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## **A macroscopic and molecular study for a complete description of technetium (VII) and uranium (VI) co-extraction mechanism with monoamides**

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DE LA RECHERCHE À L'INDUSTRIE

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# A MACROSCOPIC AND MOLECULAR STUDY FOR A COMPLETE DESCRIPTION OF TECHNETIUM (VII) AND URANIUM (VI) CO-EXTRACTION MECHANISM WITH MONOAMIDES

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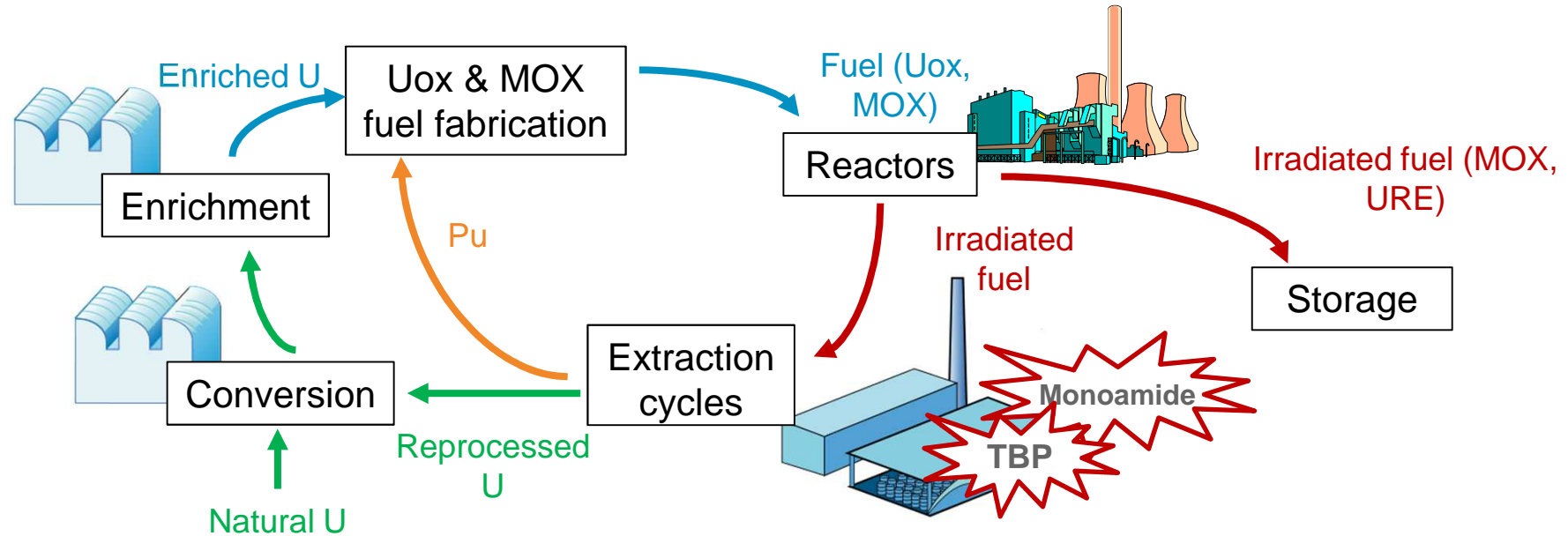
<sup>b</sup> ICSM BP 17171 30207 Bagnols sur Cèze, France

E-mail: pauline.moeyaert@cea.fr

**RANC 2016**

Budapest, April 12<sup>th</sup> 2016





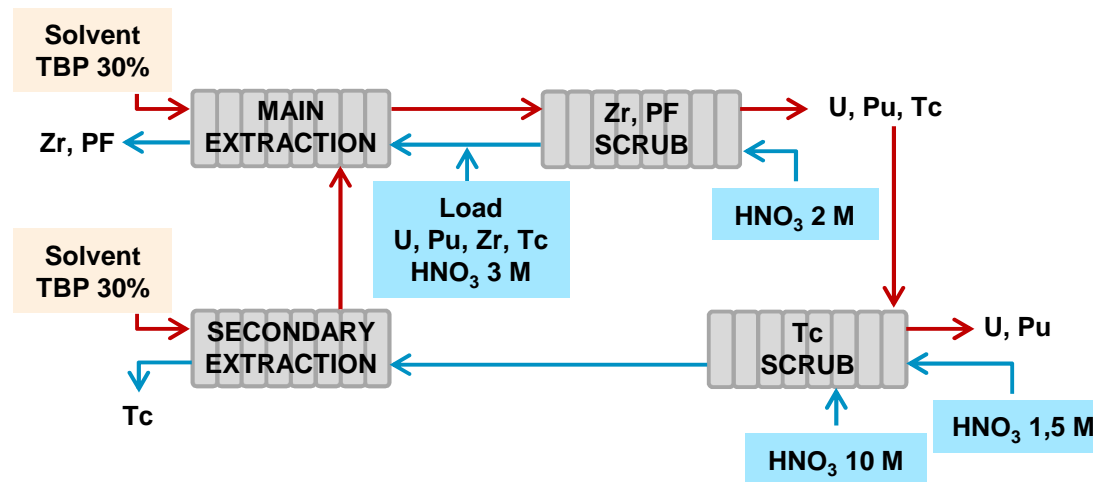
**Monoamides for U & Pu extraction ...**

- Innovative liquid-liquid extraction processes for the reprocessing of spent nuclear fuels
- Good stability towards radiolysis and hydrolysis

**... But what about fission products extraction?**

## Techneium in the PUREX process

- $^{99}\text{Tc}$  = Long-lived  $\beta$  emitting radionuclide (with a radioactive half-life of  $2.1 \times 10^5$  y)
- Radionuclide potentially mobile in the environment
- Present as  $\text{HTcO}_4$  in nitric acid dissolution solutions
- Can cause some issues in the PUREX process if not correctly scrubbed (hydrazine destruction, U & Pu contamination)
- Measurements implemented in La Hague plant

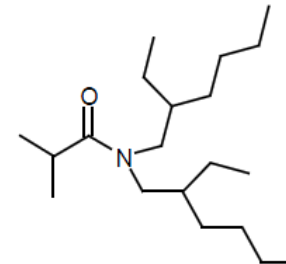


### Techneium in the PUREX process

- $^{99}\text{Tc}$  = Long-lived  $\beta$  emitting radionuclide (with a radioactive half-life of  $2.1 \times 10^5$  y)
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### Towards a new process ...

