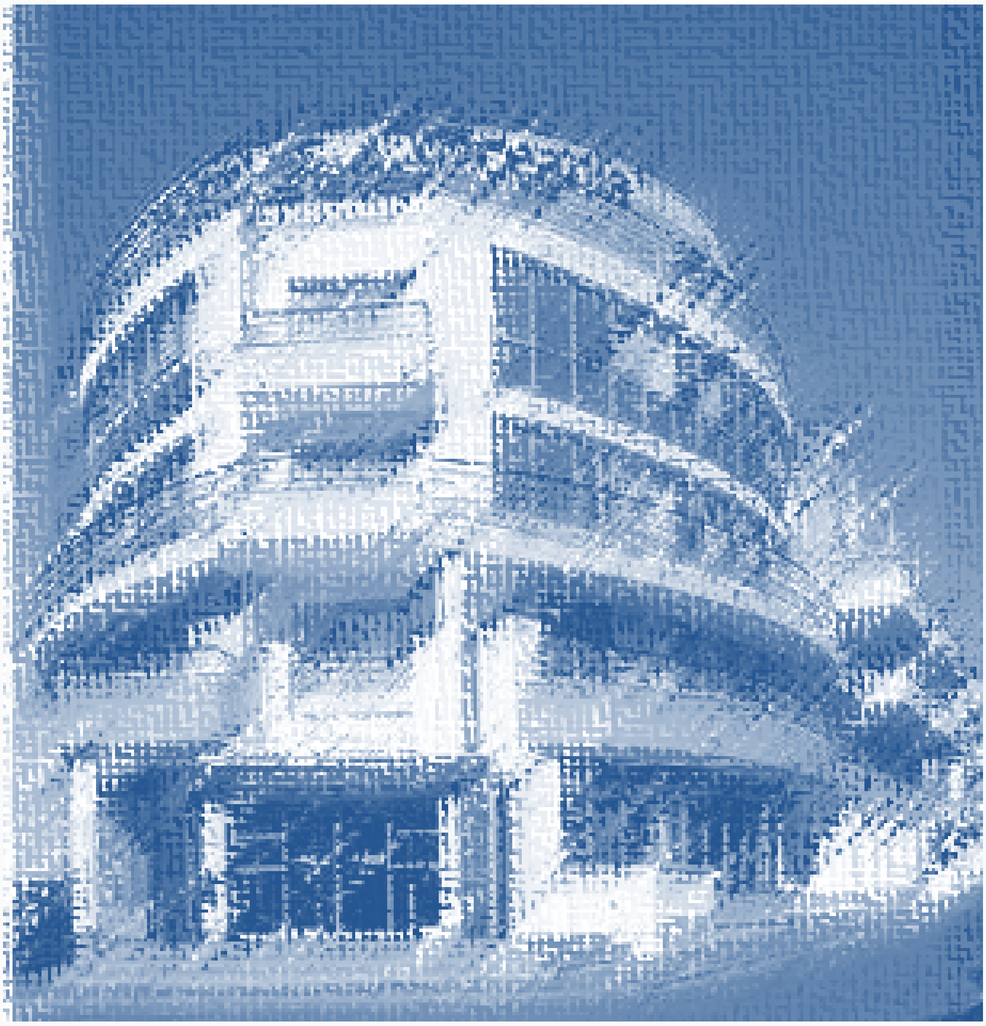
8th International Symposium on Technetium and Rhenium: Science and Utilization

ISTR 2014



La Baule - Pornichet, France
29th sept. - 3rd oct. 2014

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Nantes – Moscow – Las Vegas

Granica Publishing Group – 2014

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Technetium and Rhenium in nuclear medicine

Poster session

The 8th International Symposium on Technetium and Rhenium: Science and Utilization,

September 29th to October 3rd 2014
La Baule - Pornichet, France.

The 8th ISTR aimed at continuing 20 years of tradition on Technetium and Rhenium conferences and the symposium happening every 3 years. It was originally created in 1993 and has been successively held in 1993 (Sendai, Japan), 1996 (Moscow, Russia), 1999 (Shizuoka, Japan), 2002 (Dubna, Russia), 2005 (Oarai-Ibaraki, Japan), 2008 (Port-Elizabeth, South Africa) and 2011 (Moscow, Russia).

The aims of the 8th ISTR was to cover all aspects of Technetium and Rhenium chemistry. The conference was organized around plenary lectures (30-40 minutes), short lectures (15-20) minutes and poster sessions. The technical program has covered the following topics :

- Chemistry of Technetium in the nuclear fuel cycle (separation, disposal, waste form…)
- Technetium and Rhenium in nuclear medicine (isotopes production, labeling, coordination chemistry…)
- Radioanalytical chemistry (Measure of Tc an Re in biosphere…)
- Fundamental chemistry of Technetium and Rhenium (synthetic, materials and coordination chemistry, inorganic and organometallic complexes, properties...)
- Rhenium in the industry (mining, metallurgy, catalysis…)

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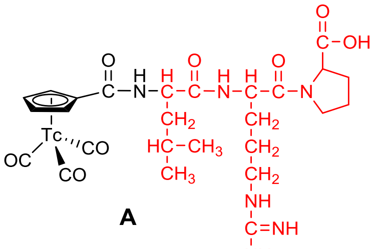
Multiple Facets of Technetium and Rhenium Chemistry in Molecular Imaging and Therapy

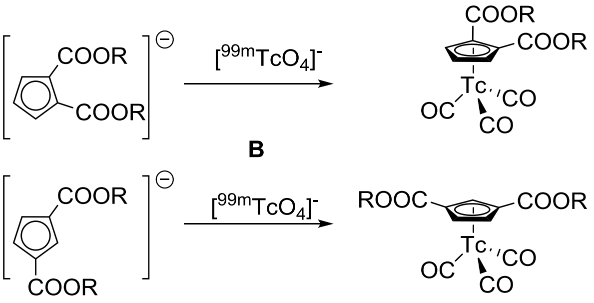
Roger Alberto, Samer Ursillo, Henrik Braband, Michael Benz, Michael Felber, Sebastian Imstepf

Department of Chemistry, University of Zurich, Winterthurerstr. 190, CH-8057 Zurich

PET is becoming more and more important, but ^{99m}Tc as a radionuclide for Single Photon Emission Computed Tomography (SPECT) has still the strongest impact on diagnostic health care. Whereas SPECT cameras can compete with PET cameras, chemical research efforts are required for keeping the role of Tc alive. Complementing diagnosis with ^{99m}Tc by therapeutic modalities is a clear asset over PET strategies (with ^{18}F). Adapting the theranostic concept, we aim at synthesizing ^{99m}Tc complexes which mimic pharmacophores (imaging) with cold Re homologues (therapy), the ^{99m}Tc complex is a structural moiety in pharmaceutically active lead structures. This strategy requires demanding organometallic reactions. The preparation of cyclopentadienyl based bioorganometallic compounds is a focus since the Cp-ring can mimic phenyls in pharmaceuticals. Complexes of the type [(Cp-R)^{99m}Tc(CO)$_3$] opened the so-called Cp-phenyl analogy.[1] The Cp complex can be a tag, as will be shown with peptides (A),[2] but also an integral part of structure in which it plays an essential role for receptor recognition. Examples with CA and HDAC inhibitors will be presented.[3] Replacing Tc by Re will yield homologues with almost identical, pharmacological properties but with therapeutic potential.



A



B

We have extended the approach to cyclopentadienyl derivatives with two carboxylato groups (B) allowing to couple two bioactive functionalities to one ^{99m}Tc or Re complex. Finally, for replacing a phenyl ring in a pharmaceutical by a "true" phenyl ring, first insights in arene chemistry will be given. These aspects from low valent, organometallic chemistry will be rounded up by insights from high valent ^{99m}Tc and Re chemistry.[4]

1. Liu, Y.; Spingler, B.; Alberto, R. et al., *J. Am. Chem. Soc.*, **2008**, 130, 1554.
2. Nadeem, Q.; Can, D.; Alberto, R. et al., *Org. & Biomol. Chem.*, **2014**, 12, 1966.
3. Can, D.; Spingler, B.; Alberto, R.; et al., *Angew. Chem. Int. Edit.*, **2012**, 51, 3354.
4. Braband, H., Benz, M., Tooyama, Y. Alberto, R. *Chem. Commun.,* **2014**, 50, 4126.

Multiple Facets of Technetium and Rhenium Chemistry in Molecular Imaging and Therapy

Roger Alberto

Department of Chemistry
University of Zürich

La Baule - Pornichet, France, September 29, 2014

Outline

- A bit of history…
- Organometallic Chemistry and **Coordination Chemistry**
- **Organometallic Chemistry** and Coordination Chemistry
- What can we learn from „**Metals in Medicine**“
- Integrated Molecular Imaging Agents: **Theranostics**
- Phenyl – **Cyclopentadienyl** Analogy
- **Functionalized** Cyclopentadienyl complexes
- Missed Opportunities

A bit of History..

“During the past five years, there has been a dramatic surge of activity in technetium chemistry, this activity has been driven to a large extent by the desire of inorganic chemists to obtain a basic understanding of this largely unexplored element.
An even greater driving force has been provided by the extensive use of Tc-99m in diagnostic nuclear medicine procedures and the growing realization that significant advance in this applied field will depend upon basic research in the field of inorganic Technetium chemistry”

E. Deutsch, K. Libson and S. Jurisson, L.F. Lindoy in *Progress in Inorganic Chemistry*, **1983**, *30*, 75

… the several oxidation states of technetium exhibit diverse chemistries which will allow Tc-99m to be incorporated into a variety of formulations that are specific for different organs, thus, various chemical forms of the single isotope …

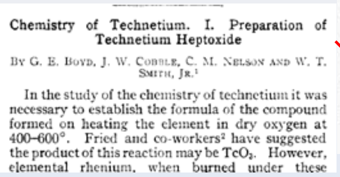
E. Deutsch, K. Libson and S. Jurisson, L.F. Lindoy in *Progress in Inorganic Chemistry*, **1983**, *30*, 75

A bit of History..

One of the reasons for the increased interest in technetium chemistry during the last few years is the widespread use of radiopharmaceutical labelled with ^{99m}Tc.

{..} However, Fig.2 shows that the number of studies reported on new ^{99m}Tc radio-pharmaceuticals has decreased from 1977 to 1980. This fact evidences a stall position in radiopharmaceutical research that will only be alleviated by Further development of technetium chemistry. Fortunately studies on the coordination chemistry are expanding. G. Bandoli, U, Mazzi, E. Roncari, Coord. Chem. Rev. **1982**, *44*, 191

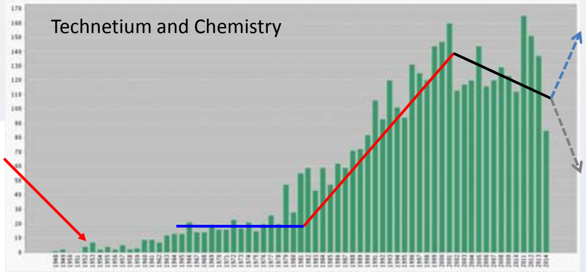
JACS, 1952



Chemistry of Technetium. I. Preparation of Technetium Heptoxide

By G. E. Boyd, J. W. Cobble, C. M. Nelson and W. T. Smith, Jr.[1]

In the study of the chemistry of technetium it was necessary to establish the formula of the compound formed on heating the element in dry oxygen at 400–600°. Fried and co-workers[2] have suggested the product of this reaction may be TcO_2. However, elemental rhenium, when burned under these



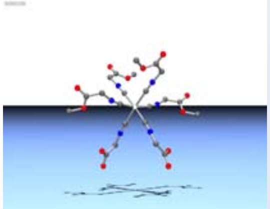
Technetium and Chemistry

A bit of History..

"During this period of time*, the coordination chemistry of technetium played a significant role. The successful development of ^{99m}Tc imaging agents **was totally dependent on the design of technetium complexes** since the biodistribution and targeting capability depend exclusively on their lipophilicity, size and charge."

"Although the focus of radiopharmaceutical research has shifted towards biological characterization of radiolabeled receptor ligands in the last several years, coordination chemistry still plays a significant role in the design and development of new target-specific radiopharmaceuticals."

The role of coordination chemistry in the development of target specific radiopharmaceuticals
S. Liu, *Chem. Soc. Rev.* **2004**, *33*, 445



A bit of History..

Much of this work has been directed toward the investigation of kinetically inert complexes formed in oxidation states that are readily accessible in aqueous media by the reduction of the pertechnetate ion. These studies have demonstrated that it is possible to prepare classes of stable complexes in both the **V and the III oxidation states with the** appropriate choice of ligand.

This in turn has enabled us (a) to synthesize this class of air- and water-stable complexes at tracer concentrations (ca. 10^{-8}-10^{-9} M) with metastable ^{99m}Tc (b,) to begin to evaluate the biological distributions of these complexes in animals, and (c) to establish structure function correlations on a potentially large class of well-characterized complexes.

Synthesis and Characterization of Hexakis(alkyl isocyanide) and Hexakis(aryl-isocyanide) Complexes of Technetium(I)
M. J. Abrams, A. Davison, A. G. Jones, C. E. Costello, H. Pang, *Inorg. Chem.*, **1983**, *22*, 2798

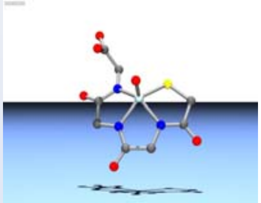
A bit of History..

For the synthesis of specific radiopharmaceuticals, the versatile chemistry of this transition element, apparent from the existence of compounds in a large number of technetium oxidation states, is an advantage.
However. the labeling requires the complexing of ^{99m}Tc with suitable functional groups.

K. Schwochau, *Angew. Chem. Int. Ed.*, **1994**, *33*, 2258

The early history of technetium and technetium radiopharmaceuticals is best characterized by the quote from Louis Pasteur:
"*In the fields of observations, chance favors only the prepared mind*"

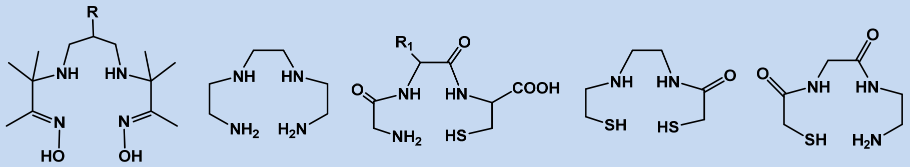
Unparalleled contributions of Techentium-99m to Medicine over 5 decades
W.C. Eckelman, *Cardiovascular Imaging*, **2009**, **2**, 364



Organometallic chemistry and **Coordination chemistry**

- ➡ Complexes; no M-C bonds
- ➡ Coordination compounds are generally thermodynamically very stable
- ➡ Chelate effect plays an important role; entropic control
- ➡ pH dependencies; competition metal-binding-H$^+$

In Technetium coordination chemistry: a few basic ligand types

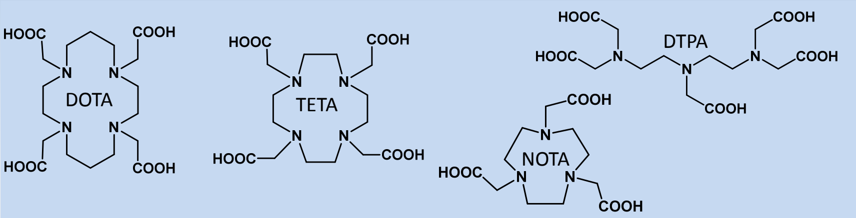


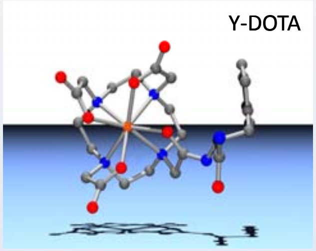
PnAO, MAMA, MAGs, DADT etc … and derivatives

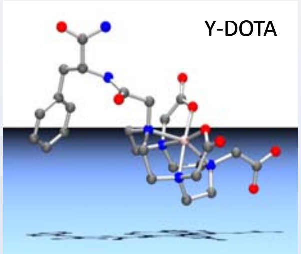
Designed for the {Tc=O}$^{3+}$ and the {Tc≡N}$^{2+}$ core

Organometallic chemistry and **Coordination chemistry**

Ligands for the “3+” family, Ga^{3+}, Lu^{3+}, In^{3+}, Gd^{3+} etc

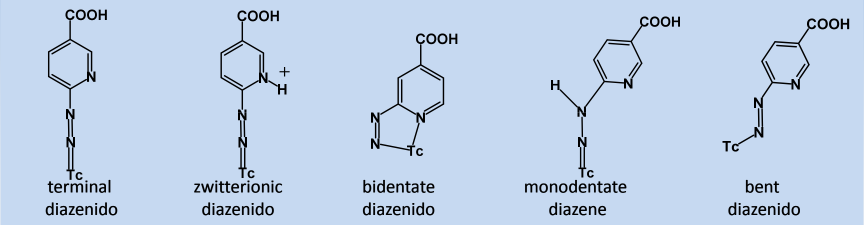




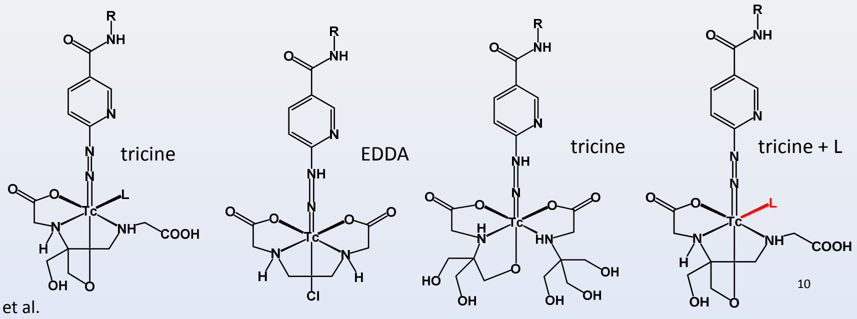


Organometallic chemistry and **Coordination chemistry**

HYNIC, a wonderful coordination chemistry approach..



..but requires multidentate coligands



J. Dilworth et al.

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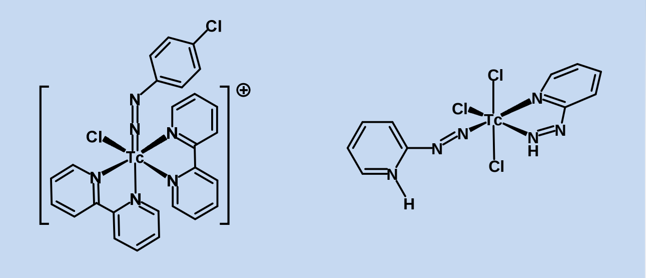
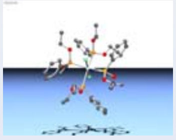
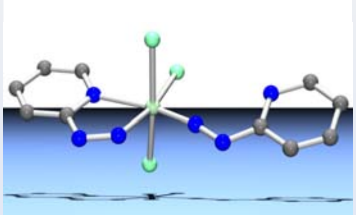
Organometallic chemistry and **Coordination chemistry**

HYNIC, a wonderful coordination chemistry approach..

Model complexes







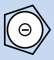
J. Dilworth J. et al., *J. Chem. Soc. Dalton T.* **1994**, 1251;
T. Nicholson, J. Zubieta, J. Babich et al., *Inorg. Chim. Acta,* **1996,** *252*, 421; *Inorg. Chem.*, **1998**, *37*, **2701**.

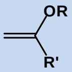
Universität Zürich

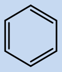
Organometallic chemistry and Coordination chemistry

- ➡ one or more M-C bonds
- ➡ bonds essentially covalent
- ➡ stability rather kinetic than thermodynamic
- ➡ chelate effect plays a minor role (robustness)
- ➡ closed shell complexes, diamagnetic, often redox inert
- ➡ rarely pH dependencies due to covalent bonds

Organometallic compounds rely on a few basic ligand classes







$[Tc_2(CO)_{10}]$	$[Tc(\eta^5\text{-}C_5H_5)(CO)_3]$	$[Tc_2(CO)_9(=C(COMe)R)]$	$[Tc(C_6H_6)_2]^+$
Carbon monoxide	Cyclopentadienyl	Carbene	arene

Ch. Palm et al.
Naturwissenschaften, **1962**, *49*, 279

F. Baumgärtner et al.
Chem. Ber., **1961**, *94*, 2198

J.C. Hileman et al., *JACS*, **1961**, *83*, 2953
W. Hieber et al. ANIE, **1961**, *73*, 579

E.O. Fischer et al.,
Chem. Ber., **1972**, *105*, 3027

Organometallic chemistry and Coordination chemistry

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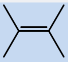
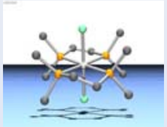
Organometallic compounds rely on a few basic ligand classes

$C{\equiv}N{-}R$	$-R$		other π-ligands
$[Tc(CN\text{-}^tBu)_6]^+$	$[Tc_2O_4(CH_3)_4]$	?	?
isonitrile	alkyle	alkene alkine	

M.J. Abrams et al.
J. Labelled Comp. Radiopharm., **1982**, *14*, 1596

W.A. Herrmann et al.
ANIE., **1990**, *29*, 189

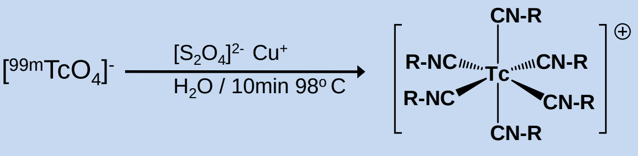


Organometallic chemistry and Coordination chemistry

Difficulties with organometallic (technetium) compounds

- low oxidations states; reduction
- prone to **back oxidation**
- solubilities of ligands in water
- **hydrolytic stability** of complexes
- Stability of ligands in water
- **accessibility of ligands** and derivatives
- ligand-centred reactivities

not very attractive conditions for radiopharmaceutical approaches!

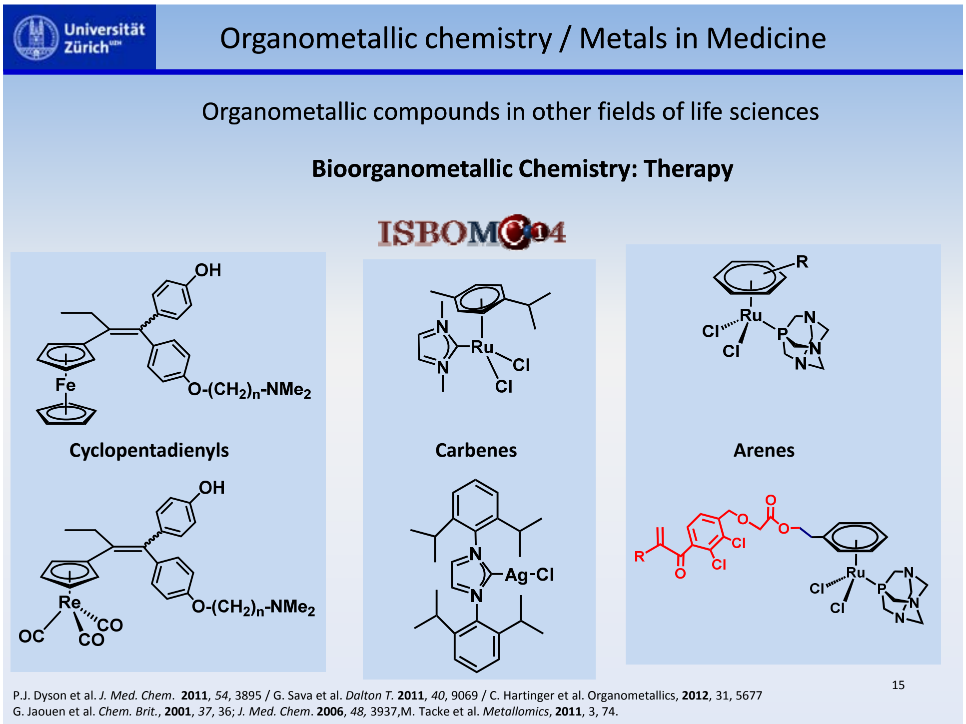


$[^{99m}TcO_4]^- \xrightarrow[H_2O\ /\ 10min\ 98^o\ C]{[S_2O_4]^{2-}\ Cu^+}$

a rock !!

yield > 98%

M.J. Abrams et al. *Inorg. Chem*. **1983**, *22*, 2798

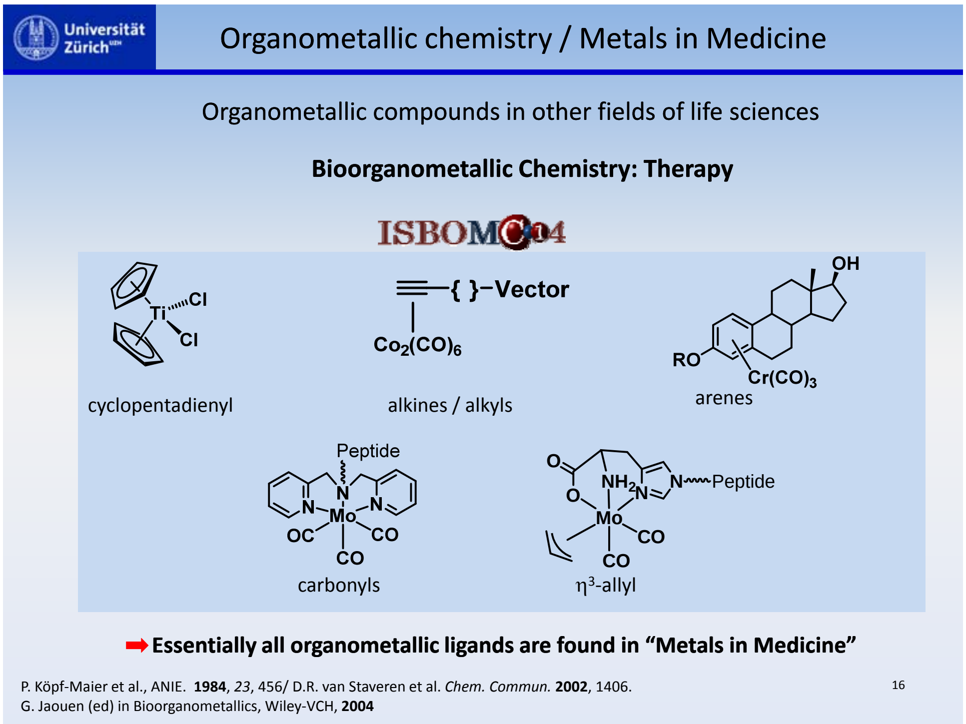


Organometallic chemistry / Metals in Medicine

Organometallic compounds in other fields of life sciences

Bioorganometallic Chemistry: Therapy

P.J. Dyson et al. *J. Med. Chem.* **2011**, *54*, 3895 / G. Sava et al. *Dalton T.* **2011**, *40*, 9069 / C. Hartinger et al. Organometallics, **2012**, 31, 5677
G. Jaouen et al. *Chem. Brit.*, **2001**, *37*, 36; *J. Med. Chem.* **2006**, *48*, 3937, M. Tacke et al. *Metallomics*, **2011**, 3, 74.



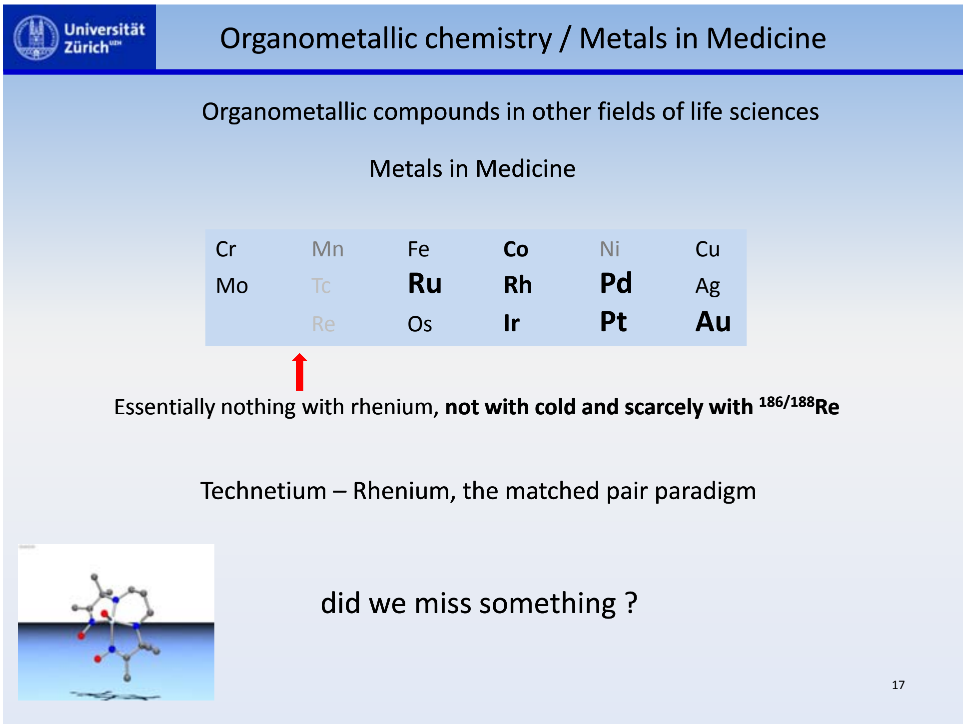
Organometallic chemistry / Metals in Medicine

Organometallic compounds in other fields of life sciences

Bioorganometallic Chemistry: Therapy

➡ **Essentially all organometallic ligands are found in "Metals in Medicine"**

P. Köpf-Maier et al., ANIE. **1984**, *23*, 456/ D.R. van Staveren et al. *Chem. Commun.* **2002**, 1406.
G. Jaouen (ed) in Bioorganometallics, Wiley-VCH, **2004**



Organometallic chemistry / Metals in Medicine

Organometallic compounds in other fields of life sciences

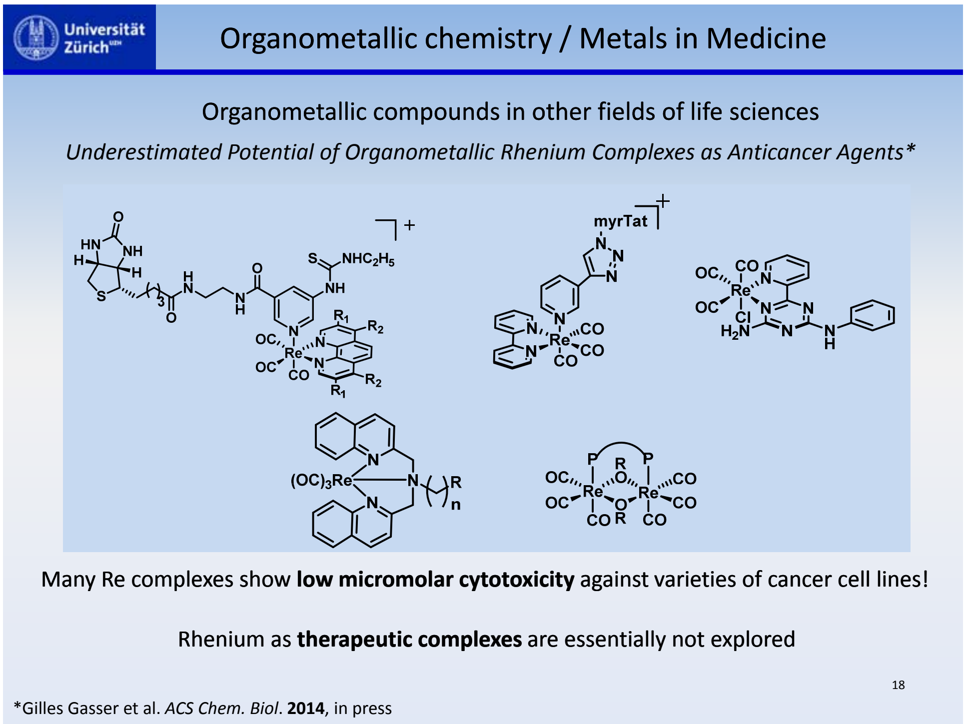
Metals in Medicine

Cr	Mn	Fe	**Co**	Ni	Cu
Mo	Tc	**Ru**	**Rh**	**Pd**	Ag
	Re	Os	**Ir**	**Pt**	**Au**

Essentially nothing with rhenium, **not with cold and scarcely with $^{186/188}$Re**

Technetium – Rhenium, the matched pair paradigm

did we miss something ?



Organometallic chemistry / Metals in Medicine

Organometallic compounds in other fields of life sciences

*Underestimated Potential of Organometallic Rhenium Complexes as Anticancer Agents**

Many Re complexes show **low micromolar cytotoxicity** against varieties of cancer cell lines!

Rhenium as **therapeutic complexes** are essentially not explored

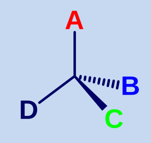
*Gilles Gasser et al. *ACS Chem. Biol*. **2014**, in press

Organometallic chemistry / Metals in Medicine

Recent developments in bioorganometallic chemistry

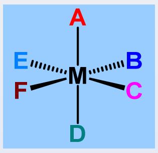
most complexes in bomc are **non-targeting**, cisplatin-like

Extension of the concept



<= **2 stereoisomers**

Metal complexes offer more structural opportunities



<= **30 stereoisomers**

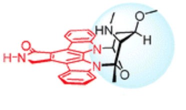
octahedral metal complexes as scaffolds

E. Meggers, Chem. Commun. **2009**, 1001.

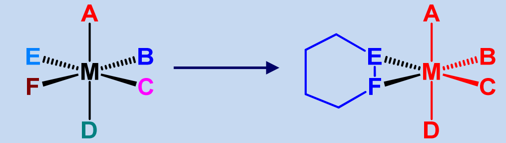
Organometallic chemistry / Metals in Medicine

Metals in Medicine: “Complex”-mediated activity

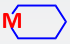
Metal complex as **an integral part** of structure recognition scaffold

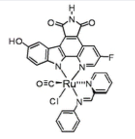


staurosporine
lead structure

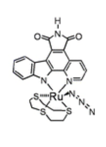


specificity affinity

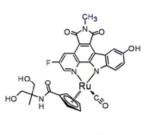




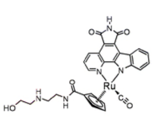
IC_{50}= 130 nM
PAK-1



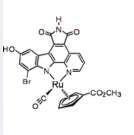
IC_{50}= 70 nM
MSK-1



IC_{50}= 40 nM
Pi3Kγ



IC_{50}= 0.5 nM
Pim-1



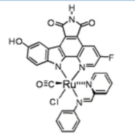
IC_{50}= 0.4 nM
GSK-3β

Metal complex directs specificity and affinity

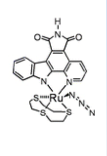
E. Meggers, Chem. Commun. **2009**, 1001; Angew. Chem. Int. Ed. **2011**, 50, 2442

Organometallic chemistry / Metals in Medicine

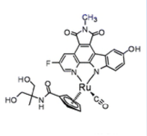
Metals in Medicine: “Complex”-mediated activity



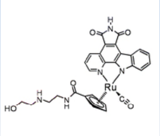
IC_{50}= 130 nM
PAK-1



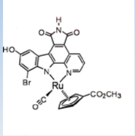
IC_{50}= 70 nM
MSK-1



IC_{50}= 40 nM
Pi3Kγ

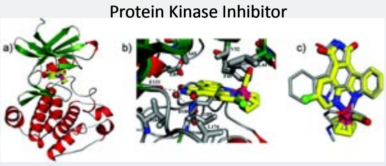


IC_{50}= 0.5 nM
Pim-1

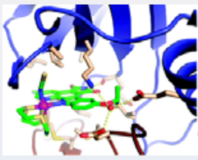


IC_{50}= 0.4 nM
GSK-3β

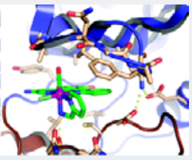
Protein Kinase Inhibitor



MLCK inhibitor 4.4 nM



Pim1 inhibitor 0.07 nM



Fine tuning of metal complex guides affinity and selectivity

can we establish similar for matched-pair elements

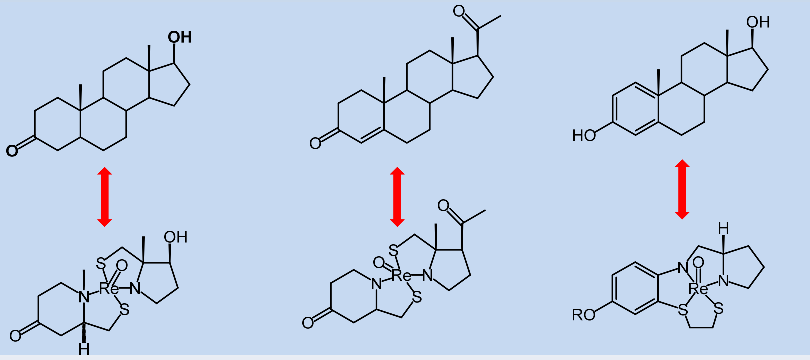
➡ **Rhenium** for therapy – **Technetium** for diagnosis

E. Meggers et al., Chem. Commun. **2009**, 1001; *JACS.* **2011**, 133, 5976; *ANIE* **2011**, 50, 2442

Organometallic chemistry / Metals in Medicine

Metals in Medicine: “Complex”-mediated activity

Structural mimics of steroid hormones

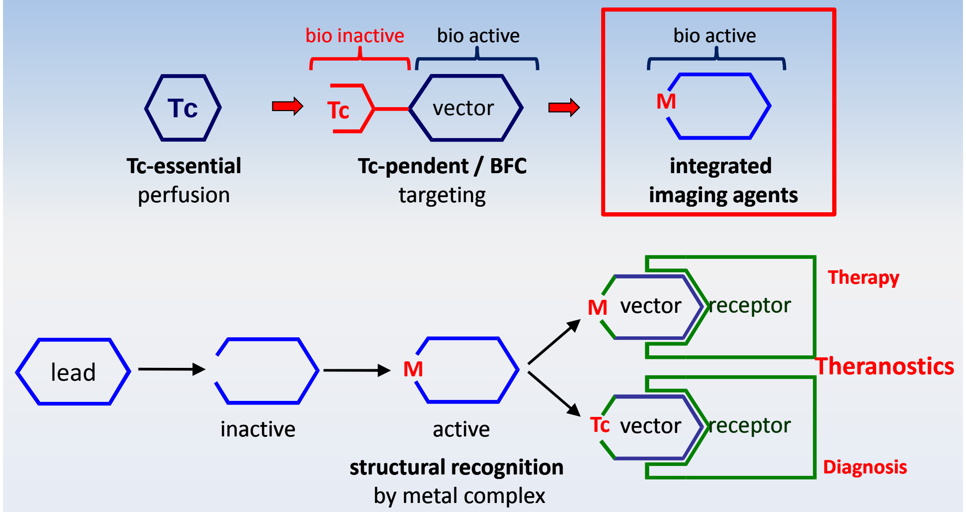


De novo **inhibitors** for receptors

Challenging for ^{99m}Tc chemistry with coordination compounds

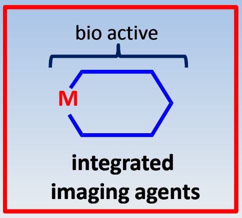
J.A. Katzenellenbogen et al., JACS, **1993**, *115*, 7045; *J. Med. Chem.*, **1994**, *37*, 928; *J. Org. Chem.*, **1997**, *62*, 6290; *J. Org. Chem.*, **1996,** *61*, 2624

Integrated Molecular Imaging Agents



Organometallic Complexes are well suited for the concept

Integrated Molecular Imaging Agents

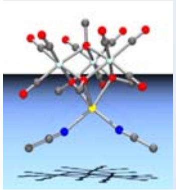


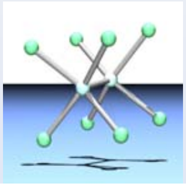
Organometallic Complexes are well suited for the concept

Technetium for imaging and its Rhenium homologue for therapy

since..

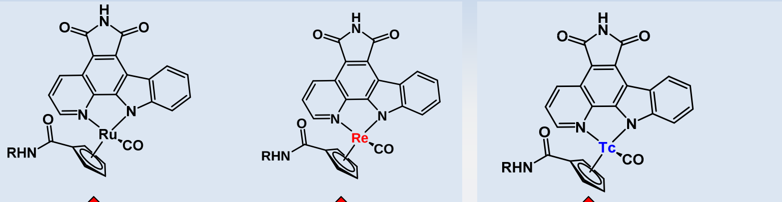
.. many lead structures comprise “organometallic” **structural motives**





Therapy and Imaging with Metal Complexes

Practical limitations



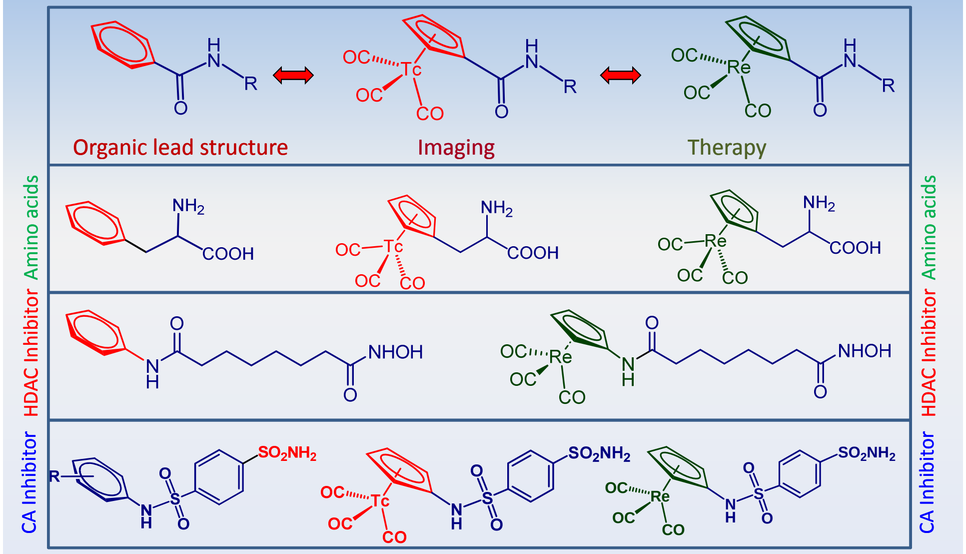
Optimized structure recognizing complexes can be synthesized by any means

inaccessible

$[^{99m}TcO_4]^- \xrightarrow[\text{30-60 min / r.t. or 100°C}]{\text{saline}}$ products

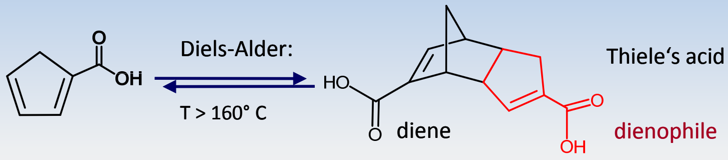
“True” Tc-Re (and Mn) homology only in low oxidation states

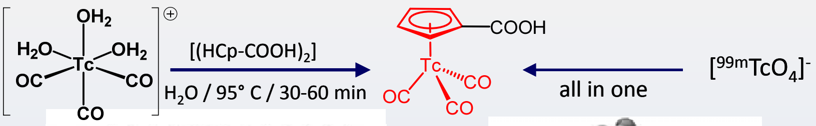
Therapy and Imaging with Metal Complexes



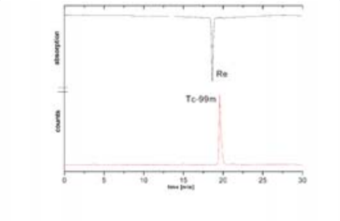
The Cyclopentadienyl – Phenyl Analogy

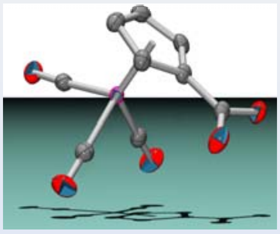
Synthesis of $[(\eta^5\text{-Cp-R})^{99m}Tc(CO)_3]^+$ complexes from water





> 97%

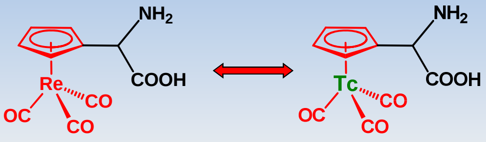




Liu, Y. et al. *J. Am. Chem. Soc.* **2008**, 130, 155

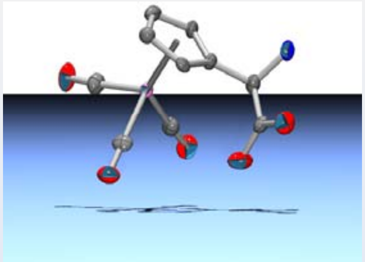
The Cyclopentadienyl – Phenyl Analogy

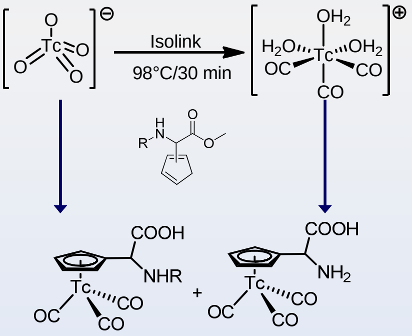
Synthesis of $[(\eta^5\text{-Cp-R})^{99m}Tc(CO)_3]^+$ complexes from water

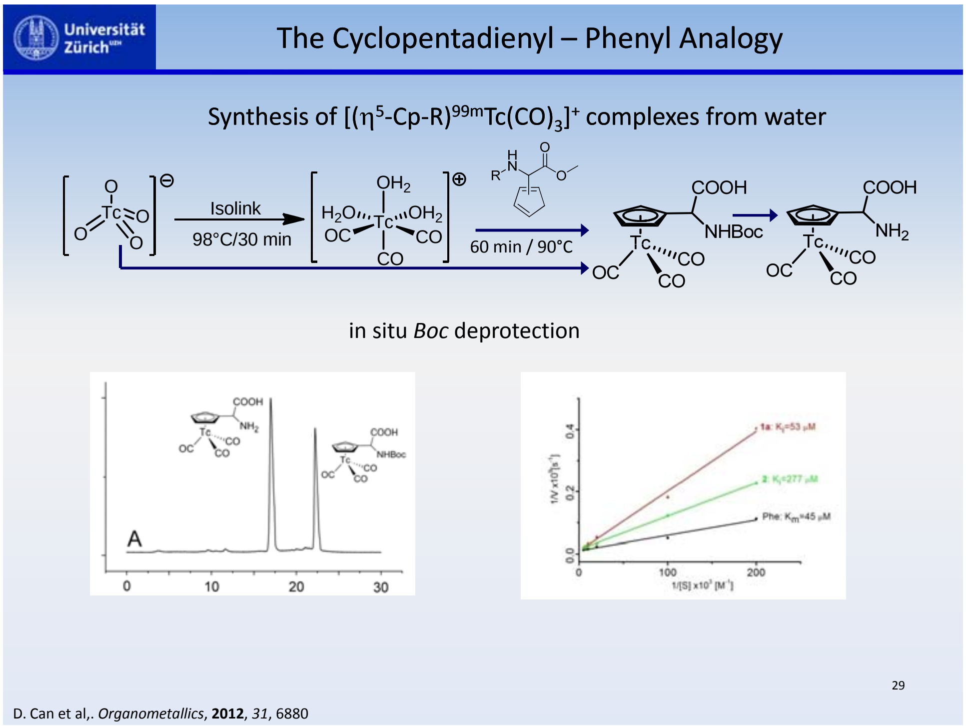


therapy

diagnosis







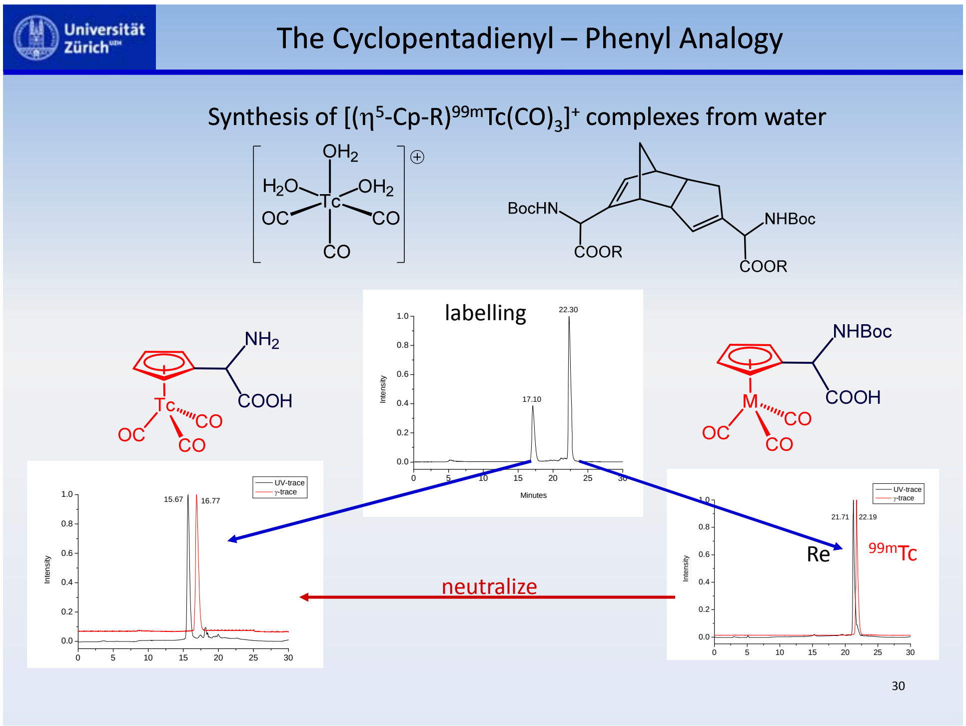
The Cyclopentadienyl – Phenyl Analogy

Synthesis of $[(\eta^5\text{-Cp-R})^{99m}Tc(CO)_3]^+$ complexes from water

in situ *Boc* deprotection

29

D. Can et al,. *Organometallics*, **2012**, *31*, 6880



The Cyclopentadienyl – Phenyl Analogy

Synthesis of $[(\eta^5\text{-Cp-R})^{99m}Tc(CO)_3]^+$ complexes from water

labelling

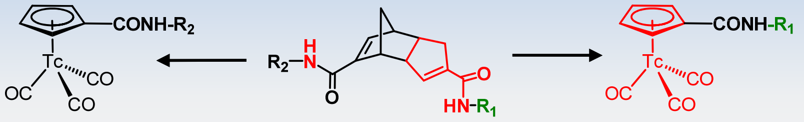
neutralize

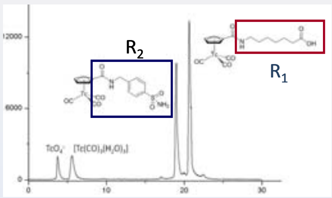
30

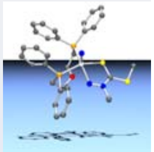
The Cyclopentadienyl – Phenyl Analogy

Synthesis of $[(\eta^5\text{-Cp-R})^{99m}Tc(CO)_3]^+$ complexes from water

Which is the labeling site?



