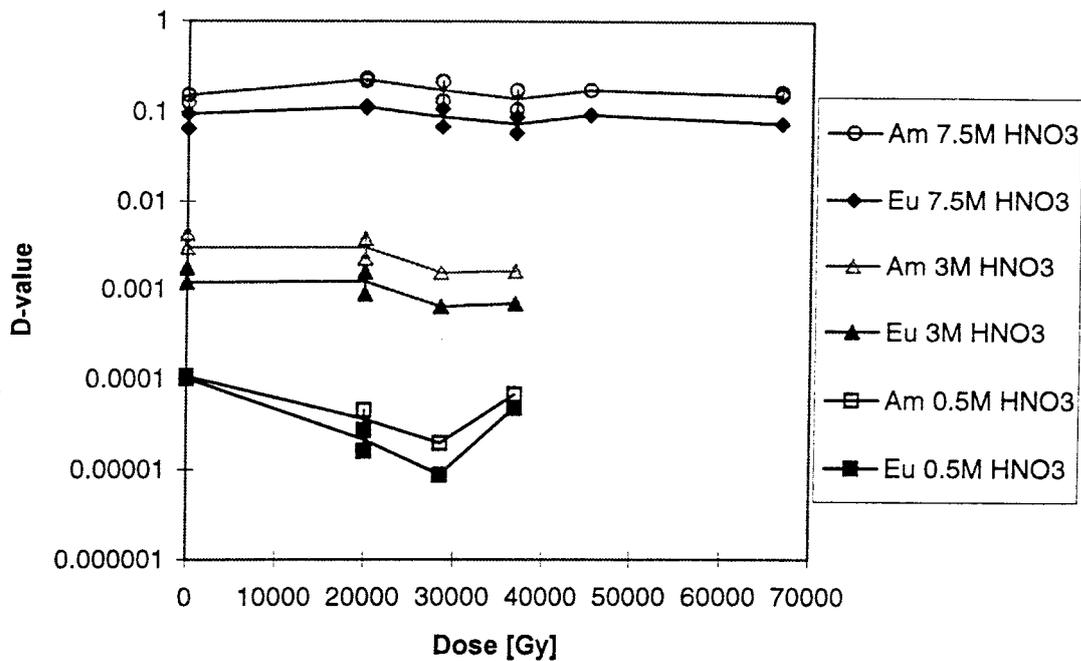
Figure 13. Am and Eu extracted from 0.5 M, 3 M and 7.5 M HNO₃ with irradiated 0.1 M DMDPHTDMA in DIPB. Appendix 1, table 7-9
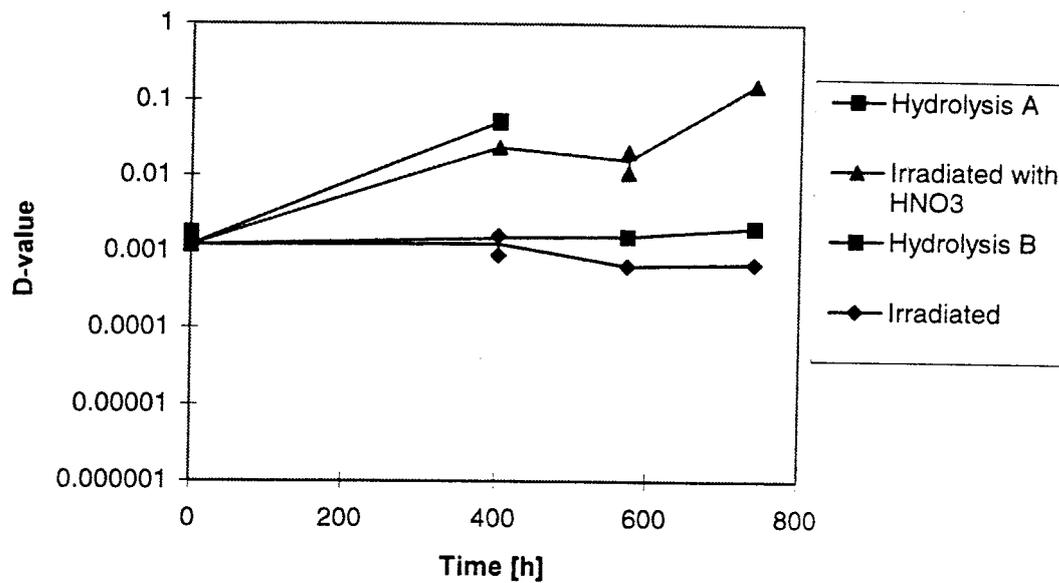
Figure 14. Eu extracted from 3M HNO₃ with irradiated 0.1 M DMDPHTDMA in DIPB, treated in different ways (Appendix 1, table 8, 10, 11 and 12).
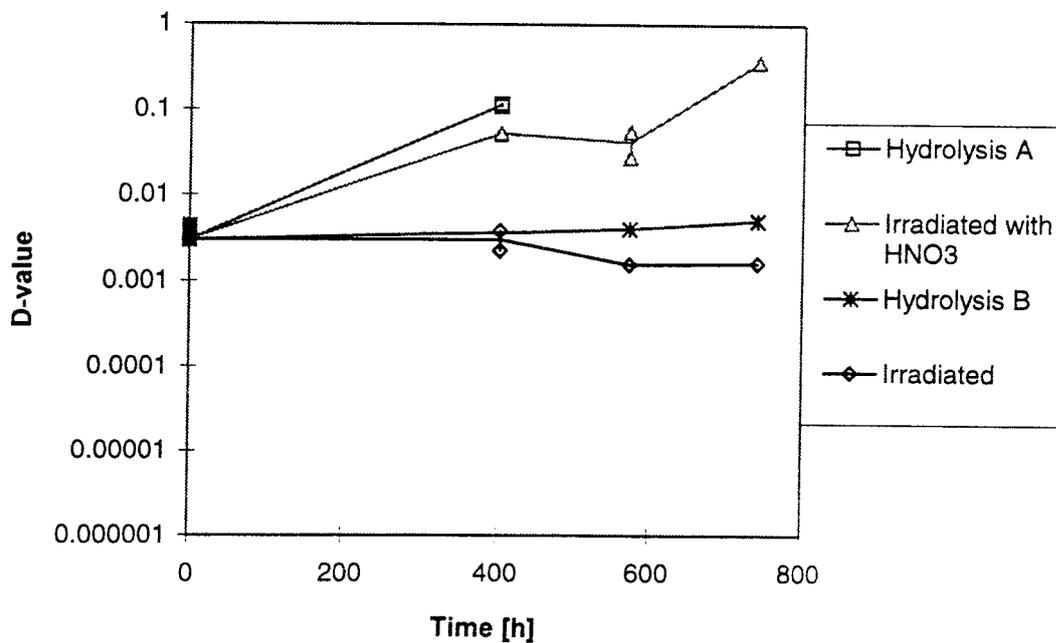
Figure 15. Am extracted from 3M HNO₃ with 0.1 M DMDPHTDMA in DIPB, treated in different ways (Appendix 1, table 8, 10, 11 and 12).

Degradation products

The degradation product shown in figure 17 was observed in all samples with DMDPHTDMA. It has previously been reported that the structure shown in figure 16 is a degradation product to malonamide and the structure shown in figure 16 is the rest of DMDPHTDMA when the structure shown in figure 17 is observed [5]. In this work the structure shown in figure 16 was not analysed due to the low mass which interfere with for example DIPB.
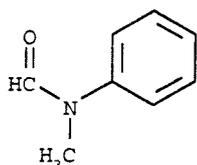
Figure 16.

The irradiated samples and the hydrolysed A sample had a tiny peak at channel 1080, figure 18, which indicate that a double bond has been formed in the carbon chain on the middle carbon. The peak probably exists in the hydrolysed B sample too, but can not be seen since degradation is not that severe in the sample that had less contact with air. It seems as if the carbon chain is vulnerable at the double bond because the carbon chain has been broken in the double bond, see figure 19-20. The structure in figure 19 and 20 are alcohols and they are only observed when DMDPHTDMA has been in contact with nitric acid [Appendix 2].

Irradiated DMDPHTDMA

The observed degradation products are:

Figure 17. [Appendix 2] $R1=C_{14}H_{29}$

17
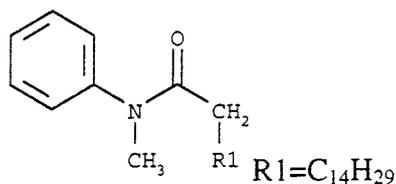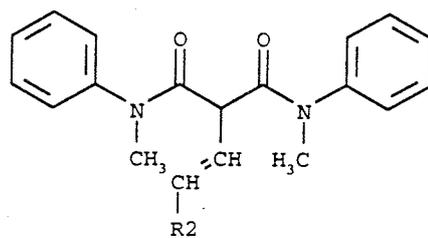
Figure 18. [Appendix 2]   R2 $=C_{12}H_{25}$
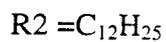
DMDPHTDMA in contact with nitric acid during irradiation

The observed degradation products are:
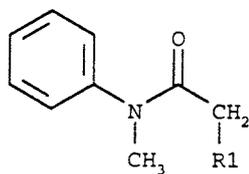
Figure 17. [Appendix 2]   R1=$C_{14}H_{29}$

Figure 18. [Appendix 2]   R2 $=C_{12}H_{25}$

Figure 19. [Appendix 2]

Figure 20. [Appendix 2]

18
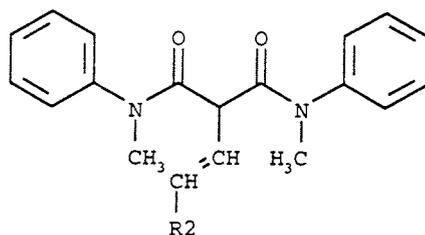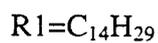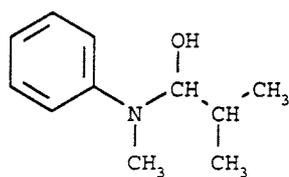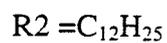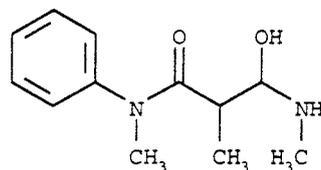
Hydrolysis A by the DMDPHTDMA

The observed degradation products are:

Figure 17. [Appendix 2]

R1=$C_{14}H_{29}$

Figure 18. [Appendix 2]

R2 =$C_{12}H_{25}$

Figure 19. [Appendix 2]

Figure 20. [Appendix 2]

19
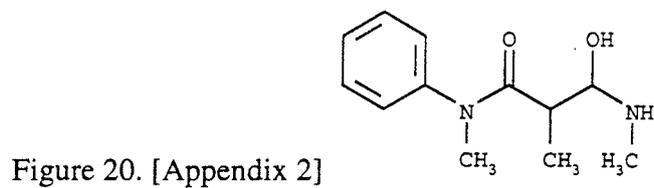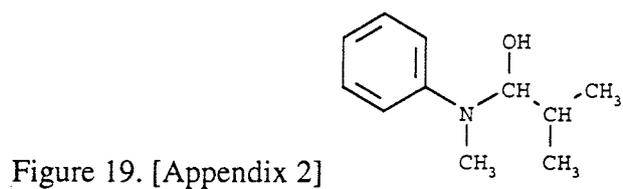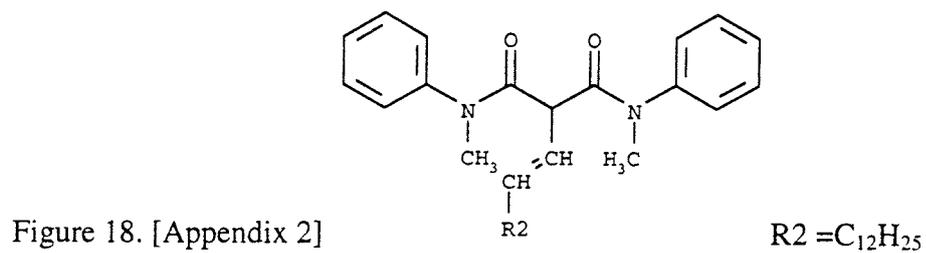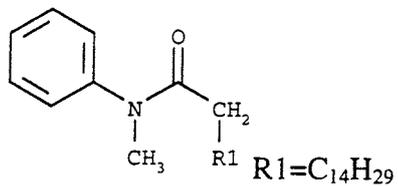
Hydrolysis B by the DMDPHTDMA

The observed degradation products are:

Figure 17. [Appendix 2]

$R1=C_{14}H_{29}$
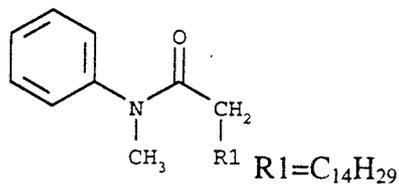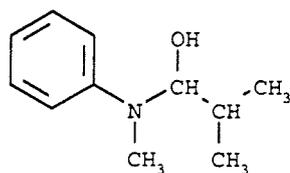
Figure 19. [Appendix 2]

Stability of DMDPHTDMA

Irradiated DMDPHTDMA, 37 kGy, in contact with nitric acid, was degraded with 35 % [Appendix 3]. Irradiated DMDPHTDMA, 67 kGy, and unirradiated DMDPHTDMA in contact with nitric acid were not degraded in detectable amounts, but the uncertainties are large because the samples had to be diluted in order to be analysed by GC-MS since a wide peak otherwise appears. Approximately less than 20 % are degraded [Appendix 3].

Spectrophotometry

The colour of the samples from different tests had changed during irradiation and hydrolysis. The spectrophotometric curves follow each other and show that the coloured compound exists in both samples, as a blank sample unirradiated DIPB was used. Only DIPB and its degradation products exist in both samples so it is probably one of the degradation products of DIPB that cause the colour change. Spectrophotometric measurements were not performed on the hydrolysed samples or the sample that was irradiated in contact with nitric acid, see figure 28.
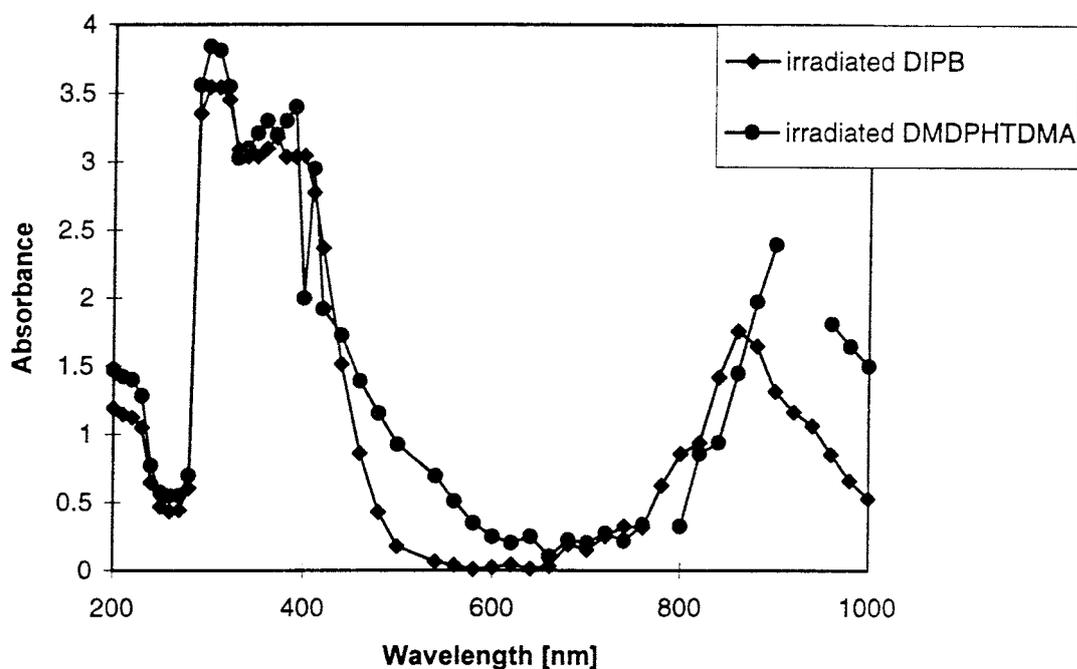
Figure 28 Spectrophotometric scan of colour change with irradiated samples.

Diluent

D-value

The D-value for Aliquat-336 extraction of Am and Eu decreased if DIPB and dodecanol were irradiated compared to the D-values obtaind if fresh Aliquat-336 and fresh DIPB and dodecanol was used (Appendix 1, table 6).

Discussion and conclusions

Diluent

DIPB was evaporated during the experiments which might have changed the concentration of extractant in the experiments. For DMDPHTDMA in TBB all the diluent, 20 ml, was evaporated in two weeks. For the other experiments, one estimation is that 6 % of the diluent evaporated each week. In future radiolysis experiments the concentration has to be checked if the system is ventilated. Distribution ratio of Am and Eu with Aliquat-336 is not only influenced by the degradation products of Aliquat-336 but also from degradation products from DIPB and/or dodecanol. DIPB also causes the colour change of the samples. Further investigation must be performed on the effect of the degradation of the diluent on the metal extraction.

Aliquat-336

An increase in concentration of Aliquat-336 caused by evaporation can not explain the increase in D-value for Am and Eu in the irradiated samples, which have been in contact with nitric acid, because the evaporation was similar for the hydrolysed samples, which show no increase in D-value. Therefore, careful investigation of the degradation products and their extraction ability is necessary. One of the degradation products, from the irradiated samples in contact with nitric acid, was identified as a secondary amine but this would rather suggest a decrease in the extraction ability.

DMDPHTDMA

It seemed as if the distribution ratio for Am and Eu did not change during irradiation, but a small increase of the concentration of DMDPHTDMA is suggested due to evaporation of the diluent. The expected decrease in metal extraction is compensated by an increase in the extractant concentration. For the hydrolysed A sample and the irradiated sample, which has been in contact with nitric acid, the metal extraction increased. It is possible that the increase in distribution ratio is caused by an increase in the extractant concentration.

Analysis methods

To analyse how much of the extractants that had been degraded the samples were first analysed by titration with acetic anhydride but due to evaporation of the diluent it was impossible to determine the concentration change due to irradiation or hydrolysis. Instead GC-MS was used. GC-MS was very useful tool giving information about how much of the extractant that had been degraded, what degradation products that had been formed and how much of each degradation product that had been formed. GC-MS shows a lot of peaks for molecules with a mass under 162 g/mole and it was difficult to determine if a peak was a degradation product from the extractants or a degradation product from DIPB. This was especially a problem for DMDPHTDMA, which have degradation products similar to DIPB.
When the samples changed colour, spectrophotometric spectra indicated that a DIPB degradation product causes the colour change.
The metal extraction was measured radiometrically, using a HPGe detector. Am was used as an analogue for trivalent actinides and Eu as an analogue for the lanthanides.

References

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[2] Cuillerdier, C., Musikas, C., Hoel, P., Nigond, L., Vitart, X., Malonamides as new extractants for nuclear waste solution., Separation science and technology, 26(9), pp 1229-1244, 1991.

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[4] Gasparini, G. M., Grossi, G., Long chain disubstituted aliphatic amides as extracting agents in industrial applications of solvent extraction., Solvent extraction and ion exchange, 4(6), pp 1233-1271, 1986.

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Acknowledgement

Appendix 1. Experimental data

Irradiated Aliquat 336: Extraction from 0.5 M HNO$_3$

Table 1 Am and Eu extracted from 0.5 M HNO$_3$ with irradiated 0.1 M Aliquat 336 in DIPB and 5 vol% dodecanol.

Irradiation time [h]	Dose [Gy]	D_{Am}	$\sigma D_{tot,Am}$	D_{Eu}	$\sigma D_{tot,Eu}$
0	0	1.2E-3	4.2 %	3.6E-4	4.2 %
170	8300	4.0E-4	5.3 %	1.5E-4	5.6 %
170	8300	5.5E-4	5.8 %	1.9E-4	5.2 %
400	20000	7.4E-4	5.3 %	3.0E-4	5.3 %
400	20000	5.8E-4	6.6 %	2.2E-4	5.8 %
580	29000	3.5E.5	9.2 %	2.3E-4	6.3 %
580	29000	1.0E-5	8.1 %	5.7E-5	5.9 %
740	37000	1.4E-5	11 %	1.0E-5	6.7 %
740	37000	3.9E-5	7.6 %	3.4E-5	5.4 %

Irradiated Aliquat-336: Extraction from 3 M HNO_3

Table 2 Am and Eu extracted from 3 M HNO_3 with irradiated 0.1 M Aliquat-336 in DIPB and 5 vol% dodecanol.

Irradiation time [h]	Dose [Gy]	D_{Am}	$\sigma D_{tot,Am}$	D_{Eu}	$\sigma D_{tot,Eu}$
0	0	3.2E-3	5.4 %	1.4E-3	5.5 %
170	8300	1.7E-3	5.9 %	7.0E-4	5.9 %
170	8300	1.8E-3	6.3 %	7.7E-4	6.6 %
400	20000	9.6E-4	5.8 %	4.1E-4	5.8 %
400	20000	1.3E-3	6.4 %	7.0E-4	5.2 %
580	29000	5.8E-4	6.0 %	3.0E-4	5.1 %
580	29000	7.5E-4	6.2 %	3.4E-4	5.1 %
740	37000	2.9E-4	6.1 %	1.5E-4	5.2 %
740	37000	3.0E-4	6.1 %	1.6E-4	5.1 %

Irradiated Aliquat-336: Extraction from 7.5 M HNO₃

Table 3 Am and Eu extracted from 7.5 M HNO₃ with irradiated 0.1 M Aliquat-336 in DIPB and 5 vol% dodecanol.

Irradiation time [h]	Dose [Gy]	D_{Am}	$\sigma D_{tot,Am}$	D_{Eu}	$\sigma D_{tot,Eu}$
0	0	6.8E-4	4.2 %	3.9E-4	4.2 %
170	8300	5.1E-4	6.6 %	3.9E-4	5.9 %
170	8300	6.6E-4	5.9 %	2.7E-4	5.2 %
400	20000	3.6E-4	5.6 %	2.4E-4	5.4 %
400	20000	2.9E-4	5.6 %	1.9E-4	4.8 %
580	29000	2.8E-4	6.2 %	2.0E-4	5.1 %
580	29000	3.1E-4	6.0 %	2.2E-4	4.9 %
740	37000	1.6E-4	7.0 %	1.1E-4	5.3 %
740	37000	2.8E-4	4.6%	2.0E-4	5.2 %

Radiolysis of Aliquat-336 from 3 M HNO₃

Table 4 Am and Eu extracted from 3 M HNO_3 with irradiated 0.1 M Aliquat-336 in DIPB and 5 vol% dodecanol which have been in contact with 3 M HNO_3 during the irradiation.

Irradiation time [h]	Dose [Gy]	D_{Am}	$\sigma D_{tot,Am}$	D_{Eu}	$\sigma D_{tot,Eu}$
0	0	3.2E-3	5.4 %	1.4E-3	5.6 %
170	8300	2.3E-2	4.7 %	1.5E-3	4.6 %
170	8300	2.2E-2	6.1 %	1.4E-2	5.3 %
400	20000	6.2E-3	6.0 %	4.8E-3	4.9 %
400	20000	9.5E-3	5.6 %	7.4E-3	5.2 %
580	29000	1.6E-2	6.7 %	1.1E-2	5.3 %
580	29000	1.5E-2	6.6 %	1.0E-2	5.3 %
740	37000	3.4E-3	5.1 %	2.7E-3	5.0 %
740	37000	3.0E-3	6.3 %	2.4E-3	5.1 %

Hydrolysis of Aliquat-336 from 3 M HNO₃

Table 5 Am and Eu extracted from 3 M HNO_3 with hydrolysed 0.1 M Aliquat-336 in DIPB and 5 vol% dodecanol which have been hydrolysed in contact with nitric acid

Hydrolysis time [h]	Dose [Gy]	D_{Am}	$\sigma D_{tot,Am}$	D_{Eu}	$\sigma D_{tot,Eu}$
0	0	3.1E-3	5.4 %	1.4E-3	5.6 %
170	0	1.5E-3	6.2 %	7.2E-3	5.2 %
170	0	1.5E-3	6.6 %	7.0E-4	5.5%
170	0	2.1E-3	6.3 %	1.4E-3	5.2 %
401,9	0	9.4E-4	6.8 %	5.2E-4	5.5 %
401,9	0	9.5E-4	6.2 %	5.2E-4	5.0 %
578	0	4.9E-4	6.2 %	3.3E-4	5.0 %
578	0	6.0E-4	7.0 %	4.3E-4	5.1 %
740	0	6.8E-4	5.4 %	5.4E-4	5.1 %

Not irradiated Aliquat-336 extracted with irradiated diluent

Table 6 Am and Eu extracted from 3 M and 7.5 M HNO_3 with 0.1 M Aliquat-336 in irradiated DIPB and dodecanol.

HNO₃ [M]	D_{Am}	$\sigma D_{tot,Am}$	D_{Eu}	$\sigma D_{tot,Eu}$
3	2.7E-4	6.9 %	2.1E-4	6.0 %
3	1.8E-4	5.8 %	1.4E-4	5.3 %
7.5	8.0E-5	6.7 %	6.0E-5	5.9 %
7.5	1.3E-4	6.7 %	1.1E-4	5.8 %

Irradiated DMDPHTDMA: Extraction from 0.5 M HNO$_3$

Table 7 Am and Eu extracted from 0.5 M HNO$_3$ with irradiated 0.1 M DMDPHTDMA in DIPB.

Irradiation time [h]	Dose [Gy]	D$_{Am}$	σD$_{tot,Am}$	D$_{Eu}$	σD$_{tot,Eu}$
0	0	1.1E-4	5.3 %	1.0E-4	5.3 %
400	20000	4.5E-5	8.9 %	2.7E-5	7.7%
400	20000	2.7E-5	10 %	1.6E-5	7.4 %
580	29000	2.0E-5	11.0 %	8.9E-6	8.8 %
740	37000	6.8E-5	7.9 %	4.8E-5	6.4 %

Irradiated DMDPHTDMA: Extraction from 3 M HNO$_3$

Table 8 Am and Eu extracted from 3 M HNO$_3$ with irradiated 0.1 M DMDPHTDMA in DIPB.

Irradiation time [h]	Dose [Gy]	D_{Am}	$\sigma D_{tot,Am}$	D_{Eu}	$\sigma D_{tot,Eu}$
0	0	4.3E-3	8.3%	1.8E-3	6.8%
0	0	3.0E-3	5.3%	1.2E-3	5.3%
400	20000	3.8E-3	6.4%	1.5E-4	6.0%
400	20000	2.3E-3	6.9%	8.9E-4	5.9%
580	29000	1.6E-3	8.3%	6.5E-4	7.0%
740	37000	1.6E-3	7.4%	7.0E-4	6.1%

Irradiated DMDPHTDMA: Extraction from 7.5 M HNO$_3$

Table 9 Am and Eu extracted from 7.5 M HNO$_3$ with irradiated 0.1 M DMDPHTDMA in DIPB.

Irradiation time [h]	Dose [Gy]	D_{Am}	$\sigma D_{tot,Am}$	D_{Eu}	$\sigma D_{tot,Eu}$
0	0	1.2E-1	7.2%	0.06.6E-2	6.7%
0	0	1.5E-1	5.3%	9.4E-2	5.3%
400	20000	2.3E-1	6.3%	1.1E-2	6.1%
400	20000	2.2E-1	6.6%	1.1E-2	6.2%
580	29000	1.3E-1	7.2%	7.0E-2	6.3%
580	29000	2.2E-1	7.9%	1.1E-2	7.4%
740	37000	1.1E-1	7.8%	6.0E-2	6.4%
740	37000	2.4E-1	7.9%	1.3E-2	6.4%
910	55000	2.5E-1	8.0%	1.3E-2	6.9%
1340	67000	1.5E-1	6.9%	7.6E-2	6.5%
1340	67000	1.7E-1	7.2%	7.2E-2	6.7%

Radiolysis of DMDPHTDMA from 3 M HNO_3

Table 10 Am and Eu extracted from 3 M HNO_3 with irradiated 0.1 M DMDPHTDMA in DIPB which have been in contact with 3 M HNO_3 during irradiation.

Irradiation time [h]	Dose [Gy]	D_{Am}	$\sigma D_{tot,Am}$	D_{Eu}	$\sigma D_{tot,Eu}$
0	0	4.3E-3	6.3%	1.8E-3	6.9%
0	0	3.0E-3	5.3%	1.2E-2	5.3%
400	20000	5.3E-2	6.7%	2.4E-2	6.2%
400	20000	5.2E-2	7.2%	2.4E-2	6.8%
580	29000	3.0E-2	7.5%	3.0E-2	7.2%
580	29000	5.5E-2	6.2%	2.1E-2	6.1%
580	29000	2.8E-2	7.2%	1.1E-2	6.5%
740	37000	3.6E-2	7.2%	1.6E-2	6.9%

Hydrolysis of DMDPHTDMA from 3 M HNO_3

Table 11 Am and Eu extracted from 3 M HNO_3 with hydrolysed (A) 0.1 M DMDPHTDMA in DIPB which have been in contact with nitric acid.

Hydrolysis time [h]	Dose [Gy]	D_{Am}	$\sigma D_{tot,Am}$	D_{Eu}	$\sigma D_{tot,Eu}$
0	0	4.3E-3	6.3%	1.8E-3	6.9%
0	0	3.0E-3	5.3%	1.2E-3	5.3%
400	20000	1.1E-1	7.1%	5.0E-2	6.6%
400	20000	1.2E-1	7.1%	5.2E-2	6.6%

Table 12 Am and Eu extracted from 3 M HNO_3 with hydrolysed (B) 0.1 M DMDPHTDMA in DIPB which have been in contact with nitric acid. The experiment was performed with less air than the experiment presented in table 10

Hydrolysis time [h]	Dose [Gy]	D_{Am}	$\sigma D_{tot,Am}$	D_{Eu}	$\sigma D_{tot,Eu}$
0	0	4.3E-3	6.3%	1.8E-3	6.9%
0	0	3.0E-3	5.3%	1.2E-3	5.3%
580	290000	4.1E-3	7.2%	1.6E-3	6.9%
740	37000	5.1E-3	7.4%	2.1E-3	7.0%

Appendix 2. GC-MS spectra

For every GC-spectra the biggest peaks are selected and the MS-spectra are shown. A number of small peaks are observed in the GC-spectra but they were neglected. Every peak is referred to by the channel number.

DIPB

GC spectrum of unirradiated DIPB.

Channel 55 is toluene, which is used to wash the injection needle.

Channel 163 is DIPB and channel 239, 316 and 620 are impurities in the diluent.

GC 70_10_300_20   kolonn GC2 OV1   50kPa
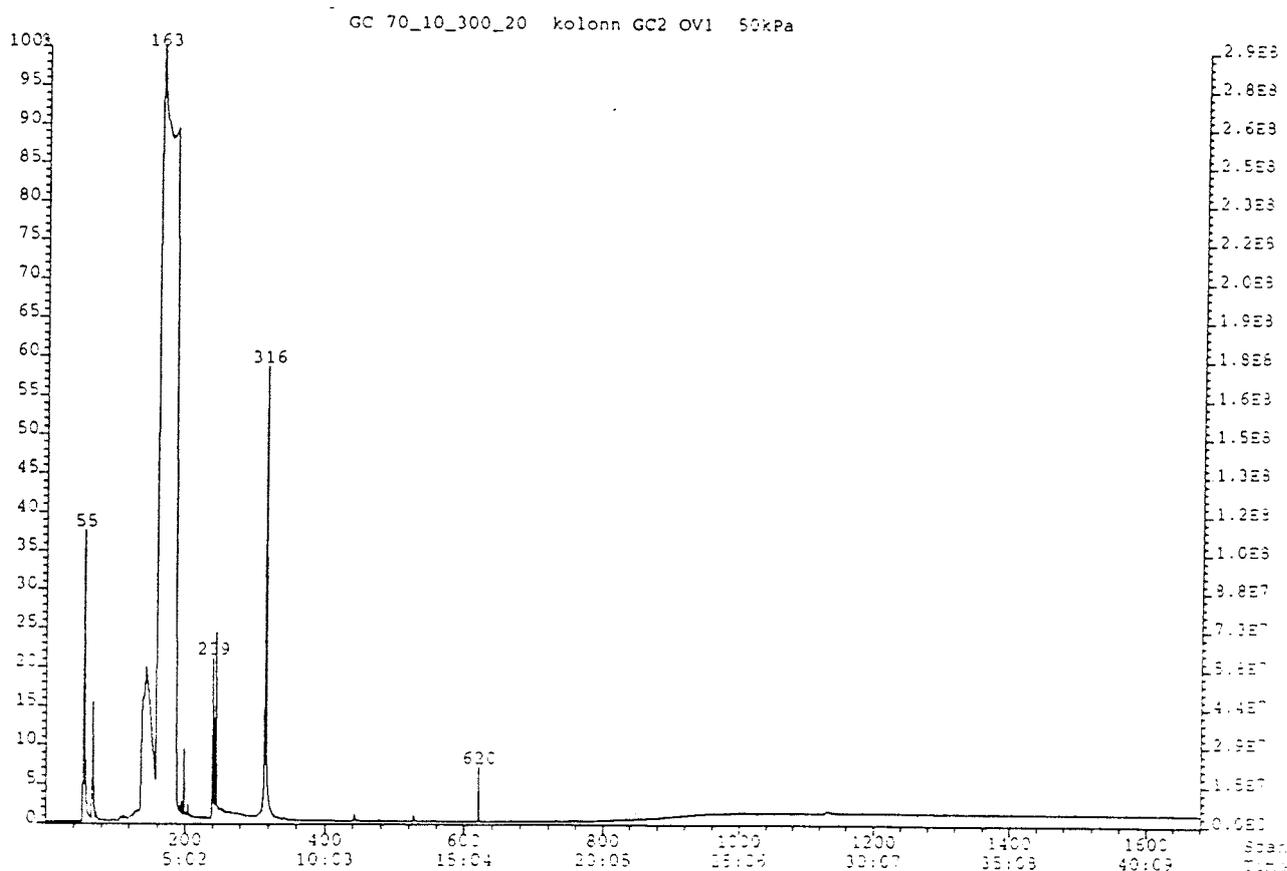
MS spectrum found in GC spectrum for unirradiated DIPB at channel 239.
The MS spectrum is similar to DIPB.
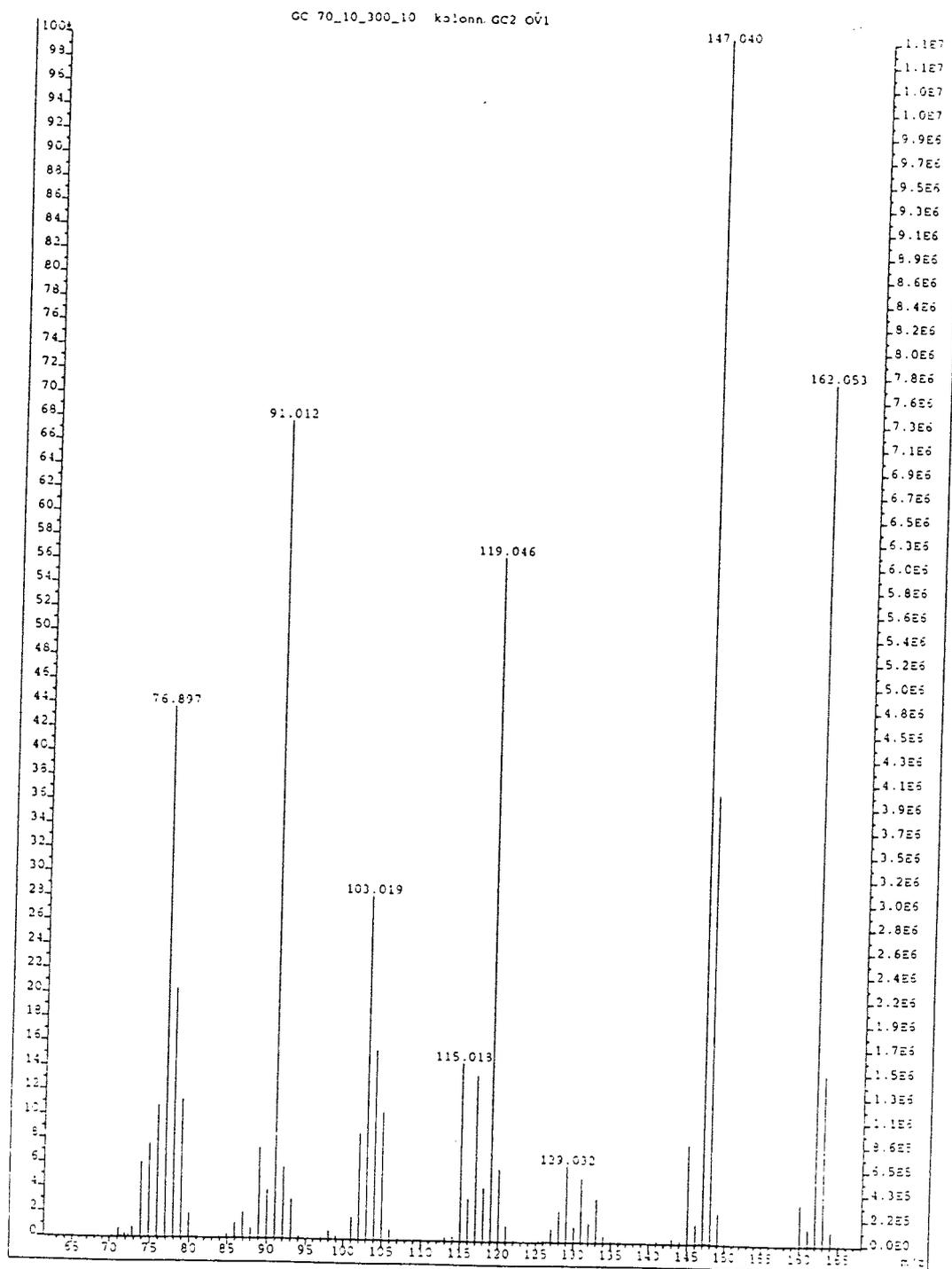
MS spectrum found in GC spectrum for unirradiated DIPB at channel 316.
The MS spectrum is similar to DIPB.
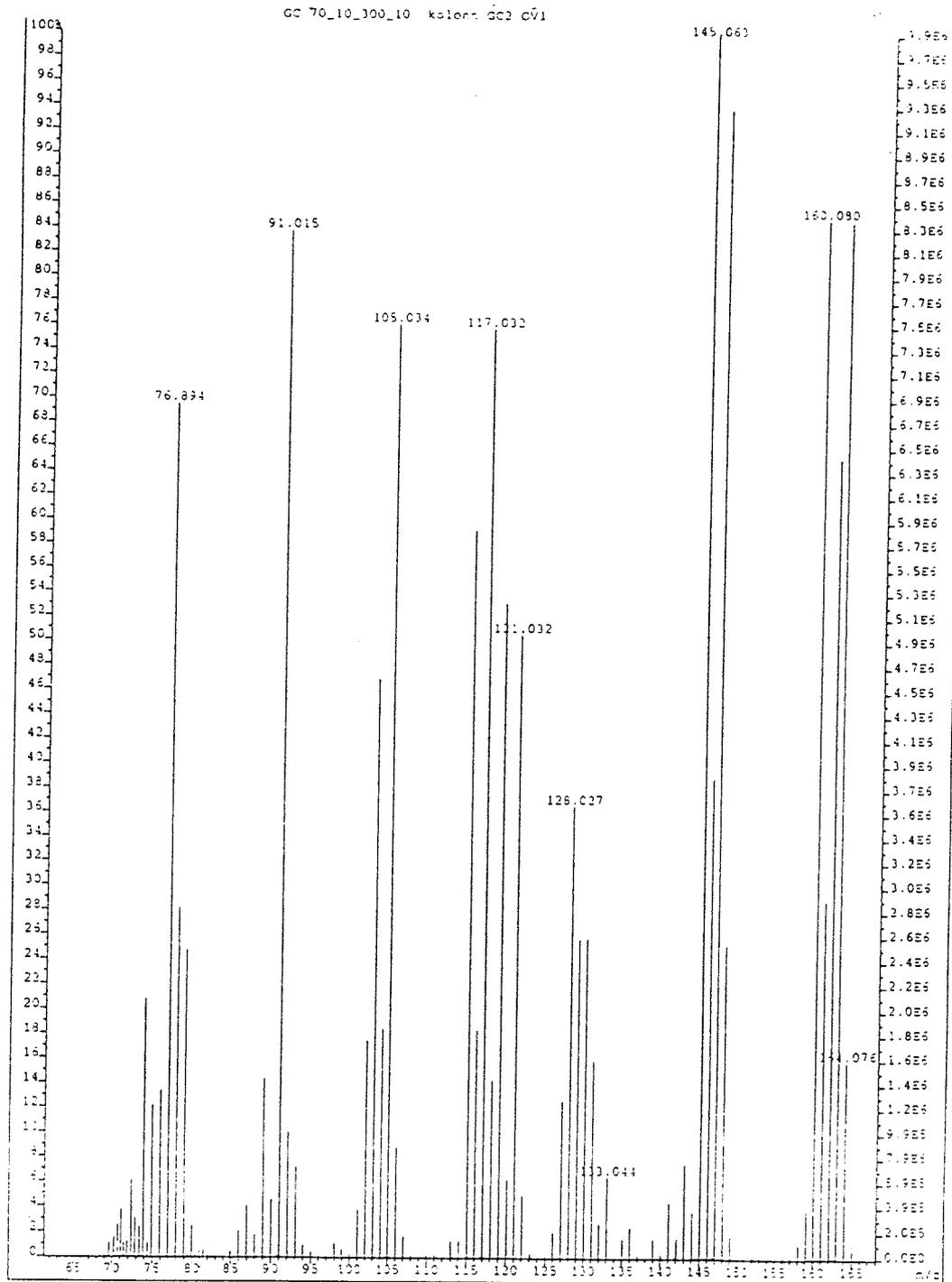
MS spectrum found in GC spectrum for unirradiated DIPB at channel 620

The MS spectrum is similar to DIPB.