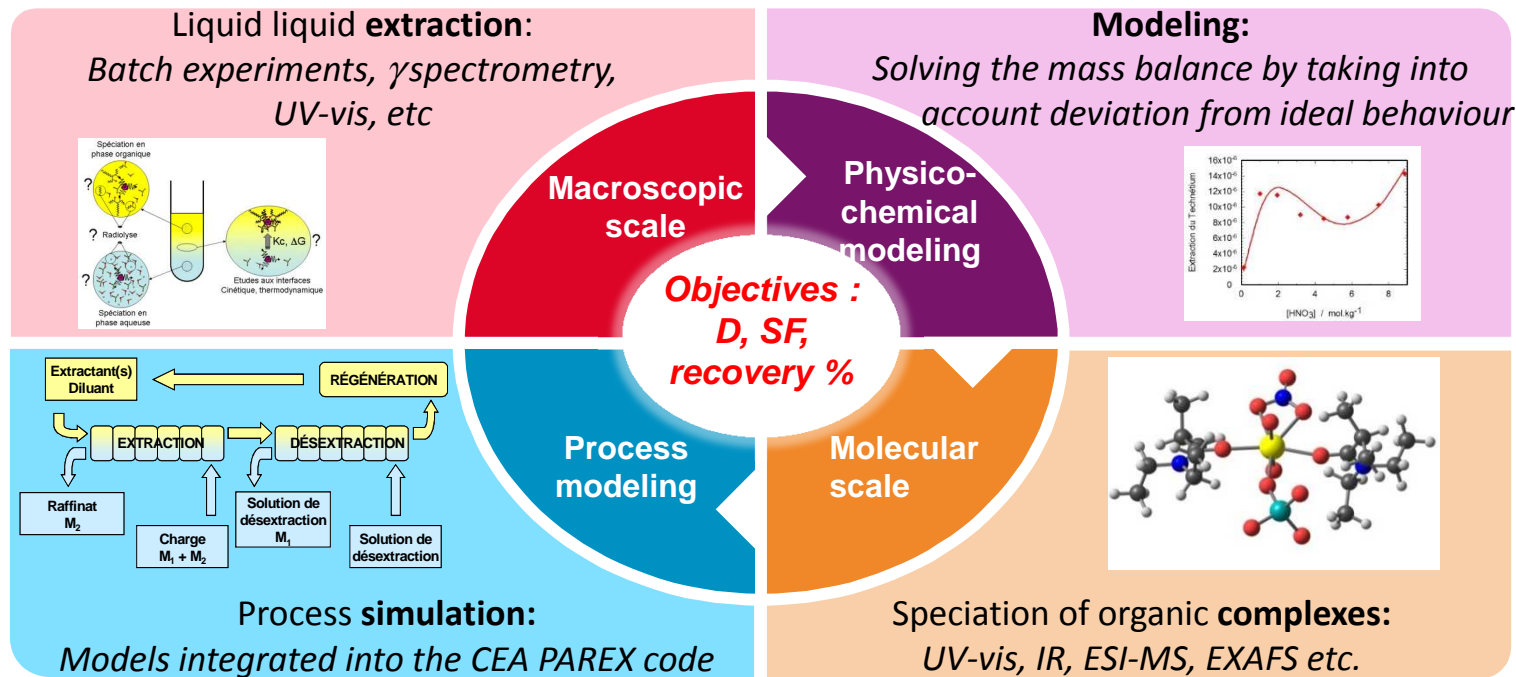
- DEHiBA (N,N-di-2-ethylhexyl-isobutyramide) = promising extractant for future processes



DEHiBA

## Objectives:

- Understanding the mechanisms involved in the extraction of technetium with DEHiBA
  - Modeling technetium extraction
- Integrating the model into the CEA PAREX code to improve the modeling of extraction processes and help flowsheets design



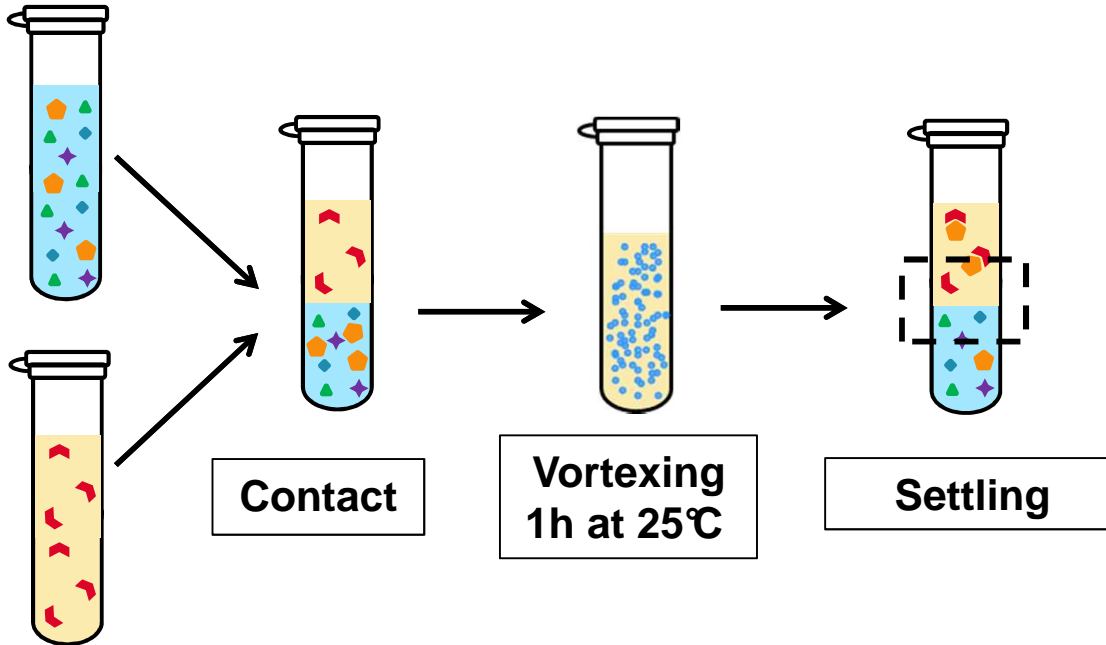
# TECHNETIUM EXTRACTION EXPERIMENTAL PROTOCOLE

## Aqueous phase:

H<sub>2</sub>O  
HNO<sub>3</sub> 0.1-6 M  
UO<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub> 0-120 g.L<sup>-1</sup>  
HTcO<sub>4</sub> 10<sup>-3</sup> M + <sup>99m</sup>Tc as  $\gamma$  spiker

