



Selective Separation of Am(III) using the Hydrophilic Complexing Agent $\text{SO}_3\text{Ph-BTPhen}$

SACSESS Workshop | 23rd April 2015

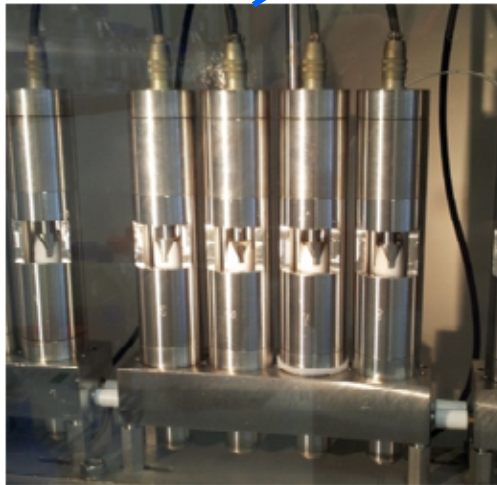
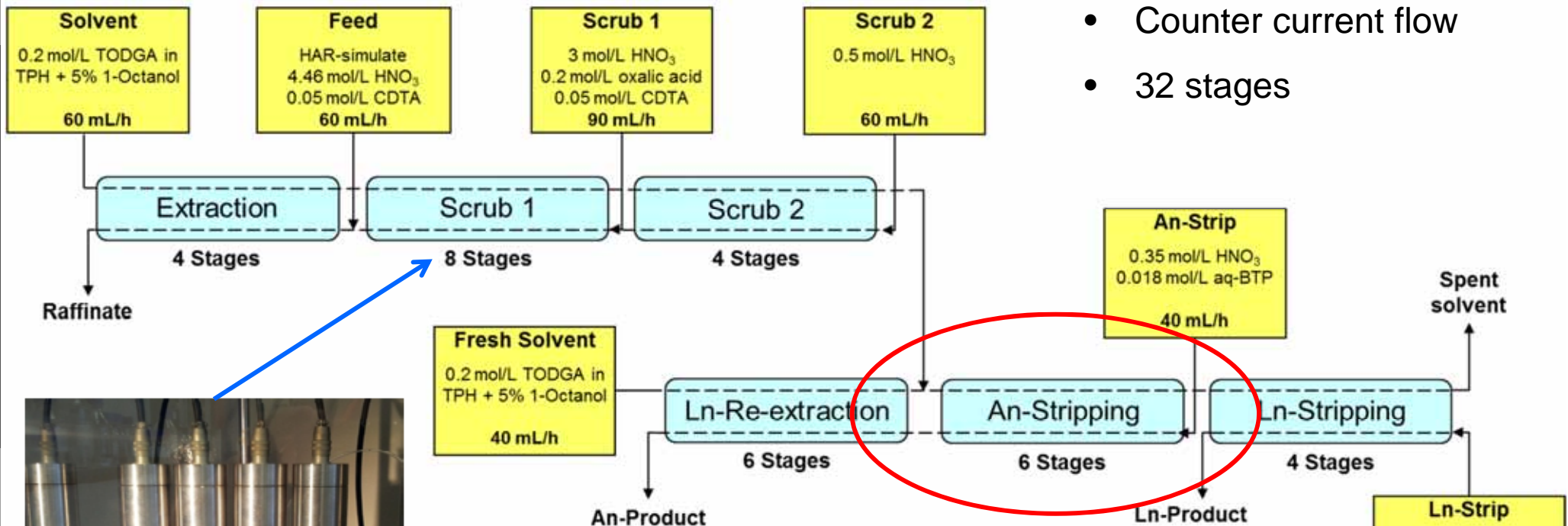
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P. Panak, A. Geist

The innovative-SANEX process

Process demonstrated in a spiked test at FZ-Jülich

Properties:

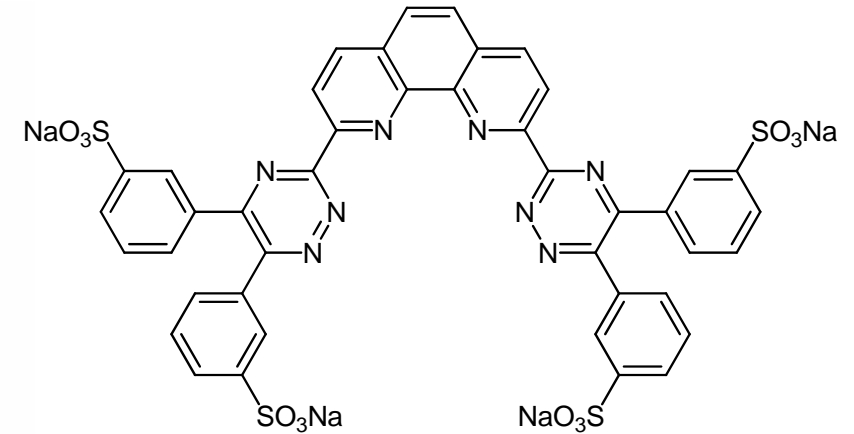
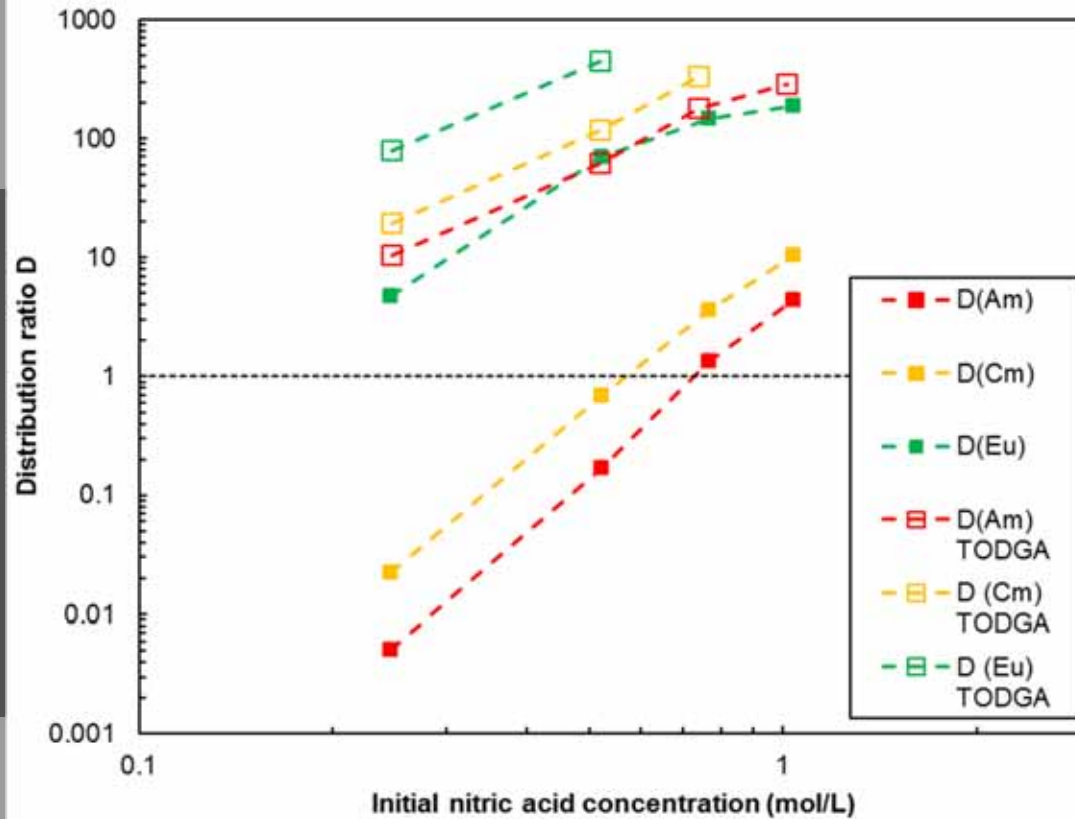
- Centrifugal contactors
- Counter current flow
- 32 stages



Am	> 99.8%
Cm	> 99.8%
Ln	< 0.1%
other	< 0.5%

Ln	~ 100%
An	< 0.1%
Y	~ 99%
other	< 0.5%

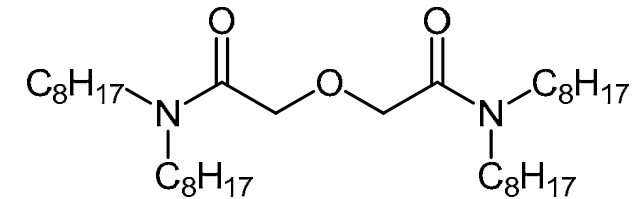
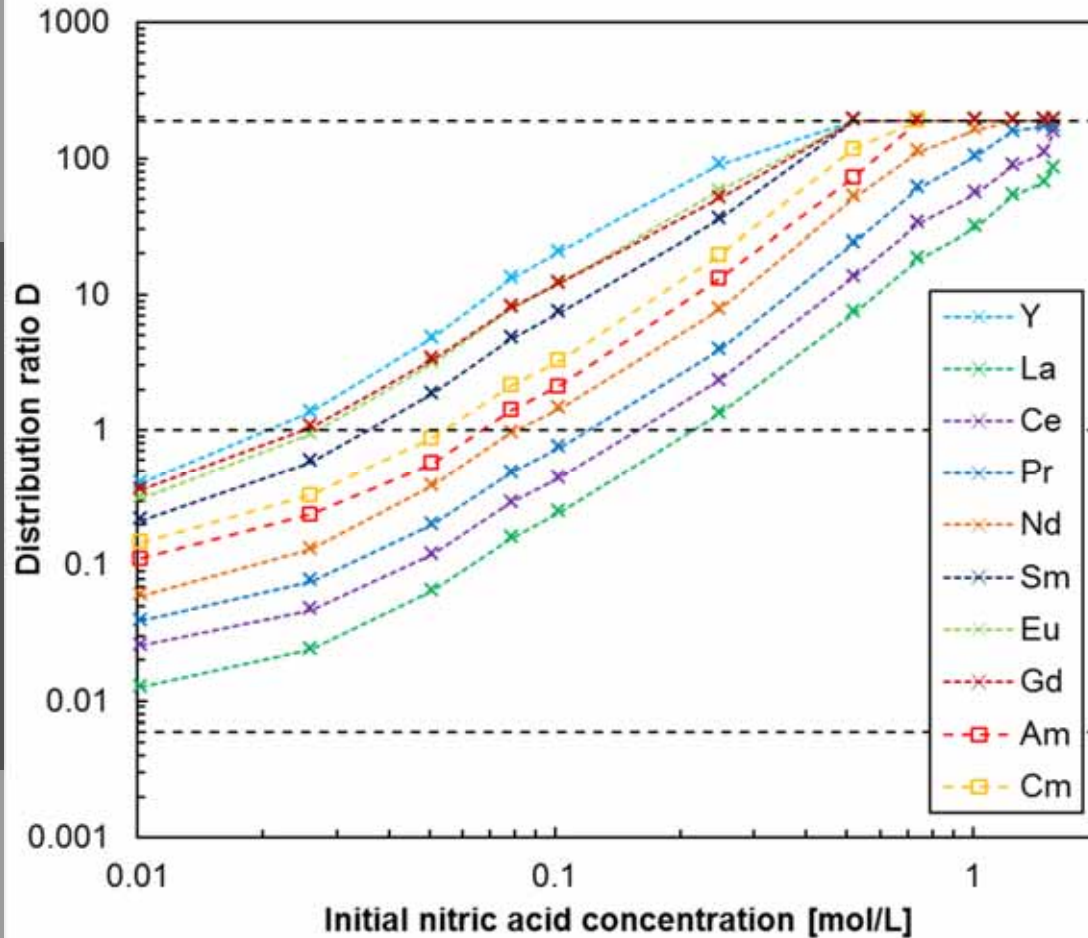
TODGA + SO₃Ph-BTPhen