GC 70_10_300_10 kolonn GC2 ÖV1
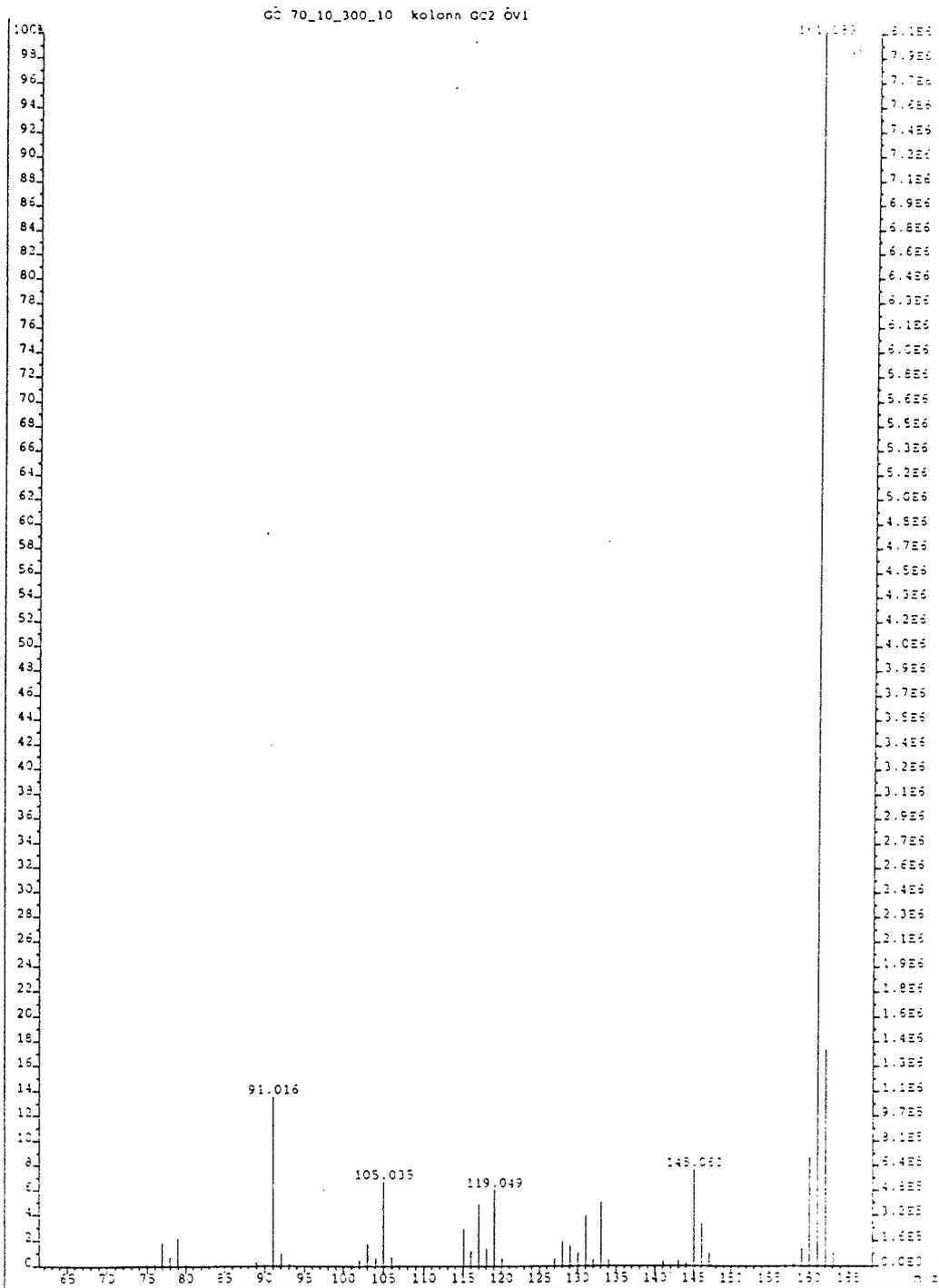
Irradiated DIPB

GC spectrum of irradiated DIPB. The sample was irradiated for 3 months(110 kGy).

Channel 55 is toluene, which was used to wash the injection needle.

Channel 166 is DIPB and channels 250, 332 and 623 are impurities in the diluent, see page 2-4.

Channel 100 and 149 are degradation products to DIPB.

The rest of the peaks found in the GC spectrum correspond well to DIPB and they might have a bulky structure that retain them in the column.
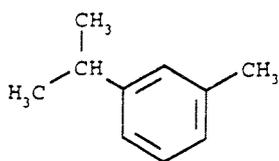
GC 70_10_300_20   kolonn GC2 OV1   50kPa

MS spectrum found in GC spectrum for irradiated DIPB at channel 100.

The MS-spectrum could bee explain by

GC 70_10_300_10 kolonn GC2 OVl
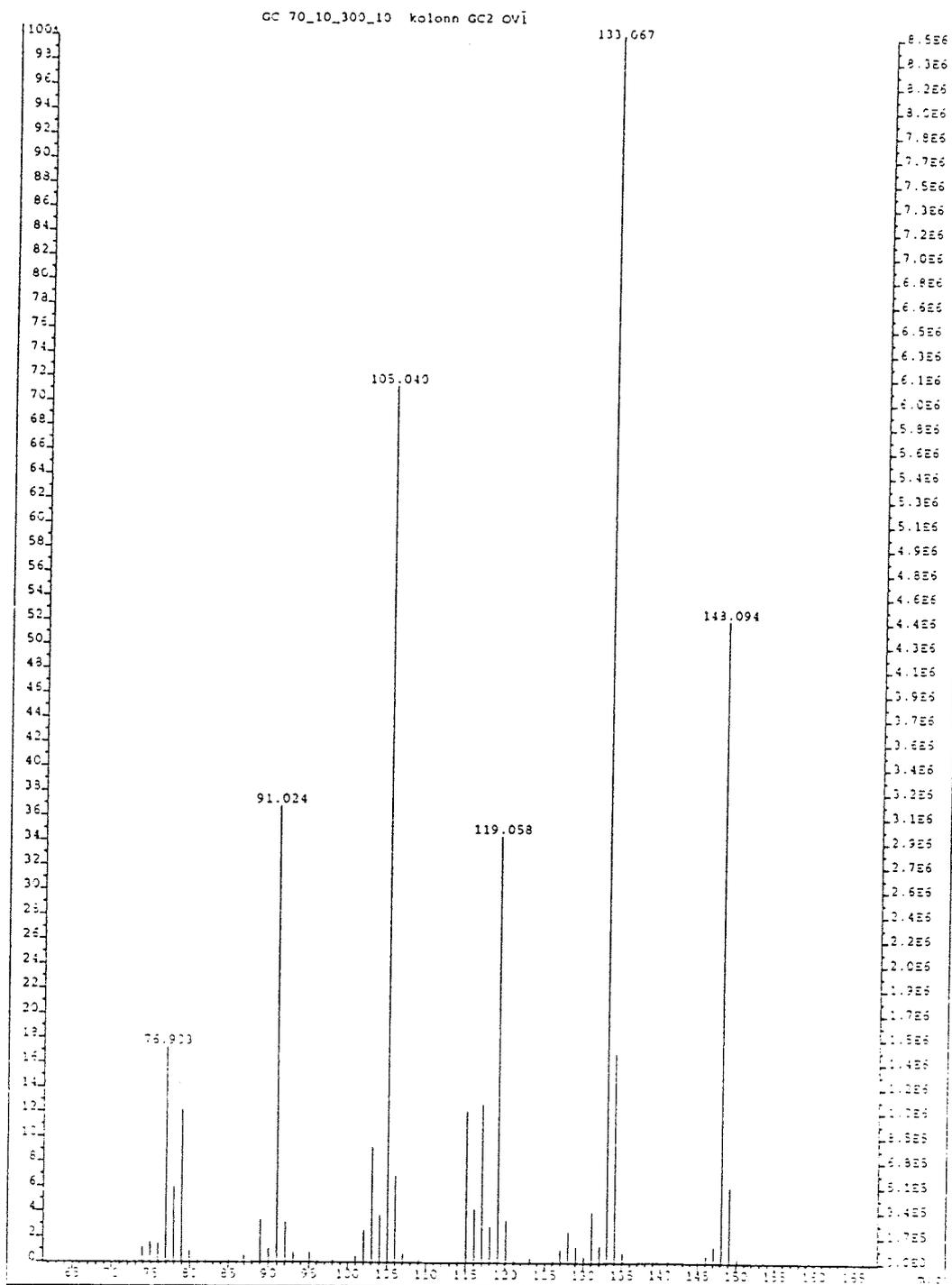
MS spectrum found in GC spectrum for irradiated DIPB at channel 149.

The MS-spectrum could bee explain by

GC 70_10_300_10 kolonn GC2 OV1

Appendix 2. 7
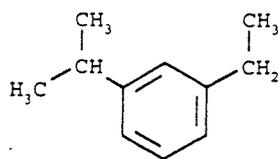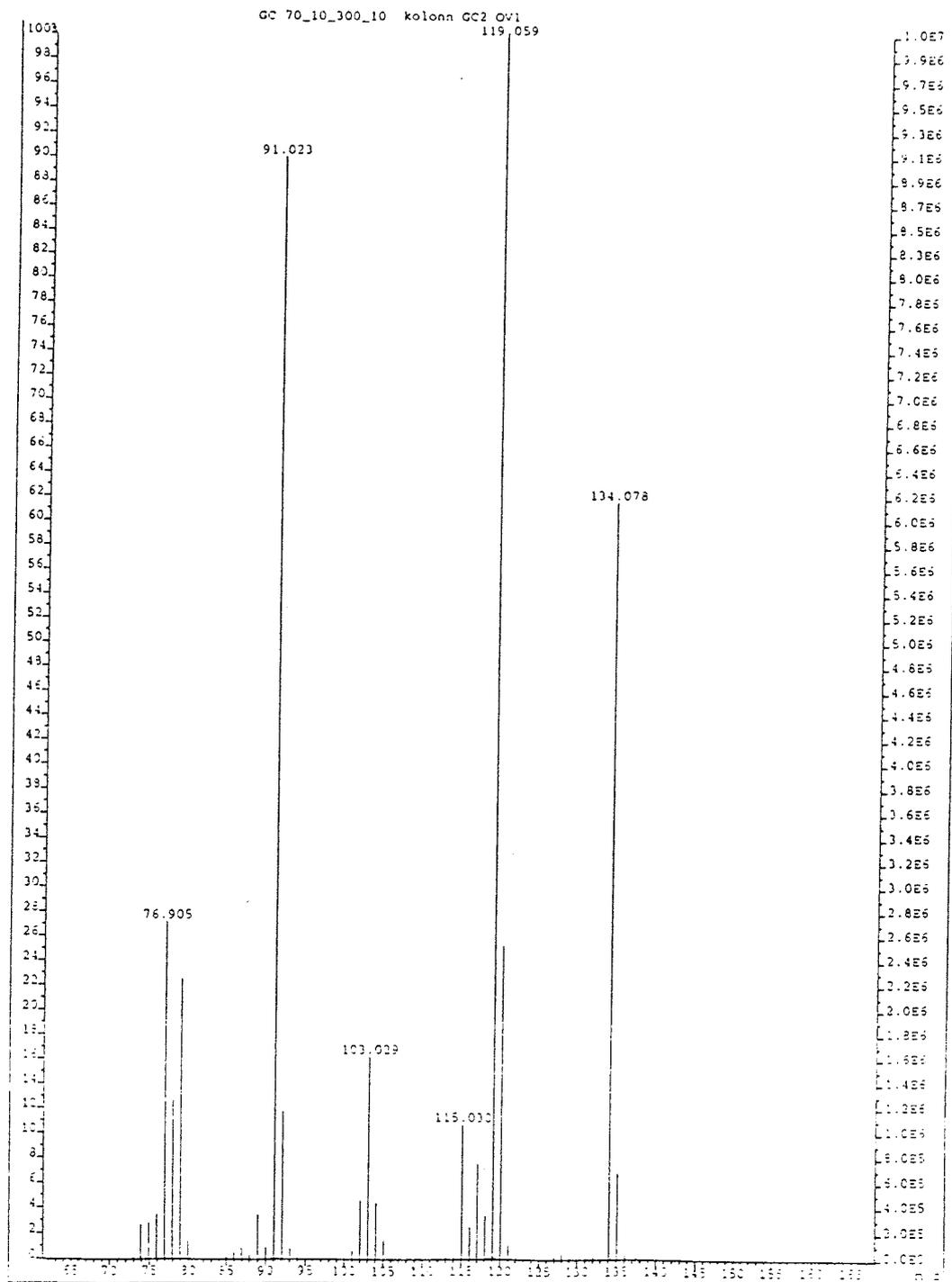
DIPB and dodecanol

GC spectrum of unirradiated DIPB and 5 vol% dodecanol.

Channel 55 is toluene, which is used to wash the injection needle.

Channel 175 is DIPB and channel 257, 329 and 637 are impurities in the diluent, see page 2-4.

Channel 344 is 1-dodecanol

GC 70_10_300_10   kolonn GC2 OV1
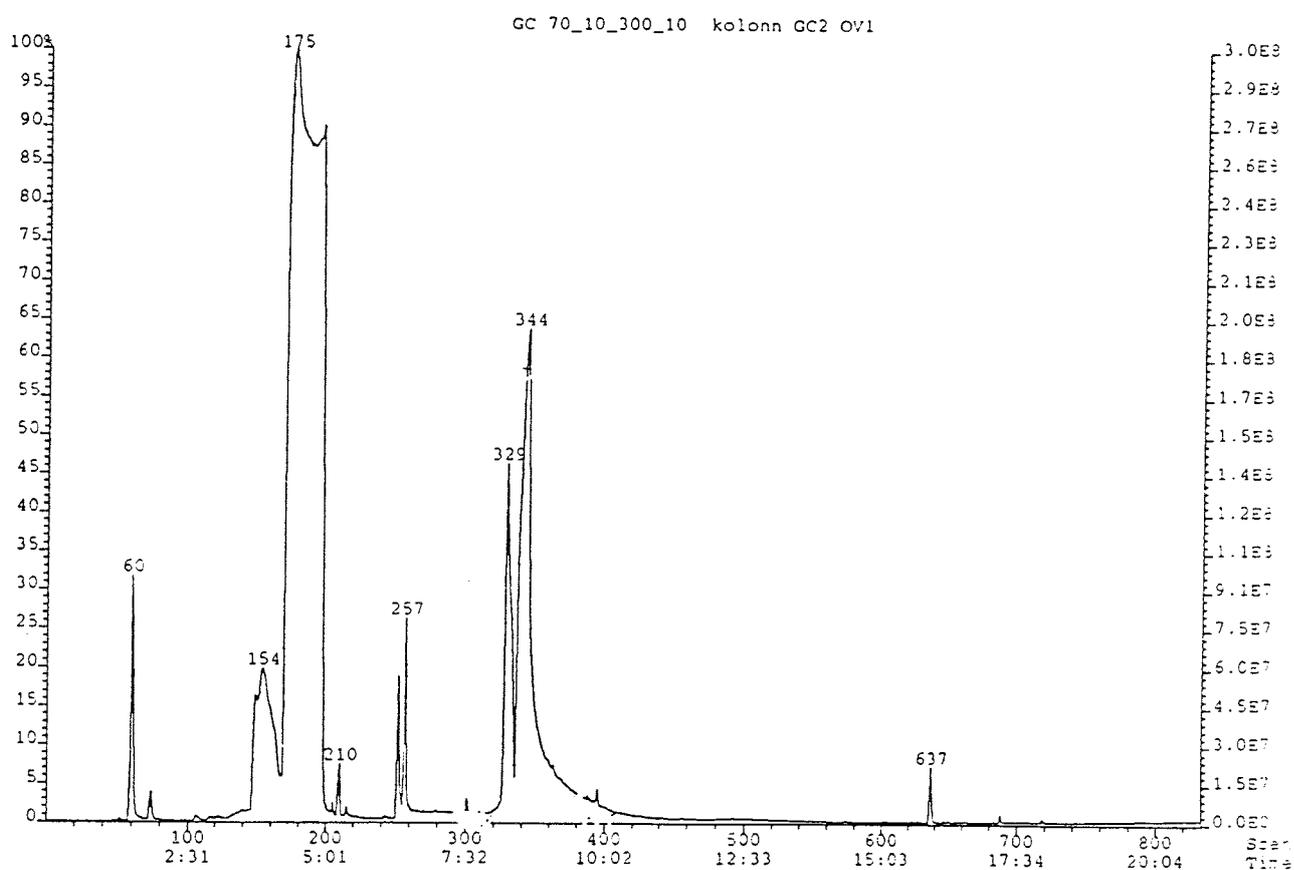
MS spectrum. Unirradiated DIPB and 5 vol% 1-dodecanol found in the GC spectrum at channel 344

The MS-spectrum are 1-dodecanol

GC 70_10_300_10 "kolonn GC2 C:\"
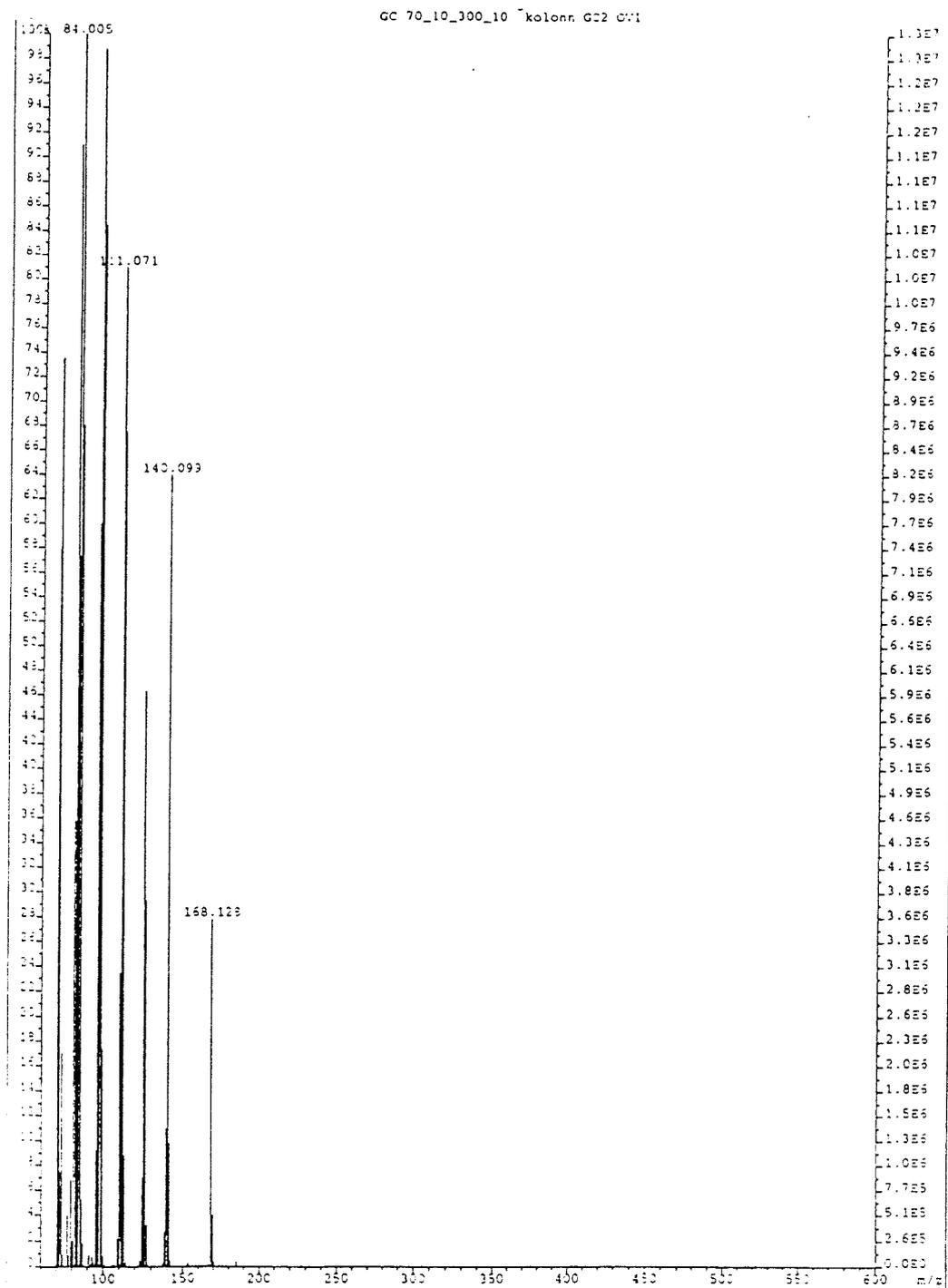
Irradiated DIPB and dodecanol

GC spectrum of irradiated DIPB and 5 vol% dodecanol. The sample was irradiated for 3 months (110 kGy).

Channel 55 is toluene, which is used to wash the injection needle.

Channel 174 is DIPB and channel 261, 329 and 638 are impurities of the diluent, see page 2-4.

Channel 341 is 1-dodecanol, see page 9.

Channel 689 and 719 are not identified.

GC 70_10_300_10   kolonn GC2 OV1
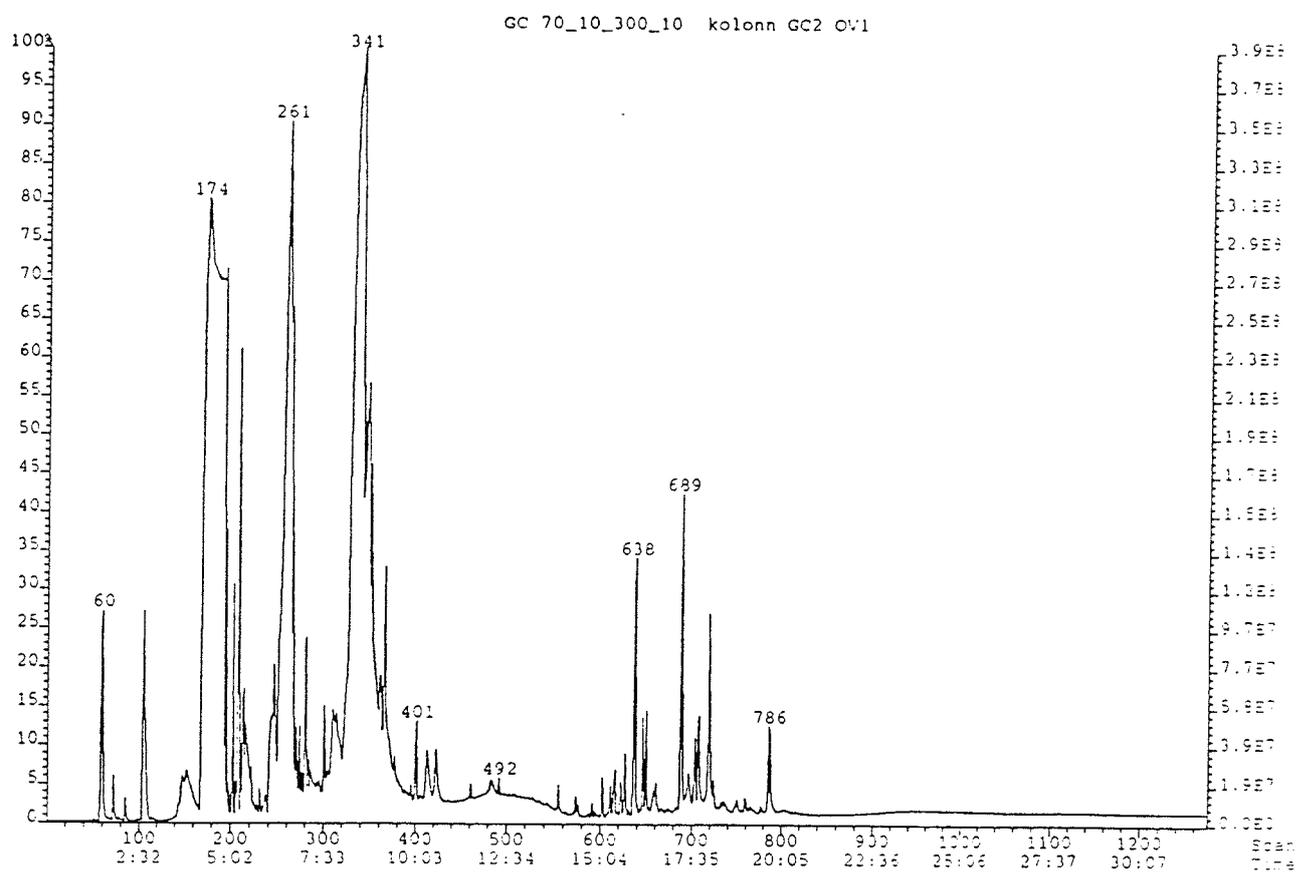
MS spectrum found in GC spectrum for irradiated DIPB and 5 vol% 1-dodecanol at channel 689.

The samples should not contain anything heavier than 170 (1-dodecanol).

The mass of DIPB+1-dodecanol are=162 + 170 = 332

The peak might be due to a chemical reaction between DIPB and dodecanol

GC 70_10_300_10 kolonn GC2 CV1
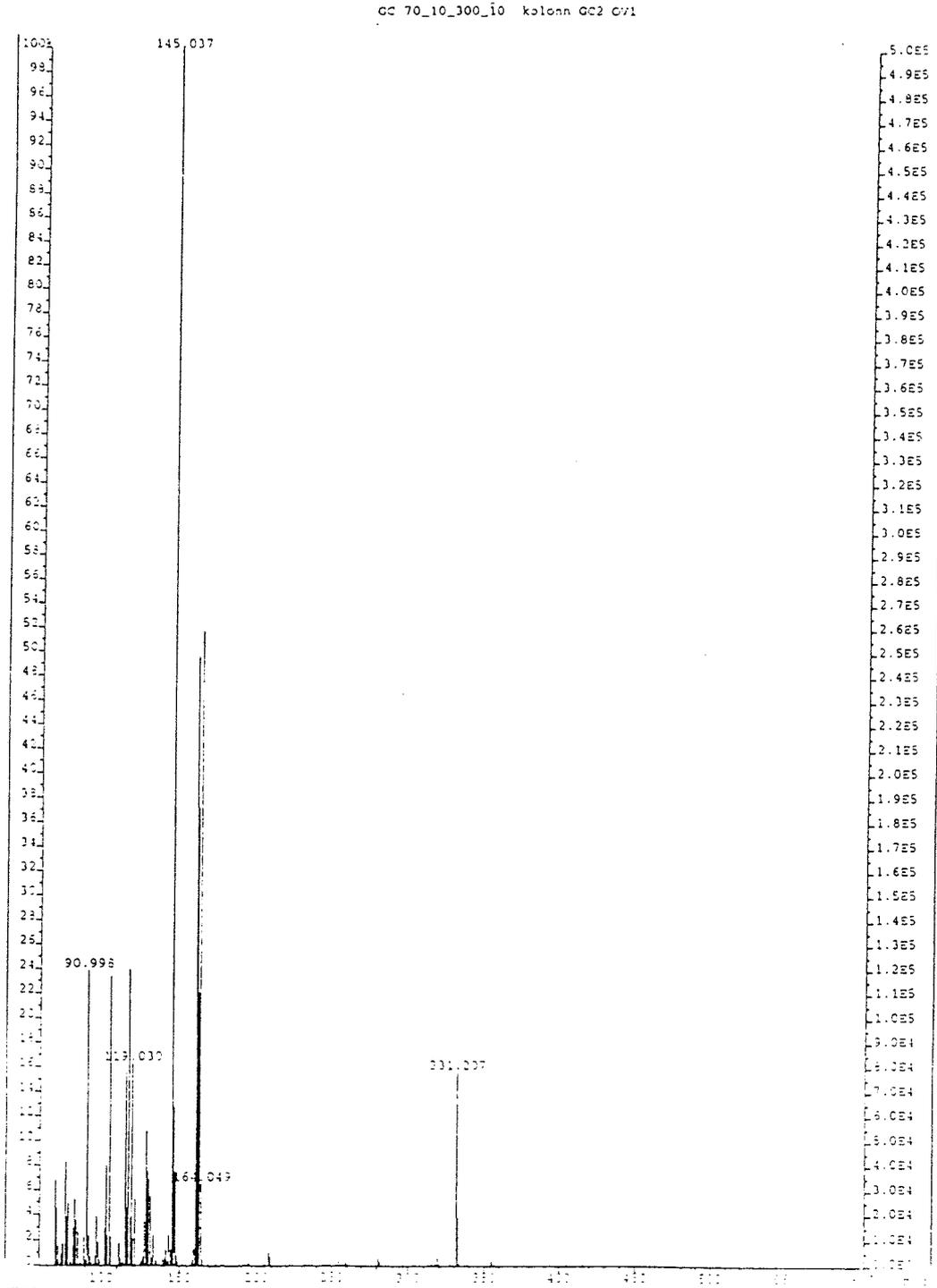
MS spectrum found in GC spectrum for irradiated DIPB and 5 vol% 1-dodecanol at channel 719.

The samples should not contain anything heavier than 170 (1-dodecanol).

The MS-spectrum might be due to a chemical reaction between DIPB and dodecanol

GC 70_10_300_10 kolonn GC2 CV1
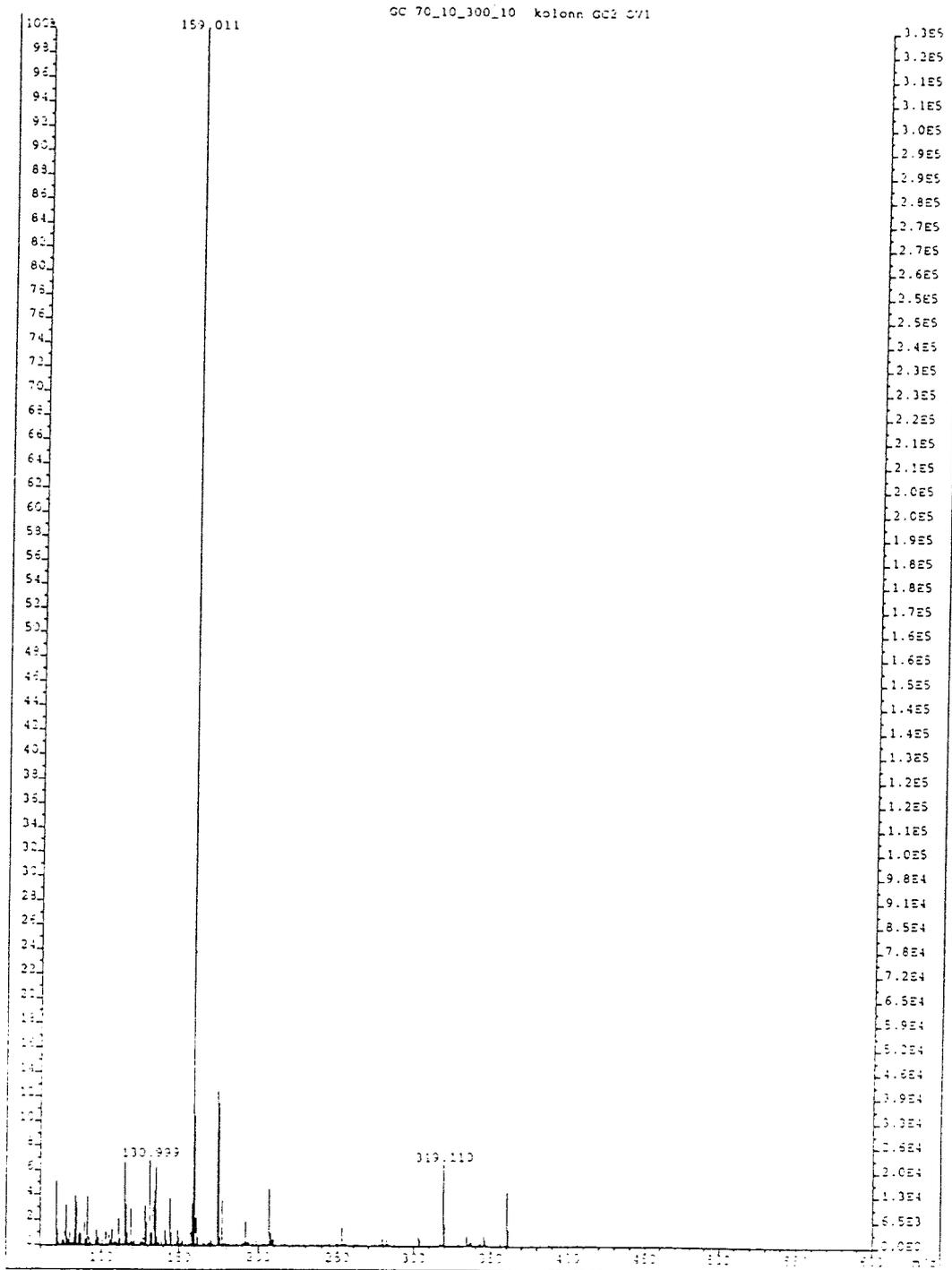
Aliquat-336 in DIPB and 1-dodecanol

GS spectrum of unirradiated Aliquat-336 in DIPB and 5 vol% 1-dodecanol.

Channel 61 is toluene, which is used to wash the injection needle.

Channel 176 is DIPB and channel 252, 329 and 638 are impurities of the diluent, see page 2-4.

Channel 341 is 1-dodecanol, see page 9

Channel 692 is not identified, see page 11.

Channel 755 and 825 are Aliquat-336.
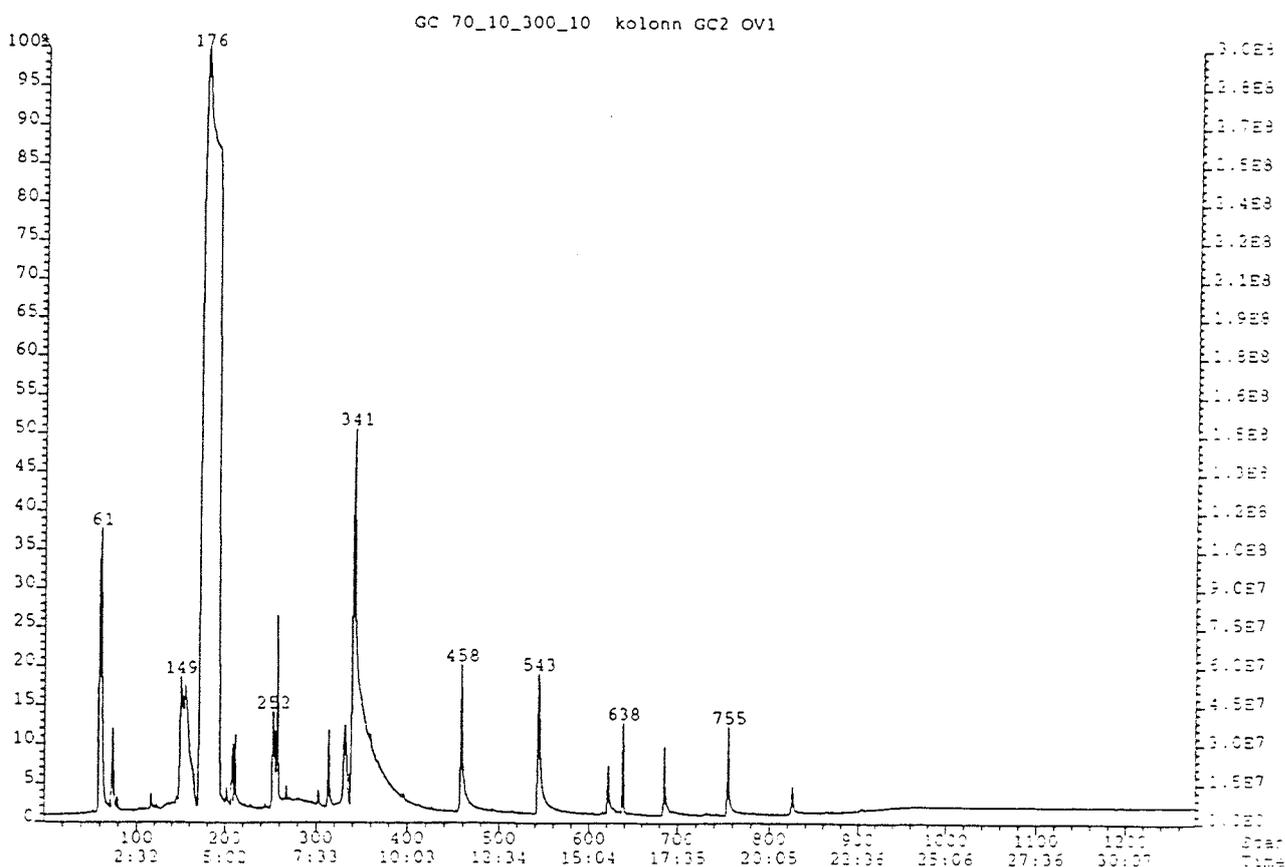
GC 70_10_300_10 kolonn GC2 OV1

MS-spectrum found in GC spectrum for unirradiated Aliquat-336 in DIPB and 5 vol% dodecanol at channel 755.