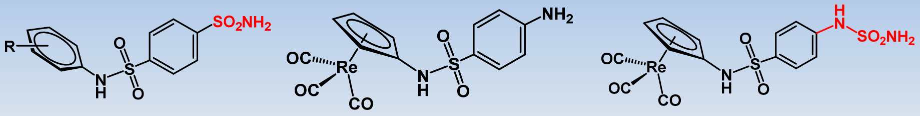




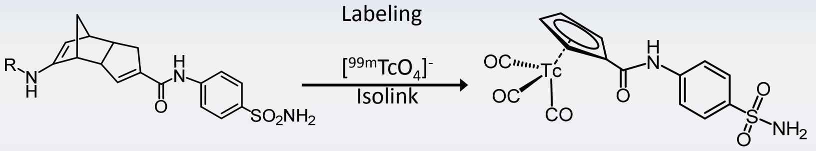
Two radiopharmaceuticals
from one single precursor !

D. Can et all, *Chem. Biodivers.* **2012**, *9*, 1849

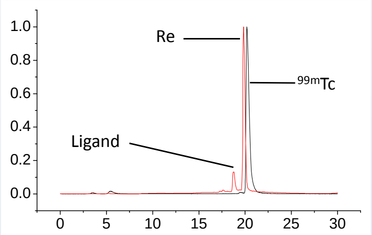
Carbonic Anhydrase (CA) Inhibitors

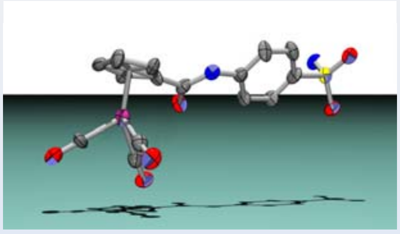


Labeling

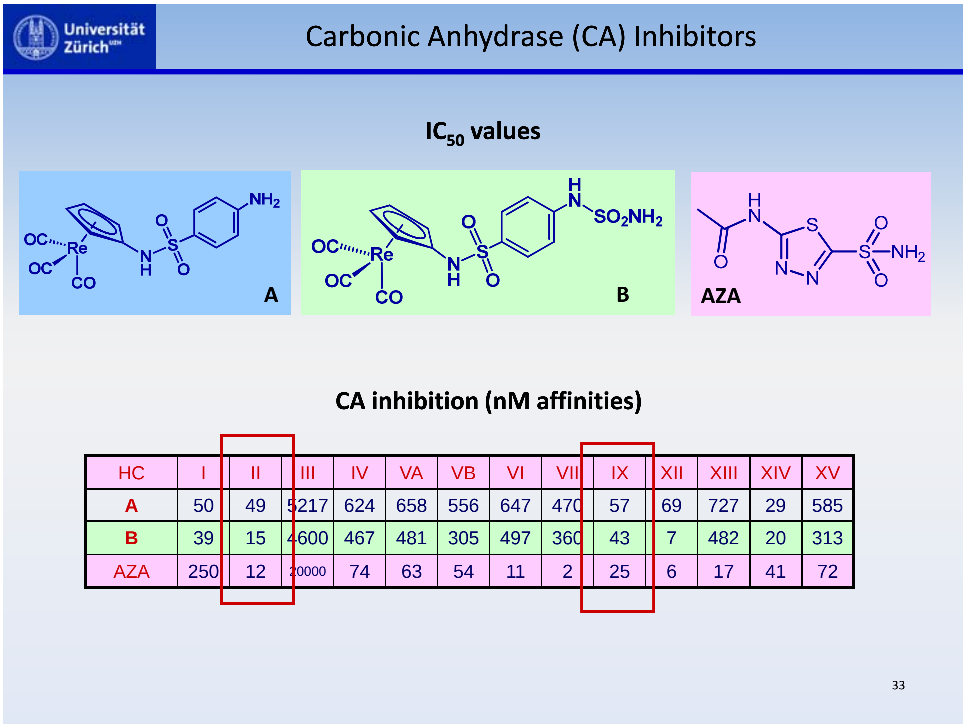


$[^{99m}TcO_4]^-$
Isolink





C. Supuran, *Nature*, **2008**, *7*, 168-181

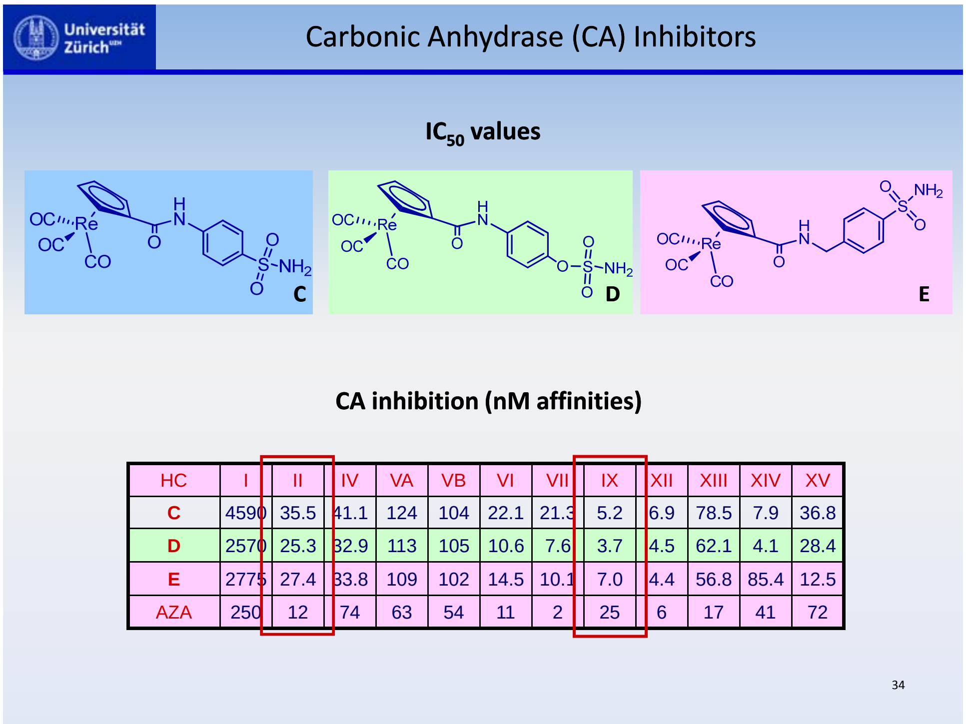


Carbonic Anhydrase (CA) Inhibitors

IC_{50} values

CA inhibition (nM affinities)

HC	I	II	III	IV	VA	VB	VI	VII	IX	XII	XIII	XIV	XV
A	50	49	5217	624	658	556	647	470	57	69	727	29	585
B	39	15	4600	467	481	305	497	360	43	7	482	20	313
AZA	250	12	20000	74	63	54	11	2	25	6	17	41	72

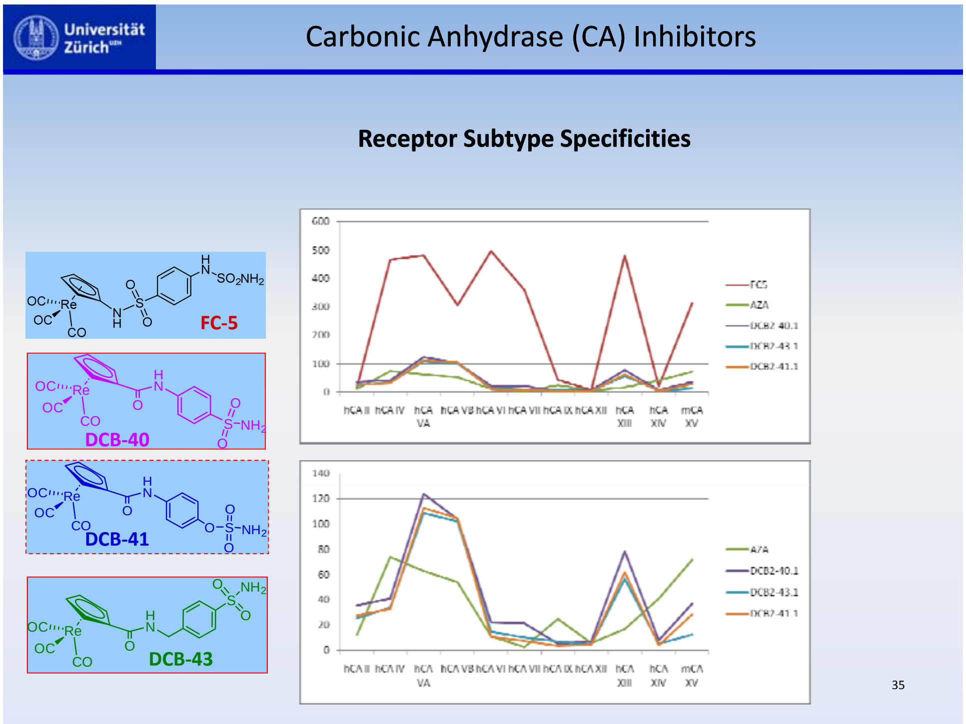


Carbonic Anhydrase (CA) Inhibitors

IC_{50} values

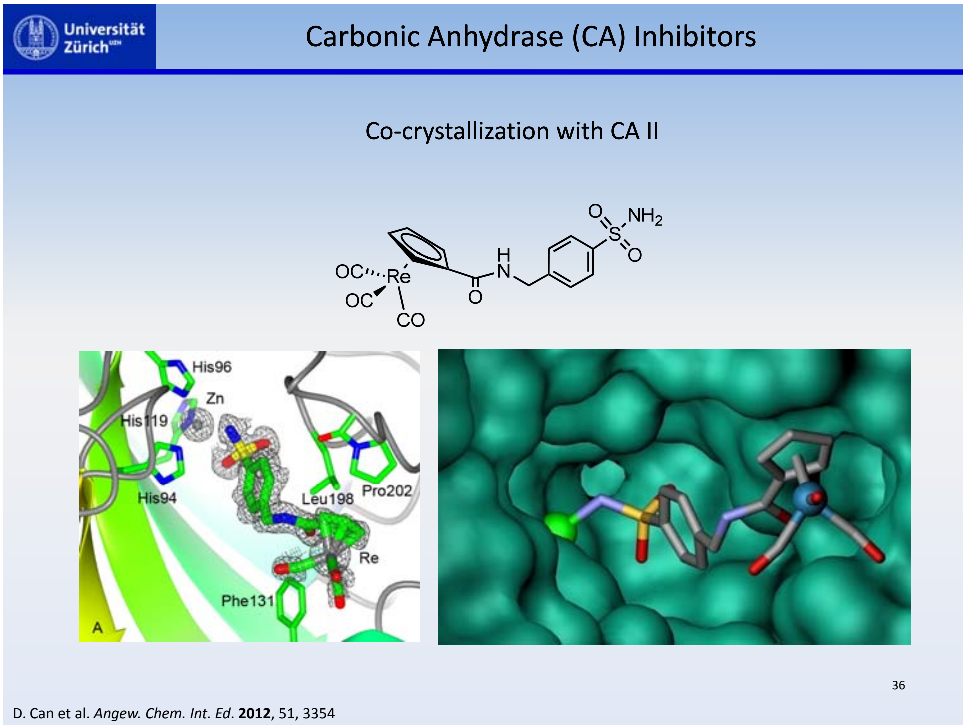
CA inhibition (nM affinities)

HC	I	II	IV	VA	VB	VI	VII	IX	XII	XIII	XIV	XV
C	4590	35.5	41.1	124	104	22.1	21.3	5.2	6.9	78.5	7.9	36.8
D	2570	25.3	32.9	113	105	10.6	7.6	3.7	4.5	62.1	4.1	28.4
E	2775	27.4	33.8	109	102	14.5	10.1	7.0	4.4	56.8	85.4	12.5
AZA	250	12	74	63	54	11	2	25	6	17	41	72



Carbonic Anhydrase (CA) Inhibitors

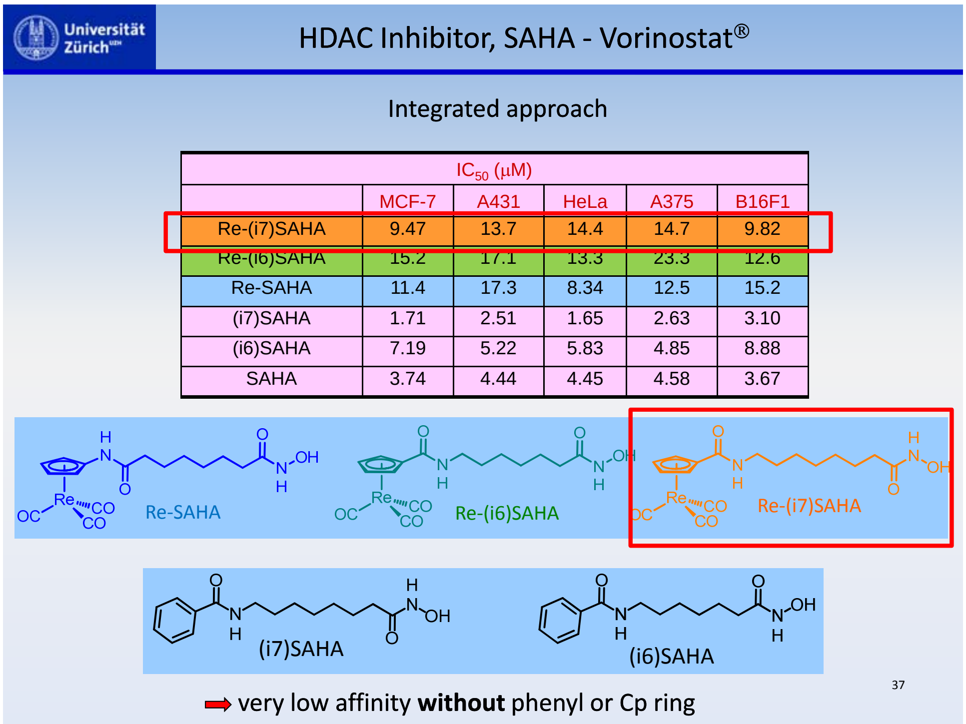
Receptor Subtype Specificities



Carbonic Anhydrase (CA) Inhibitors

Co-crystallization with CA II

D. Can et al. *Angew. Chem. Int. Ed.* **2012**, 51, 3354



HDAC Inhibitor, SAHA - Vorinostat®

Integrated approach

IC$_{50}$ (μM)					
	MCF-7	A431	HeLa	A375	B16F1
Re-(i7)SAHA	9.47	13.7	14.4	14.7	9.82
Re-(i6)SAHA	15.2	17.1	13.3	23.3	12.6
Re-SAHA	11.4	17.3	8.34	12.5	15.2
(i7)SAHA	1.71	2.51	1.65	2.63	3.10
(i6)SAHA	7.19	5.22	5.83	4.85	8.88
SAHA	3.74	4.44	4.45	4.58	3.67

Re-SAHA

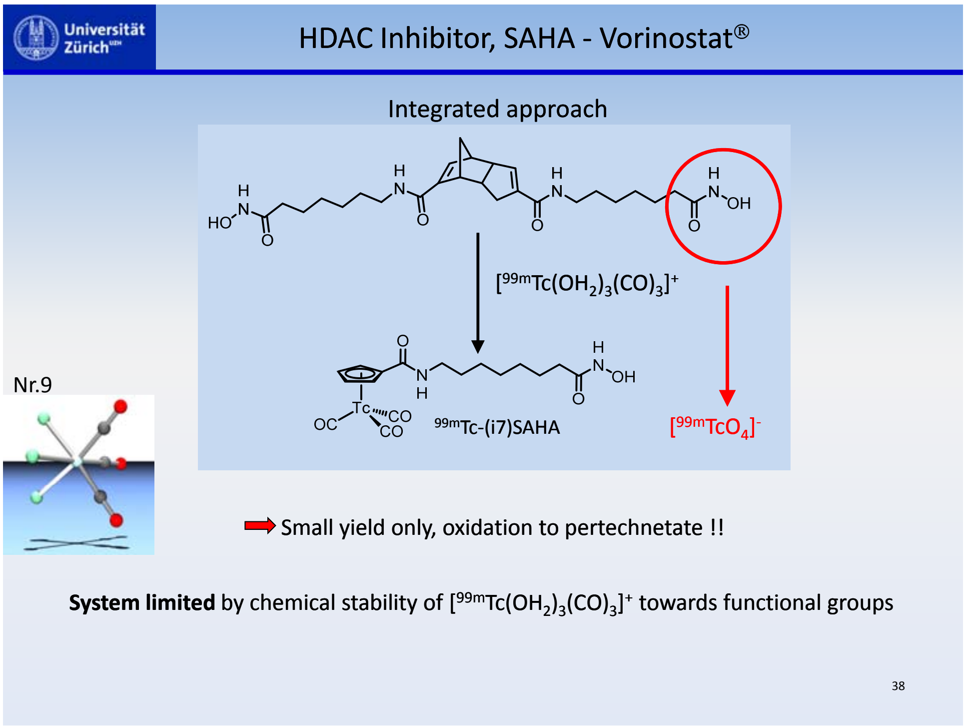
Re-(i6)SAHA

Re-(i7)SAHA

(i7)SAHA

(i6)SAHA

➡ very low affinity **without** phenyl or Cp ring



HDAC Inhibitor, SAHA - Vorinostat®

Integrated approach

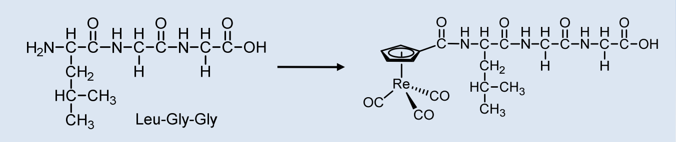
➡ Small yield only, oxidation to pertechnetate !!

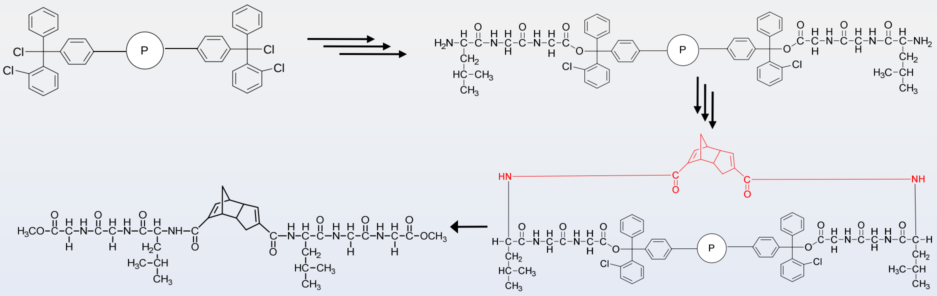
System limited by chemical stability of $[^{99m}Tc(OH_2)_3(CO)_3]^+$ towards functional groups

Cyclopentadienyl - Peptides

Pendent vs integrated approach

Peptide Transporter 2 (PEP2) inhibitors: small tripeptides

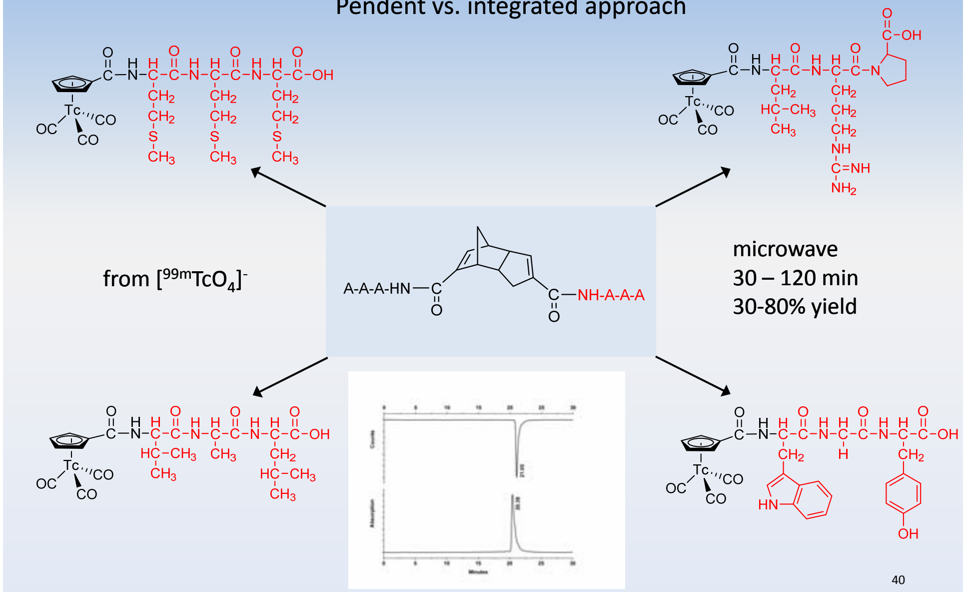




Q. Nadeem et al., *Org. & Biomol. Chem.*, **2014**, *12*, 1966; Y. Liu et al., *Bioconjugate Chem.*, **2013**, *24*, 26

Cyclopentadienyl - Peptides

Pendent vs. integrated approach

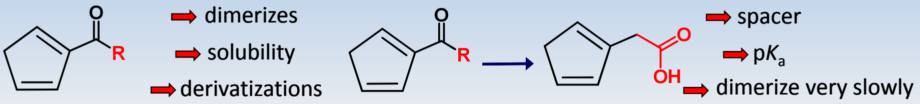


from [$^{99m}TcO_4$]$^-$

microwave
30 – 120 min
30-80% yield

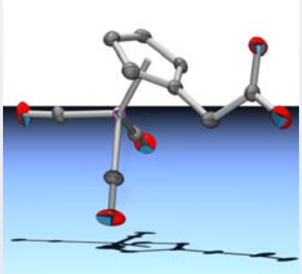
Functionalized Cp-Derivatives

Extending the cyclopentadienyl scaffold

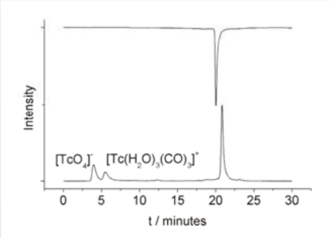


- dimerizes
- solubility
- derivatizations

- spacer
- p*K*$_a$
- dimerize very slowly



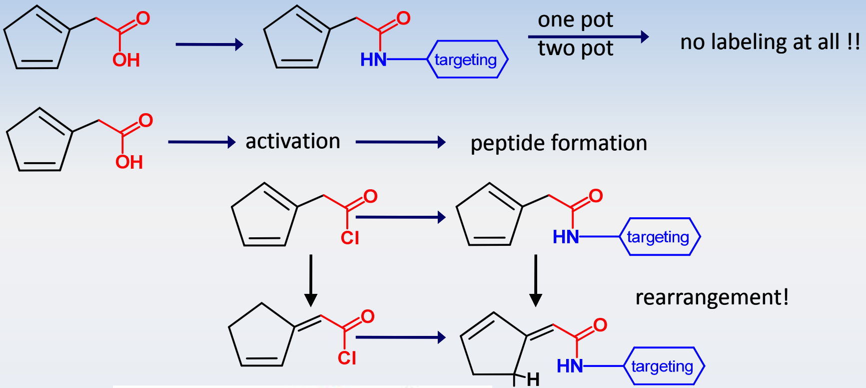
Labeling, 30 min 60°C



faster, more efficient than „C0“

Functionalized Cp-Derivatives

Introducing a targeting function



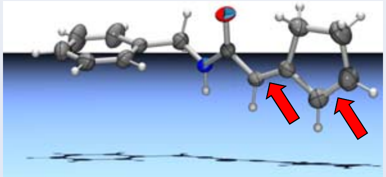
one pot
two pot

no labeling at all !!

activation

peptide formation

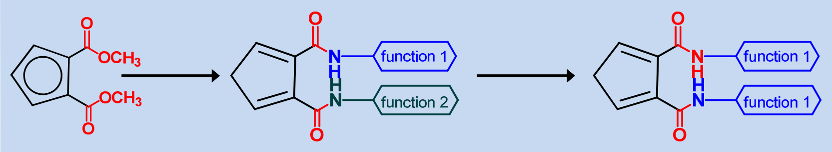
rearrangement!



Functionalized Cp-Derivatives

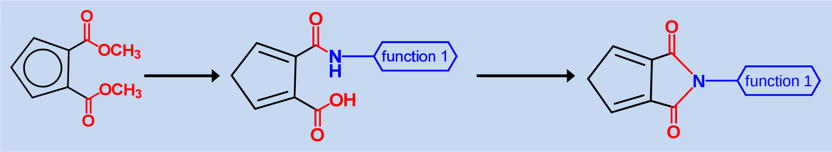
Introducing a second functionality

➡ Pharmaceutically active lead structures often comprise an **integrated** and not a terminal phenyl group



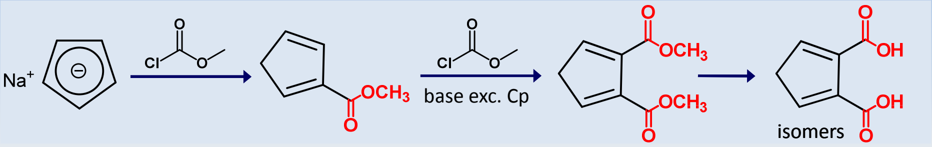
➡ two different functions can be conjugated via the metal complex..

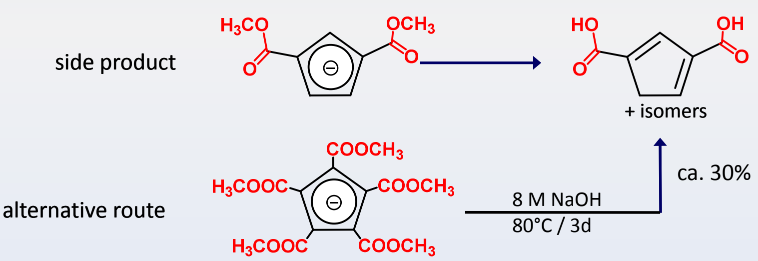
.. or only a single one in different modalities

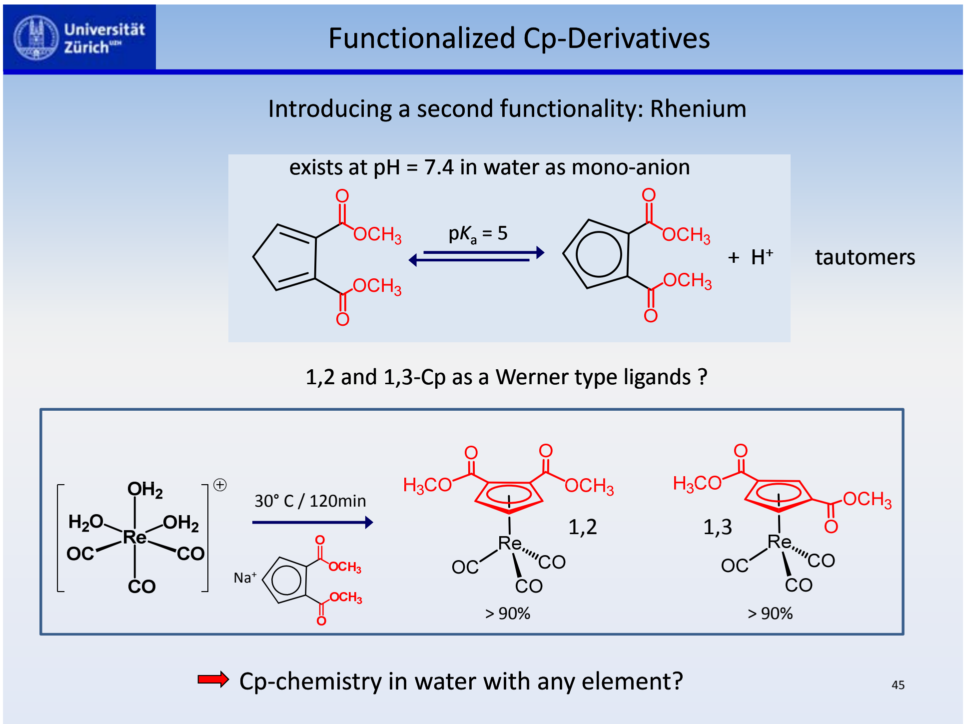


Functionalized Cp-Derivatives

Introducing a second functionality







Functionalized Cp-Derivatives

Introducing a second functionality: Rhenium

exists at pH = 7.4 in water as mono-anion

$pK_a = 5$

+ H^+

tautomers

1,2 and 1,3-Cp as a Werner type ligands ?

30° C / 120min

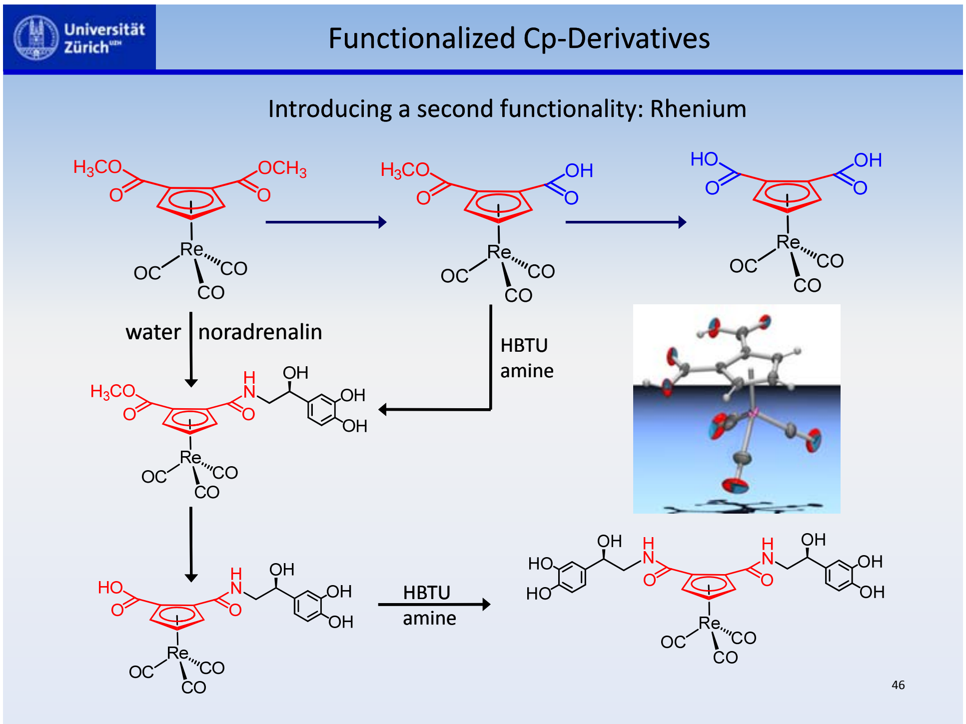
1,2

1,3

> 90%

> 90%

Cp-chemistry in water with any element?



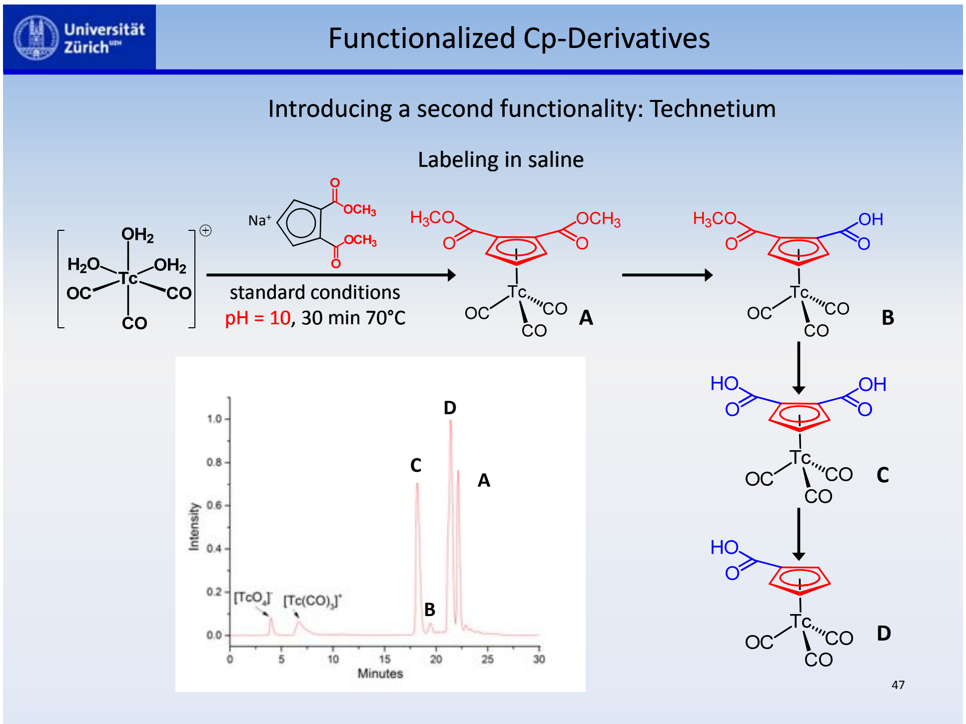
Functionalized Cp-Derivatives

Introducing a second functionality: Rhenium

water | noradrenalin

HBTU
amine

HBTU
amine



Universität Zürich

Functionalized Cp-Derivatives

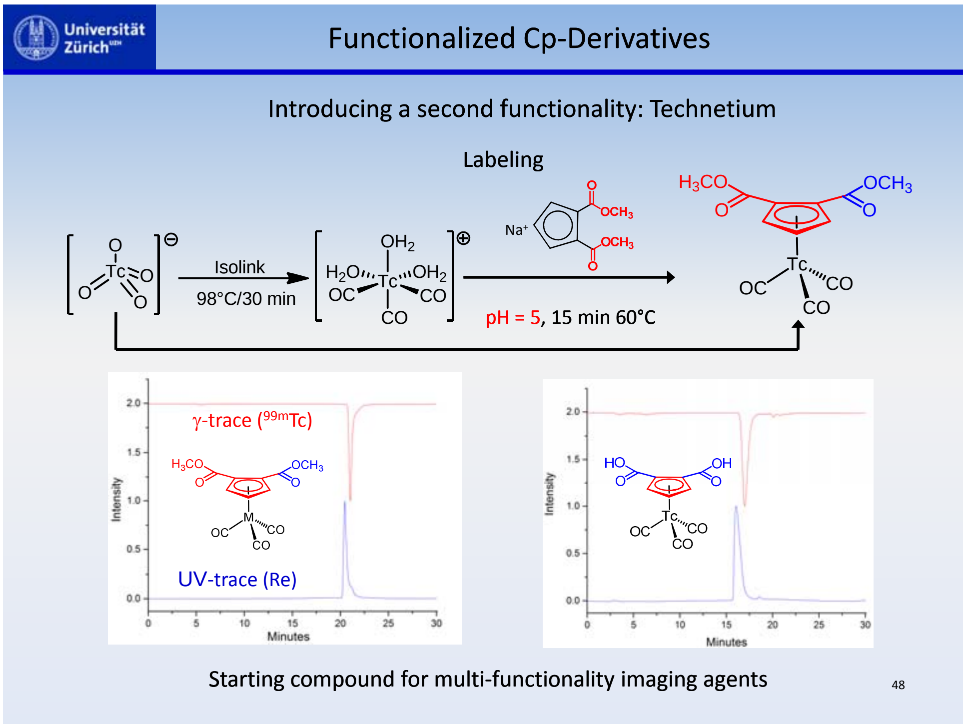
Introducing a second functionality: Technetium

Labeling in saline

standard conditions

pH = 10, 30 min 70°C

47



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Functionalized Cp-Derivatives

Introducing a second functionality: Technetium

Labeling

Isolink

98°C/30 min

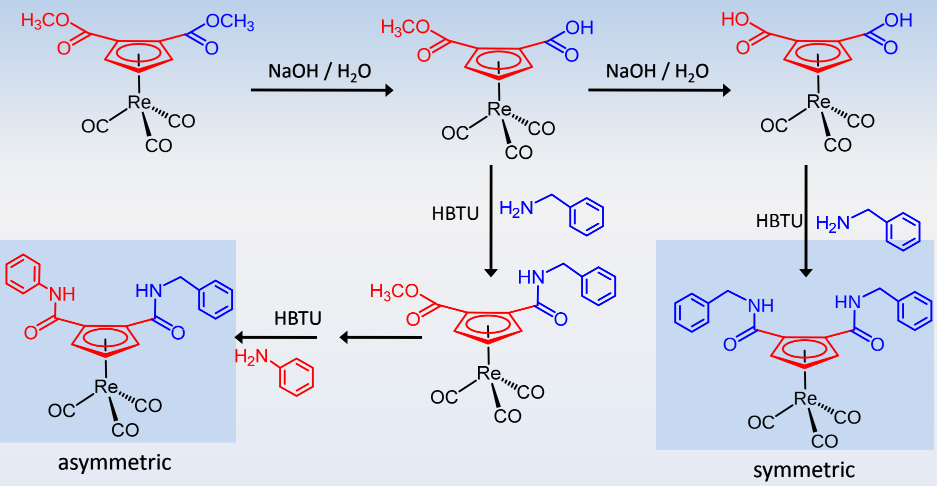
pH = 5, 15 min 60°C

Starting compound for multi-functionality imaging agents

48

Functionalized Cp-Derivatives

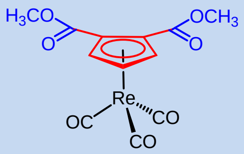
Rhenium: stepwise introduction of bio-functions

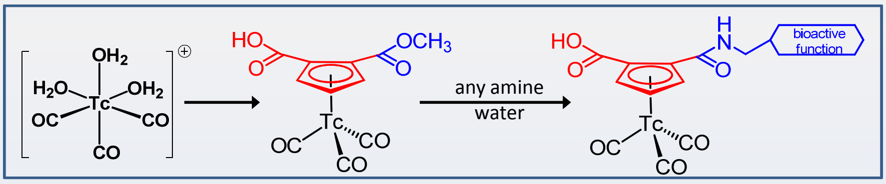


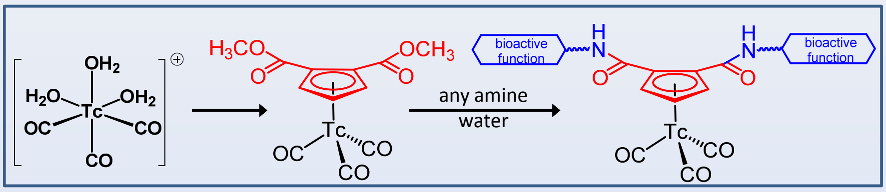
Functionalized Cp-Derivatives

Technetium: direct labeling with amines in water

Building block
for mono and homo di-functionalized complexes



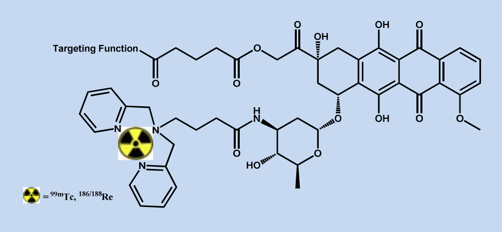




Targeting the Nucleus

Nuclear Targeting with Auger Emitters

Doxorubicin, a nucleus targeting, fluorescent molecule



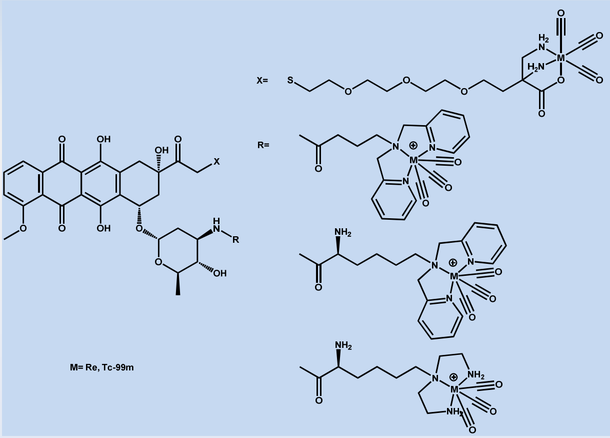
Nucleus Targeting Bifunctional Tc-99m Complexes
Bioconjugate Chem., **2011**, *22*, 958.

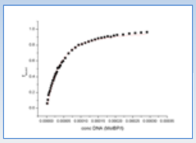
Radiotoxic Doxorubicin Tc-99m Conjugates
Imstepf *et al.* in preparation

Targeting the Nucleus

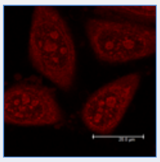
Nuclear Targeting with Auger Emitters

A systematic approach: Synthesis, Properties and *in vitro* Profil

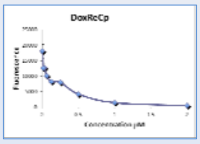


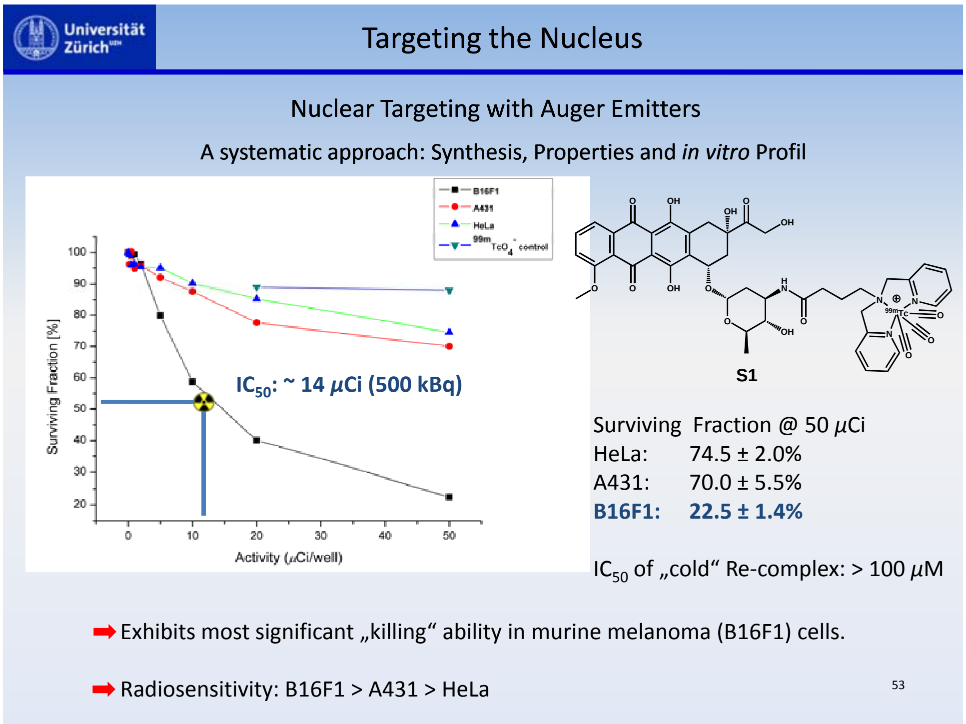


**ctDNA Titration:
DNA Binding**



**IC$_{50}$:
Cytotoxicity**





Targeting the Nucleus

Nuclear Targeting with Auger Emitters

A systematic approach: Synthesis, Properties and *in vitro* Profil

IC_{50}: ~ 14 µCi (500 kBq)

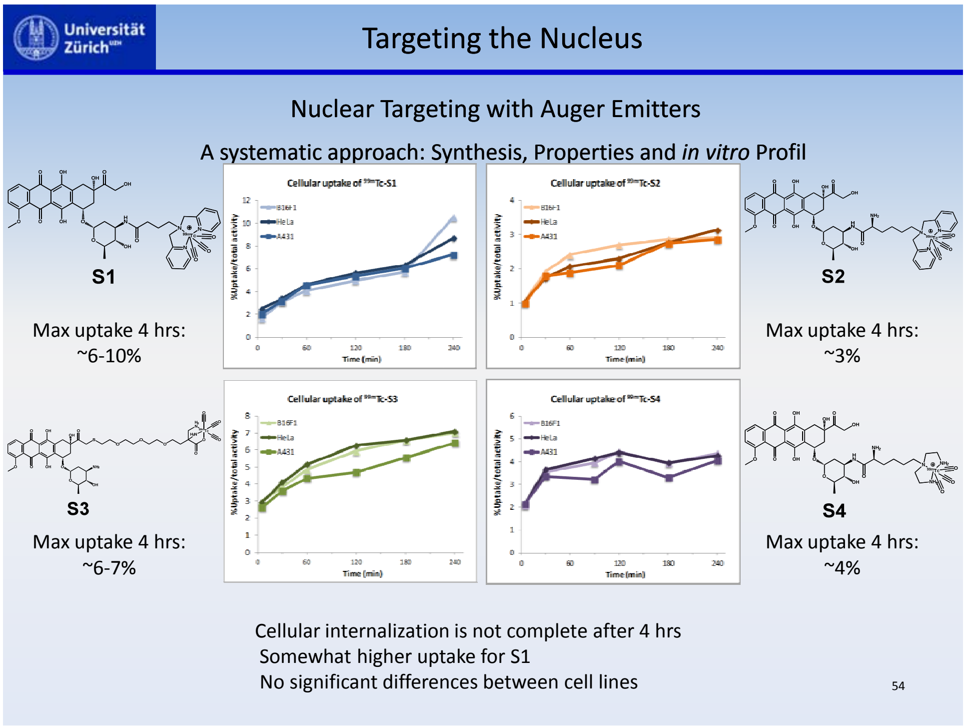
S1

Surviving Fraction @ 50 µCi
HeLa: 74.5 ± 2.0%
A431: 70.0 ± 5.5%
B16F1: 22.5 ± 1.4%

IC_{50} of „cold" Re-complex: > 100 µM

➡ Exhibits most significant „killing" ability in murine melanoma (B16F1) cells.

