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# Development and demonstration of a new SANEX process for actinide(III)/lanthanide(III) separation using a mixture of $CyMe_4BTBP$ and TODGA as selective extractant

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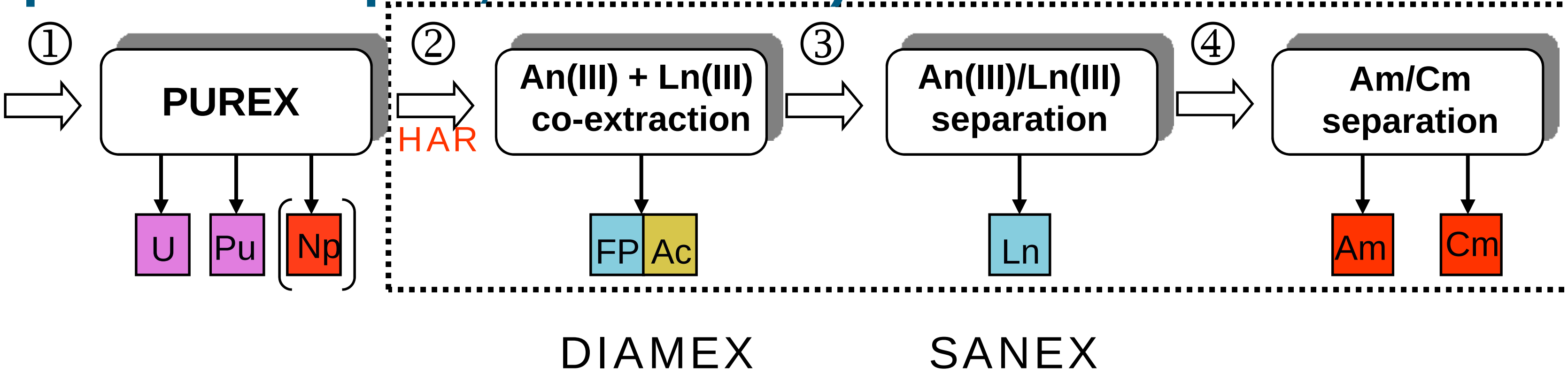
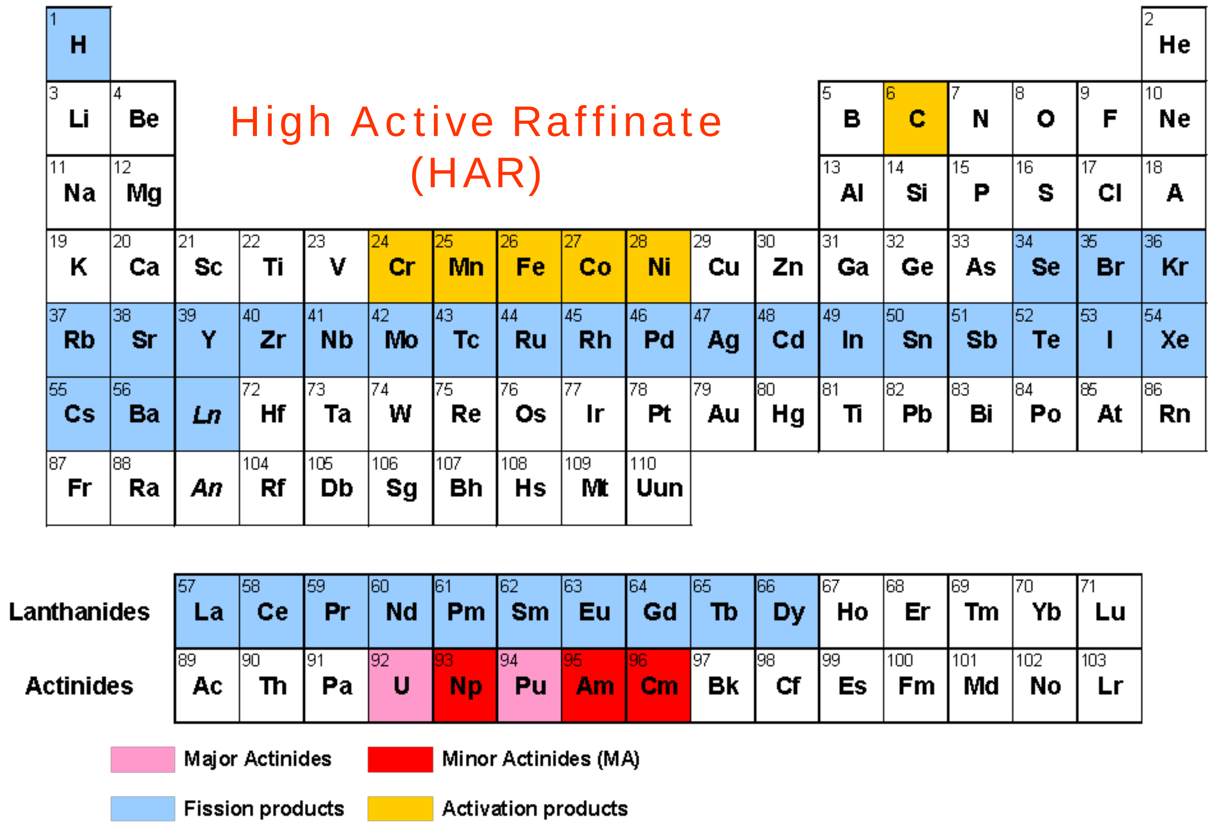
# Outline of the presentation

- European hydrometallurgical separation strategy
- TODGA/TBP process for co-extraction of An(III) + Ln(III)
- Status of EUROPART research on An(III)/Ln(III) separation
- $CyMe_4BTBP$, an effective extracting agent for An(III)/Ln(III)
- Optimisation studies and CC tests using centrifugal contactors
- Conclusions and Outlook

# European hydrometallurgical separation strategy (Newpart to Europart, 1996 - 2007)

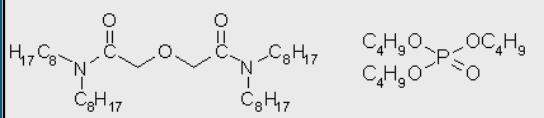
spent fuel

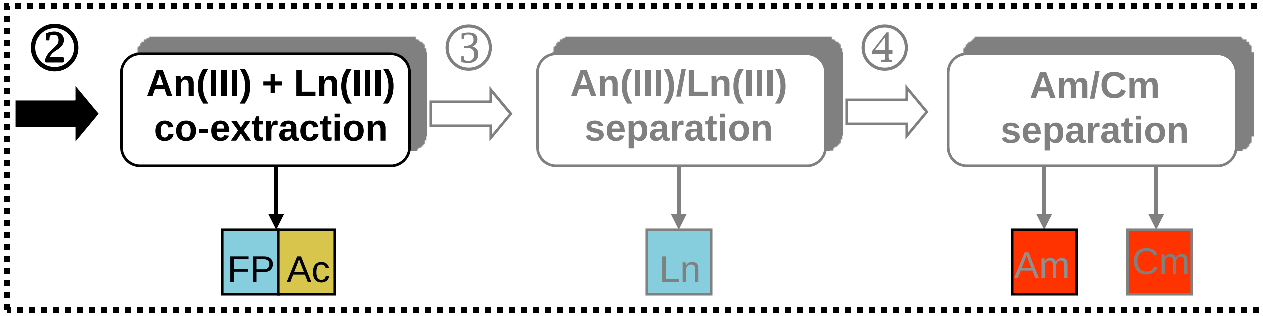


# Co-extraction of Actinides(III) and Lanthanides(III)

TODGA + TBP






**Recovery rates: Am + Cm + Ln > 99.99%, low non-Ln impurities**


*Modolo et al, Part I, Solv. Extr. Ion Exch., 25, 703-721 (2007)*
*Modolo et al, Part II, Solv. Extr. Ion Exch., 26 (1), 62 – 76 (2008)*
*Magnusson et al, Part III, Solv. Extr. Ion Exch., in press*

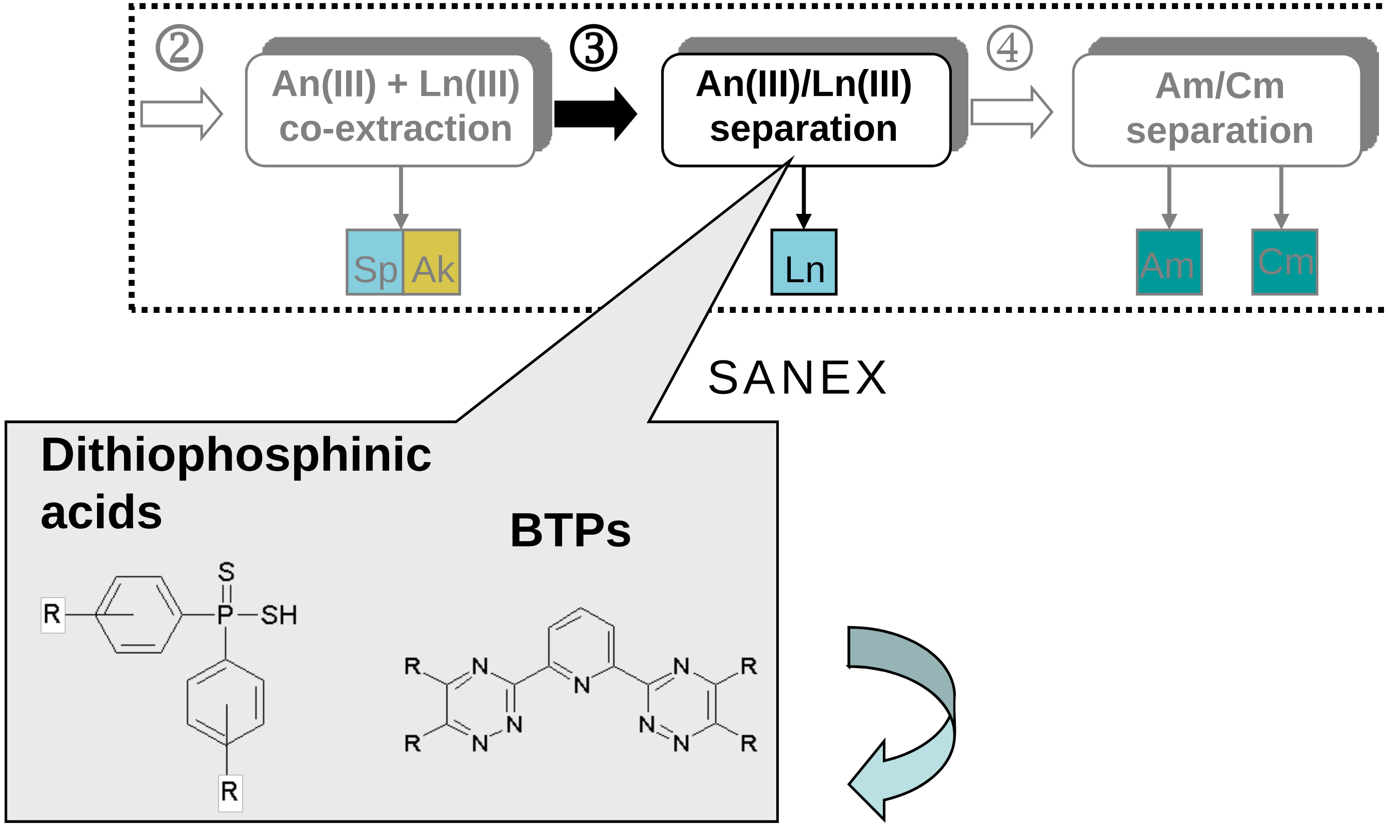
Work done in EUROPART

# Separation of Actinides(III) from Lanthanides(III)

**NEWPART**

⇩

**PARTNEW**




- Low hydrolytic stability at $HNO_3 > 1$ M $HNO_3$
- Needs a synergist, which complicates regeneration