- Application with TODGA
- SF_(Cm/Am) rises to 3.6

organic: 0.2 mol/L TODGA in TPH + 5 vol-% 1-octanol
 aqueous: diff. c(HNO₃) with (PhSO₃Na)₂-BTPhen
 T= 22°C; 5 min centrifuge

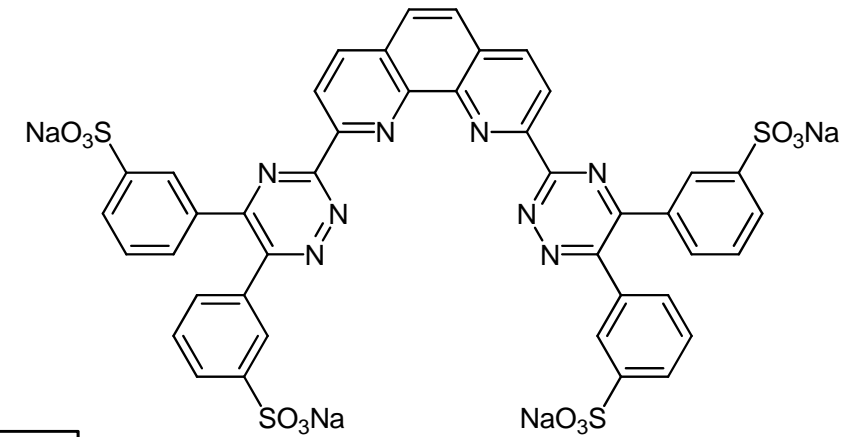
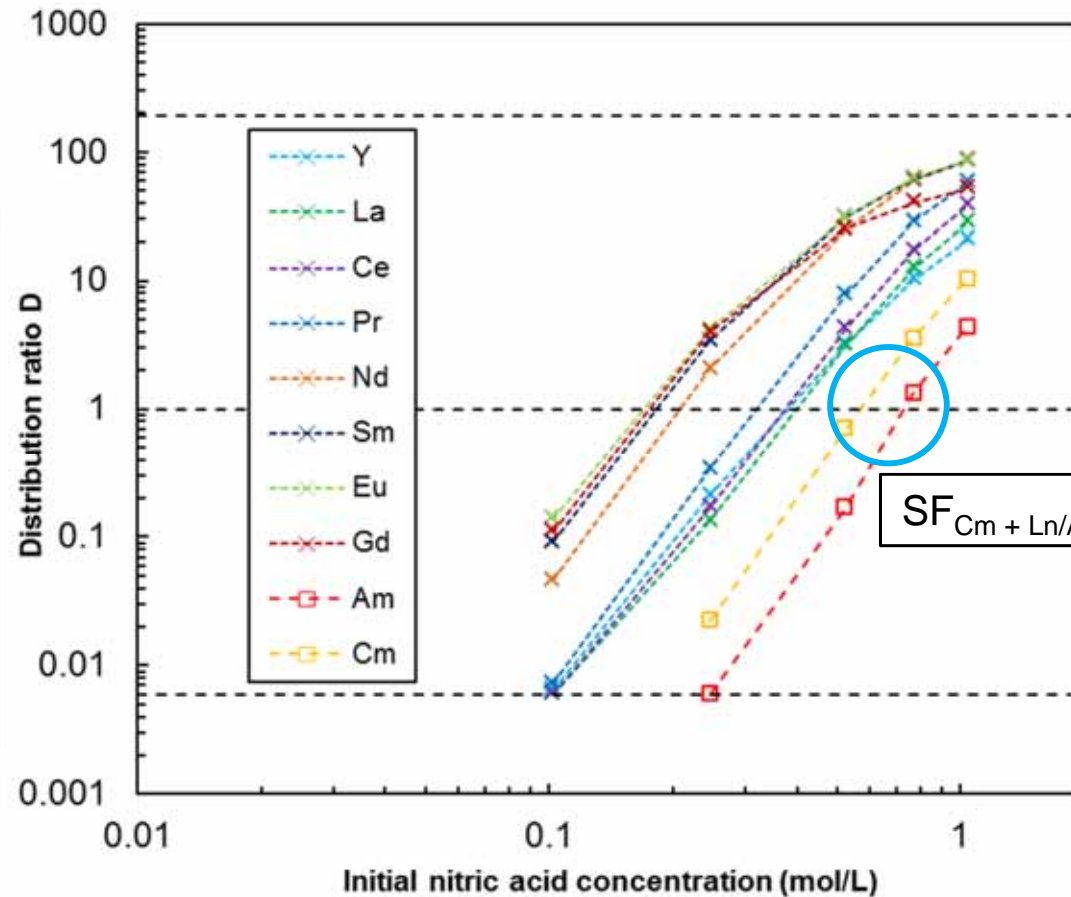
TODGA