## Organic phase:

DEHiBA / TPH

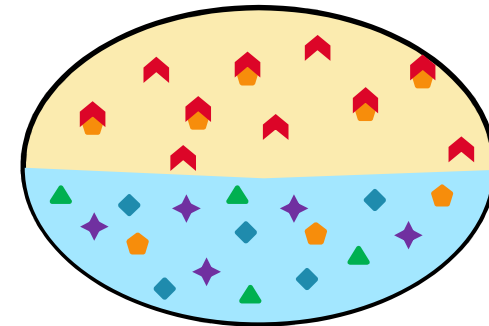


<sup>99m</sup>Tc = short-lived  $\gamma$  emitter ( $T_{1/2} \approx 6$  h)  
Used as spiker for Tc measurements

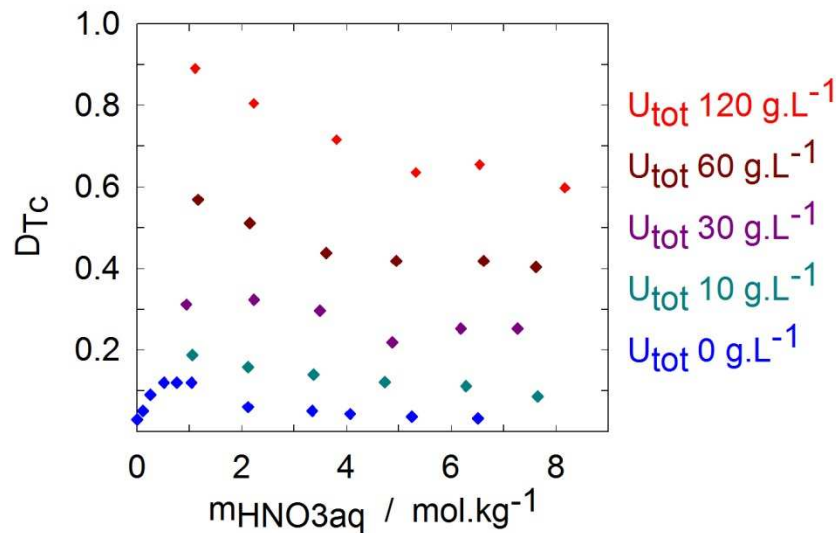


- Acid base titration
- $\gamma$  spectrometry
- UV-vis spectrophotometry

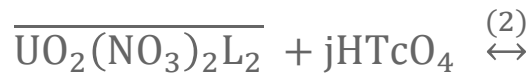
- Acid base titration
- $\gamma$  spectrometry
- UV-vis spectrophotometry



### Experimental results



- $D_{Tc} = [Tc]_{org}/[Tc]_{aq} \nearrow$  when  $U_{tot} \nearrow$
- Assumption of the following extraction equilibria:



### Mass balance equations

#### Equilibrium constants:

$$K_1 = \frac{\overline{(HTcO_4)L_i}}{[L]^i [HTcO_4]} \frac{\gamma_{\overline{(HTcO_4)L_i}}}{\gamma_{HTcO_4} \gamma_L^i}$$

$$K_2 = \frac{\overline{UO_2(NO_3)_{2-j}(TcO_4)_jL_2} [HNO_3]^j}{[L]^2 [UO_2(NO_3)_2] [HTcO_4]^j} \frac{\gamma_{\overline{UO_2(NO_3)_{2-j}(TcO_4)_jL_2}} \gamma_{HNO_3}^j}{\gamma_{UO_2(NO_3)_2} \gamma_{HTcO_4}^j \gamma_L^2}$$

#### Method:

- Free extractant concentration determined by an iterative method based on dichotomy resolution
- Calculation of U, Tc, H, H<sub>2</sub>O concentrations in organic phase
- Optimization of the unknown parameter K by an iterative method based on least-squares analysis corresponding to the minimization of:

$$\min \sum \left( \frac{[\overline{X}]_{calc} - [\overline{X}]_{exp}}{[\overline{X}]_{exp}} \right)^2$$



## In aqueous phase: the simple solutions theory

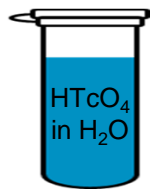
- Simple behaviour of isopiestic solutions (Zdanovskii-Stokes-Robinson)
- Mikulin equation to calculate activity coefficients

$$\gamma_{\text{HTcO}_4} = \frac{\nu_{\text{HTcO}_4} \gamma_{\text{HTcO}_4}^{\text{bi}} m_{\text{HTcO}_4}^{\text{bi}}}{\nu_{\text{HTcO}_4} m_{\text{HTcO}_4} + \nu_{\text{HNO}_3} m_{\text{HNO}_3} + \nu_{\text{UO}_2(\text{NO}_3)_2} m_{\text{UO}_2(\text{NO}_3)_2}}$$

Binary mixture data  
= f(a<sub>w</sub>)

Real mixture  
composition

### Procedure for binary data acquisition = triplet (Φ, γ, m)



Measurements of water  
activity a<sub>w</sub>



Osmotic coefficient  
calculation

$$\phi = -\frac{\ln a_w}{\nu m M_{\text{H}_2\text{O}}}$$



Activity coefficient of the  
electrolyte by integrating  
Gibbs-Duhem equation

$$\ln \gamma = \phi - 1 + \int_0^m \frac{\phi - 1}{m} dm$$

Fitting according to a semi-empirical  
equation (ex: NIST, Pitzer, ...)

$$\phi = f(m)$$

m = molality  
(mole per kg of solvent)