- CC tests with real HAR gave promising results
- Low hydrolytic and radiolytic stability

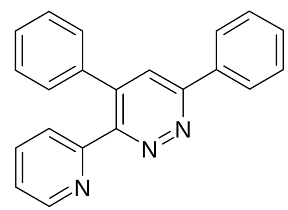
⇨ Call for improvements

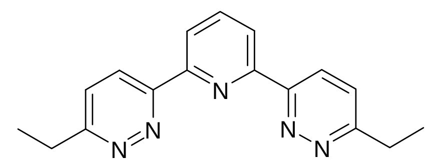
# Separation of Actinides(III) from Lanthanides(III)

## *Main achievements during EUROPART*

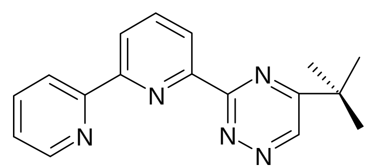
- **Sulphur containing ligands (dithiophosphinic acids)**
  - 😐 No improvement of systems developed during FP5 (PARTNEW)

- **Nitrogen containing ligands (heterocyclic rings)**
  - ☹ No extraction efficiency for molecules such as
    - Pyridine-diazines,




    - Bis-diazine-pyridine,
    - Hemi-BTPs




**Require synergists (carboxylic acid) to extract at higher acidity**

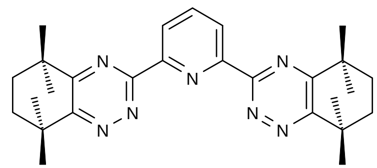
# Separation of Actinides(III) from Lanthanides(III)

## *Main achievements during EUROPART*

- **Nitrogen containing ligands (heterocyclic rings)**

☺ Very good extraction efficiency for

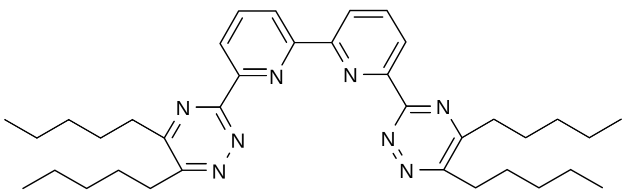
**BATPs**



**CyMe$_4$-BTP**

☺ $D_{Am} > 1$; $SF_{Am/Eu} > 1000$
☹ Low solubility
☹ Radiolytic instability
☹ **No An(III) stripping**

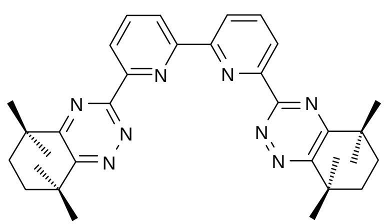
**BTBPs**



**C5-BTBP**

☺ $D_{Am} > 1$; $SF_{Am/Eu} > 100$
☹ Hydrolytic Instability

**BATBPs**



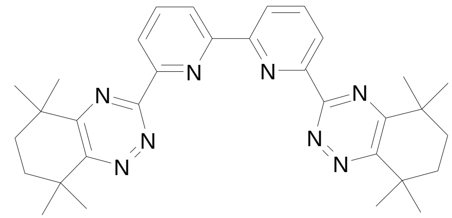
**CyMe$_4$-BTBP**

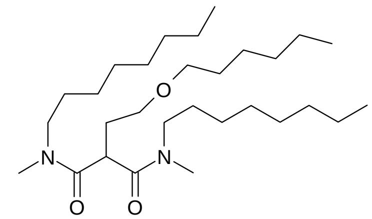
☺ $D_{Am} > 1$; $SF_{Am/Eu} > 100$
☺ High hydrolytic stability
☹ **Kinetics is slow**
😐 Radiolytic stability
☹ **Low solubility**

# Separation of Actinides(III) from Lanthanides(III)

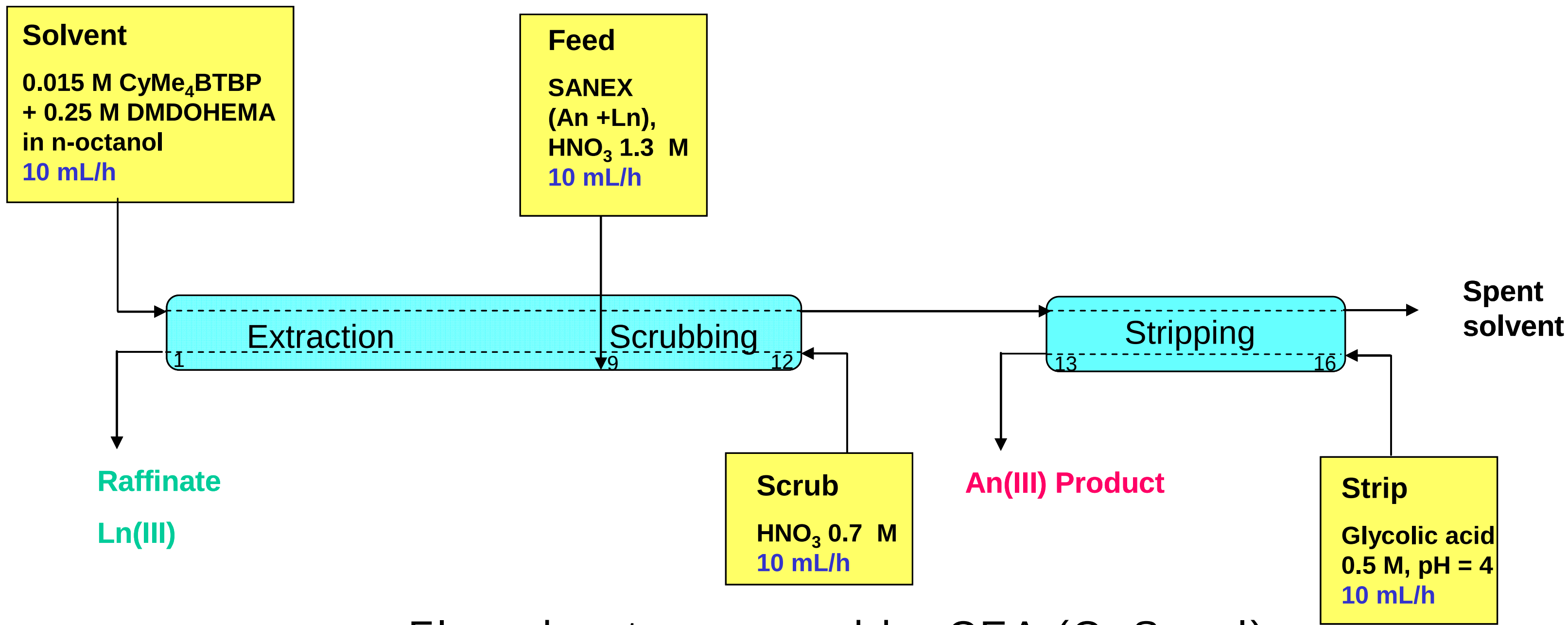
## *Optimisation studies with $CyMe_4BTBP$ + DMDOHEMA*

**Geist, Hill, Modolo, Foreman, Weigl,**
**Gompper, Hudson, Madic,**
**Solv. Extr. Ion Exch., 24, 463–483 (2006)**




0.015 M $CyMe_4BTBP$ + 0.25 M DMDOHEMA in n-octanol



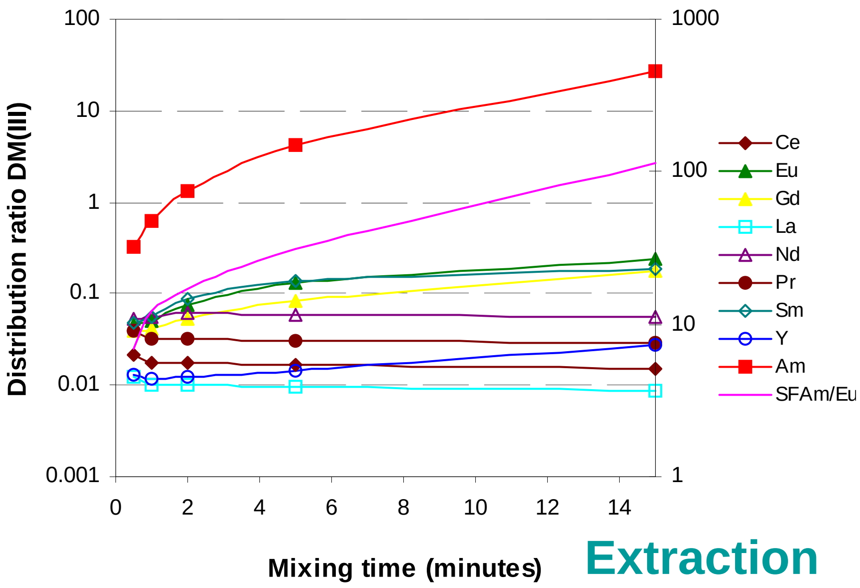

Flowsheet proposed by CEA (C. Sorel)

| Element | Y | La | Ce | Pr | Nd | Sm | Eu | Gd | $^{252}$Cf | $^{241}$Am | $^{244}$Cm | $^{152}$Eu |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| mg/L | 56 | 209 | 397 | 204 | 764 | 151 | 140 | 78 | traces | | | |