- An(III) and Ln(III) co-extraction
- $SF_{(Cm/Am)} = 1.6$
- D (An) in between D (Ln)
- No separation of Am(III) from Cm(III) an Ln(III) possible

organic: 0.2 mol/L TODGA in TPH + 5 vol-% 1-octanol
 aqueous: diff. $c(\text{HNO}_3)$ with 10^{-4} mol/L Ln(III) and tracers,
 T= 22°C; 5 min centrifuge

TODGA + SO₃Ph-BTPPhen



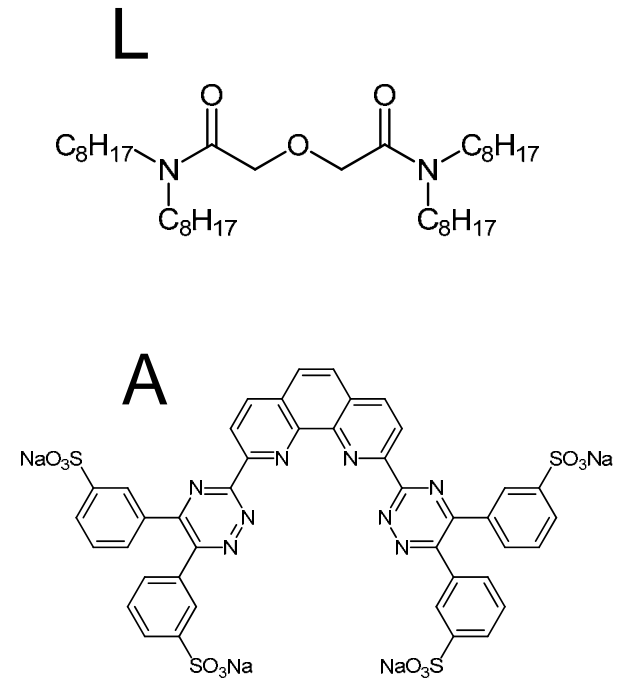
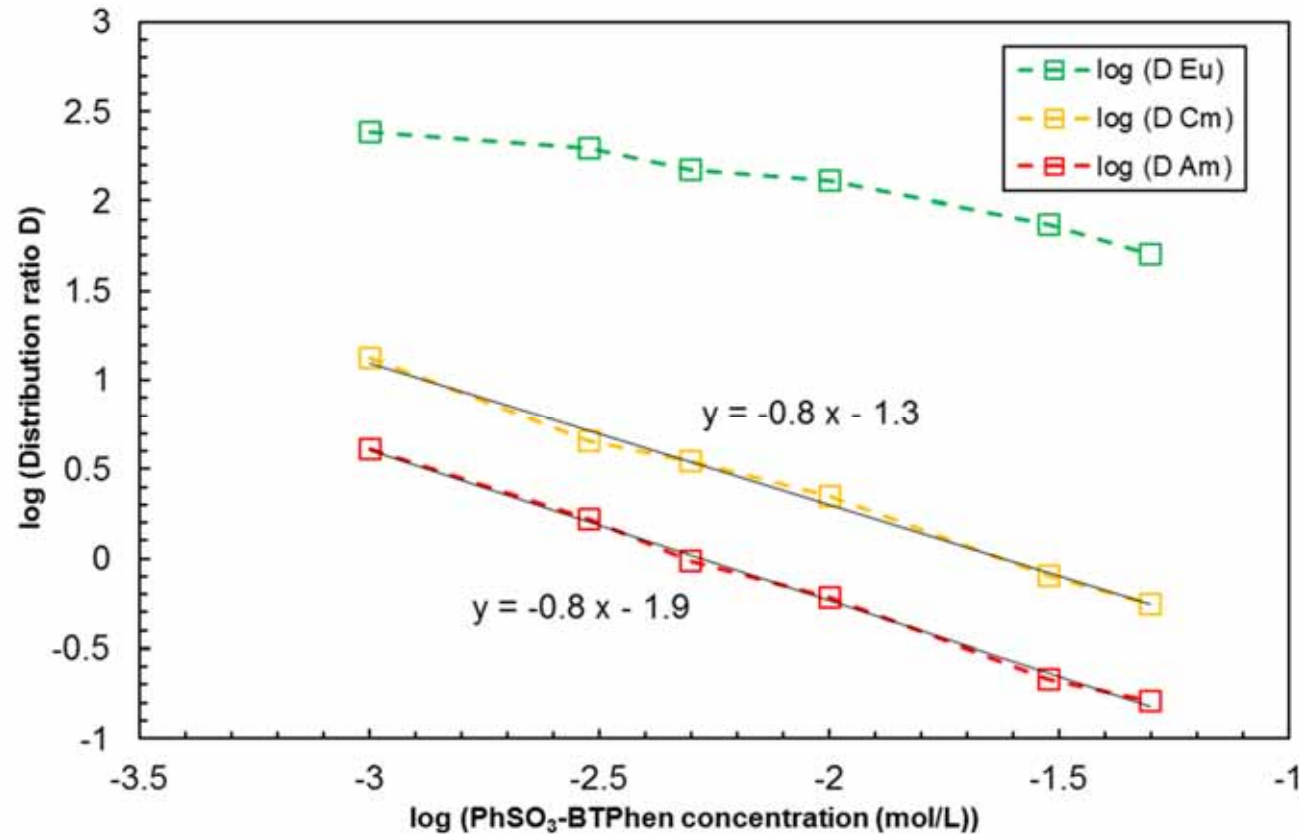
$SF_{Cm + Ln/Am} > 3.6$