In aqueous phase: the simple solutions theory

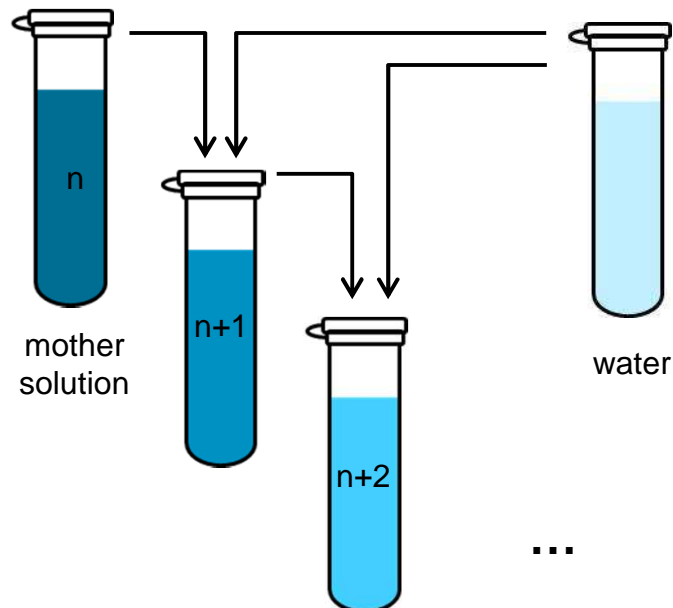
- Simple behaviour of isopiestic solutions (Zdanovskii-Stokes-Robinson)
- Mikulin equation to calculate activity coefficients

$$\gamma_{\text{HTcO}_4} = \frac{v_{\text{HTcO}_4} \gamma_{\text{HTcO}_4}^{\text{bi}} m_{\text{HTcO}_4}^{\text{bi}}}{v_{\text{HTcO}_4} m_{\text{HTcO}_4} + v_{\text{HNO}_3} m_{\text{HNO}_3} + v_{\text{UO}_2(\text{NO}_3)_2} m_{\text{UO}_2(\text{NO}_3)_2}}$$

Binary mixture data  
= f(a<sub>w</sub>)

Real mixture  
composition

Procedure for binary data acquisition = triplet (Φ, γ, m)

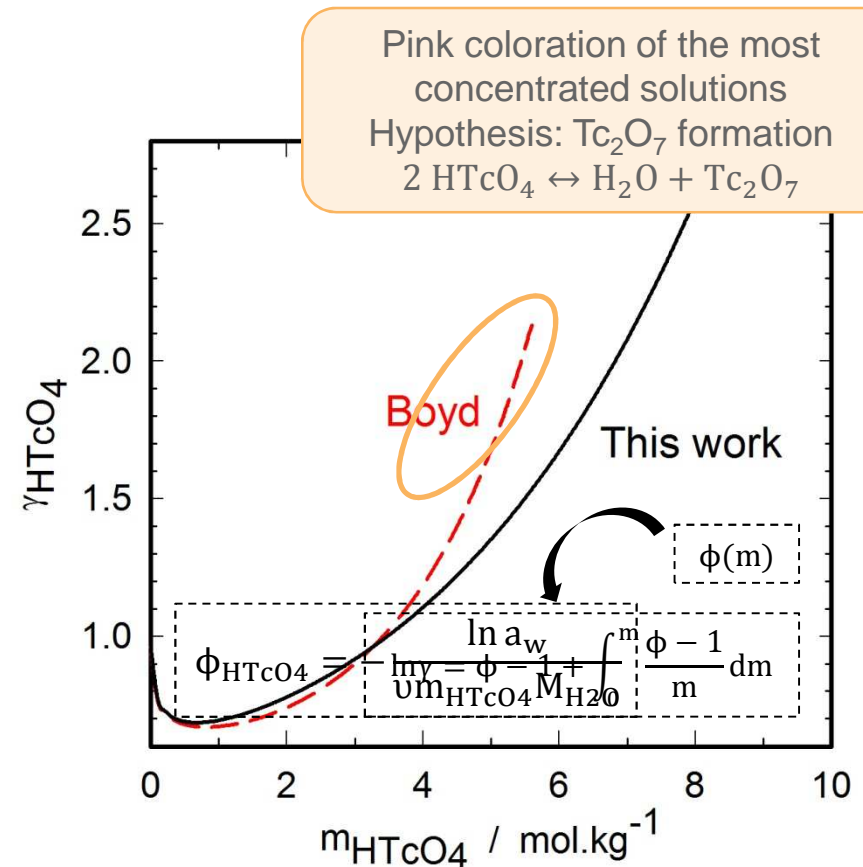


Pertechnetate acid  $\text{HTcO}_4$  binary data = triplet  $(\Phi_{\text{HTcO}_4}, \gamma_{\text{HTcO}_4}, m_{\text{HTcO}_4})$

## New variation of $\gamma = f(m)$

- Boyd's data available in the literature
- New  $a_w$  measurements
- New variation implemented in the models

$$\gamma_{\text{HTcO}_4} = \frac{\nu_{\text{HTcO}_4} \gamma_{\text{HTcO}_4}^{\text{bi}} m_{\text{HTcO}_4}^{\text{bi}}}{\nu_{\text{HTcO}_4} m_{\text{HTcO}_4} + \nu_{\text{HNO}_3} m_{\text{HNO}_3} + \nu_{\text{UO}_2(\text{NO}_3)_2} m_{\text{UO}_2(\text{NO}_3)_2}}$$



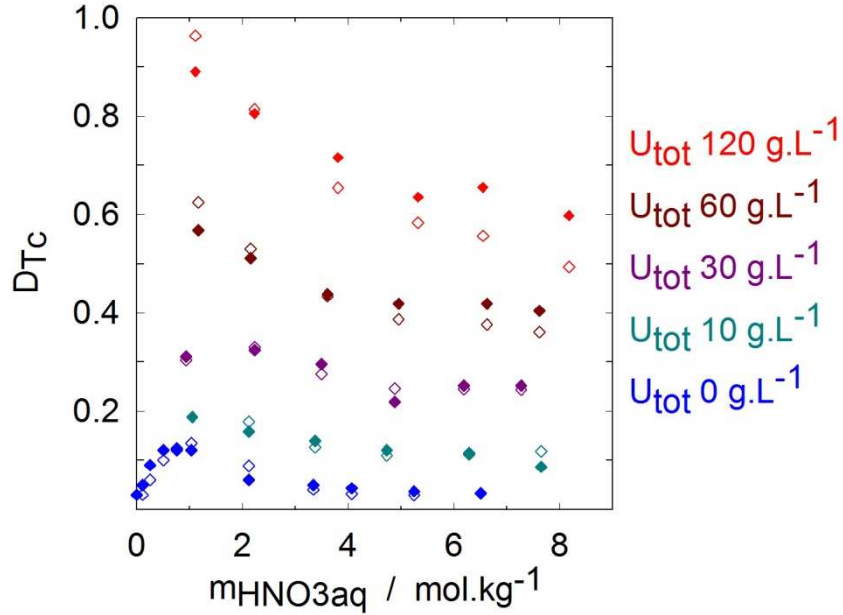
Boyd, G.E., Inorganic Chemistry, 1978. **17**(7): p. 1808-1810.