➡ Radiosensitivity: B16F1 > A431 > HeLa



Targeting the Nucleus

Nuclear Targeting with Auger Emitters

A systematic approach: Synthesis, Properties and *in vitro* Profil

S1

Max uptake 4 hrs:
~6-10%

S2

Max uptake 4 hrs:
~3%

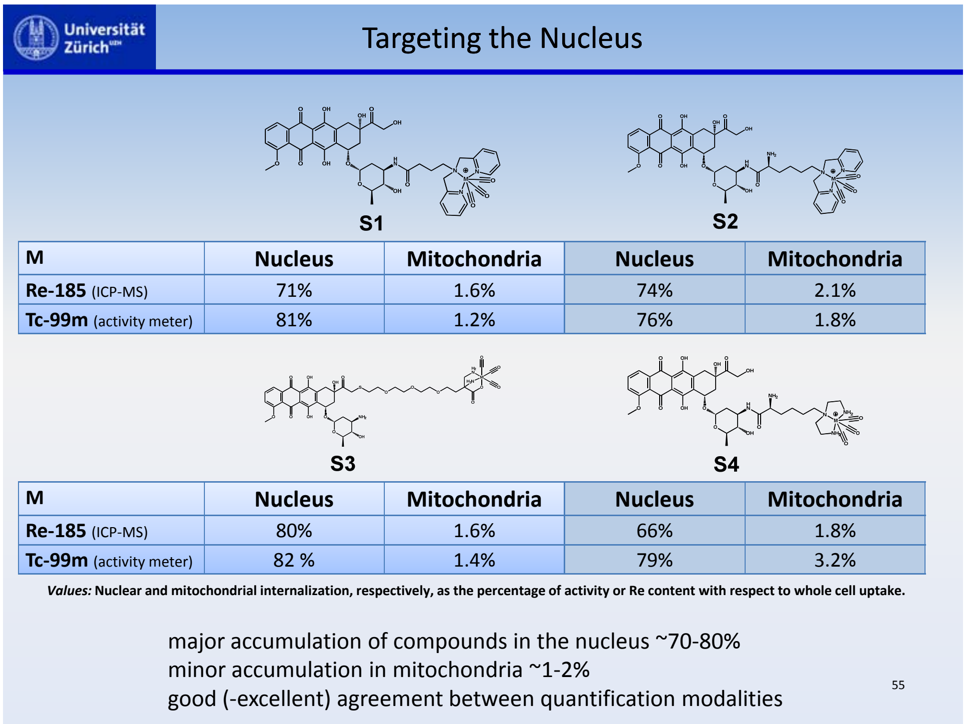
S3

Max uptake 4 hrs:
~6-7%

S4

Max uptake 4 hrs:
~4%

Cellular internalization is not complete after 4 hrs
Somewhat higher uptake for S1
No significant differences between cell lines



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Targeting the Nucleus

S1

S2

M	Nucleus	Mitochondria	Nucleus	Mitochondria
Re-185 (ICP-MS)	71%	1.6%	74%	2.1%
Tc-99m (activity meter)	81%	1.2%	76%	1.8%

S3

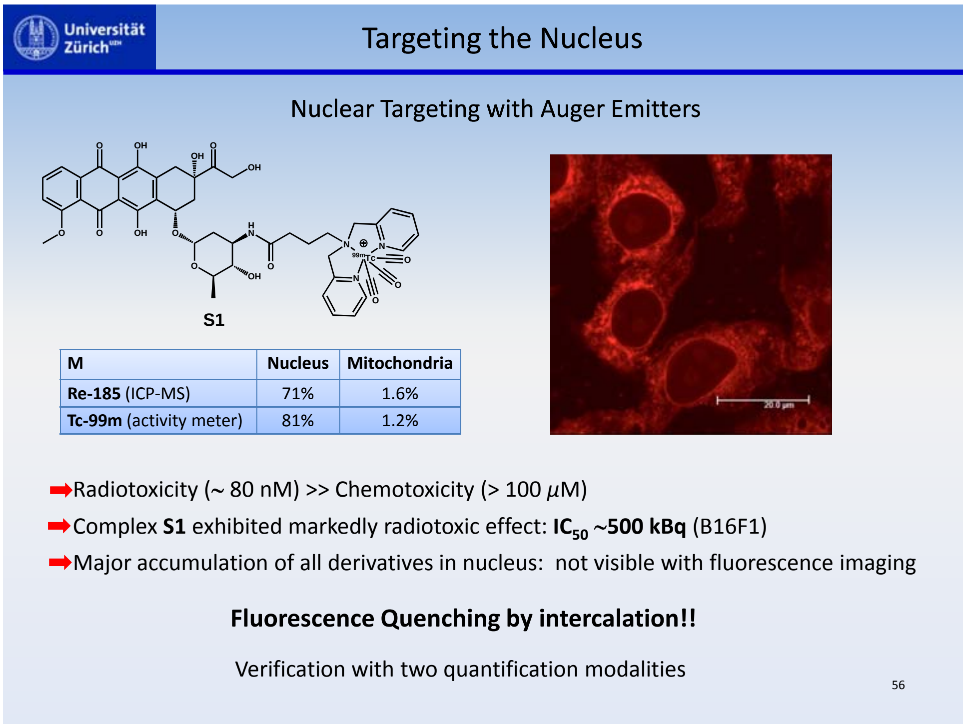
S4

M	Nucleus	Mitochondria	Nucleus	Mitochondria
Re-185 (ICP-MS)	80%	1.6%	66%	1.8%
Tc-99m (activity meter)	82 %	1.4%	79%	3.2%

Values: **Nuclear and mitochondrial internalization, respectively, as the percentage of activity or Re content with respect to whole cell uptake.**

major accumulation of compounds in the nucleus ~70-80%
minor accumulation in mitochondria ~1-2%
good (-excellent) agreement between quantification modalities

---



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Targeting the Nucleus

Nuclear Targeting with Auger Emitters

S1

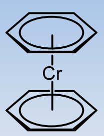
M	Nucleus	Mitochondria
Re-185 (ICP-MS)	71%	1.6%
Tc-99m (activity meter)	81%	1.2%

- ➡Radiotoxicity (~ 80 nM) >> Chemotoxicity (> 100 µM)
- ➡Complex **S1** exhibited markedly radiotoxic effect: **IC$_{50}$ ~500 kBq** (B16F1)
- ➡Major accumulation of all derivatives in nucleus: not visible with fluorescence imaging

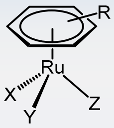
Fluorescence Quenching by intercalation!!

Verification with two quantification modalities

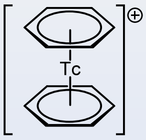
From Cyclopentadienyl to Arenes



- ➡ Chromocene: Fischer-Hafner Synthesis
- ➡ attractive since it contains “Phenyls”
- ➡ arenes can be substituted
- ➡ arenes are activated



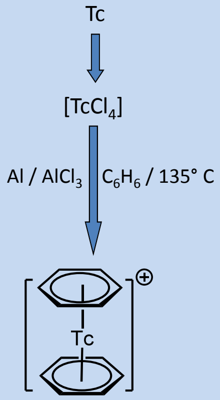
- ➡ metal-centred activity (Dyson, Sadler et al.)
- ➡ arene ring tends to be lost
- ➡ introduction of functionalities
- ➡ Multi-variations at metal (X,Y,Z)



- ➡ Synthesized by E.O. Fischer et al. from ^{99}Mo
- ➡ Chemistry essentially not investigated
- ➡ Source for higher oxidation states
- ➡ Precursor for labeling
- ➡ Rhenium analogues

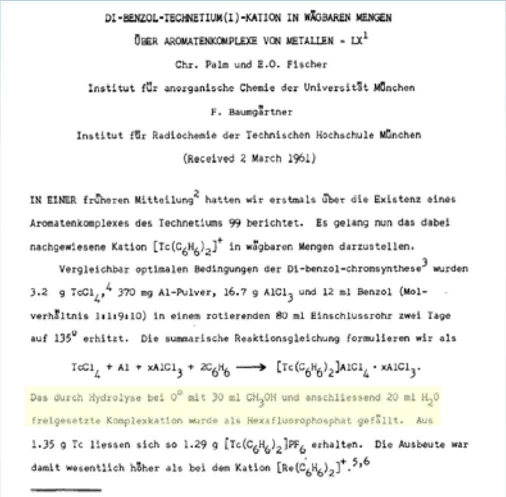
F. Baumgärtner et al. Tetrahedron Lett. **1962**, 6, 253; Chem. Ber. **1961**, 94, 2198

Missed Opportunities (Terachem 2010)



it is water stable

Fischer E.O. et al. Tetrahedron Lett., **1962**



DI-BENZOL-TECHNETIUM(I)-KATION IN WÄGBAREN MENGEN

ÜBER AROMATENKOMPLEXE VON METALLEN - LX[1]

Chr. Palm und E.O. Fischer

Institut für anorganische Chemie der Universität München

F. Baumgärtner

Institut für Radiochemie der Technischen Hochschule München

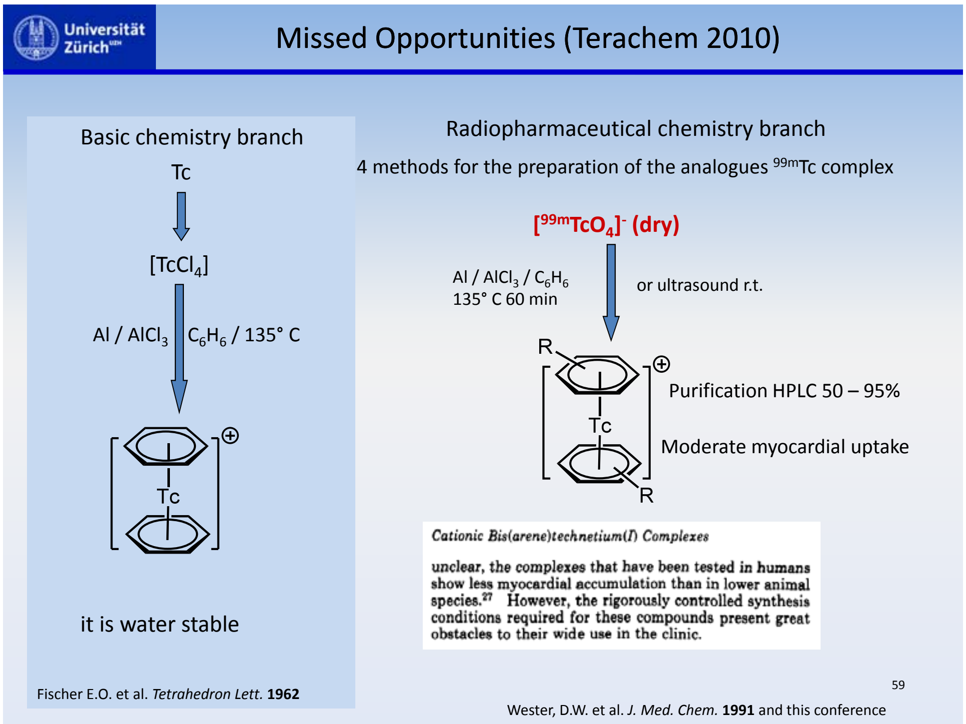
(Received 2 March 1961)

IN EINER früheren Mitteilung[2] hatten wir erstmals über die Existenz eines Aromatenkomplexes des Technetiums 99 berichtet. Es gelang nun das dabei nachgewiesene Kation $[Tc(C_6H_6)_2]^+$ in wägbaren Mengen darzustellen.

Vergleichbar optimalen Bedingungen der Di-benzol-chromsynthese[3] wurden 3.2 g $TcCl_4$,[4] 370 mg Al-Pulver, 16.7 g $AlCl_3$ und 12 ml Benzol (Molverhältnis 1:1:9:10) in einem rotierenden 80 ml Einschlussrohr zwei Tage auf 135° erhitzt. Die summarische Reaktionsgleichung formulieren wir als

$$TcCl_4 + Al + xAlCl_3 + 2C_6H_6 \longrightarrow [Tc(C_6H_6)_2]AlCl_4 \cdot xAlCl_3.$$

Das durch Hydrolyse bei 0° mit 30 ml CH_3OH und anschliessend 20 ml H_2O freigesetzte Komplexkation wurde als Hexafluorophosphat gefällt. Aus 1.35 g Tc liessen sich so 1.29 g $[Tc(C_6H_6)_2]PF_6$ erhalten. Die Ausbeute war damit wesentlich höher als bei dem Kation $[Re(C_6H_6)_2]^+$.[5,6]



Missed Opportunities (Terachem 2010)

Basic chemistry branch

Tc

$[TcCl_4]$

$Al / AlCl_3$ C_6H_6 / 135° C

it is water stable

Fischer E.O. et al. *Tetrahedron Lett.* **1962**

Radiopharmaceutical chemistry branch

4 methods for the preparation of the analogues ^{99m}Tc complex

$[^{99m}TcO_4]^-$ (dry)

$Al / AlCl_3 / C_6H_6$
135° C 60 min

or ultrasound r.t.

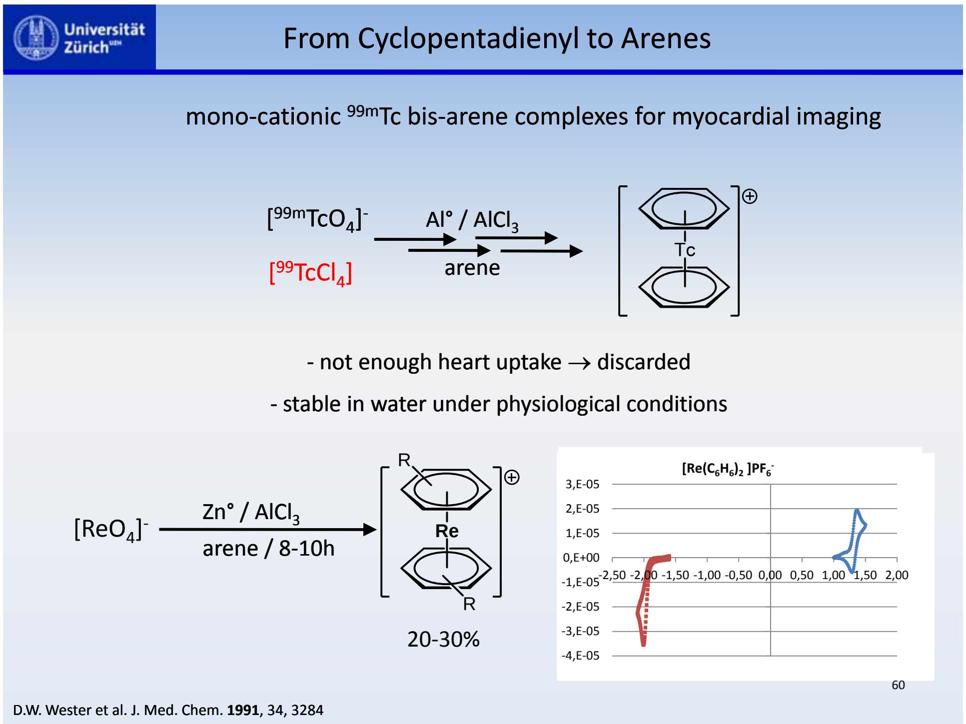
Purification HPLC 50 – 95%

Moderate myocardial uptake

Cationic Bis(arene)technetium(I) Complexes

unclear, the complexes that have been tested in humans show less myocardial accumulation than in lower animal species.[27] However, the rigorously controlled synthesis conditions required for these compounds present great obstacles to their wide use in the clinic.

Wester, D.W. et al. *J. Med. Chem.* **1991** and this conference



From Cyclopentadienyl to Arenes

mono-cationic ^{99m}Tc bis-arene complexes for myocardial imaging

$[^{99m}TcO_4]^-$
$[^{99}TcCl_4]$

Al° / $AlCl_3$
arene

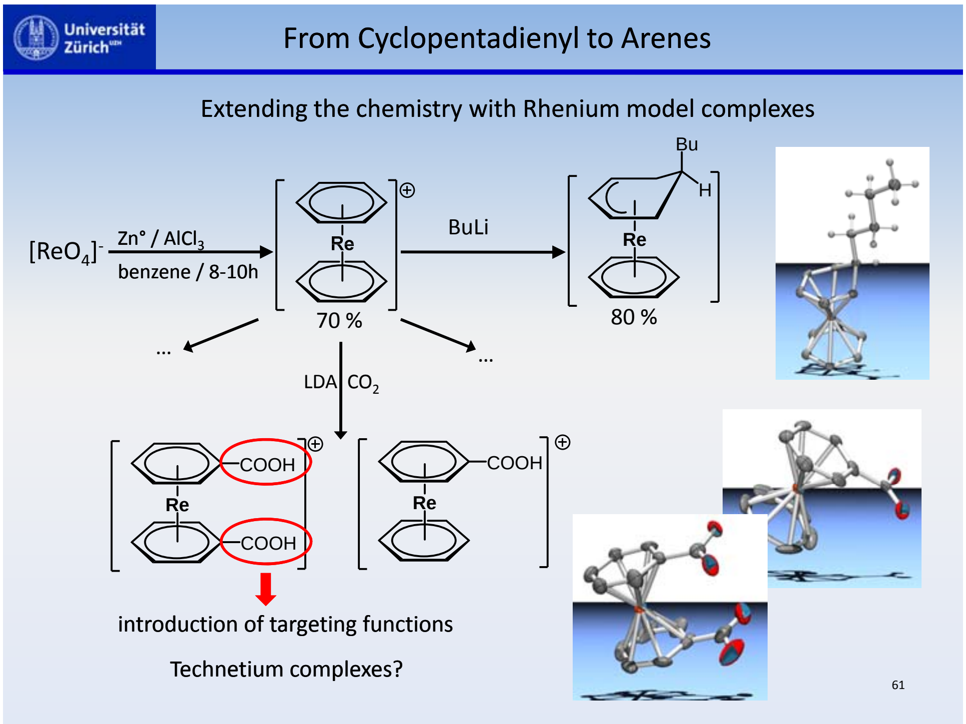
- not enough heart uptake → discarded

- stable in water under physiological conditions

$[ReO_4]^-$ $\xrightarrow[\text{arene / 8-10h}]{\text{Zn° / AlCl}_3}$

20-30%

D.W. Wester et al. J. Med. Chem. **1991**, 34, 3284



From Cyclopentadienyl to Arenes

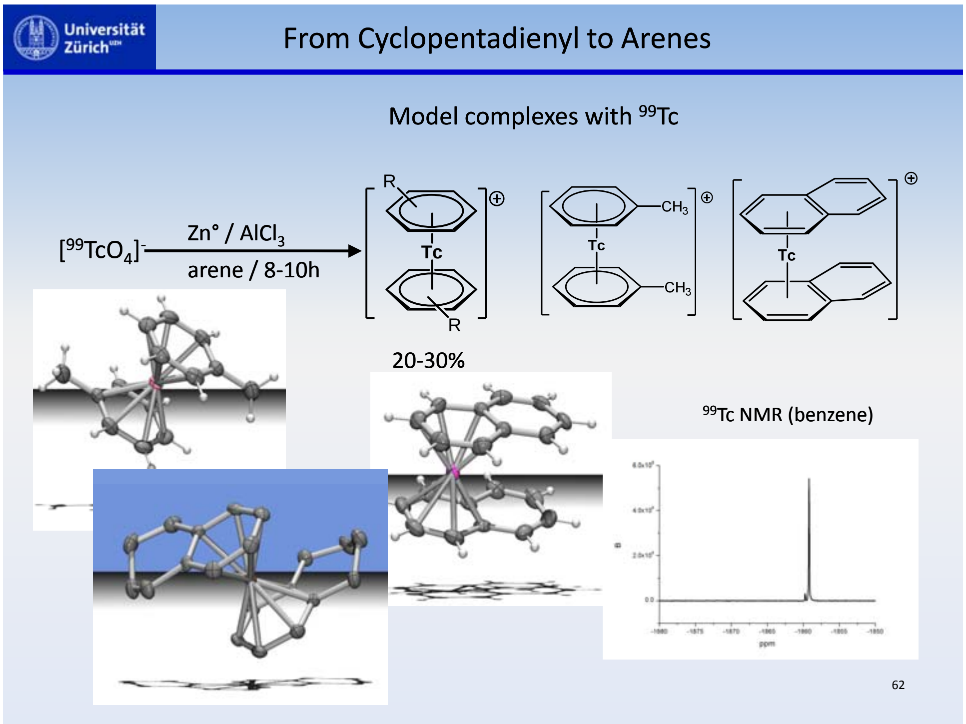
Extending the chemistry with Rhenium model complexes

$[ReO_4]^- \xrightarrow[\text{benzene / 8-10h}]{Zn° / AlCl_3}$ 70 % $\xrightarrow{BuLi}$ 80 %

LDA CO_2

introduction of targeting functions

Technetium complexes?



From Cyclopentadienyl to Arenes

Model complexes with ^{99}Tc

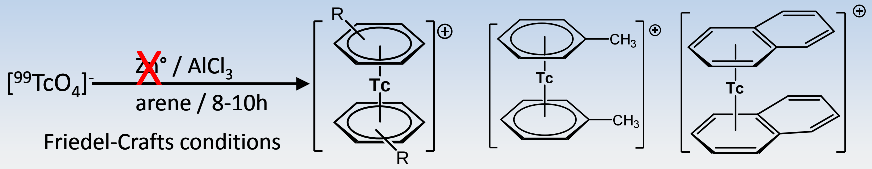
$[^{99}TcO_4]^- \xrightarrow[\text{arene / 8-10h}]{Zn° / AlCl_3}$

20-30%

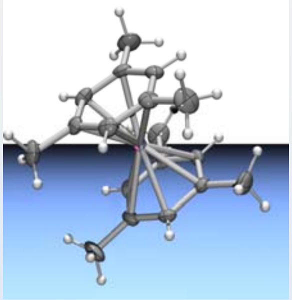
^{99}Tc NMR (benzene)

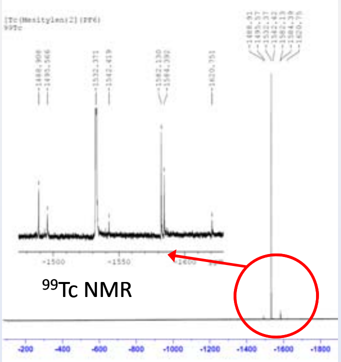
From Cyclopentadienyl to Arenes

Model complexes with ^{99}Tc


$[^{99}TcO_4]^-$ ~~Zn°~~ / $AlCl_3$ arene / 8-10h

Friedel-Crafts conditions

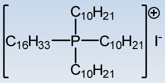


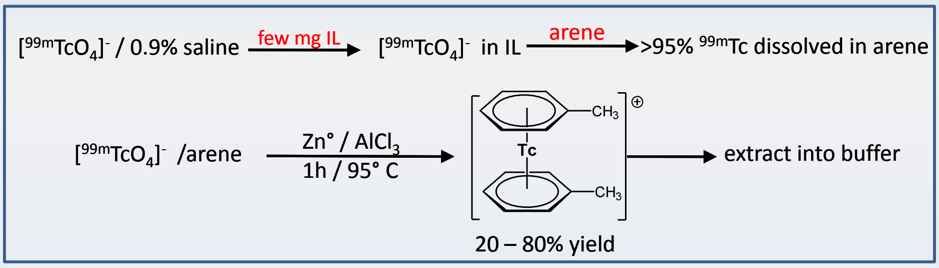

^{99}Tc NMR

From Cyclopentadienyl to Arenes

From ^{99}Tc to ^{99m}Tc

$Na[^{99m}TcO_4]$ in saline (0.9% NaCl): How to transfer into arenes ?

IL 
$$\left[C_{16}H_{33}-P(C_{10}H_{21})_3\right]^{\oplus} I^-$$


$[^{99m}TcO_4]^-$ / 0.9% saline $\xrightarrow{\text{few mg IL}}$ $[^{99m}TcO_4]^-$ in IL $\xrightarrow{\text{arene}}$ >95% ^{99m}Tc dissolved in arene

$[^{99m}TcO_4]^-$ /arene $\xrightarrow[\text{1h / 95° C}]{Zn° / AlCl_3}$ → extract into buffer

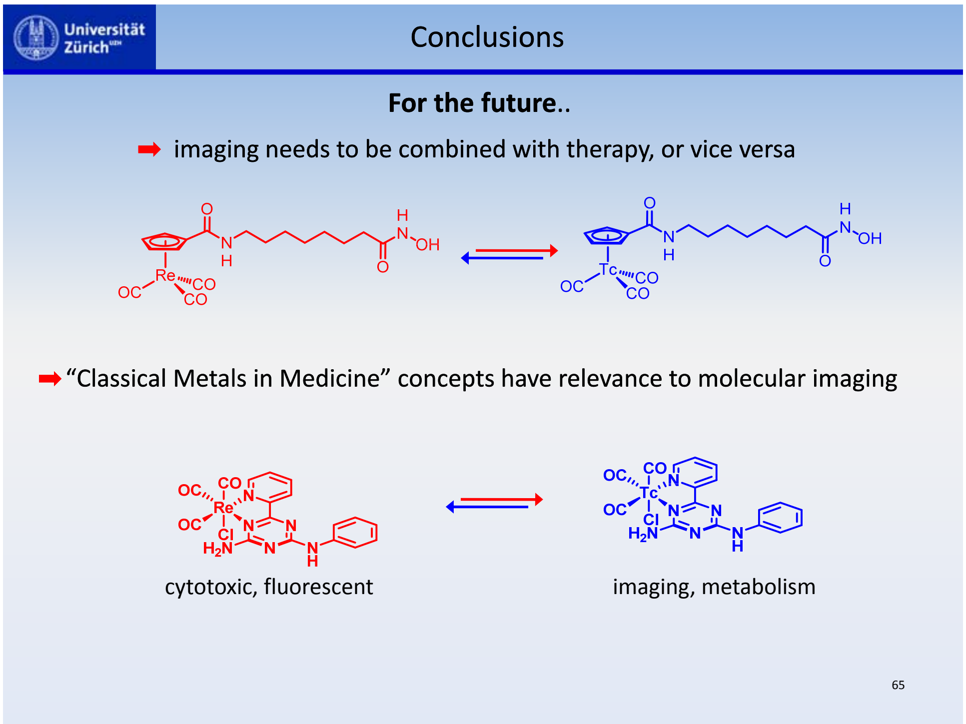
20 – 80% yield

- stable from pH = 2 – 12 at 37°C

- not air sensitive at all

⇨ arene complexes are an option for molecular imaging !

H. Braband et al. *Chem. Sci.* **2014**, in press



Conclusions

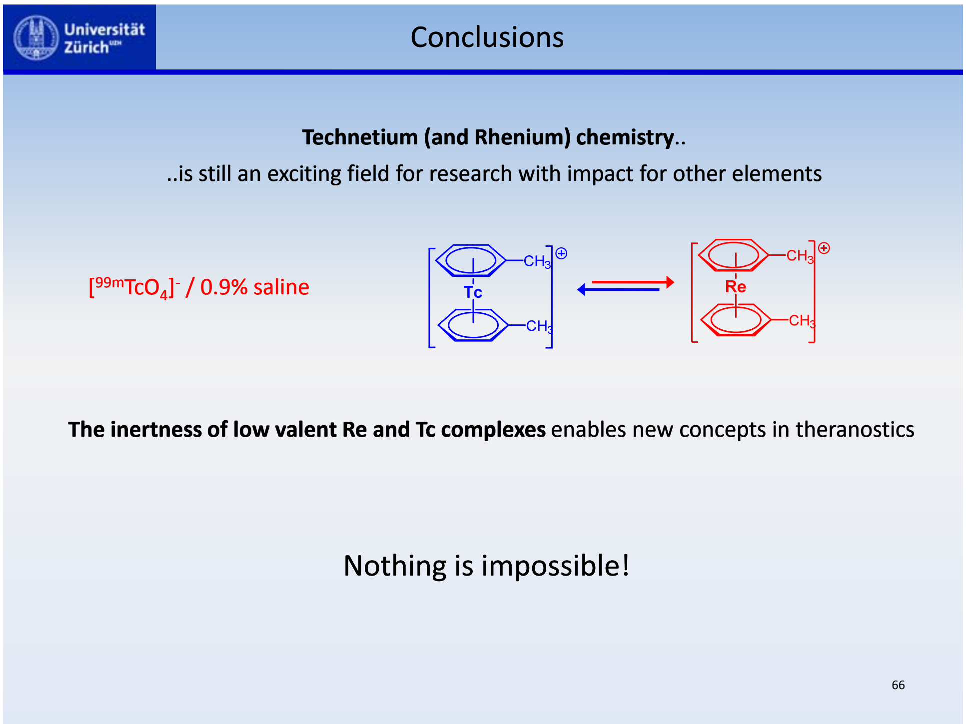
For the future..

- imaging needs to be combined with therapy, or vice versa

- “Classical Metals in Medicine” concepts have relevance to molecular imaging

cytotoxic, fluorescent

imaging, metabolism



Conclusions

Technetium (and Rhenium) chemistry..
..is still an exciting field for research with impact for other elements

$[^{99m}TcO_4]^-$ / 0.9% saline

The inertness of low valent Re and Tc complexes enables new concepts in theranostics

Nothing is impossible!

Universität Zürich

Acknowledgments

$^{99(m)}$Tc Chemistry

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Confederazione Svizzera
Confederaziun svizra
Bildung und Forschung SBF

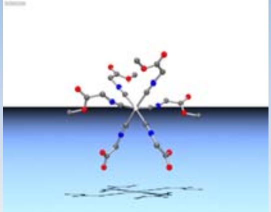
cost
EUROPEAN COOPERATION IN SCIENCE AND TECHNOLOGY

FNSNF
SWISS NATIONAL SCIENCE FOUNDATION
SSAJRP JRP-01

COVIDIEN
positive results for life

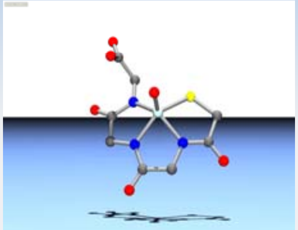
Progenics Pharmaceuticals

Solutions to Problems



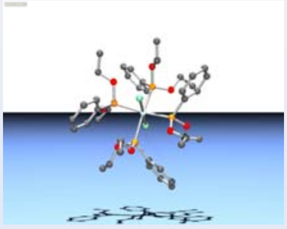
Nr. 1

B.Noll, P.Leibnitz, H.Spies, Forschungszent Rossendorf(Ber.) **1999**, 270, 153



Nr. 2

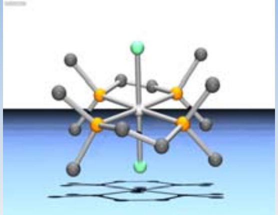
N.Bryson, J.Lister-James, A.G.Jones, W.M.Davis, A.Davison, *Inorg.Chem*. **1990**, 29, 2948.



Nr.3

U.Mazzi, D.A.Clemente, G.Bandoli, L.Magon, A.A.Orio, *Inorg.Chem*. **1977**, 16, 1042.

Solutions to Problems

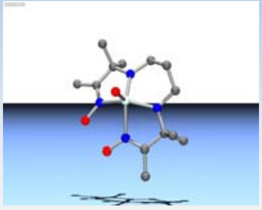


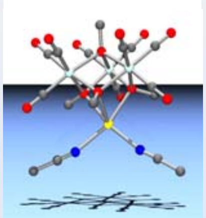
Nr. 4

J.-L.Vanderheyden, A.R.Ketring, K.Libson, M.J.Heeg, L.Roecker, P.Motz, R.Whittle, R.C.Elder, E.Deutsch, *Inorg.Chem*. **1984**, 23, 3184.

C.K.Fair, D.E.Troutner, E.O.Schlemper, R.K.Murmann, M.L.Hoppe, *Acta Crystallogr.,Sect.C:Cryst.Struct.Commun*. **1984**, 40, 1544.

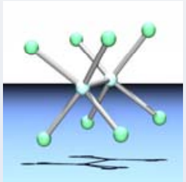
Nr.5





Nr. 6

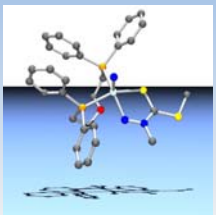
W.A.Herrmann, R.Alberto, J.C.Bryan, A.P.Sattelberger, *Chem.Ber*. **1991**, 124, 1107.



Nr.7

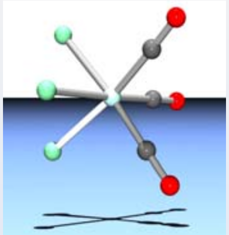
F.A.Cotton, L.Daniels, A.Davison, C.Orvig, *Inorg.Chem*. **1981**, 20, 3051.
F.Poineau, E.V.Johnstone, P.M.Forster, Longzou Ma, A.P.Sattelberger, K.R.Czerwinski, *Inorg.Chem*. **2012**, 51, 9563.

Solutions to Problems



Nr. 8

C.Bolzati, A.Boschi, L.Uccelli, F.Tisato, F.Refosco, A.Cagnolini, A.Duatti, S.Prakash, G.Bandoli, A.Vittadini, *JACS*, **2002**, 124, 11468



Nr. 9

R.Alberto, R.Schibli, D.Angst, P.A.Schubiger, U.Abram, S.Abram, T.A.Kaden, *Trans. Met. Chem.* **1997**, 22, 597

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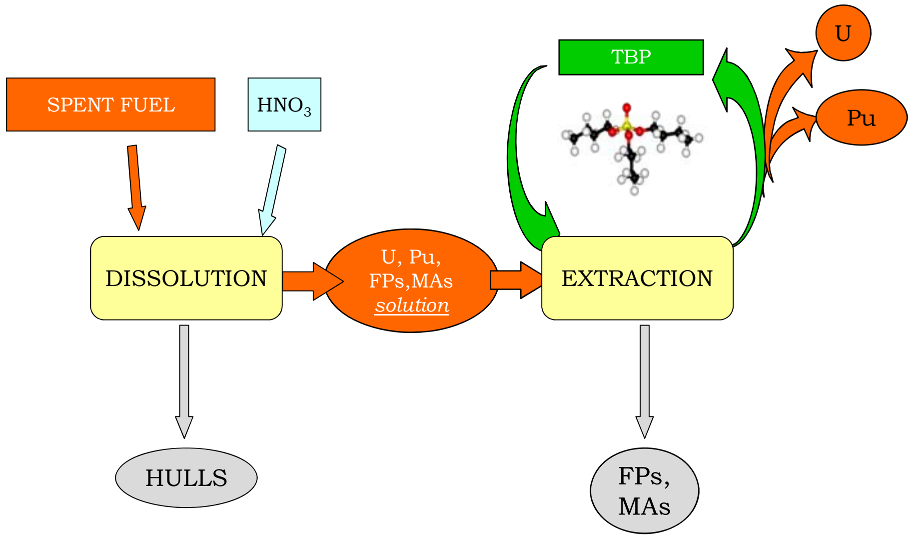
TECHNETIUM BEHAVIOR IN THE PUREX PROCESS

Pascal BARON
Current Fuel Cycle Back-End Program
CEA, Nuclear Energy Division

ISTR 2014 – 8th INTERNATIONAL SYMPOSIUM ON TECHNETIUM AND RHENIUM
29th SEPTEMBER – 3rd OCTOBER 2014, Pornichet LABAULE FRANCE

THE PUREX PROCESS



SPENT FUEL

HNO_3

DISSOLUTION

U, Pu, FPs,MAs *solution*

EXTRACTION

TBP

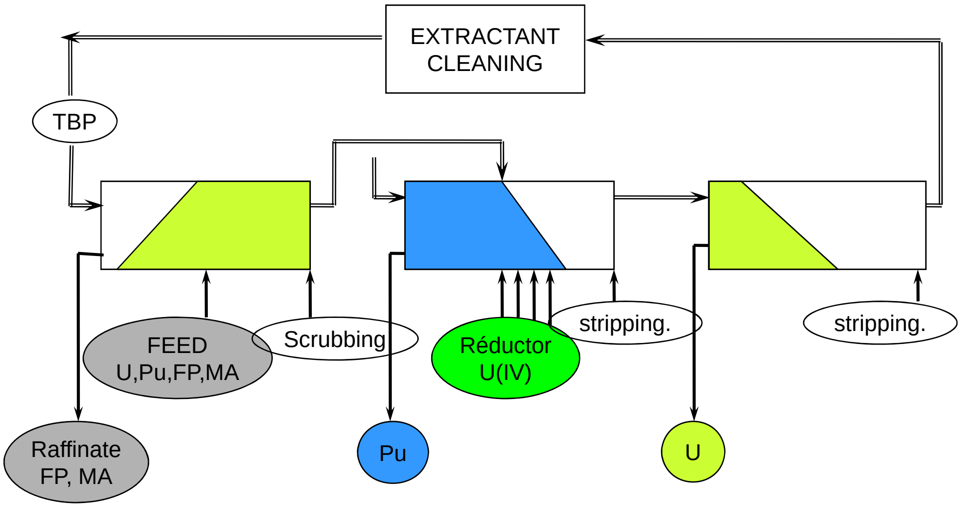
U

Pu

HULLS

FPs, MAs

1ST CYCLE U-Pu WITH U/Pu PARTITIONING


EXTRACTANT CLEANING
TBP
FEED U,Pu,FP,MA
Scrubbing
Réductor U(IV)
stripping.
stripping.
Raffinate FP, MA
Pu
U

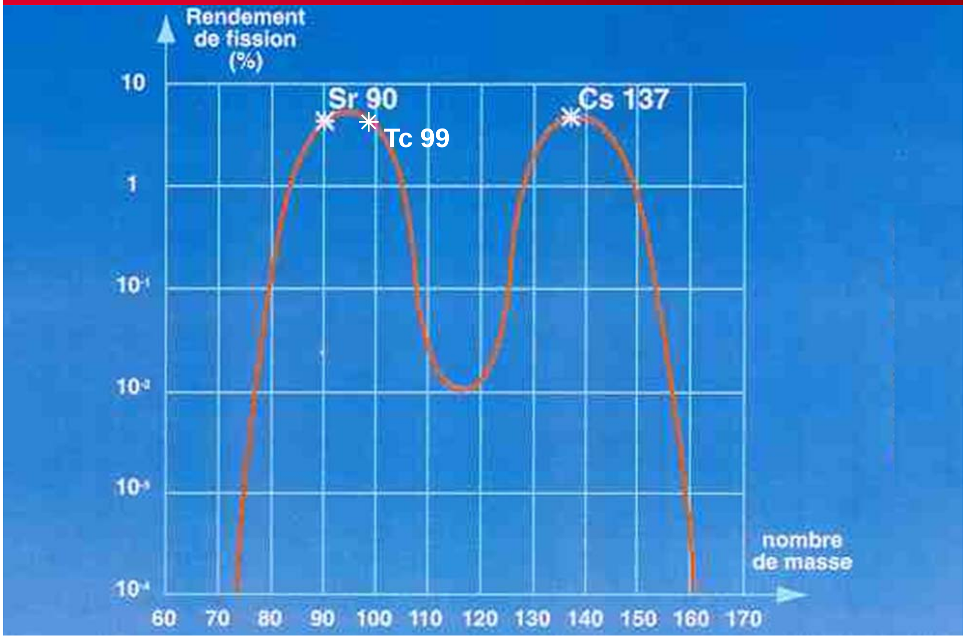
INTRODUCTION

Tc is just one FP among many others

YES, BUT:

- Tc production yield in reactor is high
- on the contrary than most of the others, Tc is able to be extracted by TBP (multiple mechanisms)
- Tc can have deleterious impact on U/Pu REDOX chemistry in the PUREX process (multiple oxydation state)

FISSION PRODUCTS YIELD



INTRODUCTION

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TECHNETIUM BEHAVIOR IN THE DISSOLUTION STEP

AMOUNT:

- About 1kg / ton (burn up dependent)
- not cooling-time dependent (^{99}Tc , half-life= 2,1.10^{5}years),

SPECIES

- TcO_2 and « poly métallic »compounds
  (*undissolved species*)
- TcO_4^- in the dissolution solution

DISSOLUTION YIELD

- Fuel type dependent at lab scale:
  UOX ~ 90 %, MOX ~ 60 %, SFR ~ 20 %
- Lower yield at industrial scale (rotating dissolver):
  ~50% for UOX and MOX

TECHNETIUM EXTRACTION BY TBP

SIMPLIFIED EXTRACTION MECHANISMS

$$H^+ + TcO_4^- + 3TBP \Leftrightarrow [HTcO_4,3TBP]$$

$$[UO_2(NO_3)_2,2TBP] + TcO_4^- \Leftrightarrow [UO_2(TcO_4)(NO_3),2TBP] + NO_3^-$$

$$[Pu(NO_3)_4,2TBP] + TcO_4^- \Leftrightarrow [Pu(TcO_4)(NO_3)_3,2TBP] + NO_3^-$$

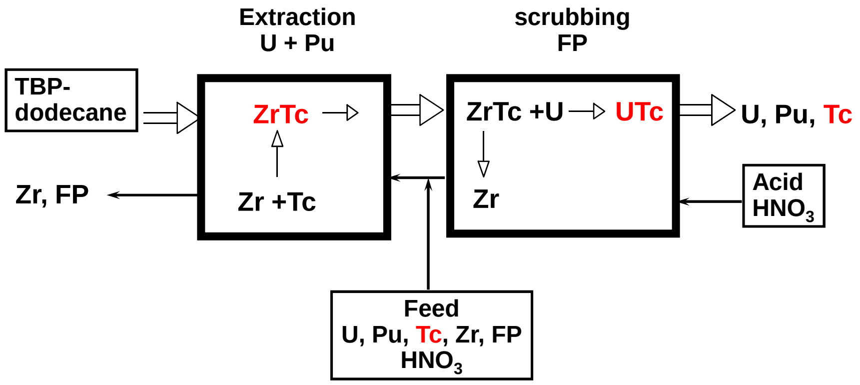
$$[Zr(NO_3)_4,2TBP] + TcO_4^- \Leftrightarrow [Zr(TcO_4)(NO_3)_3,2TBP] + NO_3^-$$

Co-extraction:

–Higher for Zr >> Pu > U

– Reduced at high [NO_3^-] (competition)

TECHNETIUM BEHAVIOR IN EXTRACTION STEP



TECHNETIUM BEHAVIOR IN EXTRACTION STEP
OPTIONS TO LIMIT THE IMPACT

CHEMICAL ADJUSTMENT

Introduction of Zr complexing agent: carboxylic acids

- Oxalic acid (forgiven / Pu leakage risk)
- Other acids (ex.: KMA)

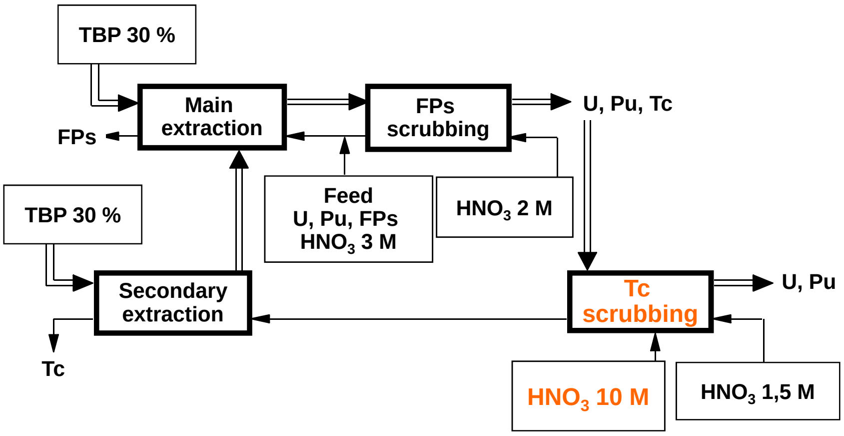
➡ NOT READY FOR UP3

OPERATING ADJUSTMENT / TOPOLOGY

- Adjunction of a complementary operation the "Tc scrubbing"
- (allow separate management of Tc / others FPs)

➡ SOLUTION CHOOSEN FOR UP3 AND UP2-800

TECHNETIUM BEHAVIOR IN EXTRACTION STEP



TBP 30 %

Main extraction

FPs scrubbing

U, Pu, Tc

FPs

TBP 30 %

Feed
U, Pu, FPs
HNO_3 3 M

HNO_3 2 M

Secondary extraction

Tc scrubbing

U, Pu

Tc

HNO_3 10 M

HNO_3 1,5 M

TECHNETIUM SCRUBBING FOR LA HAGUE

PRINCIPLES:

- Zr scrubbing at first step
- Tc back extraction (high acidity)

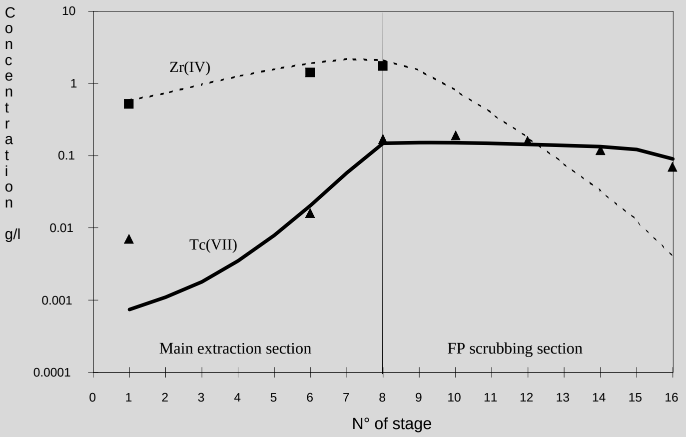
DESIGN CONSTRAINT (1985, active start of UP3 1989)

Minimization of the impact on upstream/downstream steps (mainly acid effluents)

OPTIMISATION USING PAREX CODE:

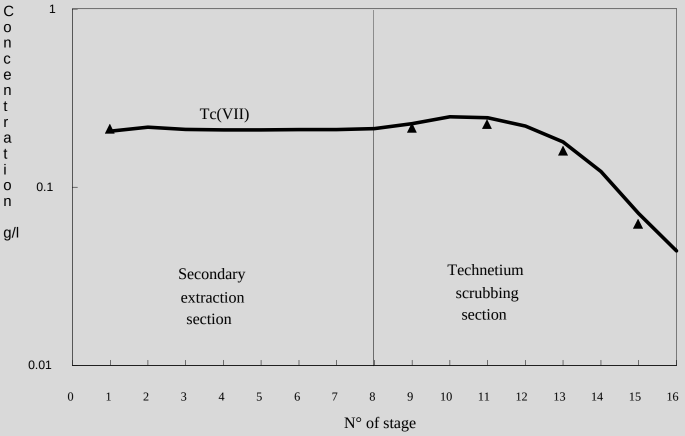
➔ DF Tc = 2,8 UP3 (1989)
(validated at lab scale on genuine solution and confirmed by UP3)

Today DF > 30 routinely performed at UP2800 and UP3



Aqueous technetium profile: experimental (▲), calculated (▬)

Aqueous zirconium profile: experimental (■), calculated (⋯⋯)



Profils technétium aqueux: experimental (▲), calculé (▬)

U/Pu SPLITTING STEP

« FUNCTIONAL » REACTION : Pu(IV) Reduction

$$U^{4+} + 2Pu^{4+} + 2H_2O \longrightarrow UO_2^{2+} + 2Pu^{3+} + 4H^+$$

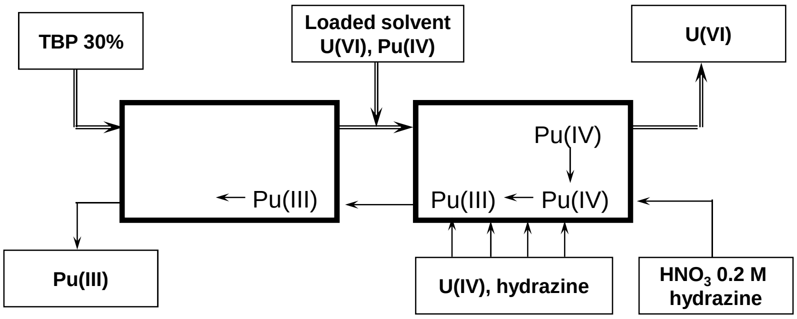
« PARASISTIC »REACTION : Pu(III) Oxydation

$$Pu^{3+} + HNO_2 + H^+ + 0{,}5HNO_3 \longrightarrow Pu^{4+} + 0{,}5H_2O + 1{,}5HNO_2$$

« USEFULL » or « STABILIZING » REACTION : HNO_2 Destruction

$$N_2H_5NO_3 + HNO_2 \longrightarrow HN_3 + HNO_3 + 2H_2O$$

U/Pu SPLITTING STEP



TBP 30%

Loaded solvent U(VI), Pu(IV)

U(VI)

Pu(IV)

Pu(III) ← Pu(IV)

← Pu(III)

Pu(III)

U(IV), hydrazine

HNO_3 0.2 M hydrazine

TECHNETIUM BEHAVIOR IN URANIUM/PLUTONIUM SPLITTING STEP

SIMPLIFIED REDOX MECHANISM

$$\mathrm{Tc(VII)} + w\mathrm{U}^{4+} + \ldots \rightarrow \mathrm{Tc}_{\mathrm{ox}} + w\mathrm{UO}_2^{2+} + \ldots \quad \text{(very fast)}$$

$$\mathrm{Tc}_{\mathrm{ox}} + x\mathrm{N}_2\mathrm{H}_5^{+} + \ldots \rightarrow \mathrm{Tc}_{\mathrm{red}} + \ldots \quad \text{(fast)}$$

$$\mathrm{Tc}_{\mathrm{ox}} + y\mathrm{U}^{4+} + \ldots \rightarrow \mathrm{Tc}_{\mathrm{red}} + y\mathrm{UO}_2^{2+} + \ldots \quad \text{(very fast)}$$

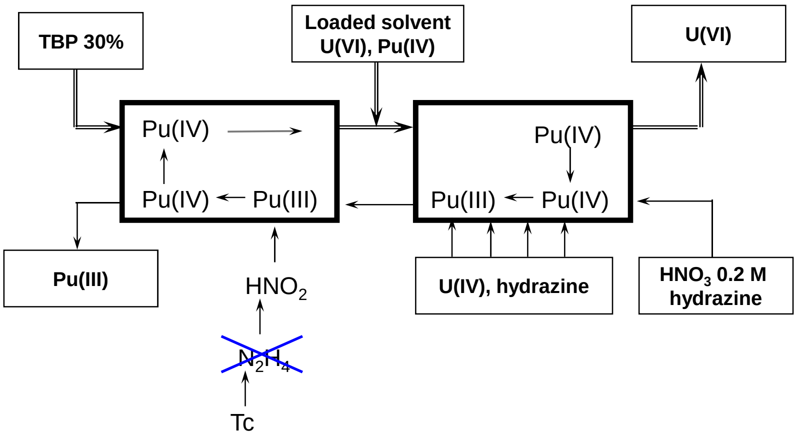
$$\mathrm{Tc}_{\mathrm{red}} + z\mathrm{HNO}_3 + \ldots \rightarrow \mathrm{Tc}_{\mathrm{ox}} + z\mathrm{HNO}_2 + \ldots \quad \text{(limiting reaction)}$$

where Tc_{ox} is for Tc(V) and/or Tc(VI)
Tc_{red} is for Tc(IV) (ou Tc(III) ?)