- Application with TODGA
- $SF_{(Cm/Am)}$ rises to 3.6
- An(III) stripped from Ln(III)
- Americium selective strip possible

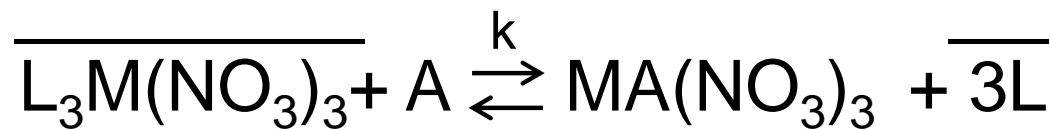
organic: 0.2 mol/L TODGA in TPH + 5 vol-% 1-octanol
 aqueous: diff. c(HNO₃) with (PhSO₃Na)₂-BTPPhen
 T= 22°C; 5 min centrifuge

SO₃Ph-BTPhen concentration variation

Slope analysis against TODGA



Slope of -0.8 indicates 1:1 complexes for Am(III) and Cm(III)



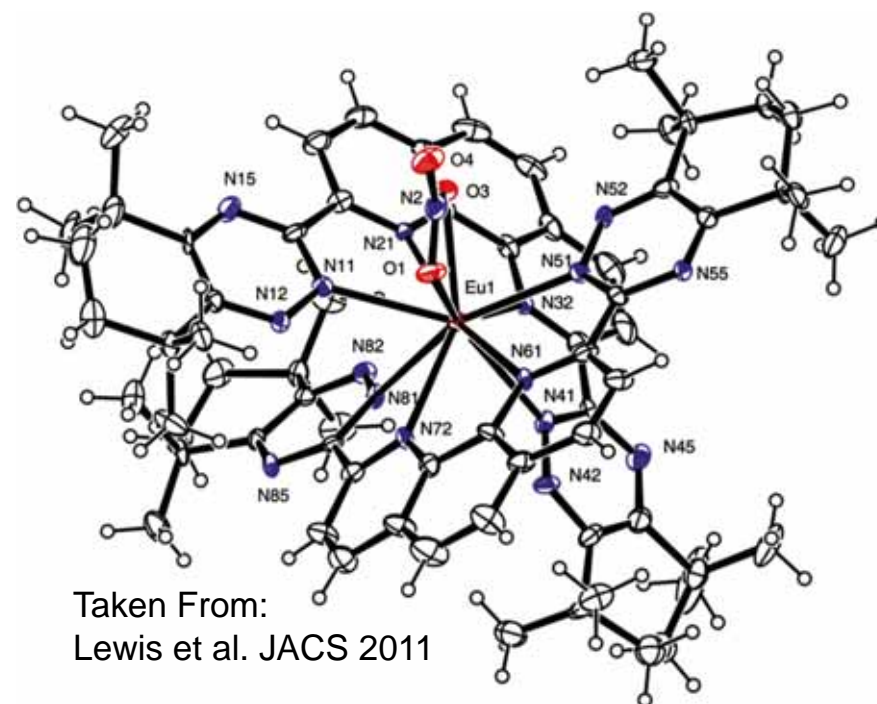
organic: 0.2 mol/L TODGA in TPH + 5 vol-% 1-octanol
 aqueous: diff c(SO₃Ph-BTPhen) in 0.5 mol/L HNO₃
 T=22°C; t= 30 min; 5 min centrifuge

Comparison to lipophilic BTPPhen

- CyMe₄-BTPPhen also shows selectivity for Am(III)
- Literature of lipophilic BTBP and BTPPhen shows 1:2 complexes

Information about stoichiometry of [An^(III)(SO₃Ph-BTPPhen)_x] complexes is missing