The MS-spectrum could bee explain by$(C_8H_{17})_2(C_9H_{19})CH_3N^+$
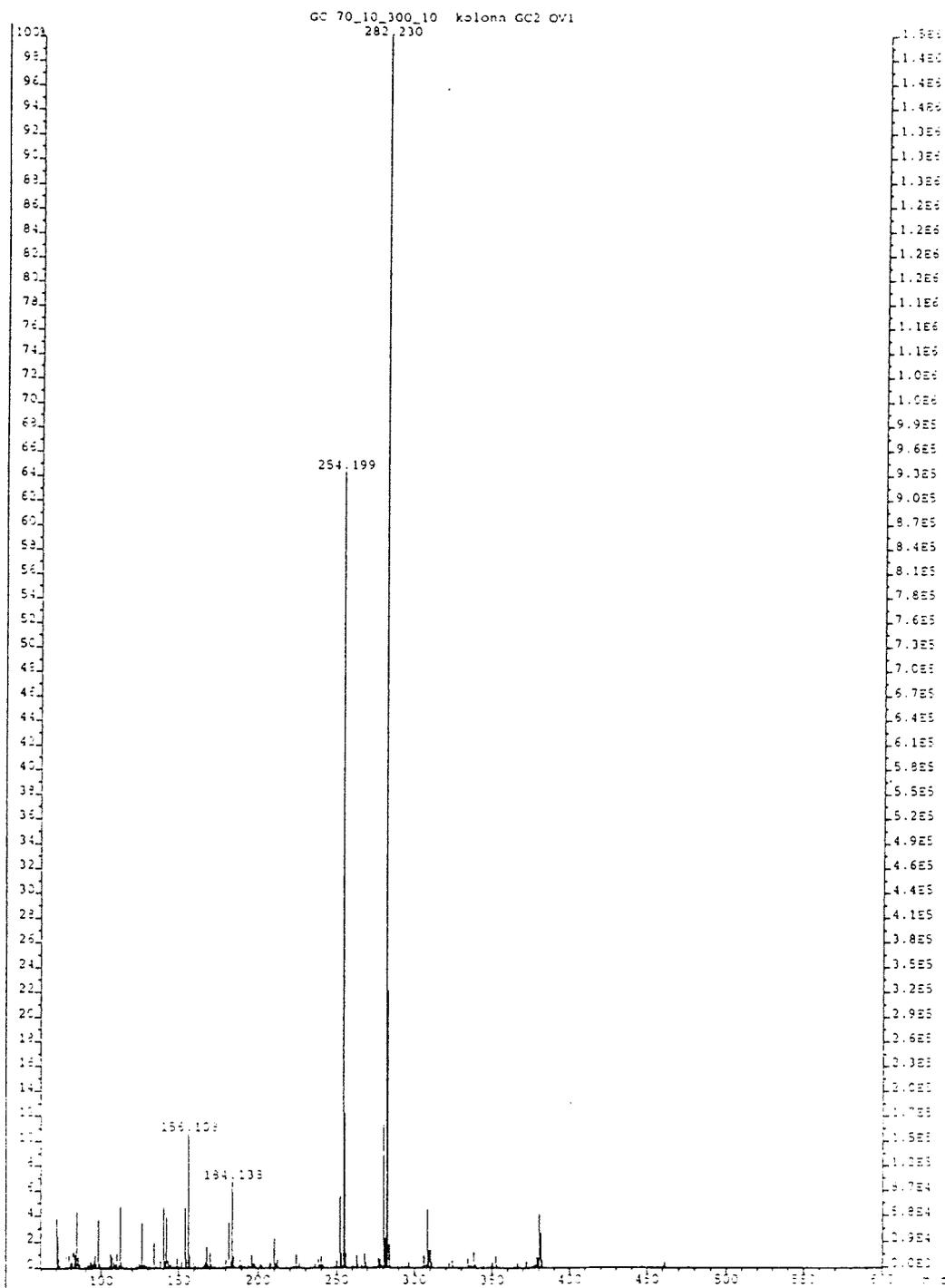
MS-spectrum found in GC spectrum for unirradiated Aliquat-336 in DIPB and 5 vol% dodecanol at channel 825

The MS-spectrum could bee explain by $(C_9H_{19})_3CH_3N^+$
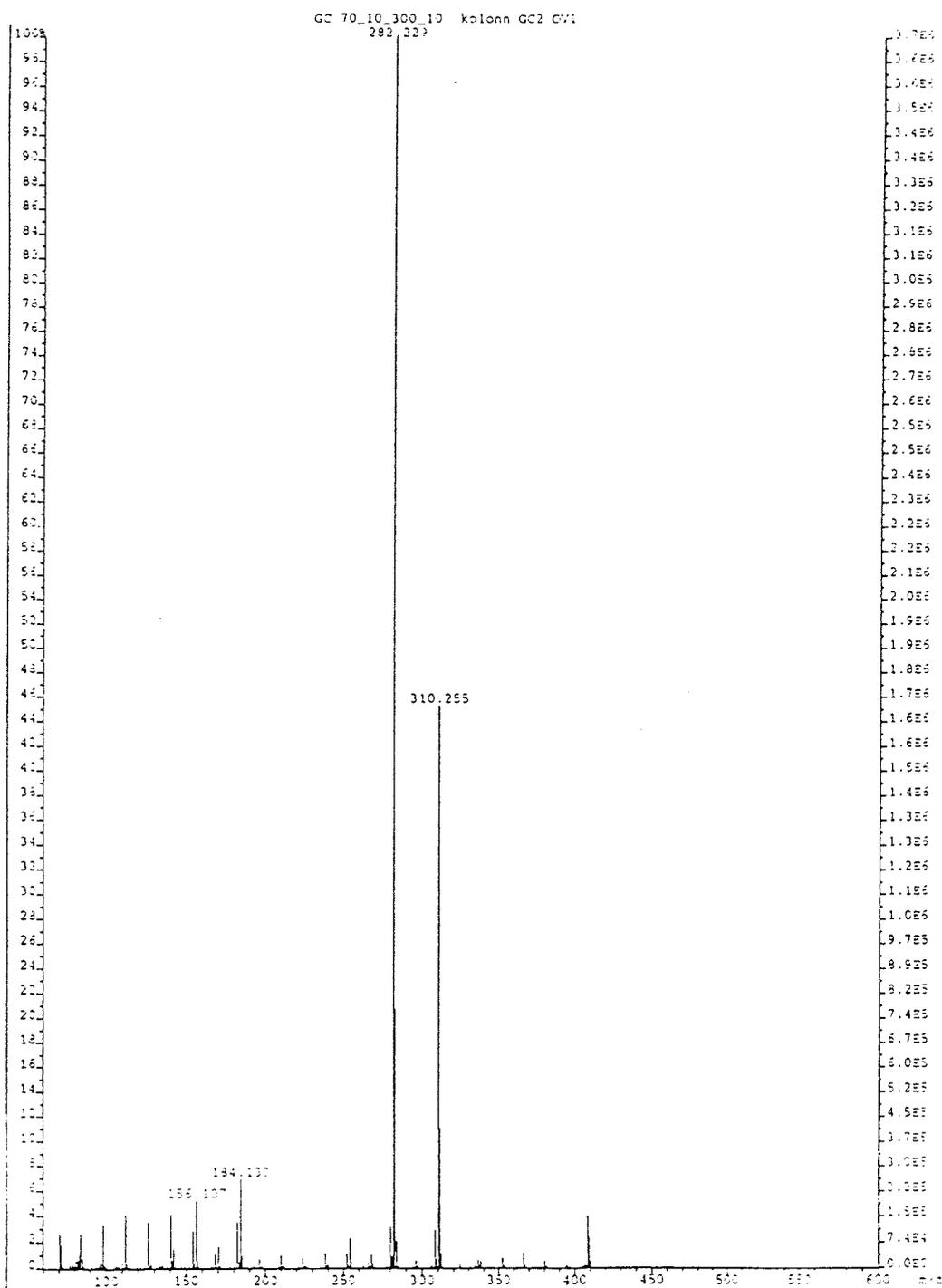
Irradiated Aliquat-336, DIPB and 1-dodecanol

GC spectrum of irradiated Aliquat-336 in DIPB and 5 vol% 1-dodecanol. The sample was irradiated for one month (37 kGy).

Channel 62 is toluene, which is used to wash the injection needle.

Channel 175 is DIPB and channel 261 and 639 are impurities of the diluent, see page 2, 4.

Channel 336 is 1-dodecanol, see page 9

Channel 689 and 719 are not identified, see pages 11 and 12.

Channel 756 and 8287 are Aliquat-336, see pages 14 and 15.

Channel 459 and 544 are degradation products to Aliquat-336.
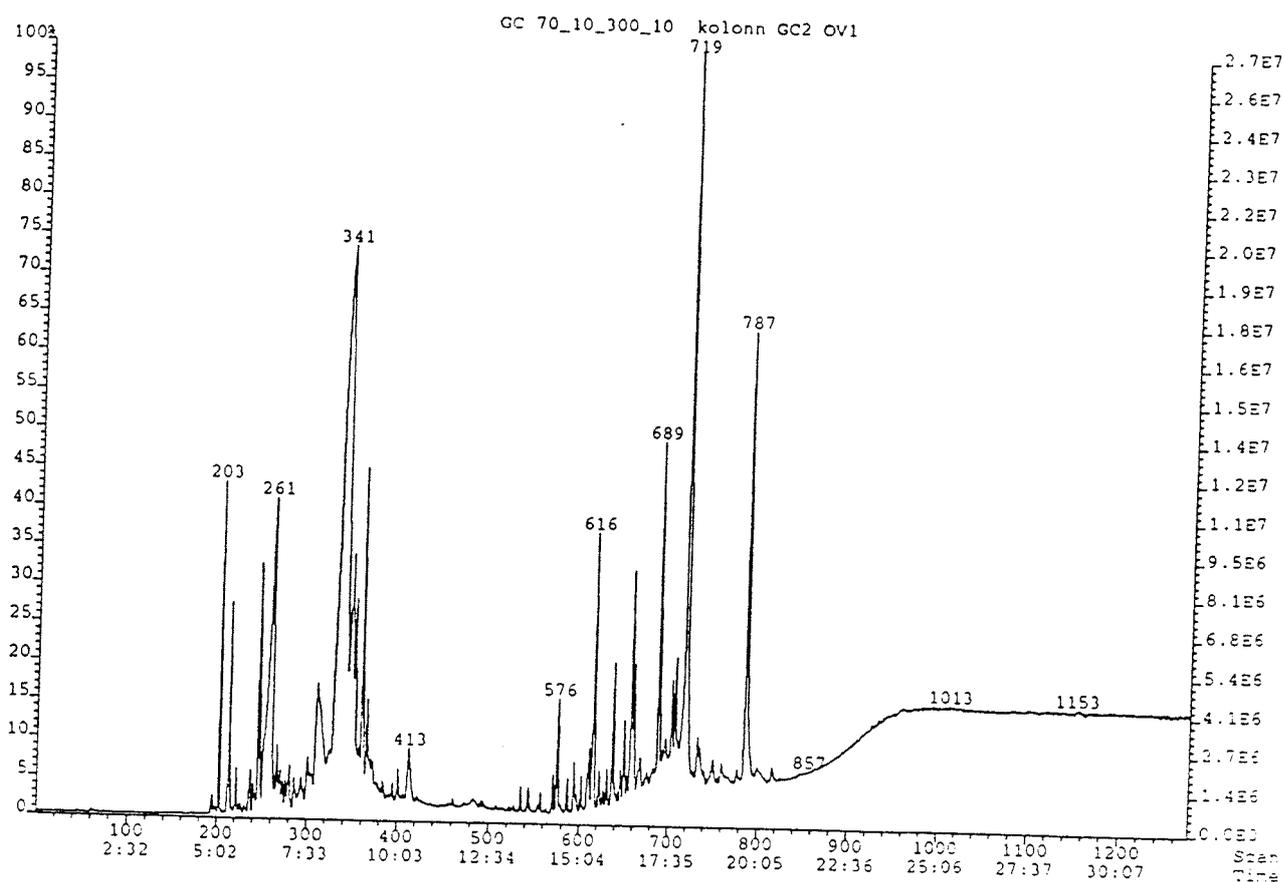
GC 70_10_300_10   kolonn GC2 OV1

MS-spectrum found in GC spectrum for irradiated Aliquat-336 in DIPB and 5 vol%
dodecanol at channel 459

The MS-spectrum could bee explain by $(C_8H_{17})_2CH_3HN^+$
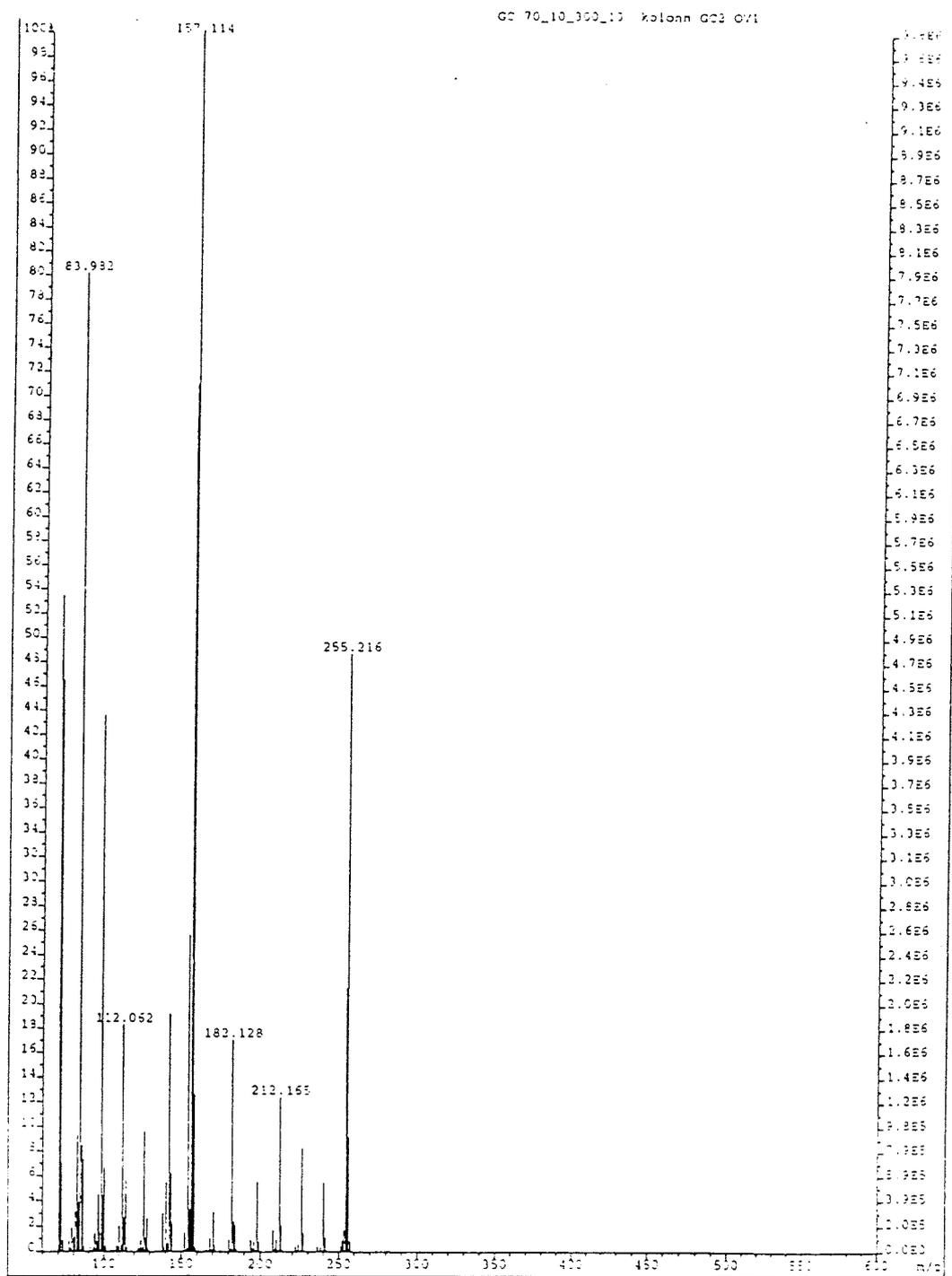
MS-spectrum found in GC spectrum for irradiated Aliquat-336 in DIPB and 5 vol% dodecanol at channel 576

The MS-spectrum could bee explain by $(C_9H_{19})_2CH_3HN^+$

GC 70_10_300_10 kolonn GT2 GV1
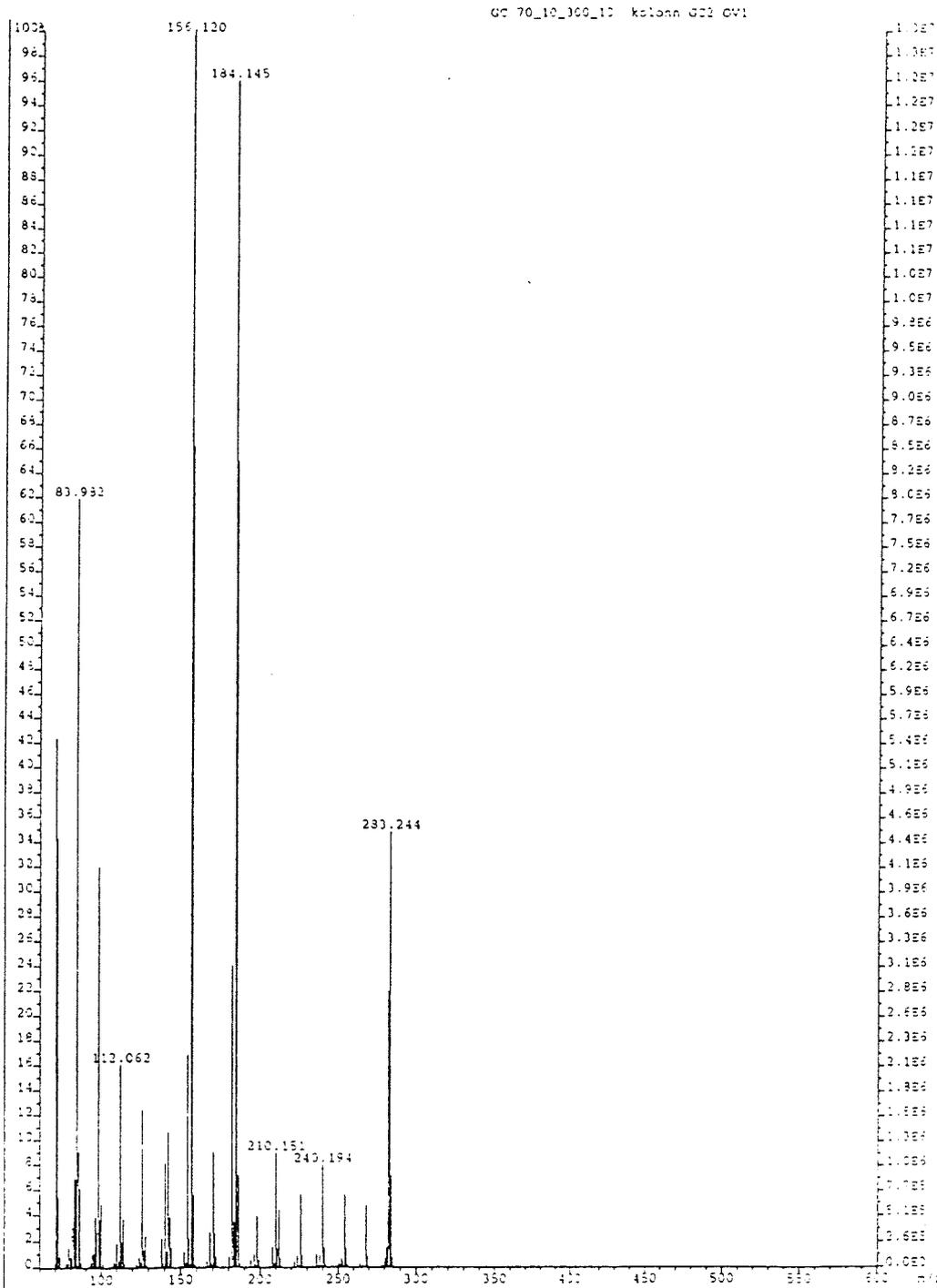
Hydrolysis of Aliquat-336 in DIPB and 1-dodecanol

GC spectrum of unirradiated Aliquat-336 in DIPB and 5 vol% 1-dodecanol that was in contact with nitric acid during one month. The spectra looks as if a lot of new compounds have been formed which are lighter than 165 g/mole and have a structure similar to DIPB.

Channel 60 is toluene, which is used to wash the injection needle.

Channel 174 is DIPB and channel 260, 329 and 637 are impurities of the diluent, see page 2-4.

Channel 362 is 1-dodecanol, see page 9.

Channel 690 and 719 are not identified, see pages 11 and 12.

Channel 757 and 833 are Aliquat-336, see pages 14 and 15.

Channel 459 and 548 are degradation products to Aliquat-336, see pages 17-18.

GC 70_10_300_10 kolonn GC3 OV1
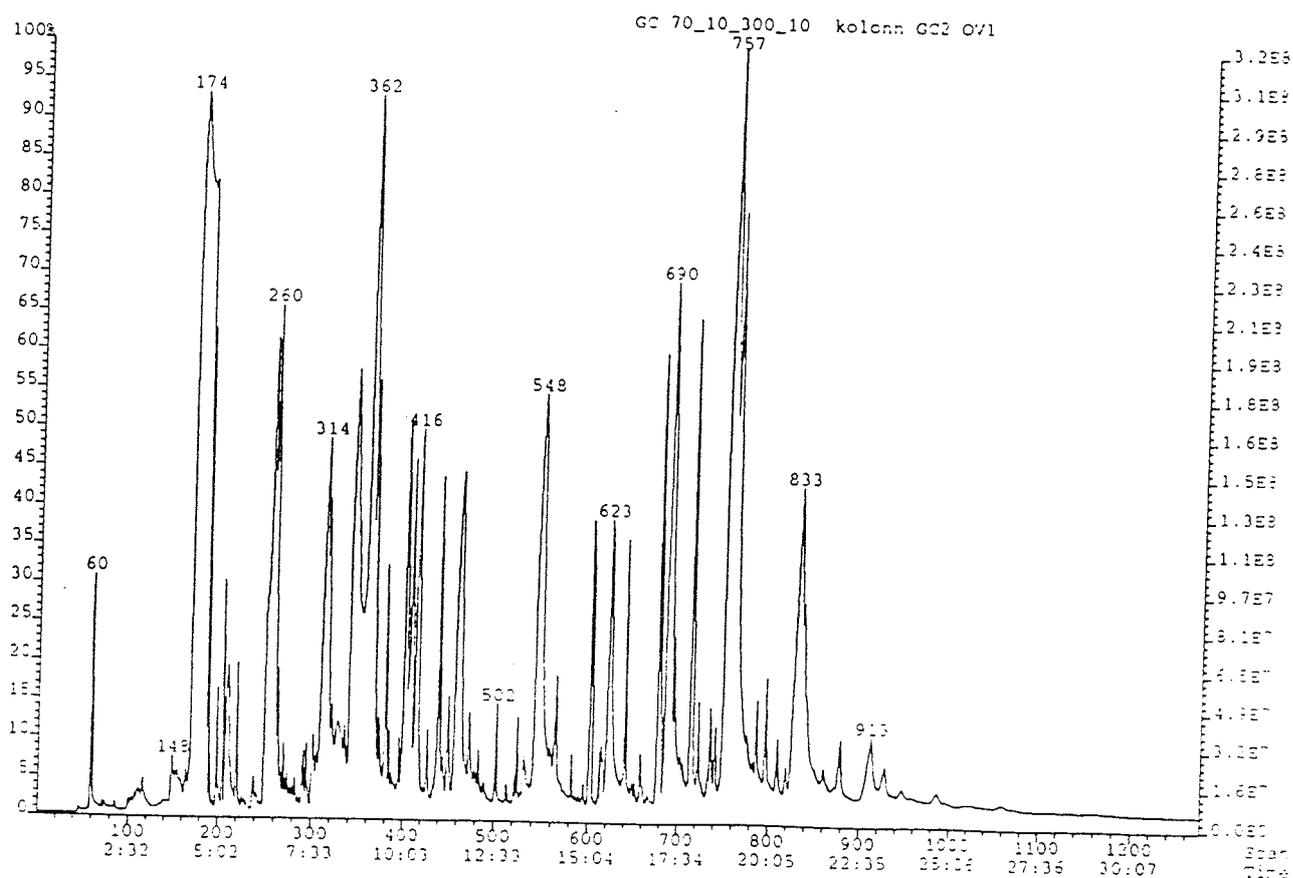
Irradiation of Aliquat-336 in DIPB and 1-dodecanol in contact with nitric acid

GC spectrum of irradiated Aliquat-336, DIPB and 5 vol% 1-dodecanol in contact with nitric acid. The spectra looks as if a lot of new compounds have been formed which are lighter than 165 g/mole and have a structure similar to DIPB.

Channel 61 is toluene, which is used to wash the injection needle.

Channel 175 is DIPB and channel 258, 329 and 637 are impurities in the diluent, see page 2-4.

Channel 360 is 1-dodecanol, see page 9.

Channel 679 and 715 are not identified, see pages 11 and 12.

Channel 754 and 825 are Aliquat-336, see pages 14 and 15.

Channel 454 and 548 are degradation products of Aliquat-336, see pages 17 and 18.

Channel 450 and 754 are degradation products of Aliquat-336
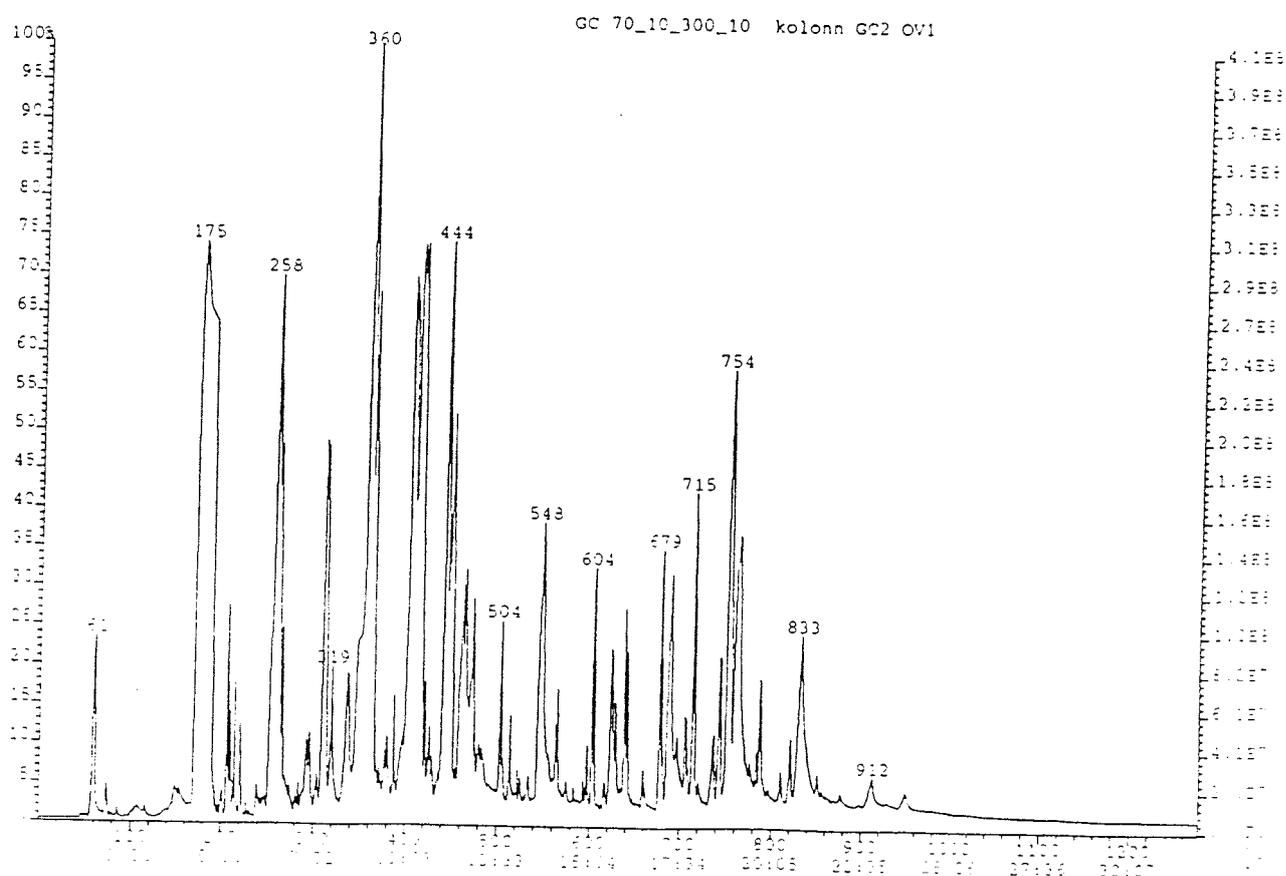
GC 70_1C_300_10 kolonn GC2 OV1

MS-spectrum found in GC spectrum for irradiated Aliquat-336 in DIPB and 5 vol%
dodecanol which have been in contact with nitric acid at channel 450.
The MS-spectrum could bee explain by$(C_8H_{17})_2H_2N^+$
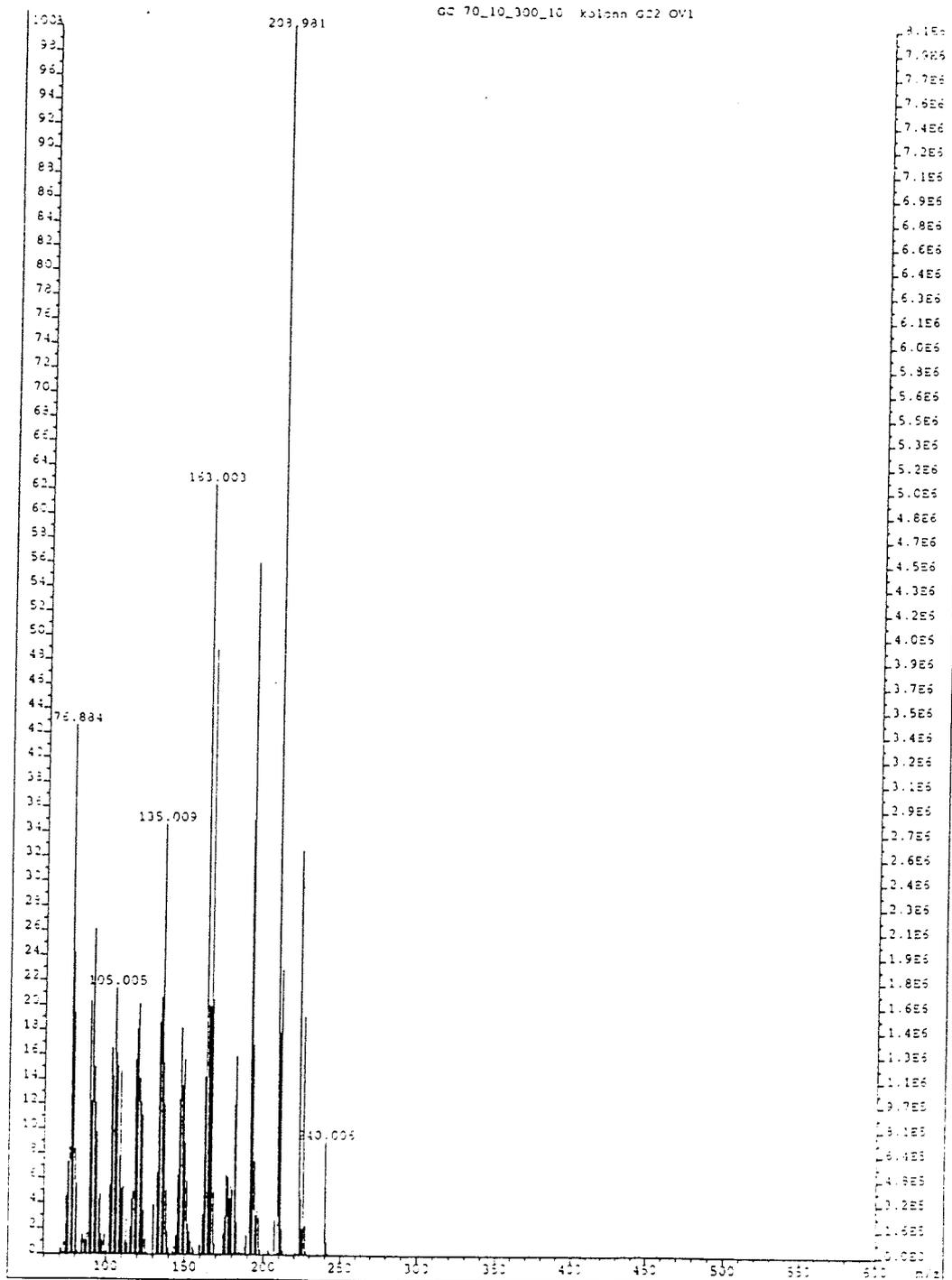
MS-spectrum found in GC spectrum for irradiated Aliquat-336 in DIPB and 5 vol%
dodecanol which have been in contact with nitric acid at channel 753.
The MS-spectrum could bee explain by $(C_8H_{17})_3HN^+$

GC 70_10_300_10 kolonn 572 OV1
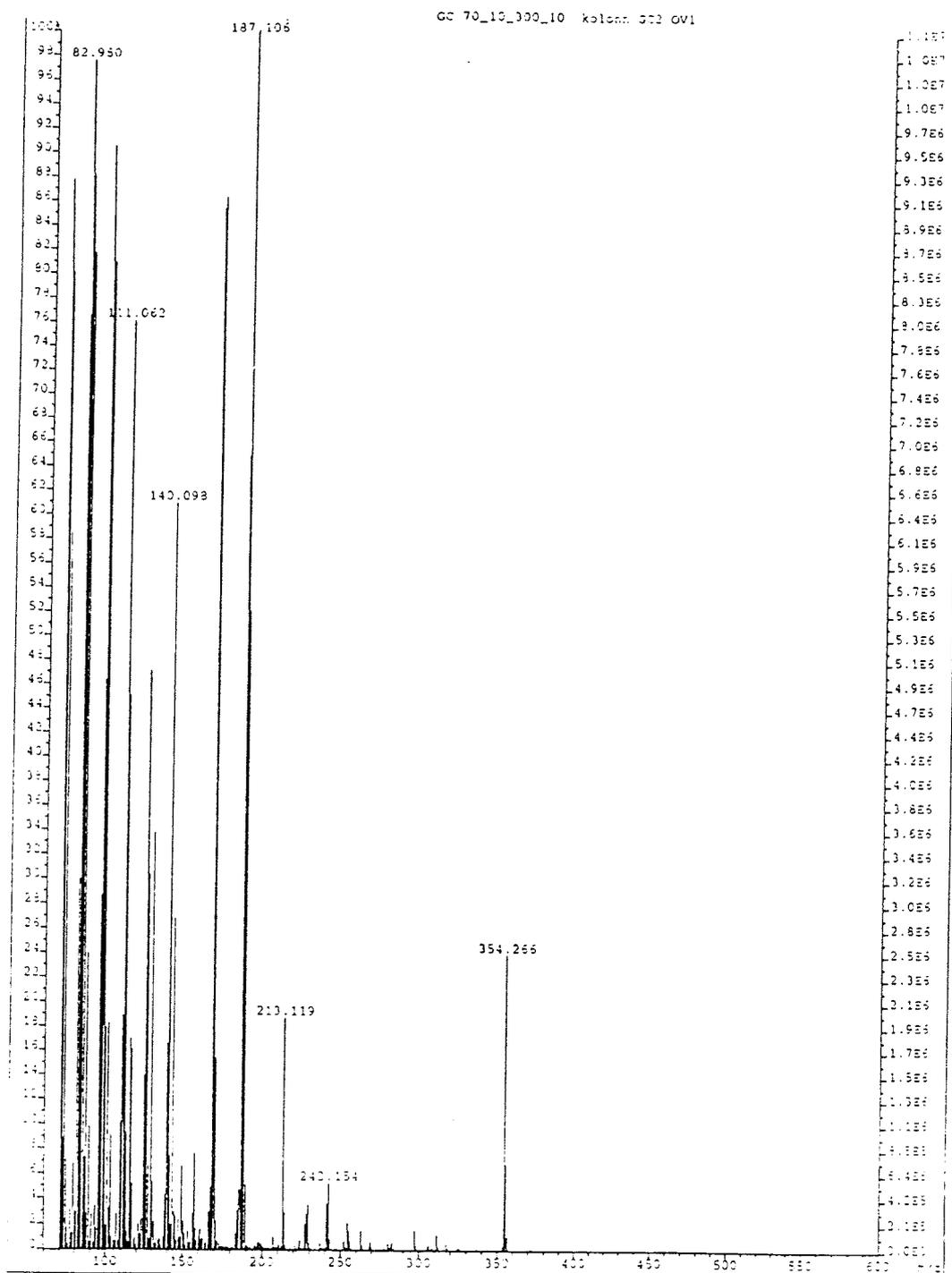
DMDPHTDMA in DIPB

GC spectrum of unirradiated DMDPHTDMA in DIPB

Channel 51 is toluene, which is used to wash the injection needle.

Channel 154 is DIPB and channel 234, 313 and 620 are impurities of the diluent, see page 2-4.

Channel 1192 is DMDPHTDMA

GC 70_10_300_20 kolonn GC2 OV1 50kPa
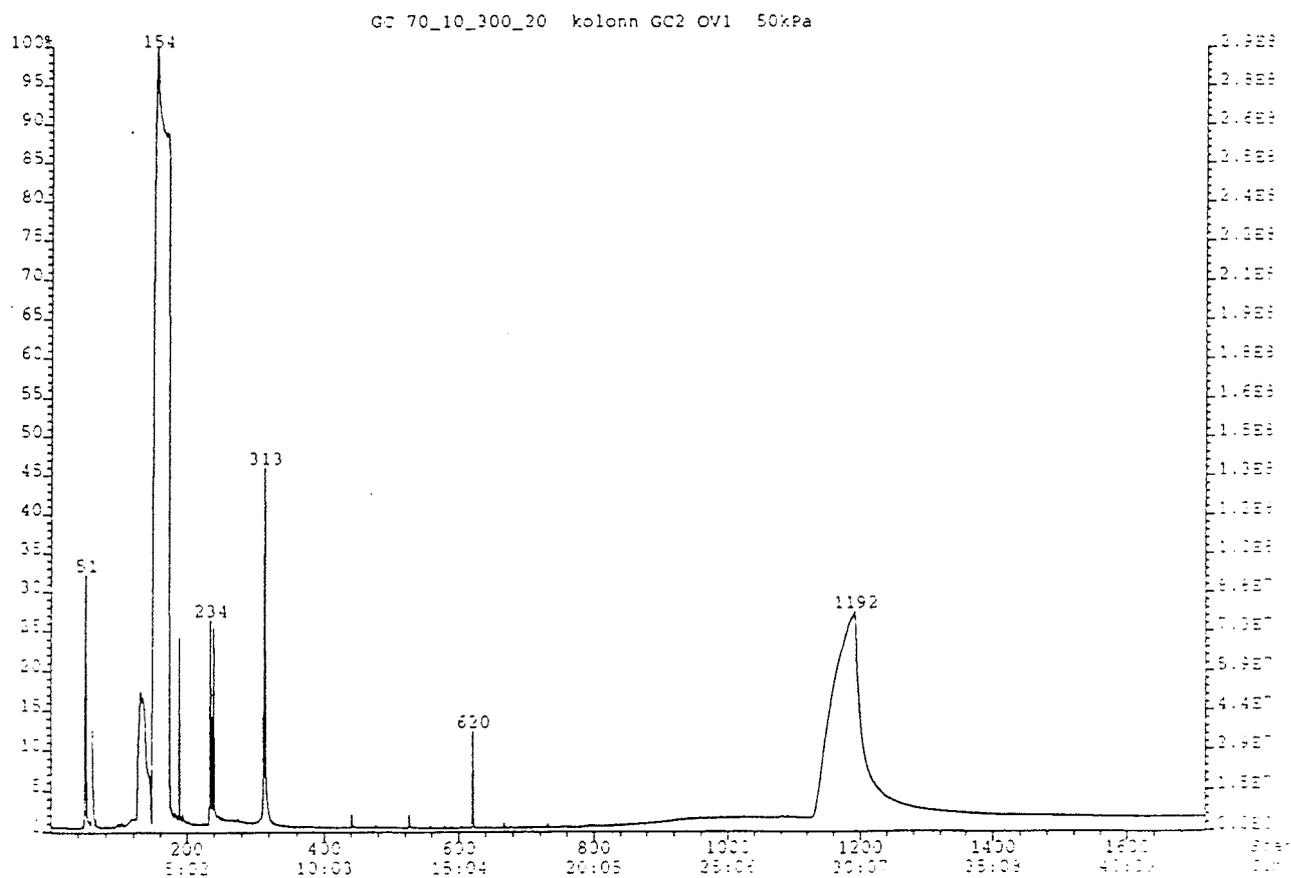
MS-spectrum found in GC spectrum for unirradiated DMDPHTDMA in DIPB at channel 1192
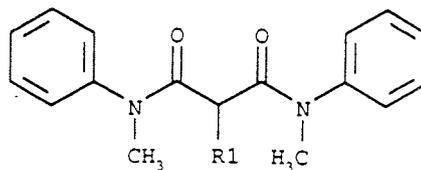
The MS-spectrum is DMDPHTDMA

$R1 = C_{14}H_{29}$

GC 70_10_300_20 kolonn GC2 OV1 50kPa
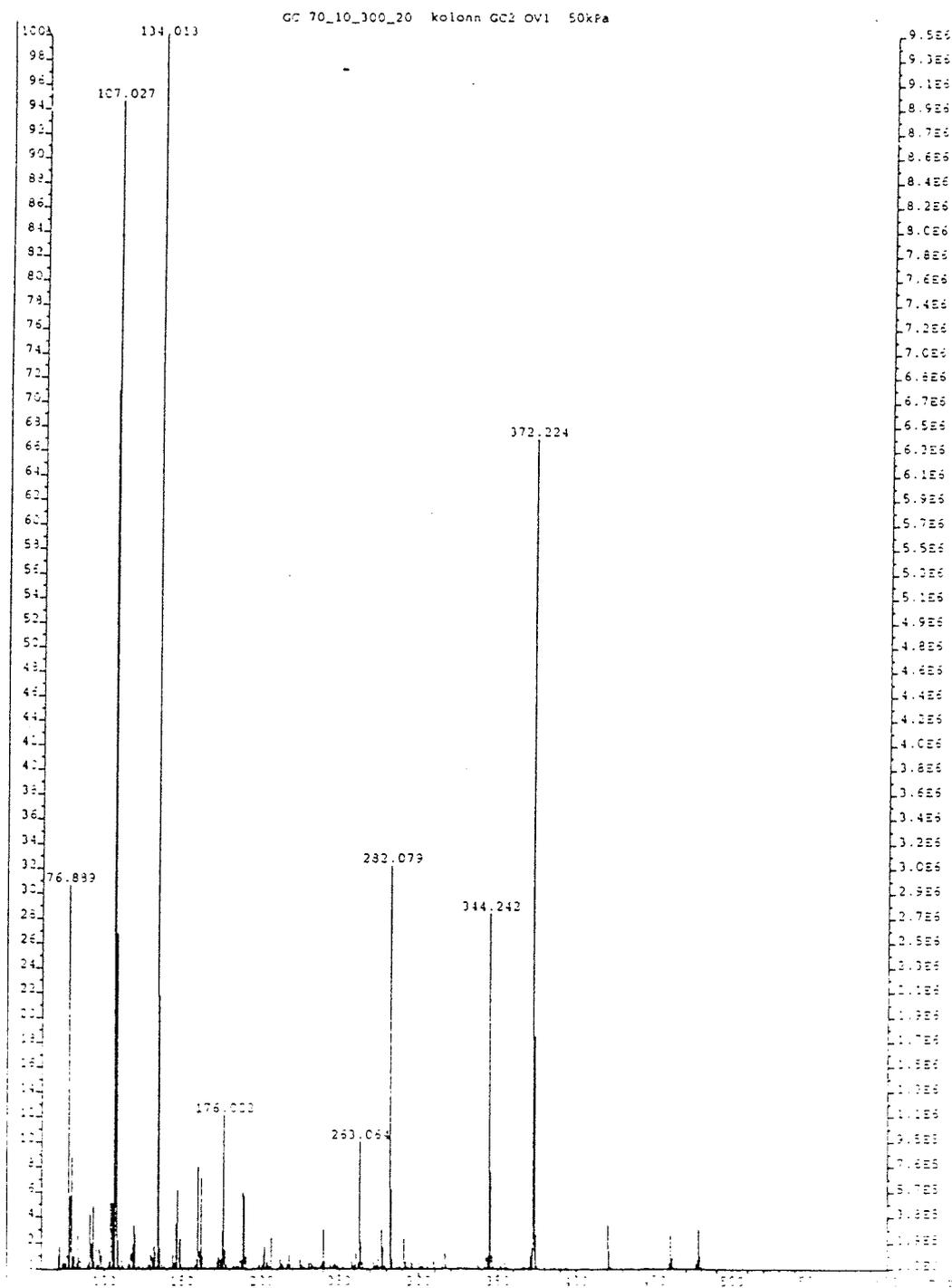
Irradiated DMDPHTDMA in DIPB

GS spectrum of irradiated DMDPHTDMA in DIPB. The sample was irradiated one month (37 kGy).

