7th International Symposium on Technetium and Rhenium Science and Utilization

TECHNETIUM CATALYTIC EFFECT AND SPECIATION IN NITRIC ACID SOLUTIONS IN PRESENCE OF Np(V), Th(IV) and Zr(IV) AND REDUCING NITROGEN DERIVATIVES

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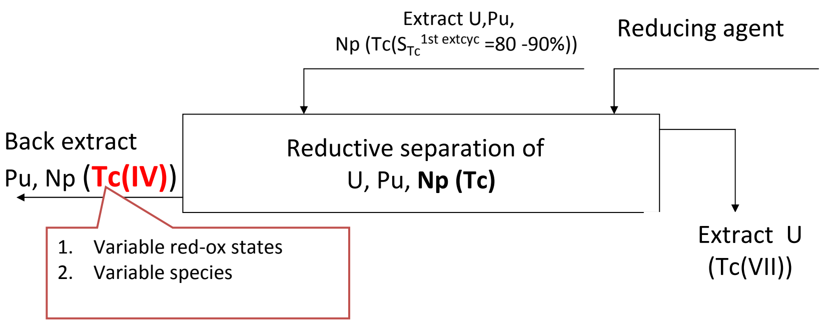
Technetium interfering role in the scenario of PUREX development



- Difficulties in stability of U/Pu separation at UK, Russian and French facilities
- Catalytic Tc effects in many chem. reactions
- Variable Tc redox states
- Tc - Waste problems

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Sellafield (UK)

Mayak (Russia)

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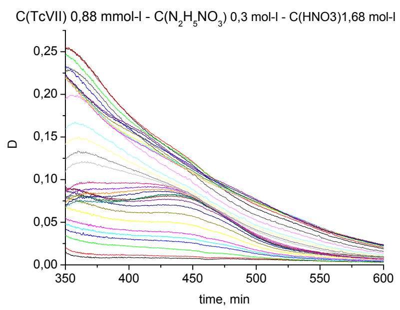
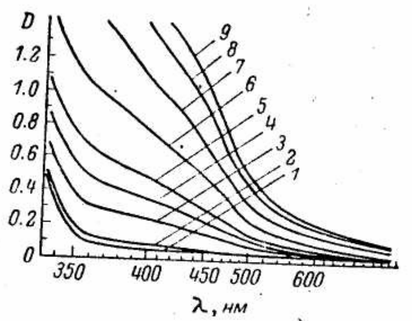
Tc reduction by hydrazine





Time increases from 1 to 9.

No peaks at 470 nm

Tc(VII) - no visible peaks

Tc(IV) – shoulder at 400 nm

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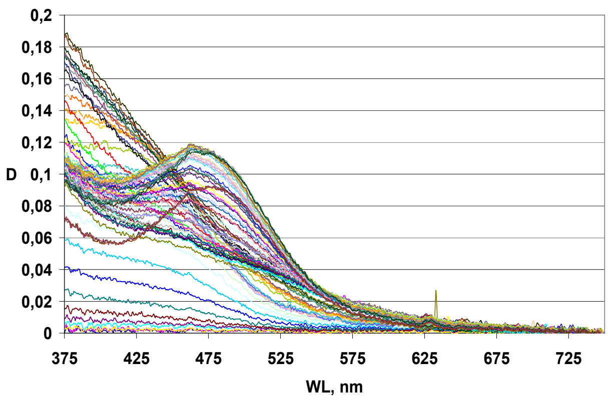
Our experiment



Peak at 470 nm

- Without deconvolution nothing could be explained
- Final species are not stable but could be stabilized in different conditions
- Huge set of chemical conditions should be studied