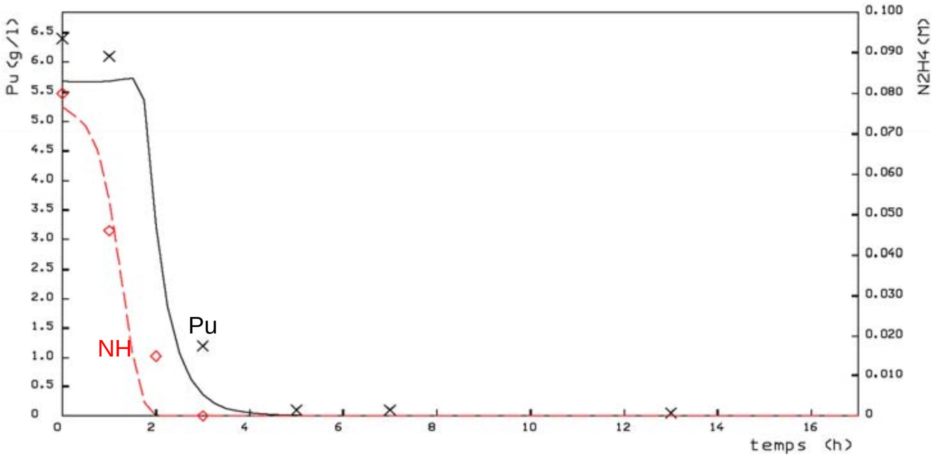
Globally

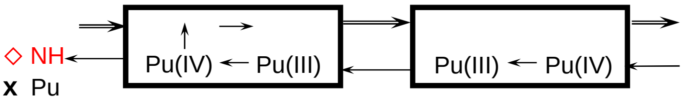
- **Kinetic of first-order versus [Tc]**
- **With relatively high activation energy (22 kcal/mol)**

DELETERIOUS IMPACT OF Tc ON PUREX PROCESS

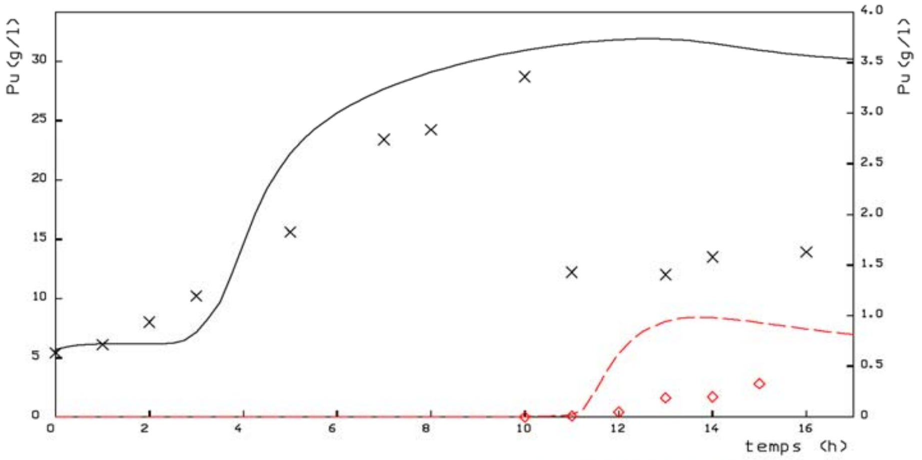

TBP 30%
Loaded solvent U(VI), Pu(IV)
U(VI)
Pu(IV)
Pu(IV) ← Pu(III)
Pu(IV)
Pu(III) ← Pu(IV)
Pu(III)
HNO_2
~~N_2H_4~~
Tc
U(IV), hydrazine
HNO_3 0.2 M hydrazine

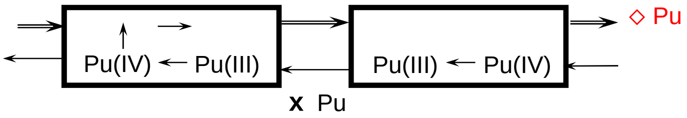
DELETERIOUS IMPACT OF Tc ON PUREX PROCESS





DELETERIOUS IMPACT OF Tc ON PUREX PROCESS





TECHNETIUM BEHAVIOR
ARRANGEMENT TAKEN FOR U/Pu SPLITTING STEP

OPERATING CONDITIONS

- Increase excess of hydrazine
- Limiting operating temperature
- Neutron’s on line monitoring

UP3 - UP2 800 RESULTS

- Outstanding stable operation
- DF of uranium vs plutonium > 10^6
- Good agreement with model predictions

IN CONCLUSION

Tc is just one FP among many others

YES, BUT:

- **It has an atypical behavior in the PUREX process**

- **That must be taken into account in the flowsheet design step**

- **Its chemistry needs to be deepen in the frame of FR fuel reprocessing (high Pu)**

DE LA RECHERCHE À L'INDUSTRIE

ISTR 2014

Pornichet LA BAULE, FRANCE

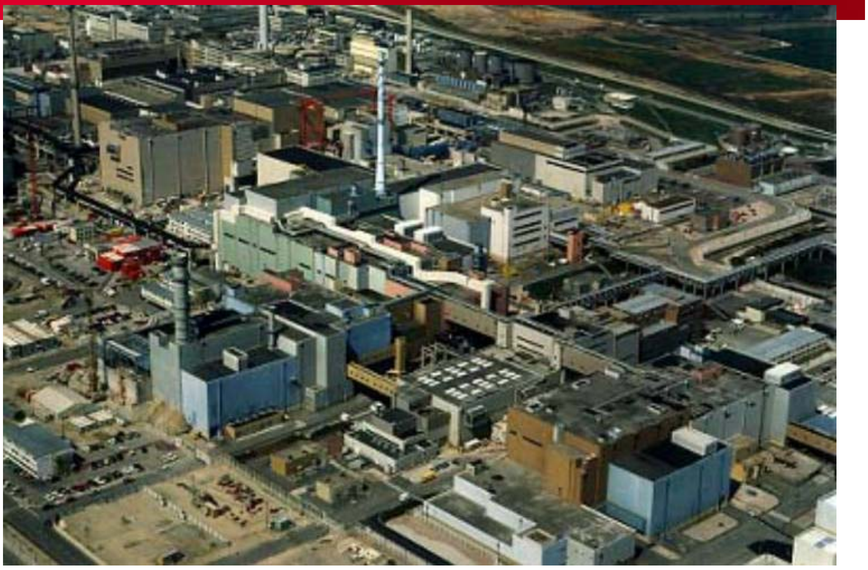
29TH *SEPTEMBER*, 3RD *OCTOBER 2014*

Pascal BARON

www.cea.fr

THANK YOU

FOR YOUR ATTENTION !

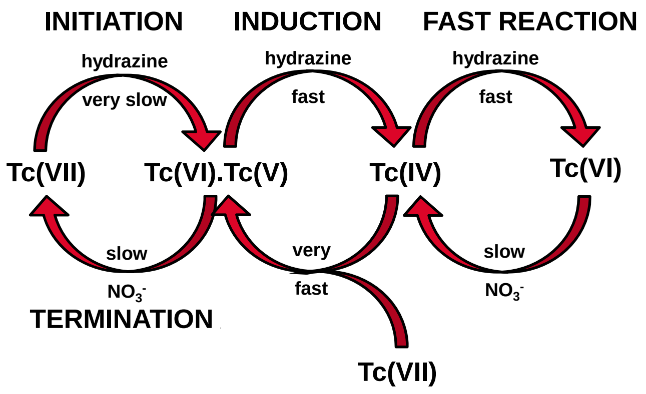


FISSION PRODUCTS :AVERAGE DISTRIBUTION

(1 ton UOX, 3,5 % ^{235}U ,33 GWj/t)

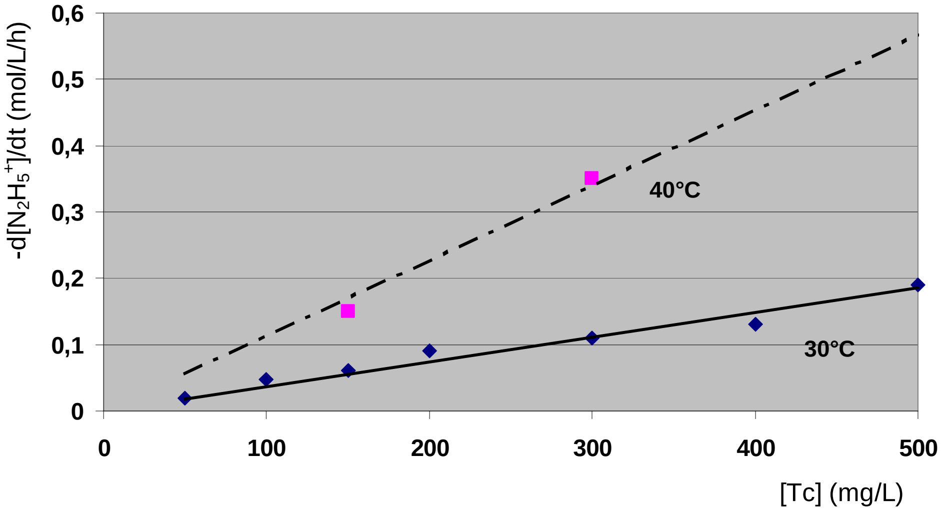
Family	Amount (kg/t)
Rare Gas (Kr, Xe)	Kr : 96 Ndm^3 (0,3 PBq) Xe : 736 Ndm^3
^{3}T & Alkali (Cs, Rb)	^{3}T = 16 TBq ; 3,977
Alkaline earth (Sr, Ba)	2,407
Yttrium & Lanthanides	10,198
Zirconium	3,586
Chalcogens (Se, Te)	0,527
Molybdenum	3,335
Technetium	**0,814**
Platinoids (Ru, Rh, Pd)	3,892
Ag, Cd, Sn, Sb, *etc…*	0,216

TECHNETIUM BEHAVIOR OF IN NITRIC ACID

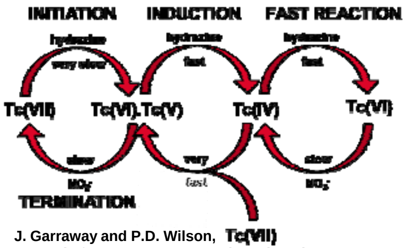


J. Garraway and P.D. Wilson,
Journal of Less-Common Metals, 97(1984) 191-203

CINÉTIQUE DE DÉCOMPOSITION DE L'HYDRAZINE EN PRÉSENCE DE TECHNÉTIUM



TECHNETIUM BEHAVIOR IN URANIUM/PLUTONIUM SPLITTING STEP



J. Garraway and P.D. Wilson,
Journal of Less-Common Metals, 97(1984) 191-203

THE ROLE OF A CHOICE OF THE TARGET FORM FOR ^{99}Tc TRANSMUTATION

A.A. Kozar’, **V.F. Peretrukhin, K.E. German**

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^{99}Tc transmutation can be the source of artificial stable ruthenium $^{100–102}$Ru. Such ruthenium has been received as a result of a neutron irradiation of Tc targets up to 20 – 70 % burn-up (for 3 different groups of Tc targets) in experiments on SM high-flux reactor. Metal homogeneous Tc targets had the form of disks in diameter 6мм and with thickness of 0.3 mm [1, 2]. They have been irradiated in geometry of a thin plate and consequently occupied irradiated volume corresponding to the cylinder in diameter and with height of 6 mm.

Artificial ruthenium demanded exposure during 8 – 10 years for application without restrictions, as it contained fission fragment ^{106}Ru ($T_{1/2}$ = 369 days) which can not be removed from this material by chemical methods.

Application of heterogeneous targets with nuclear-inert stuff to reduce a ^{106}Ru radioactivity in artificial Ru and to lower its exposure time before application or to exclude a technological step on additional preliminary purification of commercial Tc from actinide impurities [3]. Hence, the target form has effect on the artificial ruthenium purity at equal Tc nuclear density in irradiated volume.

Transformation of disks in cylinders in the conditions of identical irradiated volume could allow to lower ^{106}Ru concentration in artificial ruthenium. The minimum fission-fragment path length in Tc metal makes about 5 microns (average fission-fragment path length is about 8 microns). The corresponding form of a heterogeneous target is a tablet consisting of a mix of spherical Tc metal particle in diameter of 5 microns and a nuclear-inert stuff with Tc average density which in 20 times is less, than Tc metal. In this case all fission-fragments, including ^{106}Ru, escape the Tc (Tc-Ru) grains to stuff. The average distance between Tc spherical grains is about 23 microns, between their surfaces is about 18 microns at regular distribution of Tc particles in a target.

Fission-fragment path length in the most applicable nuclear-inert materials (such as ZrO_2, Y_2O_3, $MgAl_2O_4$, MgO, $Y_3Al_5O_{12}$, SiC, Al_2O_3, ZrO_2-Y_2O_3, ZrO_2-CaO and many others) makes 12 – 15 microns, hence hit probability of ^{106}Ru fission-fragments in the next Tc grain is negligibly small. Artificial ruthenium from such target would be almost free from ^{106}Ru nuclei. Additional purification of commercial Tc from actinide impurities would be not necessary at a choice of such target form instead of metal disks. In this case artificial ruthenium could be applied in non-nuclear field through 3 – 3.5 years after an irradiation, necessary to decay of transmutation product ^{103}Ru ($T_{1/2}$ = 39.3 days).

References

1. V. Peretroukhine, V. Radchenko, A. Kozar’ et al. Technetium transmutation and production of artifical stable ruthenium. // Comptes Rendus. – Ser. Chimie. – 2004. – Tome 7. – Fascicule 12. – P. 1215 – 1218.

2. A.A. Kozar’, V.F. Peretroukhin, K.V. Rotmanov, V.A. Tarasov. The elaboration of technology bases for the artificial stable ruthenium preparation from technetium-99 transmutation products. // 7th International Symposium on Technetium and Rhenium – Science and Utilization. Moscow, Russia, July 4 – 8, 2011. – Book of Proceedings. – P. 113. – Publishing House GRANITSA, Moscow, 2011. – 460 p.

3. A.A. Kozar’, V.F. Peretroukhin, K.V. Rotmanov, V.A. Tarasov. The elaboration of technology bases for the artificial stable ruthenium preparation from technetium-99 transmutation products. // Ibid. – P. 113.

THE ROLE OF A CHOICE OF THE TARGET FORM FOR ^{99}Tc TRANSMUTATION

ISTR 2014
8th International Symposium on Technetium and Rhenium
Pornichet LA BAULE, France
29th September - 3rd October 2014

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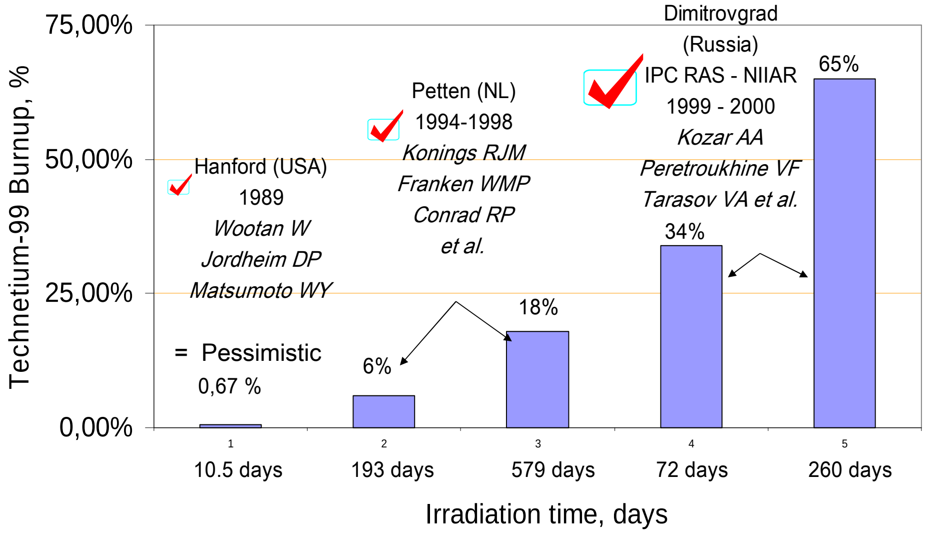
IT'S WELL KNOWN (SINCE 2000) - ^{99}Tc transmutation can be the source of artificial stable ruthenium $^{100–102}$Ru, the second of the mjst interesting elements of the Periodic table.
Such ruthenium has been synthesized as a result of a neutron irradiation of Tc targets up to 20 – 70 % burn-up (for 3 different groups of Tc targets) in experiments at SM high-flux reactor in 1999 – 2003 .

Russian Tc - Transmutation program (1992-2003)

$^{99}Tc(n,\gamma)^{100}Tc(\beta)^{100}Ru$



Tc transmutation experiment (IPCE RAS – NIIAR, 1999-2008)

✓ In IPC RAS a set of metal disc targets (10x10x0.3 mm) prepared and assembled in two batches with total weight up to 5 g.

✓ Transmutation experiment was carried out at high flux SM-3 reactor (NIIAR, Dimitrovgrad)

2nd batch: $F_t > 2\times 10^{15}$ $cm^{-2}s^{-1}$
1st batch: $F_t = 1.3\times 10^{15}$ $cm^{-2}s^{-1}$

^{99}Tc burnups have made:

34 ± 6 % and 65 ± 11 %

for the 1st and 2nd targets batches

- The high ^{99}Tc burn-ups were reached and about 2.5 g of new matter - **transmutation ruthenium were** accumulated as a result of experiments on SM-3 reactor
- These values are significantly higher of burnups 6 and 16 % achieved on HFR in Petten earlier

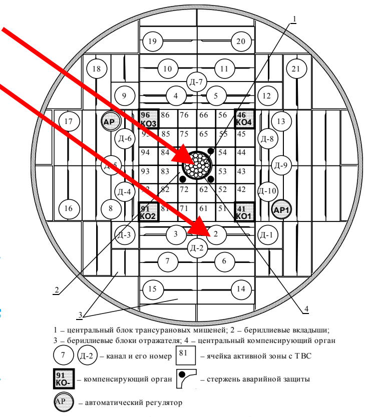


Рис.5. Картограмма реактора СМ

IRRADIATION OF ^{99}Tc METAL TARGETS IN NUCLEAR HIGH FLUX REACTORS

Petten transmutation experiment

^{99}Tc targets: metal cylinders Ø 4.8 mm and with height of 25 mm

^{99}Tc burn-up in Petten reactor are **6 % (T1)** and **16 – 18 % (T2).**

Dimitrovgrad transmutation experiment on SM high-flux reactor

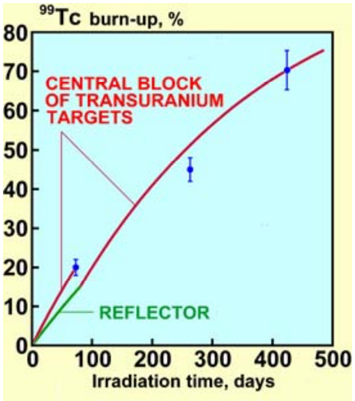
^{99}Tc targets: metal disks Ø 6.0 ± 0.3 mm and with thickness of 0.3 ± 0.02 mm

Total targets mass is ~10 g

^{99}Tc BURN-UP AND HALF-CONVERSION PERIOD

Measured and calculated ^{99}Tc burn-up and half-conversion periods in SM reactor.

№ of group	Burn-up, %		Irradiation time, eff. days	Half-conversion period $T_{1/2}^{burn}$, eff. days
	measured	calculated		
1	**19±2**	20±2	72.7	**240**
2	**45±3**	50±5	262.7	**305**
3	**70±5**	70±7	424.8	**245**



^{99}Tc burn-up in Petten reactor are **6 % (T1)** and **16 – 18 % (T2).**

^{99}Tc half-conversion period

$T_{1/2}^{burn}$ ≈ **2160 eff. days.**

Fig. 2. Calculated dependence of ^{99}Tc burn-up on irradiation time (—) and its experimental values (•) for 3 groups of targets.

ARTIFICIAL Ru ACTIVITY DECAY

Actinide content in Tc: $5 \cdot 10^{-8}$ g An per g of Tc (better values are expensive!)
Actinide fission product ^{106}Ru ($T_{1/2}$=371.6 days) can't be separated from artificial Ru by chemical methods.

Activity of ^{106}Ru + ^{106}Rh in artificial Ru

$$^{106}\text{Ru (pure } \beta\text{-radiator, } \gamma \text{ is absent)} \xrightarrow{\beta^-,\ 371.6\text{ days}} {}^{106}\text{Rh} \xrightarrow{\beta^-,\ 29.8\text{ sec}} {}^{106}\text{Pd (stable)}$$

^{106}Rh has 2 main γ -lines with energies 511.8 keV and 621.8 keV

In 2006 ^{106}Rh activity in Ru from 20 % burn-up targets later ~ 2100 days {5.7 $T_{1/2}$ (^{106}Ru)} after irradiation stop:

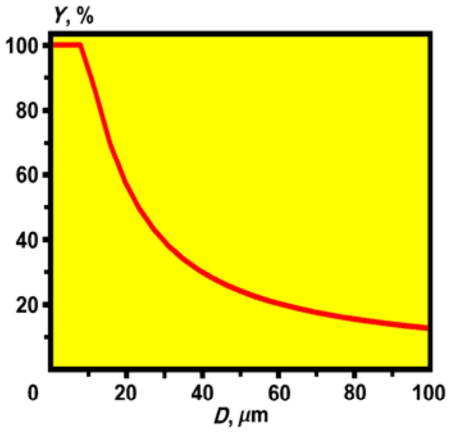
15 ± 2 Bk/g of Ru ⇒ total activity of pair ^{106}Ru + ^{106}Rh A^{106} ~ **30 Bk/g of Ru**

Later 10 years after irradiation stop: A^{106} = **3.2 ± 0.4 Bk/g of Ru** < A^{1}_{lim} = **3.7 Bk/g** ⇒

⇒ Since 2010 artificial Ru from 20% burn-up targets can be used without limitation

Artificial Ru separated from 45 % and 70 % burn-up targets can be used in non-nuclear industry ~9 and ~8 years after synthesis correspondingly

ARTIFICIAL STABLE RUTHENIUM PURIFICATION FROM ^{106}Ru



Relative yield Y of ^{106}Ru nuclei recoiling from spherical grains of technetium powder, in dependence on their diameter D (average fission-fragment path length is about 8 microns).

Transformation of disks Ø 6 mm × 0.3 mm in cylindrical targets Ø 6 mm × 6 mm

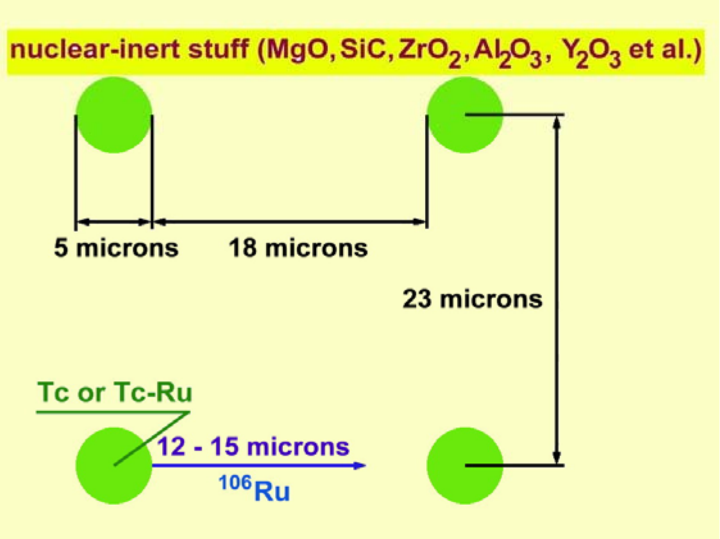


Fig. 4. Relative position of Tc (Tc-Ru) grains in heterogeneous target.

Possible target chemical substances

Tc Metal	- Tc
Tc Carbide	- Tc_6C
Tc Dioxide	- TcO_2
Tc Disulfide	- TcS_2

- and its mixtures with inert matter

Target substances
1. Metal

Sample type :

- Ordinary Powder metal
- Fused metal
- Single crystal
- Foil

Starting material :

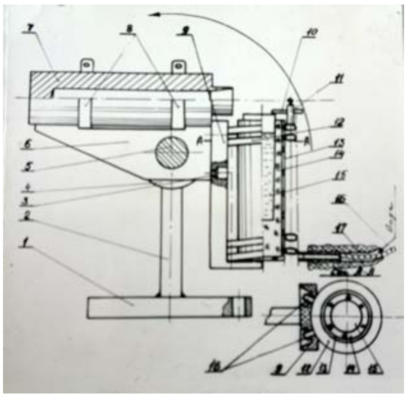
- TcO_2
- NH_4TcO_4
- R_4NTcO_4

Instrumentation

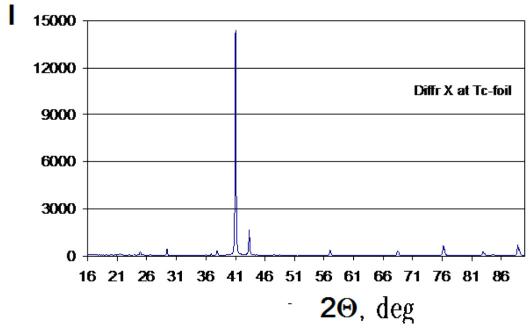
- Furnaces
- 6% H_2|Ar industurial balloon mixture
- Ingots
- Rolling-mill
- et cetera…

1. Bulk Tc metal

- Set-up used for fusion and casting of Tc metal
- Single crystal Tc metal

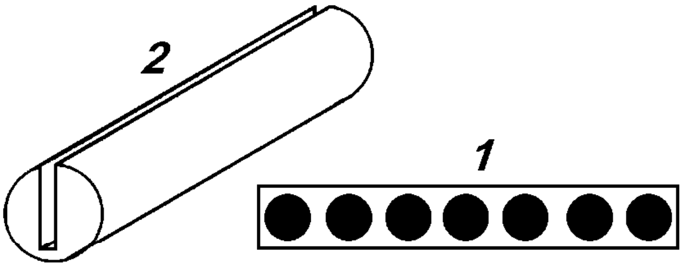


1. **Tc metal** – foil, X-ray study



- d: 20 micrometers
- Systematic absence of X-ray reflex
- = Preferential orientation of crystallites with C axe perpendicular to the foil surface

1. **Tc metal** – foil, assembling



- Spacer grid-bush with ^{99}Tc targets (*1*) and aluminium core (*2*) of capsule for loading in reactor.

1. Tc metal – foil chemical consequences

- Dissolution in HNO_3 dramatically slowed-down starting from 20% Tc to Ru conversion
- Possible to increase the dissolution rate by aggressive agents addition (Ag^{2+}, IO_4^-) but corrosion problems arises
- Possibly the best reprocessing procedure – burning in O_2 – not approved by industry to date

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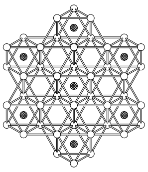
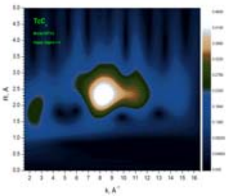
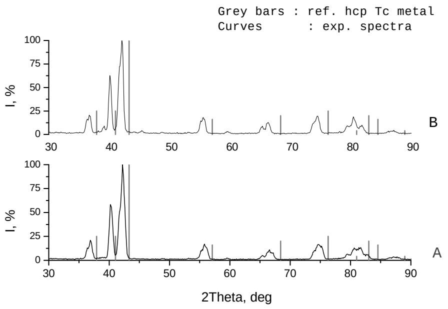
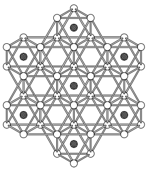


Target substances 2. Tc Carbide

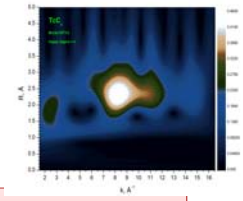


- Orthorhombic Tc metal is formed at low C content



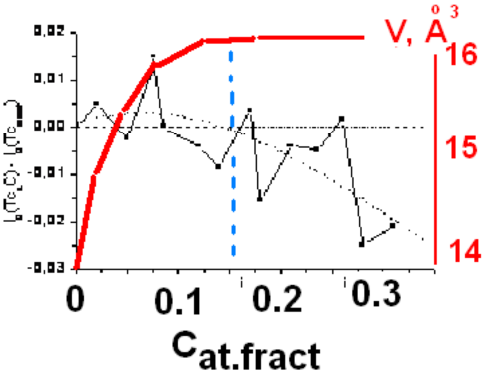


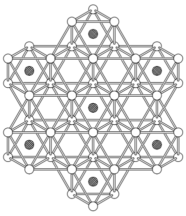
Target substances
2. Tc Carbide



- Tc_6C – non-stoechiometry
- Tc_6C + nC excess carbon for ***n°*** slowing-down

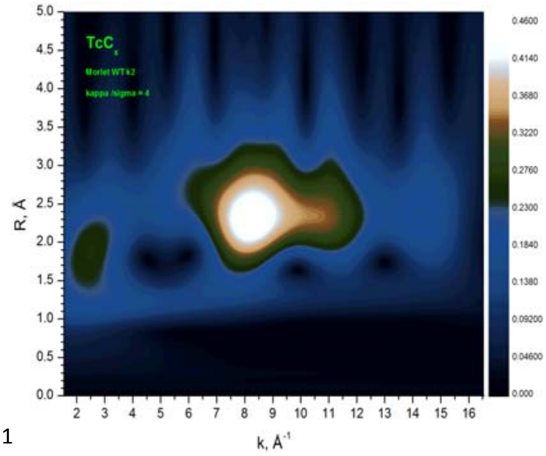
- Tc_6C – formed by :
- Tc + C reaction
- Tc + C6H6
- R_4NTcO_4 thermal decomposition in Ar





Target substances – Tc carbide
2. Tc_6C + nC excess carbon

- EXAFS study of Tc_6C + nC [1] – wavelet presentation



[1] K.German, Ya.Zubavichus ISTR2011

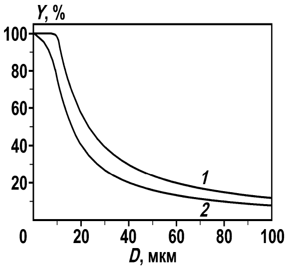
1. Tc carbide
chemical consequences

- Dissolution of Tc is more active as no RuC is known and so it is’nt formed during transmutation of Tc carbide to Ru - Tc and Ru being stabilized in separate phases
- Drawback: Possible mechanical inclusions of Tc in Ru residue at high burn-ups
- **Mixtures with C excess could be the best choice** because resonance energy neutrons are participating in transmutation due to enhanced thermolisation inside the target

1. Tc dioxide
chemical consequences

- Preparation by chemical reduction – high impurity content
- Preparation from NH4TcO4 – similar to Tc metal
- Target instability due to excess O released (Ru is stabilised as metal)
- Some Tc2O7 formed at high burn-up
- This target material is not recommended

Preparation of artificial stable Ruthenium by transmutation of Technetium



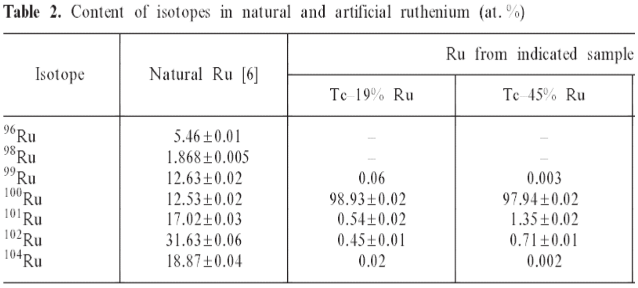


Table 2. Content of isotopes in natural and artificial ruthenium (at. %)

Isotope	Natural Ru [6]	Ru from indicated sample	
		Tc–19% Ru	Tc–45% Ru
^{96}Ru	5.46±0.01	–	–
^{98}Ru	1.868±0.005	–	–
^{99}Ru	12.63±0.02	0.06	0.003
^{100}Ru	12.53±0.02	98.93±0.02	97.94±0.02
^{101}Ru	17.02±0.03	0.54±0.02	1.35±0.02
^{102}Ru	31.63±0.06	0.45±0.01	0.71±0.01
^{104}Ru	18.87±0.04	0.02	0.002

- **Tc target material:**
- **Tc metal powder / Kozar (2008)**
- **Tc – C composite Tc carbide / German (2005)**
- **Rotmanov K. et all. *Radiochemistry,* 50 (2008) 408 :**

- **New Ruthenium is almost monoisotopic Ru-100, it has different spectral properties**
- **It is available only to several countries that develop nuclear industry**

Conclusions

- ^{99}Tc transmutation can be the source of artificial stable ruthenium $^{100–102}$Ru.
- Metal homogeneous Tc targets are possible
- Tc carbide targets are favorabale
- Artificial ruthenium demanded exposure during 8 – 10 years for application without restrictions
- Application of heterogeneous targets with nuclear-inert stuff to reduce a ^{106}Ru radioactivity in artificial Ru
- The target form effect the artificial ruthenium purity at equal Tc nuclear density in irradiated volume.

- Transformation of disks in cylinders in the conditions of identical irradiated volume could allow to lower ^{106}Ru concentration in artificial ruthenium. The minimum fission-fragment path length in Tc metal makes about 5 microns (average fission-fragment path length is about 8 microns). The corresponding form of a heterogeneous target is a tablet consisting of a mix of spherical Tc metal particle in diameter of 5 microns and a nuclear-inert stuff with Tc average density which in 20 times is less, than Tc metal. In this case all fission-fragments, including ^{106}Ru, escape the Tc (Tc-Ru) grains to stuff. The average distance between Tc spherical grains is about 23 microns, between their surfaces is about 18 microns at regular distribution of Tc particles in a target.
- Fission-fragment path length in the most applicable nuclear-inert materials (such as ZrO_2, Y_2O_3, $MgAl_2O_4$, MgO, $Y_3Al_5O_{12}$, SiC, Al_2O_3, ZrO_2-Y_2O_3, ZrO_2-CaO and many others) makes 12 – 15 microns, hence hit probability of ^{106}Ru fission-fragments in the next Tc grain is negligibly small. Artificial ruthenium from such target would be almost free from ^{106}Ru nuclei. Additional purification of commercial Tc from actinide impurities would be not necessary at a choice of such target form instead of metal disks. In this case artificial ruthenium could be applied in non-nuclear field through 3 – 3.5 years after an irradiation, necessary to decay of transmutation product ^{103}Ru ($T_{1/2}$ = 39.3 days).

- **References**
- 1. V. Peretroukhine, V. Radchenko, A. Kozar' et al. Technetium transmutation and production of artifical stable ruthenium. // Comptes Rendus. – Ser. Chimie. – 2004. – Tome 7. – Fascicule 12. – P. 1215 – 1218.
- 2. A.A. Kozar', V.F. Peretroukhin, K.Vразличные химические методы, а ские методы, а общий технеций, ка мишеналла рутения трансмутацией . Rotmanov, V.A. Tarasov. The elaboration of technology bases for the artificial stable ruthenium preparation from technetium-99 transmutation products. // 7th International Symposium on Technetium and Rhenium – Science and Utilization. Moscow, Russia, July 4 – 8, 2011. – Book of Proceedings. – P. 113. – Publishing House GRANITSA, Moscow, 2011. – 460 p.
- 3. A.A. Kozar', V.F. Peretroukhin, K.Vразличные химические методы, а ские методы, а общий технеций, ка мишеналла рутения трансмутацией . Rotmanov, V.A. Tarasov. The elaboration of technology bases for the artificial stable ruthenium preparation from technetium-99 transmutation products. // Ibid. – P. 113.

Complexation and extraction of Pu(IV) in the presence of pertechnetic acid

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CEA Marcoule, DEN/DRCP, BP 17171, 30207 Bagnols-sur-Cèze Cedex, France

The hypothesis that pertechnetate ion can form extractible complexes with actinides at the +IV or +VI oxidation state in nitric acid is quite commonly pointed out. Therefore, in nitric acid, the pertechnetate anion could act as a co-ligand with the nitrate ion and then could replace it in the extracted species. It can be noticed that in the absence of nitric acid a complex of U(VI) with the pertechnetate anion $\overline{UO_2(TcO_4)_2.2TBP}$ has already been identified in an organic phase made of TBP. However, even in the presence of nitric acid, a mixed complex can be formed by replacing a nitrate anion by a pertechnetate one:

$$\overline{UO_2(NO_3)_2.2TBP} + TcO_4{}^- \leftrightarrows \overline{UO_2(NO_3)(TcO_4).2TBP} + NO_3{}^-$$

To check the ability of pertechnetate ions to give rise to complexes with actinides, the study of the complexation of Pu(IV) by TcO_4^- was carried out by spectrophotometry in perchloric acid media. Absorption spectra of Pu(IV)-Tc(VII) mixtures, according to the temperature, enable the calculation of the complexation constant β_i of the complex present in solution by chemometric treatment. It was found that for [Tc]/[Pu] ratio up to 1300, two species are present in solution: the aquo ion Pu^{4+} and a complex which could either be $Pu(TcO_4)_3^+$ or $Pu(TcO_4)_4$.The complexation constants have been respectively estimated to $\beta_3 \sim 2.3 \pm 0.1$ and $\beta_4 \sim 3.5 \pm 0.2$ at T = 298 K.

Onthe other hand, some measurements of the distribution of Tc(VII) and Pu(IV) in biphasic system ($HClO_4$ – TBP 30%/cyclohexane) were carried out. Firstly, it has been shown that the extraction of pertechnetic acid alone involves 2.5 molecules of TBP perpertechnetic acid, indicating that the extracted species are both $\overline{HTcO_4.2TBP}$and $\overline{HTcO_4.3TBP}$.Secondly, in the presence of Pu(IV), this latter is highly extracted when the ratio [Tc]/[Pu] is close to 2500 with $D_{Pu} \sim 10$. Therefore, two extraction equilibria for the extracted neutral complex $Pu(TcO_4)_4$ in organic phase are proposed:

$$8TcO_4{}^- + 2Pu^{4+} + 3\overline{TBP} \rightleftharpoons \overline{Pu(TcO_4)_4.TBP} + \overline{Pu(TcO_4)_4.2TBP}$$

$$8TcO_4{}^- + 2Pu^{4+} + 3\overline{TBP} \rightleftharpoons \overline{(Pu(TcO_4)_4)_2.TBP} + \overline{Pu(TcO_4)_4.2TBP}$$

Nevertheless, as the [Tc]/[Pu] ratio becomes lower than 1400, Pu(IV) is then poorly extracted with D-values not higher than 1. It is in accordance with the spectrophotometric observations and chemometric calculations assuming that, in these conditions the complex formed is $Pu(TcO_4)^{3+}$. The thermodynamic characteristics of this complex have thenbeen calculated.