Channel 55 is toluene, which is used to wash the injection needle.

Channel 164 is DIPB and channel 246, 322 and 622 are impurities in the diluent, see page 2-4.

Channel 100 and 149 are degradation products of DIPB, see pages 6 and 7.

Channel 1241 are DMDPHTDMA, see page 24.

Channel 799 and 1081 are degradation products of DMDPHTDMA.
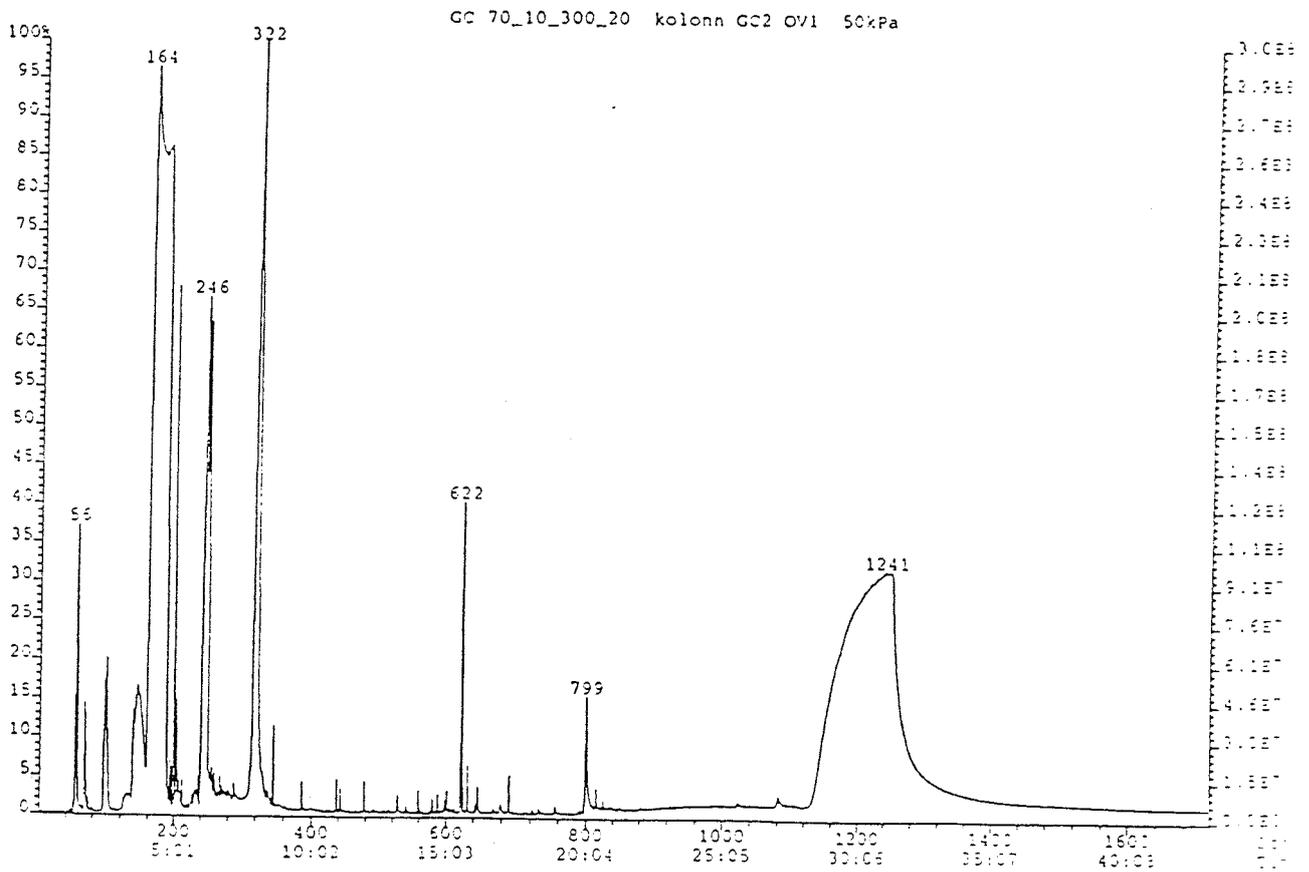
MS-spectrum found in GC spectrum for irradiated DMDPHTDMA in DIPB at channel 799
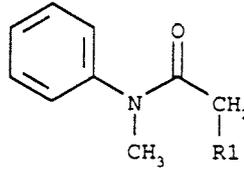
The MS-spectrum could bee explain by

R1 = C₁₄H₂₉
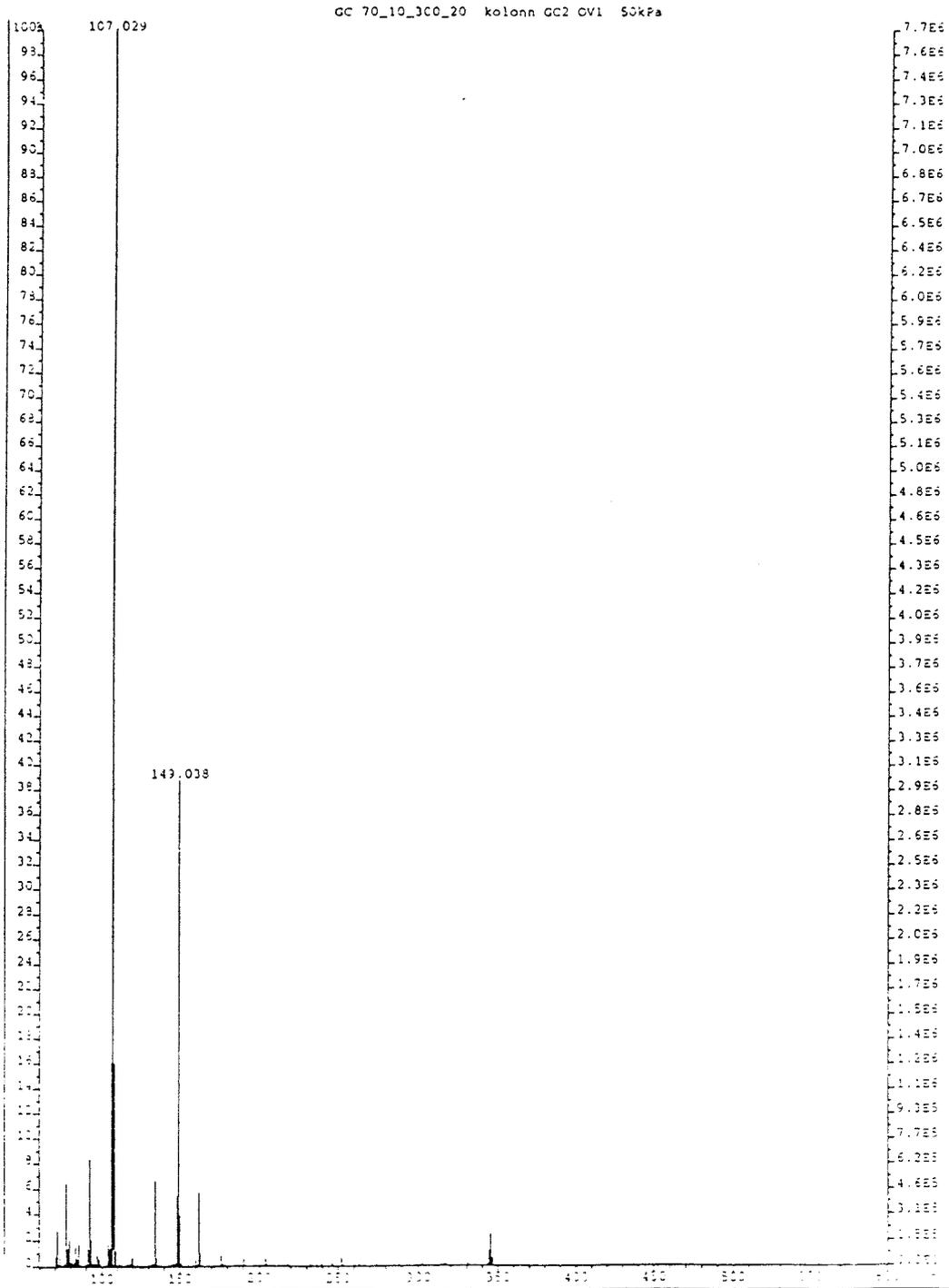
MS-spectrum found in GC spectrum for irradiated DMDPHTDMA in DIPB at

channel 1081
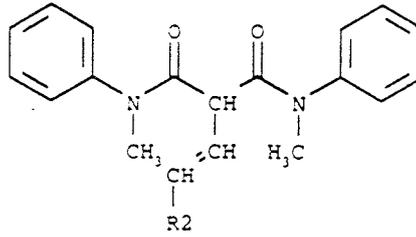
The MS-spectrum could bee explain by
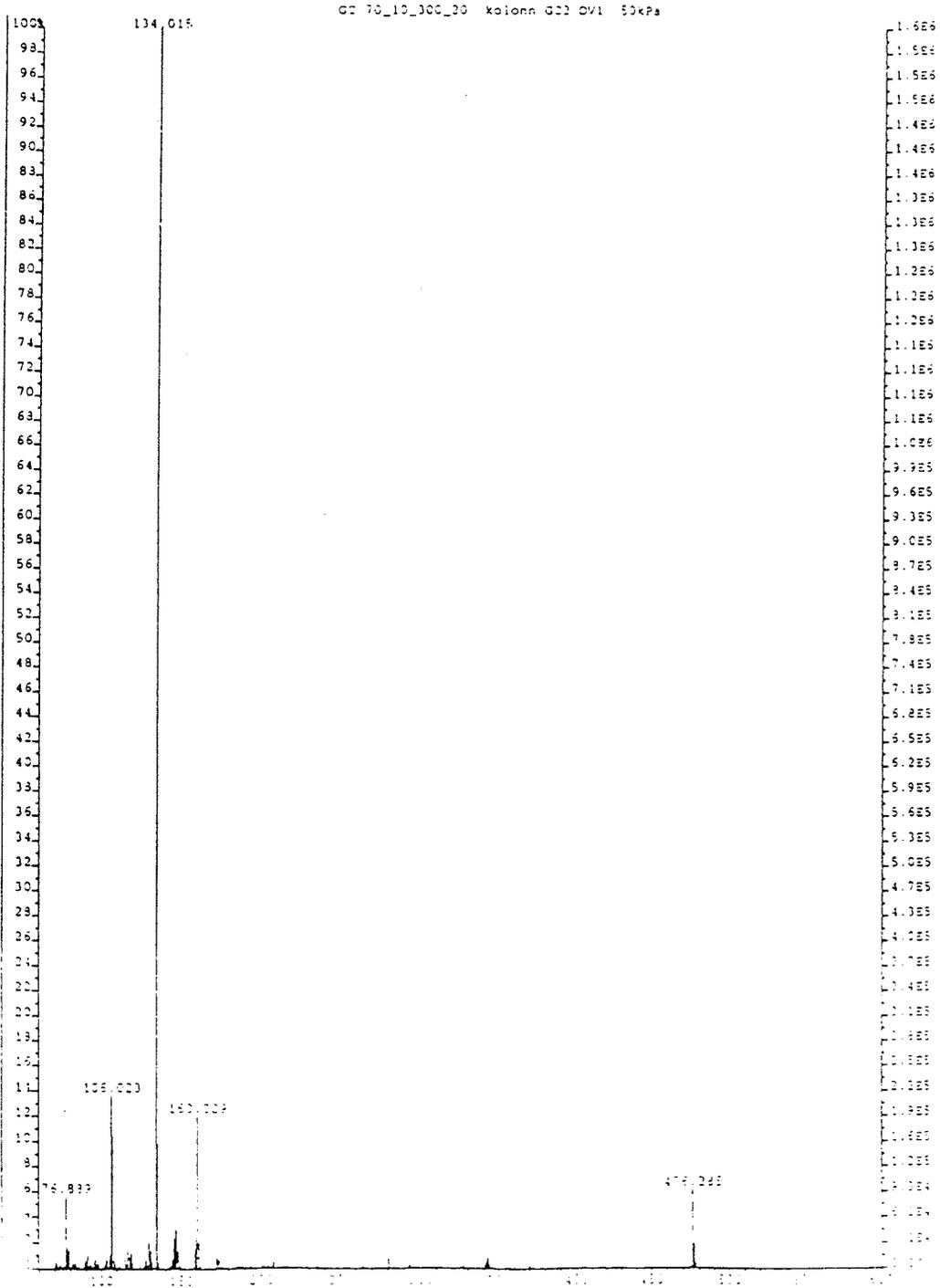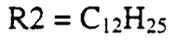
R2 = C$_{12}$H$_{25}$

Hydrolysis A of DMDPHTDMA in DIPB

GC spectrum of unirradiated DMDPHTDMA in DIPB which been in contact with nitric acid, during one month.

Channel 55 is toluene, which is used to wash the injection needle.

Channel 163 is DIPB and channel 241, 344 and 622 are impurities of the diluent, see page 2-4.

Channel 1320 are DMDPHTDMA, see page 24.

Channel 801 and 1079 are degradation products of DMDPHTDMA, see pages 26-27.

Channel 300 and 390 are degradation products to DMDPHTDMA.
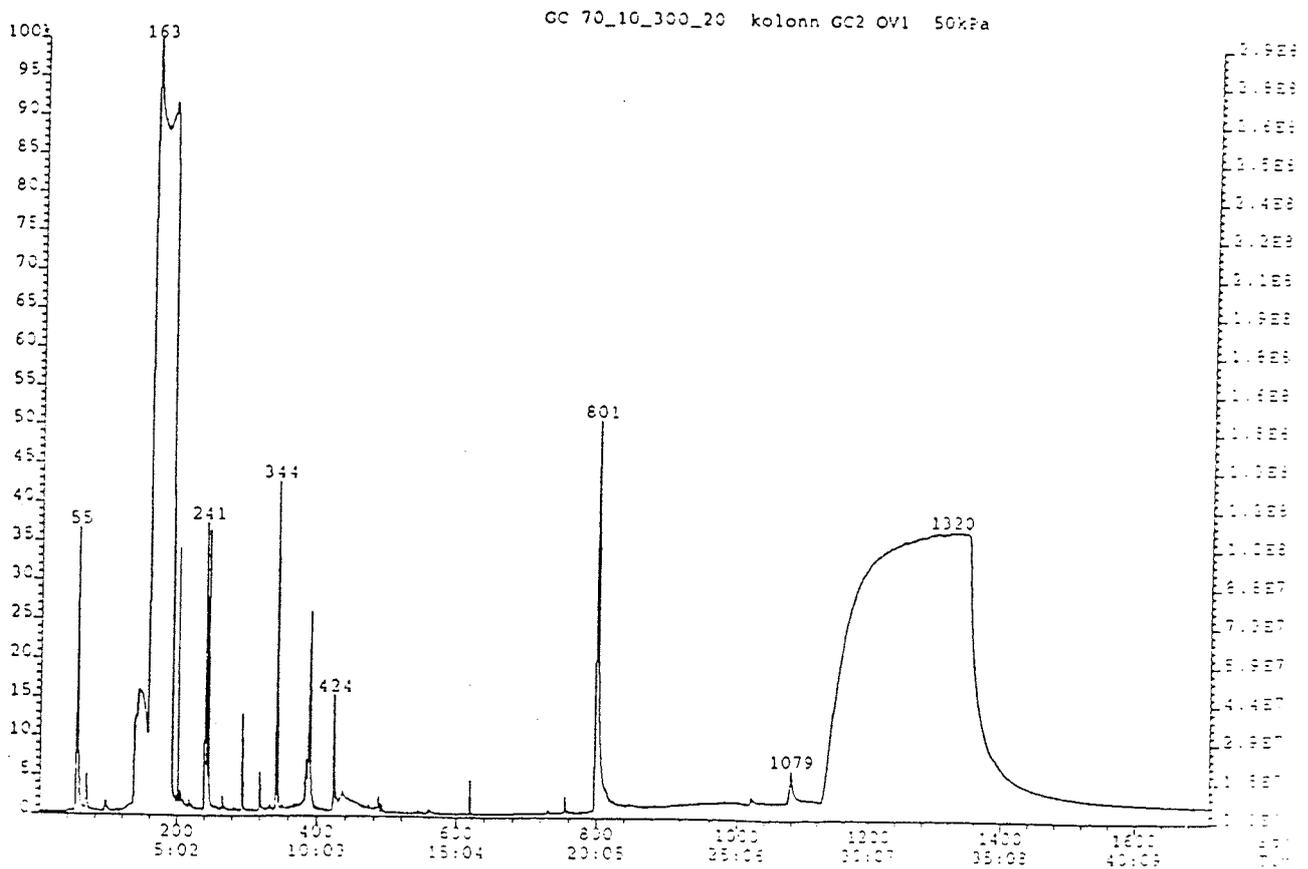
MS-spectrum found in GC spectrum for unirradiated DMDPHTDMA in DIPB which
been in contact with nitric acid, at channel 300.
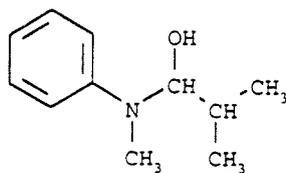
The MS-spectrum could bee explain by
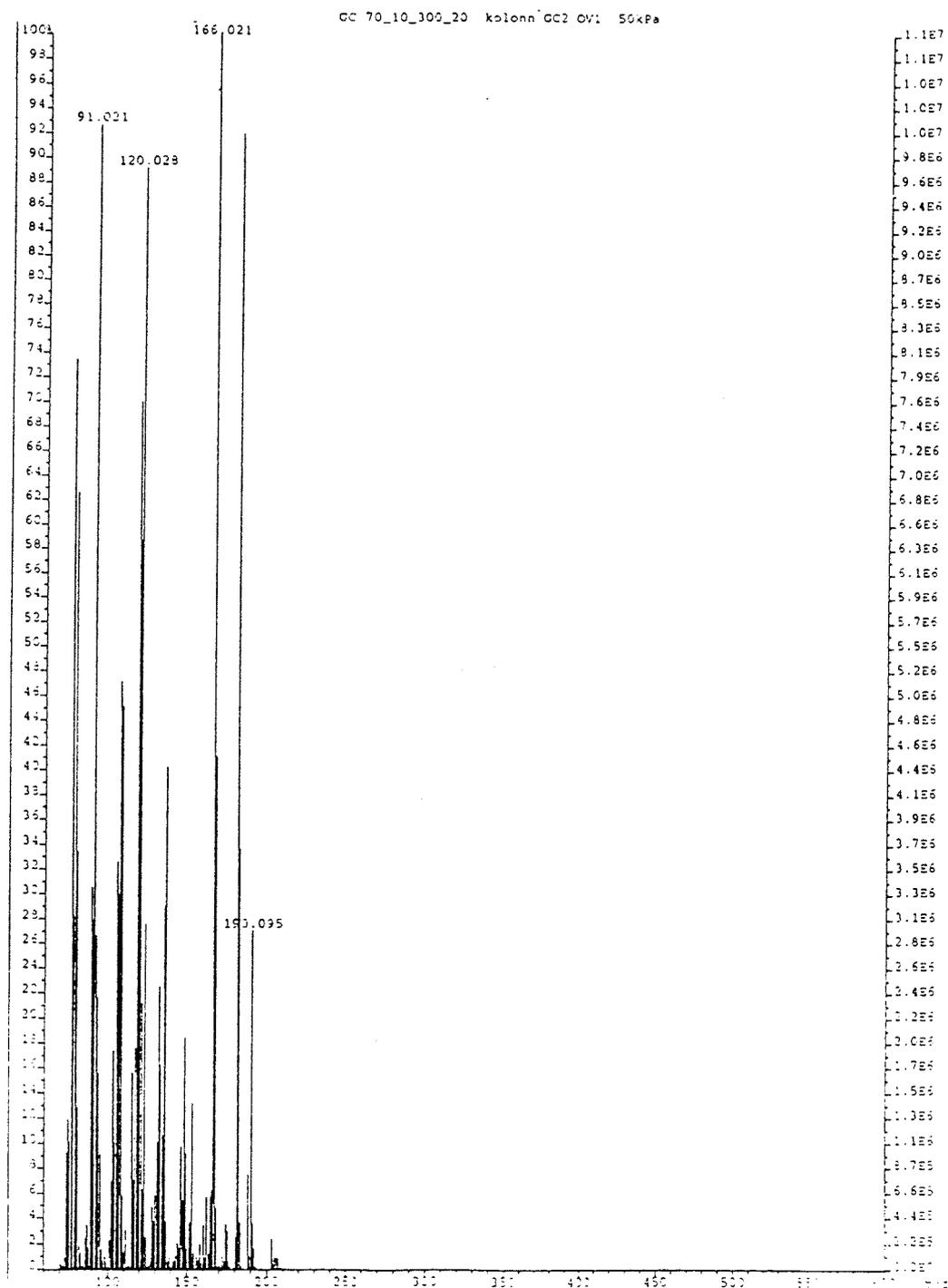
GC 70_10_300_20   kolonn GC2 OV1   50kPa

MS-spectrum found in GC spectrum for unirradiated DMDPHTDMA in DIPB which been in contact with nitric acid, at channel 396.

The MS-spectrum could bee explain by

GC 70_10_300_20   kolonn GC2 OV1   50kPa

163.079

91.021

119.053

223.092
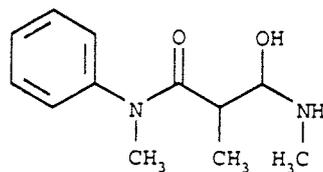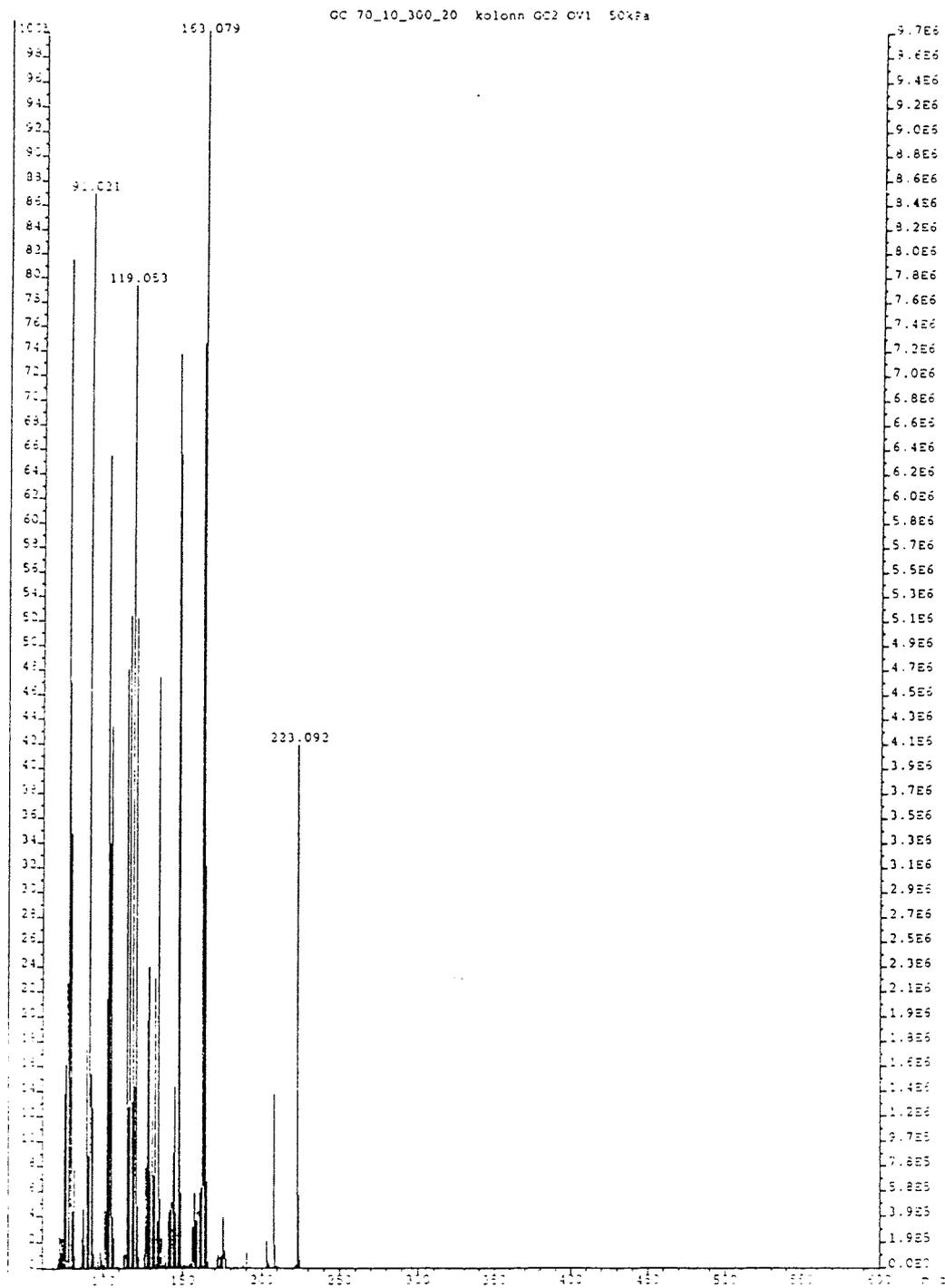
Hydrolysis B of DMDPHTDMA in DIPB

GC spectrum of unirradiated DMDPHTDMA in DIPB which been in contact with nitric acid, during one month..

Channel 22 is toluene, which is used to wash the injection needle.

Channel 65 is DIPB and channel 97, 137 and 317 are impurities in the diluent, see page 2-4.

Channel 490 is DMDPHTDMA, see page 24.

Channel 118 and 317 are degradation products of DMDPHTDMA, see pages 29-30.

GC 70_10_300_20
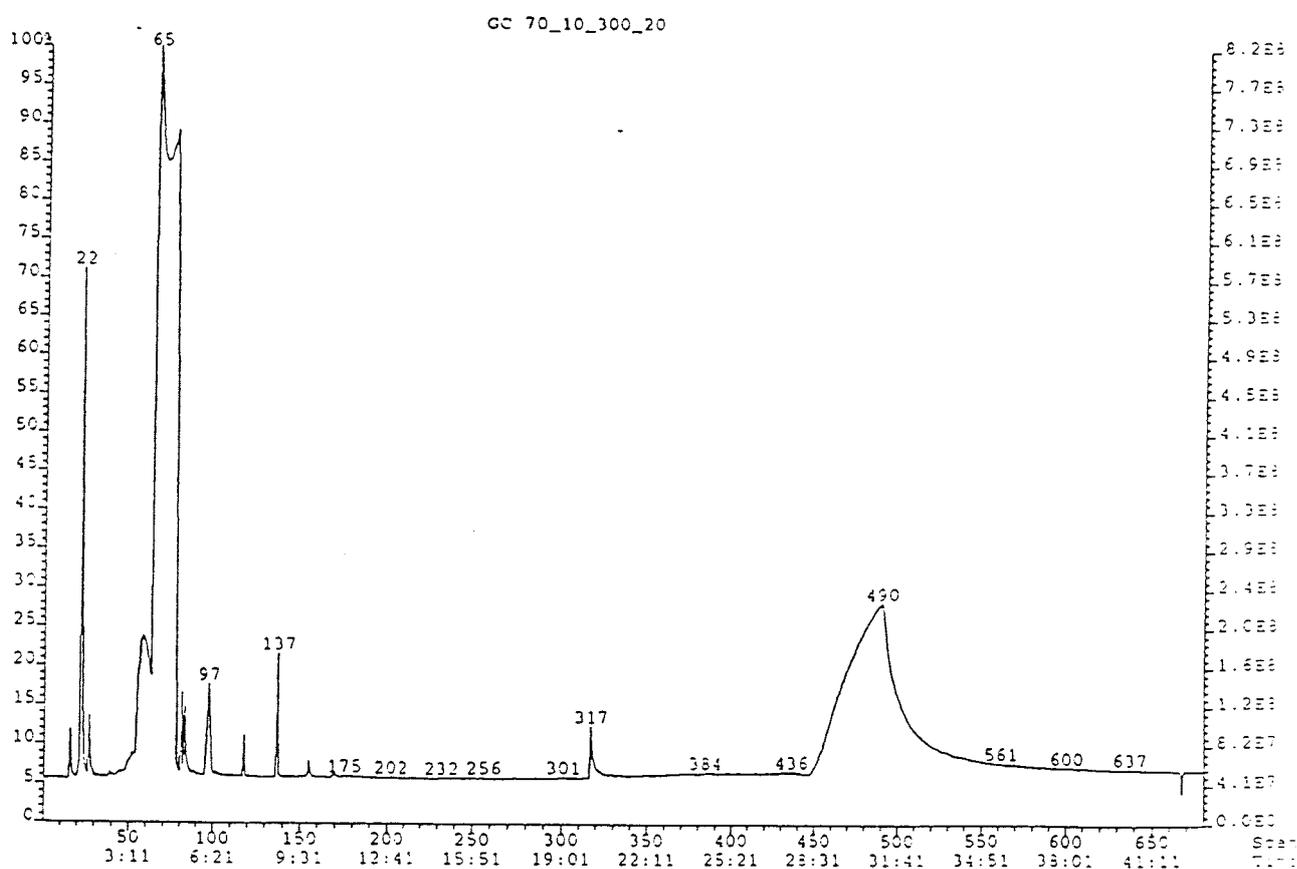
Irradiated DMDPHTDMA in DIPB which been in contact with acid

GC spectrum of irradiated DMDPHTDMA in DIPB which been in contact with acid.

The sample was irradiated one month (37 kGy).

Channel 55 is toluene, which is used to wash the injection needle.

Channel 164 is DIPB and channel 246, 322 and 620are impurities of the diluent, page 2-4.

Channel 1367 is DMDPHTDMA, see page 24.

Channel 800 and 1081 are degradation products of DMDPHTDMA, see page 29-30.

GC 70_10_300_20   kolonn GC2 OV1   50kPa
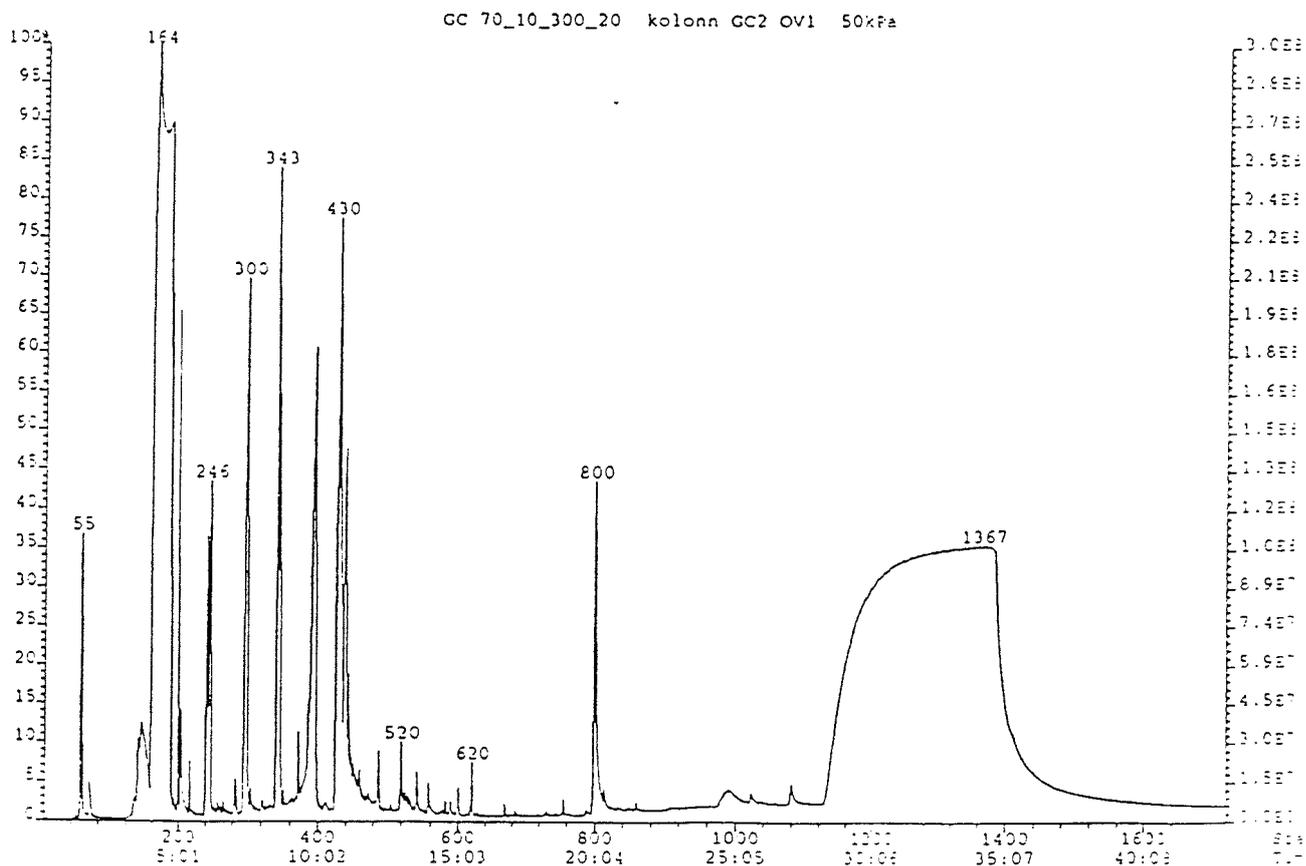
Appendix 3. Stability during irradiation or hydrolysis

Tables over all compounds, larger than 1% of DIPB, from the GC.spectra. The channel number every compound are named after comes from the GC-spectra. The compounds are sorted in three different types, DIPB and degradation products of DIPB, the extractants and the extractants degradation products.

Aliquat-336

Irradiated Aliquat-336 in DIPB and 5 vol% 1-dodecanol

Channel	Type	Relative area %
62	*	12,13
74	**	1,77
103	*	1,07
149	***	1,95
154	***	1,82
174	*	73,38
202	*	3,74
209	*	14,08
212	*	3,00
214	*	3,06
219	***	1,90
244	*	2,82
247	*	3,52
261	*	100,00
269	*	1,88
273	*	1,25

Channel	Type	Relative area %
281	*	3,36
313	*	3,47
324	*	6,25
336	*	65,46
344	*	28,48
348	*	21,80
360	*	6,30
365	*	9,99
459	**	12,57
492	***	1,03
544	**	17,59
556	***	1,09
561	***	1,25
622	*	4,38
628	*	2,08
639	*	12,03
651	*	1,27
661	***	1,24
686	*	4,44
689	**	6,34
697	***	2,37
708	*	2,11
719	*	2,45
756	**	10,45
787	*	3,08
828	***	4,07

Appendix 3. 2

*= diluent or degradation products from diluent

**= Aliquat-336

***=Aliquat-336 degradation products

% degraded Aliquat-336 = ***/(***+**)=21% Aliquat-336 was degraded, then

Aliquat-336 in DIPB and 5 vol% 1-dodecanol was irradiated for one month (37 kGy).

Irradiated Aliquat-336 in DIPB and 1-dodecanol, in contact with nitric acid

Channel	Type	Relative area %
61	*	6,41
148	***	1,05
175	*	100,00
206	*	2084
209	*	2,16
214	*	2,01
220	*	1,57
258	***	26,14
261	*	10,89
265	*	4,84
292	***	1,82
295	***	2,20
310	*	17,02
319	*	4,18
336	*	6,31
360	*	50,88
364	*	16,13
379	***	2,28
387	***	1,39
397	***	2,46
404	*	35,56
413	*	32,52
416	***	13,79
421	*	1,83
426	***	1,92
440	***	19,77
450	**	18,02

Channel	Type	Relative area %
462	***	8,42
464	***	7,96
473	***	7,78
480	***	1,54
483	***	1,32
504	***	3,84
514	***	1,50
548	**	17,49
565	***	3,13
604	***	5,75
623	*	5,86
628	*	2,18
638	*	3,83
641	*	2,77
679	**	6,48
690	*	8,74
706	*	1,95
715	*	7,46
737	***	2,11
743	***	4,07
754	**	19,93
763	*	20,61
787	*	2,88
821	***	1,49
833	**	11,69
912	**	1,64

Appendix 3. 5

*= diluent or degradation products from diluent

**= Aliquat-336

***=Aliquat-336 degradation products

% degraded Aliquat-336 = ***/(***+**)=55% Aliquat-336 was degraded, then Aliquat-336 in DIPB and 5 vol% 1-dodecanol was irradiated, in contact with nitric acid, for one month (37 kGy).