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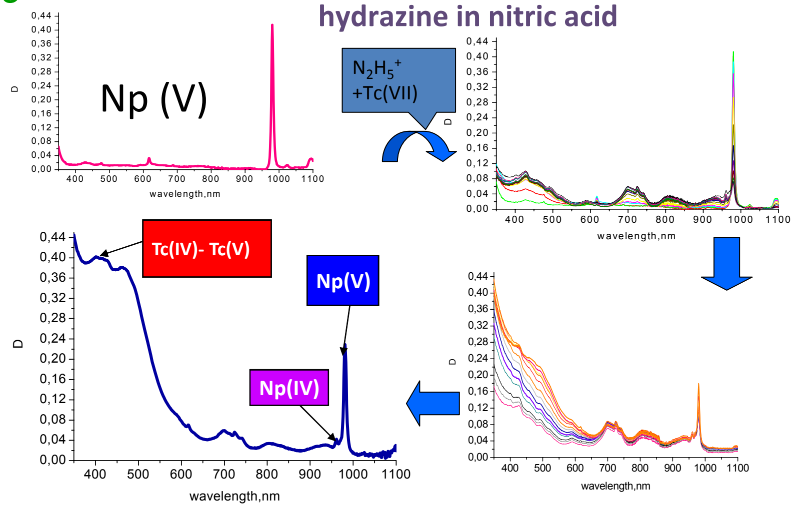
Np Reduction (Np(V) →Np(IV)) in the presence of Tc(VII) by hydrazine in nitric acid



C(Np)= 1,6*10^{-3} mol/l
C(Tc)= 1,15*10^{-3} mol/l
C(HNO_3)=1,67 mol/l
C_0($N_2H_5NO_3$)= 0,3 mol/l
t=45^{o}C

- **Kinetic studies of Tc-Np-Hydrazine system have proved the zero order for Np(V) reduction at 35<T<45^{o}C**
- **Tc(VII or V) accelerates the Np reduction but causes the destruction of hydrazine and partial back oxidation of Np(IV)**
- **Np(IV) forms some complexes, their composition should be the subject of another study**

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An example of chemical composition of the solution series for kinetic studies

№	t, ^0C	C_0 (Tc(VII)), $*10^3$ M	C_0 (Th), $*10^3$ M	C (HNO_3), M	C ($N_2H_5NO_3$), M
1		1,52			
2		1,26			
3		1,14			
4		1,01			
5	55	0,84	3,32	1,5	0,255
6		0,63			
7		0,50			
8		0,40			
1			2,32		
2			3,32		
3	60	1,01	4,32	1,5	0,255
4			5,32		
5			6,32		

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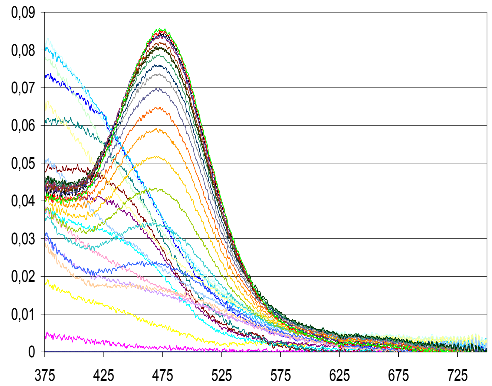
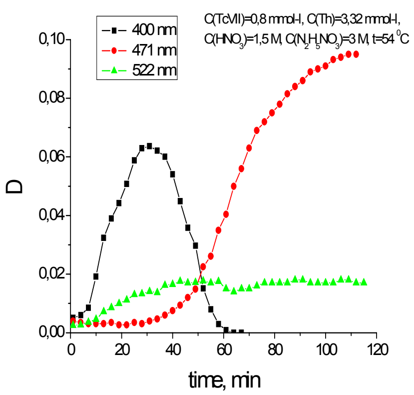
Kinetics of Tc(VII) reduction with $N_2H_5NO_3$ in presence of Th(4+)





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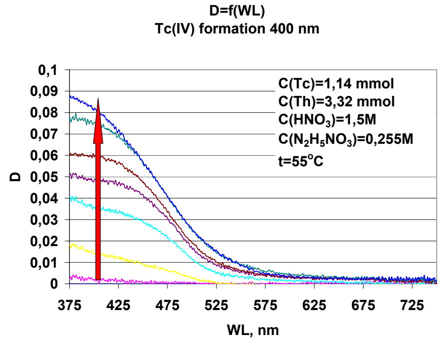
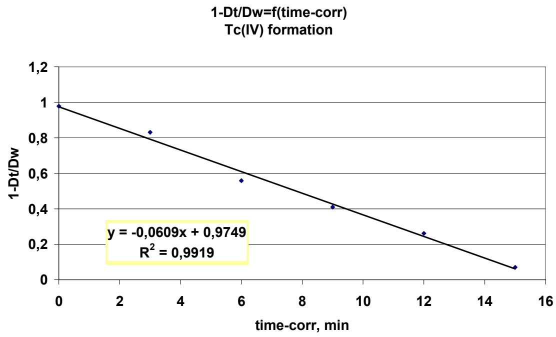
First stage:
Tc(VII) → Tc(IV)
quantified by the shoulder at 400 nm
several elementary reactions co-proceed
Reaction order
n = 0