Applied speciation method:
TRLFS in the aqueous phase



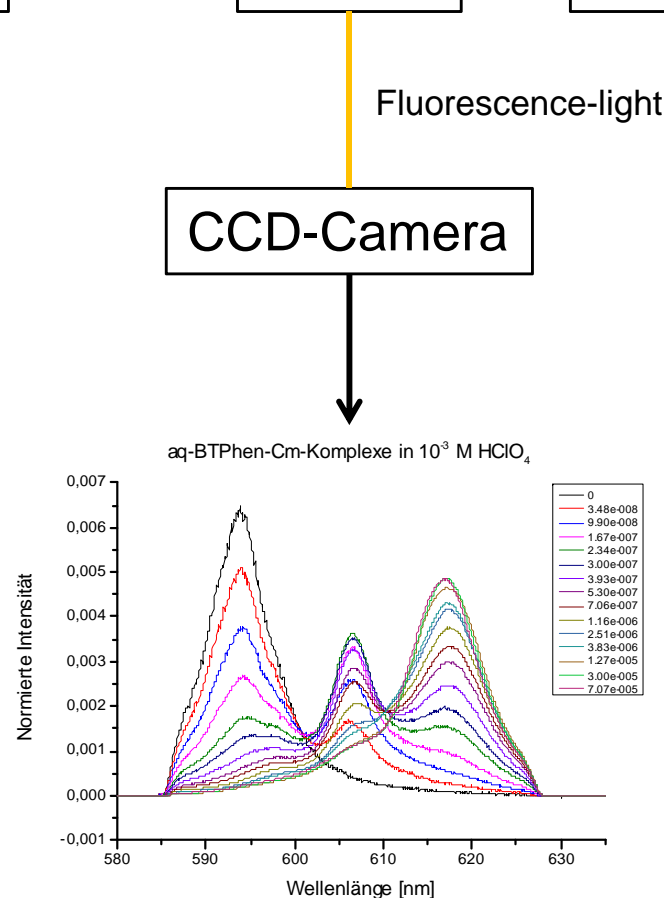
Taken From:
Lewis et al. JACS 2011

Curium TRLFS

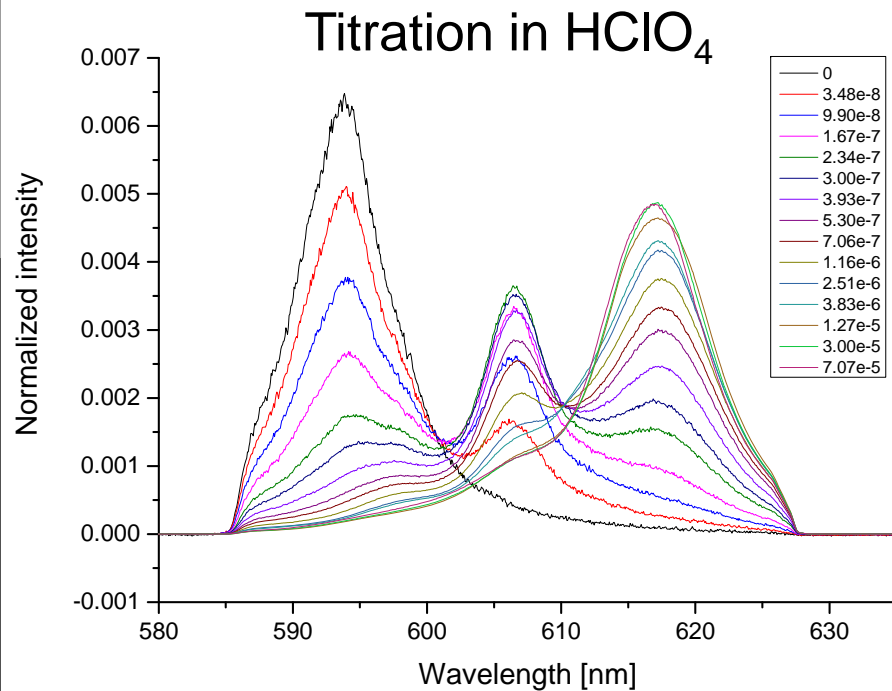
TRLFS = Time Resolved Laser Fluorescence Spectroscopy



- excitation by monochromatic laser-pulse at excitation energy of central ion
- de-excitation by fluorescence
- fluorescence shift related to complex environment
- measurement of Cm(III) fluorescence
- information on complex stoichiometry and inner coordination shell



Cm(III)-TRLFS with SO₃Ph-BTPPhen

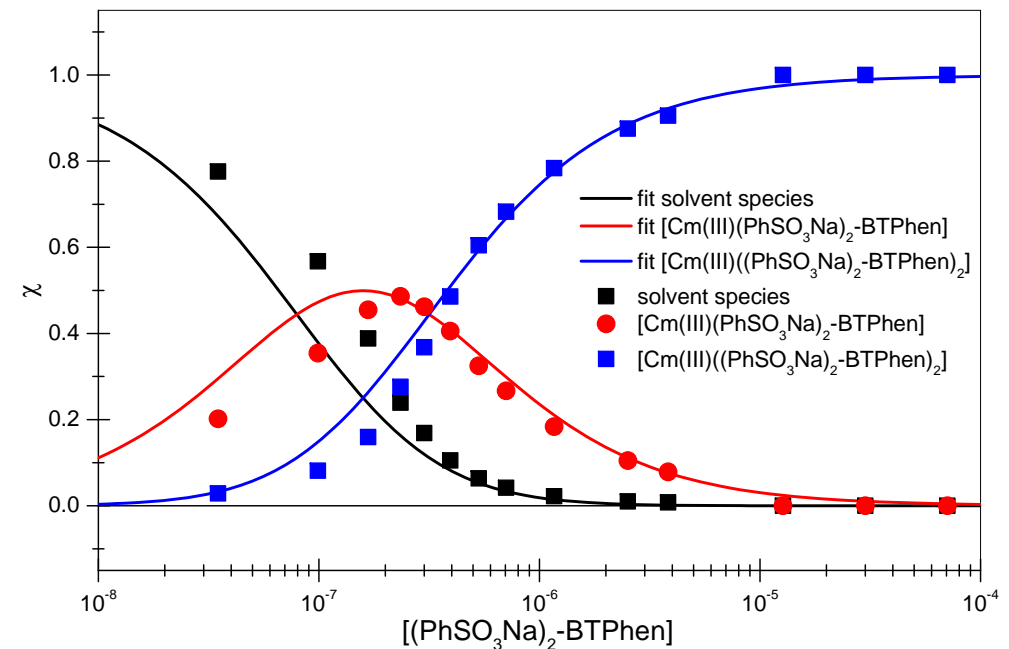


Speciation diagram

- Solvent species (black)
- 50 % of 1:1 species at about 1:2 Cm/Ligand (red)
- >90 % 1:2 species at 1:100 Cm/L (blue)