DE LA RECHERCHE À L'INDUSTRIE

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Pu(IV) COMPLEXATION AND EXTRACTION IN PRESENCE OF PERTECHNETIC ACID

L. ABIAD, L. VENAULT, Ph. MOISY

CEA Marcoule

Nuclear Energy Division

Radiochemistry and Process Department

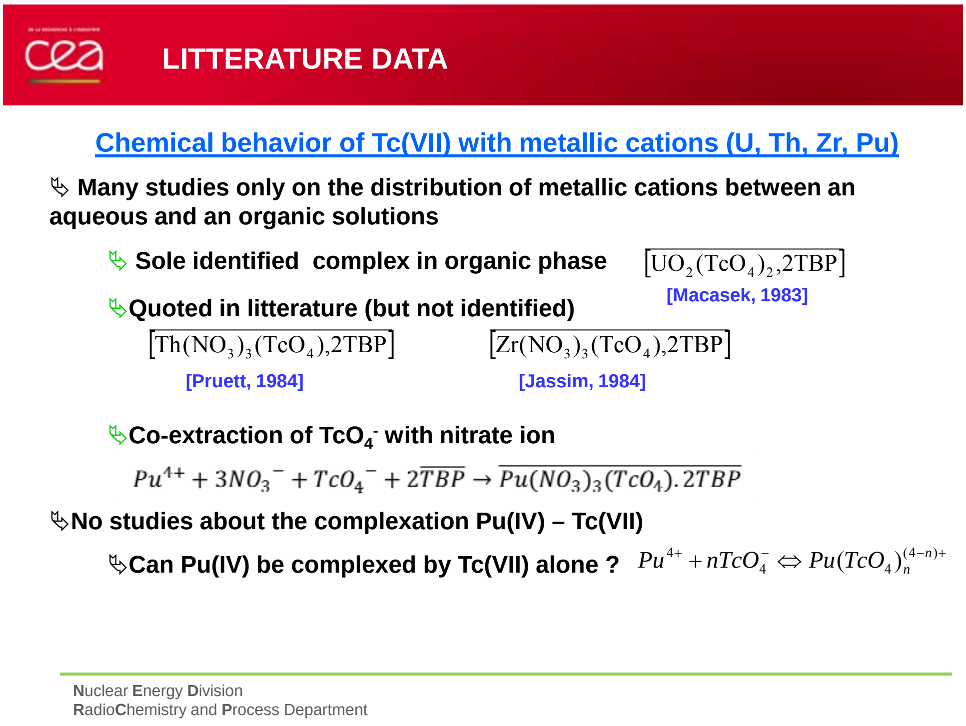
GOALS & CONTEXT

✓ **Main Goal**

To improve knowledge about Tc complexation chemistry with actinides

✓ **Industrial interest: PUREX process**

- **Disturbances in actinide extraction due to Tc**
- **Specific Tc scrubbing step**
- **Chemistry of Tc in the process still not well described**



LITTERATURE DATA

Chemical behavior of Tc(VII) with metallic cations (U, Th, Zr, Pu)

- Many studies only on the distribution of metallic cations between an aqueous and an organic solutions
  - Sole identified complex in organic phase $[UO_2(TcO_4)_2,2TBP]$ [Macasek, 1983]
  - Quoted in litterature (but not identified)

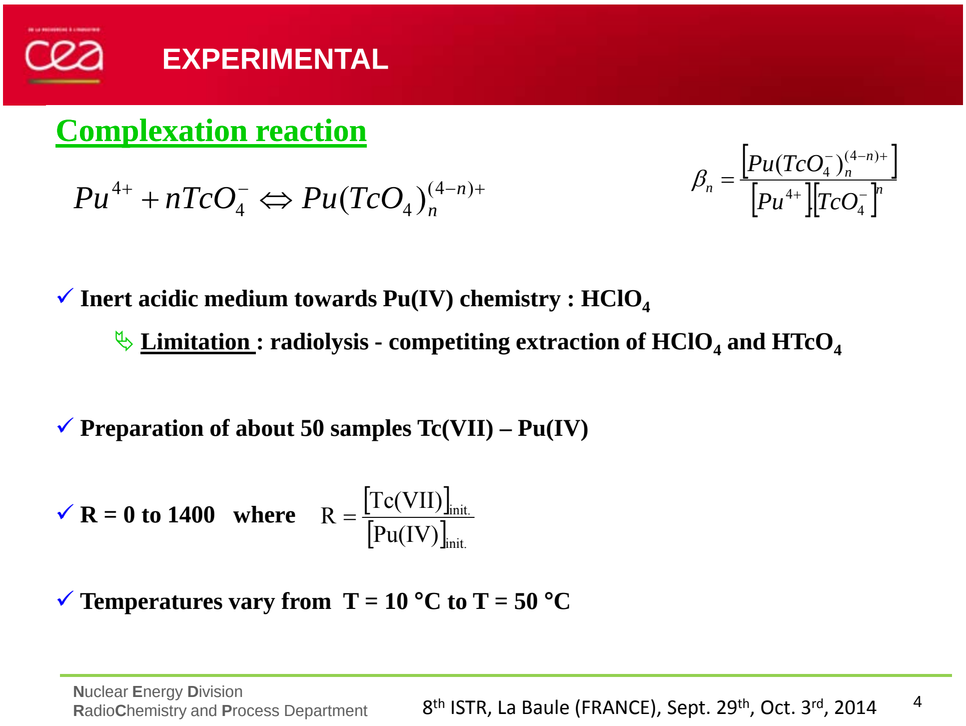
    $[Th(NO_3)_3(TcO_4),2TBP]$ [Pruett, 1984]

    $[Zr(NO_3)_3(TcO_4),2TBP]$ [Jassim, 1984]
  - Co-extraction of TcO_4^- with nitrate ion

$$Pu^{4+} + 3NO_3^- + TcO_4^- + 2\overline{TBP} \rightarrow \overline{Pu(NO_3)_3(TcO_4).2TBP}$$

- No studies about the complexation Pu(IV) – Tc(VII)
  - Can Pu(IV) be complexed by Tc(VII) alone ? $Pu^{4+} + nTcO_4^- \Leftrightarrow Pu(TcO_4)_n^{(4-n)+}$

Nuclear Energy Division
RadioChemistry and Process Department



EXPERIMENTAL

Complexation reaction

$$Pu^{4+} + nTcO_4^- \Leftrightarrow Pu(TcO_4)_n^{(4-n)+}$$

$$\beta_n = \frac{[Pu(TcO_4^-)_n^{(4-n)+}]}{[Pu^{4+}][TcO_4^-]^n}$$

- ✓ **Inert acidic medium towards Pu(IV) chemistry : $HClO_4$**
  - **Limitation : radiolysis - competiting extraction of $HClO_4$ and $HTcO_4$**
- ✓ **Preparation of about 50 samples Tc(VII) – Pu(IV)**
- ✓ **R = 0 to 1400 where** $R = \frac{[Tc(VII)]_{init.}}{[Pu(IV)]_{init.}}$
- ✓ **Temperatures vary from T = 10 °C to T = 50 °C**

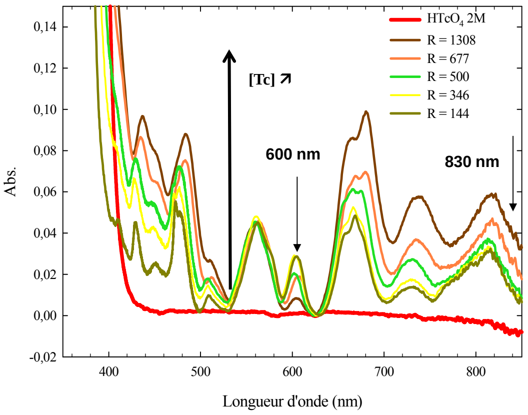
Nuclear Energy Division
RadioChemistry and Process Department

8th ISTR, La Baule (FRANCE), Sept. 29th, Oct. 3rd, 2014

RESULTS

Experimental absorption spectra for 5 mixtures Pu(IV)-Tc(VII)

I = 2 ($HClO_4$ 2 M), $[Pu]_{total}$ = 2.10^{-3}M à 25°C

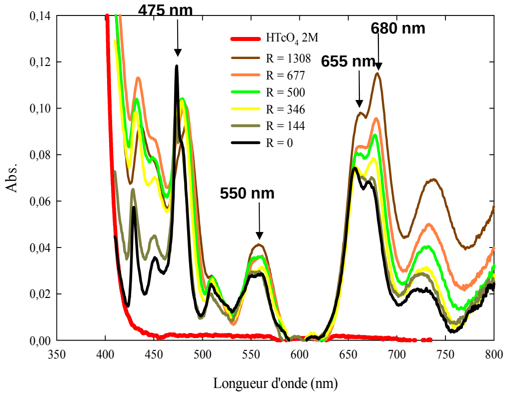


- ✓ **No Pu(VI) at λ = 830 nm**
- ✓ **No band for $HTcO_4$**
- ✓ **Increase and changes in UV bands at λ < 500 nm as R ↑**
- ✓ **Pu(III) at λ = 600 nm**
  - ➔ **due to radiolysis in Pu(IV) sol.**
  - ➔ **subtraction of Pu(III) spectra**

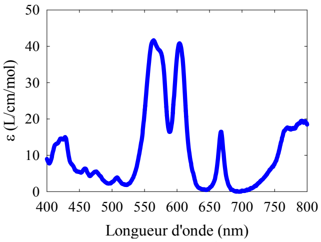
RESULTS

For every spectrum, at every T ➔ **subtraction of Pu(III) spectrum**

$$A(\lambda) = A_{tot.}(\lambda) - A_{Pu(III)}(\lambda)$$



Absorption spectra of Pu(IV)-Tc(VII) mixtures corrected from Pu(III) contribution
I = 2 ($HClO_4$ 2 M, $[Pu]_{total}$ = 2.10^{-3}M à 35°C



Extinction coefficient for a 10^{-3} M Pu(III) solution in $HClO_4$ 2 M at 25°C

- ➢ **Increase of Abs. / Changes in bands**
  - ➔ **complexation of Pu(IV) ?**
  - ➔ **Changes in hydratation sphere ?**
- ➢ **a_w and $[H^+]$ kept constant**
  - ➔ **Complexation of Pu(IV) with Tc(VII)**

RESULTS

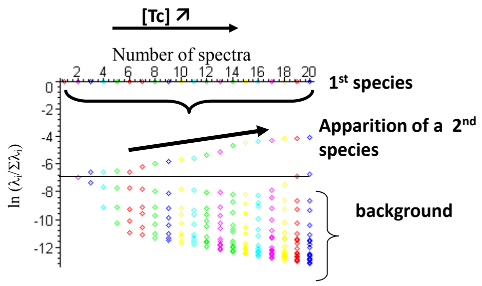
- **Qualitative study**
  - ✓ **Changes in spectra ➔ Existence of one or several complexes** **$Pu(TcO_4)_i^{(4-i)+}$**
  - ✓ **Effect of T ➔ determination of thermodynamic data**
- **Quantitative study**
  - ✓ **Spectrum λ = 520 – 760 nm**
  - ✓ **Small changes in spectrum**
  - ✓ **Free Pu(IV) & complexes in the same wavelength range**
  - ✓ **No reference spectra for the complexes**
    - **➔ Direct treatment of spectra impossible**
    - **➔ Chimiometric method**
      - ❖ **Treatment of a lot of data**
      - ❖ **Few hypothesis about the chemical composition**

CHIMIOMETRIC METHOD

1st step: Principal Component Analysis

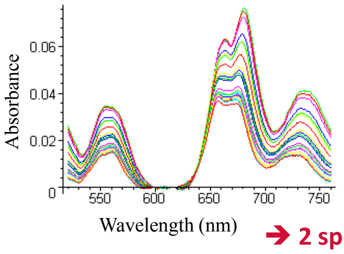
⇨ Number of species

- **Program *NBESPECE***
  - ➔ statistical & empirical tests
  - **➔ 2 species ∀ T**



At T = 40°C

- **Program *RECONS***
  - ➔ Hypothesis : 2 species
  - ➔ Reconstruction of spectra
    - **➔ reconstructed spectra similar to experimental ones**

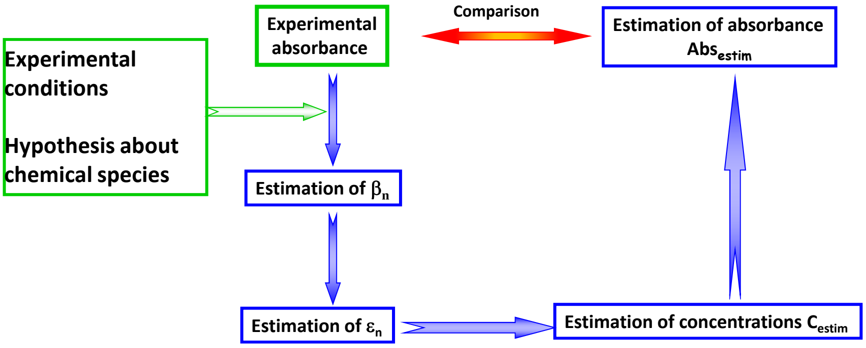


➔ 2 species

CHIMIOMETRIC METHOD

2^{nd} step: Modeling Factors Analysis (MFA)

⇨ Complexation constants & reference spectra



Experimental absorbance

Comparison

Estimation of absorbance Abs_{estim}

Experimental conditions

Hypothesis about chemical species

Estimation of β_n

Estimation of ε_n

Estimation of concentrations C_{estim}

- If $Abs_{estim} = Abs_{exper}$ ➔ Estimated concentrations = real
- Criterion : calculated reference spectra & relative deviation

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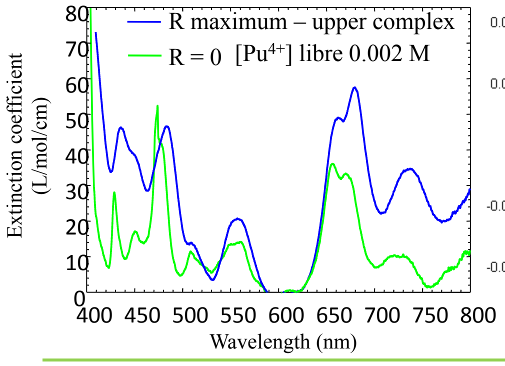
CHIMIOMETRIC METHOD

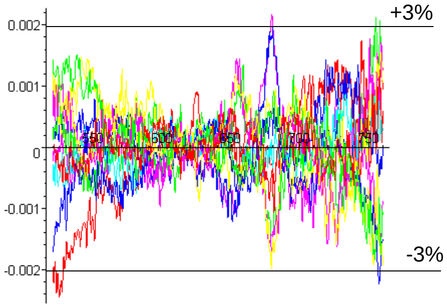
2^{nd} step: Modeling Factor Analysis (MFA)

Reference spectra for the two species



Relative deviation

Abs_{exp} - Abs_{est}



CHIMIOMETRIC METHOD

Results from MFA calculations

$[Pu^{4+}]_o$ = 0.002 M, I = 2, et $[TcO_4^-]$ = 0 to 2 M)

T	β_3	β_4
10°C	2,8 ± 5%	7,3 ± 16%
18°C	4,8 ± 21%	9,5 ± 21%
25°C	2,3 ± 4%	3,4 ± 5%
35°C	3,5 ± 2%	6,2 ± 2%
40°C	4,5 ± 2%	8,3 ± 4%
50°C	7,9 ± 14%	19,1± 14%

MFA calculations are consistent with ML_3 & ML_4

$$3\,TcO_4^- + Pu^{4+} \xleftrightarrow{\beta_3} Pu(TcO_4)_3^+$$

or

$$4\,TcO_4^- + Pu^{4+} \xleftrightarrow{\beta_4} Pu(TcO_4)_4$$

EXTRACTION

Pu(IV) Distribution Ration in presence of Tc(VII)

Goal

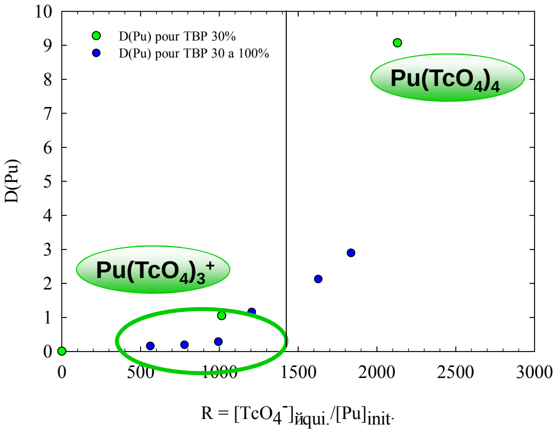
- To (undoubtedly) identify the complex in solution $\Rightarrow ML_3$ ou ML_4 ?
- Determination of the distribution ratio D_{Pu} as a function of R = [Tc(VII)]/[Pu(IV)]

Method

- Thermodynamic equilibrium TcO_4^-/ TBP without Pu
- Adding small known amounts of Pu
- α counting $\Rightarrow D_{Pu} = f(R)$

EXTRACTION - RESULTS

Variation of D_{Pu} as a function of R = $[TcO_4^-]/[Pu(IV)]$



- **1400 > R > 2500**
  ⇒ 2 > D(Pu) > 10
- ✓ **Extraction of Pu(IV)**
- ✓ **Formation of a neutral complex**
- **1400 > R > 0**
  ⇒ D(Pu) < 1
- ✓ **No extraction of Pu(IV)**
- ✓ **Formation of the charged complex**

EXTRACTION OF Pu IN PRESENCE OF $HTCO_4$

Complexation of Pu(IV)

$$Pu^{4+} + 3TcO_4^- \xrightarrow{\beta_3} Pu(TcO_4)_3^+$$

$$\beta_3 = \frac{[Pu(TcO_4)_3^+]}{[Pu^{4+}][TcO_4^-]^3}$$

$$Pu^{4+} + 4TcO_4^- \xrightarrow{\beta_4} Pu(TcO_4)_4$$

$$\beta_4 = \frac{[Pu(TcO_4)_4]}{[Pu^{4+}][TcO_4^-]^4}$$

Extraction of Pu(IV)

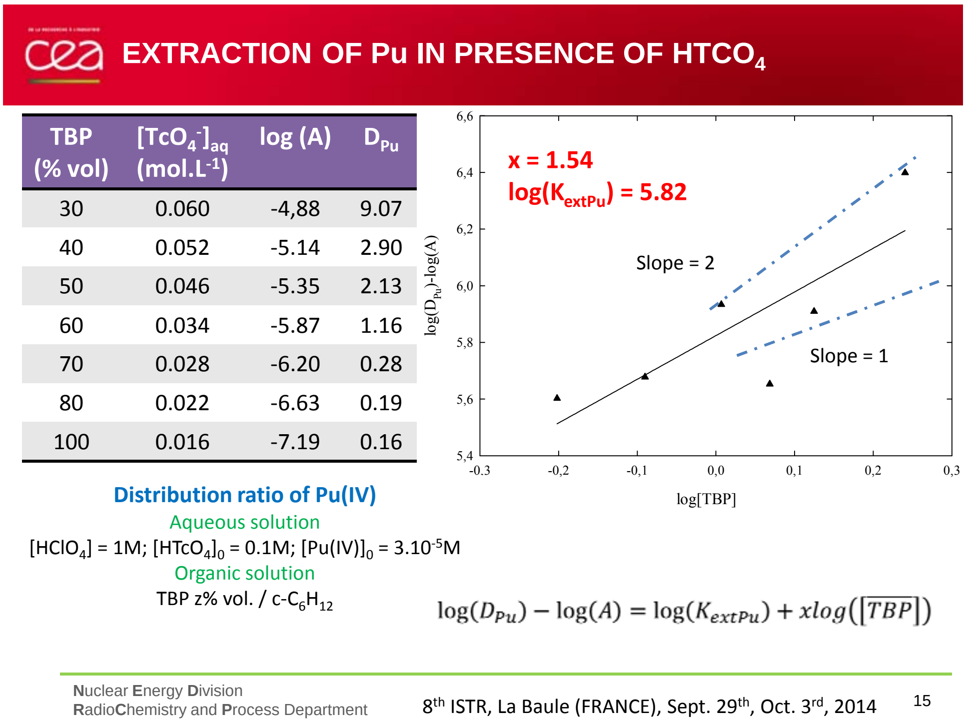
$$Pu^{4+} + 4TcO_4^- + x\overline{TBP} \rightarrow \overline{Pu(TcO_4)_4.xTBP}$$

$$K_{ext\ Pu} = \frac{[\overline{Pu(TcO_4)_4.xTBP}]}{[Pu^{4+}][TcO_4^-]^4[\overline{TBP}]^x}$$

$$D_{Pu} = \frac{[\overline{Pu(TcO_4)_4.xTBP}]}{[Pu^{4+}] + [Pu(TcO_4)_3^+] + [Pu(TcO_4)_4]}$$

$$\log(D_{Pu}) = \log(K_{extPu}) + x\log([\overline{TBP}]) + \log(A)$$

$$A = \frac{[TcO_4^-]^4}{1 + \beta_3[TcO_4^-]^3 + \beta_4[TcO_4^-]^4}$$



EXTRACTION OF Pu IN PRESENCE OF HTCO$_4$

TBP (% vol)	$[TcO_4^-]_{aq}$ (mol.L^{-1})	log (A)	D_{Pu}
30	0.060	-4,88	9.07
40	0.052	-5.14	2.90
50	0.046	-5.35	2.13
60	0.034	-5.87	1.16
70	0.028	-6.20	0.28
80	0.022	-6.63	0.19
100	0.016	-7.19	0.16

Distribution ratio of Pu(IV)

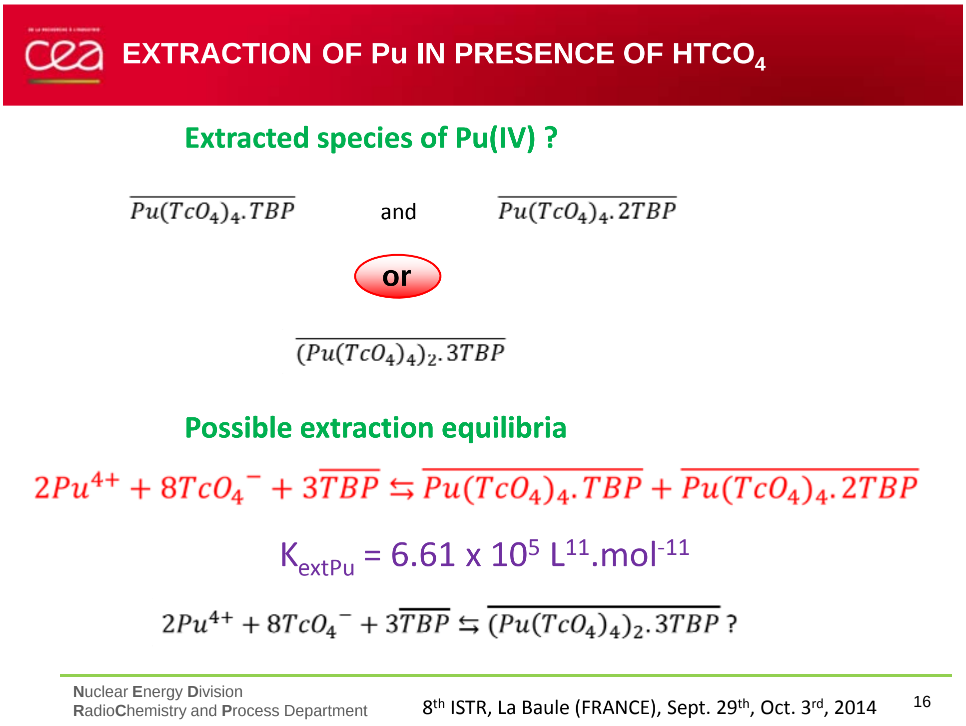
Aqueous solution

$[HClO_4] = 1M$; $[HTcO_4]_0 = 0.1M$; $[Pu(IV)]_0 = 3.10^{-5}M$

Organic solution

TBP z% vol. / c-C_6H_{12}

$$\log(D_{Pu}) - \log(A) = \log(K_{extPu}) + x\log([\overline{TBP}])$$



EXTRACTION OF Pu IN PRESENCE OF HTCO$_4$

Extracted species of Pu(IV) ?

$\overline{Pu(TcO_4)_4.TBP}$ and $\overline{Pu(TcO_4)_4.2TBP}$

or

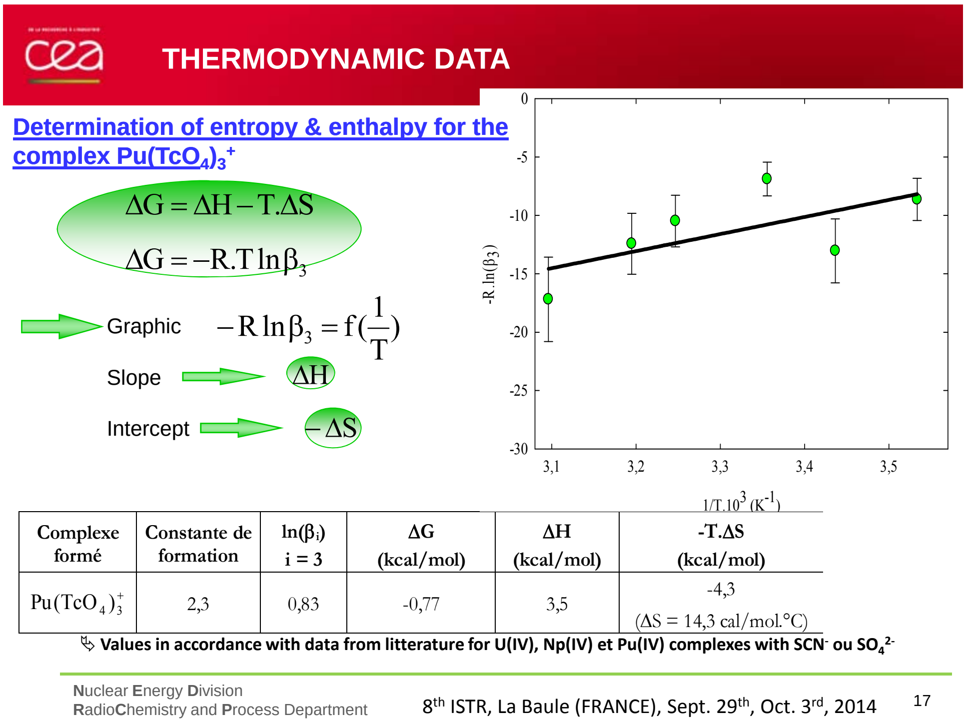
$\overline{(Pu(TcO_4)_4)_2.3TBP}$

Possible extraction equilibria

$$2Pu^{4+} + 8TcO_4^- + 3\overline{TBP} \leftrightharpoons \overline{Pu(TcO_4)_4.TBP} + \overline{Pu(TcO_4)_4.2TBP}$$

$K_{extPu} = 6.61 \times 10^5$ L^{11}.mol^{-11}

$$2Pu^{4+} + 8TcO_4^- + 3\overline{TBP} \leftrightharpoons \overline{(Pu(TcO_4)_4)_2.3TBP}\ ?$$



THERMODYNAMIC DATA

Determination of entropy & enthalpy for the complex $Pu(TcO_4)_3^+$

$$\Delta G = \Delta H - T.\Delta S$$

$$\Delta G = -R.T \ln \beta_3$$

Graphic $-R \ln \beta_3 = f(\frac{1}{T})$

Slope ΔH

Intercept $-\Delta S$

Complexe formé	Constante de formation	$\ln(\beta_i)$ i = 3	ΔG (kcal/mol)	ΔH (kcal/mol)	$-T.\Delta S$ (kcal/mol)
$Pu(TcO_4)_3^+$	2,3	0,83	-0,77	3,5	-4,3 (ΔS = 14,3 cal/mol.°C)

Values in accordance with data from litterature for U(IV), Np(IV) et Pu(IV) complexes with SCN^- ou SO_4^{2-}

Nuclear Energy Division
RadioChemistry and Process Department

8th ISTR, La Baule (FRANCE), Sept. 29th, Oct. 3rd, 2014

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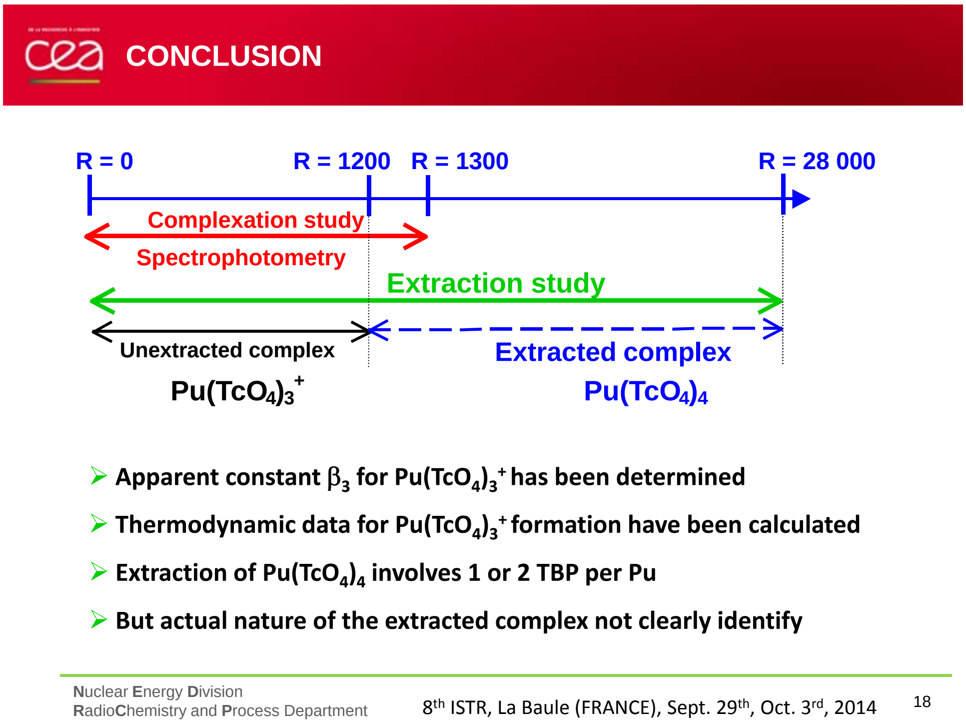

CONCLUSION

$Pu(TcO_4)_3^+$

$Pu(TcO_4)_4$

- **Apparent constant β_3 for $Pu(TcO_4)_3^+$ has been determined**
- **Thermodynamic data for $Pu(TcO_4)_3^+$ formation have been calculated**
- **Extraction of $Pu(TcO_4)_4$ involves 1 or 2 TBP per Pu**
- **But actual nature of the extracted complex not clearly identify**

Nuclear Energy Division
RadioChemistry and Process Department

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PROSPECTS

- **Spectrophotometry / Chimiometry for higher R**
  - ✓ Existence of $Pu(TcO_4)_4$ in aqueous solutions
  - ✓ Calculation of β_4
- **Structural study of $Pu(TcO_4)_3^+$ complex**
  - ✓ EXAFS
- **Determination of the thermodynamical complexation constant β°**
  - ✓ Effect of ionic strength – SIT $\log\beta = f(\Delta\varepsilon).I + f(\log\beta°)$
- **Pursuit of Pu(IV)-Tc(VII) extraction study**
  - ✓ Higher $[Pu(IV)]_0$, lower $[HTcO_4]_0$, other $[HClO_4]$…
  - ✓ To improve D_{Pu} determination
  - ✓ To state precisely the stoechiometry of the extracted species
- **Modeling of liquid/liquid extraction involving Tc(VII) and Pu(IV)**

DE LA RECHERCHE À L'INDUSTRIE

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Thank you for your kind attention

THE WAYS OF TECHNETIUM LOCALIZATION AT THE SNF REPROCESSING

N.D. Goletsky, B.Ya. Zilberman, Yu.S. Fedorov, A.S. Kudinov, A.A. Timoshuk, L.V. Sytniuk, E.A. Puzikov, S.A. Rodionov, A.P. Krinitsyn, V.I. Ryasantsev, D.V. Ryabkov, T.A. Boytsova

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The Tc behavior in the all operations of extraction NPP SNF reprocessing is investigated traditionally at the RPA «V.G. Khlopin Radium Institute». There are possible different variants of Tc localization in the products of the 1st extraction cycle depending on the assigned tasks. In the RT-1 and Experimental Demonstration Center (EDC) schemes Tc is output in combination with Pu and Np. Hereafter Tc is output separately on the extraction and/or sedimentation refining operations [1]. In the UP-2 and UP-3 schemes Tc is output selectively on 80-85% before re-extraction of Pu. At the centrifugal extractors stands (CES) and mixer-settler extractors (MSE) on the model and real SNF solutions different variants of Tc output on 98% and more to any flows of the 1st cycle were tested experimentally.

Localization of technetium in the flow can be achieved in the scheme with a two-zone (strong - and sub-acid) ablution of actinides and Tc combined extract. It is necessary to optimize strongly acidic ablution for this. As a consequence, the concentration of nitric acid in the flow will increase [2]. Experiments on the «warm» model SNF solution of PWR-1000 and full-scale SNF solutions system simulator of PWR and AMB were carried out.

The possibility of Tc localization in the individual flow or in the Zr flow was shown. It was tested within the framework of the EDC basic technology, where extract acid ablution placed in the independent extraction block. In this approach the flow of stripping solution is increased and the nitric acid concentration in the Tc and Zr stripping flow should be about 4 mol/l [3]. The increase of stripping flow rate leads to water-acid balance violation of the tritium-containing acid and water.

Localization of Tc in the barrier ablution uranium extract block is the optimum alternative. It is made after the Pu and Np re-extraction from the extract containing U and Tc by using «soft» reducing agent (acetohydroxamic acid (AHA) without hydrazine). The effect is achieved by using U(+4) and hydrazine as reducing agents with present of the AHA. It were tested in the CES extractor. In the future it is proposed to use an MSE extractor, where almost no aeration, which leading to partial oxidation of U(+4). MSE extractor allows to recovering U electrochemically in the stages of it.

It will be possible to make chemical or thermal denitration of condensed solution with the object to obtain mixed oxides if Tc is full separated from the Pu, Np and U stripping flows (separation $>10^3$). In this approach the operations of actinides sedimentation with precipitation ablutions and complex treatment of tail solutions is deleted from the process. The developed techniques are well combined with the selective Np(V) re-extraction which is made before reducing Pu re-extraction (process SuperPurex).

The full paper is available [4].

1. Fedorov Yu.S., Zilberman B.Ya., Aloy A.S., etc. RCJ, 2010, V. 54, № 4, p. 12-24.
2. Kudinov A.S., Goletsky N.D., Zilberman B.Ya., etc. Rus. Atomic Energy, 2013, V. 114, № 5
3. Anisimov O.P., Aloy A.S., Zilberman B.Ya., etc. VI international nuclear forum (St.Petersburg, 26-30.09.2011). The reports. CICE&T. SPb. 2011. p. 180-190.
4. Goletskiy N.D., Zilberman B.Ya., Fedorov Yu.S., Kudinov A.S., et al. Radiokhimiya, 2014, Vol. 56, No. 5, pp. 427–438.

The 8th International Symposium on Technetium and Rhenium: Science and Utilization
September 29 -- October 3, 2014
La Baule - Pornichet, France

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THE WAYS OF TECHNETIUM AND NEPTUNIUM LOCALIZATION AT THE SNF REPROCESSING

N.D. Goletsky, B.Ya. Zilberman, Yu.S. Fedorov, A.S. Kudinov, A.A. Timoshuk, L.V. Sytniuk, E.A. Puzikov, S.A. Rodionov, A.P. Krinitsyn, V.I. Ryasantsev, D.V. Ryabkov, T.A. Boytsova

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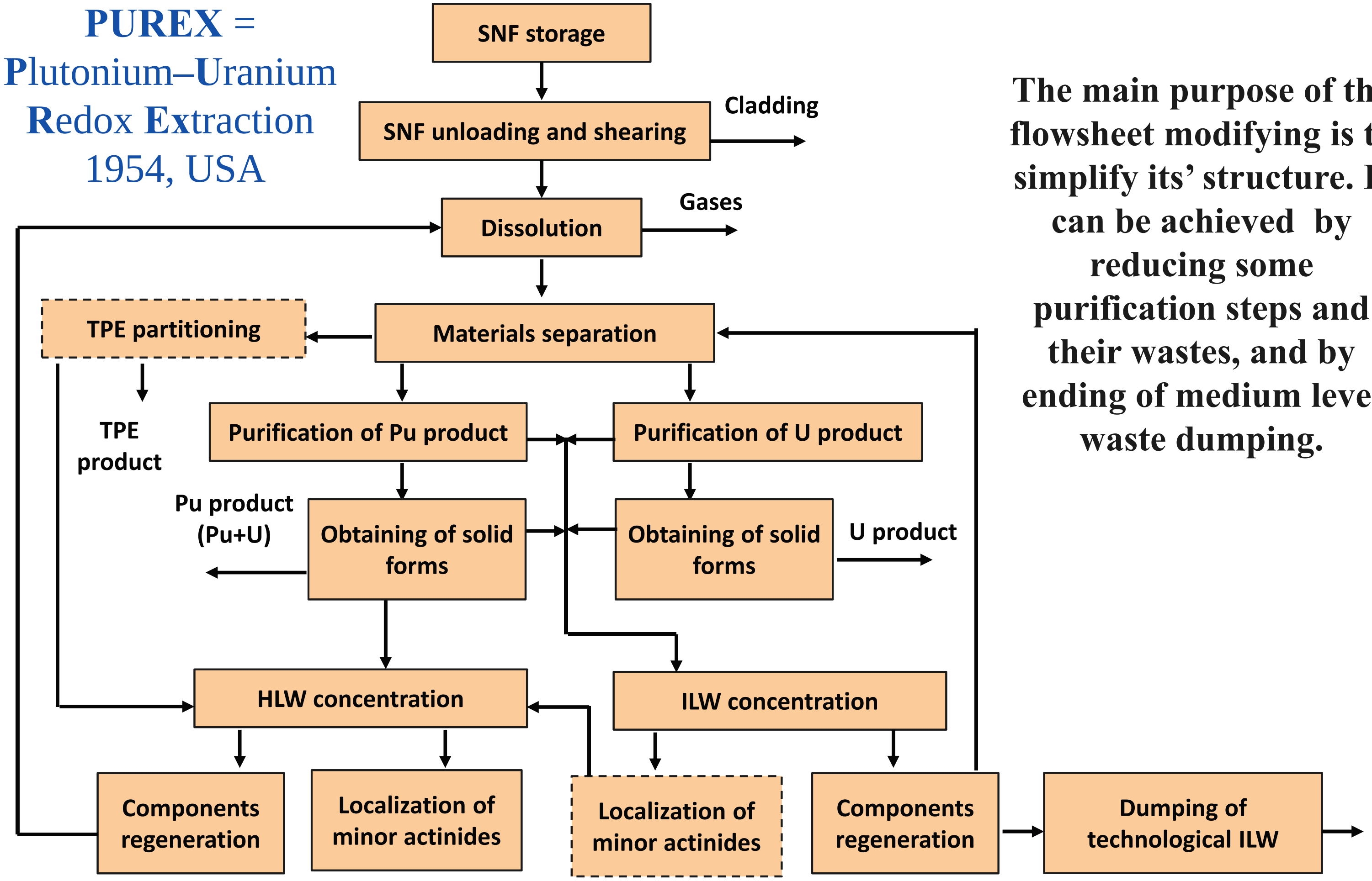
Classical flowsheet for reprocessing SNF

PUREX =
Plutonium–**U**ranium
Redox **Ex**traction
1954, USA



SNF storage

SNF unloading and shearing

Cladding

Dissolution

Gases

TPE partitioning

Materials separation

TPE product

Purification of Pu product

Purification of U product

Pu product (Pu+U)

Obtaining of solid forms

Obtaining of solid forms

U product

HLW concentration

ILW concentration

Components regeneration

Localization of minor actinides

Localization of minor actinides

Components regeneration

Dumping of technological ILW

The main purpose of the flowsheet modifying is to simplify its' structure. It can be achieved by reducing some purification steps and their wastes, and by ending of medium level waste dumping.

The negative influence of Tc and Np

The negative influence of technetium on the SNF reprocessing (Purex process)

1) Tc is a catalyst in hydrazine oxidation by the nitric acid;
2) Tc hinders the process of uranium and plutonium reduction separation;
3) Strictly limited Tc content in the final products of SNF reprocessing due to its oxide volatility: U & Pu purification factor from Tc should be about 1000.

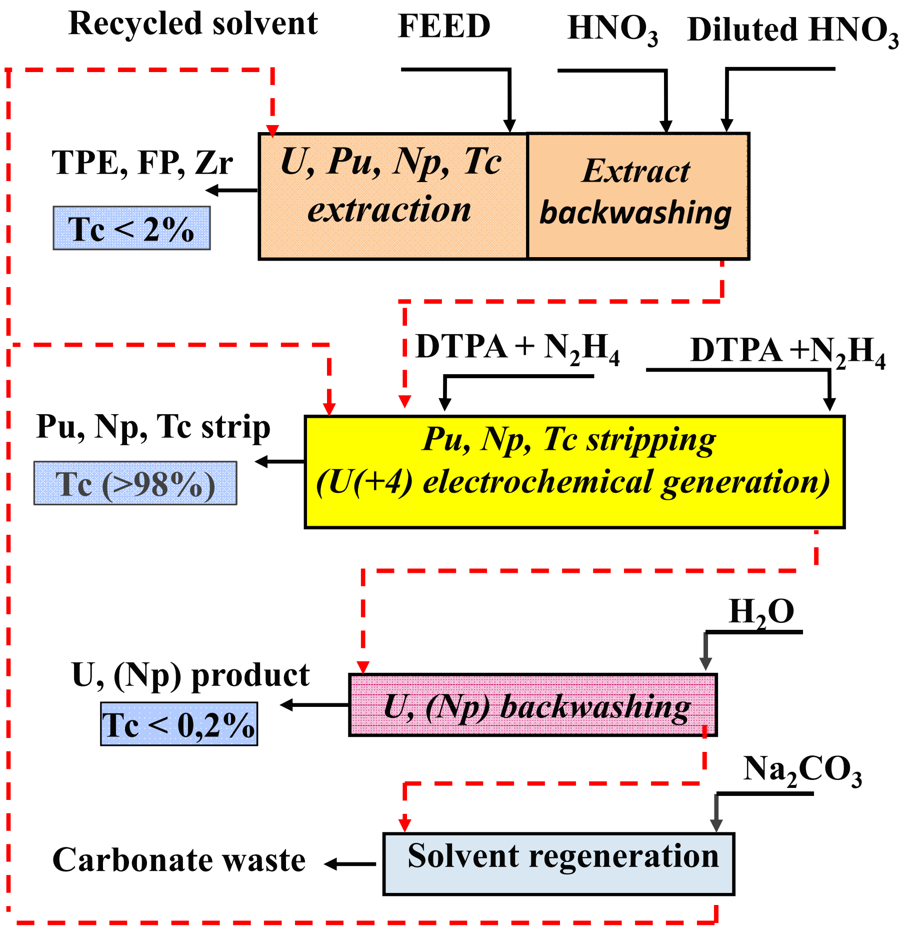
The negative influence of Neptunium on the SNF reprocessing (Purex process)

1) Strictly limited Np content in the final products of SNF reprocessing;
2) Due to the low distribution coefficients, Np distributes between all streams in the first extraction cycle.

The localization of technetium should be considered as a complex task, taking into account Tc co-extraction with U and Zr.
At the same time Np distribution should be also considered, because joint Pu and Np strip might be suitable only for fast reactor fuel preparation, while for thermal reactor Pu and Np separation is required.

The goal of this work was to consider different variants of SNF reprocessing flowsheets which allow to separate and localize in any products of the first extraction cycle.

Joint Pu, Np and Tc stripping (RT-1 plant, PA «Mayak»)



Recycled solvent

FEED

HNO_3

Diluted HNO_3

TPE, FP, Zr

Tc < 2%

U, Pu, Np, Tc extraction

Extract backwashing

DTPA + N_2H_4

DTPA + N_2H_4

Pu, Np, Tc strip

Tc (>98%)

Pu, Np, Tc stripping
(U(+4) electrochemical generation)

H_2O

U, (Np) product

Tc < 0,2%

U, (Np) backwashing

Na_2CO_3

Carbonate waste

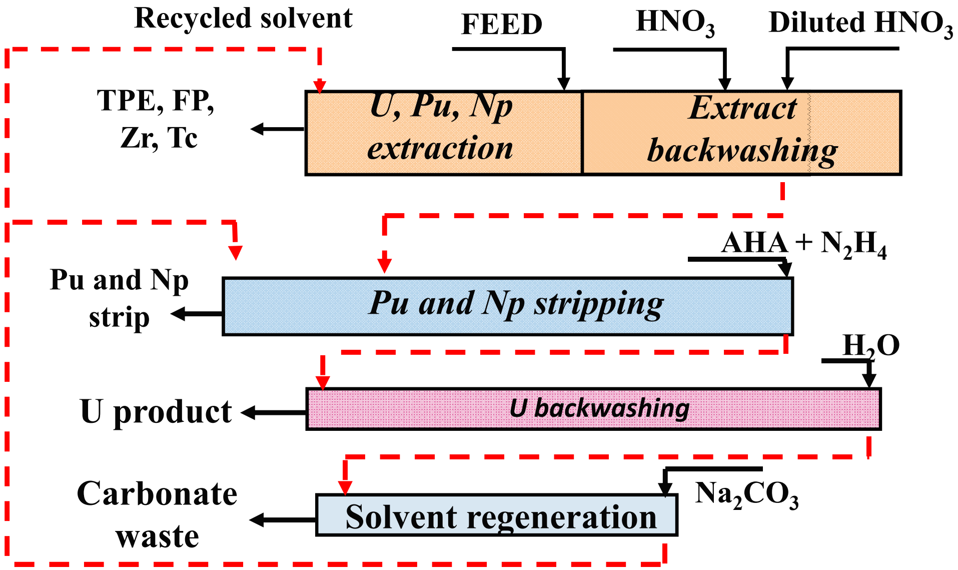
Solvent regeneration

Main drawback

Sporadic plutonium accumulation in the contactor unit and formation of hardly soluble Tc(+4) compounds with DTPA

Pu and Np separation from Tc (as well as Pu/Np partitioning) requires additional purification cycle.

Tc withdrawal to the raffinate (RT-1)



Recycled solvent

FEED

HNO_3

Diluted HNO_3

TPE, FP, Zr, Tc

U, Pu, Np extraction

Extract backwashing

$AHA + N_2H_4$

Pu and Np strip

Pu and Np stripping

H_2O

U product

U backwashing

Carbonate waste

Solvent regeneration

Na_2CO_3

Purification factor of U, Pu and Np extract from Tc is more than 40.

Pu and Np strip might be suitable for the preparation of fast reactor MOX-fuel.

Atomic energy, 2013, V. 114, № 5, p. 279-285.

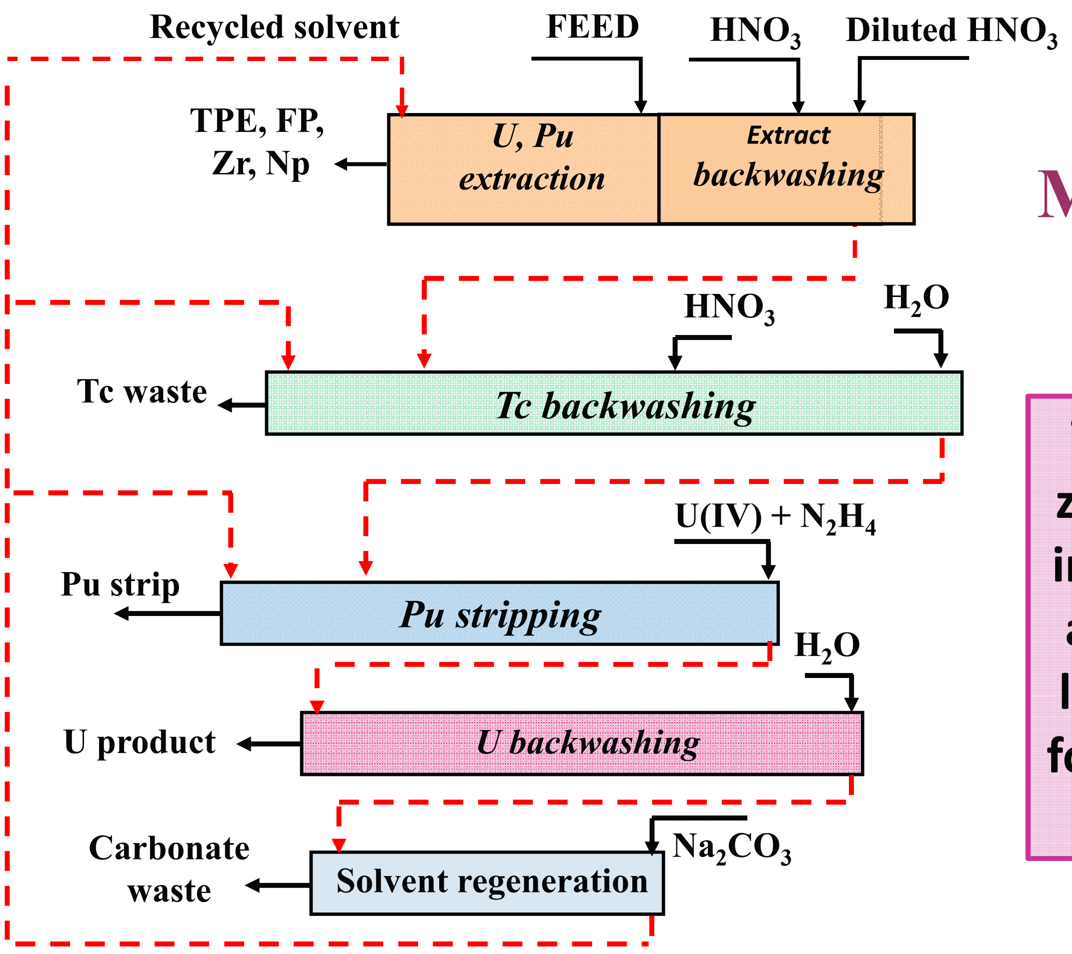
Processing of simulate SNF AMB (OM-9) and VVER-440 mixture in a ratio 1:3

Product	HNO_3, mol/L	Concentration of main components						
		U, g/L	Pu, mg/L	Np, mg/L	Tc, mg/L	Zr, mg/L	Mo, g/L	Mg, g/L
Feed	4,4	230	30	350	300	1000	5,0	6,0
Raffinate	3,9	<1	<0,5	-	170	560	2,8	3,4
U, Pu, Np solvent prod.	-	85	10	130	<2	<5	-	-

Processing of VVER-1000 "hot" simulate solution

Product	HNO_3, mol/L	Relative content of main components, %					Σα, MBq/L	Σγ, Bq/L
		U	Pu	Np	Tc	Mo		
Feed	3,2	100	100	100	100	100	$3,3*10^4$	$1*10^4$
Raffinate	3,7	<0,01	<0,1	<1	>99,9	99,9	600	3,4
U, Pu, Np solvent prod.	-	>99,9	>99,9	>99	<0,1	<0,1	$9,9*10^3$	2

Np withdrawal to the raffinate (RT-1)



Main drawback

The precipitation of zirconium molybdate in the head contactor and necessity to use large amount of salt-forming and corrosive reagents

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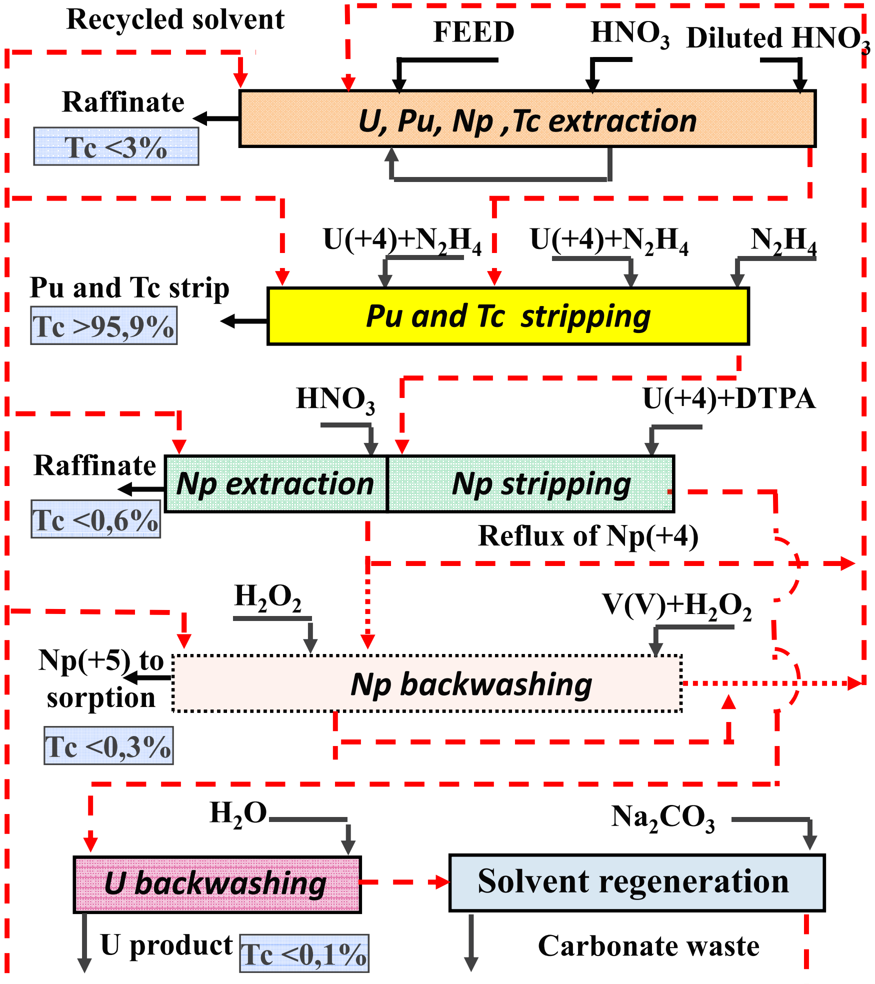
Joint Pu and Tc stripping (project of RT-1 upgrade)



Recycled solvent

FEED

HNO_3

Diluted HNO_3

Raffinate

Tc <3%

U, Pu, Np ,Tc extraction

$U(+4)+N_2H_4$

$U(+4)+N_2H_4$

N_2H_4

Pu and Tc strip

Tc >95,9%

Pu and Tc stripping

HNO_3

$U(+4)+DTPA$

Raffinate

Tc <0,6%

Np extraction

Np stripping

Reflux of Np(+4)

H_2O_2

$V(V)+H_2O_2$

Np(+5) to sorption

Tc <0,3%

Np backwashing

H_2O

Na_2CO_3

U backwashing

Solvent regeneration

U product

Tc <0,1%

Carbonate waste

Real VVER-440 solution

(39 GW*day/ton burn-up; 3 years storage)

Product	Concentration of main components					
	HNO_3, mol/L	U, g/L	Pu, mg/L	Np, mg/L	Tc, mg/L	^{106}Ru, MBq/L
Feed	3,0	210	2200	62	172	$4*10^5$
Raffinate	3,5	0,01	0,2	0,03	6	-
Pu and Tc strip	1,5	0,03	4900	1,5	340	68
Raffinate after Np extraction	2,6	0,002	0,4	0,1	0	20
Np backwash	0,9	0,6	0,03	2300	1,0	0,6
Np solvent product	-	45	-	620	-	0,14
U product	0,06	80	0,0007	0,03	0,5	0,14
Carbonate waste	-	0,04	0,1	-	-	7

Trials were carried out in collaboration with PA «Mayak» in 1986.
Radiation safety, 1998, № 4, p. 27-32

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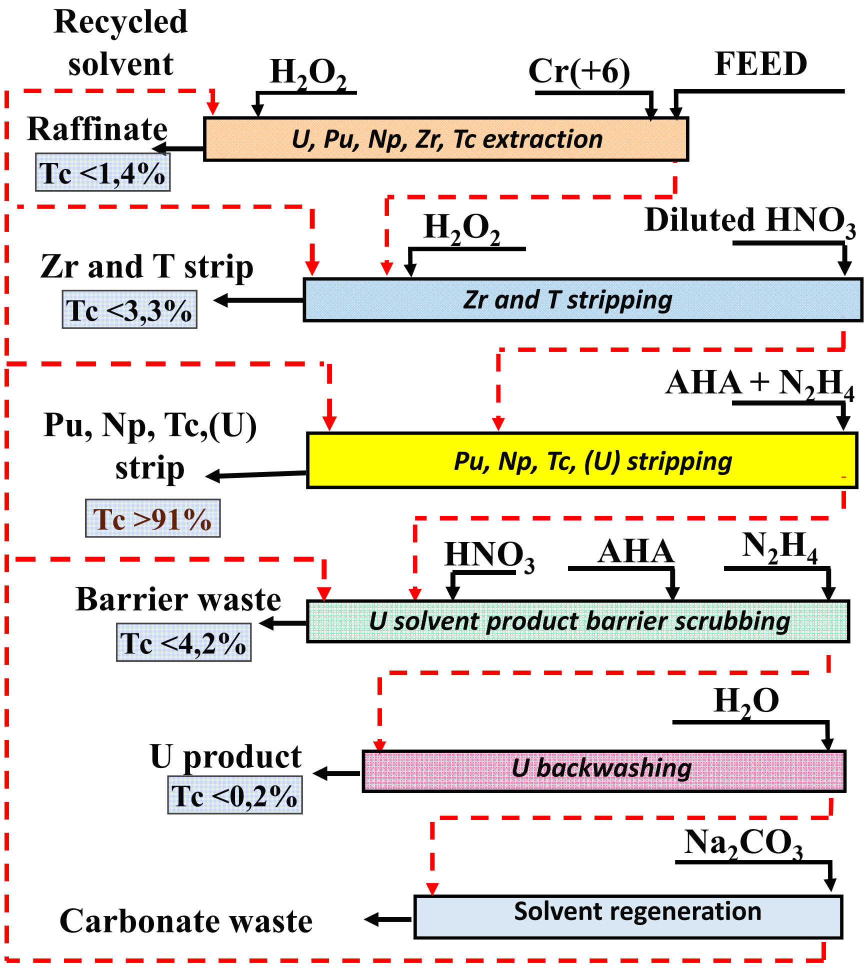
Joint Pu, Np and Tc stripping (Simplified Purex 1)

1st extraction cycle flowsheet of Experimental Demonstration Centre (EDC)



Tc stripping efficiency in the centrifugal contactors was only 90%, and the rest slipped to the barrier block.