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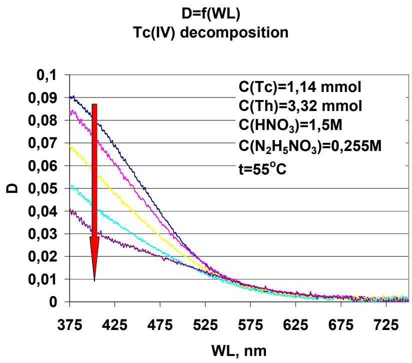
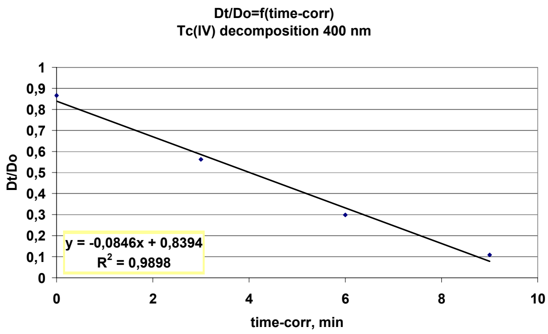
Second stage :
Tc(IV)→Tc(X)
400 nm
Reaction order
n=0





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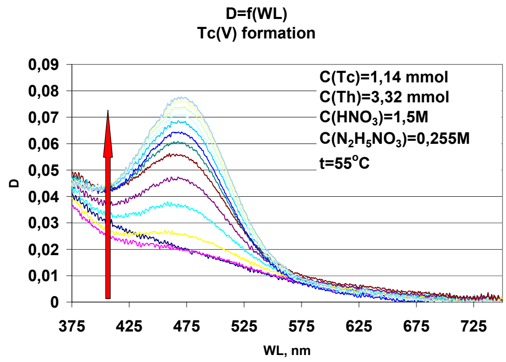
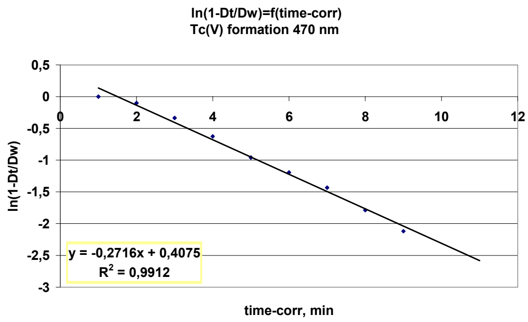
The third stage :
Tc(X)→Tc(V)
470 nm
evolution of N_2
followed by
Tc(V) formation
Reaction order
n = 1





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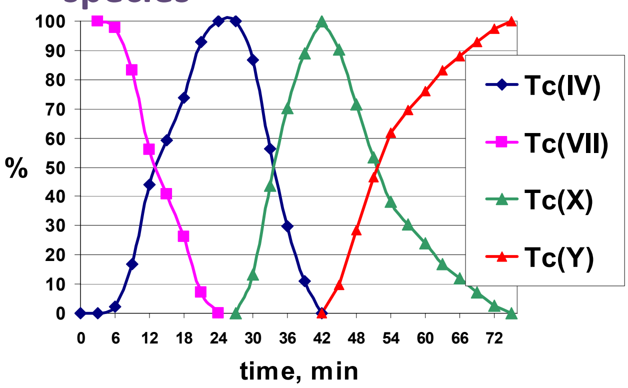
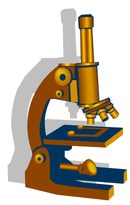
Change in content of reduced Tc species



T = 55-60°C

2 different Tc species exist simultaneously



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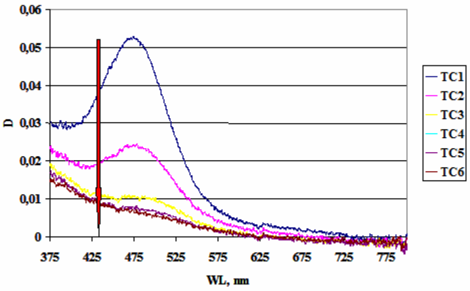
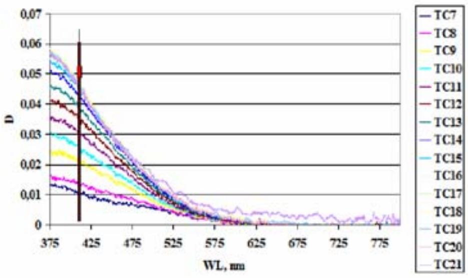
Tc(V)-Th(IV) complex back-reduction with $N_2H_5NO_3$