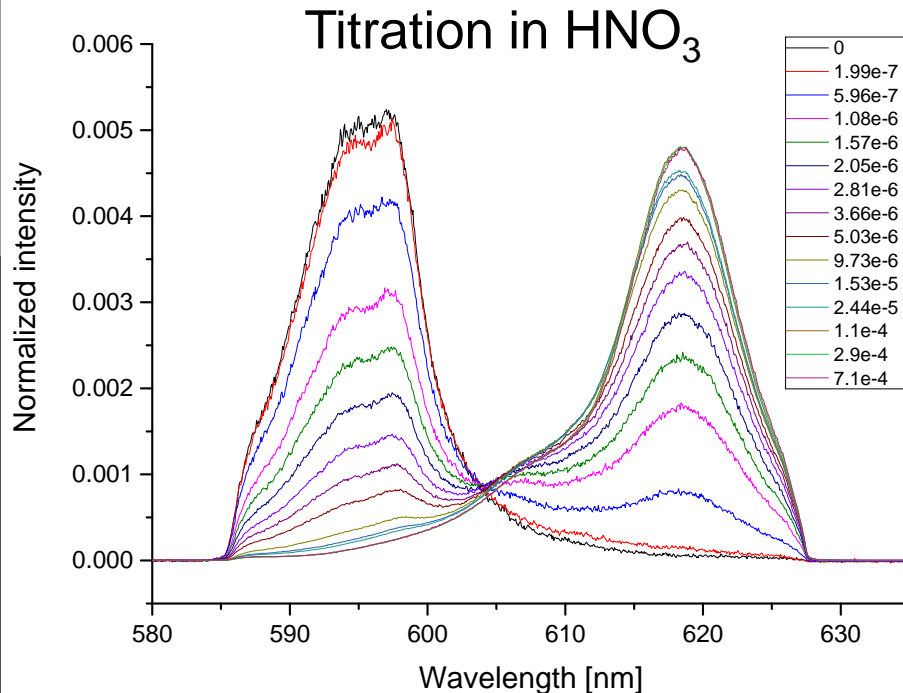
Fluorescence spectra during titration

- First formation of a 1:1 complex
- Afterwards formation of a 1:2 complex
- 1:1 completely disappearing



Conditions: titration of SO₃Ph-BTPPhen in 10⁻³ mol/L HClO₄
 Initial c(Cm(III)): 10⁻⁷ mol/L; c(SO₃Ph-BTPPhen): 0 - 7.07·10⁻⁵ mol/L

Cm(III)-TRLFS with SO₃Ph-BTPPhen

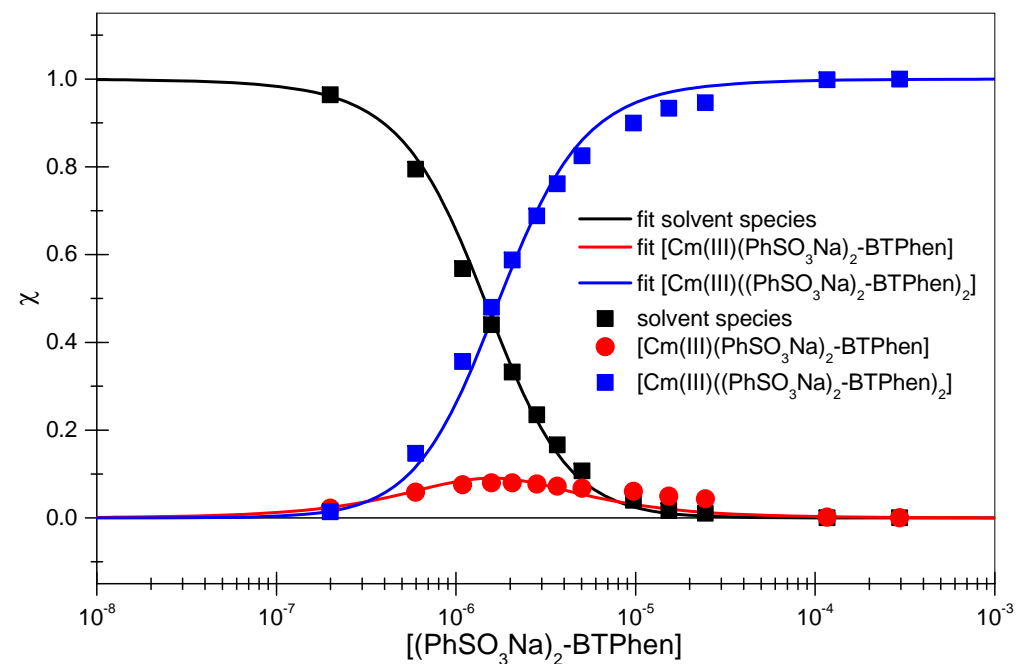


Speciation diagram

- Solvent species (black)
- Less than 10 % of 1:1 species (red)
- Changing to 1:1 species at 1:1000 Cm/L (blue)