Unirradiated Aliquat-336 in DIPB and 1-dodecanol, in contact with nitric acid

Channel	Type	Relative area %
60	*	5,09
110	*	1,23
116	***	1,33
174	*	100,00
186	***	21,68
198	***	1,82
205	*	2,82
210	*	7,54
220	*	2,48
256	*	24,72
260	*	16,77
263	*	3,82
270	*	1,19
291	***	1,23
294	***	1,13
301	*	1,70
306	*	1,65
314	*	18,22
316	*	8,27
321	***	3,03
327	***	6,59
335	*	2,52
344	*	40,30
362	*	44,65
367	*	15,31
372	***	1,94
380	***	4,43

Channel	Type	Relative area %
402	*	13,69
409	*	12,38
416	*	14,46
427	*	1,26
440	***	7,24
444	***	1,17
450	**	2,17
463	**	22,03
473	***	1,88
502	***	1,76
524	***	1,21
531	***	2,29
548	**	33,30
558	***	2,25
565	***	4,57
602	***	9,15
614	*	1,44
623	*	12,74
641	*	4,34
658	*	1,12
679	**	12,95
690	*	30,83
695	***	5,66
702	*	1,22
705	*	1,47
716	*	15,31
723	***	2,18
736	***	2,24
742	***	1,54
754	**	52,43

Channel	Type	Relative area %
763	***	34,15
776	***	1,03
787	***	1,47.
797	***	2,33
810	***	1,42
833	**	22,52
837	***	10,86
879	***	2,23
913	**	4,10
928	***	1,21

*= diluent or degradation products from diluent

**= Aliquat-336

***= Aliquat-336 degradation products

% degraded Aliquat-336 = ***/(***+**)=47% Aliquat-336 was degraded, then Aliquat-336 in DIPB and 5 vol% 1-dodecanol was in contact with nitric acid during one month.

DMDPHTDMA

The samples containing DMDPHTDMA had to be diluted, because of a too wide peak of DMDPHTDMA. Unfortunately this makes that most of the small peaks, containing the degradation product of DMDPHTDMA, are not detectable.

Irradiated DMDPHTDMA in DIPB

Channel	Type	Relative area %
55	*	28,75
66	*	5,24
143	*	32,12
163	*	100,00
184	*	30,05
198	*	2,89
240	*	5,51
245	*	6,52
316	*	26,26
620	*	1,51
1136	**	5,93

*= diluent or degradation products from diluent

**= DMDPHTDMA

***= DMDPHTDMA degradation products

The sample was irradiated for one month, (37 kGy).

No degradation products are detected because the sample was diluted and that is difficult to observe any significant peaks. They exist but have an area less than 1% compared to the largest peak. If the peak should be detectable at least 1/** = 16 % of DMDPHTDMA must be degraded.

Irradiated DMDPHTDMA in DIPB which has been in contact with nitric acid

Channel	Type	Relative area %
56	*	29,94
68	*	4,25
143	*	33,60
162	*	100,00
187	*	68,80
199	*	5,35
240	*	6,93
245	*	10,63
295	*	2,25
316	*	23,53
340	***	1,66
343	***	1,60
389	***	1,40
1143	**	13,69

*= diluent or degradation products from diluent

**= Unirradiated DMDPHTDMA

***= DMDPHTDMA degradation products

Only three degradation products are detected because the sample was diluted which make is difficult to observe other peaks. They exist but have an area less than 1% of the largest peak. If the peak should be detectable at least 1/** = 7% of DMDPHTDMA must be degraded.

% degraded DMDPHTDMA = ***/(***+**)=35 of the DMDPHTDMA are degraded, when DMDPHTDMA was irradiated, in contact with nitric acid, for one month, (37 kGy).

Hydrolysis A of DMDPHTDMA in DIPB which has been in contact with nitric acid

Channel	Type	Relative area %
55	*	22,26
67	*	3,10
138	*	8,32
142	*	24,69
162	*	100,00
183	*	44,08
197	*	2,60
128	*	4,31
244	*	6,82
315	*	21,28
619	*	1,70
1138	**	5,21

*= diluent or degradation products from diluent

**= Unirradiated DMDPHTDMA

***= DMDPHTDMA degradation products

The sample was in contact with nitric acid during one month.

No degradation products are detected because the sample was diluted and that is difficult to observe any significant peaks. They exist but have an area less than 1% compared to the largest peak. If the peak should be detectable at least 1/** = 19 % of DMDPHTDMA must be degraded.

Appendix V

Extraction Studies and Process Calculation
for the Separation of
Trivalent Actinides and Lanthanides

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1997

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Summary

The second part of the DIAMEX process, i.e. the separation of trivalent actinides from lanthanides, has been simulated in a program. The DIAMEX process is one proposed process in a future partitioning and transmutation process, where the actinides are considered to be transmuted into less harmful elements.

To be able to simulate the liquid-liquid extraction process the ratios between different terpyridine and 2-bromodecanoic acid complexes in the aqueous and organic phase were determined. From the two-phase titration of terpyridine and 2-bromodecanoic acid a model has been adapted, which express the ratios between different terpyridine and 2-bromodecanoic acid complexes as a function of the concentrations of free protons at equilibrium. Further the distribution ratios of some lanthanides (La, Nd, Pm and Tb) and actinides (Am and Cm) were determined experimentally. A model, for the determined distribution ratios for the actinides and lanthanides, has been adapted with the model for the ratios of different species of terpyridine and 2-bromodecanoic acid as a basis. The model for the distribution ratios was expressed as a function of the concentration of dissociated 2-bromodecanoic acid in the aqueous phase and the concentration of free terpyridine in the organic phase. These two models have been inserted into the program.

The program was written in FORTRAN77 and simulates the process dynamically from the start of the process and stops when the changes in outgoing streams are small, i.e. when equilibrium is reached. The program was verified manually for a simple case and has been run for a various number of cases to see the effect on the percentage extraction of different input variables. Then a suitable operating point, which should not be too sensitive to disturbances in e.g. concentrations and flow rates in the different feeds to the batteries, was determined.

For the suggested operating point there are 5 wash stages, 10 extraction stages and 2 strip stages. The concentration of nitric acid in the wash feed, aqueous feed and strip feed was 0.01 M, 0.01 M and 0.2 M respectively. The concentrations of terpyridine and 2-bromodecanioc acid in the organic feed to the extraction battery were 0.02 M and 1.0 M respectively. The flow ratio between the organic feed and the aqueous feed was 0.44, between the wash feed and the aqueous feed 1.0 and between the strip feed and the organic feed 0.2. For these values the criterions of 99.9% extraction of the actinides and 0.1% extraction of the lanthanides are achieved.

Table of Contents

Appendices 1-18

1. Introduction

One of the problems with nuclear-generated electricity are the radioactive wastes, that the production generates. The composition of some lanthanides and actinides in the irradiated fuel are presented in table 1.1.

Table 1.1 Composition of some lanthanides and actinides in the irradiated fuel [JOL].

Element	m (g/ton U)	n (mole/ton U)	ratio (mole Me^{3+}/ mole Am^{3+})
La	843	6.069	23.2159
Ce	2005	14.310	54.740
Pr	737	5.230	20.008
Nd	2428	16.833	64.393
Pm	139	0.9456	3.617
Sm	444	2.953	11.296
Eu	109	0.7173	2.744
Gd	44	0.2798	1.070
Tb	1.3	0.00818	0.0313
Dy	0.56	0.00345	0.132
Ho	0.06	0.00036	$1.38 \cdot 10^{-3}$
Er	0.01	0.00006	$2.30 \cdot 10^{-4}$
Am	63	0.2614	1.0
Cm	19	0.07787	0.298

The irradiated fuel is treated in different ways in different countries. In Sweden, a deep geological repository storage of the irradiated fuel for hundred of thousands of years. A problem with this method is to predict the behaviour of the geological barriers for the long time that has to be considered apart from the squander of fissile and fertile materials that are left in the irradiated fuel. In France, the irradiated fuel is reprocessed by the PUREX process (Plutonium Uranium Redox EXtraction) to recover uranium and plutonium.

The wastes from the PUREX process are fission products, minor actinides and activation products and still contributes to a large potential radiotoxicity. Since the actinides represent a potential radiotoxicity about 10 000 times higher than the fission products, [Bau 93], it would be useful to separate and convert the actinides to less harmful species. This is the concept of partitioning and transmutation (P&T) projects around the world. An important step in a future partitioning process of spent nuclear fuel is the separation of trivalent actinides from lanthanides. The lanthanides are neutron absorbing species and if they are present during the irradiation, the transmutation process would become very inefficient [Skå 95]. The contribution from the lanthanides to the total radiotoxicity is also very low in the long term. In a

transmutation process the americium nuclides (^{241}Am and ^{243}Am) and the curium nuclide (^{245}Cm) could be transmuted into short-lived nuclides by neutron irradiation.

The separation of the actinides from the lanthanides can be performed in different ways. The best way would be to selectively extract all actinides from the wastes from a modified PUREX process, but this can not be done with any extractant available today. One possible way is to use the DIAMEX process (DIAMide EXtraction), where extractants and solvents are suggested to only contain carbon, hydrogen, oxygen and nitrogen atoms (the CHON-principle), which make them totally incinerable and thus do not generate secondary waste. In the modified PUREX process neptunium is also considered to be recovered. Neptunium is present in two valences, 20-30% Np(V) and 70-80% Np(VI) where the pentavalent state is non-extractible and the hexavalent Np is coextracted with plutonium. This implies that Np(V) has to be oxidised to Np(VI) before the extraction.

1.1 The DIAMEX process

The first step in the DIAMEX process, figure 1.1, is to coextract the lanthanides and actinides from the HLLW (High Level Liquid Waste) from the modified PUREX process. This is performed using a malonamide extractant with the semideveloped formulae, (RR'NCO)$_2$CHR", where R, R' and R" denotes alkyl or oxyalkyl groups. The malonamide is able to extract the nitrato complexes of lanthanides and actinides from high nitric acid concentration, such as the HLLW, and to strip these species into a diluted aqueous nitric acid solution [Bau 93].
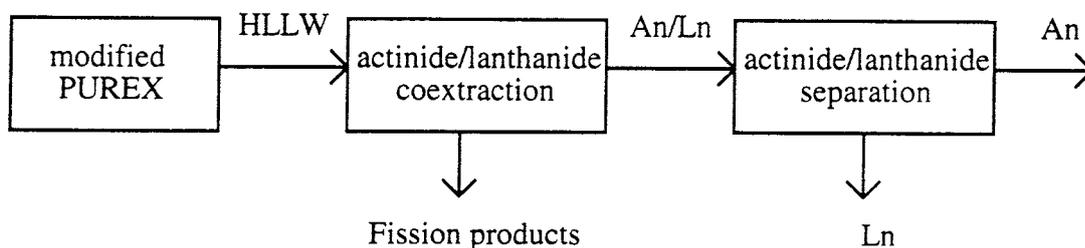
Figure 1.1 The DIAMEX process

An advantage of using a malonamide extractant is that it follows the CHON-principle. A drawback with this process is that the lanthanides, about one-third of all fission products, are extracted in the first step implying a higher dose to the extractant and this extraction of unnecessary species demand a large amount of extractant.

The second step is to separate the trivalent actinides from lanthanides and this separation is difficult due to the similar extraction behaviour because of the same valence state and ionic radius. A molar ratio of actinides to lanthanides of ~1/50 also implies that the separation is difficult. This task is performed by selective extraction of the actinides with extractants that have one or more nitrogen donor atoms, which show greater affinity to trivalent actinides than lanthanides. To be effective, the nitrogen containing extractant studied today, needs to be in a synergistic combination with a lipophilic acid with low pK$_a$ [Mad 94].

3

In this work, a process simulation of the actinide/lanthanide separation step has been performed. Terpyridine, figure 1.2, was used as the nitrogen donor extractant in a synergistic combination with 2-bromodecanoic acid (HA), figure 1.2, dissolved in *tert*-butylbenzene (tbb). To be able to do the process simulation, extraction data for the system was needed. The distribution of terpyridine and HA between the organic and aqueous phase and adduct formation of terpyridine and HA in the organic phase were also needed. A model for distribution and adduct formation of the terpyridine-HA-tbb system has been proposed and based on this model, extraction models for the lanthanides and actinides has been developed. Thereafter, a computer code has been written to simulate the process in a dynamic way.

2,2':6',2''-terpyridine

2-bromodecanoic acid (HA)
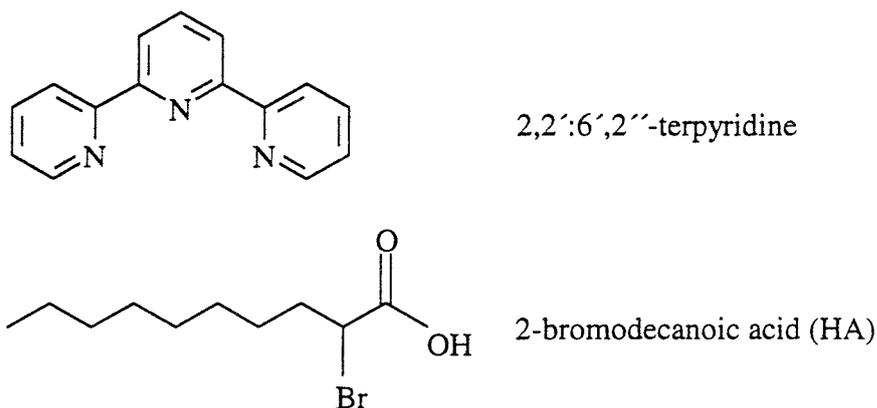
Figure 1.2 Extractants used in this work

4

2. Theory

Liquid-liquid extraction is a method to separate different species, in this work to separate trivalent actinides from lanthanides, and is based on distribution of the different species between two immiscible solvents. The two solvents often consist of an aqueous phase and an organic phase.

2.1 Distribution ratio

The extraction of a certain element M can be expressed as either the distribution ratio for element M or as the percentage extraction for element M. The distribution ratio, D_M, is defined according to equation 2.1 and the percentage extraction, $\%E_M$, is defined according to equation 2.2.

$$D_M = \frac{\text{Concentration of all species containing M in organic phase}}{\text{Concentration of all species containing M in aqueous phase}} = \frac{[M]_{tot,org}}{[M]_{tot,aq}} \qquad 2.1$$

$$\%E_M = 100 \cdot \frac{D_M \Theta}{1 + D_M \Theta} \qquad 2.2$$

Θ is the volume ratio between the organic phase and the aqueous phase.

2.2 Process calculation

For a single stage batch extraction, where a solute distributes between an aqueous and an organic phase, the weight fraction in the organic phase is described as;

$$\psi = \frac{P}{P + 1} \qquad 2.3$$

and the weight fraction in the aqueous phase is described as;

$$\varphi = \frac{1}{P + 1} \qquad 2.4$$

where P is called the extraction factor;

$$P = D\Theta \qquad 2.5$$

Denote that the percentage extraction $\%E = 100\psi$. In industry, continuous processes where the aqueous and organic phase flow countercurrent to each other are preferred. An extraction process often consists of an extraction battery, a wash battery and a strip battery, all with several stages. The purpose of the wash battery is to clean the desired product from impurities and the purpose of the strip battery is to transfer the extracted product to an aqueous phase.

5

For an industrial process both phase volumes and distribution ratios may vary for the different stages in the different batteries due to the extraction. For one stage, figure 2.1, the extraction factor is defined as;

$$P_j = D_j \frac{V_{org,j+1}}{V_{aq,j}} \qquad 2.6$$

and molar flow rates are defined according to;

$$\xi = X \cdot V_{aq} \qquad 2.7$$

$$\eta = Y \cdot V_{org} \qquad 2.8$$

where X is concentration in the aqueous phase (mol/dm^3)
       Y is concentration in the organic phase (mol/dm^3)
       V_{aq} is the flow rate of the aqueous phase (dm^3/s)
       V_{org} is the flow rate of the organic phase (dm^3/s).
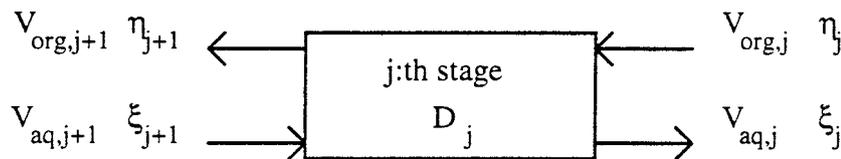
Figure 2.1 Definition of streams for one stage with countercurrent extraction.

The flow rates V_{aq} and V_{org} from any stage can usually be calculated from the apparent molar volumes, Φ_i, of the i compounds according to;

$$V_{aq} = V_{0,aq} \sum_i \left(1 + \Phi_{i,aq} X_i \right) \qquad 2.9$$

$$V_{org} = V_{0,org} \sum_i \left(1 + \Phi_{i,org} Y_i \right) \qquad 2.10$$

where $V_{0,aq}$ and $V_{0,org}$ are the flowrates of the pure phases in each stage. For a process, figure 2.2, five extraction functions can be defined.

$$e_1 = \left(1 + \sum_{i=1}^{N} \prod_{k=i}^{N} P_k \right) \qquad 2.11$$

$$e_2 = \left(1 + \sum_{i=2}^{N} \prod_{k=i}^{N} P_k \right) \qquad 2.12$$

$$s_1 = \left(1 + \sum_{i=N+2}^{M+N+1} \prod_{k=i}^{M+N+1} P_k\right) \qquad 2.13$$

$$s_2 = \left(1 + \sum_{i=N+3}^{M+N+1} \prod_{k=i}^{M+N+1} P_k\right) \qquad 2.14$$

$$\zeta = \prod_{k=N+2}^{M+N+1} P_k \qquad 2.15$$
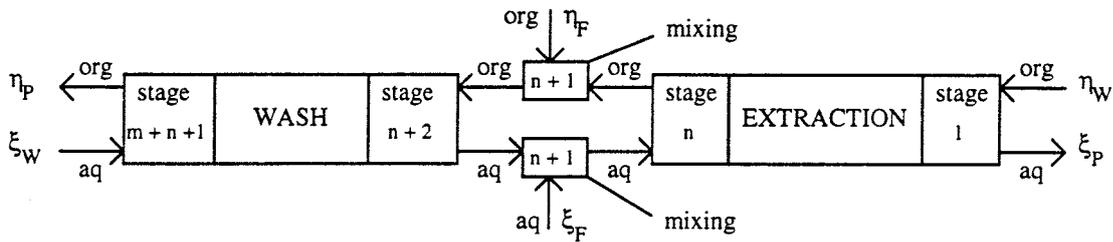
Figure 2.2 Countercurrent extraction with n extraction stages and m washing stages.

The molar flow rates of the outgoing aqueous phase, ξ_P, and the outgoing organic phase, η_P, can be calculated, through a series of molar balances.

$$\xi_P = \frac{\xi_W + \eta_W(e_2\zeta + s_2) + \xi_F s_1 + \eta_F s_2}{e_1\zeta + s_2} \qquad 2.16$$

$$\eta_P = \xi_F + \xi_W - \xi_P + \eta_F + \eta_W \qquad 2.17$$

For a more detailed description of the different molar balances, see [Per 83].

2.3 Protonation of terpyridine

Two-phase titration of terpyridine-HA-tbb and an aqueous phase shows that the pH decreases less than expected when HNO_3 is added. This effect is due to the protonation of terpyridine. It has been shown that terpyridine can be diprotonated and the protonated species are present in the aqueous phase. The mechanism for the protonation of terpyridine can be described according to equations 2.18 - 2.21.

$$T \xleftarrow{\lambda_T} \overline{T} \qquad 2.18$$

$$T + H^+ \xleftarrow{k_1} TH^+ \qquad 2.19$$

$$T + 2H^+ \xleftarrow{\quad k_2 \quad} TH_2^{2+}$$

2.20

$$H^+ + NO_3^- \xleftarrow{\quad k_a \quad} HNO_3$$

2.21

T is terpyridine and overlined species denotes species in the organic phase. The association constant for nitric acid, $k_a = 10^{-1.35}$ [Hägg], and protonation constants for terpyridine, $k_1 = 5.13 \cdot 10^4$ and $k_2 = 1.9 \cdot 10^8$ (0.1 M ionic strength and 23°C), were used [Sch 84]. The distribution constant, $\lambda_T = 239$, was used [Hag 97].

2.4 Adduct formation between terpyridine and 2-bromodecanoic acid

When 2-bromodecanoic acid is present in the organic phase the protonation of terpyridine is decreased. This is probably due to adduct formation between terpyridine and 2-bromodecanoic acid in the organic phase. The adduct formation can be described as;

$$\overline{T} + n\overline{HA} \xleftarrow{\quad k_{ad,n} \quad} \overline{(HA)_n T}$$

2.22

where HA is 2-bromodecanoic acid. No values of the adduct formation constants, $k_{ad,n}$, were available in literature.

2.5 Extraction mechanism

When 2-bromodecanoic acid is dissolved in non-polar solvents, i.e. *tert*-butylbenzene, the acid is dimerised according to;

$$2\overline{HA} \xleftarrow{\quad K_d \quad} \overline{(HA)_2}$$

2.23
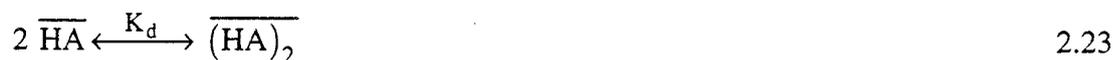
When 2-bromodecanoic acid is in contact with an aqueous phase it will be distributed between the organic phase and the aqueous phase and is slightly dissociated in the aqueous phase;

$$HA \xleftarrow{\quad \lambda_{HA} \quad} \overline{HA}$$

2.24

$$H^+ + A^- \xleftarrow{\quad K_a \quad} HA$$

2.25

No values of either the dimerisation constant, K_d, or the distribution constant, λ_{HA}, were found in literature. The dissociation constant of 2-bromodecanoic acid is $K_a = 10^{3.7}$ at 0.001 M ionic strength [Hag 97].

To study the extraction mechanism for the system with terpyridine and 2-bromodecanoic acid equations 2.18 to 2.22 have to be considered to determine the distribution of the different species of terpyridine and equations 2.22 to 2.25 have to

be considered to determine the distribution of the different species containing 2-bromodecanoic acid.

Complexation in the aqueous phase was assumed to occur between the dissociated 2-bromodecanoic acid and the free metal ion according to equation 2.26. Due to the low concentrations of nitric acid, complexation with nitrate ions is probably negligible.

$$M^{3+} + xA^- \xleftrightarrow{\alpha_x} MA_x^{3-x} \qquad\qquad 2.26$$

Neutral complexes, such as MA_3, is soluble in the organic phase and thus MA_3 will distribute between the aqueous phase and the organic phase;

$$MA_3 \xleftrightarrow{\lambda_L} \overline{MA_3} \qquad\qquad 2.27$$

No values for either the complex formation constants, α_x, or the distribution constant, λ_L, were found in literature. In the organic phase, mixed complexes with MA_3, 2-bromodecanoic acid and terpyridine may be formed;

$$\overline{MA_3} + m\overline{HA} + n\overline{T} \xleftrightarrow{Q_{mn}} \overline{MA_3(HA)_m T_n} \qquad\qquad 2.28$$
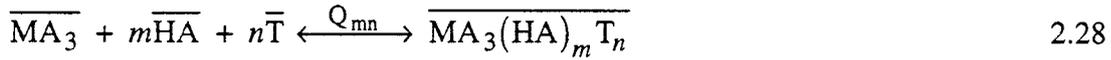
Now the distribution ratio of the metal element M can be calculated from equations 2.26 and 2.28 yielding;

$$D_M = \frac{\displaystyle\sum_{m=0}^{M}\sum_{n=0}^{N}\left[\overline{MA_3(HA)_m T_n}\right]}{\displaystyle\sum_{x=0}^{X}\left[MA_x^{3-x}\right]} \qquad\qquad 2.29$$

Equation 2.29 can be expanded by inserting equations 2.22, 2.24-2.28.

$$D_M = \frac{\displaystyle\sum_{m=0}^{M}\sum_{n=0}^{N} Q_{mn}\lambda_L \lambda_{HA}^m \alpha_3 K_a^m \left[A^-\right]^{3+m}\left[H^+\right]^m\left[\overline{T}\right]^n}{\displaystyle\sum_{x=0}^{X}\alpha_x\left[A^-\right]^x} \qquad\qquad 2.30$$

2.6 Corrections for decay

For some of the nuclides, correction for decay during acquisition has to be performed, in order to compare the activity in the aqueous and organic phase of the same sample. Each correction can be made with a correction factor, f, which is defined as the ratio between the measured activity, A_m, to the corrected activity A_0.

Due to the low activity in the organic phase when the initial concentration of HNO_3 in the aqueous phase is above 0.10 M, the measuring times has been relatively long compared with the half-lives of the nuclides ^{140}La (half-life 40.272 h), ^{147}Nd (half-life 10.98 d) and ^{160}Tb (half-life 72.3 d). Therefore, a correction for decay during the time of measurement is necessary and the correction factor is defined as;

$$f_1 = \frac{1 - e^{-\lambda_i t_m}}{\lambda_i t_m} \qquad\qquad 2.31$$

Since it was not possible to measure the aqueous phase and the organic phase of the same sample at the same time a correction for decay between sampling and measurement is necessary. This was done for the nuclides ^{140}La, ^{147}Nd, ^{160}Tb because of their short half-lives and for ^{147}Pm (half-life 2.62 y) due to long time between measurements of the different phases. The correction factor is defined as;

$$f_2 = e^{-\lambda_i t_s} \qquad\qquad 2.32$$

For the nuclides ^{140}La, ^{147}Nd and ^{160}Tb both corrections needs to be taken into account yielding equation 2.33 and for some of the samples with ^{147}Pm the correction according to equation 2.31 needs to be taken into account yielding equation 2.34.

$$A_m = A_0 \cdot f_1 \cdot f_2 = A_0 \cdot \frac{1 - e^{-\lambda_i t_m}}{\lambda_i t_m} \cdot e^{-\lambda_i t_s} \qquad\qquad 2.33$$

$$A_m = A_0 \cdot f_2 = A_0 \cdot e^{-\lambda_i t_s} \qquad\qquad 2.34$$

where A_m is the measured activity (Bq)
$\qquad$ A_0 is the corrected activity (Bq)
$\qquad$ λ_i is the decay constant for the measured nuclide (s^{-1})
$\qquad$ t_s is the time between sampling and measurement (s)
$\qquad$ t_m is the measuring time (s)

3. Experimental

Extraction data for many of the actinides and lanthanides with 0.02 M terpyridine, 1.0 M 2-bromodecanoic acid (HA) in *tert*-butylbenzene are not available in the literature. Extraction studies were therefore performed for lanthanum, neodymium, promethium, terbium and curium. The D-values were determined as a function of nitric acid concentration. Protonation of terpyridine in synergistic mixture with HA was also studied. All experiments were performed at room temperature.

3.1 Materials

Aldrich provided 2,2':6',2"-terpyridine (98% purity) and *tert*-butylbenzene (99% purity) and 2-bromodecanoic acid (HA), 98% purity, was bought from Fluka.

3.2 Determination of extraction curves

1 ml aqueous phase of different nitric acid concentration and radioactive tracers were added to a test tube. The test tube was sealed and was allowed to stand for at least an hour to equilibrate. 1 ml of the organic phase, 0.02 M terpyridine, 1.0 M HA in tbb, was added to the test tube. The tubes were shaken vigorously for five minutes at room temperature, a time which enables equilibrium between the two phases to be reached, and centrifuged at 5000 rpm for ten minutes. Depending on the radionuclide and the nitric acid concentration, different volumes of samples, 0.05-0.7 ml of the aqueous phase and 0.05-0.9 ml of the organic phase, were taken and added to the measuring vials. Depending on the radionuclide different detectors and measuring times were used, see 3.6, to determine the distribution ratio.

3.3 Two-phase titration of terpyridine

To determine the protonation of terpyridine in HA and tbb and the adducts of terpyridine with HA in tbb a two-phase titration at constant ionic strength (I = 1 M) were performed. Three titrant solutions, 0.25 M HNO_3, 0.5 M HNO_3 and 1.0 M HNO_3 in $NaNO_3$, $[NO_3^-]_{tot}$ = 1 M, were prepared. 8 ml 1 M $NaNO_3$ and 4 ml 0.02 M terpyridine, 1.0 M HA in tbb were added to a beaker. The potential (E) in mV was measured in the aqueous phase at equilibrium and then 0.1 to 1.0 ml of one of the three titrant solutions was added to achieve a slow change in potential. The solution was vigorously stirred for 3 minutes before a new measurement of the potential was performed and this was repeated several times. To determine the concentration of free protons from the potential (E) a calibration curve with the same ionic strength (I = 1 M) was determined.

3.4 Purification of Curium standard

The curium standard was slightly impure, contained ^{239}Pu. The decay product from ^{244}Cm (^{240}Pu) was negligible compared to the impurity of ^{239}Pu. To separate plutonium from curium, extraction with Aliquat-336 was used. Aliquat-336 extracts plutonium to the organic phase and curium is left in the aqueous phase. The same

11

volume of 0.2 M Aliquat-336 in 1,3-diisopropylbenzene (DIPB) was added to the curium standard. The solution was shaken for five minutes and then centrifuged for 5 minutes at 5000 rpm. As much as possible of the organic phase was discarded before fresh organic solvent was added. The plutonium extraction was repeated 10 times to achieve a sufficiently low plutonium concentration in the aqueous phase. Now, the curium standard was cleaned from the Aliquat-336 that was dissolved in the aqueous phase and this was achieved by shaking the standard with equal volume of 1,3-DIPB for 2 minutes and centrifuge it at 5000 rpm for 3 minutes. After the organic phase was discarded the cleaning was repeated once more. The curium standard was then shaken with the same volume of n-hexane for 2 minutes and centrifuged at 5000 rpm for 5 minutes. After the organic phase was discarded this was repeated once more and when the organic phase had been discarded for the second time the curium standard was ready for use.

3.5 Radionuclides

The radionuclides used in the experiments were either available at the department (^{147}Pm and ^{244}Cm) or produced by neutron irradiation in the reactor at Ife Kjeller (^{140}La, ^{147}Nd and ^{160}Tb). The curium standard was purified from plutonium on July 1st, 1997. La, Nd and Tb were produced by irradiation of the stable metal oxide (i.e. ^{139}La$_2$O$_3$). The amount of metal oxide to be irradiated was calculated as;

$$m_{Ln_2O_3} = \frac{N_t}{2N_A x_i} M_{Ln_2O_3} \qquad 3.1$$

where Ln is the lanthanide La, Nd or Tb

$m_{Ln_2O_3}$ is the amount of metal oxide in gram

$M_{Ln_2O_3}$ is the molecular weight of the metal oxide in gram/mol

x_i is the atomic fraction of the isotope i to be converted

N_A is the Avogadro constant, $6.022 \cdot 10^{23}$ mol^{-1}

N_t is the number of atoms and is calculated according to Eq 3.2

$$N_t = \frac{A}{\Phi_0 \sigma_{eff} \left(1 - e^{-\lambda t_{irr}}\right) e^{-\lambda t_{cool}}} \qquad 3.2$$

where A is radioactivity in Bequerel, 20 mCi = $7.4 \cdot 10^8$ Bq

t_{irr} is the irradiation time, 7 days

t_{cool} is the cooling time, 1 day

Φ_0 is the neutron flux in n/(cm^2·s) = $1.4 \cdot 10^{13}$

σ_{eff} is the effective neutron absorption cross-section in cm^2 and is calculated according to Eq. 3.3

$$\sigma_{eff} = \sigma_{th} + 0.1 \cdot RI \qquad 3.3$$

where σ_{th} is the thermal neutron absorption cross-section in cm^2

RI is the resonance integral in cm^2

3.6 Measuring conditions

3.6.1 Lanthanum

The radionuclide ^{140}La has γ -energies at 328.8 keV (20.7%), 487 keV (45.9%), 815.8 keV (23.6%), 1596.5 keV (95.4%) and 2521.7 keV (3.43%). The γ -energy at 487 keV was used and was measured by a high purity germanium (HPGe) detector. The measuring times varied between 2 minutes and 5 hours. Due to the relatively short half-life (40.272 h) of ^{140}La, compared to the measuring time, we had to compensate for both disintegration during measurement and for the different times, when the measurements of the different phases were done, see 2.6. The concentration of lanthanum was $3.48 \cdot 10^{-3}$ M in the 0.7 M nitric acid stock solution. A volume between 0.01 ml and 0.4 ml was added in each experiment.

3.6.2 Neodymium

The radionuclide ^{147}Nd has γ -energies at 91.1 keV (27.9%) and 531 keV (13%). The γ -energy at 91.1 keV was used and was measured by a high purity germanium (HPGe) detector. The measuring times varied between 3 minutes and 117 hours. Due to the relatively short half-life (10.98 d) of ^{147}Nd compared to the measuring time, we had to compensate for both disintegration during measurement and for the different times, when the measurements of the different phases were done, see 2.6. The concentration of neodymium was 0.22 M in the 0.82 M nitric acid stock solution. 0.01 ml of the stock solution was added in each experiment.

3.6.3 Promethium

The radionuclide ^{147}Pm, which is a β^- - and γ - emitting nuclide has very weak γ -intensities so in these experiments the β^- decay was measured with a LKB Wallac 1219 Rackbeta liqiud scintillation counter. 15 ml of scintillation cocktail, Emulsifier Safe, was added to each measuring vial. The measuring times varied between 2 and 5 minutes. Due to the relatively short half-life (2.62 y) of ^{147}Pm compared to the different times of measurement, we had to compensate for the different times of the measurements of the different phases, see 2.6. A volume between $5 \cdot 10^{-3}$ ml and 0.05 ml of the 0.8 M nitric acid stock solution was added in each experiment.

13

3.6.4 Terbium

The radionuclide ^{160}Tb has γ-energies at 46.0 keV (10.7%), 86.8 keV (13.2%), 298.6 keV (26.8%), 879.4 keV (29.8%), 966.2 keV (25.0%) and 1177.9 keV (15.2%). The γ-energy at 298.6 keV was used and was measured by a high purity germanium (HPGe) detector. The measuring times varied between 6 minutes and 64 hours. Due to the relatively short half-life (72.3 d) of ^{160}Tb compared to the measuring time, we had to compensate for both disintegration during the measurement and for the different times, when the measurements of the different phases were done, see 2.6. The concentration of terbium was $5.54 \cdot 10^{-3}$ M in the 0.61 M nitric acid stock solution. 0.01 ml of the stock solution was added in each experiment.

3.6.5 Curium

The radionuclide ^{244}Cm disintegrates by emitting α-particles with energies of 5.77 MeV and 5.80 MeV. 15 ml of scintillation cocktail, Emulsifier Safe, was added to each measuring vial, after which measurement was made by a LKB Wallac 1219 Rackbeta liqiud scintillation counter. The measuring time was 2 minutes. Volumes between 0.01 ml and 0.02 ml of the 0.63 M nitric acid stock solution were added in each experiment.

14

4. Results and discussion

4.1 Determination of the extraction curves

When the nitric acid concentration is increased the metal ion extraction is decreased, figure 4.1, due to association of 2-bromodecanoic acid and to the transfer of terpyridine from the organic phase to the aqueous phase, see appendix 3. The curium standard was impure, contained ^{239}Pu, and was purified, but the D-values for curium at 0.2 M nitric acid are higher than expected. Experiments with ^{233}U, appendix 11, indicates that U and and probably also Pu will be well extracted and even a low content of Pu could explain the increased D-values.
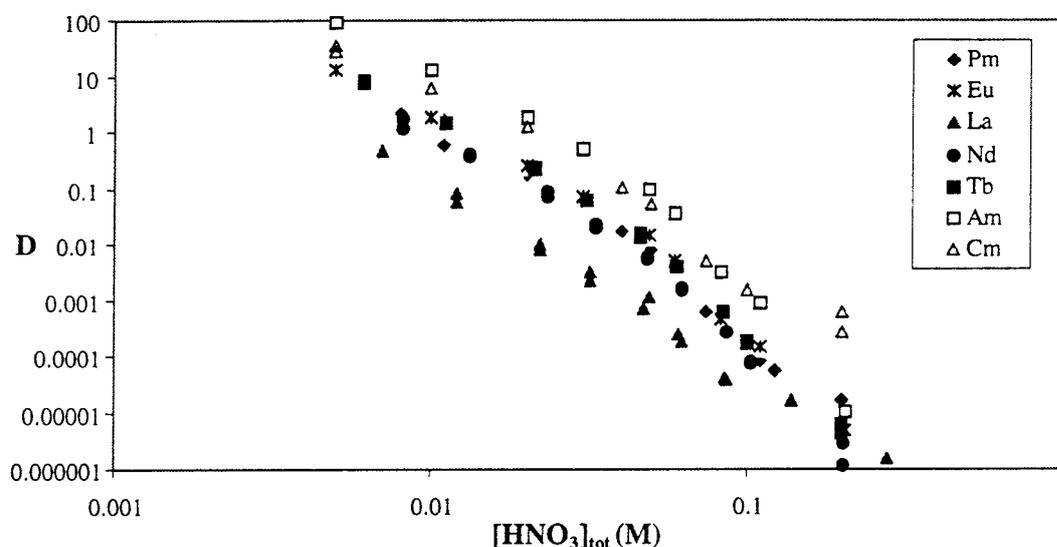
Figure 4.1 Experimental D-values for some lanthanides and actinides.

The distribution ratios obtained 0.1 M nitric acid concentrations are low and uncertain due to measuring difficulties at low distribution ratios, see appendix 4-10.
The separation factor between Cm and Tb is above 5 for the examined range in nitric acid concentration. This implies that it is possible to use the terpyridine-HA-tbb system to separate trivalent actinides from lanthanides, since Tb has the highest D-value of all the lanthanides and Cm has lower D-value than americium.

4.1.1 Effect of the ionic radius

When the atomic number is increased in the lanthanide series the ionic radius is decreased, the lanthanide contraction see table 4.1. The metal extraction increases with decreasing ionic radius, figure 4.1, due to the better coordination in the terpyridine structure.

Table 4.1 The ionic radius of some trivalent lanthanides and actinides [Sea 90].

Element	Ionic radius (Å)
Lanthanum (La^{3+})	1.061
Neodymium (Nd^{3+})	0.995
Promethium (Pm^{3+})	0.979
Europium (Eu^{3+})	0.950
Terbium (Tb^{3+})	0.923
Americium (Am^{3+})	0.982
Curium (Cm^{3+})	0.970

4.2 Model adaption to experimental data

4.2.1 Modelling of the terpyridine-HA-tbb system

From the experimental values of the two-phase titration with the organic phase 0.02 M terpyridine, 1.0 M HA in tbb and 0.1 M terpyridine, 1.0 M HA in tbb [Spj 97] respectively, a model is adapted for the system. It was assumed that terpyridine form different species according to equations 2.18-2.20 and 2.22 and that the formed adducts between HA and terpyridine in one case was HAT and in another case were both HAT and $(HA)_2T$. The total molar balance of terpyridine for the former case is;

$$\Theta c_T = \Theta\left(\left[\overline{T}\right] + \left[\overline{HAT}\right]\right) + \left[T\right] + \left[HT^+\right] + \left[H_2T^{2+}\right] \qquad 4.1$$

which can be rewritten as;

$$\Theta c_T = \Theta\left(\left[\overline{T}\right] + k_{ad,1}\left[\overline{HA}\right]\left[\overline{T}\right]\right) + \frac{\left[\overline{T}\right] + k_1\left[H^+\right]\left[\overline{T}\right] + k_2\left[H^+\right]^2\left[\overline{T}\right]}{\lambda_T} \qquad 4.2$$

and for the latter case;

$$\Theta c_T = \Theta\left(\left[\overline{T}\right] + \left[\overline{HAT}\right] + \left[\overline{(HA)_2T}\right]\right) + \left[T\right] + \left[HT^+\right] + \left[H_2T^{2+}\right] \qquad 4.3$$

which can be converted to;

$$\Theta c_T = \Theta\left(\left[\overline{T}\right] + k_{ad,1}\left[\overline{HA}\right]\left[\overline{T}\right] + k_{ad,2}\left[\overline{HA}\right]^2\left[\overline{T}\right]\right) +$$
$$\frac{\left[\overline{T}\right] + k_1\left[H^+\right]\left[\overline{T}\right] + k_2\left[H^+\right]^2\left[\overline{T}\right]}{\lambda_T} \qquad 4.4$$

where c_T is the total concentration of terpyridine. Further it was assumed that HA form the different species described in equations 2.22-2.25, which gives the total molar balance of HA for the first case;

$$\Theta c_{HA} = \Theta\left(\left[\overline{HA}\right] + \left[\overline{HAT}\right] + 2\cdot\left[\overline{(HA)_2}\right]\right) + [HA] + \left[A^-\right] \qquad 4.5$$

which can be reformulated as;

$$\Theta c_{HA} = \Theta\left(\left[\overline{HA}\right] + k_{ad,1}\left[\overline{HA}\right]\left[\overline{T}\right] + 2K_d\left[\overline{HA}\right]^2\right) + \frac{\left[\overline{HA}\right]}{\lambda_{HA}} + \frac{\left[\overline{HA}\right]}{\lambda_{HA}\cdot K_a\left[H^+\right]} \qquad 4.6$$

and for the second case;

$$\Theta c_{HA} = \Theta\left(\left[\overline{HA}\right] + \left[\overline{HAT}\right] + 2\cdot\left[\overline{(HA)_2T}\right] + 2\cdot\left[\overline{(HA)_2}\right]\right) + [HA] + \left[A^-\right] \qquad 4.7$$

which can be rewritten as;

$$\Theta c_{HA} = \Theta\left(\left[\overline{HA}\right] + k_{ad,1}\left[\overline{HA}\right]\left[\overline{T}\right] + 2k_{ad,2}\left[\overline{HA}\right]^2\left[\overline{T}\right] + 2K_d\left[\overline{HA}\right]^2\right) +$$
$$\frac{\left[\overline{HA}\right]}{\lambda_{HA}} + \frac{\left[\overline{HA}\right]}{\lambda_{HA}\cdot K_a\left[H^+\right]} \qquad 4.8$$

where c_{HA} is the total concentration of HA. The HNO_3 species according to equations 2.19-2.21, yields a total molar balance of HNO_3 for both cases;

$$c_{HNO_3} = \left[H^+\right] + \left[HT^+\right] + 2\cdot\left[H_2T^{2+}\right] + [HNO_3] \qquad 4.9$$

which can be converted to;

$$c_{HNO_3} = \left[H^+\right] + \frac{k_1\left[H^+\right]\left[\overline{T}\right] + 2k_2\left[H^+\right]^2\left[\overline{T}\right]}{\lambda_T} + k_a\left[H^+\right]\left[NO_3^-\right] \qquad 4.10$$

where c_{HNO_3} is the total concentration of HNO_3. The first case equations 4.2, 4.6 and 4.10 and the second case equations 4.4, 4.8 and 4.10 were used to model the system. The models have been fitted to the experimental data with a minimization program, [JOL], and the program was modified to fit these conditions. The results for the first model is presented in appendix 1 and for the second model in appendix 2. The ratios for different terpyridine species calculated with the second model at different nitric acid concentrations are presented in appendix 3. The constants were determined to, $\lambda_{HA} = 8.87\cdot10^3$, $k_{ad,1} = 1.62$, $k_{ad,2} = 1.02\cdot10^{10}$ and $K_d = 9.91\cdot10^7$.