Moeyaert, P., et al. The Journal of Chem. Therm., 2015. **85**(0): p. 61-67.

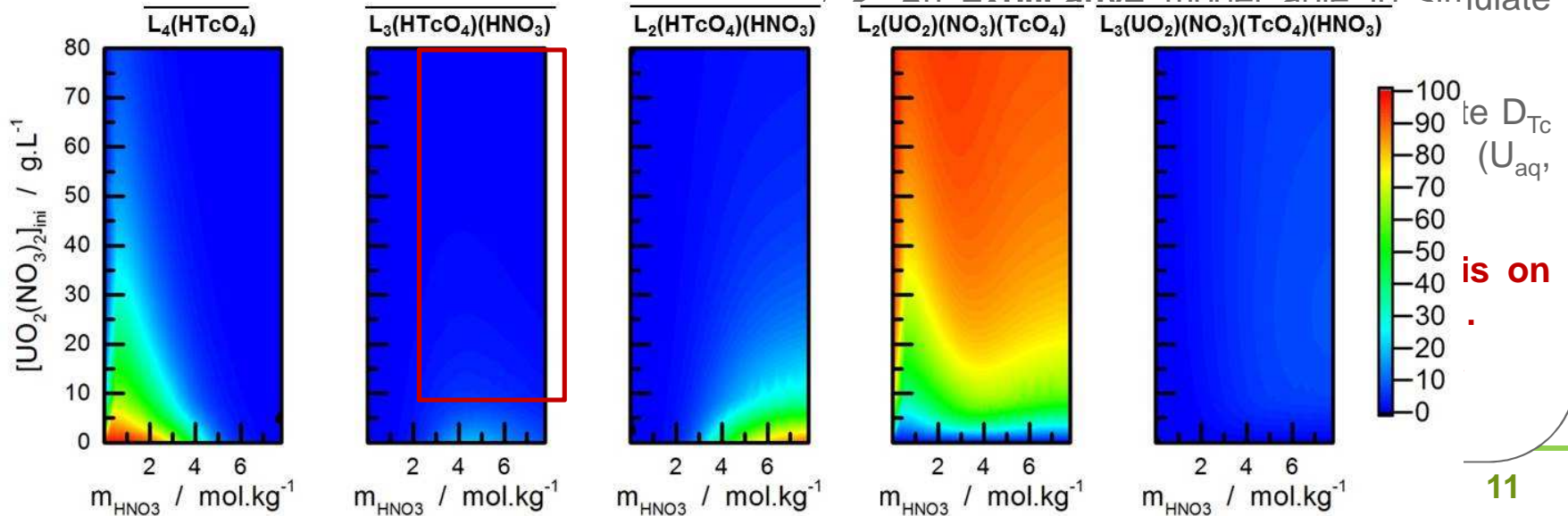
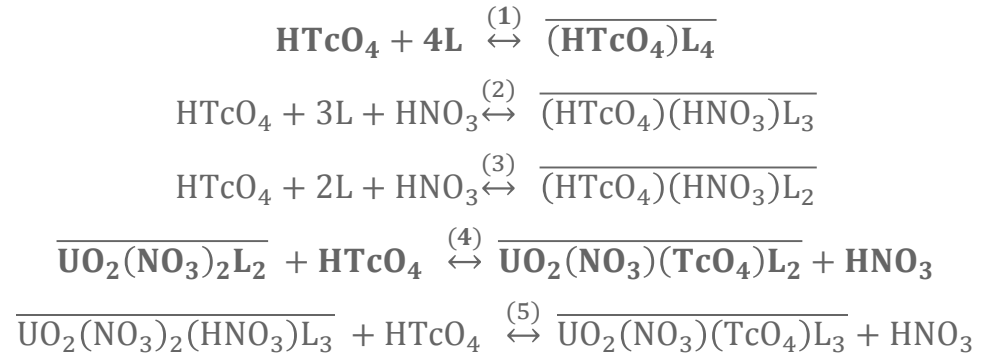
Moeyaert, P., et al. The Journal of Chem. Therm., 2015. **91**(0): p. 94-100.