Product	Concentration of main components					
	HNO_3, mol/L	U, g/L	Pu, mg/L	Np, mg/L	Tc, mg/L	Zr, mg/L
Feed	1,9	550	7000	420	660	1900
Raffinate	0,7	0,1	1	1	10	200
Zr and T strip	2,3	1	2	4	40	3100
U, Pu, Np, Tc solv. prod.	-	94	36	50	40	0
Pu, Np, Tc strip	0,7	0,04	390	560	380	-
U solvent product	-	87	<0,1	<1	~5	-
Barrier waste	0,9	0,1	0,2	~1	35	-
U product	-	79	<0,2	<1	<0,1	-

Σγ, MBq/L	Feed	Pu, Np, Tc strip	U product
	3,1E+6	25	0,01/4 (^{237}U)

Patents RU:2012075 (1994); 2454741 (2012); 2454742 (2012)

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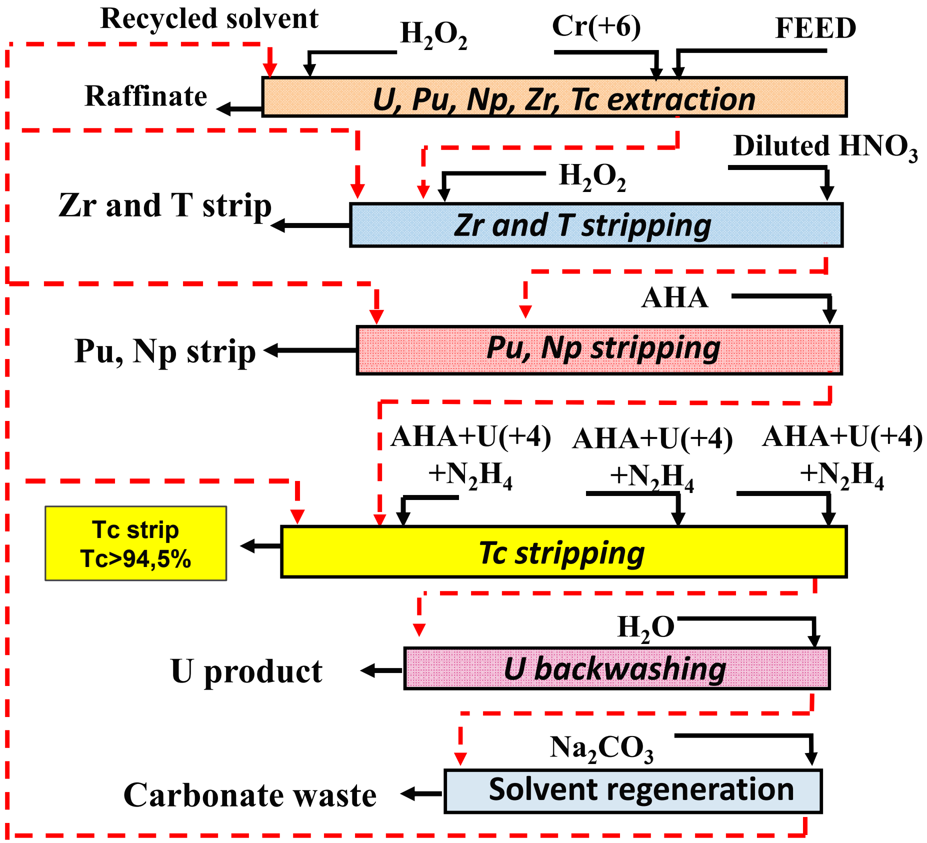
Tc stripping in the barrier unit (Simplified Purex 2)



Recycled solvent

H_2O_2

Cr(+6)

FEED

Raffinate

U, Pu, Np, Zr, Tc extraction

Diluted HNO_3

H_2O_2

Zr and T strip

Zr and T stripping

AHA

Pu, Np strip

Pu, Np stripping

AHA+U(+4) $+N_2H_4$

AHA+U(+4) $+N_2H_4$

AHA+U(+4) $+N_2H_4$

Tc strip
Tc>94,5%

Tc stripping

H_2O

U product

U backwashing

Na_2CO_3

Carbonate waste

Solvent regeneration

VVER-1000 model solution processing

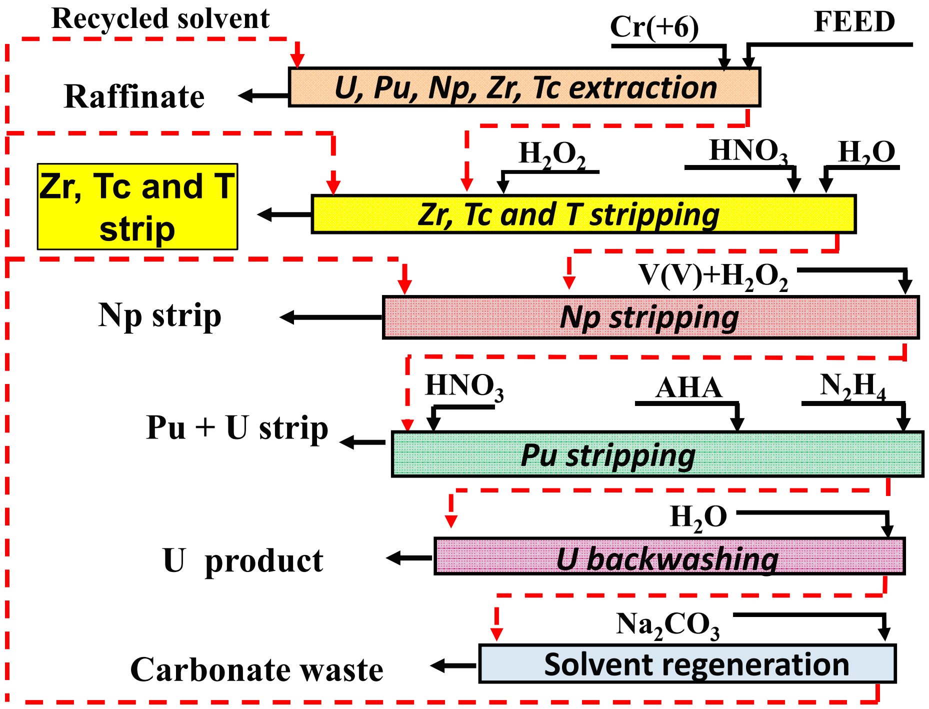
Product	HNO_3 mol/L	Main components, %				
		U(+6)	U(+4)	Pu	Np	Tc
Feed	1,9	100	-	100	100	100
Raffinate	0,7	0,02	-	<0,01	0,2	1,3
Zr and T strip	2,3	0,01	-	0,02	0,4	3,3
Pu, Np strip	0,3	0,004	-	99,96	98,4	0,6
Tc strip	1,2	0,1	<1	0,002	0,15	94,5
U product	0,1	99,95	0	0,01	0,75	0,2
Carbonate waste	-	0,01	0	0,0002	<0,1	-

Patent RU: 2012075 (1994).
Application for an invention 2013108331

It is possible to improve the purification of U from Tc and to obtain uranium product corresponding to sublimate plant standards on the Tc content using mixer-settlers (MSC) and electrochemical generation of U(+4).

Tc localization with Zr and selective Np stripping

(SuperPurex 1)



Recycled solvent
Cr(+6)
FEED
Raffinate
U, Pu, Np, Zr, Tc extraction
H_2O_2
HNO_3
H_2O
Zr, Tc and T strip
Zr, Tc and T stripping
$V(V)+H_2O_2$
Np strip
Np stripping
HNO_3
AHA
N_2H_4
Pu + U strip
Pu stripping
H_2O
U product
U backwashing
Na_2CO_3
Carbonate waste
Solvent regeneration

Main drawbacks

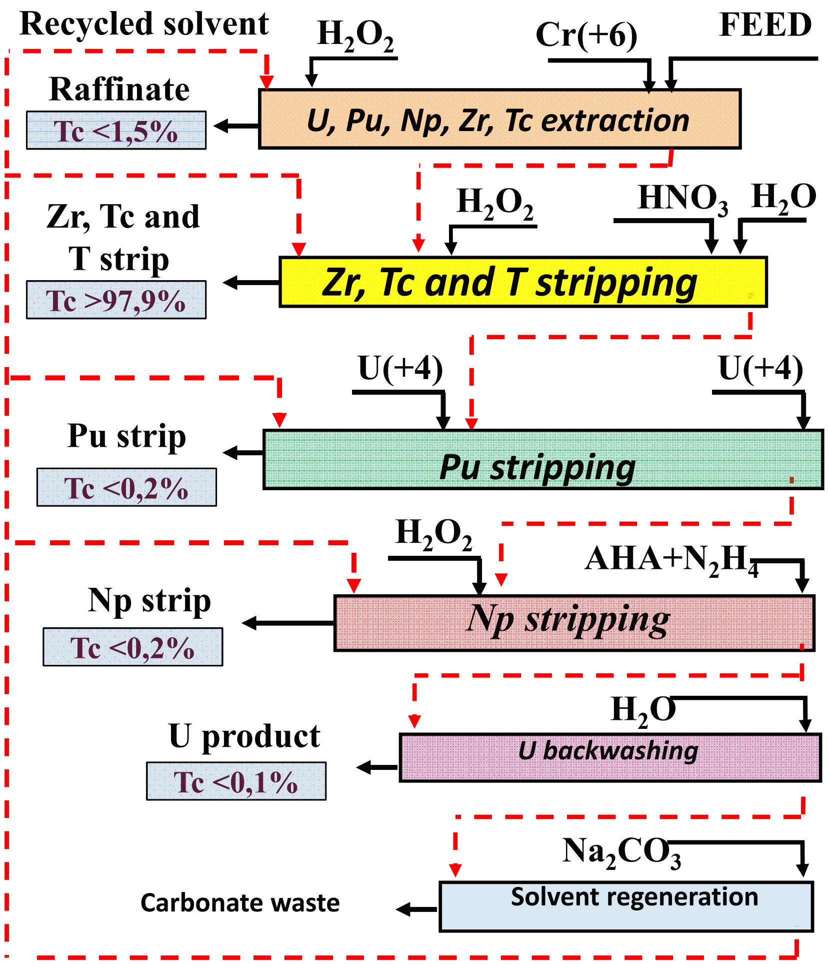
The lack of barrier unit (the 7-unit flowsheet) is needed to get U product without Pu traces.

Real SNF VVER-1000 solution processing

Product	HNO_3, mol/L	Relative content of main components, %						
		U	Pu	Np	Tc	Zr	Σα, MBq/L	Σγ, MBq/L
Feed	1,9	100	100	100	100	100	142000	140000
Raffinate	0,7	0,01	0,01	0,2	1,8	9,8	67000	104000
Zr, Tc, T strip	4,5	<0,02	<0,01	<0,1	>96	90,2	188	2810
Np strip	0,9	<0,01	0,05	99,8	<1	0	31	580
Pu + U strip	0,7	2	99,7	0,08	<1	-	71000	6,8
U product	0,1	99,9	0,2	<0,05	<0,1	-	202	2,8
Carbonate waste	-	<0,01	<0,01	-	-	-	5,2	1,3

Tc localization with Zr and selective Np stripping

(SuperPurex 2)



Recycled solvent

H_2O_2

Cr(+6)

FEED

Raffinate

Tc <1,5%

U, Pu, Np, Zr, Tc extraction

Zr, Tc and T strip

Tc >97,9%

H_2O_2

HNO_3

H_2O

Zr, Tc and T stripping

U(+4)

U(+4)

Pu strip

Tc <0,2%

Pu stripping

H_2O_2

AHA+N_2H_4

Np strip

Tc <0,2%

Np stripping

U product

Tc <0,1%

H_2O

U backwashing

Carbonate waste

Na_2CO_3

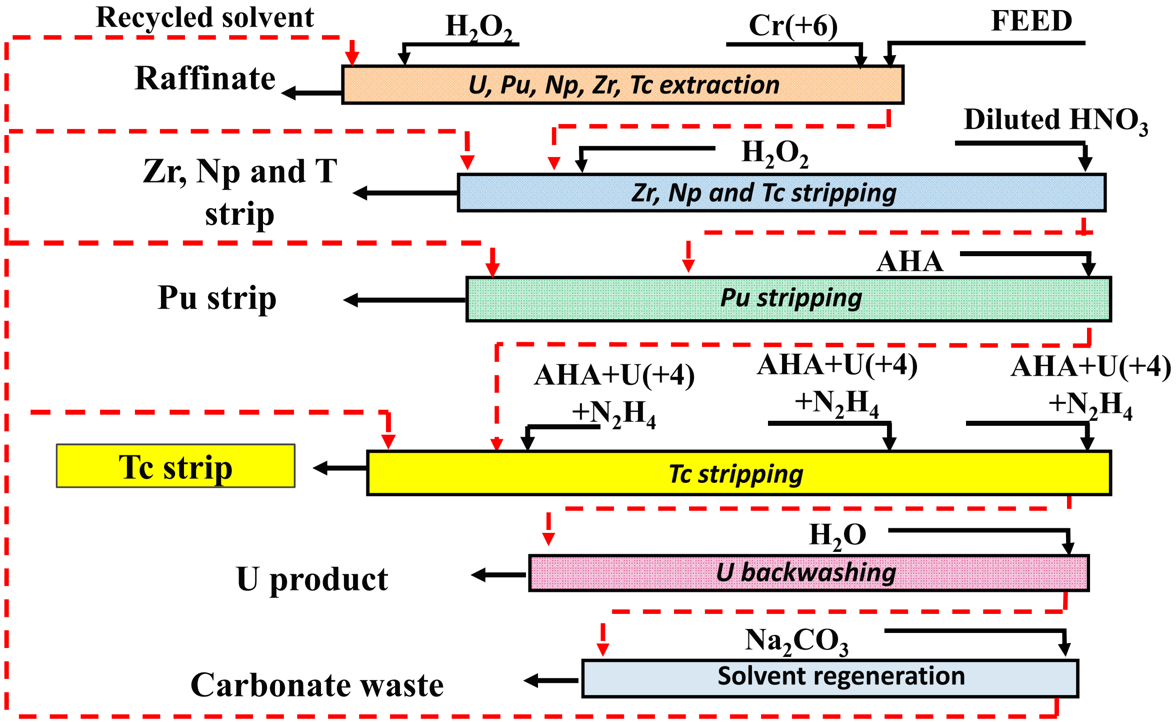
Solvent regeneration

Real VVER-1000 (burn-up is 70 GW*day/ton) solution processing

Product	HNO_3 mol/L	Main components				
		U, g/L	Pu, mg/L	Np, mg/L	Tc, mg/L	Zr
Feed	1,8	424	5700	400	270	1560
Raffinate	0,8	<0,01	3	1	<10	42
Zr, Tc, T strip	4,5	<0,01	5	3	80	540
Pu strip	1,3	<0,1	6100	<5	<2	-
Np strip	0,75	<0,01	10	490	<2	-
U product	0,2	60	<0,1	0,1	-	-

Product		
	Σα, GBq/L	Σγ, GBq/L
Feed	430	3800
Raffinate	470	3700
Zr, Tc, T strip	1,9	9,2
Pu strip	125	0,1
Np strip	0,25	0,01
U product	0,006	0,01 (^{237}U)

Np localization with Zr and selective Tc stripping
(REMIX)



Product	HNO_3, mol/L	Main components				
		U, g/L	Pu, mg/L	Np, mg/L	Tc, mg/L	Zr, mg/L
Feed	1,9	550	220	400	660	1900
Raffinate	0,8	<0,01	<0,1	0,7	10	120
Zr, Np, T strip	1,8	<0,01	0,3	360	60	2600
Pu strip	0,8	<0,01	312	80	1,2	<20
Tc strip	0,8	0,12	1,8	2,7	630	-
U product	0,08	72	<0,01	<0,1	0,04	-

Summary table of checked variants of technetium and neptunium localization in the first extraction cycle

Product	Flowsheet variant								
	RT-1				SimplePurex		SuperPurex		Remix
Variant	*№ 1*	*№ 2*	*№ 3**	*№ 4*	*№ 1*	*№ 2*	*№ 1***	*№ 2*	*№ 1*
Number of units	*4*	*4*	*5*	*5*	*6*	*6*	*6*	*6*	*6*
Raffinate	Zr	Zr+Tc	Np, Zr, (Tc)	Zr	-	-	-	-	-
Strip 1	-	-	Tc	-	Zr	Zr	Zr+Tc	Zr+Tc	Zr+Np
Strip 2	Pu+Np+Tc	Pu+Np	Pu	Pu, Tc	Pu+Np+Tc	Pu+Np	Np	Pu	Pu
Strip 3	-	-	-	Np	Barrier	Tc	Pu+(U)	Np	Tc
U product	U	U	U	U	U	U	U	U	U
Carbonate waste	Contains no main components								
Kind of MOX fuel that can be prepared from the obtained products	-	For fast reactors	-	-	-	For fast reactors	For thermal reactors	For fast and thermal reactors	For fast and thermal reactors

* - Zirconium molybdate precipitation in the U and Pu extraction unit;

** - U product with Pu traces .

CONCLUSION

- Completely purification of actinide products from Technetium, and if it is necessary, from Neptunium, could be obtained by various ways within the 1st cycle with the use of six extraction units, changing the content and flowrate of stripping solutions.
- Among all tested flowsheets of SNF reprocessing today REMIX flowsheet was the most perspective due to its generality.

Thank you for your kind attention!

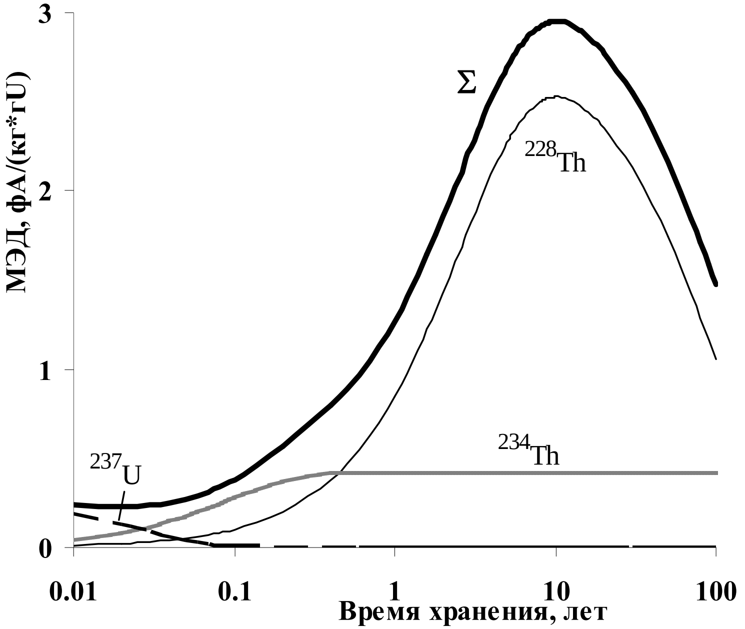
More details are given in the fresh paper:

N.D. Goletsky, B.Ya. Zilberman, Yu.S. Fedorov, A.S. Kudinov, A.A. Timoshuk, L.V. Sytniuk, E.A. Puzikov, S.A. Rodionov, A.P. Krinitsyn, V.I. Ryasantsev, D.V. Ryabkov.

Ways of Technetium and Neptunium Localization in Extraction reprocessing of Spent Nuclear Fuel from Nuclear Power Plants.

Radiochemistry, 2014, v. 56, No 5, p. 501 - 514

The change of exposure dose power of Uranium nitrate hexahydrate melt during the storage



Burn-up 50 GW day/t SNF WWER-1000;
5 years storage

The ^{228}Th accumulation, as a daughter isotope of ^{232}U, limits the time of regenerated uranium use and makes difficult it's enrichment with ^{235}U. For the same reason (^{236}Pu decay and, as a result, ^{232}U formation) stored pluronium requires deep purification before it's re-fabrication into MOX-fuel for fast reactors.

The nature of the technetium volatile species formed during vitrification in borosilicate glass

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The vitrification of sodium pertechenate into borosilicate glass was performed under air at 1100 °C. A glass with a composition similar to the one developed for vitrification of the low activity waste at the Hanford site was used. During the process, a red volatile species was observed above 600 °C. The nature of the red species was studied by XAFS spectroscopy. The EXAFS results indicate the environment of the absorbing atom to be constituted by 2.9(6) O atoms at 1.73(2) Å, 2.2(4) O atoms at 2.02(2) Å, and 0.8(2) O atoms at 2.18(2) Å. The results are consistent with the presence of a mononuclear species with a structure closely related to the one of $TcO_3(OH)(H_2O)_2$. The mechanism of formation of $TcO_3(OH)(H_2O)_2$ and the role of water on the nature of the volatile technetium species during vitrification were discussed.

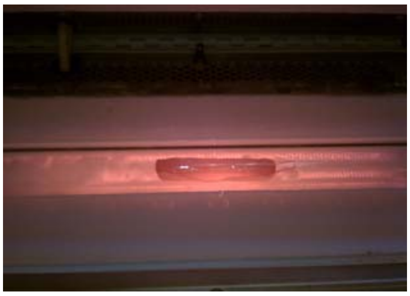
The Nature of Technetium Volatile Species formed during Vitrification in Borosilicate Glass

By: Bradley C. Childs, Frederic Poineau, Ph.D., Alfred Sattelberger Ph.D., and Ken Czerwinski, Ph.D.

8th International Symposium on Technetium and Rhenium

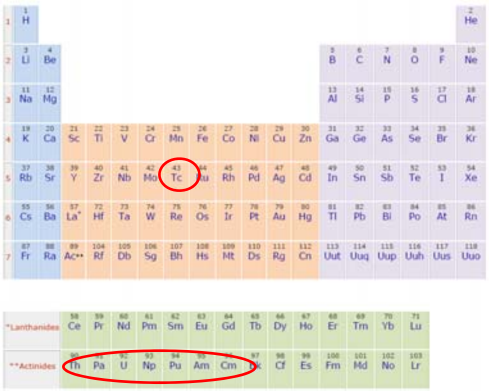
Overview

- **Introduction**
- **Experimental Methods**
- **Results**
- **Conclusion**
- **Future Work**



Glass with Tc at 1100 °C under air

Radioelement Chemistry



- 118 total elements
  - 117 recently discovered
    - UNLV involved in discovery
  - 81 stable, 37 radioactive (≈ 30 % of all elements)
- Exploration of radioelements expands understanding of period trends

- **Technetium**
  - 2nd row transition element Macroscopic chemistry with ^{99}Tc
    - half life 2.1E5 a
  - Range of oxidation states
    - 7^+ to 1^-

- **Actinides**
  - Filling 5f electron shell
  - Range of isotopes available for chemistry
    - Different half lives
  - Varied oxidation states

Applied and Fundamental Technetium Chemistry at UNLV

Chemistry relevant to the nuclear fuel cycle and radiopharmaceuticals

-Separations and waste forms

Synthetic and coordination chemistry of ^{99}Tc

-Metal-metal bonded compounds, binary halides, and oxides

U/Tc separation

Fundamental linked with applied chemistry

Capabilities

Synthesis:
Ability to work with high activity: (mg to g of ^{99}Tc)
glove box, Schlenk line, HEPA-filtered fume hoods
Characterization:
Spectroscopy: UV-Vis, IR, NMR, XRD & XAFS
Diffraction and First principles calculations

Tc laboratory at UNLV

Technetium

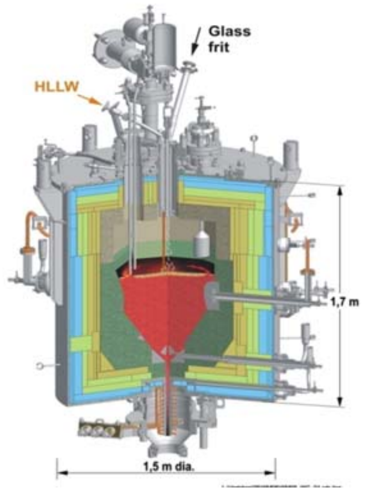
- ^{99}Tc is a fission product from ^{235}U
  - $T^{1/2} = 2.13\times10^5$ years
  - $E_{\beta^-} = 294$ keV
- Technetium has 9 oxidation states
  - [+7 to -1]
- Pertechnetate (TcO_4^-) anion mobile in environment
- High temperature conditions can affect retention (10 % - 90 %) in glass
- Tc(VII) is volatile
  - TcO_2 sublime at 900 °C
  - Tc_2O_7 boils at 311 °C
- Approximately 2 tons of ^{99}Tc produced from U.S. nuclear industry per year
- Stable waste form is needed
  - Alloys
  - Oxides

NH_4TcO_4 with TcO_2
Starting compound

Hanford Site

- Fit criteria (8) for site selection of Manhattan Project
- Primary site for production of plutonium
- Approximately 1500 kg of ^{99}Tc
- Tc (VII) dominate oxidation state

Introduction

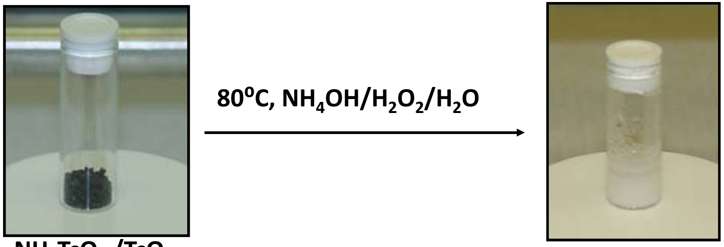


- The Hanford Tank Waste Treatment and Immobilization Plant (WTP) plans to vitrify waste for disposal
- Cold cap studies
  - Batch material goes from solid to liquid
  - Evaluate change in Tc speciation
  - Examined from 600 °C to 1100 °C
- Perform batch and glass synthesis with Tc
- Evaluate Tc speciation
- Main issue in process is Tc volatilization

[1] Ian L. Pegg, Keith S. Matlack, and Isabelle S. Muller: Technetium Retention During LAW Vitrification, DOE EM Waste Processing Technical Exchange 2010.

Experimental Methods

Synthesis of $NaTcO_4$



$80^oC, NH_4OH/H_2O_2/H_2O$

NH_4TcO_4 /TcO_2

NH_4TcO_4

- NH_4TcO_4 added to Dowex 50WX4-100 and eluted in water
  - 15 mL of $HTcO_4$ solution obtained
- Neutralized with 1.8 mL $NaHCO_3$
- Concentration determined by UV-Visible spectroscopy
- 0.171 M solution of $NaTcO_4$

Batch Preparation

Loading	Weight %	Melting Point
Al_2O_3	5.97	
B_2O_3	9.79	450-510 °C
CaO	2.46	
Fe_2O_3	5.38	
MgO	1.45	
Na_2O	21.27	1132 °C
SiO_2	44.50	1600-1725 °C
TiO_2	1.37	
ZnO	3.43	
ZrO_2	2.94	

1% Tc by mass added to batch

Pt boat used for heating

[1] Thomas May, Matlack k, Isabelle S. Muller, Innocent Joseph, and Ian Pegg: Improved Technetium Retention in Hanford LAW, Glass - Phase 1 Final Report Ref RPP-RPT-45887, Rev.

Tube Furnace Set Up

- ➢ Gas atmosphere introduced from a tank
- ➢ Water trap used to ensure no Tc leaving system

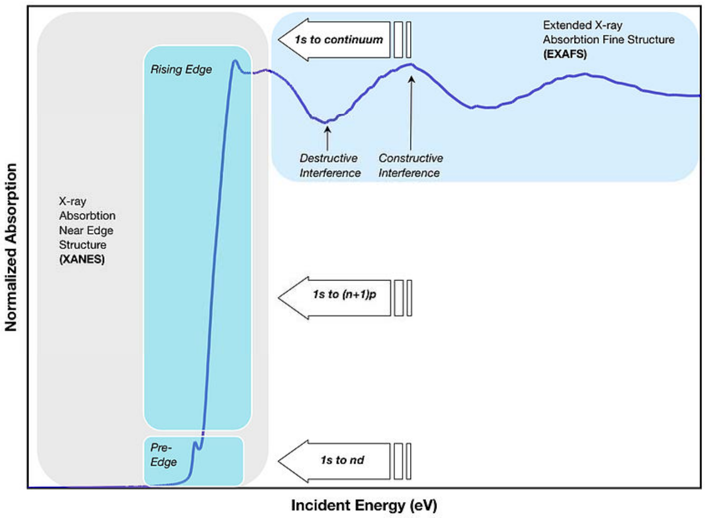
Lindberg Blue M Mini Mite M#
TF55035A-1
Tube furnace max temp: 1100 °C

XAFS Sample Preparation

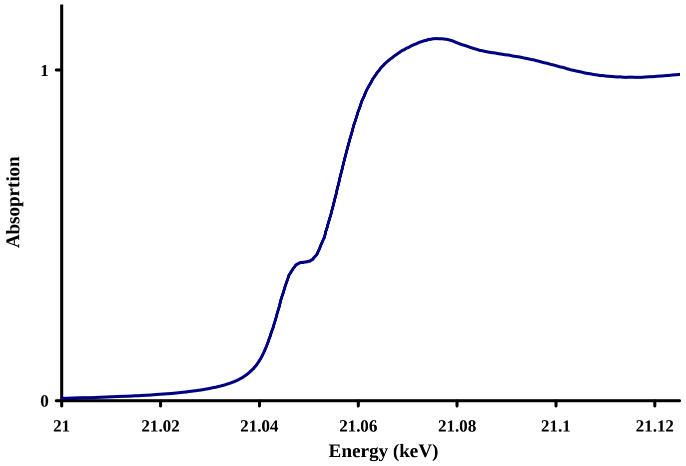
- 1% Tc by mass
- ANL XAS solid sample holders
- No boron nitride
- Samples placed in holders as solid
- Kapton placed over windows
- Experiment performed at the APS/ANL-12 BM

Results

XAFS Spectroscopy

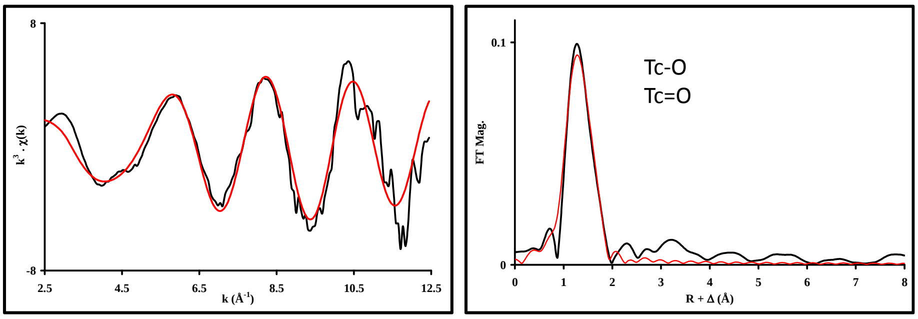


Results XANES



XANES spectrum of the volatile red species. Tc K-edge (21.044 keV) in fluorescence mode. Tc (VII) main result

Results EXAFS



Fitted k^3-EXAFS (left) spectrum and Fourier transform (right) of the k^3–weighted EXAFS spectrum of the red species. Experimental data in red and fit in black. Spectra was fit using structure

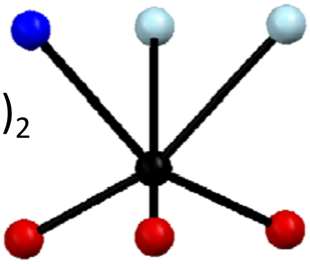
Structure was fit using $Re_2O_7 \cdot 2H_20$ model

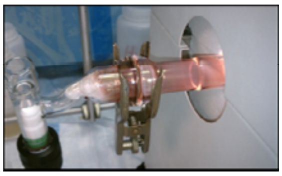
Results

Scattering	C.N	Distance (Å)	s^2 (Å^2)
Tc=O	2.9(6)	1.73(2)	**0.0022**
Tc-O	2.2(4)	2.02(2)	**0.004**
Tc-O	**0.8(2)**	**2.18(2)**	**0.004**

Table above EXAFS fit parameters obtained for the red volatile species. $\Delta E_0 = 0.07$ eV.

$TcO_3(OH)(H_2O)_2$





Proposed Formation of $TcO_3(OH)(H_2O)_2$

- **$TcO_3(OH) + 2\ H_2O \rightarrow TcO_3(OH)(H_2O)_2$**
  - **Tc transported as $TcO_3(OH)$ in gas phase and condenses**

1. $Tc(IV) + O_2 \rightarrow Tc_2O_7$
   - $Tc_2O_7 + 3H_2O \rightarrow 2\ TcO_3(OH)(H_2O)_2$
     - Hydrolysis of Tc_2O_7
2. $NaTcO_4 + 3H_2O \rightarrow TcO_3(OH)(H_2O)_2 + NaOH$
   - Hydrolysis of $NaTcO_4$
3. $2NaTcO_4 \rightarrow Na_2O + Tc_2O_7$
   - Thermal dehydration followed by hydrolysis

Conclusions and Future Work

- Vitrification of NaTcO4 into borosilicate glass performed under air at 1100 °C.
  - Red volatile species observed above 600 °C.
- XAFS results are consistent with $TcO_3(OH)(H_20)_2$
- All reactions involve Tc(VII) species with water.
- Perform same synthesis under inert and dry atmosphere.

Acknowledgements

- Trevor Low and Julie Bertoia
- Tc Group
- UNLV Radiochemistry Program
- Improved Retention of Tc in LAW Glass, Pacific Northwest National Laboratory, DE-AC05-76RL01830
- Advanced Photon Source use was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. DE-AC02-06CH11357

Questions?

Electrochemical studies of technetium-ruthenium and rhenium-ruthenium alloys in nitric acid: implications for the long term behavior of metallic technetium waste forms.

Romina Farmand[1], Frederic Poineau[1], Daniel J. Koury[1], David G. Kolman[2], Gordon D. Jarvinen[3], and Kenneth R. Czerwinski[1].

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[3] Seaborg Institute, Los Alamos National Laboratory, Los Alamos, NM 87545, USA

In order to predict the durability of metallic technetium waste form, understanding of the corrosion properties of technetium metal is of importance. One parameter that needs to be considered in those predictions is the building of ruthenium that occurs from the decay of technetium. In this context, the corrosion behavior of technetium-ruthenium and rhenium-ruthenium alloys (rhenium was used as a technetium surrogate) alloys were studied in nitric acid. Technetium-ruthenium and rhenium-ruthenium alloys with various compositions were prepared and their corrosion behavior was studied by electrochemical methods in 1M HNO_3.

Dissolution potentials of the alloys were determined by linear voltammetry. Result shows that the dissolution potential of the alloys increase with the ruthenium content. In order to understand the dissolution mechanism, electrolysis experiments above the dissolution potential were performed; the corrosion products of the alloys were characterized on the surface of the electrodes by scanning electron microscopy and Energy dispersive X-ray spectroscopy and in solution by UV-visible spectroscopy and electrospray ionization mass spectrometry. The speciation of technetium, rhenium and ruthenium was studied after dissolution of the alloys at 1.2 V/ (Ag/AgCl). Results show the formation of permetalates for rhenium and technetium and RuO_4.

Electrochemical studies of rhenium-ruthenium alloys in nitric acid: implications for the long term behavior of metallic technetium waste forms

Romina Farmand

UNIVERSITY OF NEVADA LAS VEGAS

Outline

I. Introduction
II. Preparation & Characterization of Re-Ru alloys
III. Preparation of Re-Ru Electrodes
IV. Corrosion studies on Re-Ru & Tc-Ru Electrodes in Nitric Media
V. Characterization of corrosion products
VI. Conclusions
VII. Future Work

Introduction

Background on Technetium

- ^{99}Tc is a major fission product of the nuclear industry(~6% ^{235}U)
  - *Every year in the U.S., about 2 tons of ^{99}Tc is produced
  - *long half-life ($t_{1/2} = 2.1.10^5$ a) and $^{99}Tc \rightarrow {}^{99}Ru + \beta^-$
- In the spent nuclear fuel, technetium is present as the metal and as an alloy with Mo, Ru, Rh, Pd ("epsilon-phases")
- After separation of ^{99}Tc from the spent fuel, ^{99}Tc is plan to be converted to the metal and incorporated into an alloy for long term storage in depository sites
- In the prediction of the long term behavior of the Tc-waste form, building of the Ruthenium from the radioactive beta decay of technetium needs to be considered
- Since Ru is more noble than Tc, Tc-Ru alloys should be more corrosion-resistance than pure Tc metal so study of the effect of Ru on the corrosion behavior of Tc is of importance

Binary Rhenium Ruthenium Alloys

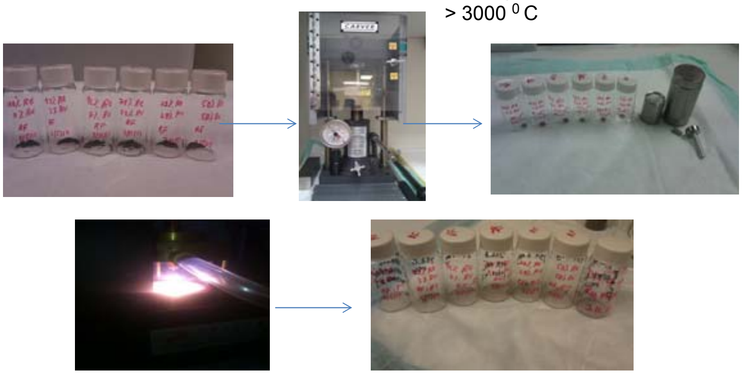
- Re and Ru metals have been studied with metallic alloys
  * Electrochemical behavior of pure Re, Mo, Ru, Tc, Mo-Re alloy, Mo-Ru alloys were studied in nitric media[1]
- Tc-Ru alloys were synthesized and characterized but no corrosion studies were performed[5 ,3]
- In studies of electrochemical properties of binary alloys simulated epsilon-phases, Re is used as a surrogate for Tc

Goal: To prepare and analyze different compositions of Re-Ru & Tc-Ru alloys by Using electrochemical techniques for better understanding of the effect of Ruthenium on the corrosion behavior of Re & Tc metal

Experimental Method

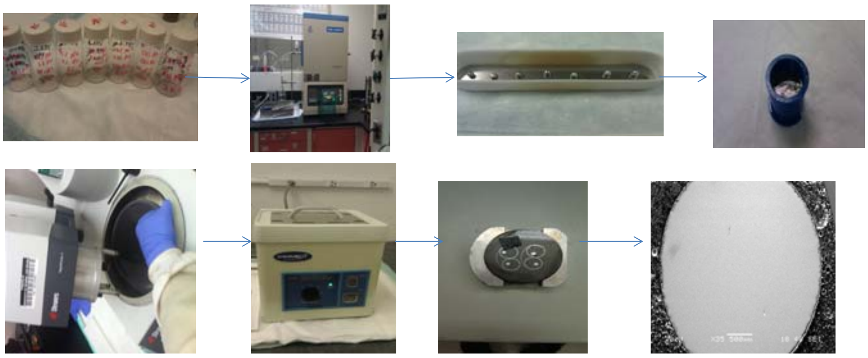
Theoretical Pellet Weight (mg)		Theoretical w.t.% before SEM		Mean Experimental w.t.% After SEM		Repository Age (years)
Re	Ru	Re	Ru	Re	Ru	Re
250	0	100	0	100	0	0
242.5	7.5	98.35	1.65	97.99	2.01	11418
230	20	95.5	4.5	93.14	6.86	39150
190	55	86.7	13.3	80.57	19.43	112986
180	70	82.6	17.4	74.05	26.2	153339
0	100	64.8	35.2	52.52	47.48	300682
		0	100	0	100	None

- Mixture of Re and Ru powders with appropriate masses
- Mixture of powders transferred via a funnel to a 6 mm die
- Used the pellet Presser to press the 6 mm die for 10 mins at 4 metric tons
- Arc-Melted the pellets 3X under a dynamic vacuum and purge of H5 (95% Ar, ,5% H_2)
  - •Re m.p. is 3182 ^{0}C , Ru is 2334 ^{0}C , Arc Temp is > 3000 ^{0}C



Continued Experimental Method

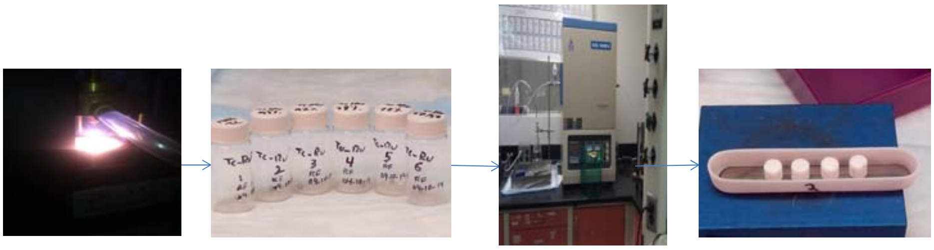
- Re-Ru alloys were annealed in the MTI furnace at 1700 ^{0}C under H-5 for 12 hrs
- Re-Ru alloys were embedded on the resin epoxy
- The epoxy was grinded coarsely with 220 and then finely with 1200 Silica Carbide grits
  - * rinsed the epoxy with Methanol and Water
- The epoxy was polished with diamond abrasives ranging from 9 micron to 1 micron
  - * rinsed the epoxy with Methanol and Water
- Residues left after polishing on Re-Ru alloys were removed by ultra-sonic cleaner for Clear SEM imaging



Continued Experimental Method

Samples (mass mg)	Experimental Compositions Tc: Ru (at. %)	Decay time (years)
a (242.3)	97: 3	10000
b (229.1)	91.7: 8.3	25000
c (234.4)	77.8: 22.2	75000
d (224.4)	71.5: 28.5	100000
e (231.0)	49.8: 50.2	213000

- Mixture of Tc and Ru powders with appropriate masses in the fume hood
- Mixture of powders transferred via a funnel to a 6 mm die in the fume hood
- Used the pellet Presser to press the 6 mm die for 10 mins at 4 metric tons in the glove box
- Arc-Melted the pellets 3X under a dynamic vacuum and purge of H5 (95% Ar, ,5% H_2)