4.2.2 Modelling of extraction curves

From the experimentally determined D-values a model is adapted. The extraction model is defined according to equation 2.30, which can be circumscribed for M=0, N=1 and X=0 as;

$$D_M = \lambda_L \alpha_3 \left[A^- \right]^3 \left(1 + Q_{01}\left[\overline{T} \right] \right)$$
4.11

The model in section 4.2.1, equations 4.4, 4.6 and 4.10, was used as a basis, for the distribution of terpyridine, HA and HNO_3, to calculate the equilibrium values of $\left[\overline{T} \right]$ and $\left[A^- \right]$ for given total concentrations of nitric acid, terpyridine and 2-bromodecanoic acid. The constants α_0 and Q_{00} equals 1 by definition. The model has been fitted to the experimental data with a minimization program, [JOL], and the program has been modified to fit these conditions. The resulting extraction curves can be viewed in appendices 4-10. The evaluated constants λ_L, α_3 and Q_{01} can be viewed in table 4.2.

Table 4.2 Calculated constants in the models for some lanthanides and actinides.

Element	λ_L	α_3	Q_{01}
La	$2.56 \cdot 10^{13}$	$2.48 \cdot 10^{13}$	49.2
Nd	$3.95 \cdot 10^{13}$	$3.86 \cdot 10^{13}$	$1.63 \cdot 10^{14}$
Pm	$9.17 \cdot 10^{13}$	$6.28 \cdot 10^{13}$	$2.56 \cdot 10^3$
Eu	$9.14 \cdot 10^{13}$	$5.74 \cdot 10^{13}$	$9.02 \cdot 10^3$
Tb	$7.85 \cdot 10^{13}$	$6.43 \cdot 10^{13}$	$9.75 \cdot 10^3$
Am	$9.99 \cdot 10^{13}$	$1.02 \cdot 10^{14}$	$4.94 \cdot 10^4$
Cm	$2.59 \cdot 10^{14}$	$2.09 \cdot 10^{14}$	$2.21 \cdot 10^3$

4.3 Dynamic simulation of the extraction process

The computer code used in the calculation was written in FORTRAN77. The flow chart is described in appendix 17 and names of the different streams are given in appendix 13. The extraction model, see 4.2.2, with the extraction constants, table 4.2, for the different elements are inserted into the program. Before the program can be run two input files have to be created. One that contain the flow rate of the aqueous feed, ratios between flows in the process and the number of stages in the different batteries, see appendix 12. The other contain the concentration of americium and the ratios between metal concentrations in the aqueous feed, see appendix 12. The extraction batteries are all operated with the aqueous and organic phase flow countercurrent to each other. The program simulates the extraction process dynamically until equilibrium for the extractants and nitric acid is reached.
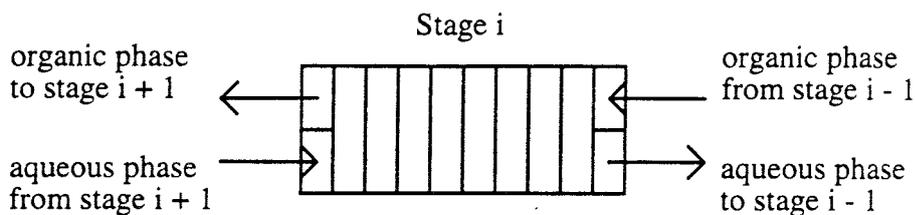
Figure 4.2 Description of a stage in the dynamic simulation with movement of the aqueous and organic phase.

In the dynamic simulation the stages in the different batteries are divided into ten parts, figure 4.2. First the organic phase is moved one step to the left and the aqueous phase one step to the right and then the equilibrium concentrations of the extractants and nitric acid are calculated for all stages with the model for the terpyridine-HA-tbb system, see 4.2.1. After this, the two phases are moved once again and this is repeated until the difference in concentrations of the extractants and nitric acid in the outgoing streams are less than $1 \cdot 10^{-9}$ M.

Then the program calculates the concentrations and percentage extraction of actinides and lanthanides in the outgoing streams using the method described in 2.2. This is achieved by calling a subroutine which simulates both an extraction and a wash battery and then calling a subroutine which simulates a strip battery. When these calculations are performed the results are written in a file for data analysis.

The concentration of Am^{3+} in the aqueous feed, LNANF, was set to $1 \cdot 10^{-6}$ M and the ratios between metal ions and Am^{3+} can be viewed in table 1.1.

4.3.1 Suitable operating conditions for the process

The nitric acid concentration in the aqueous feeds to the different batteries and the flow of the aqueous feeds and the organic feed will be varied, due to disturbances when a process is run. This implies that the process is not run in the operating point all the time and thus the process has to be able to function not only in the operating point, but also in other points around the operating point. To find a suitable operating point the process has been examined for a lot of different values of the variables and the values of the variables in the operating point are presented in table 4.3. For a process a usual condition is 99.9 % extraction of the wanted species and 0.1 % extraction of the not wanted species and this operating point fulfills this condition. The results for the operating point can be viewed in appendix 15 and 16.

Table 4.3 Specification of values of the variables in the operating point.

Specification of variables	Values in the operating point
number of stages in extraction battery	10
number of stages in wash battery ˙	5
number of stages in strip battery	2
$[HNO_3]_{tot}$ in LNANF (M)	0.01
$[HNO_3]_{tot}$ in WASHAF (M)	0.01
$[HNO_3]_{tot}$ in ANSTRAF (M)	0.2
flow ratio ORGFEED/LNANF	0.44
flow ratio WASHAF/LNANF	1.0
flow ratio ANSTRAF/ORGFEED	0.2

For the proposed operating point the strip battery is insensitive to changes in flow ratio, with 20 % variation, and concentration of nitric acid in the aqueous feed to the strip battery, above 0.1 M nitric acid concentration.

The process is sensitive to changes in flow ratios and concentrations of nitric acid in the aqueous feeds to the extraction and wash batteries, table 4.4. The operating points that fulfill the condition 99.9 % extraction of the wanted species and 0.1 % extraction of the not wanted species is marked with OK.

Table 4.4 Values of the percentage extraction for the extraction and wash batteries for different nitric acid concentrations in LNANF and WASHAF and different flow ratios.

$[HNO_3]_{tot}$ (M)	Flow ratio between ORGFEED and LNANF						
	0.4	0.42	0.44	0.45	0.47	0.48	0.5
0.009	Ln <0.17	Ln <0.43	Ln <0.94	Ln <1.34	Ln <2.57	Ln <3.46	Ln <5.93
0.010	An <99.8	OK	OK	OK	Ln <0.2	Ln <0.3	Ln <0.5
0.011	An <94.0	An <98.8	An <99.6	An <99.7	An <99.8	OK	OK

The process is sensitive to changes, but some of the points around the chosen operating point are not too bad and the process will be possible to run.

4.3.2 Verification of the process simulation

The program was verified for element Am for a simple case with the values of the different variables according to table 4.5.

Table 4.5 Values of the variables for which the program was verified.

Specification of variables	Input values used in the verification
number of stages in the extraction battery	1
number of stages in the wash battery	1
number of stages in the strip battery	1
flow ratio in extraction battery	0.5
flow ratio in wash battery	1.0
flow ratio in strip battery	1.0

First the equilibrium concentration of $\overline{T}$ and A^- in the different stages has to be calculated, table 4.6, in order to be able to calculate the distribution of metal ions. The D-values for americium were calculated;

$$D_{Am} = 9.99 \cdot 10^{13} \cdot 1.02 \cdot 10^{14} \left[A^- \right]^3 \left(1 + 4.94 \cdot 10^4 \left[\overline{T} \right] \right) \qquad 4.12$$

where the resulting D-values can be seen in table 4.6. The P-values were calculated according to equation 2.6 and can also be viewed in table 4.6.

Table 4.6 Equilibrium values of $\left[\overline{T} \right]$ and $\left[A^- \right]$ and calculated D- and P-values for the different stages.

Parameter	Wash stage	Extraction stage	Strip stage
$\left[A^- \right]$ (M)	$4.298 \cdot 10^{-10}$	$1.044 \cdot 10^{-11}$	$4.639 \cdot 10^{-10}$
$\left[\overline{T} \right]$ (M)	$2.127 \cdot 10^{-4}$	$5.788 \cdot 10^{-7}$	$2.619 \cdot 10^{-4}$
D	9.31	$1.19 \cdot 10^{-5}$	14.18
P	9.31	$1.19 \cdot 10^{-5}$	7.09

The percentage extraction for the strip stage was calculated according to equation 2.2 and for the extraction and wash battery according to section 2.2. The results from the program and the verification can be viewed in table 4.7.

Table 4.7 Calculated percentage extraction for program and verification.

Percentage extraction	Program	Verification
%E(strip)	$1.19 \cdot 10^{-3}$	$1.19 \cdot 10^{-3}$
%E(extraction + wash)	86.49	86.49

4.3.3 Effect of different variables in the process simulation

When one of the variables in the process simulation is varied the effect on the percentage extraction, %E, has been evaluated for curium and terbium. Curium and terbium was chosen because these elements are most difficult to separate, figure 4.1, between the actinides and lanthanides. The variables for the reference case are presented in appendix 14. The first variables to be varied are the number of stages in the batteries.

When the number of extraction stages are increased, the percentage extraction of both terbium and curium are increased, but the percentage extraction of terbium is increased in a larger extent than for curium, table 4.8. This indicates that a lot of terbium is extracted if almost all curium is extracted which means that other variables also needs to be varied if the process is going to work.

Table 4.8 Calculated percentage extraction for wash and extraction batteries when number of extraction stages are varied.

number of extraction stages	$\%E(Tb^{3+})$	$\%E(Cm^{3+})$
1	31.134	79.2
3	61.935	99.296
5	78.221	99.978

When the number of wash stages are increased the percentage extraction for terbium is decreased and is almost constant for curium, table 4.9. This implies that the product becomes cleaner when more wash stages are used and that some wash stages has to be present in the process.

Table 4.9 Calculated percentage extraction for wash and extraction batteries when number of wash stages are varied.

number of wash stages	$\%E(Tb^{3+})$	$\%E(Cm^{3+})$
1	64.109	99.269
2	61.935	99.296
3	60.775	99.3

The effect of the variation of strip stages are not very well seen in table 4.10 but when two or more strip stages is used almost all terbium and curium is transferred to the aqueous phase. This implies that two strip stages are sufficient in the process for the reference conditions.

22

Table 4.10 Calculated percentage extraction for strip battery when number of strip stages are varied.

number of strip stages	$\%E(Tb^{3+})$	$\%E(Cm^{3+})$
1	0.001	0.006
2	0	0
3	0	0

When the nitric acid concentration in the aqueous feed, LNANF, is increased the percentage extraction of both terbium and curium is decreased, table 4.11, due to the lower D-values at higher nitric acid concentrations. At higher nitric acid concentrations the extraction of terbium is decreased in larger extent than for curium indicating an optimum in the choice of nitric acid concentration causing curium to be extracted to a larger extent than Tb.

Table 4.11 Calculated percentage extraction for wash and extraction batteries when $[HNO_3]_{tot}$ in the aqueous feed, LNANF, is varied.

$[HNO_3]_{tot}$ in LNANF (M)	$\%E(Tb^{3+})$	$\%E(Cm^{3+})$
0.005	89.506	99.879
0.01	61.935	99.296
0.02	10.724	91.129

When the nitric acid concentration in WASHAF is increased the percentage extraction for terbium is decreased in larger extent than for curium implying a cleaner product, table 4.12. An optimum for nitric acid concentration in WASHAF can be choosen in the same way as for LNANF.

Table 4.12 Calculated percentage extraction for wash and extraction batteries when $[HNO_3]_{tot}$ in the wash feed, WASHAF, is varied.

$[HNO_3]_{tot}$ in WASHAF (M)	$\%E(Tb^{3+})$	$\%E(Cm^{3+})$
0.005	91.166	99.866
0.01	61.935	99.296
0.02	4.609	91.74

When the nitric acid concentration is increased almost all terbium and curium are transferred to the aqueous phase, table 4.13, which is the purpose of the strip battery. This indicates that high nitric acid concentrations should be used in ANSTRAF in the process. Stripping with 0.03 M nitric acid shows that if a too low nitric acid concentration is chosen the stripping is not sufficient.

Table 4.13 Calculated percentage extraction for strip battery when $[HNO_3]_{tot}$ in the strip feed, ANSTRAF, is varied.

$[HNO_3]_{tot}$ in ANSTRAF (M)	$\%E(Tb^{3+})$	$\%E(Cm^{3+})$
0.03	0.111	4.632
0. 2	0	0
0. 4	0	0

When the flow ratio between the organic feed and the aqueous feed is decreased the percentage extraction for terbium is decreased in larger extent than for curium, table 4.14, and thus implying low flow ratio is desired in the process. The flow ratio has an optimum in the separation between curium and terbium and the flow ratio is chosen to achieve enough extraction of curium but as little as possible for terbium.

Table 4.14 Calculated percentage extraction for wash and extraction batteries when the flow ratio ORGFEED/LNANF is varied.

flow ratio ORGFEED/LNANF	$\%E(Tb^{3+})$	$\%E(Cm^{3+})$
0.5	22.052	96.59
1.0	61.935	99.296
2.0	81.525	99.742

When the flow ratio beween the organic feed and the aqueous feed to the wash battery is decreased a better separation between curium and terbium is achieved and the product becomes cleaner, table 4.15. This indicates that low flow ratios between the organic feed and the aqueous feed to the wash battery should be used in the process.

Table 4.15 Calculated percentage extraction for wash and extraction batteries when the flow ratio ORGFEED/WASHAF is varied.

flow ratio ORGFEED/WASHAF	$\%E(Tb^{3+})$	$\%E(Cm^{3+})$
0.5	19.546	97.328
1.0	61.935	99.296
2.0	82.58	99.713

When the flow ratio beween the organic feed and the aqueous feed to the strip battery is decreased, almost all terbium and curium are transferred to the aqueous phase, table 4.16. The flow ratio can be as high as 5.0 and still almost all metal species in the organic phase is stripped and this indicates that flow ratios around 5.0 should be used to reach a high concentration of metal ions in the aqueous feed. The flow ratio of 20 is

used in table 4.16 to show that when the flow ratio is too high the metal ions are not stripped.

Table 4.16 Calculated percentage extraction for strip battery when the flow ratio ORGFEED/ANSTRAF is varied.

flow ratio VORGFEED/ANSTRAF	%E(Tb³⁺)	%E(Cm³⁺)
0.5	0	0
1.0	0	0
20	0.755	15.546

4.4 Assumptions made in the simulation

The simulation of the extraction process was simplified with the following assumptions.

1. The aqueous and organic phase are totally immiscible.

2. No degradation of the extraction reagents or the organic solvent occurs.

3. Equilibrium between outgoing streams in all stages.

4. No nitrate complexes are formed in the aqueous phase.

5. The extraction constants in the extraction model for the lanthanides where no extraction data was available were approximated with constants for other lanthanides. The constants for Ce and Pr were approximated with the constants for Nd and Sm was aproximated with Eu. The constants for Gd, Dy, Ho, Er, Tm, Yb, and Lu were aproximated with the constants for Tb.

6. Fresh organic phase is feed to the extraction battery.

7. Fresh nitric acid is feed to the wash and strip batteries.

8. Only trivalent actinides and lanthanides enter the process in the aqueous phase to the extraction battery.

9. Constant flow of the organic and aqueous phase due to the low concentrations of extraction reagents.

5. Conclusions

5.1 Determination of ratios of terpyridine and 2-bromodecanoic acid species

Terpyridine is diprotonated at higher nitric acid concentrations and thus almost all terpyridine is transferred to the aqueous phase. For the studied range in nitric acid concentration the dominating species of 2-bromodecanoic acid is the dimerised form in the organic phase and is thus not transferred to the aqueous phase in the same proportion as terpyridine.

5.2 Determination of metal extraction

The experimentally determined distribution ratios decreases when the nitric acid concentration is increased, due to the association of 2-bromodecanoic acid and the protonation of terpyridine. The extraction model shows that at higher nitric acid concentrations the dominating extracted specie is the neutral species with the dissociated 2-bromodecanoic acid as ligand and not as at lower nitric acid concentrations where the dominating extracted specie is the same neutral specie but now coordinated with one terpyridine molecule. The separation factor is around 5 for the entire studied range in nitric acid concentration and thus a separation of trivalent actinides from lanthanides should be possible.

5.3 Process simulation

When an extraction process is run there is a problem with the protonation of terpyridine, because almost all terpyridine is transferred to the aqueous phase at the strip battery and a way to recover terpyridine must be figured out. Another problem is the sensitivity for disturbances in the feeds to the batteries at the operating point. The extraction process is thus hard to run but at the operating point it is possible to separate trivalent actinides from lanthanides with terpyridine and 2-bromodecanoic acid in *tert*-butylbenzene.

26

6. Future work

To follow the CHON-principle another acid than 2-bromodecanoic acid has to be found.

Extractants other than terpyridine has to be used. The extractants should not be transferred to the aqueous phase when pH decreases.

Determination of D-values for the rest of the lanthanides and actinides, e.g. uranium, neptunium and plutonium. Uranium has been tested and the results are presented in appendix 11.

Determination of D- values of different concentration of extractants, which would lead to new models or verification of the used model.

Modelling of the entire DIAMEX process to find out the problems, e.g used extractants, other elements extracted and flow ratios.

7. Acknowledgements

I would like to thank my four supervisors, Prof Jan-Olov Liljenzin, M.Sc. Åsa Enarsson, M.Sc. Anders Landgren and M.Sc. Lena Spjuth, for their help with all sorts of problems this work has caused me.
I would also like to thank Christian Ekberg for help when the programs not have done what I wanted them to do and Gunnar Skarnemark for helping me with little things not always related to this work.

Finally, I would like to thank all the other people at the Department of Nuclear Chemistry for all help during the last six months.

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Experimental and calculated values of protonation of terpyridine model 1

Table 1.1 Experimental and calculated values with model 1 for protonation of terpyridine in the terpyridine-HA-tbb system.

0.02 M terpyridine			0.1 M terpyridine		
$[H^+]_{eq}$ (M)	$[HNO_3]_{tot}$ (M)	$[HNO_3]_{calc}$ (M)	$[H^+]_{eq}$ (M)	$[HNO_3]_{tot}$ (M)	$[HNO_3]_{calc}$ (M)
2.19E-03	3.28E-03	4.60E-03	1.19E-03	6.56E-03	6.68E-03
3.26E-03	6.48E-03	7.45E-03	1.82E-03	1.28E-02	1.18E-02
4.35E-03	9.60E-03	1.04E-02	2.30E-03	1.88E-02	1.62E-02
5.65E-03	1.27E-02	1.38E-02	2.60E-03	2.45E-02	1.92E-02
7.05E-03	1.56E-02	1.72E-02	3.12E-03	2.99E-02	2.44E-02
8.31E-03	1.85E-02	1.99E-02	4.28E-03	4.10E-02	3.54E-02
1.15E-02	2.42E-02	2.55E-02	5.72E-03	5.17E-02	4.75E-02
1.56E-02	2.95E-02	3.13E-02	7.50E-03	6.19E-02	5.91E-02
2.05E-02	3.47E-02	3.71E-02	9.83E-03	7.17E-02	7.00E-02
3.12E-02	4.54E-02	4.89E-02	1.31E-02	8.10E-02	7.98E-02
4.31E-02	5.56E-02	6.13E-02	2.33E-02	1.01E-01	9.79E-02
5.44E-02	6.54E-02	7.29E-02	3.90E-02	1.19E-01	1.16E-01
7.88E-02	8.55E-02	9.82E-02	5.77E-02	1.37E-01	1.35E-01
1.03E-01	1.05E-01	1.23E-01	7.53E-02	1.54E-01	1.52E-01
1.47E-01	1.41E-01	1.69E-01	9.60E-02	1.71E-01	1.73E-01
1.88E-01	1.74E-01	2.11E-01	1.21E-01	1.87E-01	1.97E-01
2.44E-01	2.19E-01	2.69E-01	1.39E-01	2.02E-01	2.15E-01
2.96E-01	2.58E-01	3.22E-01	2.11E-01	2.68E-01	2.84E-01
3.78E-01	3.12E-01	4.07E-01	2.72E-01	3.21E-01	3.44E-01
4.28E-01	3.57E-01	4.59E-01	3.40E-01	3.63E-01	4.10E-01
			3.77E-01	3.98E-01	4.46E-01
			4.18E-01	4.27E-01	4.85E-01

Figure 1.1 Experimental and calculated values of two-phase titration with model 1.

Experimental and calculated values of protonation of terpyridine model 2

Table 2.1 Experimental and calculated values with model 2 for protonation of terpyridine in the terpyridine-HA-tbb system.

0.02 M terpyridine			0.1 M terpyridine		
$[H^+]_{eq}$ (M)	$[HNO_3]_{tot}$ (M)	$[HNO_3]_{calc}$ (M)	$[H^+]_{eq}$ (M)	$[HNO_3]_{tot}$ (M)	$[HNO_3]_{calc}$ (M)
2.19E-03	3.28E-03	4.53E-03	1.19E-03	6.56E-03	5.72E-03
3.26E-03	6.48E-03	7.67E-03	1.82E-03	1.28E-02	1.13E-02
4.35E-03	9.60E-03	1.09E-02	2.30E-03	1.88E-02	1.61E-02
5.65E-03	1.27E-02	1.46E-02	2.60E-03	2.45E-02	1.92E-02
7.05E-03	1.56E-02	1.80E-02	3.12E-03	2.99E-02	2.48E-02
8.31E-03	1.85E-02	2.07E-02	4.28E-03	4.10E-02	3.66E-02
1.15E-02	2.42E-02	2.61E-02	5.72E-03	5.17E-02	4.91E-02
1.56E-02	2.95E-02	3.17E-02	7.50E-03	6.19E-02	6.07E-02
2.05E-02	3.47E-02	3.73E-02	9.83E-03	7.17E-02	7.12E-02
3.12E-02	4.54E-02	4.90E-02	1.31E-02	8.10E-02	8.05E-02
4.31E-02	5.56E-02	6.13E-02	2.33E-02	1.01E-01	9.81E-02
5.44E-02	6.54E-02	7.29E-02	3.90E-02	1.19E-01	1.16E-01
7.88E-02	8.55E-02	9.82E-02	5.77E-02	1.37E-01	1.35E-01
1.03E-01	1.05E-01	1.23E-01	7.53E-02	1.54E-01	1.52E-01
1.47E-01	1.41E-01	1.69E-01	9.60E-02	1.71E-01	1.73E-01
1.88E-01	1.74E-01	2.11E-01	1.21E-01	1.87E-01	1.97E-01
2.44E-01	2.19E-01	2.69E-01	1.39E-01	2.02E-01	2.15E-01
2.96E-01	2.58E-01	3.22E-01	2.11E-01	2.68E-01	2.84E-01
3.78E-01	3.12E-01	4.07E-01	2.72E-01	3.21E-01	3.44E-01
4.28E-01	3.57E-01	4.59E-01	3.40E-01	3.63E-01	4.10E-01
			3.77E-01	3.98E-01	4.46E-01
			4.18E-01	4.27E-01	4.85E-01

Figure 2.1 Experimental and calculated values of two-phase titration with model 2.

Calculated ratios of different terpyridine species
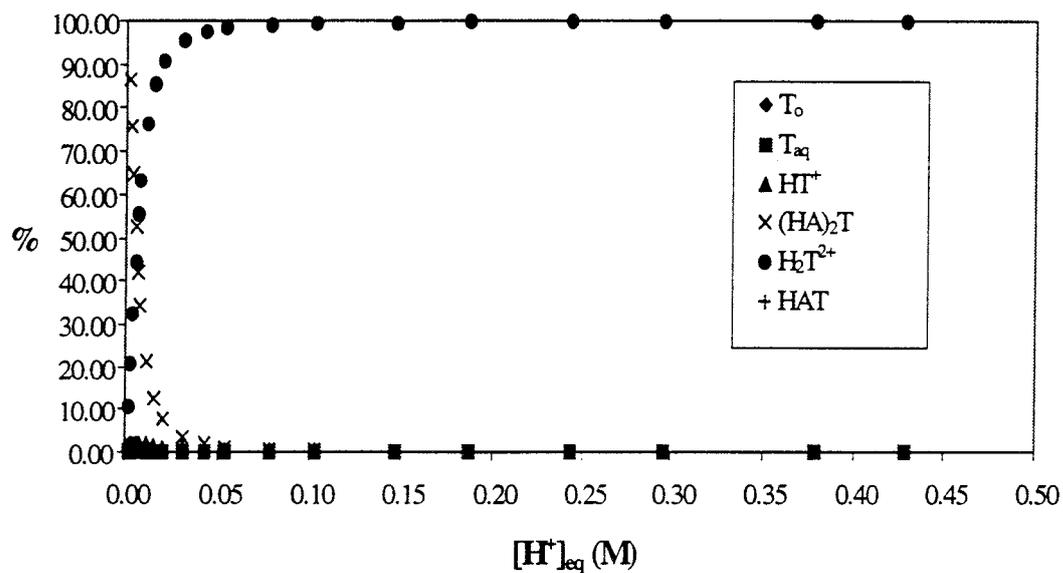
Figure 3.1 Calculated ratios of different terpyridine species with model 2.
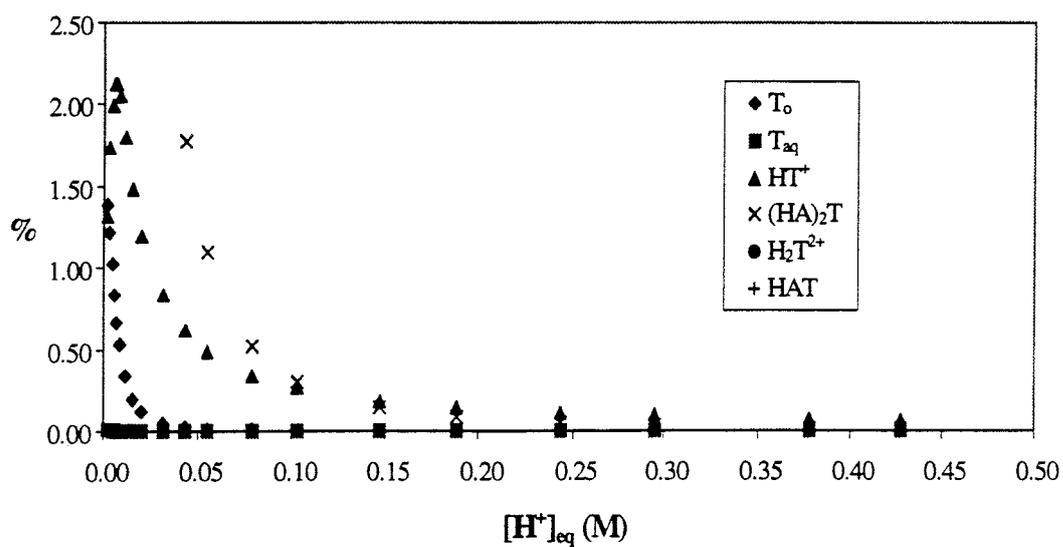
Figure 3.2 Enlargement of figure 3.1 with a maximum of 2.5%.

Experimental and calculated D-values for lanthanum

Table 4.1 Experimental and calculated D-values for lanthanum at some different nitric acid concentrations.

[HNO₃]ₜₒₜ (M)	[H⁺]ₑq (M)	experimental D	calculated D
6.98E-03	2.93E-03	4.73E-01	1.38E-01
6.98E-03	2.93E-03	4.82E-01	1.38E-01
1.20E-02	4.31E-03	8.20E-02	4.39E-02
1.20E-02	4.31E-03	5.49E-02	4.39E-02
2.20E-02	6.94E-03	1.02E-02	1.06E-02
2.20E-02	6.94E-03	8.08E-03	1.06E-02
3.20E-02	9.97E-03	3.23E-03	3.59E-03
3.20E-02	9.97E-03	2.27E-03	3.59E-03
4.70E-02	1.64E-02	6.89E-04	8.12E-04
4.90E-02	1.75E-02	1.16E-03	6.69E-04
6.10E-02	2.56E-02	2.40E-04	2.16E-04
6.30E-02	2.71E-02	1.82E-04	1.82E-04
8.50E-02	4.65E-02	3.90E-05	3.61E-05
8.70E-02	4.83E-02	3.85E-05	3.21E-05
1.40E-01	9.95E-02	1.69E-05	3.68E-06
2.80E-01	2.37E-01	1.54E-06	2.73E-07
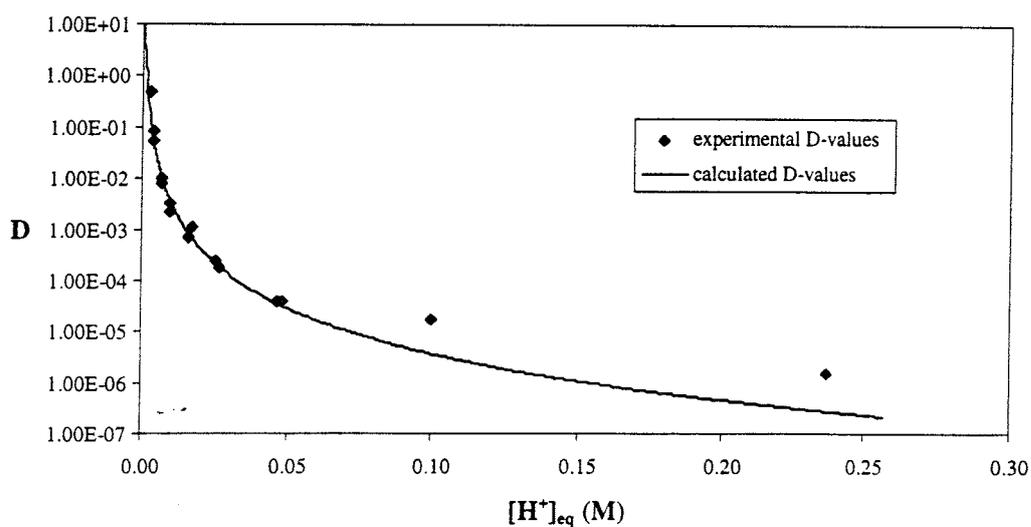
Figure 4.1 Experimental determined and calculated distribution values for lanthanum at some different nitric acid concentrations.

Experimental and calculated D-values for neodymium

Table 5.1 Experimental and calculated D-values for neodymium at some different nitric acid concentrations.

$[HNO_3]_{tot}$ (M)	$[H^+]_{eq}$ (M)	experimental D	calculated D
8.18E-03	3.28E-03	1.18E+00	1.29E+00
8.18E-03	3.28E-03	1.69E+00	1.29E+00
1.32E-02	4.62E-03	3.73E-01	4.23E-01
1.32E-02	4.62E-03	4.20E-01	4.23E-01
2.32E-02	7.27E-03	6.91E-02	8.83E-02
2.32E-02	7.27E-03	8.76E-02	8.83E-02
3.32E-02	1.04E-02	2.00E-02	2.38E-02
3.32E-02	1.04E-02	2.37E-02	2.38E-02
4.82E-02	1.71E-02	5.98E-03	3.61E-03
4.82E-02	1.71E-02	5.27E-03	3.61E-03
6.22E-02	2.65E-02	1.61E-03	7.09E-04
6.22E-02	2.65E-02	1.53E-03	7.09E-04
8.62E-02	4.76E-02	2.76E-04	9.49E-05
8.62E-02	4.76E-02	2.72E-04	9.49E-05
1.03E-01	6.39E-02	7.77E-05	3.68E-05
1.03E-01	6.39E-02	7.52E-05	3.68E-05
2.03E-01	1.62E-01	2.87E-06	2.08E-06
2.03E-01	1.62E-01	1.16E-06	2.08E-06
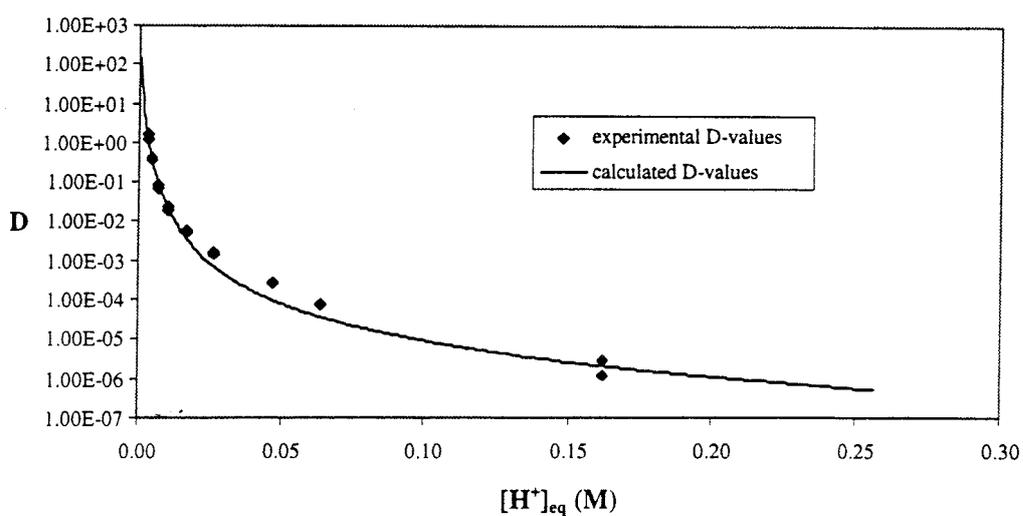
Figure 5.1 Experimental determined and calculated distribution values for neodymium at some different nitric acid concentrations.

Experimental and calculated D-values for promethium

Table 6.1 Experimental and calculated D-values for promethium at some different nitric acid concentrations.

$[HNO_3]_{tot}$ (M)	$[H^+]_{eq}$ (M)	experimental D	calculated D
8.00E-03	3.23E-03	2.11E+00	1.59E+00
1.07E-02	3.96E-03	1.84E+00	8.42E-01
1.10E-02	4.05E-03	6.05E-01	7.87E-01
2.00E-02	6.40E-03	1.77E-01	1.84E-01
4.00E-02	1.30E-02	1.66E-02	1.83E-02
5.00E-02	1.81E-02	7.95E-03	6.33E-03
7.50E-02	3.73E-02	6.15E-04	6.61E-04
1.10E-01	7.05E-02	8.16E-05	9.52E-05
1.23E-01	8.29E-02	5.67E-05	5.83E-05
2.00E-01	1.59E-01	1.69E-05	8.22E-06
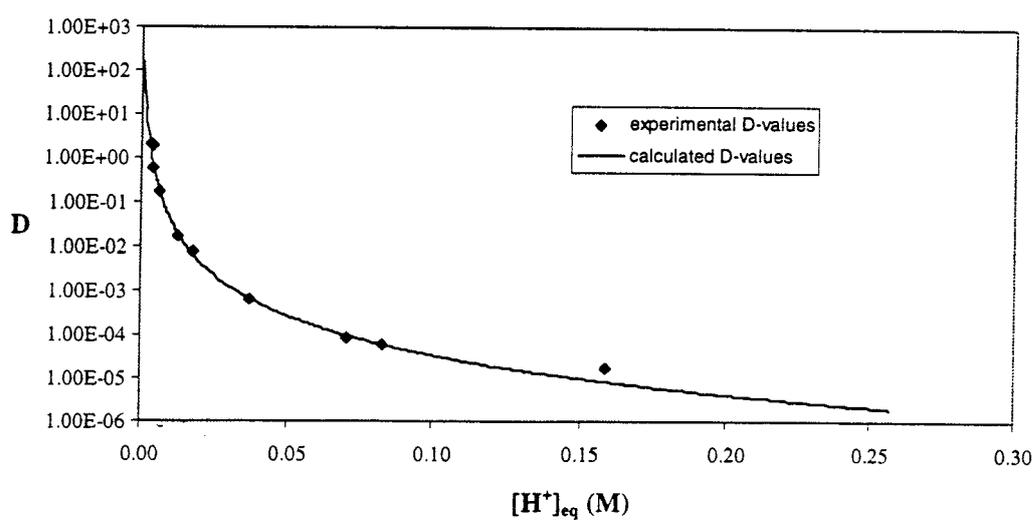
Figure 6.1 Experimental determined and calculated distribution values for promethium at some different nitric acid concentrations.

Experimental and calculated D-values for europium

Table 7.1 Experimental [Spj 97] and calculated D-values for europium at some different nitric acid concentrations.

$[HNO_3]_{tot}$ (M)	$[H^+]_{eq}$ (M)	experimental D	calculated D
5.00E-03	2.33E-03	1.27E+01	8.26E+00
1.00E-02	3.78E-03	1.82E+00	1.79E+00
2.00E-02	6.40E-03	2.50E-01	3.13E-01
3.00E-02	9.32E-03	7.03E-02	8.43E-02
4.88E-02	1.74E-02	1.42E-02	8.88E-03
5.90E-02	2.41E-02	4.97E-03	2.86E-03
8.35E-02	4.51E-02	4.68E-04	3.62E-04
1.10E-01	7.05E-02	1.41E-04	8.95E-05
2.06E-01	1.65E-01	4.81E-06	6.75E-06
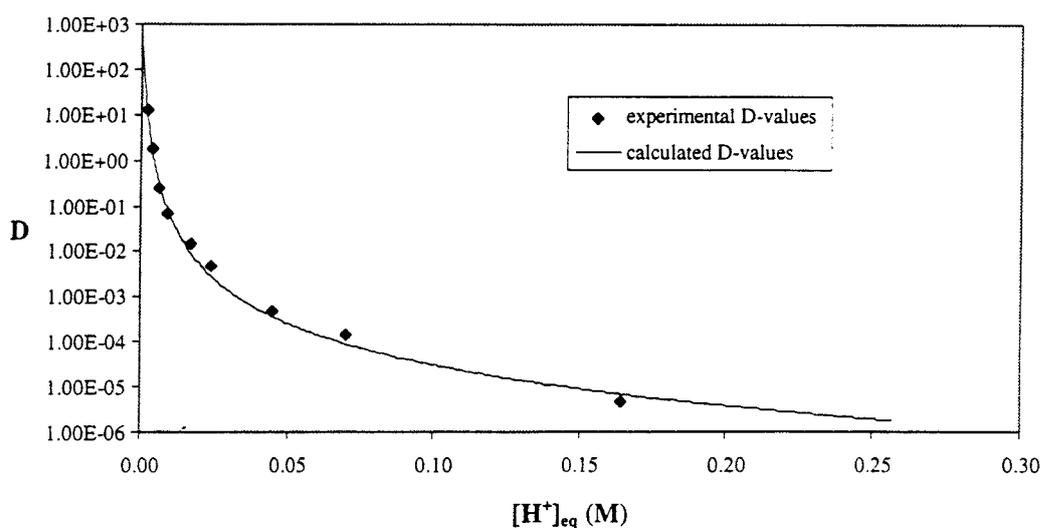
Figure 7.1 Experimental determined and calculated distribution values for europium at some different nitric acid concentrations.