Fluorescence spectra during titration

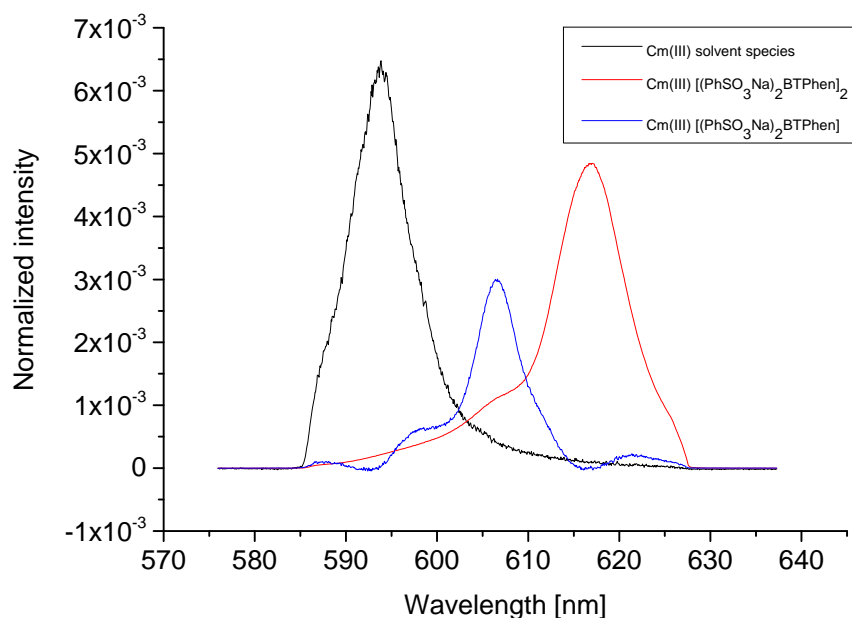
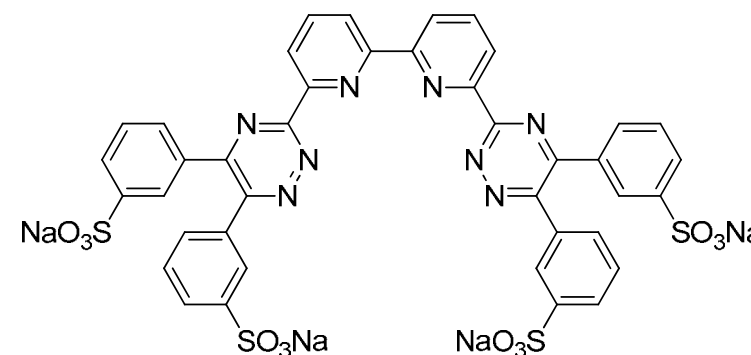
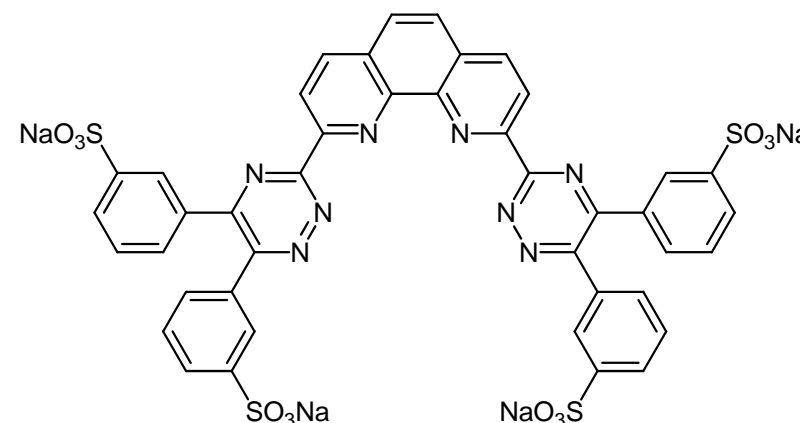
- Formation of a 1:2 complex
- less formation of a 1:1 complex



Conditions: titration of SO₃Ph-BTPPhen in 0.5 mol/L HNO₃
 Initial c(Cm(III)): 10⁻⁷ mol/L; c(SO₃Ph-BTPPhen): 0 - 7.1e⁻⁴ mol/L

Comparison of SO₃Ph-BTPhen and SO₃Ph-BTBP

- 1:1 and 1:2 complex found with Cm(III)
- 1:1 complex suppressed with HNO₃
- Similar stability constants to SO₃Ph-BTBP



Ligand	log(K) ₀₁	log(K) ₀₂	log(β) ₀₂
BTPhen	6.2	4.5	10.7
BTBP	4.2	4.6	10.4

Comparison with SO₃Ph-BTBP measurements of Christoph Wagner, KIT, presented this morning.

Conclusion and outlook

SO₃Ph-BTPhen for selective separation of Americium

- Separation of Am(III) from Cm(III) and Ln(III) possible
- Slope of ~ -1 observed
- Fast stripping kinetics
- 1:1 and 1:2 complex found by TRLFS-studies
- 1:2 complex preferred in 0.5 mol/L HNO₃
- Stability constants similar to the SO₃Ph-BTBP system
- Fluorescence-lifetime showed quenching of SO₃Ph-BTPhen

For the details I like to invite you to my Poster this afternoon.

Acknowledgement

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Thank you for your attention !