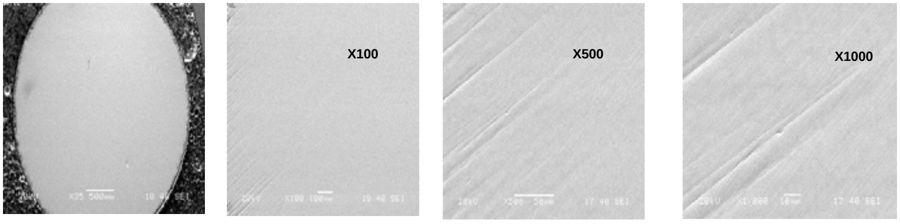


- Arc-melted Tc-Ru alloys were annealed in the MTI furnace at 1700 ^{0}C under H-5 for 12 hrs

Characterization of Re-Ru alloys by EDX/SEM

SEM Images

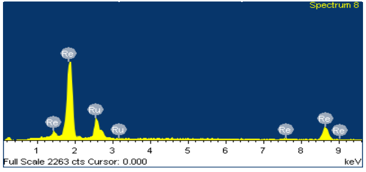
74.05:25.95 w.t.% Re-Ru alloy



- The SEM analysis of Re-Ru alloys with other compositions confirmed the homogeneity of the composition
- Re and Ru are isostructural, having a hexagonal close packed structure (hcp) and form complete solid solution with a single phase

EDX Analysis

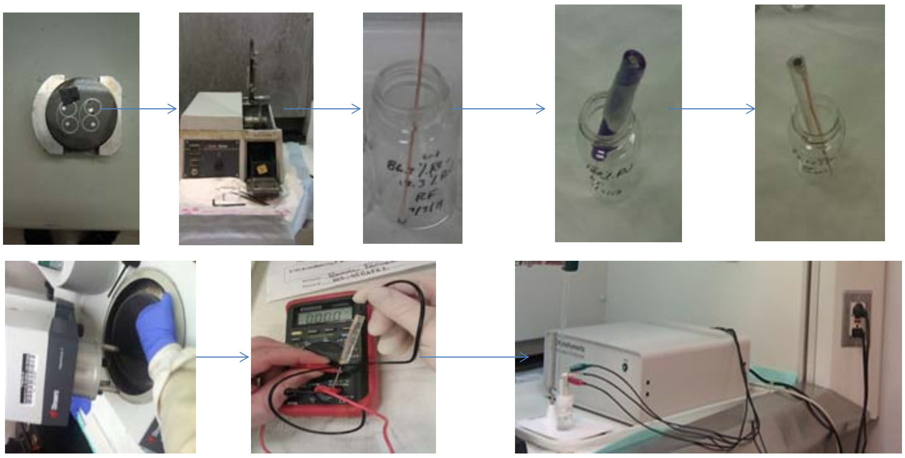
Element	Weight%	Atomic%
Ru L	26.51	39.92
Re M	73.49	60.08
Totals	100.00	



74.05:25.95 w.t.% Re-Ru alloy

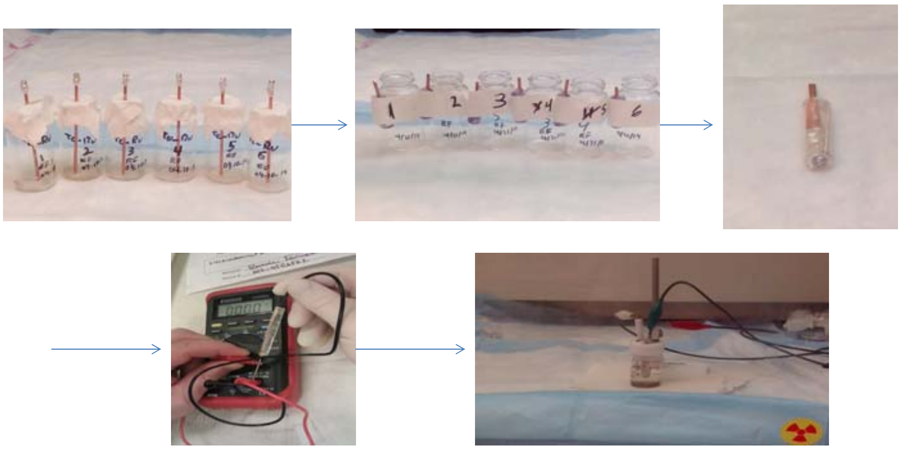
Preparation of Re-Ru Electrodes

- Diamond Saw machine was use to take each of Re-Ru beads out of the epoxy
- Each Re-Ru pellet was connected to a Copper wire (1mm width) with silver epoxy, mounted in a plastic straw (D= 6.25 mm) sealed with a temperature/acid/base epoxy resin
- The electrodes were polished with 220 girt Silican Carbide paper and washed with distilled water and methanol
- The resistance of the electrodes were measured to be 0.00 Ω



Preparation of Tc-Ru Electrodes

- Each Tc-Ru pellet was connected to a Copper wire (1mm width) with silver epoxy, mounted in a plastic straw (D= 6.25 mm) sealed with a temperature/acid/base epoxy resin in the fume hood
- The electrodes were polished with 220 girt Silican Carbide paper and washed with distilled water and methanol in the fume hood
- The resistance of the electrodes were measured to be 0.00 Ω



Preparation of Re-Ru Electrodes

compositions of Re-Ru electrodes determined by EDX spectroscopy

Samples (mass mg)	Experimental Compositions Re: Ru (at. %)
a (233.0)	96.3: 3.7
b (242.1)	87.9: 12.1
c (236.8)	69.0: 31.0
d (239.6)	60.5: 39.5
e (231.6)	37.3: 62.7

- Re-Ru electrodes were prepared and their corrosion behavior investigated in nitric acid by electrochemical techniques

Electrochemical Set up

- Three electrode configuration :
  I.Reference Electrode: Ag/AgCl KCl (1M) [E=+0.235 V/NEH]
  II.Working Electrode: metal or Re-Ru alloy
  III.Auxiliary Electrode: Platinum wire (0.5 mm diameter)

- Electrochemical Cell (volume = 9 ml)
- The Electrodes were connected to a potentiostat controlled by a computer (software CHI660b)

- Electrochemical Techniques used :
  I. Bulk Electrolysis
  II. Linear Sweep Voltammetry

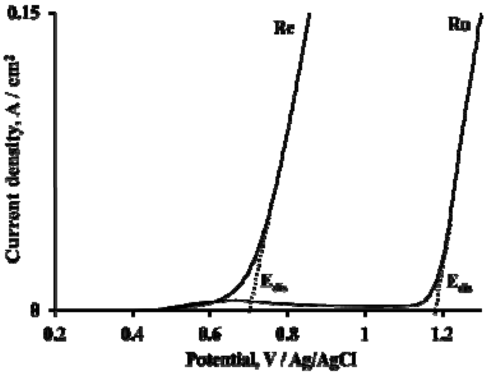
Linear Sweep Voltammetry

- Study of Re metal in 1 M HNO_3

  Re voltammogram shows the current continuously increases with the potential

- Study of Ru metal in 1 M HNO_3

  For Ru, the Voltammogram has 3 regions:
  Region I: from E = .200 – .650 V, current increases
  Region II: from E = .650 – 1.15 V, current stabilizes
  Region III: from E > 1.15 V, Current increases again



Re in 1 M HNO_3 : E_{dis} = 0.74 V /SCE
Ru in 1 M HNO_3 : E_{dis} = 1.2 V/ SCE

A. Maslennikov *et al.*

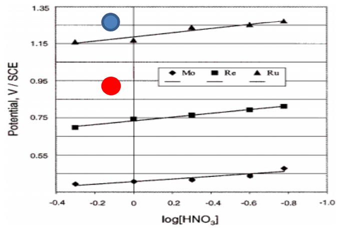
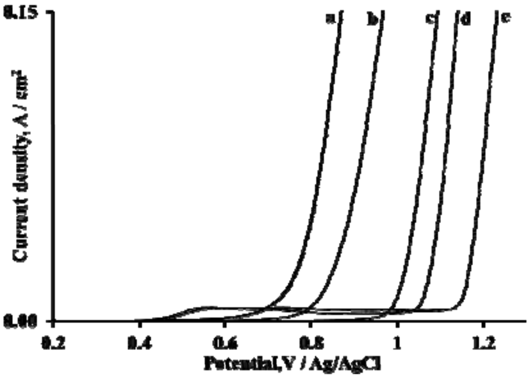


Fig. 3. Dissolution potentials of Mo, Re and Ru metals in 0.5–6.0 M HNO_3, estimated from LV curves; $t = 25$ °C.

Linear Sweep Voltammetry



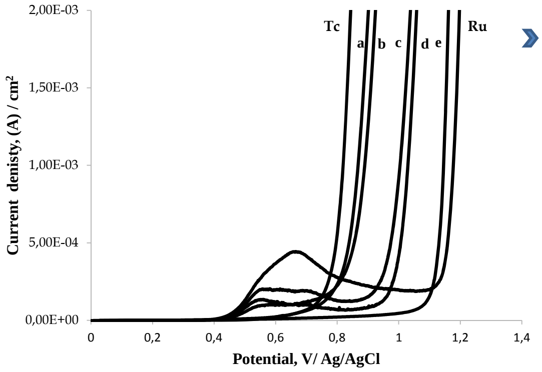
- Linear Sweep Voltammetry on Re-Ru electrodes in 1 M HNO_3

Sample (Ru content in at. %)	E_{dis} (V/Ag/AgCl)
Re	0.69
sample a (3.7)	0.77
sample b (12.1)	0.85
sample c (31.0)	1.01
sample d (39.5)	1.08
sample e (62.7)	1.15
Ru	1.18

- The voltammograms of samples a, b and c are similar to that of Re metal and their currents Increase continously with increasing potential

- The voltammograms of samples d and e are similar to that of Ru metal (plateau of the current Between 0.6 – 1 V

Linear Sweep Voltammetry

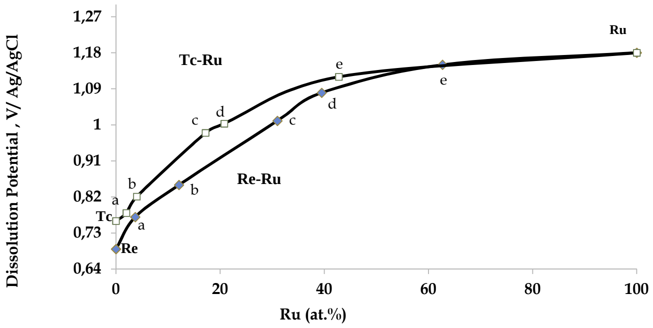


- Linear Sweep Voltammetry on Tc-Ru electrodes in 1 M HNO_3

Sample (Ru content in at. %)	E_{dis} (V/Ag/AgCl)
Tc	0.760
sample a (2.0)	0.780
sample b (4.0)	0.827
sample c (17.2)	0.980
sample d (20.8)	0.003
sample e (42.8)	1.12
Ru	1.18

- The voltammograms of samples a, b are similar to that of Tc metal and their currents Increase continously with increasing potential
- The voltammograms of samples c, d and e are similar to that of Ru metal (plateau of the curren Between 0.6 – 1 V

Linear Sweep Voltammetry

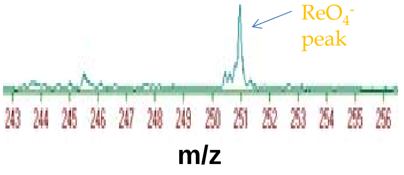


- Dissolution potentials as a function of Ru content in the electrodes
- E_{dis} increases with the Ru content : better corrosion resistance of Re-Ru & Tc-Ru alloys ; Ru has an effect on the corrosion potential of the Re-Ru & Tc-Ru electrodes
- Tc-Ru electrodes are more corrosion resistant than Re-Ru electrodes in 1 M nitric acid (with similar at.% compositions)

Corrosion Mechanism of Re Metal in 1 M HNO_3

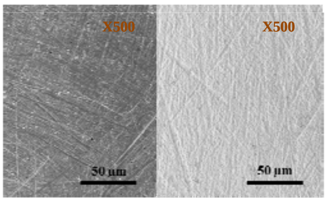
Bulk Electrolysis Technique was used to study the corrosion mechanism of Re metal at fixed potential of 0.750 V

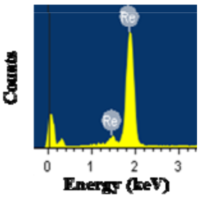
Corrosion products characterization in solution (by ESI/MS)



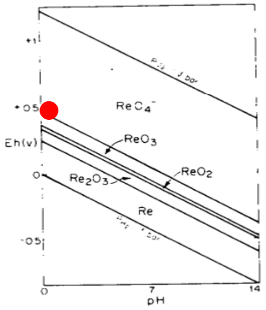
Corrosion products characterization in solid (by SEM/EDX)

before Bulk Electrolysis after Bulk Electrolysis





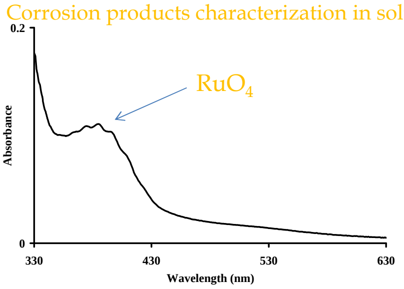
Eh-pH Diagram of Re in non-Complexing media[4]



Corrosion Mechanism of Ru Metal in 1 M HNO_3

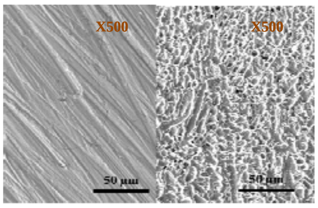
Bulk Electrolysis Technique was used to study the corrosion mechanism of Ru metal at fixed potential of 1.2 V

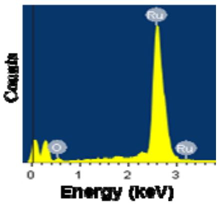
Corrosion products characterization in solution (by UV-Vis)



Corrosion products characterization in solid (by SEM/EDX)

before Bulk Electrolysis after Bulk Electrolysis





Eh-pH Diagram of Ru in non-Complexing media[4]

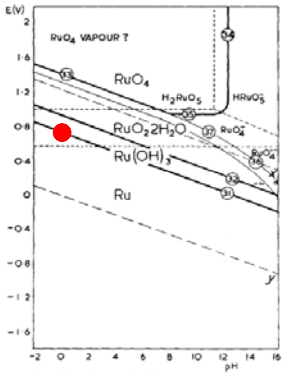
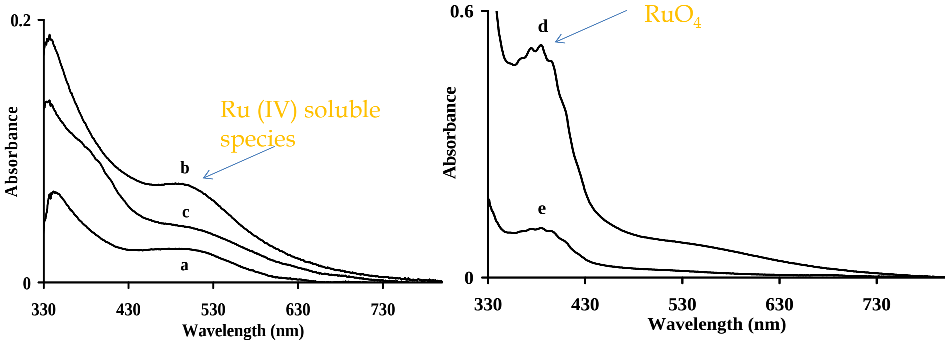


Fig. 11 Potential-pH diagram for the ruthenium-water system at 25°C

Corrosion Mechanism of Re-Ru alloys in 1 M HNO_3

Corrosion products characterization in solution (by UV-Vis)

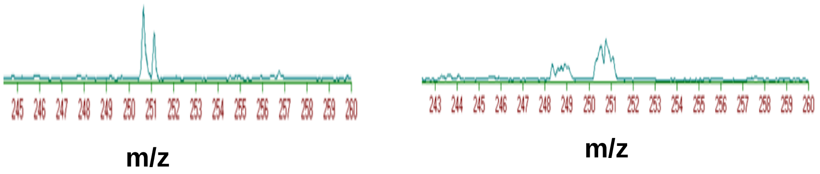


UV-Visible spectra of the solution after electrolysis of samples a - e at 1.2 V in 1 M HNO_3

- For samples a, b and c, no gas evolution was observed at the electrode and the spectra exhibit a band at 500 nm which is probably due to presence of Ru(IV) polymeric species[3]
- For samples d and e, gas evolution was observed at the electrode and the spectra exhibit a band at 380 nm which is due to the presence of RuO_4 [1]

Corrosion Mechanism of Re-Ru alloys in 1 M HNO_3

Corrosion products characterization in solution (by ESI/MS)



ESI/MS spectra of the solutions after electrolysis of sample b and sample e at 1.2 V in 1 M HNO_3

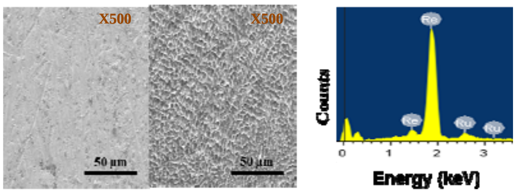
- ESI/MS spectra of solutions for samples b and e exhibit a peak at M = 251 which is characteristic of ReO_4^-

Corrosion Mechanism of Re-Ru alloys in 1 M HNO_3

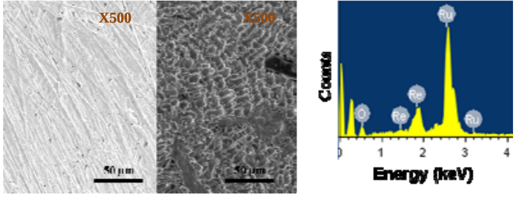
Corrosion products characterization in solid (by SEM/EDX)

SEM images & EDX spectra of the solutions after electrolysis of sample b (on the top) and sample e (on the bottom) at 1.2 V in 1 M HNO_3

before Bulk Electrolysis after Bulk Electrolysis



before Bulk Electrolysis after Bulk Electrolysis



Compositions (at. %) on the surface of samples b and e determined by EDX

Sample	Re (at. %)	Ru (at. %)	O (at. %)
b	87.2	12.8	-
e	9.3	23.6	67.1

- EDX analysis of the surface confirms The presence of O for sample e while O was absent in sample b

Conclusion

Linear Sweep Voltammetry

- As Ru content increases in the Re-Ru and Tc-Ru alloys, dissolution potential of the alloys increase

Corrosion Mechanism of Re-Ru alloys in 1 M HNO_3 at 1.2 V

- For Re, the speciation is dominated by $ReO4^-$
- For Ru,, the speciation is dependent on the composition of the alloys and oxygen evolution at the electrode;
  *For alloys with Ru content below 31 at. %, no gas evolution was observed and only Ru (IV) species was detected
  *For alloys with Ru content above 31 at. %, gas evolution was observed and RuO_4 was detected
- An oxide Layer was detected for alloys with Ru content above 31 at. %
- Similar behavior should be observed in Tc-Ru alloys in the nitric media

Future Work

- Electrochemical study of Tc-Ru alloys
- Synthesis and electrochemical study of epsilon phase (Tc-Mo-Ru-Pd-Rh alloys)

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[1] A. Maslennikov A. B Fourest. F David and M Masson "Electrochemical dissolution of simulated "white inclusions" in nitric acid. Linear Voltammetry study with Mo, Re, Ru metals and their alloys electrode," *Radio-chem Acta* 91:41-425 (2003)

[2] E. Mausolf E. D. Kolman. G. Jarvinen. F. Poineau. K. Czerwinski, *Los Alamos National Laboratory* (2010)

[3] M. Ferrier. F. Poineau. G. Jarvinen and K. Czerwinski , "Chemical and electrochemical behavior of metallic technitium in acidic media," *J. Radioanal Nucl Chem* DOI 10.1007 (2013)

[4] M.J.N. Pourbaix, J.V. Muylder and N. de Zoubov, "Electrochemical Properties of the Platinum Metals", *Platinum Metals Rev.*, **3**, 100-106 (1959).

[5] Y. Shirasu, K. Minato, "Characterization of Technetium-Ruthenium Alloys for Transmutation of Technetium Metal," *J. American Nuclear Society*, 1340-1343 (1999).

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Dr. Dan Koury
Dr. Erik Johnstone
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Questions

Review on the Tc Chemistry at SUBATECH in Inorganic Media (Chloride, Sulfate, Carbonate) with or without Radiation Effect

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Technetium is important as a long half-life multivalent radioelement within the framework of the nuclear waste storage especially in underground geological sites. So, the safety studies require the knowledge of the redox and of the chemical properties of this element in order to model its geochemical behavior in the environment.

In a first part, the results presented here [1-5], after 15 years of research studies, deal with the redox behavior and the speciation of Tc in chloride, sulfate and carbonate media in order to perform the speciation during the reduction process of Tc(VII) in Tc(V), Tc(IV) and Tc(III) either by chemical/electrochemical methods either by radiolytic process induced by α, γ irradiations. The speciation of Tc in solution was carried out by complementary techniques such as UV-VIS Spectrophotometry, Raman Spectroscopy and X-rays Absorption Spectroscopy.

In chloride medium, the Tc(IV) species produced by dissolving $K_2TcCl_6(s)$ was characterized as hydrolysed $TcCl_6^{2-}$: $TcCl_5(H_2O)^-$ or $TcCl_4(H_2O)_2$ [1]. Kinetic studies, in chloride medium, of the $TcCl_5(H_2O)^-$ species condensation leads to the characterization of a linear structure such as Tc^{IV}-O-Tc^{IV} [3]. The formula proposed for this species is $Tc_2OCl_{10}^{4-}$ and can give $Tc_n^{IV}O_y^{(4n-2y)+}$ by a cyclisation process [3]. In chloride medium, TcO_2 lead to the formation of $Tc_2OCl_{10}^{4-}$ at pH = 0.3 and $Tc_n^{IV}O_y^{(4n-2y)+}$ at pH = 1.5 [3]. The electrochemical reduction of TcO_4^- in carbonate medium leads to amorphous oxides or carbonate complexes of Tc(IV) and/or Tc(III) [1]. We have attempted to prepare sulfate compounds of Tc using ligands exchange and reduction of TcO_4^- in sulfate medium. For $pH < 4$, one reduced species of Tc is formed in solution and was characterized as a small size oxo or hydroxo polynuclear complex $Tc_n^{IV}O_y^{(4n-2y)+}$ which can be considered as a precursor of $TcO_2.xH_2O$ for $pH > 3$ [4].

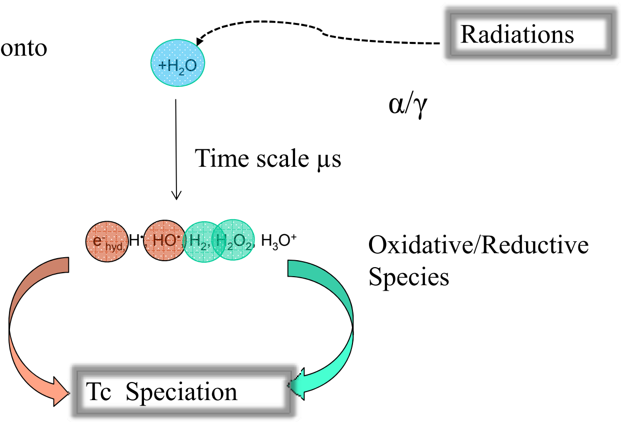
In a second part, the stability of the Tc species under α or γ irradiation has been studied: Under γ irradiation, the Tc(VII) is stable but reduced in Tc(IV) in the presence of formate when the carbonate complex of Tc(IV) is oxidized in Tc(VII) [1]. However, TcO_4^- is formed by γ radiolysis of $TcO_2.xH_2O$ and $Tc_n^{IV}O_y^{(4n-2y)+}$ under N_2O atmosphere with a strongly increased of the solubility [4]. Moreover, under α radiation the $Tc_n^{IV}O_y^{(4n-2y)+}$ species is oxidized to TcO_4^- [3]. The decomposition of $TcCl_6^{2-}$ by γ radiolysis was studied and did not lead straightly to the formation of Tc(VII) but the ligand exchange between Cl^- and H_2O is enhanced [4]. In concentrated H_2SO_4 (≥ 12 M), α-radiolysis experiments of Tc(VII) were performed in order to study the radiolytic behaviour of Tc(VII). XANES studies show that radiolytic reduction of Tc(VII) leads to the formation of Tc(V)-Tc(VII) mixture in H_2SO_4 13 M and just Tc(V) in 18 M of H_2SO_4. The analysis of EXAFS spectra is consistent with the formation of $[TcO(HSO_4)_3(H_2O)_2]$ and $[TcO(HSO_4)_3(H_2O)(OH)]^-$ monomer complexes in H_2SO_4 13 M and $[Tc(HSO_4)_3(SO_4)(H_2O)]$ and $[Tc(HSO_4)_3(SO_4)(OH)]^-$ species at 18 M of H_2SO_4 [2].

Figure 1 present the summary of these studies in the chloride, sulfate and carbonate media for reduction processes under irradiation or not.

Review on the Tc Chemistry at SUBATECH in Inorganic Media (Chloride, Carbonate) with Radiation Effect

J.Vandenborre,
M.Fattahi

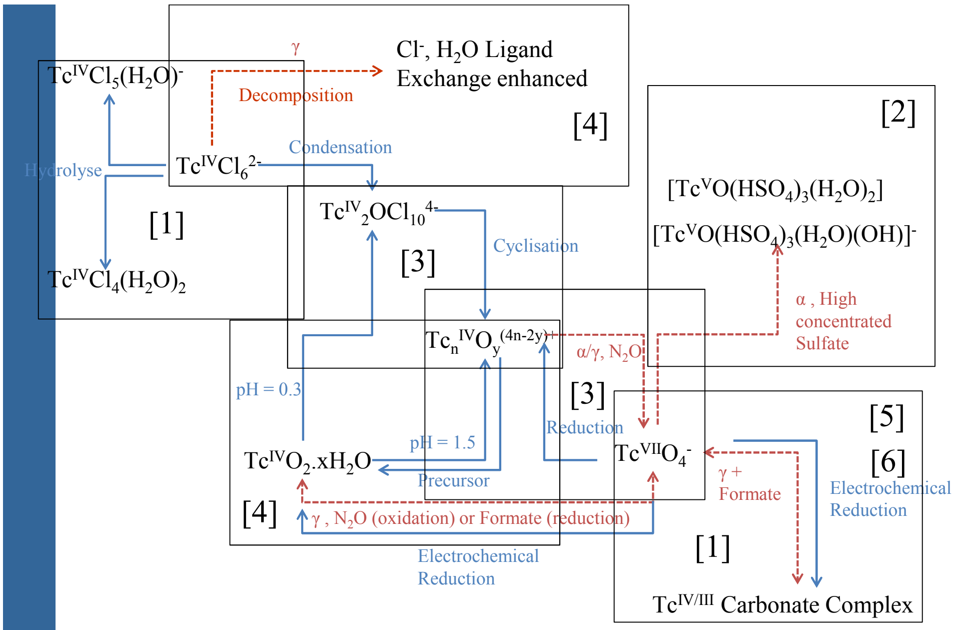
Objectives:
Radiolytic species effect onto
Tc Reduction/Oxidation?



Examples : Dosimetry with the same radiation
Oxidation $Fe^{2+} \rightarrow Fe^{3+}$
Reduction $Ce^{4+} \rightarrow Ce^{3+}$
Depends on the Redox Potential

TOPIC

First Part : Tc Chemistry + γ Radiation



$Tc^{IV}Cl_5(H_2O)^-$

γ

Decomposition

Cl^-, H_2O Ligand Exchange enhanced

[4]

[2]

Hydrolyse

$Tc^{IV}Cl_6^{2-}$

Condensation

[1]

$Tc^{IV}Cl_4(H_2O)_2$

$Tc^{IV}{}_2OCl_{10}{}^{4-}$

[3]

Cyclisation

$[Tc^VO(HSO_4)_3(H_2O)_2]$

$[Tc^VO(HSO_4)_3(H_2O)(OH)]^-$

α , High concentrated Sulfate

$Tc_n{}^{IV}O_y{}^{(4n-2y)+}$

α/γ, N_2O

pH = 0.3

[3]

Reduction

[5]

pH = 1.5

$Tc^{IV}O_2.xH_2O$

$Tc^{VII}O_4{}^-$

[6]

Precursor

γ + Formate

Electrochemical Reduction

[4]

γ , N_2O (oxidation) or Formate (reduction)

[1]

Electrochemical Reduction

$Tc^{IV/III}$ Carbonate Complex

[1].Ben Saïd, K., *Contribution à l'étude des réactions d'oxydoréduction et à la spéciation du technétium en milieu chloré et carbonaté.*, in *Ph.D.* 1999, Université de Nantes

[2].Denden, I., *La chimie du Tc en milieux très acides, effet des rayonnements alpha et gamma* in *Ph.D.* 2013, Université de Nantes TALK

[3].Poineau, F., *Mécanismes de condensation du Technétium tétravalent en milieu chloré*, in *Ph.D.* 2004, Université de Nantes

[4].Vichot, L., *Spéciation du technétium en milieu chloro-sulfate. Contribution à l'étude des effets de la radiolyse α*, in *Ph.D.* 2001, Université de Nantes

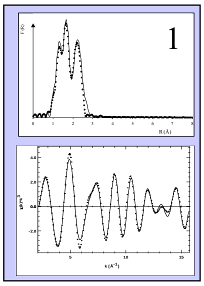
[5]. Llorens, I., *Etude de la coprécipitation du technétium-99 avec la sidérite ($FeCO_3$) comme phase d'accueil*, in *Ph.D.* 2007, Université de Nantes: Nantes.

[6].Ghalei, M., *Reduction of Mn, Tc, Re species in highly concentrated carbonate media by electrochemistry and radiolysis*, in *Ph.D.* started in 2012, Université de Nantes TALK

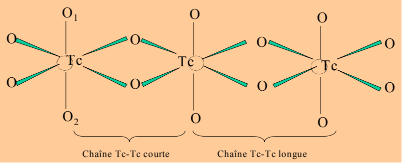
Oxide Characterisation

XAS Experiments

EXAFS: $Tc^{IV}O_2.xH_2O$



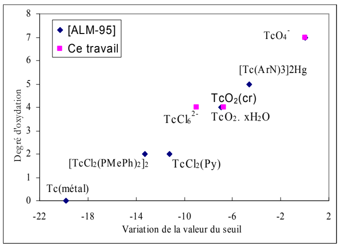
Complexe	Type de liaison	r (Å)	CN	σ (Å^2)	ΔE$_0$ (eV)	Résiduel %	
TcO_2	Tc-O$_1$	1,81	0,68	10^{-5}	4,646	14	Ce travail
	Tc-O$_2$	1,98	5,31	0,0071	4,646	14	
	Tc-O	1,98	6	0,0038			ALM-95
		(1,94-2,08)	6				ROG-69 ALM-95
	Tc-Tc	2,53	1	0,0049	10,637	14	Ce travail
		2,61	1	0,0038			ALM-95
		2,875	1				ANT-85
		(2,48)	1				ROG-69 ALM-95



First Hypothesis :

Bridge μ-O → Tc(μ-O)$_2$Tc species

XANES : $Tc_nO_y^{(4n-2y)+}$



Nature de l'espèce	Degré d'oxydation	Shift du seuil (eV)	Réferences
TcO_4^-	7	0	Ce travail
TcO_4^-	7	0	[ALM-95]
$[Tc(ArN)_3]_2Hg$	5	-4,61	[ALM-95]
TcO_2	4	-6,95	[ALM-95]
TcO_2. xH_2O (échantillon 1)	4	-6.75	Ce travail
$TcCl_6^{2-}$	4	-9	Ce travail
$[Cl^-] = 3$, $[SO_4^{2-}] = 0,1$ M	4	-6,6	Ce travail
$[SO_4^{2-}] = 0,1$ M	4	-6,4	Ce travail
$[TcCl_2(PMe_2Ph)_2]_2$	2	-13,24	[ALM-95]
$TcCl_2(py)_4$	2	-11,21	[ALM-95]
Tc(O)	0	-19,85	[ALM-95]

D.O = IV for $Tc_n^{IV}O_y^{(4n-2y)+}$

Vichot, L., *Spéciation du technétium en milieu chloro-sulfate. Contribution à l'étude des effets de la radiolyse α*, in *Ph.D.* 2001, Université de Nantes

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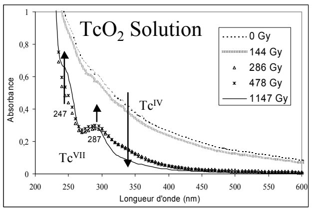
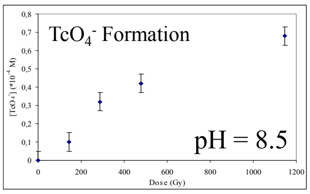
Oxides under γ Radiolysis

$Tc^{IV}O_2.xH_2O$ under γ Radiolysis





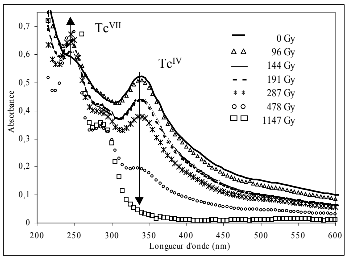
Reoxidation Process

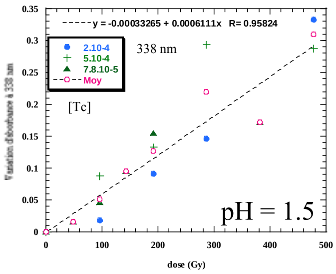
$G_{exp}(Tc(VII)) = 1,12 \times 10^{-7}$ mol.J^{-1}

By γ Irradiation :

$$TcO_2 \rightarrow TcO_4^- \leftarrow Tc_nO_y^{(4n-2y)+}$$

$Tc_nO_y^{(4n-2y)+}$ under γ Radiolysis



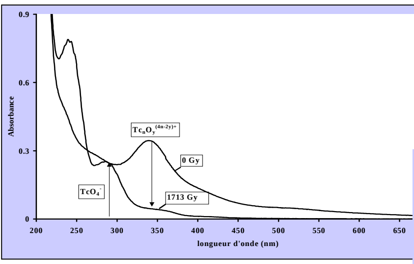


$G_{exp}(-[Tc(IV)]) = 1,46\ 10^{-7}$ mol.J^{-1}

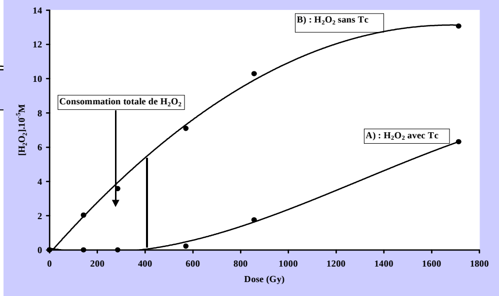
Vichot, L., *Spéciation du technétium en milieu chloro-sulfate. Contribution à l'étude des effets de la radiolyse α*, in *Ph.D.* 2001, Université de Nantes

Oxides under α Radiolysis

$Tc_nO_y^{(4n-2y)+}$ /$TcO_2.xH_2O$ under α Radiolysis



e^-_{hyd}, $H^\bullet$, $HO^\bullet$, H_2, H_2O_2, H_3O^+



OXIDATION
$TcO_2.xH_2O \rightarrow TcO_4^-$
$Tc_nO_y^{(4n-2y)+} \rightarrow TcO_4^-$
$G(-Tc_nO_y^{(4n-2y)+}) = 1.09.10^{-7}$ mole.J^{-1}

H_2O_2 CONSUMPTION BY Tc(IV)

MECHANISMS : $Tc(IV) + H_2O_2 \rightarrow Tc(V) + OH^{\cdot} + OH^-$
$2Tc(V) \rightarrow Tc(IV) + Tc(VII)$

Poineau, F., *Mécanismes de condensation du Technétium tétravalent en milieu chloré*, in *Ph.D.* 2004, Université de Nantes

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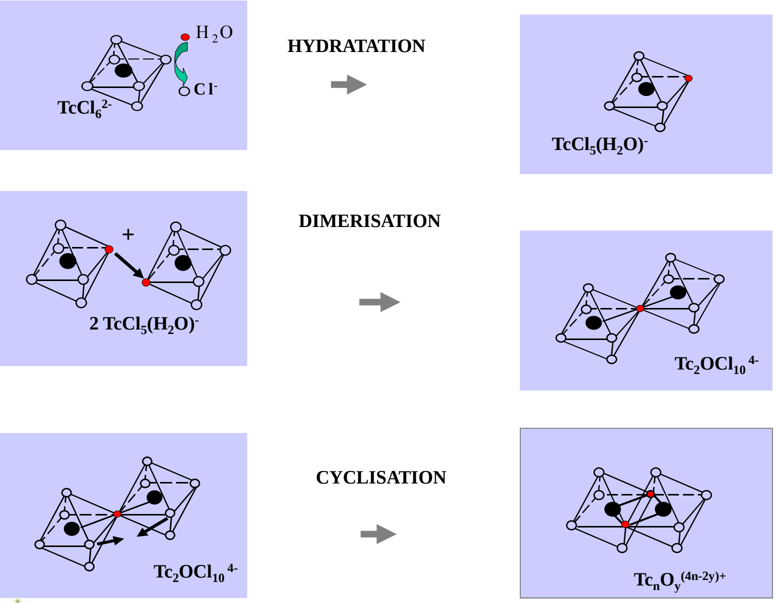
Chloride Media

XAS Experiments

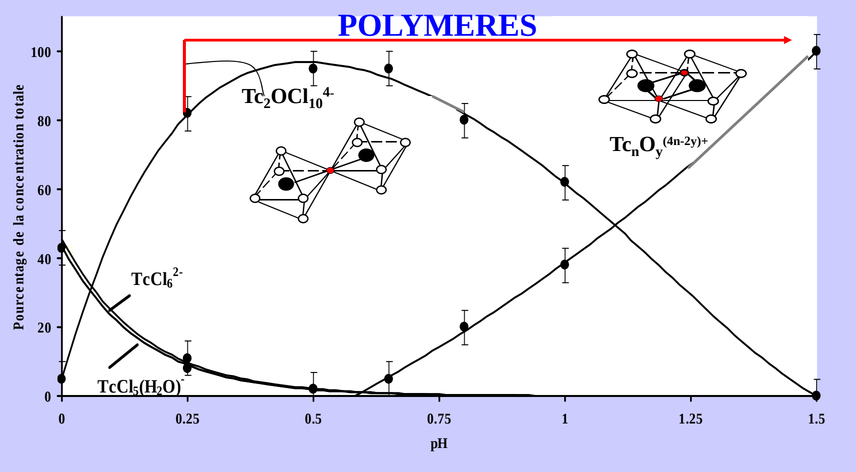
$TcCl_6^{2-} \rightarrow Tc_2OCl_{10}^{4-} \rightarrow Tc_nO_y^{(4n-2y)+}$



Poineau, F., *Mécanismes de condensation du Technétium tétravalent en milieu chloré*, in *Ph.D.* 2004, Université de Nantes

$TcCl_6^{2-}$ Speciation vs. pH

Chloride Media



vs. pH : Tc-O-Tc → $Tc(\mu\text{-}O)_2Tc$

Poineau, F., *Mécanismes de condensation du Technétium tétravalent en milieu chloré*, in *Ph.D.* 2004, Université de Nantes

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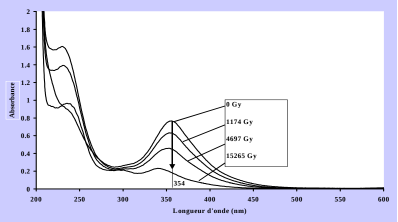
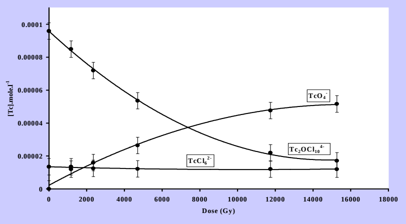
$TcCl_6^{2-}$ /$Tc_2OCl_{10}^{4-}$ under α Radiolysis

Chloride Media

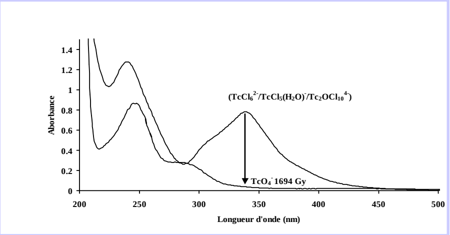




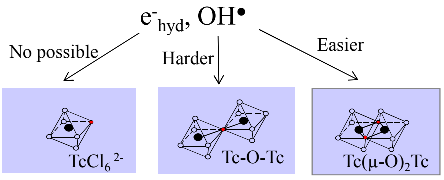
$TcCl_6{}^{2-}$ STABLE under α
OXIDATION $Tc_2OCl_{10}^{4-} \rightarrow TcO_4^-$
α : Low yield Radical Species
G ($-Tc_2OCl_{10}^{4-}$)= 9.05 10^{-9} mole.J^{-1}

$e^-_{hyd,}$ $H^\bullet$, $HO^\bullet$, H_2, H_2O_2, H_3O^+

$TcCl_6^{2-}$ /$Tc_2OCl_{10}^{4-}$ under γ Radiolysis



OXIDATION $Tc_2OCl_{10}^{4-} \rightarrow TcO_4^-$
γ : High yield Radical species


e^-_{hyd}, $OH^\bullet$

No possible

Harder

Easier

$TcCl_6{}^{2-}$

Tc-O-Tc

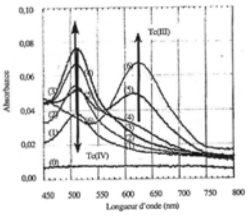
$Tc(\mu\text{-}O)_2Tc$

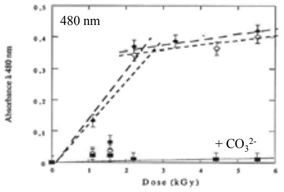
Poineau, F., *Mécanismes de condensation du Technétium tétravalent en milieu chloré*, in *Ph.D.* 2004, Université de Nantes

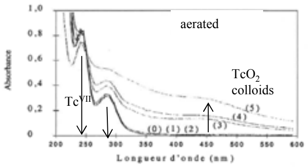
Slow rate process Electrochemistry vs. γ Radiolysis

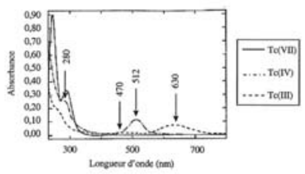
Carbonate Media

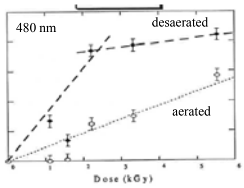
High rate process

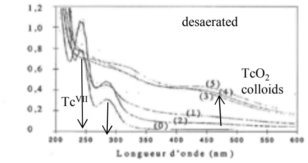












$CO_2^{-\bullet}$ reductive species of Tc
$CO_3^{-\bullet}$ oxydative species of Tc
O_2 effect = Reoxidation of Tc^{IV}
and $CO_2^{-\bullet}$ scavenging

$$HCOO^- + OH^\bullet \rightarrow CO_2^{-\bullet}$$
$$CO_3^{2-} + OH^\bullet \rightarrow CO_3^{-\bullet}$$
$$O_2 + CO_2^{-\bullet} \rightarrow O_2^{-\bullet}$$

Ben Saïd, K., *Contribution à l'étude des réactions d'oxydoréduction et à la spéciation du technétium en milieu chloré et carbonaté.*, in *Ph.D.* 1999, Université de Nantes

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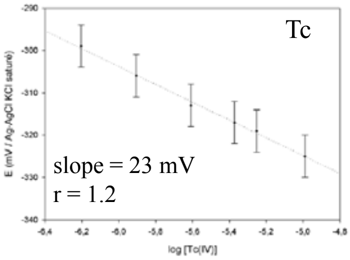
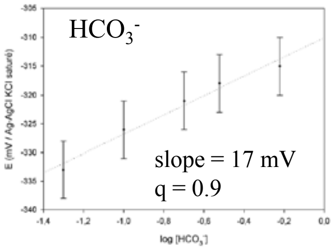
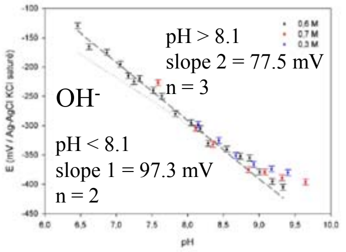
Electrochemistry Potential vs. Concentration

Carbonate Media

$(Tc(CO_3)_q(OH)_n^{4-n-2q})_r$







Hypothesis : Mononuclear Species ?

Hydrolyse Equilibrium
$TcCO_3(OH)_2 + H_2O \leftrightarrow TcCO_3(OH)_3^- + H^+$

XAS Experiment to confirm

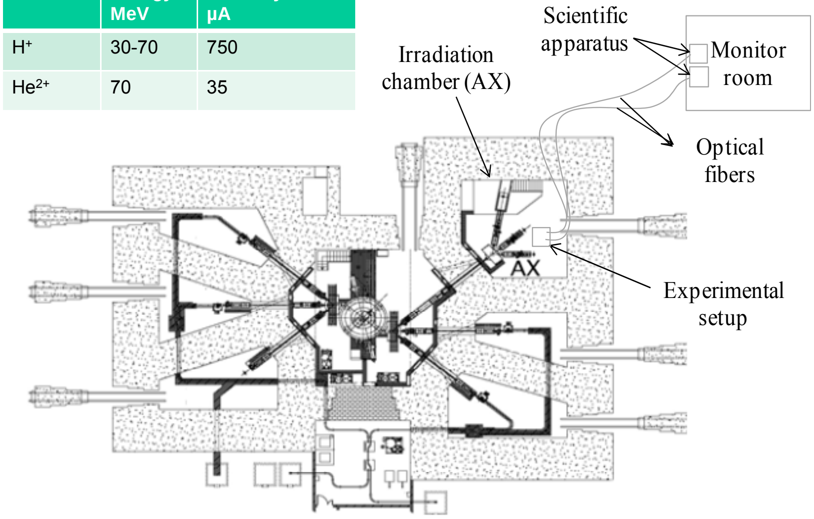
Llorens, I., *Etude de la coprécipitation du technétium-99 avec la sidérite ($FeCO_3$) comme phase d'accueil*, in *Ph.D.* 2007, Université de Nantes: Nantes.

Second Part :
Tc chemistry under α Radiation provided by ARRONAX Cyclotron Facility (started in 2009)

Coll. F.Haddad

Radiations α

Particle	Energy MeV	Intensity µA
H^+	30-70	750
He^{2+}	70	35

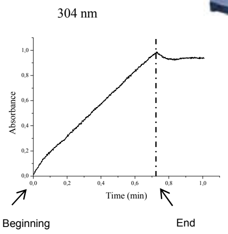


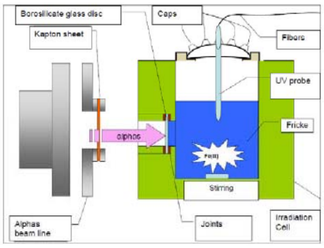
Radiations γ

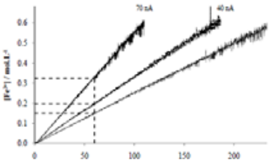
Particle	Energy keV	Dose Rate (Gy.min^{-1})
γ	660 (Cs^{137})	~ 10

Dosimeter cartography

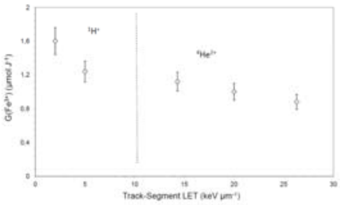
Fricke Dosimetry







Particle	Energy MeV	Intensity nA	Dose Rate Gy.min^{-1}
He^{2+}	68	100	~ 4000

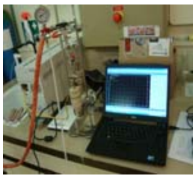


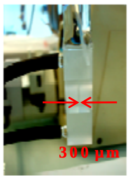
1) C. Costa et al., Am. J. Anal.Chem., 3 (2012) 6-11.
2) A. Traboulsi et al., Analytical Chemistry, in submission (2014).