1) Tc(V) → Tc(X)   2)Tc(X) → Tc(IV)

1. Back reduction of Tc(V)-Th(IV) complex with hydrazine proceeds as a reverse reaction sequence and follow first order for Tc concentration.
2. It proceeds till complete back formation of Tc(IV)
3. The experiments are absolutely reproducible (a set of 14 experiments with different Tc and Th concentrations were recorded)

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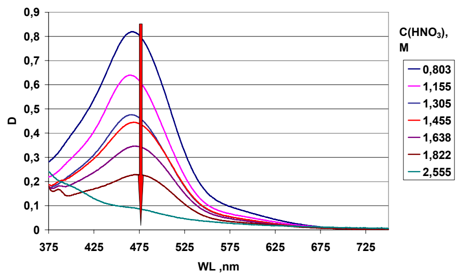
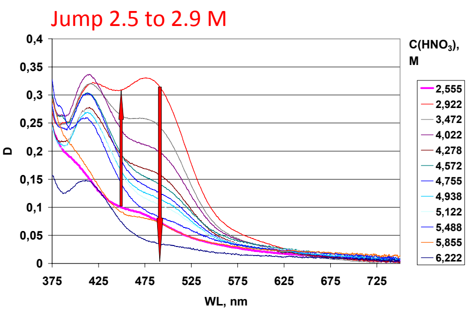
Tc + Th + hydrazine in nitric acid of various concentrations

= same *equilibrated* solutions 2 months later

Tc concentration is constant !





A:
coexistence of two species
in 0.8-2.55 M HNO3
– one with 475 nm peak Tc(1)
r with no peaks Tc(2)

B:
coexistence of two more species
in 2.9-6.0 M HNO_3
- One with 420 nm peak Tc(3)
- The other with 475 nm peak Tc(4)

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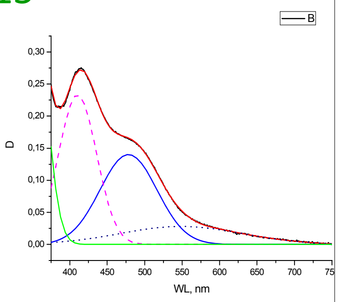

Data: Data6_B
Model: Gauss
Equation: y=y0 + (A/(w*sqrt(PI/2)))*exp(-2*((x-xc)/w)^2)
Weighting:
y No weighting

Chi^2/DoF = 1.4771E-6
R^2 = 0.99983

y0	0	±0
xc1	548.64745	±5.75322
w1	162.78133	±5.08875
A1	5.71759	±0.38224
xc2	478.40772	±0.4001
w2	76.1615	±0.8699
A2	13.37553	±0.38645
xc3	410.42528	±0.14363
w3	50.77228	±0.42957
A3	14.85117	±0.20443
xc4	352.90071	±3.17927
w4	33.79505	±2.29136
A4	15.15263	±3.23383

- Every spectrum was analyzed by deconvolution, otherwise the analysis would be impossible

1) **600 nm – Tc(III)**
2) **470 nm – Tc(Y)**
3) **420 nm – complex with products of hydrazine oxidation**
4) **400 nm – Tc(IV)**

Reactions taking place in Tc-HNO_3-$N_2H_5NO_3$ system

$TcVII + N_2H_5^+ \rightarrow TcVI + N_2H_3\cdot + H^+$
$TcV + N_2H_5^+ \rightarrow TcIV + N_2H_3\cdot + H^+$
$TcIV + TcVII \rightarrow TcVI + TcV$
$TcIV + NO_3^- \rightarrow TcVI + NO_2^-$
$TcVI + N_2H_5^+ \rightarrow TcIV + N_2H_2^+ + 3H^+$
$TcVI + NO_3^- \rightarrow TcVII + NO_2^-$
$TcV + NO_3^- \rightarrow TcVI + HNO_2$
$HNO_2 + N_2H_5^+ \rightarrow HN_3 + 2H_2O + H^+$
$HN_3 + HNO_2 \rightarrow N_2 + N_2O + H_2O$
$2N_2H_3\cdot \rightarrow N_4H_6 \rightarrow 2NH_3 + N_2$
$2N_2H_2 \rightarrow N_4H_4 \rightarrow HN_3 + NH_3$