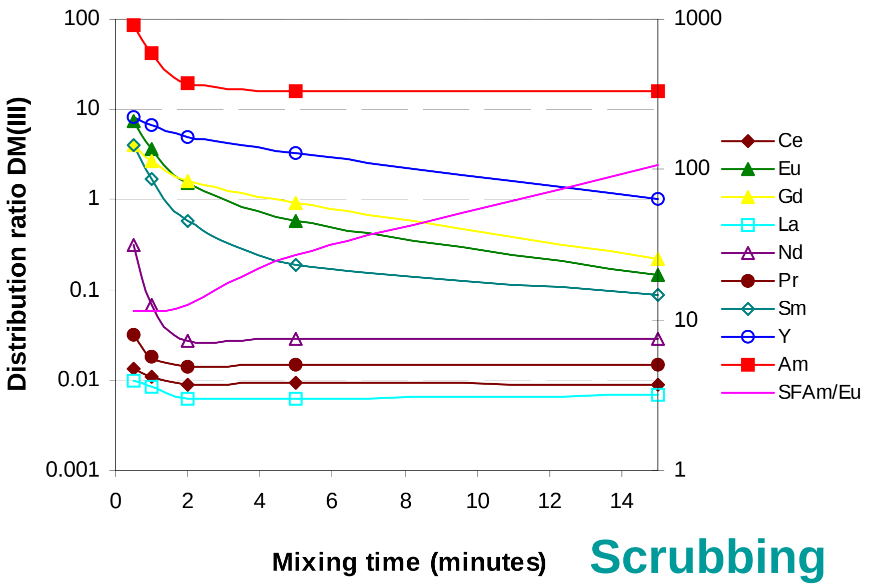
Composition of synthetic SANEX feed (generated during TODGA/TBP test)

# Separation of Actinides(III) from Lanthanides(III)

## *Kinetic tests in test tubes with $CyMe_4$BTBP + DMDOHEMA*

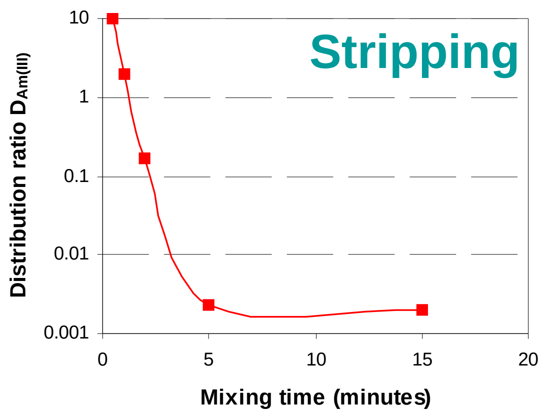



Extraction




Scrubbing

| conditions | Organic phase | Aqueous phase | A/O ratio |
|---|---|---|---|
| Extraction | 0.015 M $CyMe_4$-BTBP + 0.25 M DMDOHEMA in octanol | SANEX feed 1.15 M $HNO_3$ | 0.5 |
| Scrubbing | Loaded organic phase from extraction | 0.8 M $HNO_3$ | 1 |
| Stripping | Loaded organic phase from extraction | 0.5 M Glycolic acid set to pH 4 | 1 |



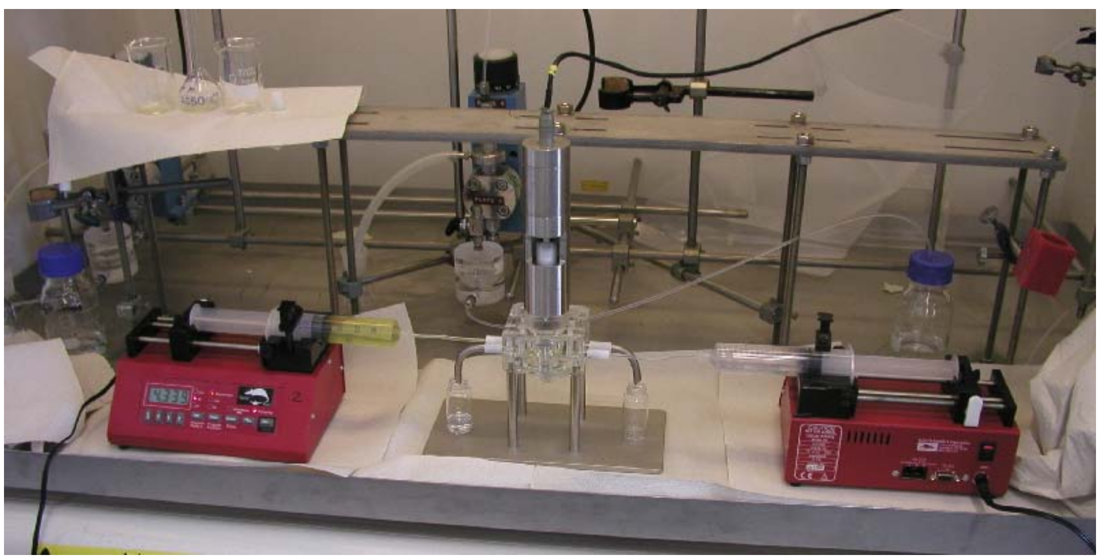

## SANEX Feed

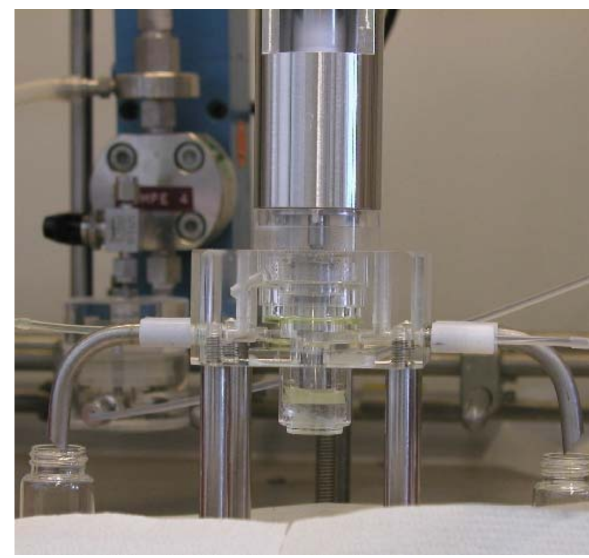
| Element | Y | La | Ce | Pr | Nd | Sm | Eu | Gd | $^{252}$Cf | $^{241}$Am | $^{244}$Cm | $^{152}$Eu |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| mg/L | 56 | 209 | 397 | 204 | 764 | 151 | 140 | 78 | traces | | | |

# Separation of Actinides(III) from Lanthanides(III)

## *Single centrifuge kinetic tests*

| Test number | Sample | Flow rate (mL/h) | |
|---|---|---|---|
| | | *Organic phase* | *Aqueous phase* |
| Test 1 | EX 1 | 20 | 40 |
| Test 2 | EX 2 | 10 | 20 |
| Test 3 | EX 3 | 5 | 10 |
| Batch Test | EX eq | Organic phase: 0.015 M $CyMe_4$-BTBP + 0.25 M DMDOHEMA in 1-octanol<br><br>Aqueous phase: SANEX Feed, A/O ratio = 2 , Mixing time 15 min, 22°C | |





# Separation of Actinides(III) from Lanthanides(III)

## *Single centrifuge kinetic tests*

| Test number | Sample | Flow rate (mL/h) | |
|---|---|---|---|
| | | *Organic phase* | *Aqueous phase* |
| Test 1 | EX 1 | 20 | 40 |
| Test 2 | EX 2 | 10 | 20 |
| Test 3 | EX 3 | 5 | 10 |
| Batch Test | EX eq | Organic phase: 0.015 M $CyMe_4$-BTBP + 0.25 M DMDOHEMA in 1-octanol<br><br>Aqueous phase: SANEX Feed,<br>A/O ratio = 2 , Mixing time 15 min, 22°C | |

| Sample | $D_{Eu}$ | $D_{Am\ \gamma}$ | $D_{Am\ \alpha}$ | $D_{Cm}$ | $D_{Cf}$ | $SF_{Am/Eu}$ | $SF_{Am/Cm}$ |
|---|---|---|---|---|---|---|---|
| EX 1 | 0.05 | 0.62 | 0.58 | 0.35 | 0.61 | 13 | 1.65 |
| EX 2 | 0.08 | 1.48 | 1.32 | 0.73 | 1.49 | 19 | 1.81 |
| EX 3 | 0.11 | 2.48 | 2.02 | 1.20 | 2.38 | 21 | 1.68 |
| EX eq | 0.21 | 27 | 25 | 13 | 183 | 133 | 1.92 |

Too slow kinetics (extraction and stripping)
to implement the current flow sheet
Needs modification

# Separation of Actinides(III) from Lanthanides(III)

## *Results of hot BTBP/DMDOHEMA (ITU 2008, CC)*

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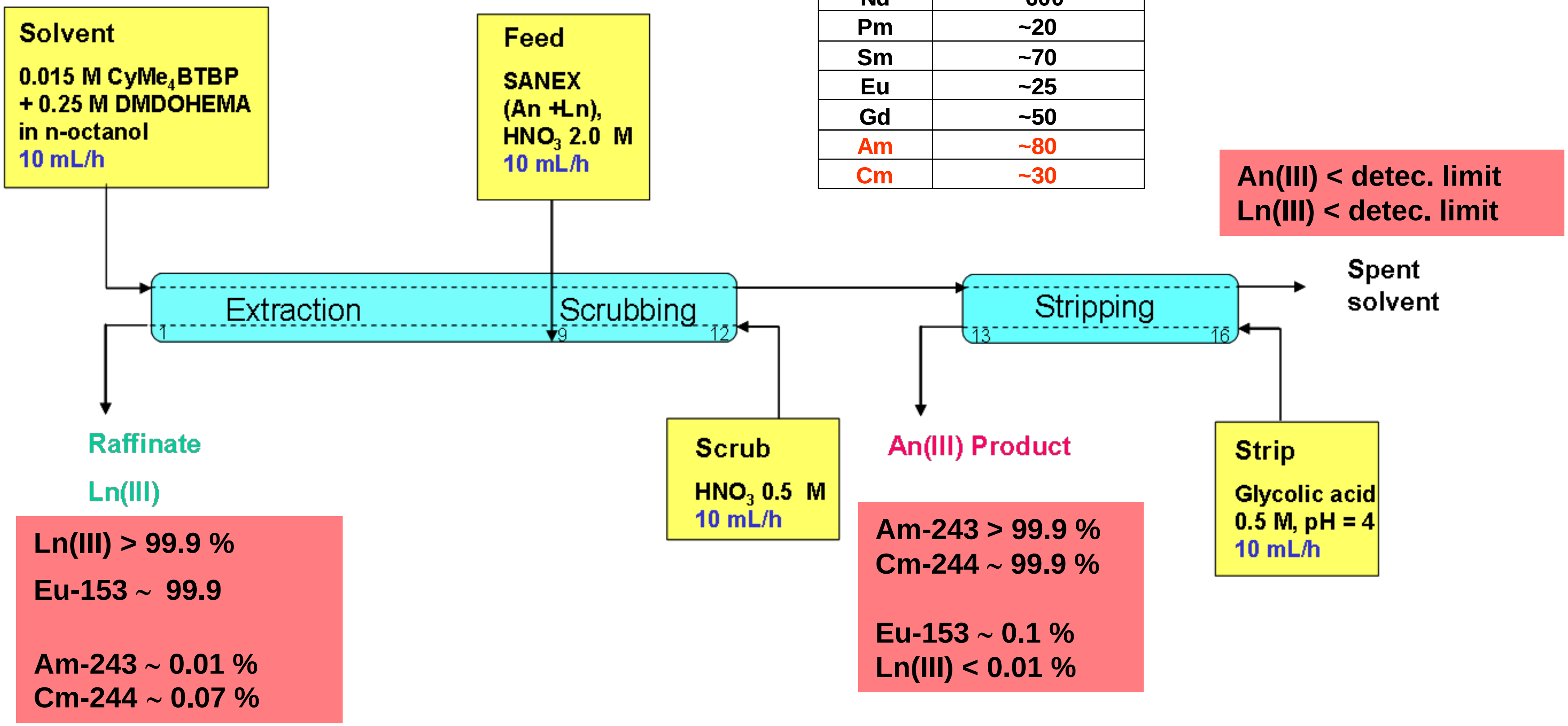
**Feed: Product fraction from the TODGA/TBP**
**Acidity adjusted to 2 M (from 0.12)**