CEA Thesis L. Abiad

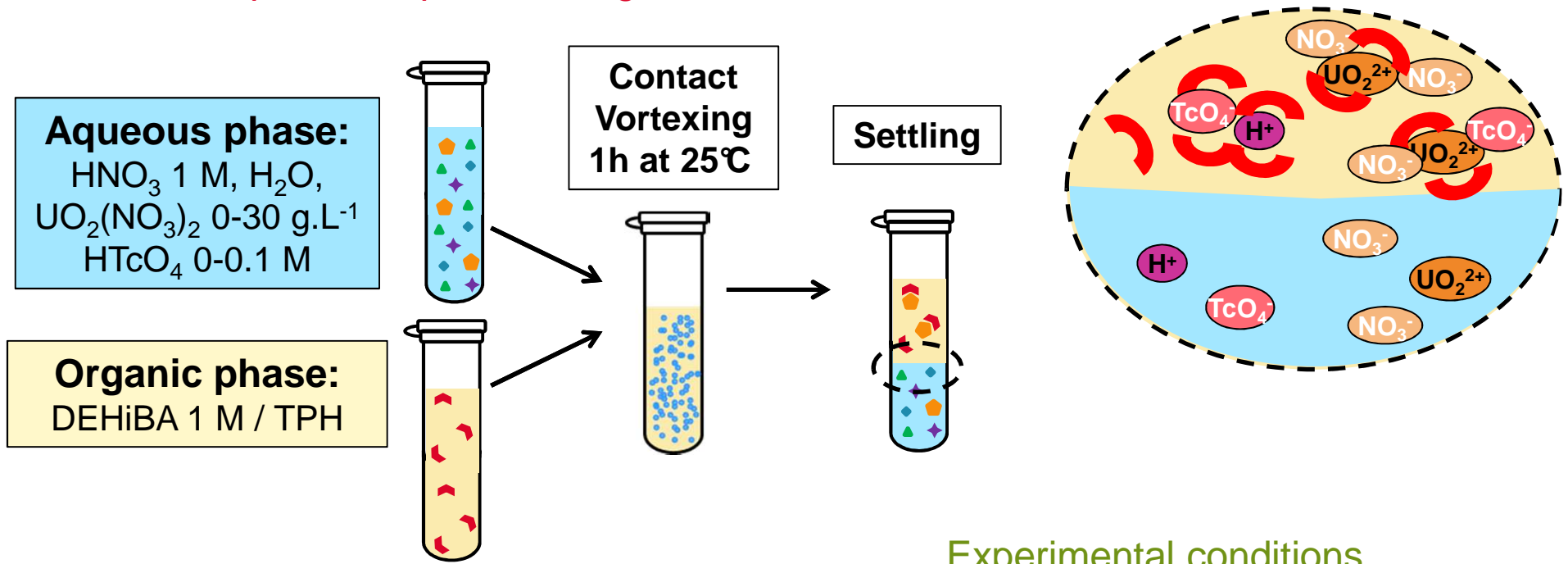
# TECHNETIUM EXTRACTION MODELING RESULTS



## Main extraction mechanisms:



## IR and XAS spectroscopies investigations



**IR spectroscopy:** influence of the Tc/U ratio

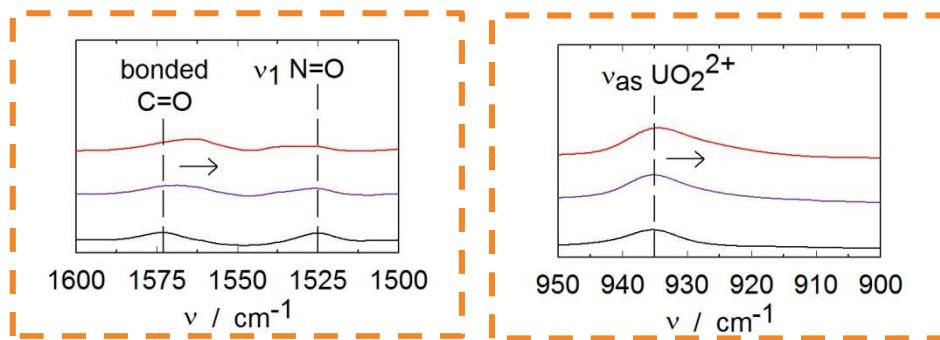
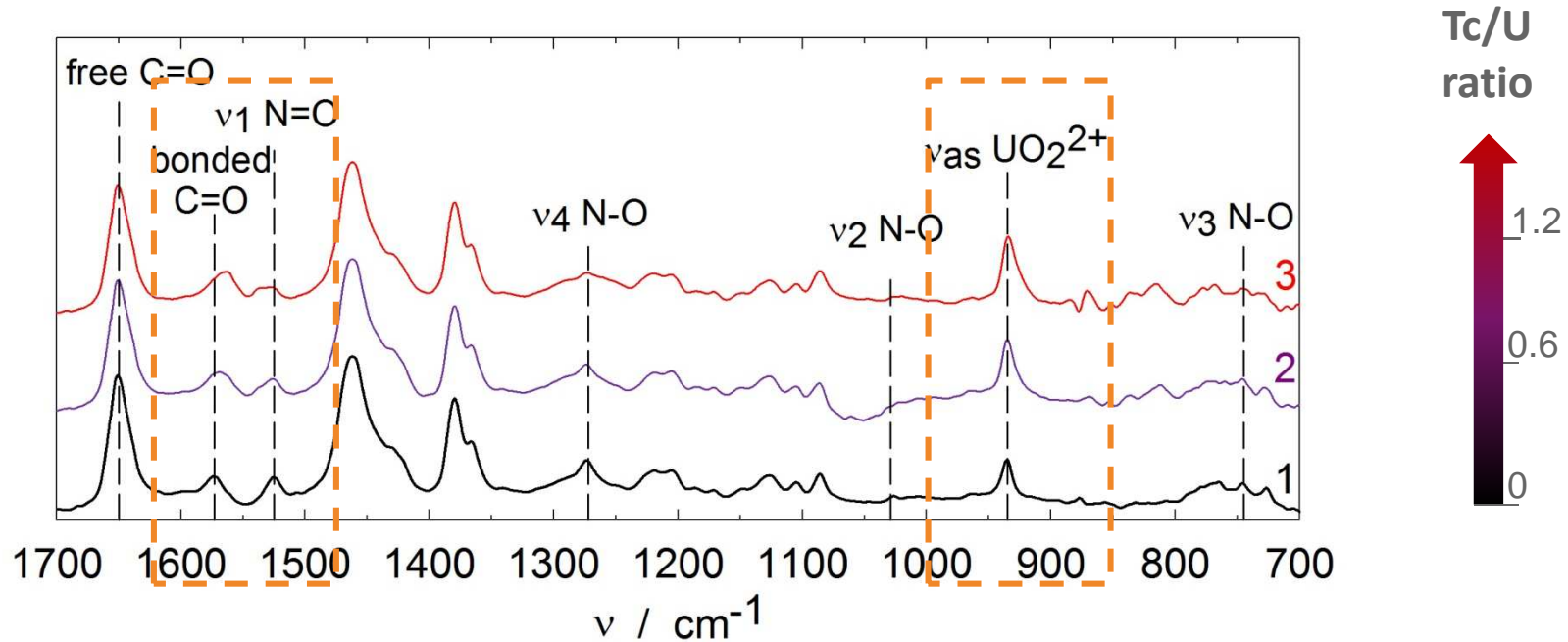
**XAS spectroscopy:** influence of the Tc/U ratio and data processing