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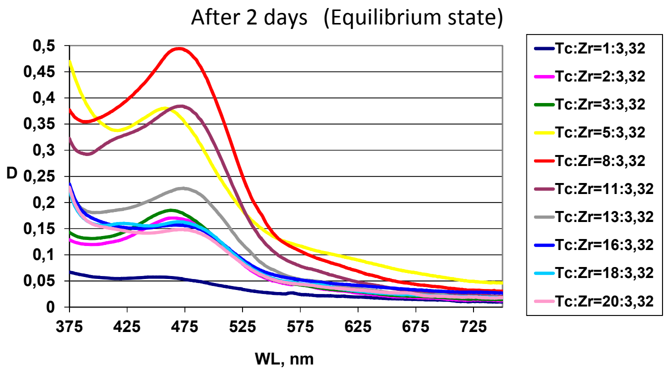
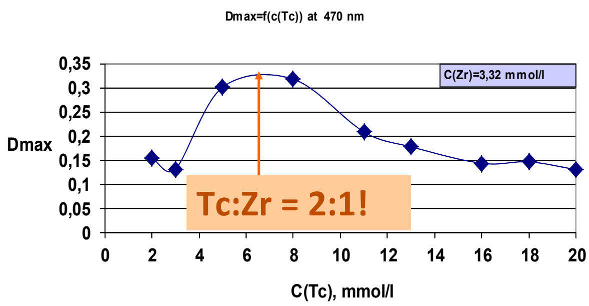
Zirconium c(Zr)=3,32 mmol/l





t = 60^0C

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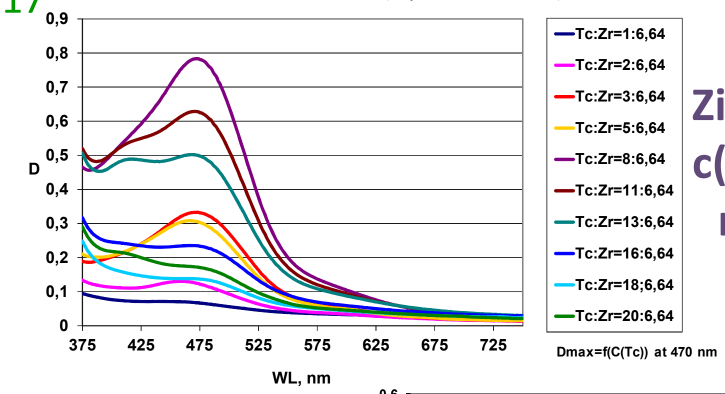
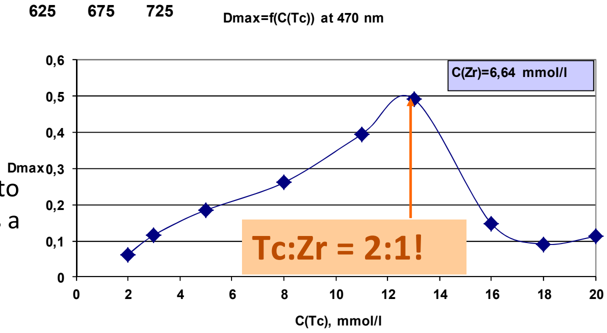


Zirconium c(Zr)=6,64 mmol/l

t = 60^{0}C



Concentration of the Tc(V) complex is increasing at the [Tc] from 2 up to 13 mM.

Futher increase of [Tc] leads to appearance of Tc(IV) which is a catalytic agent for decomposition of hydrazine.