| Element | Concentration [ppm] |
|---|---|
| Y | ~50 |
| La | ~200 |
| Ce | ~300 |
| Pr | ~150 |
| Nd | ~600 |
| Pm | ~20 |
| Sm | ~70 |
| Eu | ~25 |
| Gd | ~50 |
| Am | ~80 |
| Cm | ~30 |

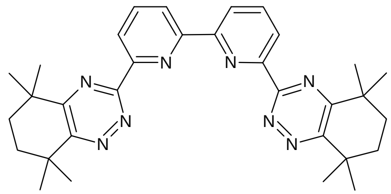
***Magnusson, Christiansen, Foreman, Geist, Glatz, Malmbeck, Modolo, Serranno-Purroy, Sorel, Solv. Extr. Ion Exch. submitted***

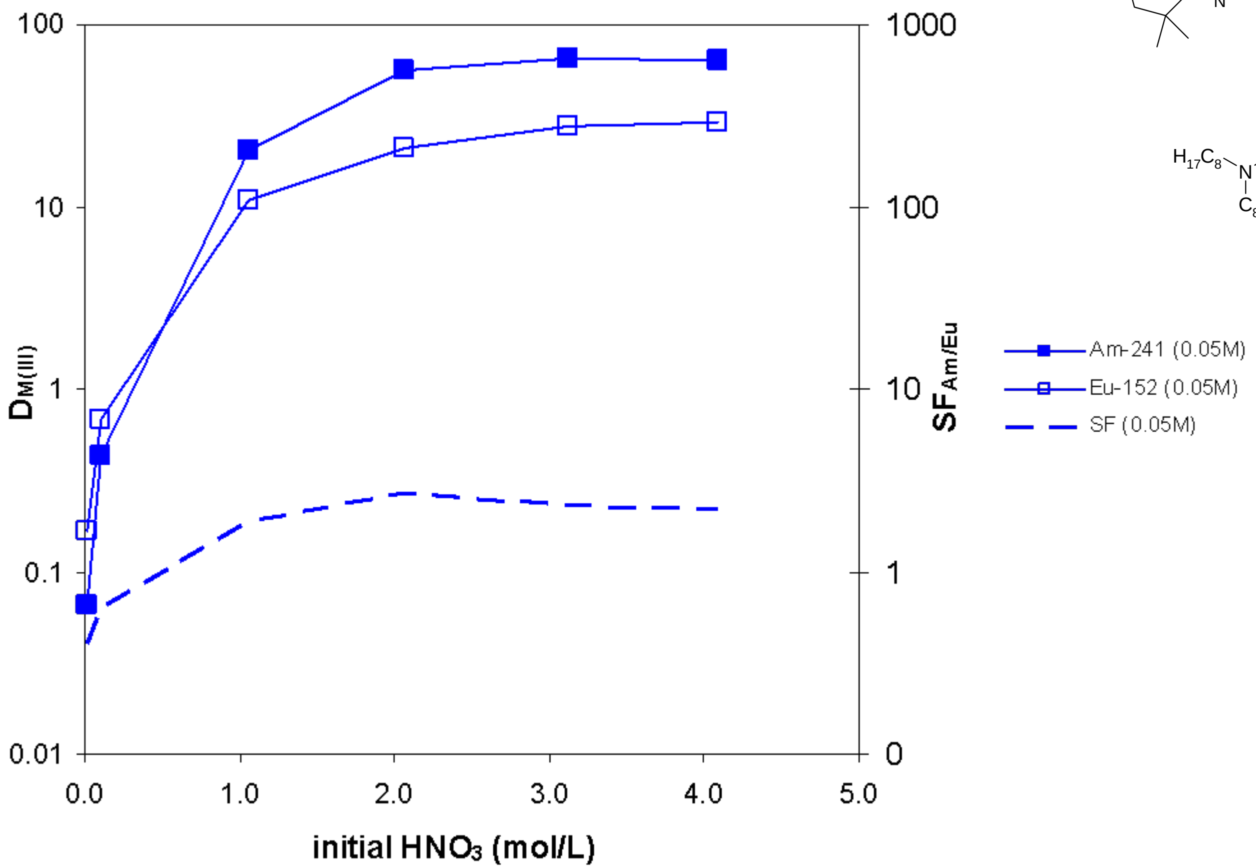


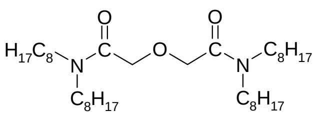

- > 99.9% of the An(III) in the product
- The Ln remained in the raffinate
- No detectable Ln or An in the spent organic phase

# Separation of Actinides(III) from Lanthanides(III)

## *Optimisation studies, influence of TODGA*





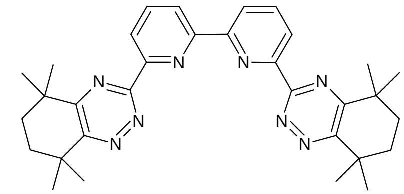



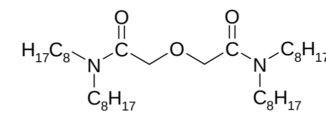
Organic phase: 0.015 mol/L $CyMe_4BTBP$ + variable TODGA in n-octanol

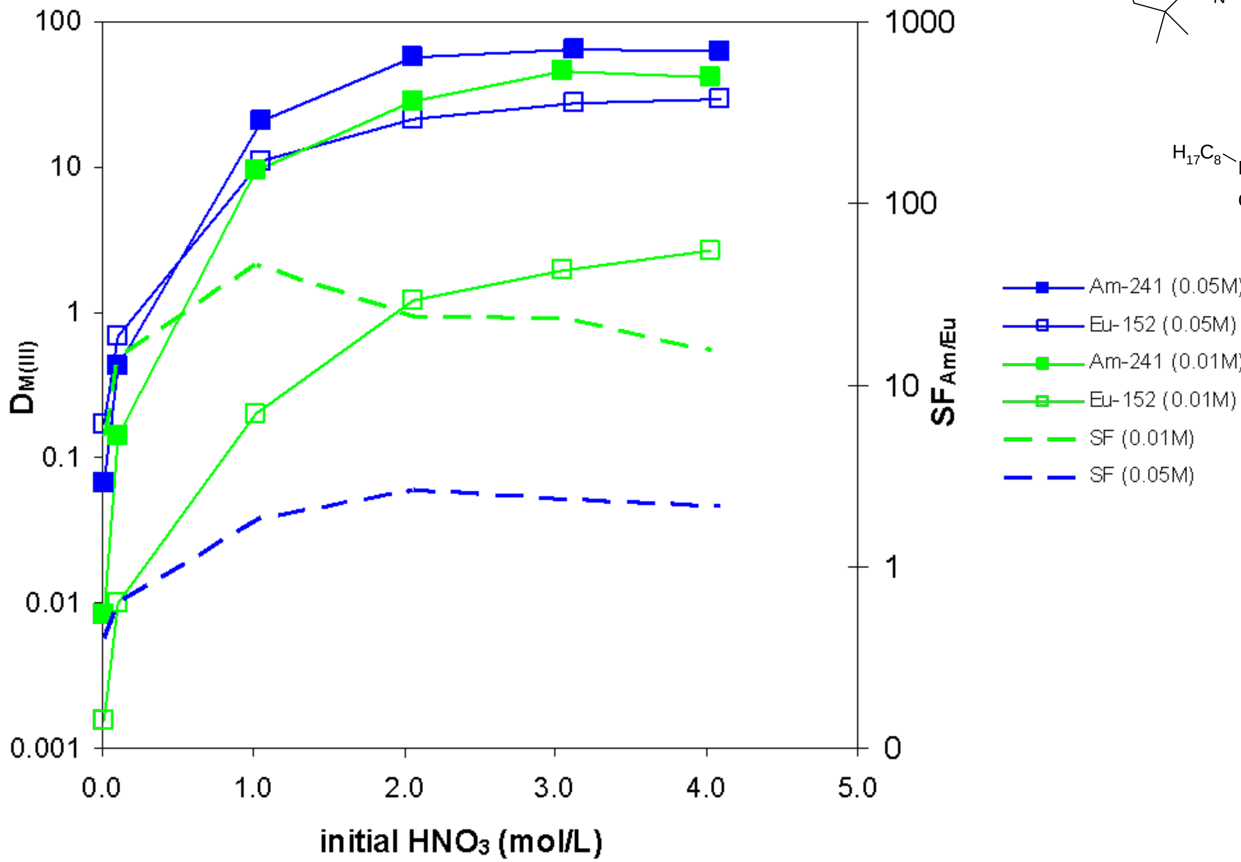
Aqueous phase: variable $HNO_3$, traces of $^{241}Am$ and $^{152}Eu$, 22 °C

# Separation of Actinides(III) from Lanthanides(III)

## *Optimisation studies, influence of TODGA*





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Aqueous phase: variable $HNO_3$, traces of $^{241}Am$ and $^{152}Eu$, 22 °C