DEHiBA- $\text{HNO}_3^-$   
 $\text{UO}_2(\text{NO}_3)_2$

DEHiBA- $\text{HNO}_3^-$   
 $\text{UO}_2(\text{NO}_3)_2$ - $\text{HTcO}_4$

DEHiBA- $\text{HNO}_3^-$   
 $\text{HTcO}_4$

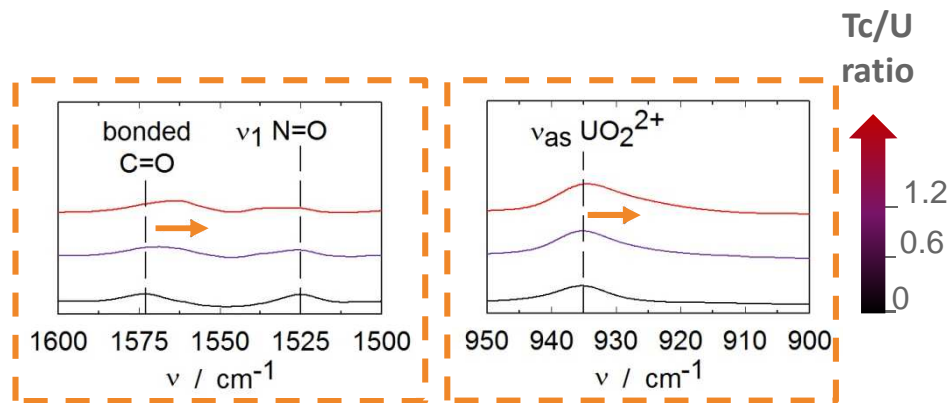
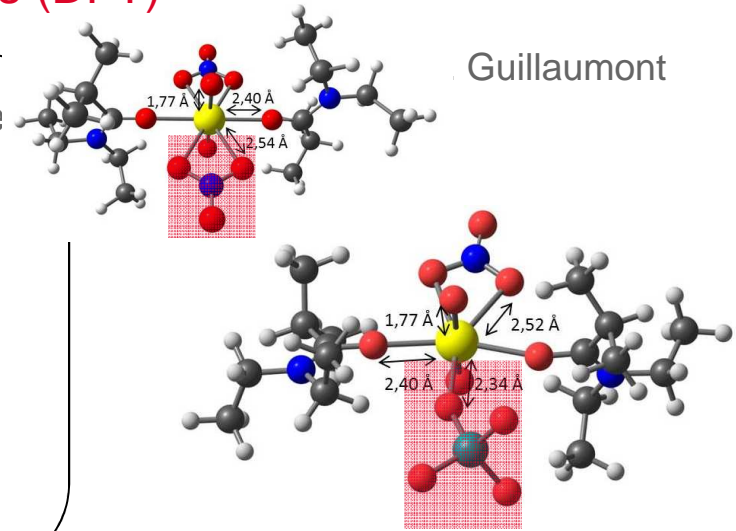
## IR spectroscopy



- Bonded C=O and  $UO_2$  stretch shifted to lower frequencies when  $[Tc] \nearrow$
- Changes in the intensity and in the shape of the nitrate  $\nu_1$  N=O stretch when  $[Tc] \nearrow$
- ➔ **Changes are occurring in the U(VI) inner coordination sphere when uranium and technetium are co-extracted**

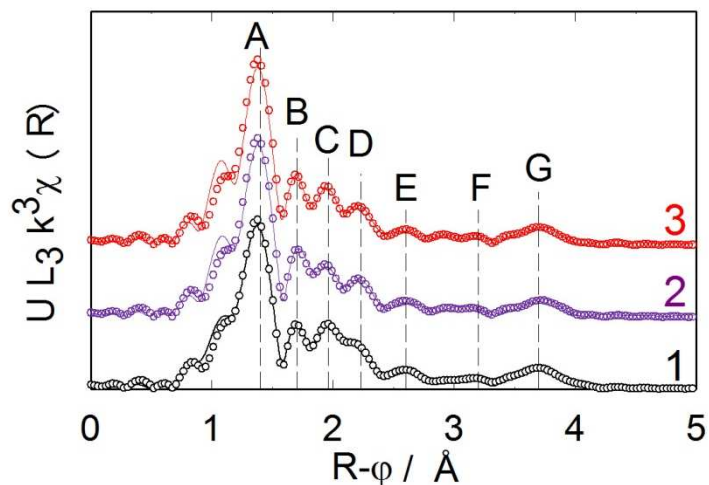
## IR spectroscopy combined with theoretical calculations (DFT)

- Optimisation of the  $\text{UO}_2(\text{NO}_3)(\text{TcO}_4)\text{L}_2$  complex structure
- Vibrational frequencies calculation for  $\text{UO}_2(\text{NO}_3)_2\text{L}_2$  and  $\text{UO}_2(\text{NO}_3)(\text{TcO}_4)\text{L}_2$  complexes
- ➔ **Confirmation that changes are occurring in the U(VI) inner coordination sphere when uranium and technetium are co-extracted**
- ➔ **Calculated  $\text{UO}_2(\text{NO}_3)(\text{TcO}_4)\text{L}_2$  structure is used as support for XAS data processing**

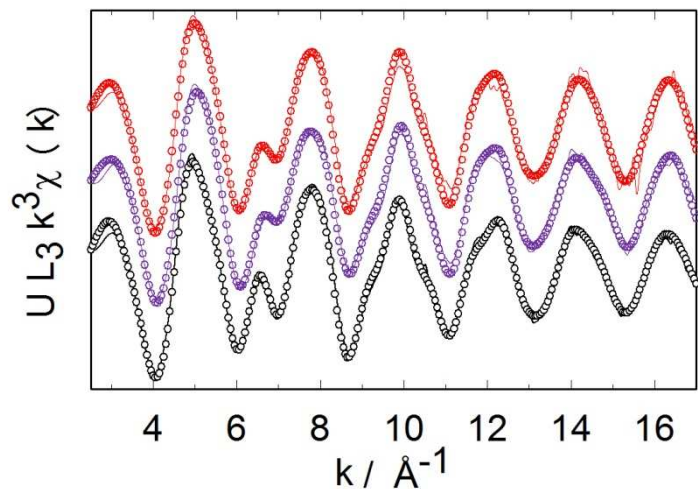


		v / cm <sup>-1</sup>	
		Bonded v C=O	ν <sub>as</sub> UO <sub>2</sub> <sup>2+</sup>
<b>exp</b>	Type of vibration		
	$\text{UO}_2(\text{NO}_3)_2\text{L}_2$	1573	935
		v / cm <sup>-1</sup>	
		Bonded v C=O	ν <sub>as</sub> UO <sub>2</sub> <sup>2+</sup>
<b>calc</b>	Type of vibration		
	$\text{UO}_2(\text{NO}_3)_2\text{L}_2$	1587	933
	$\text{UO}_2(\text{NO}_3)(\text{TcO}_4)\text{L}_2$	1576	930