Experimental and calculated D-values for terbium

Table 8.1 Experimental and calculated D-values for terbium at some different nitric acid concentrations.

[HNO₃]ₜₒₜ (M)	[H⁺]ₑq (M)	experimental D	calculated D
6.09E-03	2.67E-03	7.96E+00	5.48E+00
6.09E-03	2.67E-03	8.17E+00	5.48E+00
1.11E-02	4.07E-03	1.44E+00	1.43E+00
1.11E-02	4.07E-03	1.41E+00	1.43E+00
2.11E-02	6.70E-03	2.38E-01	2.72E-01
2.11E-02	6.70E-03	2.20E-01	2.72E-01
3.11E-02	9.67E-03	6.06E-02	7.41E-02
3.11E-02	9.67E-03	6.15E-02	7.41E-02
4.61E-02	1.59E-02	1.32E-02	1.21E-02
4.61E-02	1.59E-02	1.59E-02	1.21E-02
6.01E-02	2.49E-02	3.97E-03	2.51E-03
6.01E-02	2.49E-02	4.05E-03	2.51E-03
8.41E-02	4.56E-02	6.06E-04	3.38E-04
8.41E-02	4.56E-02	6.23E-04	3.38E-04
1.01E-01	6.19E-02	1.83E-04	1.30E-04
1.01E-01	6.19E-02	1.75E-04	1.30E-04
2.01E-01	1.60E-01	4.58E-06	7.11E-06
2.01E-01	1.60E-01	6.04E-06	7.11E-06
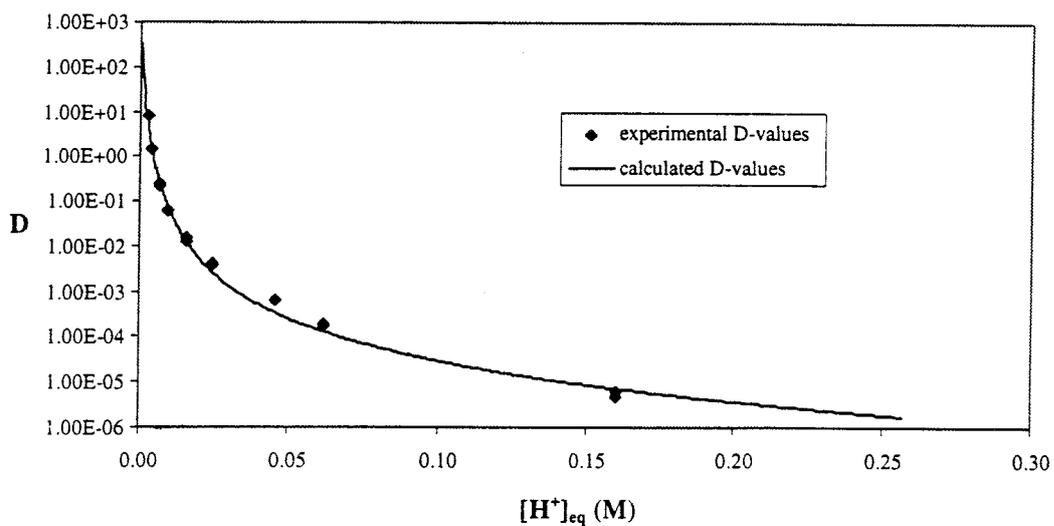
Figure 8.1 Experimental determined and calculated distribution values for terbium at some different nitric acid concentrations.

Experimental and calculated D-values for americium

Table 9.1 Experimental [Spj 97] and calculated D-values for americium at some different nitric acid concentrations.

[HNO$_3$]$_{tot}$ (M)	[H$^+$]$_{eq}$ (M)	experimental D	calculated D
5.00E-03	2.33E-03	9.05E+01	6.81E+01
1.00E-02	3.78E-03	1.30E+01	1.44E+01
2.00E-02	6.40E-03	1.81E+00	2.37E+00
3.00E-02	9.32E-03	5.18E-01	5.82E-01
4.88E-02	1.74E-02	9.87E-02	4.56E-02
5.90E-02	2.41E-02	3.73E-02	1.18E-02
8.35E-02	4.51E-02	3.28E-03	1.01E-03
1.10E-01	7.05E-02	9.00E-04	2.07E-04
2.06E-01	1.65E-01	1.05E-05	1.36E-05
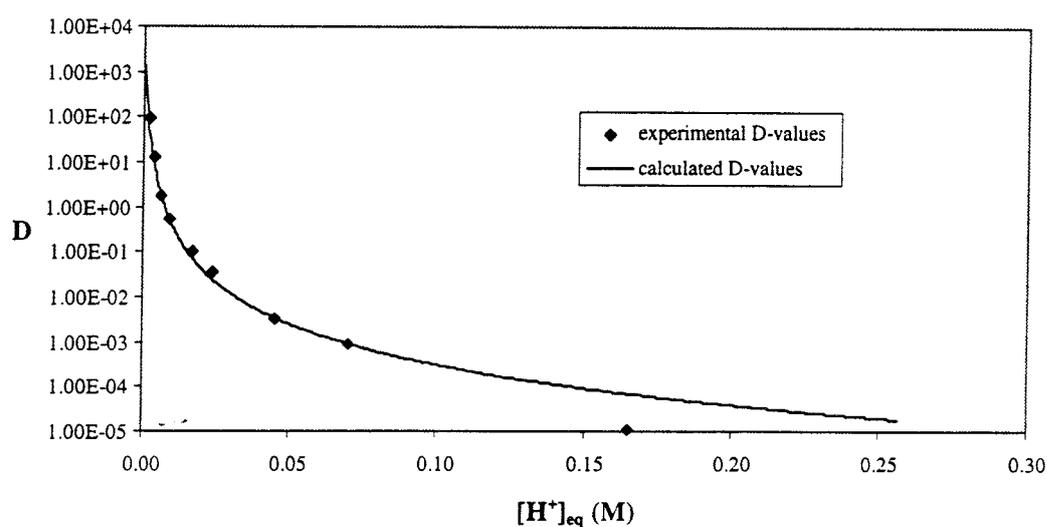
Figure 9.1 Experimental determined and calculated distribution values for americium at some different nitric acid concentrations.

Experimental and calculated D-values for curium

Table 10.1 Experimental and calculated D-values for curium at some different nitric acid concentrations.

$[HNO_3]_{tot}$ (M)	$[H^+]_{eq}$ (M)	experimental D	calculated D
6.25E-03	2.72E-03	2.68E+01	2.39E+01
6.25E-03	2.72E-03	3.49E+01	2.39E+01
1.18E-02	4.25E-03	6.07E+00	5.98E+00
2.12E-02	6.74E-03	1.25E+00	1.40E+00
4.12E-02	1.36E-02	1.07E-01	1.46E-01
5.12E-02	1.89E-02	5.09E-02	5.13E-02
7.62E-02	3.84E-02	5.11E-03	5.63E-03
1.01E-01	6.20E-02	1.51E-03	1.32E-03
2.02E-01	1.62E-01	6.11E-04	7.36E-05
2.02E-01	1.62E-01	2.68E-04	7.36E-05
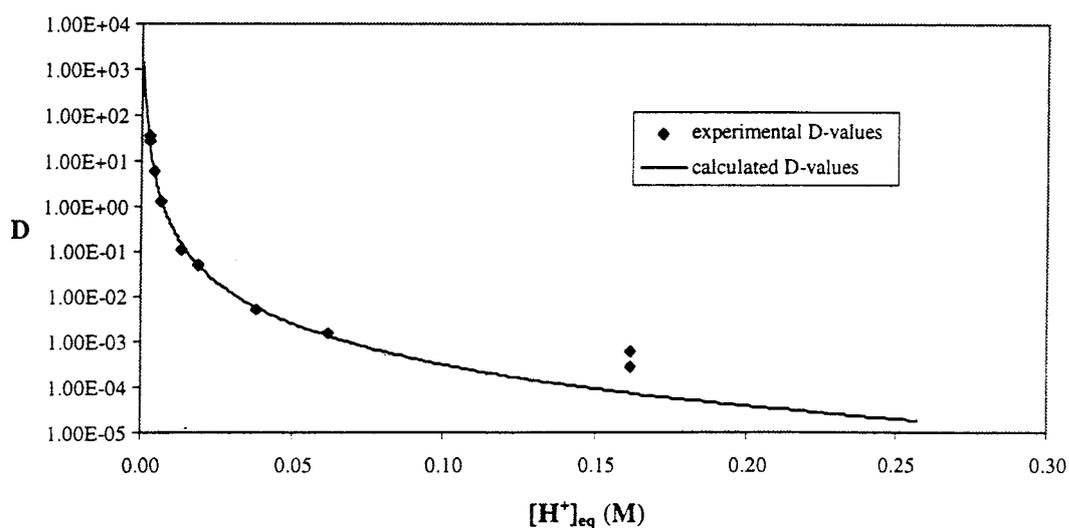
Figure 10.1 Experimental determined and calculated distribution values for curium at some different nitric acid concentrations.

Experimental D-values for uranium

Table 11.1 Experimental D-values for uranium at some different nitric acid concentrations.

[HNO₃]ₜₒₜ (M)	[H⁺]eq (M)	experimental D-values
4.00E-02	1.30E-02	1.08E+00
7.50E-02	3.73E-02	8.81E-02
2.00E-01	1.59E-01	1.20E-03
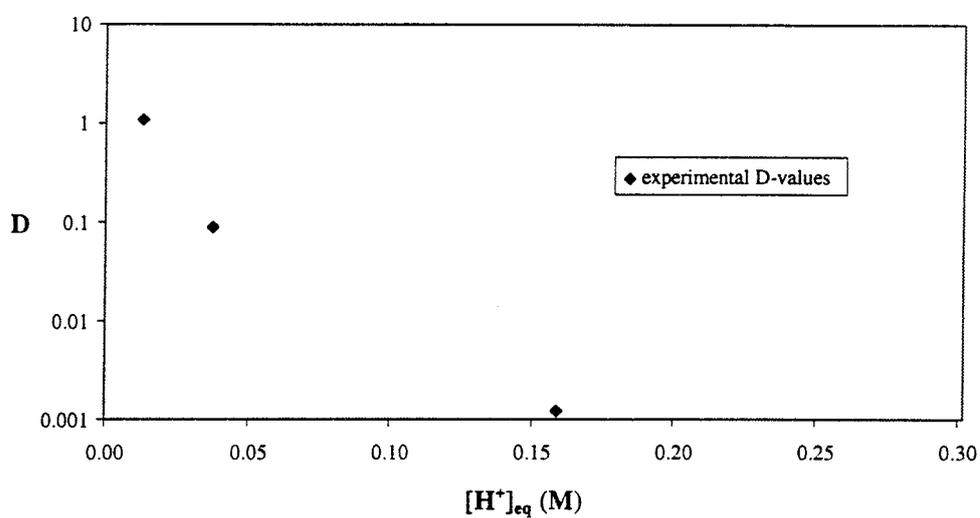
Figure 11.1 Experimental determined distribution values for uranium at some different nitric acid concentrations.

Specification of the input values in the input files

Table 12.1 Specification of variables in the input file ANLNFS.IN and the input values used in the simulation.

Specification of variables in the input file ANLNFS.IN	Input values in the simulation
flow rate in the aqueous feed	10 (dm^3/s)
flow ratio WASHAF/LNANF	1.0
flow ratio ORGFEED/LNANF	0.44
flow ratio ANSTRAF/ORGFEED	0.2
number of stages in wash battery	5
number of stages in extraction battery	10
number of stages in strip battery	2

Table 12.2 Specification of variables in the input file ANLNFC.IN and the input values used in the simulation.

Specification of variables in the input file ANLNFC.IN	Input values in the simulation
concentration of americium in the aqueous feed (M)	$1.0 \cdot 10^{-6}$
ratio $[La^{3+}]/[Am^{3+}]$ in the aqueous feed	23.2159
ratio $[Ce^{3+}]/[Am^{3+}]$ in the aqueous feed	54.740
ratio $[Pr^{3+}]/[Am^{3+}]$ in the aqueous feed	20.008
ratio $[Nd^{3+}]/[Am^{3+}]$ in the aqueous feed	64.393
ratio $[Pm^{3+}]/[Am^{3+}]$ in the aqueous feed	3.617
ratio $[Sm^{3+}]/[Am^{3+}]$ in the aqueous feed	11.296
ratio $[Eu^{3+}]/[Am^{3+}]$ in the aqueous feed	2.744
ratio $[Gd^{3+}]/[Am^{3+}]$ in the aqueous feed	1.070
ratio $[Tb^{3+}]/[Am^{3+}]$ in the aqueous feed	0.0313
ratio $[Dy^{3+}]/[Am^{3+}]$ in the aqueous feed	0.132
ratio $[Ho^{3+}]/[Am^{3+}]$ in the aqueous feed	$1.38 \cdot 10^{-3}$
ratio $[Er^{3+}]/[Am^{3+}]$ in the aqueous feed	$2.30 \cdot 10^{-4}$
ratio $[Am^{3+}]/[Am^{3+}]$ in the aqueous feed	1.0
ratio $[Cm^{3+}]/[Am^{3+}]$ in the aqueous feed	0.298

Flow sheet over the process with names used in the simulation
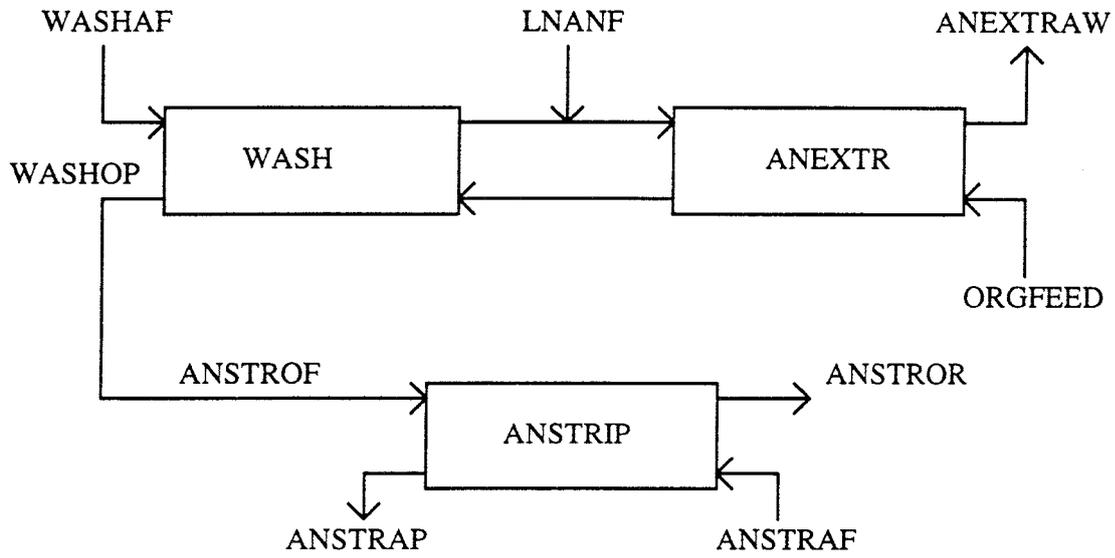
Figure 13.1 Flow sheet over the process with the names used in the simulation program

Specification of variables for reference case

Table 14.1 Specification of variables and values for the reference case.

Specification of variables	Input values in the reference case
number of stages in extraction battery	3
number of stages in wash battery	2
number of stages in strip battery	2
$[HNO_3]_{tot}$ in LNANF (M)	0.01
$[HNO_3]_{tot}$ in WASHAF (M)	0.01
$[HNO_3]_{tot}$ in ANSTRAF (M)	0.2
flow ratio ORGFEED/LNANF	1.0
flow ratio WASHAF/ORGFEED	1.0
flow ratio ANSTRAF/ORGFEED	1.0

Composition of streams connected with the extraction and wash batteries for the operating point

Table 15.1 Composition of streams connected with the extraction and wash batteries for the operating point.

Element	LNANF (M)	WASHAF (M)	ANEXTRAW (M)	ORGFEED (M)	WASHOP (M)	%E	100-%E
La	2.32E-05	0.00E+00	1.16E-05	0.00E+00	3.30E-16	0	100
Ce	5.47E-05	0.00E+00	2.74E-05	0.00E+00	2.76E-10	0	100
Pr	2.00E-05	0.00E+00	1.00E-05	0.00E+00	1.01E-10	0	100
Nd	6.44E-05	0.00E+00	3.22E-05	0.00E+00	3.25E-10	0	100
Pm	3.62E-06	0.00E+00	1.81E-06	0.00E+00	2.33E-10	0.003	99.997
Sm	1.13E-05	0.00E+00	5.65E-06	0.00E+00	1.38E-08	0.054	99.946
Eu	2.74E-06	0.00E+00	1.37E-06	0.00E+00	3.36E-09	0.054	99.946
Gd	1.07E-06	0.00E+00	5.35E-07	0.00E+00	1.39E-09	0.057	99.943
Tb	3.13E-08	0.00E+00	1.56E-08	0.00E+00	4.06E-11	0.057	99.943
Dy	1.32E-08	0.00E+00	6.60E-09	0.00E+00	1.71E-11	0.057	99.943
Ho	1.38E-09	0.00E+00	6.90E-10	0.00E+00	1.79E-12	0.057	99.943
Er	2.30E-10	0.00E+00	1.15E-10	0.00E+00	2.98E-13	0.057	99.943
Am	1.00E-06	0.00E+00	6.21E-13	0.00E+00	2.27E-06	100	0
Cm	2.98E-07	0.00E+00	5.17E-11	0.00E+00	6.77E-07	99.965	0.035

Table 15.2 Equilibrium concentrations of A^- and $\overline{T}$ in the different stages in the extraction and wash batteries.

Battery and stage number	$\overline{T}$ (M)	A^- (M)
EXTR 1	3.17E-04	4.99E-10
EXTR 2	3.17E-04	4.99E-10
EXTR 3	3.17E-04	4.99E-10
EXTR 4	3.17E-04	4.99E-10
EXTR 5	3.17E-04	4.99E-10
EXTR 6	3.17E-04	4.98E-10
EXTR 7	3.16E-04	4.98E-10
EXTR 8	3.10E-04	4.94E-10
EXTR 9	2.81E-04	4.76E-10
EXTR 10	1.76E-04	4.01E-10
WASH 1	1.75E-04	4.01E-10
WASH 2	1.75E-04	4.01E-10
WASH 3	1.70E-04	3.97E-10
WASH 4	1.47E-04	3.78E-10
WASH 5	7.26E-05	3.02E-10

Composition of streams connected with the strip battery for the operating point

Table 16.1 Composition of streams connected with the strip battery for the operating point.

Element	ANSTRAF (M)	ANSTRAP (M)	ANSTROF (M)	ANSTROR (M)	%E	100-%E
La	0.00E+00	6.60E-17	3.30E-16	2.90E-30	0	100
Ce	0.00E+00	5.52E-11	2.76E-10	1.43E-23	0	100
Pr	0.00E+00	2.02E-11	1.01E-10	5.21E-24	0	100
Nd	0.00E+00	6.50E-11	3.25E-10	1.68E-23	0	100
Pm	0.00E+00	4.65E-11	2.33E-10	1.72E-22	0	100
Sm	0.00E+00	2.76E-09	1.38E-08	8.45E-21	0	100
Eu	0.00E+00	6.71E-10	3.36E-09	2.05E-21	0	100
Gd	0.00E+00	2.77E-10	1.39E-09	7.86E-22	0	100
Tb	0.00E+00	8.12E-12	4.06E-11	2.30E-23	0	100
Dy	0.00E+00	3.42E-12	1.71E-11	9.70E-24	0	100
Ho	0.00E+00	3.58E-13	1.79E-12	1.01E-24	0	100
Er	0.00E+00	5.96E-14	2.98E-13	1.69E-25	0	100
Am	0.00E+00	4.55E-07	2.27E-06	5.26E-18	0	100
Cm	0.00E+00	1.35E-07	6.77E-07	4.41E-17	0	100

Table 16.2 Equilibrium concentrations of A^- and $\overline{T}$ in the different stages in the strip battery.

Battery and stage number	$\overline{T}$ (M)	A^- (M)
STRIP 1	3.08E-08	9.11E-12
STRIP 2	1.29E-11	9.03E-12

Program structure
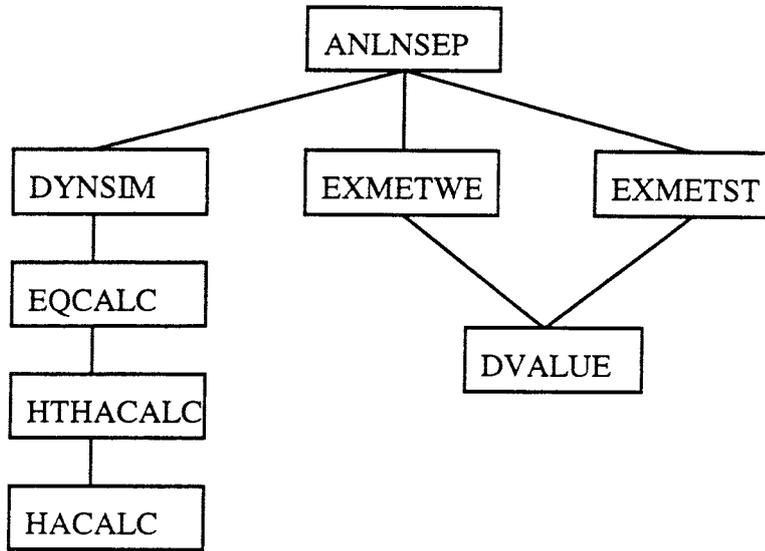
Figure 17.1 Hierarchical structure of ANLNSEP

1 = All elements done?

Figure 17.2 A

1 = [HNO3]calc ok?
2 = Outgoing conc. ok?
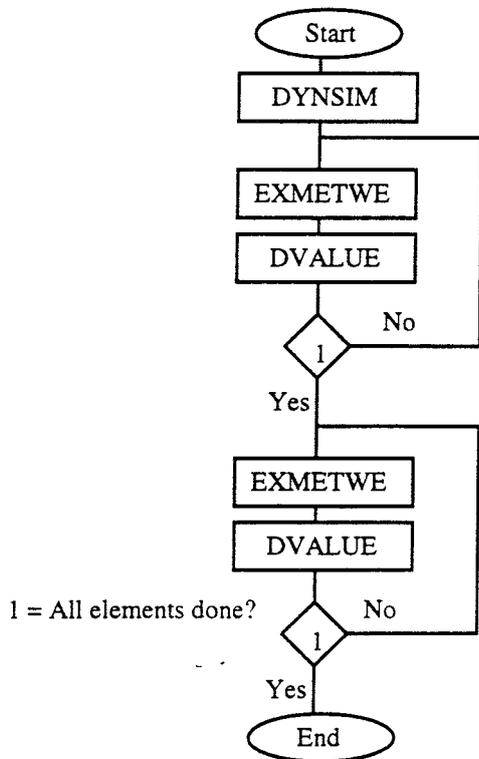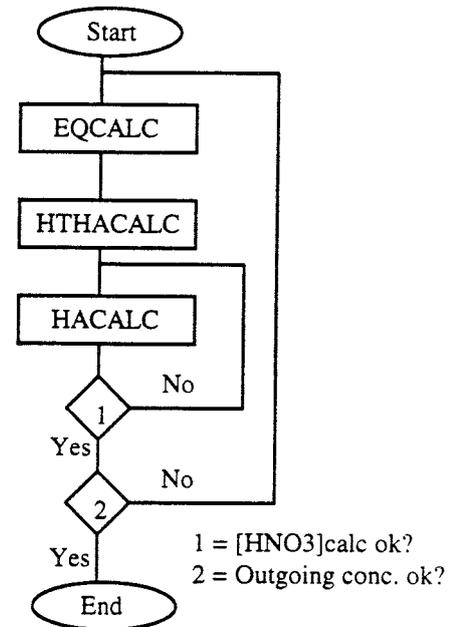
Figure 17.2 B

Figure 17.2 Flow charts of ANLNSEP (A) and DYNSIM (B).