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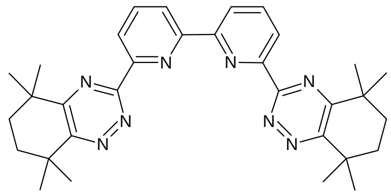
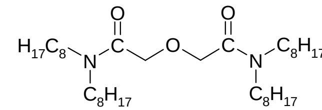
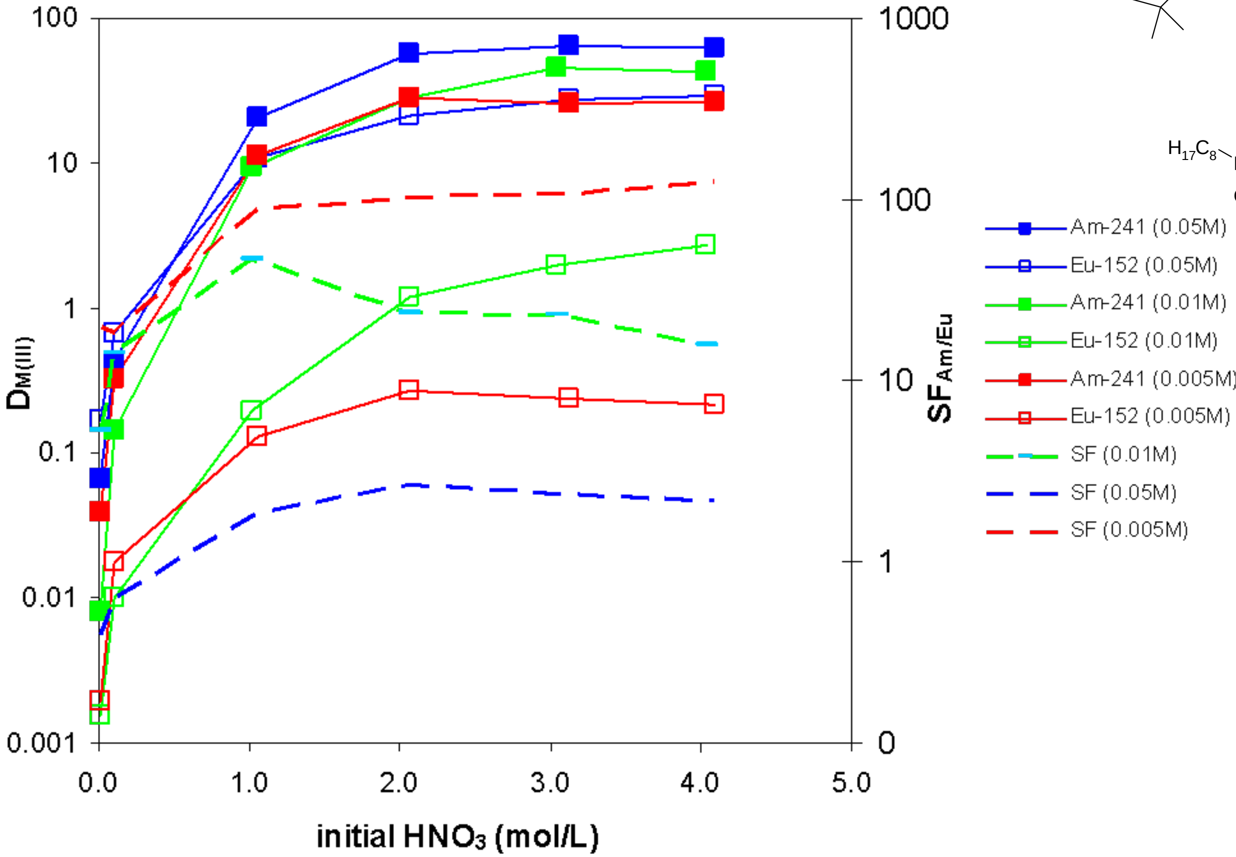