## XAS spectroscopy



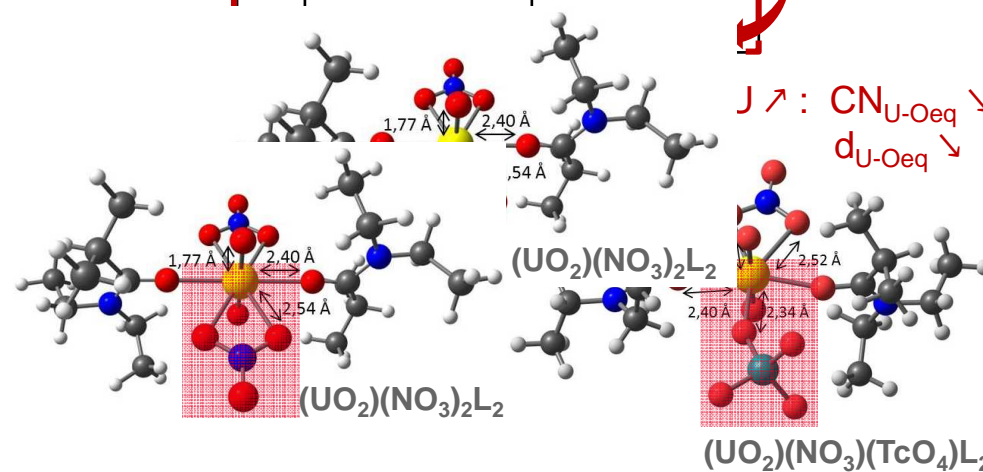
Fourier transform of the  $k^3$ -weighted EXAFS spectra at uranium  $L_3$  edge for U-Tc complexes



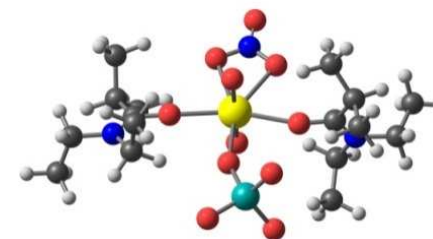
$k^3$ -weighted EXAFS spectra at uranium  $L_3$  edge for U-Tc complexes



	$CN_{U-O_{eq}}$	$d_{U-O_{eq}} / \text{\AA}$
1	6	2.48
2	5.7	2.47



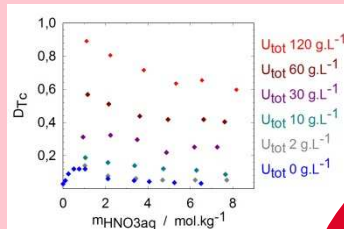
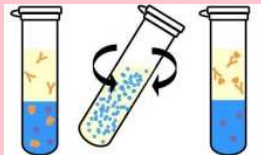
**Confirmation of the suggested co-extraction mechanism of U(VI) and Tc(VII)**





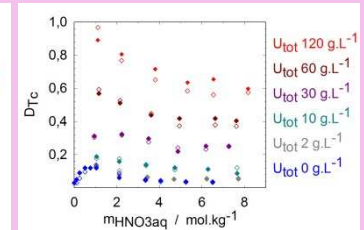
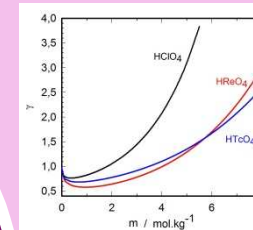
## Liquid liquid extraction:

Batch experiments,  $\gamma$  spectrometry, UV-vis, etc



## Modeling:

Solving the mass balance by taking into account deviation from ideal behaviour



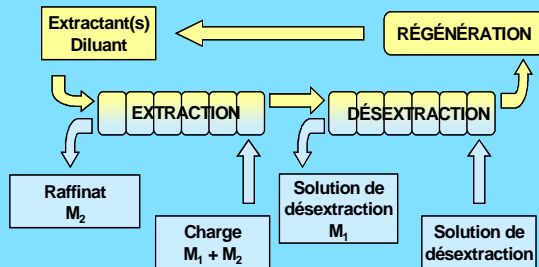
Macroscopic scale

Physico-chemical modeling

Objectives :  
D, SF,  
recovery %

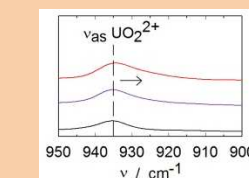
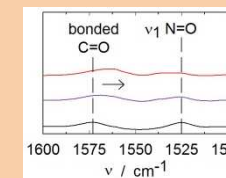
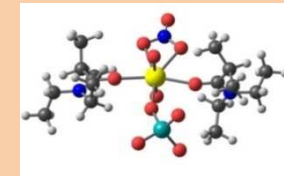
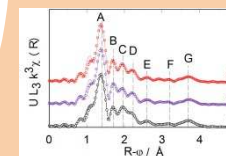
Process modeling

Molecular scale



## Process simulation :

Models integrated into the CEA PAREX code



## Speciation of organic complexes:

UV-vis, IR, ESI-MS, EXAFS etc.

Moeyaert, P., et al. Inorg. Chem., 2016. Submitted

## Aknowledgements

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Dr. Christian Sorel  
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Dr. Thomas Dumas  
Dr. Dominique Guillaumont  
Dr. Kristina Kvashnina  
Pr. Philippe Moisy  
Pr. Jean-François Dufrêche



# THANK YOU FOR YOUR ATTENTION



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