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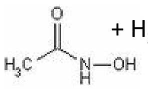
Hydroxylamine NH_2OH

Technetium Reduction and Complexation by Acetohydroxamic Acid in Nitric and Perchloric Acids: Formation of $[Tc(II)(NO)(AHA)_2(H_2O)]+$ and its Effects on the Nuclear Fuel Cycle *by C. S. Gong, W. W. Lukens, F. Poineau, and K. R. Czerwinski*



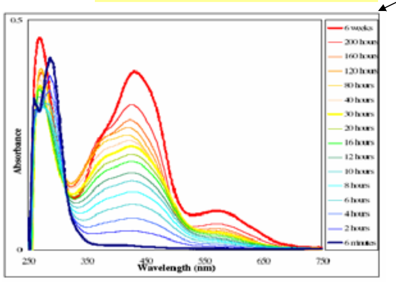
$+ H_2O = NH_2OH + CH_3COOH$

AHA-acetohydroxamic acid

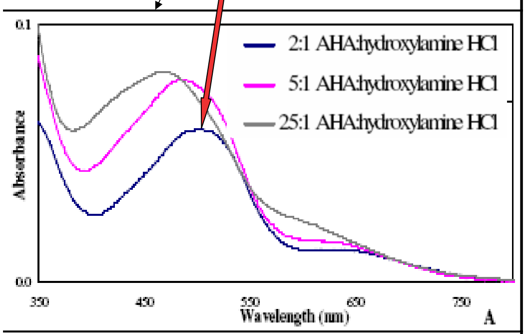
λmax=428 nm (only AHA)

Without Th or Zr:

λmax=500 nm (AHA and NH_2OH)



Monitoring the production of $Tc^{II}NO(AHA)_2H_2O^+$ over time via UV-vis spectroscopy. Here, 0.16 mM Tc in 3.66 M AHA and 1.0 M $HClO_4$ in a sealed quartz cuvette was monitored for 6 weeks. The final spectrum (red) is the equilibrium spectrum observed for all reaction solutions in $HClO_4$ and HNO_3 at all temperatures.



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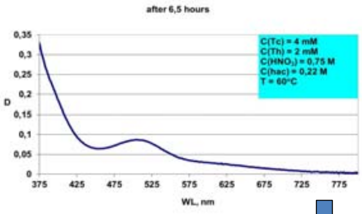
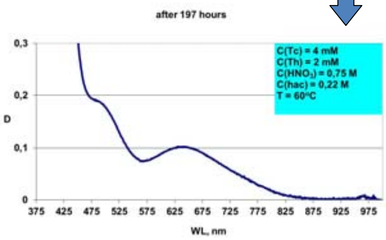
Tc(VII) reduction with NH_2OH in presence of Th(IV) or Zr(IV)

Under constant heating:

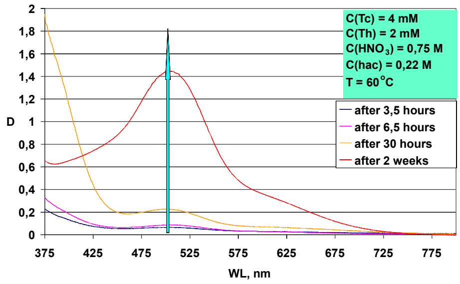


500 nm ⟶ 675 nm



Reaction goes faster with Zr than with Th

Under heating during 2 days, then room temperature:



- **Complex formation is very slow**
- **Complex is stable for months at 20°C**

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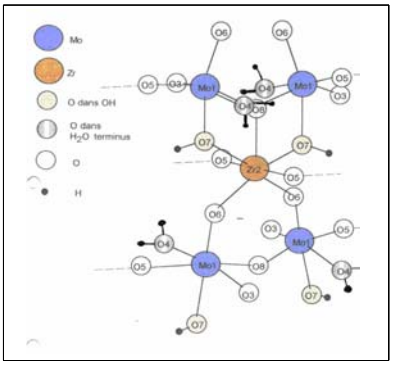
Hypotheses on Tc observed behavior

a) Tc Hydrolyses

b) Cation-cation interaction of actinides with $[O=Tc^{V}]^{3+}$

c) $[N \equiv Tc^{V}]^{2+}$ or $[N \equiv Tc^{IV}]^{+}$ bond formation

d) ZrMo2-type complexation ($ZrMo_2O_7(OH)_2{*}2H_2O$)



Conclusions

- Tc(V) forms stable complexes with M(IV) (M=Th,Zr) in 1.3 M HNO_3 when Tc:Zr(Th)=2:1
- The system Th(Zr)-Tc-$N_2H_5NO_3$ (NH_2OH*HCl)-HNO_3 is so complicated that to answer all the questions we need supplementary study of the solid phases

Thank you for attention!