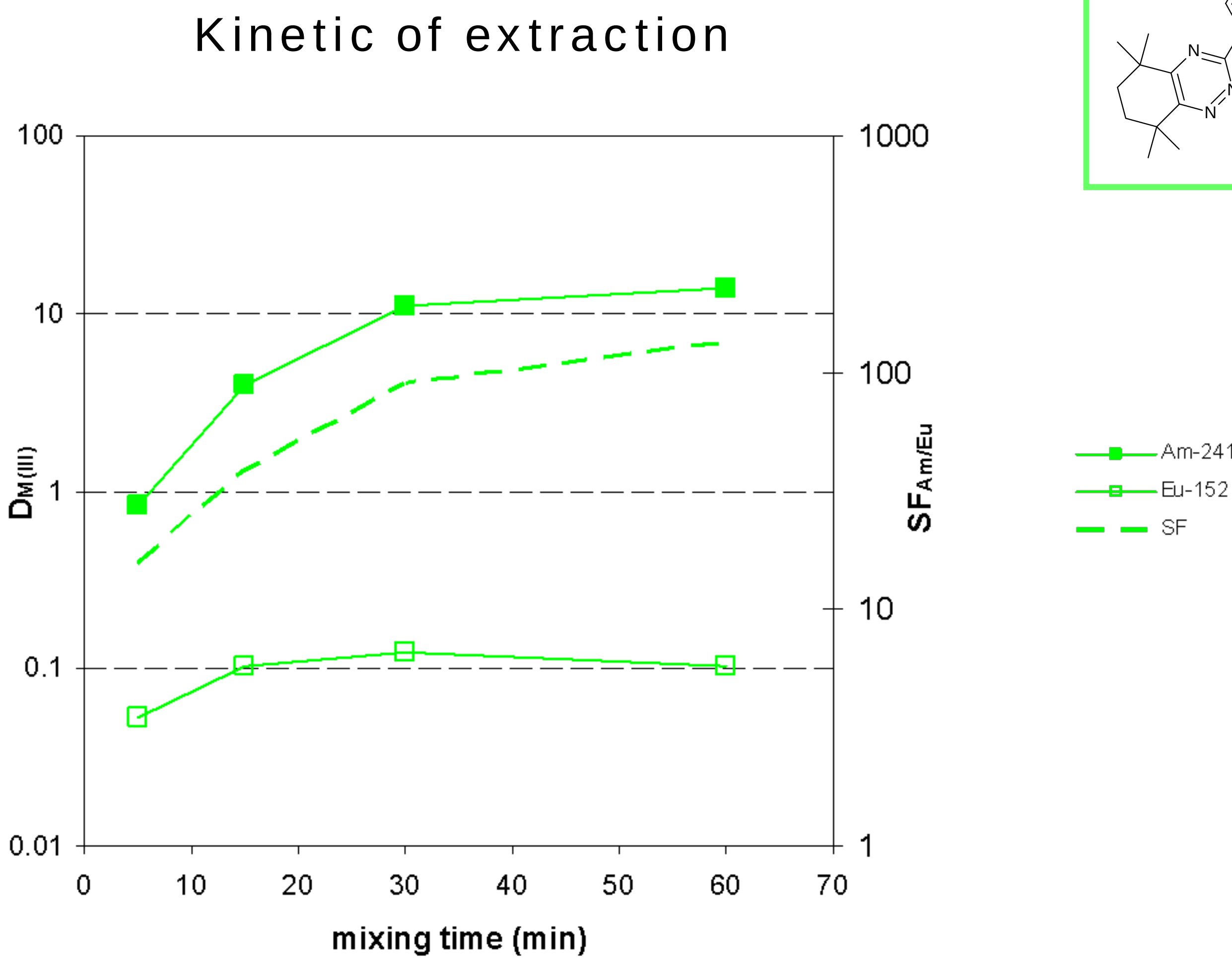


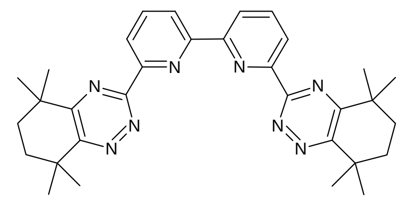

Organic phase: 0.015 mol/L $CyMe_4BTBP$ + variable TODGA in n-octanol

Aqueous phase: variable $HNO_3$, traces of $^{241}Am$ and $^{152}Eu$, 22 °C

# Separation of Actinides(III) from Lanthanides(III)

## *Optimisation studies with $CyMe_4BTBP$*



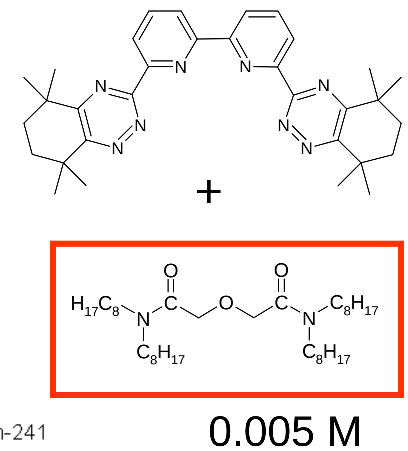



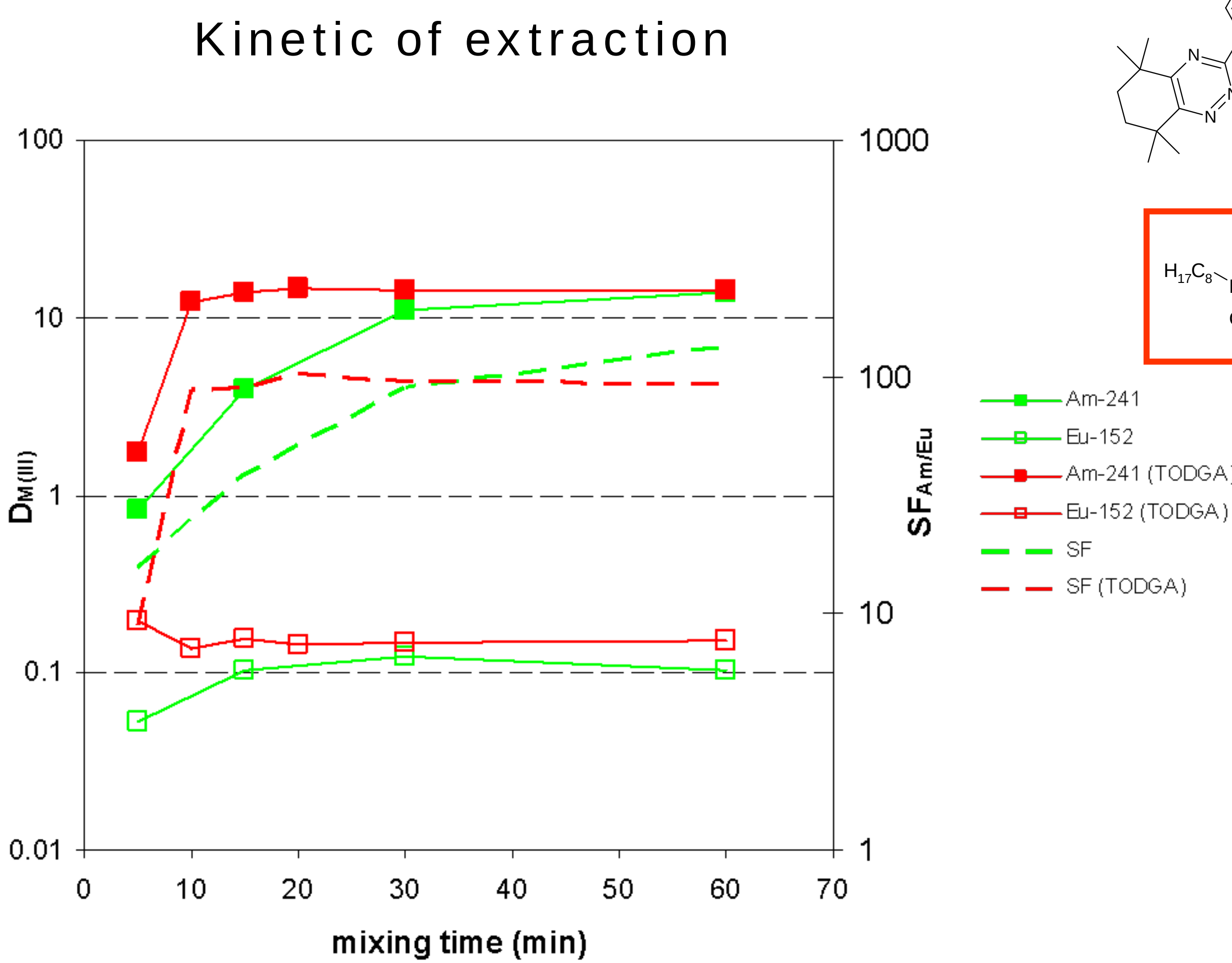

Organic phase: 0.015 mol/L $CyMe_4BTBP$ in n-octanol

Aqueous phase: 1.0 mol/L $HNO_3$, traces of $^{241}Am$ and $^{152}Eu$, 22 °C

# Separation of Actinides(III) from Lanthanides(III)

## *Optimisation studies with $CyMe_4BTBP$*

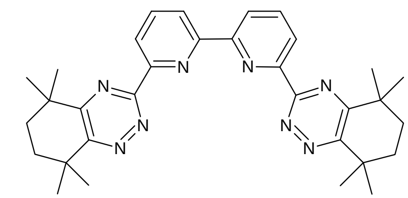


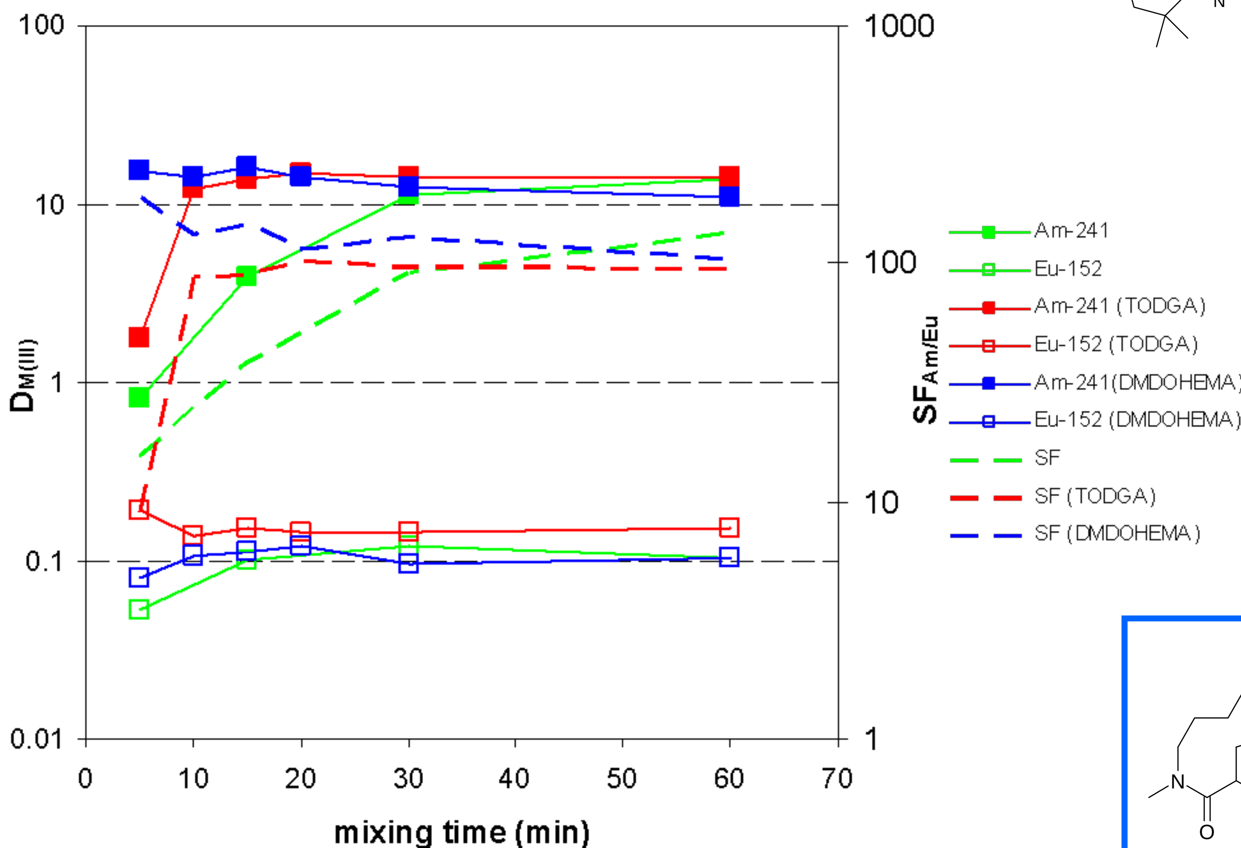

Organic phase: 0.015 mol/L $CyMe_4BTBP$ (+ 0.005 mol/L TODGA) in n-octanol
Aqueous phase: 1.0 mol/L $HNO_3$, traces of $^{241}Am$ and $^{152}Eu$, 22 °C

# Separation of Actinides(III) from Lanthanides(III)

## *Optimisation studies with $CyMe_4BTBP$*



Kinetic of extraction

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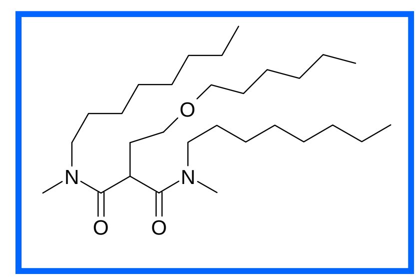

| | | |
|---|---|---|
| Organic phase: | 0.015 mol/L $CyMe_4BTBP$ without and with (0.005 mol/L TODGA or 0.25 mol/L DMDOHEMA) in n-octanol | 0.25 M |
| Aqueous phase: | 1.0 mol/L $HNO_3$, traces of $^{241}Am$ and $^{152}Eu$, 22 °C | |

# Separation of Actinides(III) from Lanthanides(III)

## *Single centrifuge kinetic tests*

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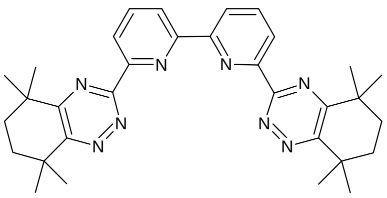
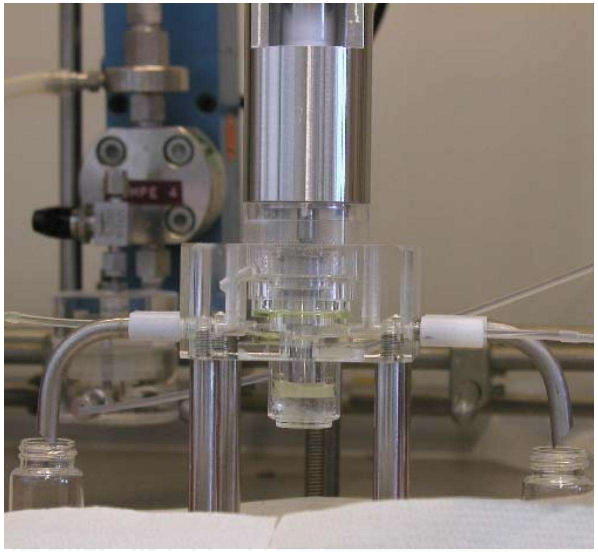



## Extraction from SANEX feed

| Flow | TODGA | | | DMDOHEMA | | |
|---|---|---|---|---|---|---|
| mL/h (aq/org) | $D_{Eu}$ | $D_{Am}$ | $SF_{Am/Eu}$ | $D_{Eu}$ | $D_{Am}$ | $SF_{Am/Eu}$ |
| 40/20 | 0.16 | 0.8 | 5 | 0.048 | 0.6 | 13 |
| 20/10 | 0.18 | 1.3 | 7 | 0.079 | 1.5 | 19 |
| Batch eq. | 0.28 | 22 | 80 | 0.21 | 25 | 120 |

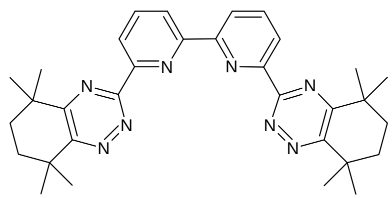


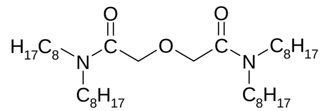
## Stripping with glycolic acid

| Flow | TODGA | | | DMDOHEMA | | |
|---|---|---|---|---|---|---|
| mL/h (aq/org) | $D_{Eu}$ | $D_{Am}$ | $SF_{Am/Eu}$ | $D_{Eu}$ | $D_{Am}$ | $SF_{Am/Eu}$ |
| 20/20 | 0.099 | 0.22 | 2.2 | 1.7 | 5.5 | 3.2 |
| 10/10 | 0.095 | 0.08 | 0.8 | 0.65 | 1.8 | 2.7 |
| Batch eq. | 0.044 | 0.003 | 0.07 | 0.02 | 0.002 | 0.08 |

# Separation of Actinides(III) from Lanthanides(III)

## *Results of spiked BTBP/TODGA (FZJ 2008, CC)*





| Element | Concentration (mg/L) | Nuclide/Activity (MBq/L) |
|---|---|---|
| Am | traces | Am-241 (2.5) |
| Cm | traces | Cm-244 (2.4) |
| Cf | traces | Cf-252 (1.6) |
| Ce | 383 | |
| Eu | 129 | Eu-152 (3.3) |
| Gd | 85 | |
| La | 205 | |
| Nd | 716 | |
| Pr | 192 | |
| Sm | 142 | |
| Y | 55 | |