Program code

```
$DEBUG
$LARGE
C     PROGRAM FOR FLOWSHEET EVALUATION DIAMEXPROCESS ••••••••••••••••
C     AN/LN SEPARATION DYNAMIC SIMULATION ••••••••••••••••••••••••••
C
C     97-10-20 M.JOHANSSON DIAMEX PROCESS STEP 3 SEPARATION •••••••••
C     OF ACTINIDES FROM LANTHANIDES, DYNAMIC SIMULATION •••••••••••••
C
C     SYMBOLIC NAMES FROM FLOWSHEET OF PROCESS•••••••••••••••••••••••••
C
C     CONCENTRATIONS IN EXTRBEST ARE NR 1=T, 2=HA, 3=HA2, 4=HAT, ••••
C     5=HA2T, 6=TAQ, 7=HT+, 8=H2T2+, 9=HAAQ, 10=AAQ, 11=H+, 12=NO3-,•
C     13=HNO3, 21 TO 35 LANTHANIDES, 39=AM, 40=CM ••••••••••••••••••••••
C     A MAXIMUM OF 40 ELEMENTS ARE PERMITTED
C
C     A MAXIMUM OF 20 STAGES ARE PERMITTED IN THE BATTERIES •••••••••
C
C
             IMPLICIT REAL*8 (A-H,O-Z)
             INTEGER I,J
             INTEGER NWASH,NANEXTR,NANSTRIP
             REAL*8 LNANF(40),WASHAF(40),ANSTRAF(40),ORGFEED(40)
             REAL*8 RWASHAF,RANSTRAF,RORGFEED
             REAL*8 VWASHAF,VLNANF,VANSTRAF,VORGFEED
             REAL*8 RCLNANF(14),CAMLNANF,METHALT
             REAL*8 WASH(40,200),ANEXTR(40,200),ANSTRIP(40,200)
             REAL*8 ANEXTRAW(40),ANSTRAP(40),ANSTROR(40)
             REAL*8 WASHOP(40),ANSTROF(40),ANSTRAPP(40)
             REAL*8 WASHOPP(40),ANEXTRAWP(40),ANSTRORP(40)

             CHARACTER*4 NA(40)
             CHARACTER*9 NFIL(3)
C
C     THE INTERBATTERY FLOW PATTERN IS PRESCRIBED USING A SERIES•••••
C     OF EQUIVALENCE STATEMENTS BETWEEN THE IN- AND OUT-GOING STREAMS
C     THIS PERMITS A RELATIVELY EASY WAY TO MODIFY THE FLOWSHEET.••••
             EQUIVALENCE (WASHOP,ANSTROF)
C
C     SPECIFICATION OF ELEMENTS USED IN THIS CALCULATION ••••••••••
C     ACCORDING TO DESCRIPTION ABOVE •••••••••••••••••••••••••••••••••
C
             DATA NA/'T  ','HA ','HA2 ','HAT ','HA2T',TAQ ',
      1      'HT  ','H2T ','HAAQ','AAQ ','H ','NO3 ','HNO3',
      2      '0014','0015','0016','0017','0018','0019','0020',
      3      'LA  ','CE ','PR ','ND ','PM ','SM ','EU ',
      4      'GD  ','TB ','DY ','HO ','ER ','TM ','YB ',
      5      'LU  ','0036','0037','0038','AM ','CM '/
C
C
C     OPEN DIFFERENT INPUT FILES TO READ DATA •••••••••••••••••••••••••
             DATA NFIL/'ANLNFS.IN','ANLNFC.IN','ANLN.UT  '/
             OPEN(4,FILE='ANLN.TXT',STATUS='NEW')
             OPEN(9,FILE=NFIL(1),STATUS='OLD')
C
C     READ DATA FROM FILE09•••••••••••••••••••••••••••••••••••••••••••
C
C     READ FIRST FLOW-RATES••••••••••••••••••••••••••••••••••••••••••••
             READ(9,1)VLNANF,RWASHAF,RORGFEED,RANSTRAF
      1      FORMAT(F10.0)
C
C     THEN READ NUMBER OF STAGES IN EACH BATTERY•••••••••••••••••••••••
             READ(9,2)NWASH,NANEXTR,NANSTRIP
      2      FORMAT(I2)
C
C     CLOSE THIS INPUT FILE AND OPEN NEXT INPUT FILE••••••••••••••••••
             CLOSE(9)
             OPEN(9,FILE=NFIL(2),STATUS='OLD')
C
C     READ CONCENTRATION OF AMERICIUM AND RELATIVE CONCENTRATION ••••
C     VECTOR OF LNANF ••••••••••••••••••••••••••••••••••••••••••••••••
             READ(9,3)CAMLNANF,RCLNANF
      3      FORMAT(F13.0)
C
C     CLOSE THIS INPUT FILE••••••••••••••••••••••••••••••••••••••••••••
             CLOSE(9)
C
C     COMPUTE FLOW RATES•••••••••••••••••••••••••••••••••••••••••••••••
             VWASHAF=VLNANF*RWASHAF
             VORGFEED=VLNANF*RORGFEED
             VANSTRAF=VORGFEED*RANSTRAF
C
C     COMPUTE TOTAL METAL CONCENTRATION •••••••••••••••••••••••••••••••
             METHALT=0.0
             DO I=1,14
              METHALT=METHALT+CAMLNANF*RCLNANF(I)
             END DO
C
C     THESE FEED CONCENTRATIONS ARE PRESCRIBED•••••••••••••••••••••••••
             DO I=1,40
```

```fortran
                WASHAF(I)=0.0
                ORGFEED(I)=0.0
                ANSTRAF(I)=0.0
                LNANF(I)=0.0
                END DO
             ORGFEED(1)=0.02
             ORGFEED(2)=1.0
             ANSTRAF(13)=0.2
             WASHAF(13)=0.01
             LNANF(13)=0.01
             ANSTRAF(11)=-1.0/(2*10**(-1.35))+
     1          SQRT((1.0/(2*10**(-1.35)))**2+ANSTRAF(13)/10**(-1.35))
             ANSTRAF(12)=ANSTRAF(11)
             ANSTRAF(13)=ANSTRAF(13)-ANSTRAF(11)
             WASHAF(11)=-1.0/(2*10**(-1.35))+
     1          SQRT((1.0/(2*10**(-1.35)))**2+WASHAF(13)/10**(-1.35))
             WASHAF(12)=WASHAF(11)
             WASHAF(13)=WASHAF(13)-WASHAF(11)
             LNANF(11)=-(10**(-1.35)*3*METHALT+1)/(2*10**(-1.35))+
     1          SQRT(((10**(-1.35)*3*METHALT+1)/
     2          (2*10**(-1.35)))**2+LNANF(13)/10**(-1.35))
             LNANF(12)=3*METHALT+LNANF(11)
             LNANF(13)=LNANF(13)-LNANF(11)
C
C       COMPUTE CONCENTRATION VECTOR OF LNANF ***************************
             DO I=1,12
                LNANF(I+20)=CAMLNANF*RCLNANF(I)
                END DO
             DO I=13,14
                LNANF(I+26)=CAMLNANF*RCLNANF(I)
                END DO
C
C       INITIALIZE CONCENTRATIONS IN THE STAGES ************************
C       ALL STAGES ARE FILLED WITH WATER AT THE START *****************
             DO I=1,40
                ANEXTRAW(I)=0.0
                ANSTRAP(I)=0.0
                ANSTROR(I)=0.0
                WASHOP(I)=0.0
                ANSTROF(I)=0.0
                ANEXTRAWP(I)=0.0
                ANSTRAPP(I)=0.0
                ANSTRORP(I)=0.0
                WASHOPP(I)=0.0
                DO J=1,NWASH*10
                   WASH(I,J)=0.0
                   WASH(11,J)=1.0E-7
                   END DO
                DO J=1,NANEXTR*10
                   ANEXTR(I,J)=0.0
                   ANEXTR(11,J)=1.0E-7
                   END DO
                DO J=1,NANSTRIP*10
                   ANSTRIP(I,J)=0.0
                   ANSTRIP(11,J)=1.0E-7
                   END DO
                END DO
C
C       INITIALISATION DONE TIME TO START PROCESS SIMULATION **********
C       COMPUTE T, HA,... CONCENTRATIONS IN THE BATTERIES FIRST *******
C
             CALL DYNSIM(NWASH,NANEXTR,NANSTRIP,WASHAF,
     1          LNANF,ANSTRAF,ORGFEED,ANEXTR,ANSTRIP,WASH,
     2          ANSTROR,ANSTRAP,ANEXTRAW,VORGFEED,VWASHAF,
     3          VLNANF,VANSTRAF)
C
C
C       COMPUTE METAL CONCENTRATIONS***********************************
C
             DO I=21,40
             CALL EXMETWE(VORGFEED,VWASHAF,VWASHAF+VLNANF,
     1          WASHOP(I),ORGFEED(I),ANEXTRAW(I),LNANF(I),
     2          WASHAF(I),NANEXTR,NWASH,I,ANEXTRAWP(I),WASHOPP(I),
     3          WASH,ANEXTR)

             CALL EXMETST(VORGFEED,VANSTRAF,ANSTROR(I),
     1          ANSTROF(I),ANSTRAF(I),ANSTRAP(I),NANSTRIP,
     2          I,ANSTRAPP(I),ANSTRORP(I),ANSTRIP)
             END DO
C
C
C       CALCULATIONS DONE TIME TO PRINT RESULTS ***********************
C       PRINT RESULTS TO FILE*****************************************
C
C       PRINT NUMBER OF STAGES AND CONCENTRATIONS IN STREAMS **********
             WRITE(4,300)
300          FORMAT(13X,2HAF,10X,2HAW,10X,2HAR,10X,2HOF,10X,2HOW,
     1          10X,2HOP,10X,4HE(%),8X,4HS(%))
C
             WRITE(4,100)NANEXTR,NWASH,VLNANF,VWASHAF,
     1          VLNANF+VWASHAF,VORGFEED,VORGFEED
100          FORMAT(3HE+W,2I2,4F12.3,12X,F12.3)
C
             WRITE(4,101)(NA(I),LNANF(I),WASHAF(I),ANEXTRAW(I),
                ORGFEED(I),WASHOP(I),WASHOPP(I),ANEXTRAWP(I),I=1,40)
101          FORMAT(3X,A4,2X,1P4E12.3,12X,E12.3,0P2F12.3)
C
             WRITE(4,300)
```

```
C
            WRITE(4,103)NANSTRIP,VANSTRAF,VANSTRAF,VORGFEED,
     1      VORGFEED
103         FORMAT(3HSTR,I2,2X,F12.3,12X,2F12.3,12X,F12.3)
C
            WRITE(4,120)(NA(I),ANSTRAF(I),ANSTRAP(I),ANSTROF(I),
     1      ANSTROR(I),ANSTRORP(I),ANSTRAPP(I),I=1,40)
120         FORMAT(3X,A4,2X,1PE12.3,12X,2E12.3,12X,E12.3,0P2F12.3)
C
C     PRINT STAGE CONCENTRATIONS OF T AND AAQ IN THE BATTERIES ••••••
C
            WRITE(4,129)
129         FORMAT(13X,1HT,11X,3HAAQ)
            WRITE(4,130)(I,ANEXTR(1,I*10),ANEXTR(10,I*10),
     1      I=1,NANEXTR)
130         FORMAT(4HEXTR,I3,2X,1P2E12.3)
C
            WRITE(4,131)(I,WASH(1,I*10),WASH(10,I*10),
     1      I=1,NWASH)
131         FORMAT(4HWASH,I3,2X,1P2E12.3)
C
            WRITE(4,132)(I,ANSTRIP(1,I*10),ANSTRIP(10,I*10),
     1      I=1,NANSTRIP)
132         FORMAT(5HSTRIP,I3,1X,1P2E12.3)
C
            CLOSE(4)
C
            END
C
C
            SUBROUTINE EXMETST(VORG,VAQ,YP,YF,XF,XR,NS,IZ,
     1      RAFF,EXTR,CONC)
C
C   METAL EXTRACTION OR STRIP WITH P-METHOD USING EXTRACTANT AND ••••
C   NITRIC ACID DEPENDENT P-VALUES FOR EACH STAGE ••••••••••••••••••••
C
C   YF,VORGF ---------- YP,VORGP
C         ------->ISTRIP/I-------->
C                 I EXTR I
C         <-------I  NS  I<--------
C   XR,VAQR    ---------- XF,VAQF
C
C
            INTEGER NS,IZ,N,I,K
            REAL*8 P(10),E,PI,S
            REAl*8 VAQ,VORG,VAQR,VAQF,VORGF,VORGP
            REAL*8 METTOT,XR,XF,YF,YP,RAFF,EXTR,CONC(40,200)
            REAL*8 T,AAQ,DVALUE
C
C   SET DIFFERENT STREAMS •••••••••••••••••••••••••••••••••••••••••
            VAQF=VAQ
            VAQR=VAQ
            VORGF=VORG
            VORGP=VORG
C
C   COMPUTE FLOW OF METALSPECIE TO THE BATTERY •••••••••••••••••••••••
            METTOT=XF*VAQF+YF*VORGF
C
            IF (METTOT.GT.0.0) THEN
C   COMPUTE P(K) VALUES ••••••••••••••••••••••••••••••••••••••••••••••
            DO N=1,NS
            T=CONC(1,10*N-5)
            AAQ=CONC(10,10*N-5)
            P(N)=VORG*DVALUE(T,AAQ,IZ)/VAQ
            END DO
C
C   COMPUTE E AND S SUMS •••••••••••••••••••••••••••••••••••••••••••
            E=1.0
            DO I=2,NS
            PI=1.0
            DO K=I,NS
             PI=PI*P(K)
            END DO
            E=E+PI
            END DO
C
            PI=1.0
            DO K=1,NS
             PI=PI*P(K)
            END DO
            S=E+PI
C
C   COMPUTE RAFFINATE CONCENTRATION ••••••••••••••••••••••••••••••••••
            XR=((XF*VAQF)+(YF*VORGF)*E)/(S*(VAQR))
            IF(XR.LT.0.0)XR=0.0
C
C   COMPUTE EXTRACT CONCENTRATION ••••••••••••••••••••••••••••••••••••
            YP=(METTOT-XR*VAQR)/VORGP
            IF(YP.LT.0.0)YP=0.0
C
C   COMPUTE RELATIVE AMOUNTS IN RAFFINATE OR EXTRACT •••••••••••••••••
            RAFF=100.0*XR*VAQR/METTOT
            EXTR=100.0-RAFF
C
            RETURN
C
            ELSE
C   SPECIAL CASE, NO FEED ••••••••••••••••••••••••••••••••••••••••••••
```

```
                XR=0.0
                YP=0.0
                RAFF=0.0
                EXTR=0.0
                RETURN
                ENDIF
C
      END
C
C
                SUBROUTINE EXMETWE(VORG,VAQINW,VAQINE,YP,YF,XR,XF,
      I         XW,NS,MS,IZ,RAFF,EXTR,WASH,ANEXTR)
C
C     METAL EXTRACTION AND WASH WITH P-METHOD USING EXTRACTANT AND ••••
C     NITRIC ACID DEPENDENT P-VALUES FOR EACH STAGE ••••••••••••••••••••
C
C     YF,VORGF ----------          ----------- YP,VORGP
C          -------->I EXTR I---------->I WASH I-------->
C                I    I    I      I    I    I
C          <--------I  NS  I<--------- I  MS  I<--------
C     XR,VAQR ----------   !          ----------- XW,VAQW
C                          !
C                        XF,VAQF
C
C
                IMPLICIT REAL*8 (A-H,O-Z)
                INTEGER NS,MS,NM,I,K
                REAL*8 EF,XIW,XIF,XIR,XW,XF,XR,YP,YF
                REAL*8 VORG,VAQINW,VAQINE
                REAL*8 VAQF,VAQW,VAQR,VORGF,VORGP
                REAL*8 WASH(40,200),ANEXTR(40,200),DVALUE
                REAL*8 P(20),PI,E1,E2,S1,S2
                REAL*8 T,AAQ
C
C     SET DIFFERENT STREAMS •••••••••••••••••••••••••••••••••••••••••••••
                VAQW=VAQINW
                VAQF=VAQINE-VAQW
                VAQR=VAQINE
                VORGF=VORG
                VORGP=VORG
C
C     COMPUTE P(K)-VALUES ••••••••••••••••••••••••••••••••••••••••••••••
                NM=NS+MS+1
                DO K=1,NS
                T=ANEXTR(1,10*K-5)
                AAQ=ANEXTR(10,10*K-5)
                P(K)=VORGF*DVALUE(T,AAQ,IZ)/(VAQW+VAQF)
                END DO
                DO K=NS+2,NM
                T=WASH(1,10*(K-NS-1)-5)
                AAQ=WASH(10,10*(K-NS-1)-5)
                P(K)=VORGF*DVALUE(T,AAQ,IZ)/VAQW
                END DO
C
C     CALCULATE MASS FLOWS•••••••••••••••••••••••••••••••••••••••••••••••
                EF=YF*VORGF
                XIW=XW*VAQW
                XIF=XF*VAQF
C
                IF(EF+XIW+XIF.GT.0.0) THEN
C   COMPUTE E AND S-SUMS•••••••••••••••••••••••••••••••••••••••••••••••••
                E2=1.0D+00
                DO I=2,NS
                PI=1.0D+00
                DO K=I,NS
                PI=PI*P(K)
                END DO
                E2=E2+PI
                END DO
                PI=1.0D+00
                DO K=1,NS
                PI=PI*P(K)
                END DO
                E1=E2+PI
C
                S2=1.0D+00
                DO I=NS+3,NM
                PI=1.0D+00
                DO K=I,NM
                PI=PI*P(K)
                END DO
                S2=S2+PI
                END DO
                PI=1.0D+00
                DO K=NS+2,NM
                PI=PI*P(K)
                END DO
                S1=S2+PI
C
C     COMPUTE XR MASS FLOW•••••••••••••••••••••••••••••••••••••••••••••••
                XIR=(EF*E2*PI+XIW+XIF*S1+EF*S2)/(PI*E1+S2)
C
C     COMPUTE RAFFINATE AND EXTRACT CONCENTRATIONS••••••••••••••••••••••••
                XR=XIR/VAQR
                IF(XR.LT.0.0)XR=0.0
                YP=(XIF+XIW+EF-XIR)/VORGP
                IF(YP.LT.0.0)YP=0.0
                RAFF=100.0*XIR/(XIF+XIW+EF)
```

```
                EXTR=100.0-RAFF
C
                RETURN
                ELSE
                  XR=0.0
                  YP=0.0
                  RAFF=0.0
                  EXTR=0.0
                  RETURN
                END IF
C
                END
C
C
                REAL*8 FUNCTION DVALUE(T,AAQ,IZ)
C
C   CALCULATES D-VALUES FOR ELEMENTS •••••••••••••••••••••••••••••••••
C
                INTEGER IZ,N
                REAL*8 T,AAQ
                REAL*4 K(40,4)
C
C   T, IZ=1, N=1•••••••••••••••••••••••••••••••••••••••••••••••••••••
                DATA K(1,1),K(1,2),K(1,3),K(1,4)
     1          /0.0,0.0,0.0,0.0/
C
C   HA, IZ=2, N=2•••••••••••••••••••••••••••••••••••••••••••••••••••••
                DATA K(2,1),K(2,2),K(2,3),K(2,4)
     1          /0.0,0.0,0.0,0.0/
C
C   HA2, IZ=3, N=3•••••••••••••••••••••••••••••••••••••••••••••••••••••
                DATA K(3,1),K(3,2),K(3,3),K(3,4)
     1          /0.0,0.0,0.0,0.0/
C
C   HAT, IZ=4, N=4•••••••••••••••••••••••••••••••••••••••••••••••••••••
                DATA K(4,1),K(4,2),K(4,3),K(4,4)
     1          /0.0,0.0,0.0,0.0/
C
C   HA2T, IZ=5, N=5•••••••••••••••••••••••••••••••••••••••••••••••••••••
                DATA K(5,1),K(5,2),K(5,3),K(5,4)
     1          /0.0,0.0,0.0,0.0/
C
C   TAQ, IZ=6, N=6•••••••••••••••••••••••••••••••••••••••••••••••••••••
                DATA K(6,1),K(6,2),K(6,3),K(6,4)
     1          /0.0,0.0,0.0,0.0/
C
C   HT, IZ=7, N=7•••••••••••••••••••••••••••••••••••••••••••••••••••••
                DATA K(7,1),K(7,2),K(7,3),K(7,4)
     1          /0.0,0.0,0.0,0.0/
C
C   H2T, IZ=8, N=8•••••••••••••••••••••••••••••••••••••••••••••••••••••
                DATA K(8,1),K(8,2),K(8,3),K(8,4)
     1          /0.0,0.0,0.0,0.0/
C
C   HAAQ, IZ=9, N=9•••••••••••••••••••••••••••••••••••••••••••••••••••••
                DATA K(9,1),K(9,2),K(9,3),K(9,4)
     1          /0.0,0.0,0.0,0.0/
C
C   AAQ, IZ=10, N=10•••••••••••••••••••••••••••••••••••••••••••••••••••••
                DATA K(10,1),K(10,2),K(10,3),K(10,4)
     1          /0.0,0.0,0.0,0.0/
C
C   H, IZ=11, N=11•••••••••••••••••••••••••••••••••••••••••••••••••••••
                DATA K(11,1),K(11,2),K(11,3),K(11,4)
     1          /0.0,0.0,0.0,0.0/
C
C   NO3, IZ=12, N=12•••••••••••••••••••••••••••••••••••••••••••••••••••••
                DATA K(12,1),K(12,2),K(12,3),K(12,4)
     1          /0.0,0.0,0.0,0.0/
C
C   HNO3, IZ=13, N=13•••••••••••••••••••••••••••••••••••••••••••••••••••••
                DATA K(13,1),K(13,2),K(13,3),K(13,4)
     1          /0.0,0.0,0.0,0.0/
C
C   BLANK, IZ=14, N=14•••••••••••••••••••••••••••••••••••••••••••••••••••••
                DATA K(14,1),K(14,2),K(14,3),K(14,4)
     1          /0.0,0.0,0.0,0.0/
C
C   BLANK, IZ=15, N=15•••••••••••••••••••••••••••••••••••••••••••••••••••••
                DATA K(15,1),K(15,2),K(15,3),K(15,4)
     1          /0.0,0.0,0.0,0.0/
C
C   BLANK, IZ=16, N=16•••••••••••••••••••••••••••••••••••••••••••••••••••••
                DATA K(16,1),K(16,2),K(16,3),K(16,4)
     1          /0.0,0.0,0.0,0.0/
C
C   BLANK, IZ=17, N=17•••••••••••••••••••••••••••••••••••••••••••••••••••••
                DATA K(17,1),K(17,2),K(17,3),K(17,4)
     1          /0.0,0.0,0.0,0.0/
C
C   BLANK, IZ=18, N=18•••••••••••••••••••••••••••••••••••••••••••••••••••••
                DATA K(18,1),K(18,2),K(18,3),K(18,4)
     1          /0.0,0.0,0.0,0.0/
C
C   BLANK, IZ=19, N=19•••••••••••••••••••••••••••••••••••••••••••••••••••••
                DATA K(19,1),K(19,2),K(19,3),K(19,4)
     1          /0.0,0.0,0.0,0.0/
C
```

```
C     BLANK, IZ=20, N=20••••••••••••••••••••••••••••••••••••••••••••••••
              DATA K(20,1),K(20,2),K(20,3),K(20,4)
       1          /0.0,0.0,0.0,0.0/
C
C     LA, IZ=21, N=21••••••••••••••••••••••••••••••••••••••••••••••••••
              DATA K(21,1),K(21,2),K(21,3),K(21,4)
       1          /2.56E+13,2.48E+13,49.2,0.0/
C
C     CE, IZ=22, N=22••••••••••••••••••••••••••••••••••••••••••••••••••
              DATA K(22,1),K(22,2),K(22,3),K(22,4)
       1          /3.95E+13,3.86E+13,1.63E+4,0.0/
C
C     PR, IZ=23, N=23••••••••••••••••••••••••••••••••••••••••••••••••••
              DATA K(23,1),K(23,2),K(23,3),K(23,4)
       1          /3.95E+13,3.86E+13,1.63E+4,0.0/
C
C     ND, IZ=24, N=24••••••••••••••••••••••••••••••••••••••••••••••••••
              DATA K(24,1),K(24,2),K(24,3),K(24,4)
       1          /3.95E+13,3.86E+13,1.63E+4,0.0/
C
C     PM, IZ=25, N=25••••••••••••••••••••••••••••••••••••••••••••••••••
              DATA K(25,1),K(25,2),K(25,3),K(25,4)
       1          /9.17E+13,6.28E+13,2.56E+3,0.0/
C
C     SM, IZ=26, N=26••••••••••••••••••••••••••••••••••••••••••••••••••
              DATA K(26,1),K(26,2),K(26,3),K(26,4)
       1          /9.14E+13,5.74E+13,9.02E+3,0.0/
C
C     EU, IZ=27, N=27••••••••••••••••••••••••••••••••••••••••••••••••••
              DATA K(27,1),K(27,2),K(27,3),K(27,4)
       1          /9.14E+13,5.74E+13,9.02E+3,0.0/
C
C     GD, IZ=28, N=28••••••••••••••••••••••••••••••••••••••••••••••••••
              DATA K(28,1),K(28,2),K(28,3),K(28,4)
       1          /7.85E+13,6.43E+13,9.75E+3,0.0/
C
C     TB, IZ=29, N=29••••••••••••••••••••••••••••••••••••••••••••••••••
              DATA K(29,1),K(29,2),K(29,3),K(29,4)
       1          /7.85E+13,6.43E+13,9.75E+3,0.0/
C
C     DY, IZ=30, N=30••••••••••••••••••••••••••••••••••••••••••••••••••
              DATA K(30,1),K(30,2),K(30,3),K(30,4)
       1          /7.85E+13,6.43E+13,9.75E+3,0.0/
C
C     HO, IZ=31, N=31••••••••••••••••••••••••••••••••••••••••••••••••••
              DATA K(31,1),K(31,2),K(31,3),K(31,4)
       1          /7.85E+13,6.43E+13,9.75E+3,0.0/
C
C     ER, IZ=32, N=32••••••••••••••••••••••••••••••••••••••••••••••••••
              DATA K(32,1),K(32,2),K(32,3),K(32,4)
       1          /7.85E+13,6.43E+13,9.75E+3,0.0/
C
C     TM, IZ=33, N=33••••••••••••••••••••••••••••••••••••••••••••••••••
              DATA K(33,1),K(33,2),K(33,3),K(33,4)
       1          /7.85E+13,6.43E+13,9.75E+3,0.0/
C
C     YB, NZ=34, N=34••••••••••••••••••••••••••••••••••••••••••••••••••
              DATA K(34,1),K(34,2),K(34,3),K(34,4)
       1          /7.85E+13,6.43E+13,9.75E+3,0.0/
C
C     LU, IZ=35, N=35••••••••••••••••••••••••••••••••••••••••••••••••••
              DATA K(35,1),K(35,2),K(35,3),K(35,4)
       1          /7.85E+13,6.43E+13,9.75E+3,0.0/
C
C     BLANK, IZ=36, N=36••••••••••••••••••••••••••••••••••••••••••••••••
              DATA K(36,1),K(36,2),K(36,3),K(36,4)
       1          /0.0,0.0,0.0,0.0/
C
C     BLANK, IZ=37, N=37••••••••••••••••••••••••••••••••••••••••••••••••
              DATA K(37,1),K(37,2),K(37,3),K(37,4)
       1          /0.0,0.0,0.0,0.0/
C
C     BLANK, IZ=38, N=38••••••••••••••••••••••••••••••••••••••••••••••••
              DATA K(38,1),K(38,2),K(38,3),K(38,4)
       1          /0.0,0.0,0.0,0.0/
C
C     AM, IZ=39, N=39••••••••••••••••••••••••••••••••••••••••••••••••••
              DATA K(39,1),K(39,2),K(39,3),K(39,4)
       1          /9.99E+13,1.02E+14,4.94E+4,0.0/
C
C     CM, IZ=40, N=40••••••••••••••••••••••••••••••••••••••••••••••••••
              DATA K(40,1),K(40,2),K(40,3),K(40,4)
       1          /2.59E+14,2.09E+14,2.21E+3,0.0/
C
C
              N=IZ
              DVALUE=K(N,1)*AAQ**3*K(N,2)*(1+K(N,3)*T)
C
              RETURN
              END
C
C
              SUBROUTINE DYNSIM(NWASH,NANEXTR,NANSTRIP,WASHAF,
       1      LNANF,ANSTRAF,ORGFEED,ANEXTR,ANSTRIP,WASH,
       2      ANSTROR,ANSTRAP,ANEXTRAW,VORGFEED,VWASHAF,
       3      VLNANF,VANSTRAF)
C
C     DYNAMIC SIMULATION OF PROCESS ••••••••••••••••••••••••••••••••••••
```

```fortran
C    CALCULATION OF CONCENTRATIONS ALL SPECIES IN ALL *************
C    STREAMS AND STAGES UNTIL THE PROCESS IS STABLE ****************
C    I.E. THE CHANGE IN OUTGOING STREAMS ARE SMALL ******************
C
C
             INTEGER I,J,K
             INTEGER NWASH,NANEXTR,NANSTRIP
             REAL*8 WASHAF(40),LNANF(40),ANSTRAF(40),ORGFEED(40)
             REAL*8 VORGFEED,VWASHAF,VLNANF,VANSTRAF
             REAL*8 WASH(40,200),ANEXTR(40,200),ANSTRIP(40,200)
             REAL*8 WASHNEW(13,200),ANEXTRNEW(13,200)
             REAL*8 ANSTRIPNEW(13,200)
             REAL*8 ANSTROR(40),ANEXTRAW(40),ANSTRAP(40)
             REAL*8 ANEXTRAWOLD(40),ANSTRAPOLD(40)
             REAL*8 TEST(5)
C
C
C    SET INITIAL CONDITIONS, DIFFERENCE GREATER THAN 0.000001 ******
             F=1.0
C
C    CALCULATION OF EQUILIBRIUM CONCENTRATION FOR THE STAGES *******
C    FOR 10 MOVEMENTS AND CHECK CHANGE IN CONCENTRATION ************
C          AND CHECK TOTAL MASSBALANCE OF TERPY AND ********************
C          MASSBALANCE OF H+ OVER WASH AND EXTRACT BATTERY ***************
C    DO UNTIL DIFFERENCE IS LESS THAN 1E-9 **************************
             DO WHILE(F.GT.0.000000001)
C
C    SAVE OLD VALUES FOR OUTGOING STREAMS ***************************
             DO K=6,12
               ANEXTRAWOLD(K)=ANEXTRAW(K)
               ANSTRAPOLD(K)=ANSTRAP(K)
             END DO
C
             DO I=1,10
C
C    DYNAMIC SIMULATION MOVE VALUES ONE STEP ************************
C    FIRST THE ORGANIC CONCENTRATIONS LEFT *************************
             DO K=1,5
               DO J=1,NWASH*10-1
                 WASHNEW(K,J+1)=WASH(K,J)
               END DO
               DO J=1,NANEXTR*10-1
                 ANEXTRNEW(K,J+1)=ANEXTR(K,J)
               END DO
               DO J=1,NANSTRIP*10-1
                 ANSTRIPNEW(K,J+1)=ANSTRIP(K,J)
               END DO
               WASHNEW(K,1)=ANEXTR(K,10*NANEXTR)
               ANSTRIPNEW(K,1)=WASH(K,10*NWASH)
               ANEXTRNEW(K,1)=ORGFEED(K)
             END DO
C
C    THEN AQUEOUS CONCENTRATIONS RIGHT *****************************
             DO K=6,13
               DO J=2,NWASH*10
                 WASHNEW(K,J-1)=WASH(K,J)
               END DO
               DO J=2,NANEXTR*10
                 ANEXTRNEW(K,J-1)=ANEXTR(K,J)
               END DO
               DO J=2,NANSTRIP*10
                 ANSTRIPNEW(K,J-1)=ANSTRIP(K,J)
               END DO
               WASHNEW(K,10*NWASH)=WASHAF(K)
               ANEXTRNEW(K,10*NANEXTR)=(WASH(K,1)*VWASHAF+
     1         LNANF(K)*VLNANF)/(VWASHAF+VLNANF)
               ANSTRIPNEW(K,10*NANSTRIP)=ANSTRAF(K)
             END DO
C
C    PUT VALUES BACK INTO THE WORK VECTOR**************************
             DO K=1,13
               DO J=1,NWASH*10
                 WASH(K,J)=WASHNEW(K,J)
               END DO
               DO J=1,NANEXTR*10
                 ANEXTR(K,J)=ANEXTRNEW(K,J)
               END DO
               DO J=1,NANSTRIP*10
                 ANSTRIP(K,J)=ANSTRIPNEW(K,J)
               END DO
             END DO
C
C    CALCULATE NEW EQUILIBRIUM CONCENTRATIONS IN ALL STAGES IN *****
C    ALL BATTERIES ************************************************
             DO J=1,NWASH
               CALL EQCALC(J,WASH,VWASHAF,VORGFEED)
             END DO
             DO J=1,NANEXTR
               CALL EQCALC(J,ANEXTR,VWASHAF+VLNANF,VORGFEED)
             END DO
             DO J=1,NANSTRIP
               CALL EQCALC(J,ANSTRIP,VANSTRAF,VORGFEED)
             END DO
C
             END DO
C
C    SET VALUES IN OUTGOING STREAMS ********************************
             DO K=1,5
```

```
                ANSTROR(K)=ANSTRIP(K,10*NANSTRIP)
                END DO
                DO K=6,13
                  ANEXTRAW(K)=ANEXTR(K,1)
                  ANSTRAP(K)=ANSTRIP(K,1)
                END DO
C
C      CALCULATE DIFFERENCE IN MASSBALANCE OF TERPY ******************
                TEST(1)=ORGFEED(1)-(ANSTROR(1)+ANSTROR(4)+
       1        ANSTROR(5)+(ANEXTRAW(6)+ANEXTRAW(7)+ANEXTRAW(8))*
       2        (VWASHAF+VLNANF)/VORGFEED+
       3        (ANSTRAP(6)+ANSTRAP(7)+ANSTRAP(8))*VANSTRAF/
       4        VORGFEED)
C
C      CALCULATE DIFFERENCE IN MASSBALANCE OF HNO3 OVER WASH *********
C      AND ANEXTR ****************************************************
                TEST(2)=VWASHAF*(WASHAF(13)+WASHAF(11))+
       1        VLNANF*(LNANF(13)+LNANF(11))-
       1        (ANEXTRAW(7)+2*ANEXTRAW(8)+ANEXTRAW(11)+
       2        ANEXTRAW(13))*(VWASHAF+VLNANF)
C
C      CALCULATE MASSBALANCE OF TERPY OVER STRIP *******************
                TEST(3)=WASH(1,10*NWASH)+WASH(4,10*NWASH)+
       1        WASH(5,10*NWASH)-(ANSTROR(1)+ANSTROR(4)+
       2        ANSTROR(5)+(ANSTRAP(6)+ANSTRAP(7)+ANSTRAP(8))*
       3        VANSTRAF/VORGFEED)
C
C      CALCULATE MASSBALANCE OF TERPY OVER WASH ********************
                TEST(4)=ANEXTR(1,10*NANEXTR)+ANEXTR(4,10*NANEXTR)+
       1        ANEXTR(5,10*NANEXTR)-(WASH(1,10*NWASH)+
       2        WASH(4,10*NWASH)+WASH(5,10*NWASH))-(WASH(6,1)+
       3        WASH(7,1)+WASH(8,1))*VWASHAF/VORGFEED
C
C      CALCULATE MASSBALANCE OF TERPY OVER EXTR ********************
                TEST(5)=ORGFEED(1)+
       1        VWASHAF/VORGFEED*(WASH(6,1)+WASH(7,1)+WASH(8,1))-
       1        (ANEXTR(1,10*NANEXTR)+ANEXTR(4,10*NANEXTR)+
       2        ANEXTR(5,10*NANEXTR)+(ANEXTRAW(6)+ANEXTRAW(7)+
       3        ANEXTRAW(8))*(VWASHAF+VLNANF)/VORGFEED)
C               WRITE(*,*)TEST
C
C
C      CALCULATE THE MAXIMUM DIFFERENCE BETWEEN OLD VALUES AND *******
C      NEW VALUES IN OUTGOING STREAMS AFTER 10 MOVEMENTS *************
                F=MAX(ABS(ANSTRAP(6)-ANSTRAPOLD(6)),
       1        ABS(ANSTRAP(7)-ANSTRAPOLD(7)),
       2        ABS(ANSTRAP(8)-ANSTRAPOLD(8)),
       3        ABS(ANSTRAP(9)-ANSTRAPOLD(9)),
       4        ABS(ANSTRAP(10)-ANSTRAPOLD(10)),
       5        ABS(ANSTRAP(11)-ANSTRAPOLD(11)),
       6        ABS(ANSTRAP(12)-ANSTRAPOLD(12)),
       7        ABS(ANEXTRAW(6)-ANEXTRAWOLD(6)),
       8        ABS(ANEXTRAW(7)-ANEXTRAWOLD(7)),
       9        ABS(ANEXTRAW(8)-ANEXTRAWOLD(8)),
       A        ABS(ANEXTRAW(9)-ANEXTRAWOLD(9)),
       B        ABS(ANEXTRAW(10)-ANEXTRAWOLD(10)),
       C        ABS(ANEXTRAW(11)-ANEXTRAWOLD(11)),
       D        ABS(ANEXTRAW(12)-ANEXTRAWOLD(12)))
C
                WRITE(*,123)
123             FORMAT(' ',\)
                END DO
C
                RETURN
                END
C
C
C
                SUBROUTINE EQCALC(P,CONC,VAQ,VORG)
C
C      CALCULATION OF CONCENTRATIONS OF ALL SPECIES ******************
C      AT EQUILIBRIUM FOR THE STAGE GIVEN AQUEOUS AND ORGANIC FLOW, ***
C      CONCENTRATIONS OF ALL SPECIES IN ALL PARTS OF THE STAGE *******
C
                INTEGER P,I,J
                REAL*8 CONC(40,200),VAQ,VORG,TETA
                REAL*8 CTBER,CHABER,CHNO3BER,CNO3BER
                REAL*8 HJMV,TJMV,HAJMV,NO3JMV
                REAL*8 CT(10),CHA(10),CHNO3(10),CNO3(10)
                REAL*8 T(10),HA(10),HA2(10),HAT(10),HA2T(10),TAQ(10)
                REAL*8 HT(10),H2T(10),HAAQ(10),AAQ(10)
                REAL*8 H(10),NO3(10),HNO3(10)
C
C      SET INITIAL CONDITIONS
                CTBER=0.0
                CHABER=0.0
                CHNO3BER=0.0
                CNO3BER=0.0
                HJMV=0.0
                TJMV=0.0
                HAJMV=0.0
                NO3JMV=0.0
C
C      COMPUTE TETA VALUE **********************************************
                TETA=VORG/VAQ
C
C      CALCULATION OF CT, CHA AND CHNO3 FOR THE STAGE *****************
C      FIRST ASSIGN CONCENTRATIONS OF THE DIFFERENT SPECIES FOR ******
C      ONE PART OF THE STAGE ******************************************
```

```fortran
              J=(P-1)*10+1
              DO I=1,10
               T(I)=CONC(1,J)
               HA(I)=CONC(2,J)
               HA2(I)=CONC(3,J)
               HAT(I)=CONC(4,J)
               HA2T(I)=CONC(5,J)
               TAQ(I)=CONC(6,J)
               HT(I)=CONC(7,J)
               H2T(I)=CONC(8,J)
               HAAQ(I)=CONC(9,J)
               AAQ(I)=CONC(10,J)
               H(I)=CONC(11,J)
               NO3(I)=CONC(12,J)
               HNO3(I)=CONC(13,J)
               J=J+1
              END DO
C
C     THEN CALCULATE CT, CHA AND CHNO3 FOR ONE PART OF THE STAGE ****
              DO I=1,10
               CT(I)=T(I)+HAT(I)+HA2T(I)+TAQ(I)/TETA+HT(I)/TETA+
     1           H2T(I)/TETA
               CHA(I)=HA(I)+HAT(I)+2*HA2T(I)+2*HA2(I)+
     1           HAAQ(I)/TETA+AAQ(I)/TETA
               CNO3(I)=NO3(I)+HNO3(I)
               CHNO3(I)=H(I)+HT(I)+2*H2T(I)+HNO3(I)
C
C     SUMMATION OF CT, CHA, CHNO3 AND CNO3 OVER THE STAGE ***********
               CTBER=CTBER+CT(I)/10.0
               CHABER=CHABER+CHA(I)/10.0
               CHNO3BER=CHNO3BER+CHNO3(I)/10.0
               CNO3BER=CNO3BER+CNO3(I)/10.0
              END DO
C
              CALL HTHACALC(CHNO3BER,CTBER,CHABER,CNO3BER,HJMV,
     1          TJMV,HAJMV,NO3JMV,TETA)
C
C     RETURN CALCULATED EQUILIBRIUM VALUES INTO THE DIFFERENT *******
C     PARTS OF THE STAGE ********************************************
              DO I=(P-1)*10+1,(P-1)*10+10
               CONC(1,I)=TJMV
               CONC(2,I)=HAJMV
               CONC(3,I)=7.905148E+7*HAJMV**2
               CONC(4,I)=1.624513*HAJMV*TJMV
               CONC(5,I)=1.020960E+10*HAJMV**2*TJMV
               CONC(6,I)=TJMV/239
               CONC(7,I)=51300*TJMV*HJMV/239
               CONC(8,I)=1.9E+8*TJMV*HJMV**2/239
               CONC(9,I)=HAJMV/8869.181
               CONC(10,I)=HAJMV/(8869.181*10**3.7*HJMV)
               CONC(11,I)=HJMV
               CONC(12,I)=NO3JMV
               CONC(13,I)=CNO3BER-NO3JMV
              END DO
C
              RETURN
              END
C
C
C
C
              SUBROUTINE HTHACALC(CHNO3,CT,CHA,CNO3,HJMV,TJMV,
     1          HAJMV,NO3JMV,TETA)
C
C     CALCULATION OF CONCENTRATIONS OF H, T AND HA AT EQUILIBRIUM ***
C     FOR GIVEN CHNO3, CT, CHA, NO3 AND TETA *********************
C
      INTEGER I
      REAL*8 CHNO3,CT,CHA,CNO3
              REAL*8 HJMV,TJMV,HAJMV,NO3JMV,TETA
      REAL*8 K(3),TP(3),HAP(3),F(3),SGN,HACALC
C
C
C     START APPROXIMATION *****************************************
      K(1)=CHNO3/1E+3
      K(2)=CHNO3
C
C     CALCULATION OF ERRORS FOR THE TWO GUESSED VALUES *************
      DO I=1,2
       HAP(I)=HACALC(K(I),CHA,CT,TETA)
       TP(I)=TETA*CT/
     1   (TETA+TETA*1.624513*HAP(I)+
     2        TETA*1.02096E+10*HAP(I)**2+1.0/239+51300*K(I)/239+
     3        1.9E+8*K(I)**2/239)
       F(I)=CHNO3-(K(I)+TP(I)*51300*K(I)/239+
     1   TP(I)*2*1.9E+8*K(I)**2/239+
     2        K(I)*10**(-1.35)*CNO3/(1+10**(-1.35)*K(I)))
      END DO
C
C     CONTINUE UNTIL DIFFERENT SIGN OF ERRORS ********************
      DO WHILE(SGN(F(1)).EQ.SGN(F(2)))
C
C     SAME SIGN OF ERRORS CHANGE ONE OF THE GUESSED VALUES **********
C     RETURN IF F(2) IS ZERO ***********************************
      IF(F(2).EQ.0.0) THEN
       HJMV=K(2)
       TJMV=TP(2)
       HAJMV=HAP(2)
```

```fortran
                NO3JMV=CNO3/(1+10**(-1.35)*K(2))
          RETURN
          ELSE
          K(1)=0.1*K(1)
          HAP(1)=HACALC(K(1),CHA,CT,TETA)
          TP(1)=TETA*CT/
     1    (TETA+TETA*1.624513*HAP(1)+
     2           TETA*1.02096E+10*HAP(1)**2+1.0/239+51300*K(1)/239+
     3           1.9E+8*K(1)**2/239)
          F(1)=CNO3-(K(1)+TP(1)*51300*K(1)/239+
     1    TP(1)*2*1.9E+8*K(1)**2/239+
     2           K(1)*10**(-1.35)*CNO3/(1+10**(-1.35)*K(1)))
          END IF
          END DO
C
C     OK DIFFERENT SIGNS OF ERRORS ••••••••••••••••••••••••••••••••••••
C
C     CONTINUE UNTIL ERROR IS LESS THAN 0.000000001 ••••••••••••••••••••
          DO WHILE(ABS(F(2)).GT.0.000000001)
C
C     CALCULATION OF NEXT GUESSED VALUE ••••••••••••••••••••••••••••••••
          K(3)=K(2)-(K(2)-K(1))*F(2)/(F(2)-F(1))
          HAP(3)=HACALC(K(3),CHA,CT,TETA)
          TP(3)=TETA*CT/
     1    (TETA+TETA*1.624513*HAP(3)+
     2           TETA*1.02096E+10*HAP(3)**2+1.0/239+51300*K(3)/239+
     3           1.9E+8*K(3)**2/239)
          F(3)=CHNO3-(K(3)+TP(3)*51300*K(3)/239+
     1    TP(3)*2*1.9E+8*K(3)**2/239+
     2           K(3)*10**(-1.35)*CNO3/(1+10**(-1.35)*K(3)))
C
C     RETURN IF F(3) IS ZERO OTHERWISE CHANGE THE OLD VALUE WITH ••••
C     SAME SIGN OF ERROR ••••••••••••••••••••••••••••••••••••••••••••••
                IF(F(3).EQ.0.0) THEN
                HJMV=K(3)
                TJMV=TP(3)
                HAJMV=HAP(3)
                NO3JMV=CNO3/(1+10**(-1.35)*K(3))
                RETURN
                ELSEIF(SGN(F(3)).EQ.SGN(F(2))) THEN
                K(2)=K(3)
                TP(2)=TP(3)
                HAP(2)=HAP(3)
                F(2)=F(3)
                F(1)=0.5*F(1)
                ELSE
                K(1)=K(2)
                TP(1)=TP(2)
                HAP(1)=HAP(2)
                F(1)=F(2)
                K(2)=K(3)
                TP(2)=TP(3)
                HAP(2)=HAP(3)
                F(2)=F(3)
                END IF
                END DO
C
C     ERROR IS SMALL ENOUGH RETURN EQUILIBRIUM VALUES OF ••••••••••••••
C     H+, T, HA AND NO3- ••••••••••••••••••••••••••••••••••••••••••••••
                HJMV=K(2)
                TJMV=TP(2)
                HAJMV=HAP(2)
                NO3JMV=CNO3/(1+10**(-1.35)*K(2))
                RETURN
                END
C
C
C
          REAL*8 FUNCTION HACALC(K,CHA,CT,TETA)
C
C     CALCULATION OF HA CONCENTRATION AT EQUILIBRIUM FOR ••••••••••••••
C     GIVEN H+, CT, CHA AND TETA ••••••••••••••••••••••••••••••••••••••
C
          INTEGER I
          REAL*8 K,CHA,CT,TP(3),HAP(3),F(3),TETA,SGN
C
C
C     START APPROXIMATION ••••••••••••••••••••••••••••••••••••••••••••••
          HAP(1)=CHA/1.0E+3
          HAP(2)=CHA
C
C     CALCULATION OF ERRORS FOR THE TWO GUESSED VALUES ••••••••••••••••
          DO I=1,2
          TP(I)=TETA*CT/
     1    (TETA+TETA*1.624513*HAP(I)+
     2           TETA*1.02096E+10*HAP(I)**2+1.0/239+51300*K/239+
     3           1.9E+8*K**2/239)
          F(I)=CHA-(HAP(I)+HAP(I)/(TETA*8869.181)+
     1           HAP(I)/(TETA*8869.181*10**3.7*K)+
     2           2*7.905148E+7*HAP(I)**2+1.624513*HAP(I)*TP(I)+
     3           2*1.02096E+10*HAP(I)**2*TP(I))
          END DO
C
C     DO UNTIL DIFFERENT SIGN OF ERRORS ••••••••••••••••••••••••••••••••
          DO WHILE(SGN(F(1)).EQ.SGN(F(2)))
C
C     SAME SIGN OF ERRORS CHANGE ONE OF THE GUESSED VALUES ••••••••••••
C     RETURN IF F(2) IS ZERO ••••••••••••••••••••••••••••••••••••••••••
```

```fortran
      IF(F(2).EQ.0.0) THEN
        HACALC=HAP(2)
        RETURN
      ELSE
        HAP(1)=0.1*HAP(1)
        TP(1)=TETA*CT/
     1    (TETA+TETA*1.624513*HAP(1)+
     2          TETA*1.02096E+10*HAP(1)**2+1.0/239+51300*K/239+
     3          1.9E+8*K**2/239)
        F(1)=CHA-(HAP(1)+HAP(1)/(TETA*8869.181)+
     1          HAP(1)/(TETA*8869.181*10**3.7*K)+
     2          2*7.905148E+7*HAP(1)**2+1.624513*HAP(1)*TP(1)+
     3          2*1.02096E+10*HAP(1)**2*TP(1))
      END IF
      END DO
C
C     OK DIFFERENT SIGN OF ERRORS ••••••••••••••••••••••••••••••••••••••
C
C     DO UNTIL ERROR IS LESS THAN 0.000000001 ••••••••••••••••••••••••••
      DO WHILE(ABS(F(2)).GT.0.000000001)
C
C     CALCULATION OF NEW GUESSED VALUE ••••••••••••••••••••••••••••••••••
      HAP(3)=HAP(2)-(HAP(2)-HAP(1))*F(2)/(F(2)-F(1))
      TP(3)=TETA*CT/
     1    (TETA+TETA*1.624513*HAP(3)+
     2          TETA*1.02096E+10*HAP(3)**2+1.0/239+51300*K/239+
     3          1.9E+8*K**2/239)
        F(3)=CHA-(HAP(3)+HAP(3)/(TETA*8869.181)+
     1          HAP(3)/(TETA*8869.181*10**3.7*K)+
     2          2*7.905148E+7*HAP(3)**2+1.624513*HAP(3)*TP(3)+
     3          2*1.02096E+10*HAP(3)**2*TP(3))
C
C     RETURN IF F(3) IS ZERO OTHERWISE CHANGE THE OLD VALUE WITH ••••
C           SAME SIGN OF ERROR ••••••••••••••••••••••••••••••••••••••••••••
      IF(F(3).EQ.0) THEN
        HACALC=HAP(3)
        RETURN
      ELSEIF(SGN(F(3)).EQ.SGN(F(2))) THEN
        HAP(2)=HAP(3)
        F(2)=F(3)
        F(1)=0.5*F(1)
      ELSE
        HAP(1)=HAP(2)
        F(1)=F(2)
        HAP(2)=HAP(3)
        F(2)=F(3)
      END IF
      END DO
C
C     ERROR IS SMALL ENOUGH RETURN EQUILIBRIUM VALUE OF HA ••••••••••
      HACALC=HAP(2)
      RETURN
      END
C
C
C
C
          REAL*8 FUNCTION SGN(H)
C
C     SGN=1.0 IF H>0
C     SGN=1.0 IF H=0
C     SGN=-1.0 IF H<0
C
          REAL*8 H
C
          IF(H)11,12,12
11        SGN=-1.0
          RETURN
12        SGN=1.0
          RETURN
          END
C
C
C.
```

Appendix VI

Travel Report

University of Reading
March 10-14, 1997
Lena Spjuth

In connection with the european collaboration (NEWPART FI41-CT-96-0010) I spent a week at the University of Reading, March 10-14. I took part in their research work concerning synthesis and crystal determination. A lot of discussions were held about the future work and future synthesis of new interesting extractants.

We synthesised a new nitrogen-containing extractant which is expected to have good selectivity for actinides(III) over lanthanides. The extractant, tolylterpyridine (see figure 1), is a toluene-substituted terpyridine and is more lipophilic than the unsubstituted terpyridine that previously has been investigated (in synergistic systems with 2-bromodecanoic acid). Hopefully a lipophilic anion won't be needed in the extraction by this new extractant because of its more lipophilic character. Extraction studies with this new extractant is planned to start at Chalmers in the beginning of April. Other similar structures are planned to be synthesised in Reading this spring and extraction studies are then planned to be performed at Chalmers and in France (CEA).
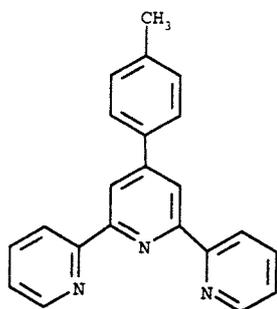
Figure 1. Tolylterpyridine.

When trying to grow a crystal of the extracted Sm-nitrate-complex from a synergistic mixture of terpyridine and 2-bromodecanoic acid, a new crystal of samarium, nitrate and terpyridine was found and its structure was determined by X-ray diffraction. The crystal didn't contain 2-bromodecanoic acid even though the acid was present in solution. The correlation between the crystal structure and species in solution is always hard to predict. Are the crystals that we find totally different from the extracting complexes we have in solution??

The molecular modelling program, Cerius2, that they are using at the University of Reading, was demonstrated and its advantages and disadvantages over other similar packages (e.g. Sybyl) were presented.

Appendix VII

OECD / NEA

conference on

Long-Lived Radionuclide Chemistry in Nuclear Waste Treatment

Villeneuve-Lès-Avignon, France, 18-20 June, 1997

In June, Anders Landgren and Jan-Olov Liljenzin participated in the OECD/NEA conference on "Long-Lived Radionuclide Chemistry in Nuclear Waste Treatment" held in Villeneuve-Lès-Avignon, France. About 80 people from 10 different countries attended the conference.

There were 4 sessions concerning: radwaste inventory, long-lived radionuclide (LLR) contents and nature of the problems; speciation of LLRs; thermodynamic properties of LLRs relevant to their separation and separation methods of LLRs. Anders Landgren presented the paper "Extraction Behaviour of Technetium and Actinides in the Aliquat-336 / Nitric Acid System".

On the last day there was a technical visit to ATALANTE at Marcoule. The objectives for ATALANTE are to provide the Commissariat à l'Energie Atomic (CEA) with modern research and development facilities in the areas of high-level chemistry and radiochemistry, to replace older laboratories located in the heavily populated Paris suburbs, centralise radioactive research and development activities at Marcoule in the areas of reprocessing, actinide and fission product separation, waste treatment and related analyses and to promote co-operation with other R&D activities already present on site and closer collaboration with COGEMA.

Appendix VIII

Travelling report

IVA's International Conference
"Why Research on Accelerator-driven Transmutation Technology"
October 24, Stockholm, Sweden (1997)

In October 1997, the Royal Swedish Academy of Engineering Sciences (IVA) arranged an international conference on accelerator-driven transmutation technology and its applications. Four invited speakers talked about different concepts and aspects of this new technology.

Dr. Stanley Schreiber presented the research on accelerator-driven technology that is being performed at the Los Alamos National Laboratory, USA. A linear accelerator with a lead-bismuth target is considered and the separation process planned is based on pyrochemistry. The national laboratories in Argonne and Oak Ridge are also involved in this research, pyrochemistry and liquid metal research, respectively.

Professor Carlo Rubbia presented his Energy Amplifier, a thorium fueled reactor driven by a cyclotron. Actinides separated from conventional reactor fuels are also considered to be burnt in this reactor, thus both energy production and waste minimisation are possible at the same time.

Dr. Massimo Salvatores from the CEA compared the transmutation efficiency between fast breeder reactors and accelerator-driven systems in terms of percentage of the total reactor park that has to be used for actinide burning. If fast breeder reactors are used for transmutation about 25% of all reactors have to be fast breeders. If accelerator-driven systems are used only 6% of the reactor park has to be used for this purpose.

Finally, Professor Lars Ingelstam gave a lecture about complex systems and their acceptance among the general population.