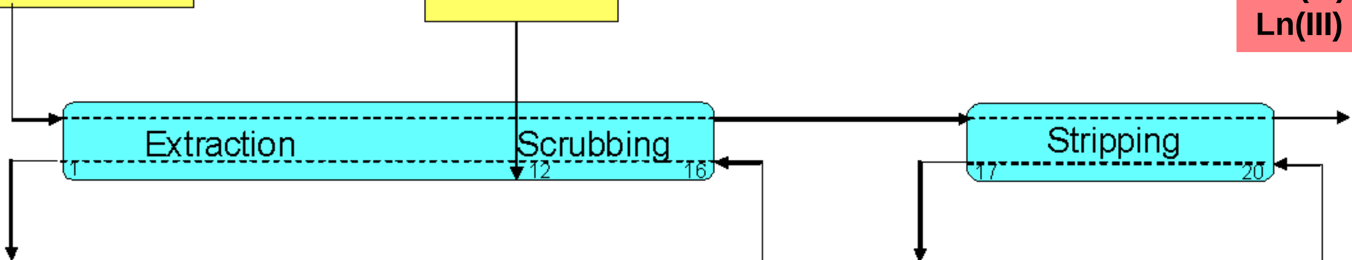
**An(III) ~ detec. limit**
**Ln(III) ~ detec. limit**

**Solvent**

**0.015 M $CyMe_4BTBP$ + 0.005 M TODGA in n-octanol**
**10 mL/h**

**Feed**

**SANEX (An +Ln), $HNO_3$ 1.3 M**
**10 mL/h**




**Raffinate**

**Ln(III)**

**Ln(III) > 99.9 %**
**Eu-152 ~ 99.9 %**

**Am-241 ~ 0.08 %**
**Cm-244 ~ 0.32 %**
**Cf-252 ~ detec. limit**

**Scrub**

**$HNO_3$ 0.7 M**
**10 mL/h**

**An(III) Product**

**Am-241 > 99.9 %**
**Cm-244 ~ 99.7 %**
**Cf-252 > 99.9 %**

**Eu-152 ~ 0.8 %**
**Ln(III) < 0.1 %**
**Y(III) ~ 3.2%**

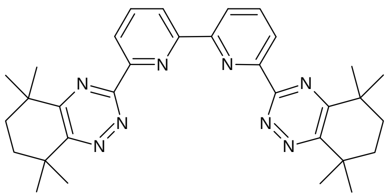
**Strip**

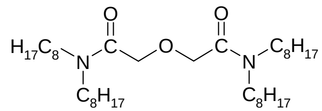
**Glycolic acid 0.5 M, pH = 4**
**10 mL/h**

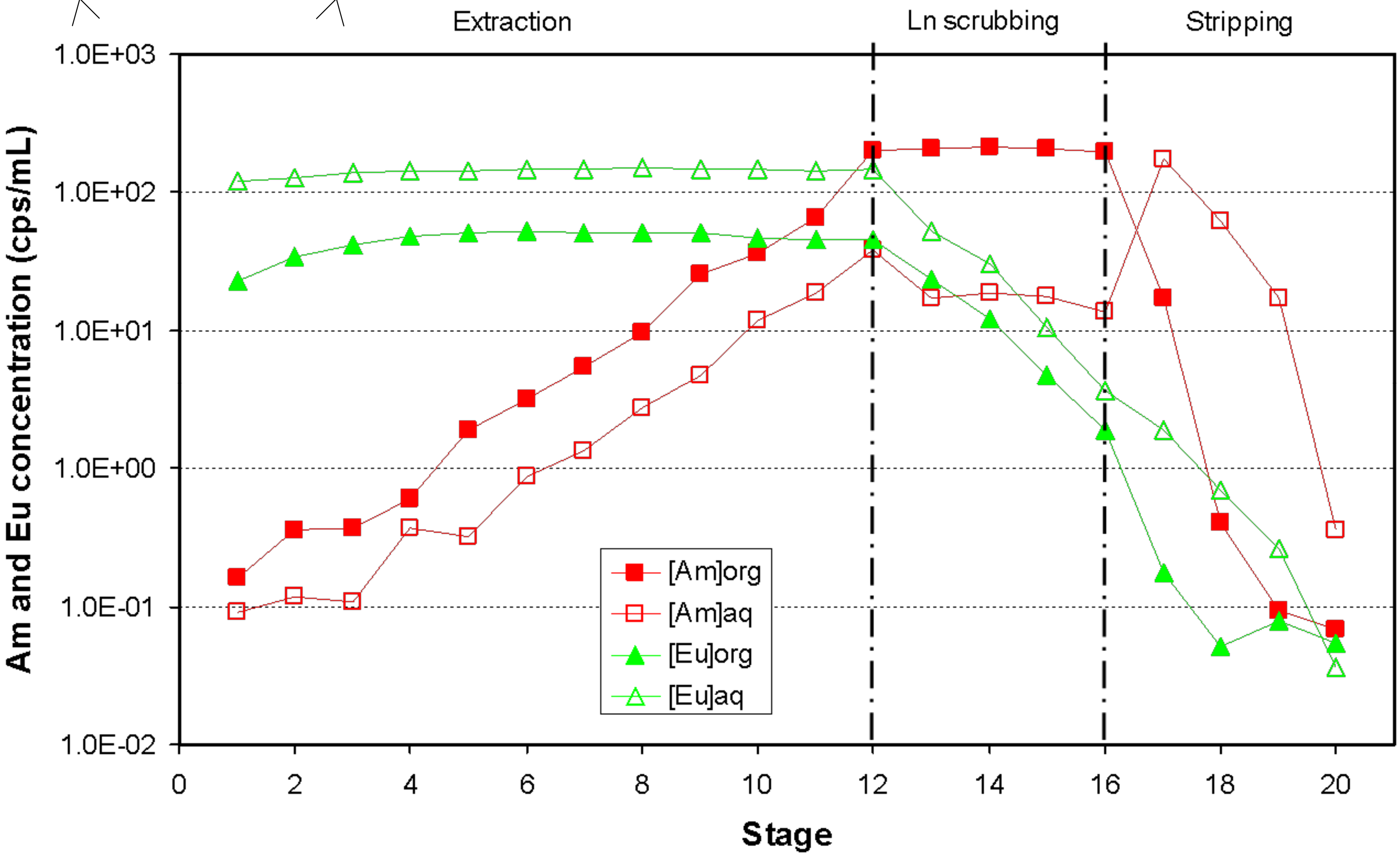
- >99.9% of the An(III) in the product, < 0.5 % Ln (mass)
- The Ln remained in the raffinate,
- No detectable Ln or An in the spent organic phase

# Separation of Actinides(III) from Lanthanides(III)

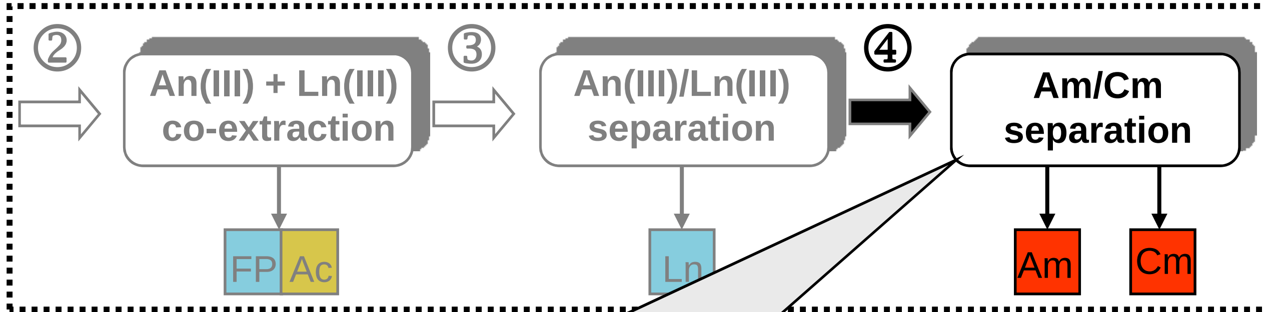
## *Results of spiked BTBP/TODGA (FZJ 2008, CC)*



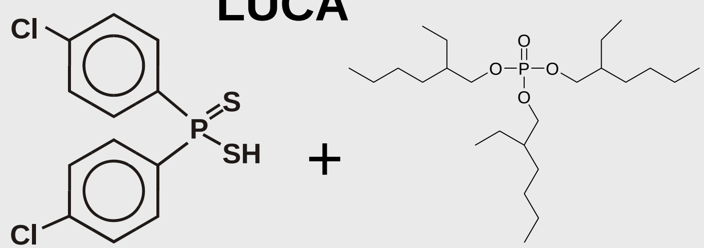


# Separation of Americium(III) from Curium(III)




**LUCA**




Separationfactor$_{Am/Cm}$~ 8-10

**Lanthaniden Und Curium/Americium separation**

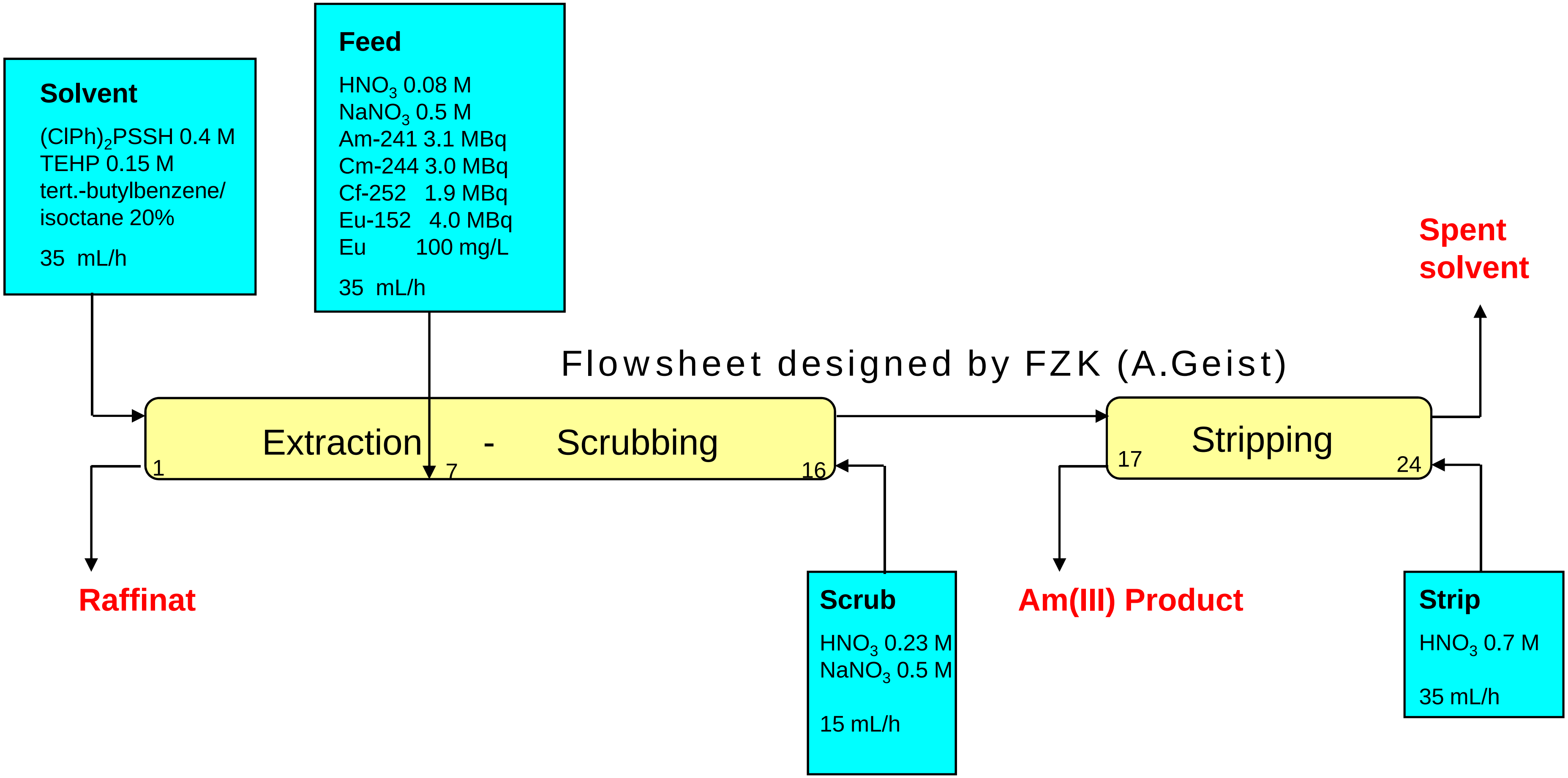
*Modolo, Odoj, European Patent 1664359B1, (2007)*

*Modolo, Nabet, Solv. Extr. Ion Exch., 23, 359-373 (2005)*

# Separation of Americium(III) from Curium(III)

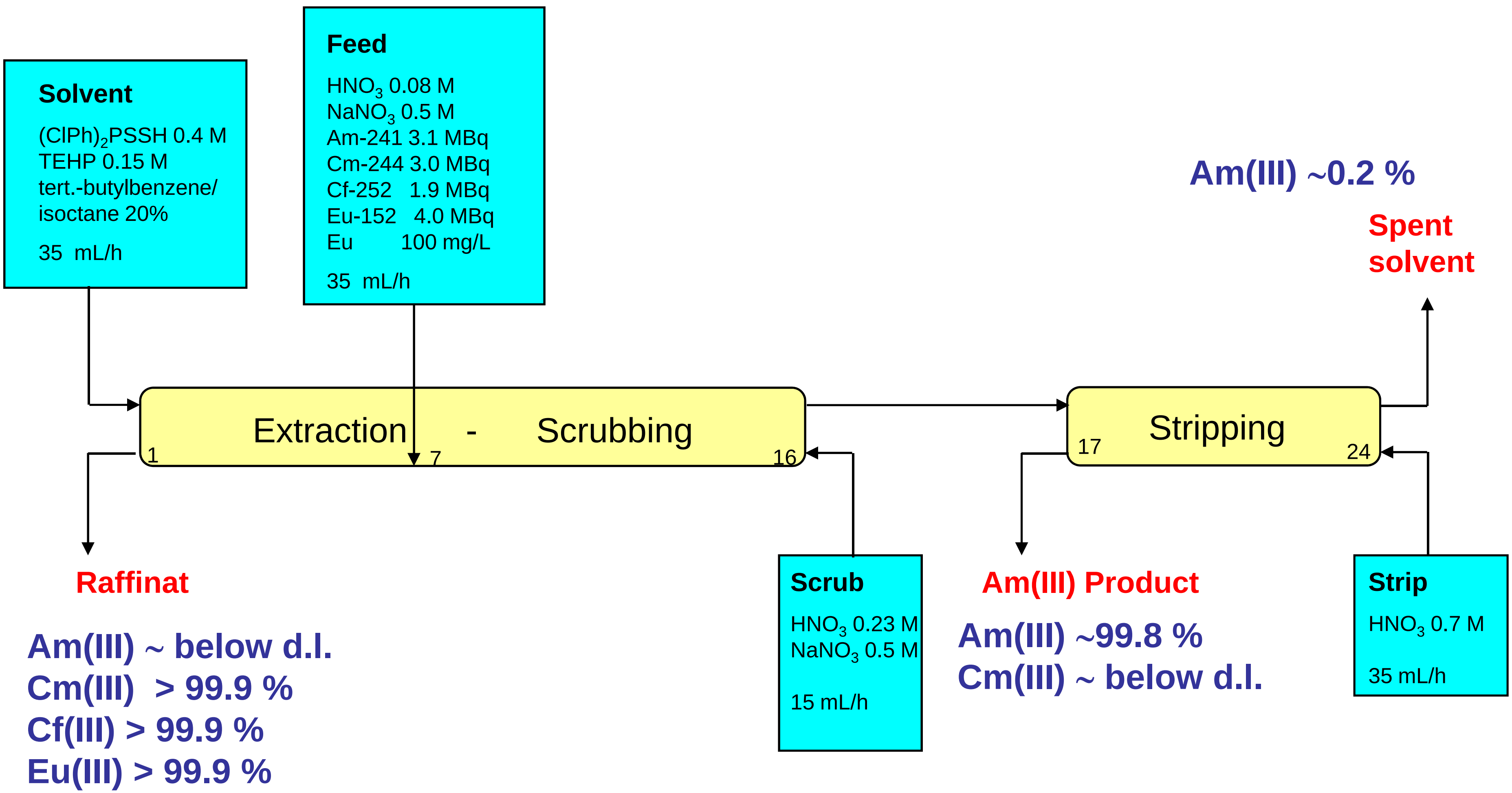
## *LUCA demonstration*





# Separation of Americium(III) from Curium(III)

## *LUCA demonstration*




- >99.9% of the Am(III) extraction, no Cm(III) contamination
- The Ln + Cm(III) + Cf(III) remained in the raffinate,
- Stripping can easily be optimized

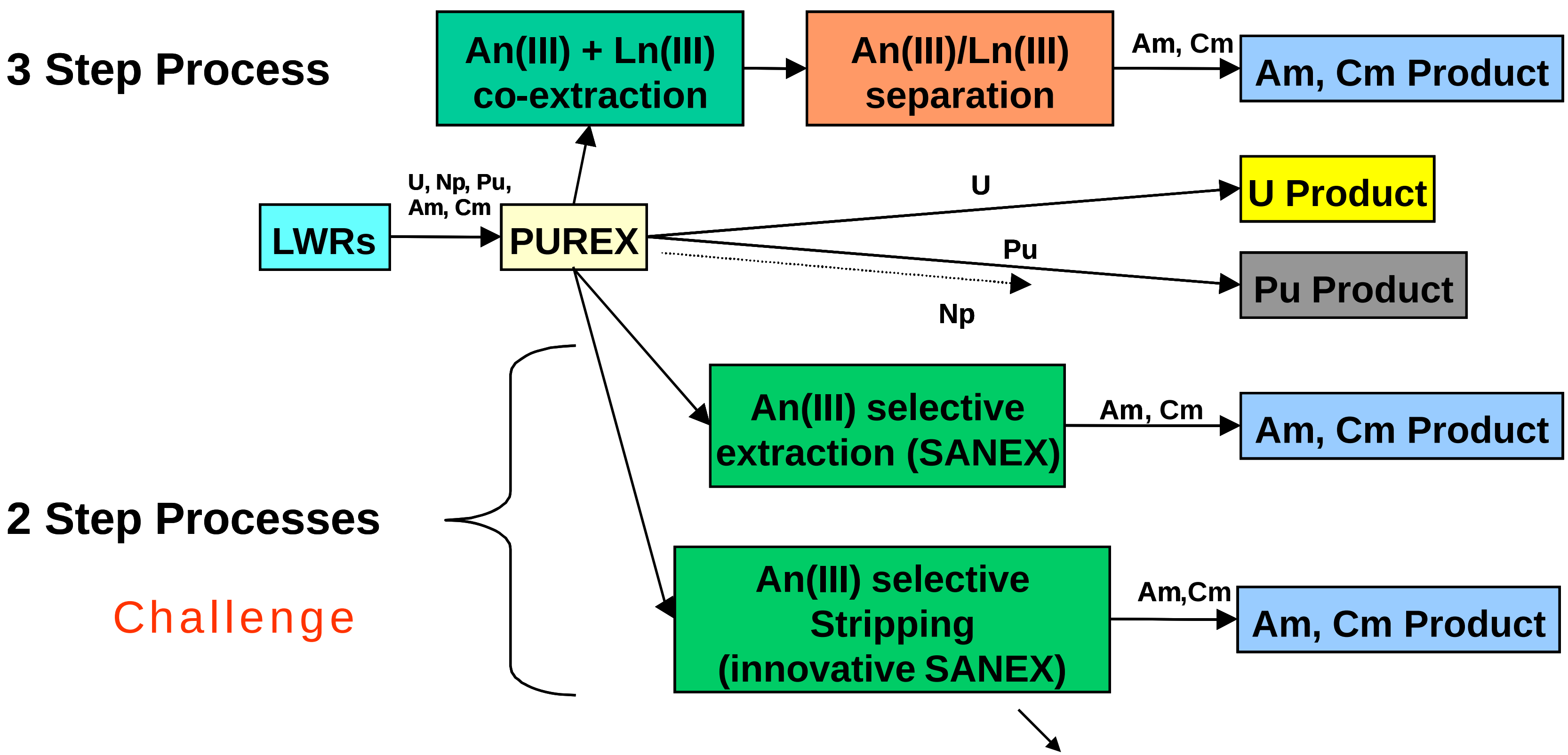
# Conclusions

- $CyMe_4BTBP$ is a promising extractant for An(III)/Ln(III)
- Kinetic of extraction is low, can be improved by a phase transfer catalyst such as DMDOHEMA or TODGA
- Optimisation studies leads to the development of reversible extraction processes
- Hot $CyMe_4BTBP$ + DMDOHEMA extraction process
- Spiked $CyMe_4BTBP$ + TODGA extraction process
- Am(III)/Cm(III) separation is possible by the LUCA process

# Outlook

- Hot $CyMe_4BTBP$ + TODGA demonstration
- Hot Am(III)/Cm(III) demonstration

FP 7 ACSEPT 2008-2011 (Actinide reCycling by SEparation and Transmutation)




(See Poster III-7: C. Hill et al.)

# Acknowledgement

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and

*ACSEPT (FP-7-CP-2007-211267)*

Thank you for your attention...