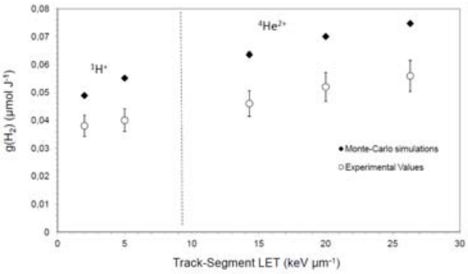
H_2 gas measurment

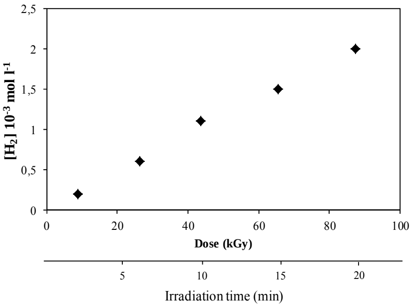
e^-_{hyd}, $H^\bullet$, $HO^\bullet$, H_2, H_2O_2, H_3O^+

H_2 reductive species
Impact onto Tc speciation?



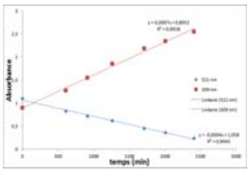


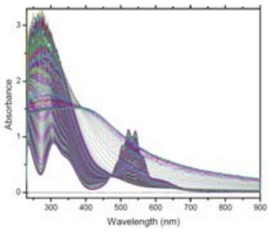


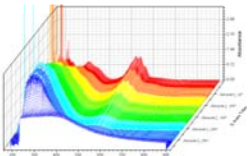


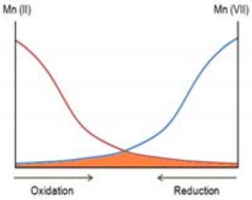
Crumière, F., *Etudes de l'effet des rayonnements ionisants sur l'eau : Rendements radiolytiques de l'hydrogène moléculaire*, in *Ph.D.* 2012, Université de Nantes: Nantes.

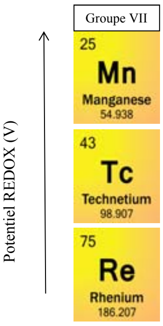
Carbonate Media





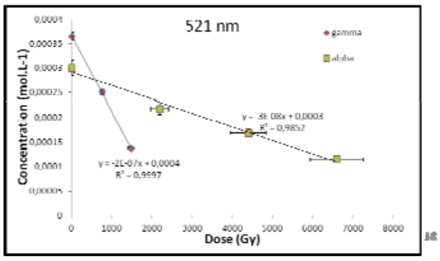






Groupe VII

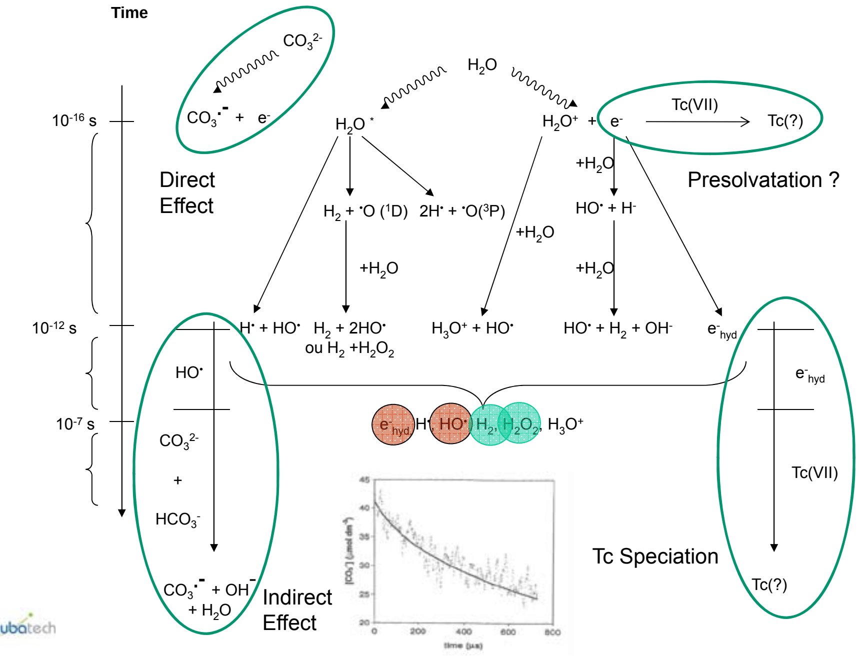
25	**Mn** Manganese 54.938
43	**Tc** Technetium 98.907
75	**Re** Rhenium 186.207



See TALK M.Ghalei

Ghalei, M., *Reduction of Mn, Tc, Re species in highly concentrated carbonate media by electrochemistry and radiolysis*, in *Ph.D.* started in 2012, Université de Nantes: Nantes.

α Pulsed Radiolysis



Time

10^{-16} s

10^{-12} s

10^{-7} s

CO_3^{2-}

$CO_3^{\bullet -}$ + e^-

Direct Effect

H_2O

H_2O^*

H_2O^+ + e^-

Tc(VII) → Tc(?)

Presolvatation ?

H_2 + $^{\bullet}O(^1D)$ 2H$^{\bullet}$ + $^{\bullet}O(^3P)$

+H_2O

$HO^{\bullet}$ + H^-

$H^{\bullet}$ + $HO^{\bullet}$ H_2 + $2HO^{\bullet}$ ou H_2 + H_2O_2

H_3O^+ + $HO^{\bullet}$

$HO^{\bullet}$ + H_2 + OH^-

e^-_{hyd}

$HO^{\bullet}$

CO_3^{2-} + HCO_3^-

$CO_3^{\bullet -}$ + OH^- + H_2O

Indirect Effect

e^-_{hyd}, $H^{\bullet}$, $HO^{\bullet}$, H_2, H_2O_2, H_3O^+

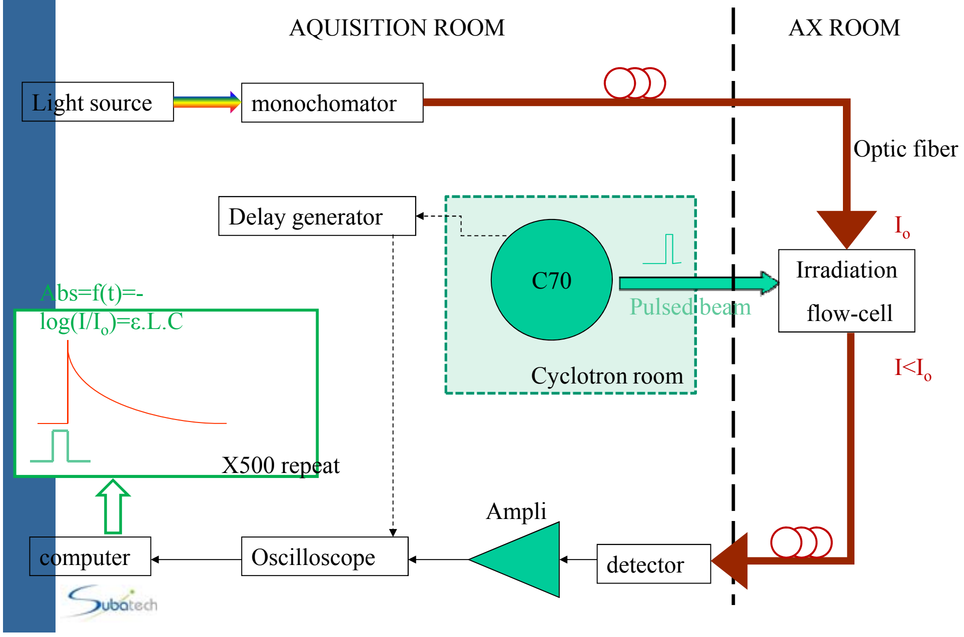
Tc Speciation

e^-_{hyd}

Tc(VII)

Tc(?)

α Pulsed Radiolysis



AQUISITION ROOM

AX ROOM

Light source

monochomator

Optic fiber

Delay generator

C70

Pulsed beam

Cyclotron room

Irradiation flow-cell

I_o

$I<I_o$

Abs=f(t)=-log(I/I_o)=ε.L.C

X500 repeat

computer

Oscilloscope

Ampli

detector

Thank you for your attention

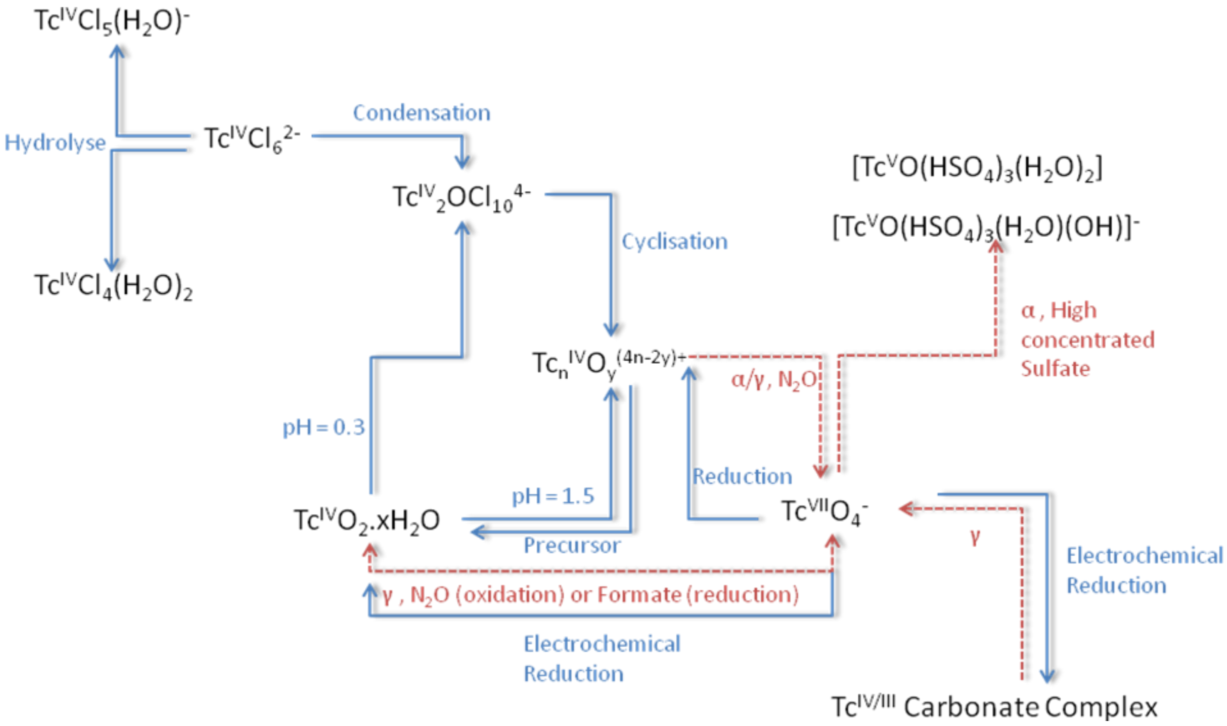


Figure 1: Graphical summarize of the Tc speciation work in SUBATECH in chloride, sulfate and carbonate media under irradiation

[1]. Ben Saïd, K., *Contribution à l'étude des réactions d'oxydoréduction et à la spéciation du technétium en milieu chloré et carbonaté.*, in *Ph.D.* 1999, Université de Nantes: Nantes.

[2]. Denden, I., *La chimie du Tc en milieux très acides, effet des rayonnements alpha et gamma* in *Ph.D.* 2013, Université de Nantes: Nantes.

[3]. Poineau, F., *Mécanismes de condensation du Technétium tétravalent en milieu chloré*, in *Ph.D.* 2004, Université de Nantes: Nantes.

[4]. Vichot, L., *Spéciation du technétium en milieu chloro-sulfate. Contribution à l'étude des effets de la radiolyse α*, in *Ph.D.* 2001, Université de Nantes: Nantes, France.

[5]. Ghalei, M., *Reduction of Mn, Tc, Re species in highly concentrated carbonate media by electrochemistry and radiolysis*, in *Ph.D.* started in 2012, Université de Nantes: Nantes.

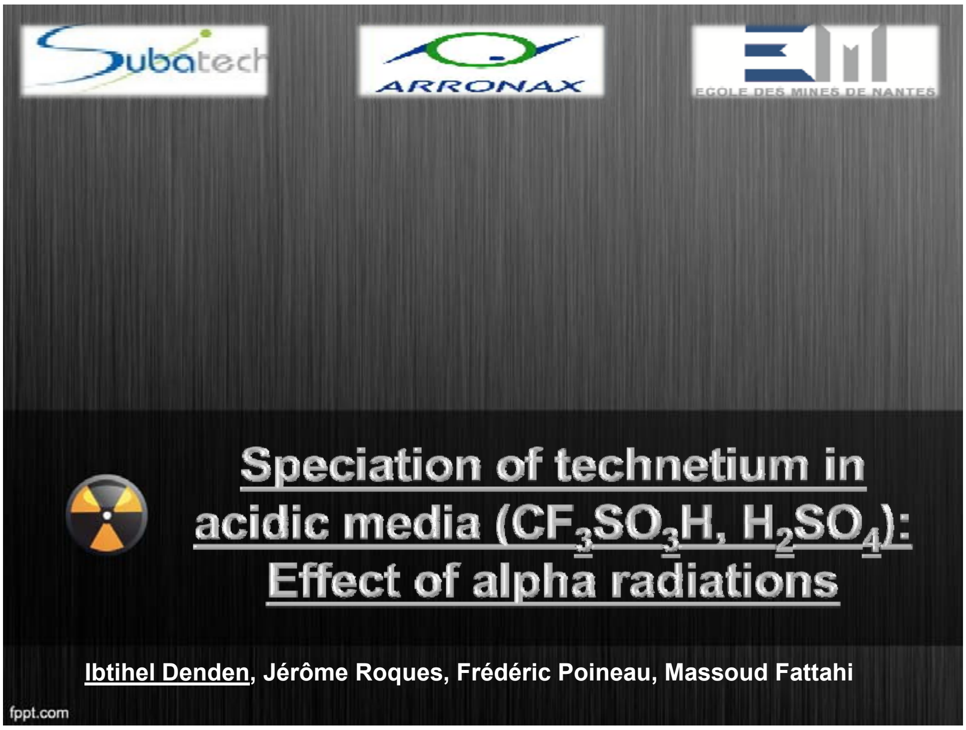
Speciation of technetium in acidic media (CF_3SO_3H, H_2SO_4): Effect of alpha radiations

Ibtihel Denden, Jérôme Roques, Frédéric Poineau, Massoud Fattahi

This project focuses on the fundamental study of technetium speciation in highly acidic medium. The behaviour of technetium trifluoromethanesulfonic acid was investigated first in the absence, then in the presence of α irradiation. Given these two different conditions, spectrophotometric results of Tc(VII) reduction are similar. XAS analysis indicates the formation of a cyclic dimer of Tc(IV) complexed to triflate ligands and formulated as $Tc_2O_2(CF_3SO_3)_4(H_2O)_4$. This compound is linearized to Tc^{IV}-O-Tc^{IV} with the increase of HTFMS concentration. At high concentration of HTFMS +98% (11.15 M), the protonated species $TcO_3(OH)(H_2O)_2$ which is formed in the absence of external ionizing radiations, is reduced to the (V) oxidation state under α irradiation. Structural characterization by EXAFS spectroscopy and DFT calculations suggests the formation of monomer species of Tc(V)-triflate complexes where $[OTc(F_3CSO_3)_2(H_2O)_2]^+$ and $[OTc(F_3CSO_3)_2(OH)_2]^-$ compounds were proposed.

α-radiolysis experiments of Tc(VII) were performed in order to compare the radiolytic behaviour of Tc(VII) in both comparable media HTFMS and H_2SO_4 ($C_{H2SO4} \geq 12$ M). XANES studies show that radiolytic reduction of Tc(VII) leads to the formation of Tc(V)/Tc(VII) mixture in H_2SO_4 13 M and Tc(V) in 18 M of H_2SO_4. The analysis of EXAFS spectra is consistent with the formation of $[TcO(HSO_4)_3(H_2O)_2]$ and $[TcO(HSO_4)_3(H_2O)(OH)]^-$ monomer complexes in H_2SO_4 13 M and $[Tc(HSO_4)_3(SO_4)(H_2O)]$ and $[Tc(HSO_4)_3(SO_4)(OH)]^-$ species at 18 M of H_2SO_4.

Keywords: technetium, HTFMS, H_2SO_4, α-radiolysis, speciation, XAS (XANES and EXAFS), DFT.



Subatech ARRONAX ECOLE DES MINES DE NANTES

Speciation of technetium in acidic media (CF_3SO_3H, H_2SO_4): Effect of alpha radiations

Ibtihel Denden, Jérôme Roques, Frédéric Poineau, Massoud Fattahi

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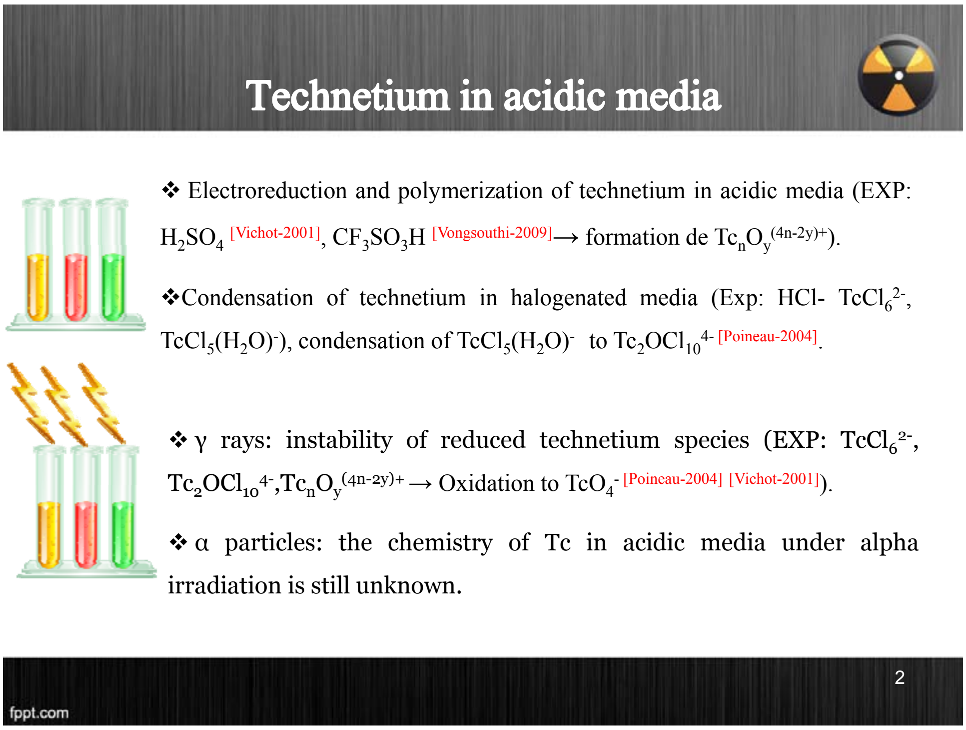

Technetium in acidic media

❖ Electroreduction and polymerization of technetium in acidic media (EXP: H_2SO_4 [Vichot-2001], CF_3SO_3H [Vongsouthi-2009]⟶ formation de $Tc_nO_y^{(4n-2y)+}$).

❖Condensation of technetium in halogenated media (Exp: HCl- $TcCl_6^{2-}$, $TcCl_5(H_2O)^-$), condensation of $TcCl_5(H_2O)^-$ to $Tc_2OCl_{10}^{4-}$ [Poineau-2004].

❖ γ rays: instability of reduced technetium species (EXP: $TcCl_6^{2-}$, $Tc_2OCl_{10}^{4-}$,$Tc_nO_y^{(4n-2y)+}$ ⟶ Oxidation to TcO_4^- [Poineau-2004] [Vichot-2001]).

❖ α particles: the chemistry of Tc in acidic media under alpha irradiation is still unknown.

2

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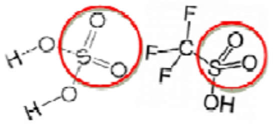
Acidic media

Trifluoromethanesulfonic acid/triflic acid (CF_3SO_3H , HTFMS)

- **Important catalyst in organic syntheses (Exp: phenol alkylation) and polymerization reactions (Exp: polyethers, polyols and silicones syntheses).**
- **Very weak complexing agent.**
- **Stability toward oxidation and reduction reactions.**

Sulfuric acid (H_2SO_4)



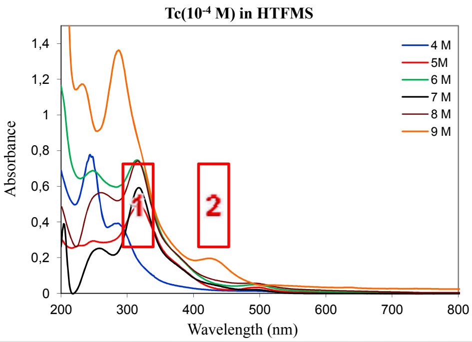
PRESENTATION PLAN

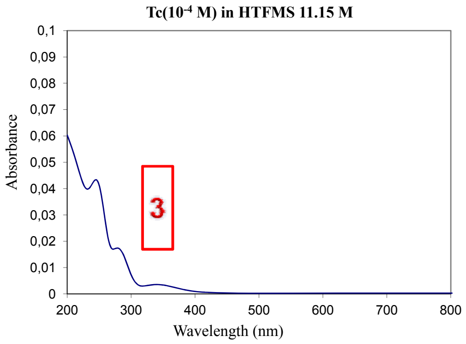
- BEHAVIOUR OF TECHNETIUM IN TRIFLIC ACID MEDIA IN THE ABSENCE OF EXTERNAL IRRADIATION
- BEHAVIOUR OF TECHNETIUM IN ACIDIC MEDIA UNDER α IRRADIATION
  - CF_3SO_3H
  - H_2SO_4
- SPECIATION OF TECHNETIUM BY X-RAY ABSORPTION SPECTROSCOPY (XANES/EXAFS)
  - CF_3SO_3H
  - H_2SO_4

BEHAVIOUR OF TECHNETIUM IN TRIFLIC ACID MEDIA IN THE ABSENCE OF EXTERNAL IRRADIATION

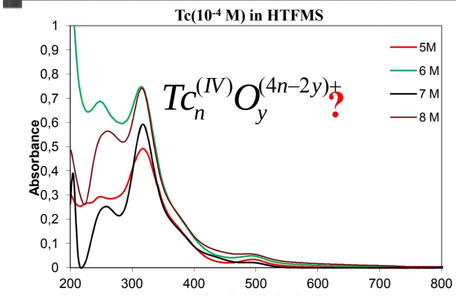
Spectrophotometric instability of TcO_4^- in HTFMS

- Stability of TcO_4^- in HTFMS< 4M.
- Formation of new species of Tc in HTFMS> 4 M.

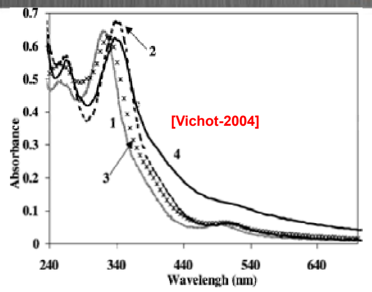


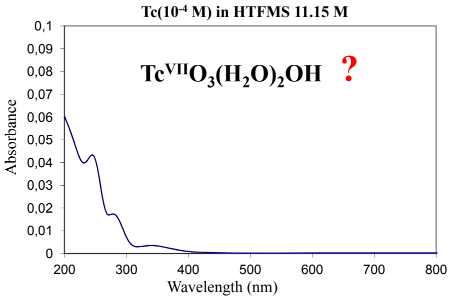


BEHAVIOUR OF TECHNETIUM IN TRIFLIC ACID MEDIA IN THE ABSENCE OF EXTERNAL IRRADIATION

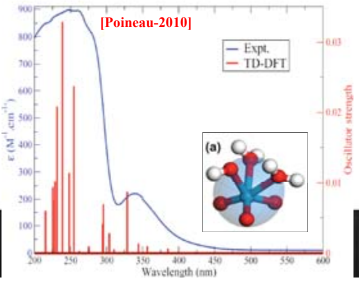


$Tc_n^{(IV)}O_y^{(4n-2y)+}$?

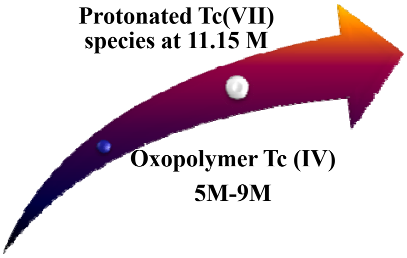




$Tc^{VII}O_3(H_2O)_2OH$?



BEHAVIOUR OF TECHNETIUM IN TRIFLIC ACID MEDIA IN THE ABSENCE OF EXTERNAL IRRADIATION



Protonated Tc(VII) species at 11.15 M

Oxopolymer Tc (IV) 5M-9M

First approach: **Partial thermal decomposition of HTFMS**

CO_2, CO, SO_2, F_2CO, CS_2, HF, HCO_3^-, $H_2SO_4^-$, HSO_3^-.

Second approach: **Hydrolysis of HTFMS by nucleophilic attack of water molecules on the C atoms:**

$$H_2O + CF_3\!-\!SO_3H \longrightarrow HOCF_3 + H_2SO_3$$

PRESENTATION PLAN

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  - H_2SO_4
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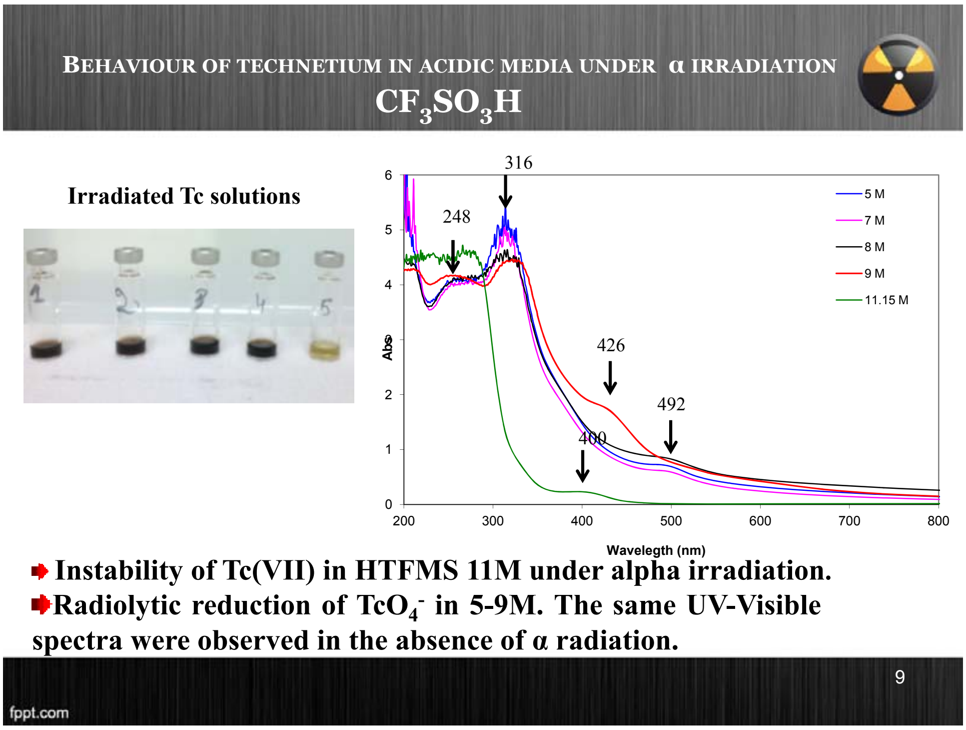
  - CF_3SO_3H
  - H_2SO_4
- CONCLUSION GÉNÉRALE



BEHAVIOUR OF TECHNETIUM IN ACIDIC MEDIA UNDER α IRRADIATION

CF_3SO_3H

Irradiated Tc solutions

- **Instability of Tc(VII) in HTFMS 11M under alpha irradiation.**
- **Radiolytic reduction of TcO_4^- in 5-9M. The same UV-Visible spectra were observed in the absence of α radiation.**

9

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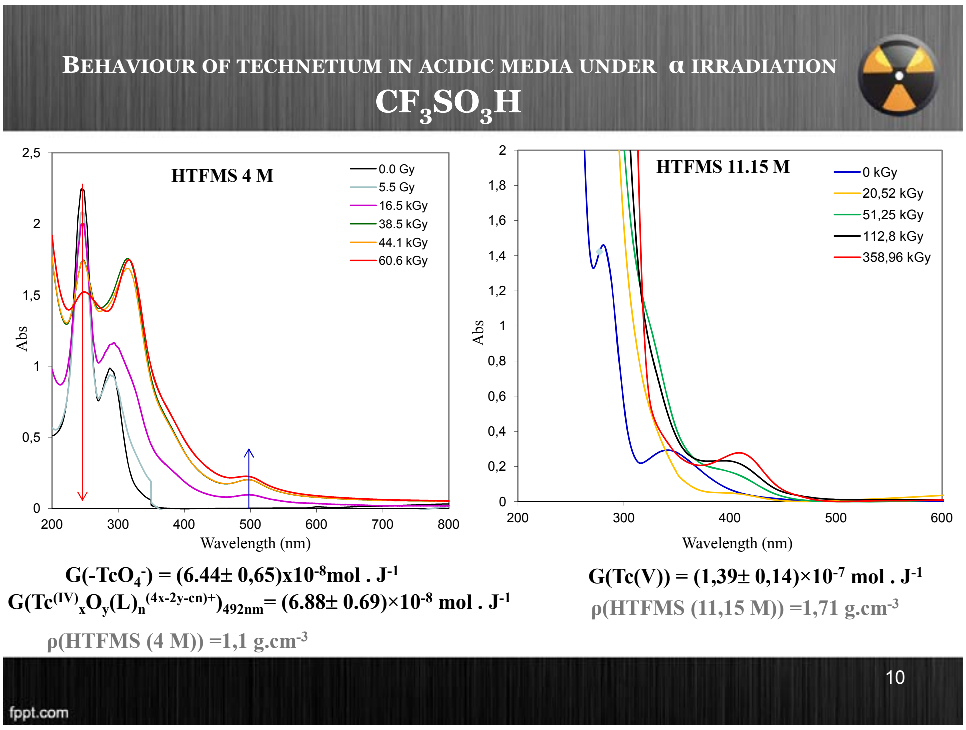

BEHAVIOUR OF TECHNETIUM IN ACIDIC MEDIA UNDER α IRRADIATION

CF_3SO_3H

$G(-TcO_4^-) = (6.44 \pm 0,65)x10^{-8} mol . J^{-1}$

$G(Tc^{(IV)}{}_xO_y(L)_n{}^{(4x-2y-cn)+})_{492nm} = (6.88 \pm 0.69)\times10^{-8}$ mol . J^{-1}

ρ(HTFMS (4 M)) =1,1 $g.cm^{-3}$

$G(Tc(V)) = (1,39 \pm 0,14)\times10^{-7}$ mol . J^{-1}

ρ(HTFMS (11,15 M)) =1,71 $g.cm^{-3}$

10

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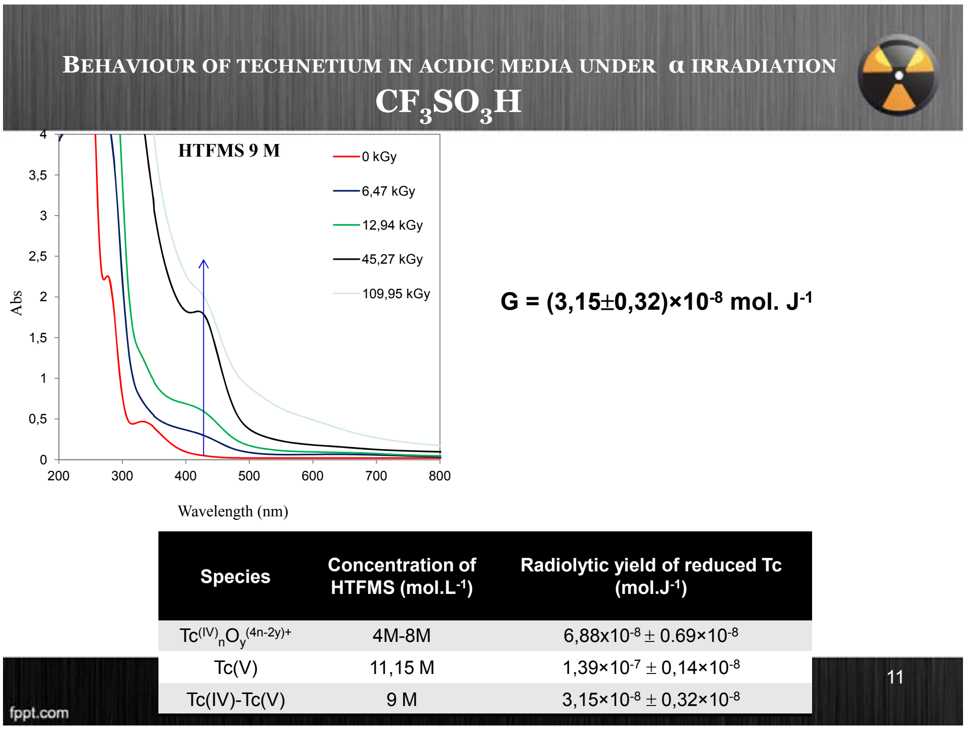
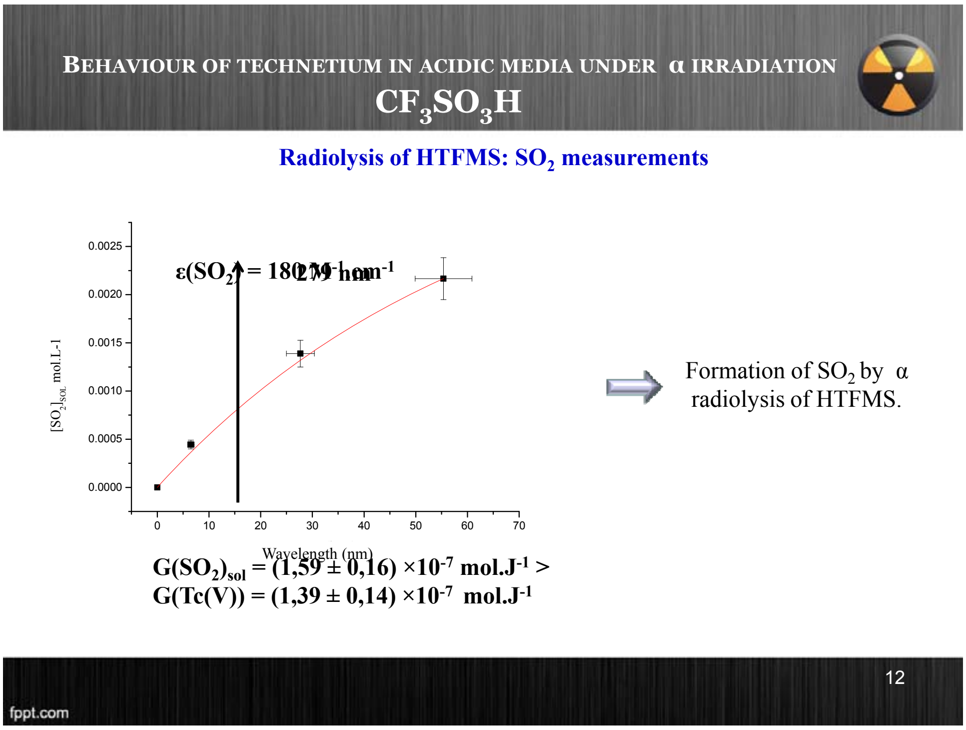


BEHAVIOUR OF TECHNETIUM IN ACIDIC MEDIA UNDER α IRRADIATION
CF_3SO_3H

G = (3,15±0,32)×10^{-8} mol. J^{-1}

Species	Concentration of HTFMS (mol.L^{-1})	Radiolytic yield of reduced Tc (mol.J^{-1})
$Tc^{(IV)}{}_nO_y{}^{(4n-2y)+}$	4M-8M	$6{,}88\times10^{-8} \pm 0.69\times10^{-8}$
Tc(V)	11,15 M	$1{,}39\times10^{-7} \pm 0{,}14\times10^{-8}$
Tc(IV)-Tc(V)	9 M	$3{,}15\times10^{-8} \pm 0{,}32\times10^{-8}$



BEHAVIOUR OF TECHNETIUM IN ACIDIC MEDIA UNDER α IRRADIATION
CF_3SO_3H

Radiolysis of HTFMS: SO_2 measurements

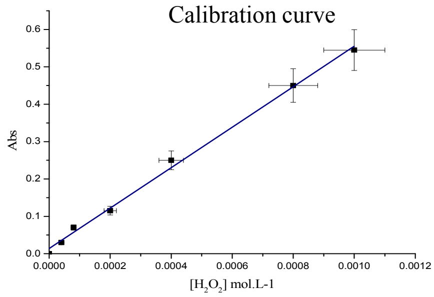
Formation of SO_2 by α radiolysis of HTFMS.

$G(SO_2)_{sol} = (1{,}59 \pm 0{,}16) \times10^{-7}$ mol.J^{-1} >
$G(Tc(V)) = (1{,}39 \pm 0{,}14) \times10^{-7}$ mol.J^{-1}

BEHAVIOUR OF TECHNETIUM IN ACIDIC MEDIA UNDER α IRRADIATION

CF_3SO_3H

Radiolysis of HTFMS: H_2O_2 measurements (Ti(IV) complexation)



Results of H_2O_2 measurements in HTFMS (4 M, 9 M et 11,15 M): No H_2O_2 is detected.

$$CF_3SO_3-H + {}^{\bullet}OH \rightarrow CF_3SO_3^{\bullet} + H_2O$$

$$CF_3SO_3^{\bullet} + {}^{\bullet}OH \rightarrow CF_3SO_3-OH$$

$$^{\bullet}CF_3 + {}^{\bullet}OH \rightarrow CF_3OH$$

BEHAVIOUR OF TECHNETIUM IN ACIDIC MEDIA UNDER α IRRADIATION

CF_3SO_3H

α radiolysis mechanism of HTFMS

$$CF_3SO_3H \xrightarrow{Irradiation} CF_3SO_3H^*$$

$$CF_3SO_3H \xrightarrow{Irradiation} CF_3\overset{\bullet}{S}\overset{+}{O_3}H + e^-$$

$$CF_3\overset{\bullet}{S}\overset{+}{O_3}H + CF_3SO_3H \rightarrow {}^{\bullet}CF_3 + SO_3 + CF_3SO_3H_2^+$$

$$CF_3SO_3H \rightarrow {}^{\bullet}CF_3 + {}^{\bullet}SO_3H$$

$$^{\bullet}CF_3 + {}^{\bullet}CF_3 \rightarrow C_2F_6$$

$$\boxed{\begin{array}{c} ^{\bullet}CF_3 + CF_3SO_3H \rightarrow CF_3OH + {}^{\bullet}CF_3 + \underline{SO_2} \\ ^{\bullet}CF_3 + {}^{\bullet}SO_3H \rightarrow CF_3OH + \underline{SO_2} \\ H^{\bullet} + {}^{\bullet}HSO_3 \rightarrow H_2O + \underline{SO_2} \\ ^{\bullet}HSO_3 + {}^{\bullet}HSO_3 \rightarrow H_2SO_4 + \underline{SO_2} \end{array}}$$

BEHAVIOUR OF TECHNETIUM IN ACIDIC MEDIA UNDER α IRRADIATION

CF_3SO_3H

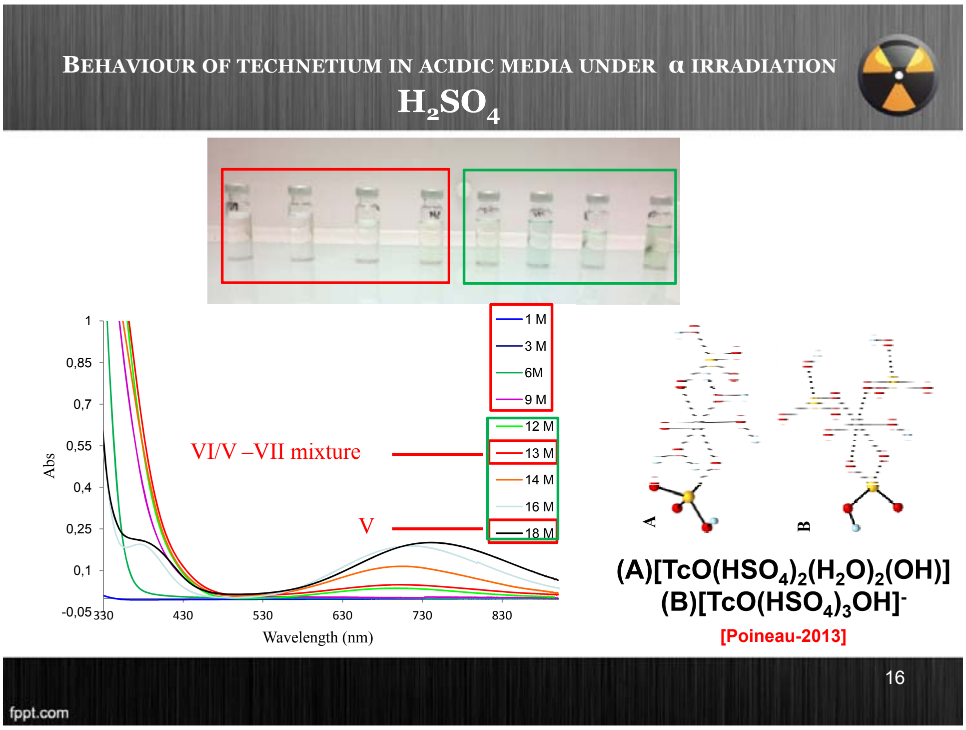
HTFMS 11,15 M

$$Tc(VII) + SO_2 \rightarrow Tc(V) + SO_4^{2-}$$

HTFMS-xH_2O mixtures

$$2Tc(V) \rightarrow Tc(IV) + Tc(VI)$$

$$2Tc(VI) \rightarrow Tc(V) + Tc(VII)$$

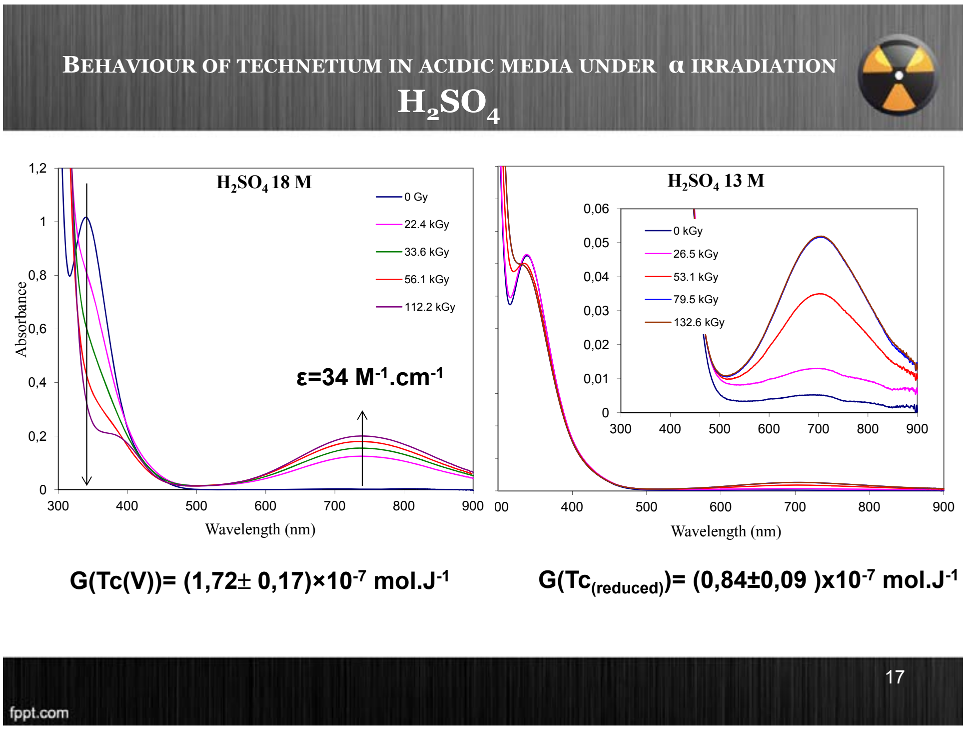


BEHAVIOUR OF TECHNETIUM IN ACIDIC MEDIA UNDER α IRRADIATION

H_2SO_4

(A)$[TcO(HSO_4)_2(H_2O)_2(OH)]$
(B)$[TcO(HSO_4)_3OH]^-$

[Poineau-2013]



BEHAVIOUR OF TECHNETIUM IN ACIDIC MEDIA UNDER α IRRADIATION

H_2SO_4

ε=34 $M^{-1}.cm^{-1}$

G(Tc(V))= (1,72± 0,17)×10^{-7} $mol.J^{-1}$

G($Tc_{(reduced)}$)= (0,84±0,09)x10^{-7} $mol.J^{-1}$

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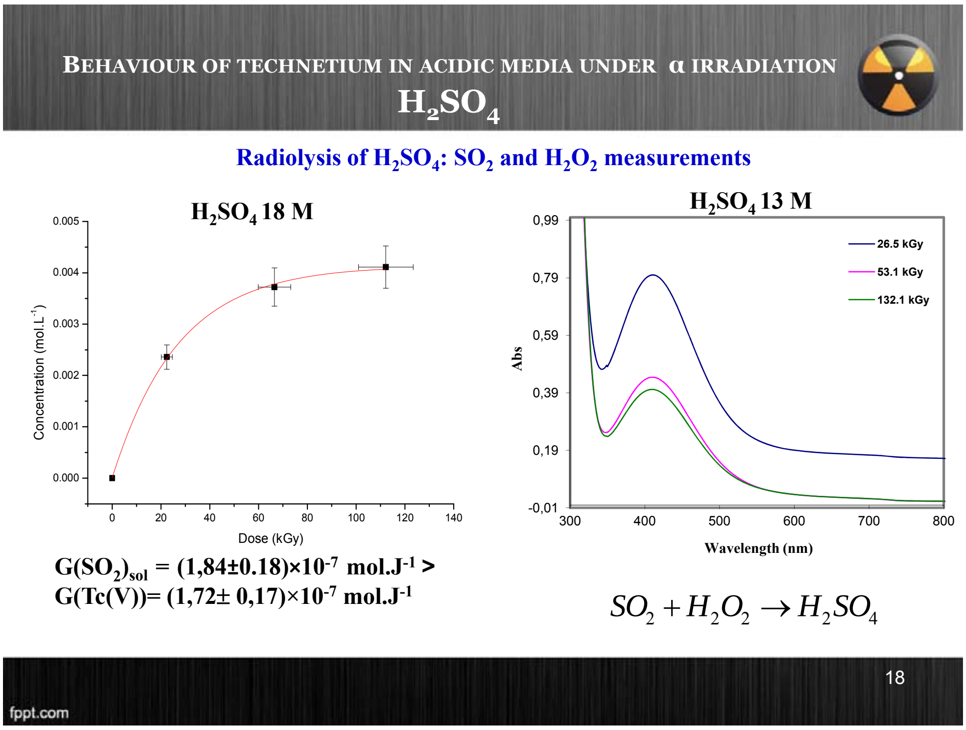

BEHAVIOUR OF TECHNETIUM IN ACIDIC MEDIA UNDER α IRRADIATION

H_2SO_4

Radiolysis of H_2SO_4: SO_2 and H_2O_2 measurements

$G(SO_2)_{sol}$ = (1,84±0.18)×10^{-7} $mol.J^{-1}$ >
G(Tc(V))= (1,72± 0,17)×10^{-7} $mol.J^{-1}$

$$SO_2 + H_2O_2 \rightarrow H_2SO_4$$

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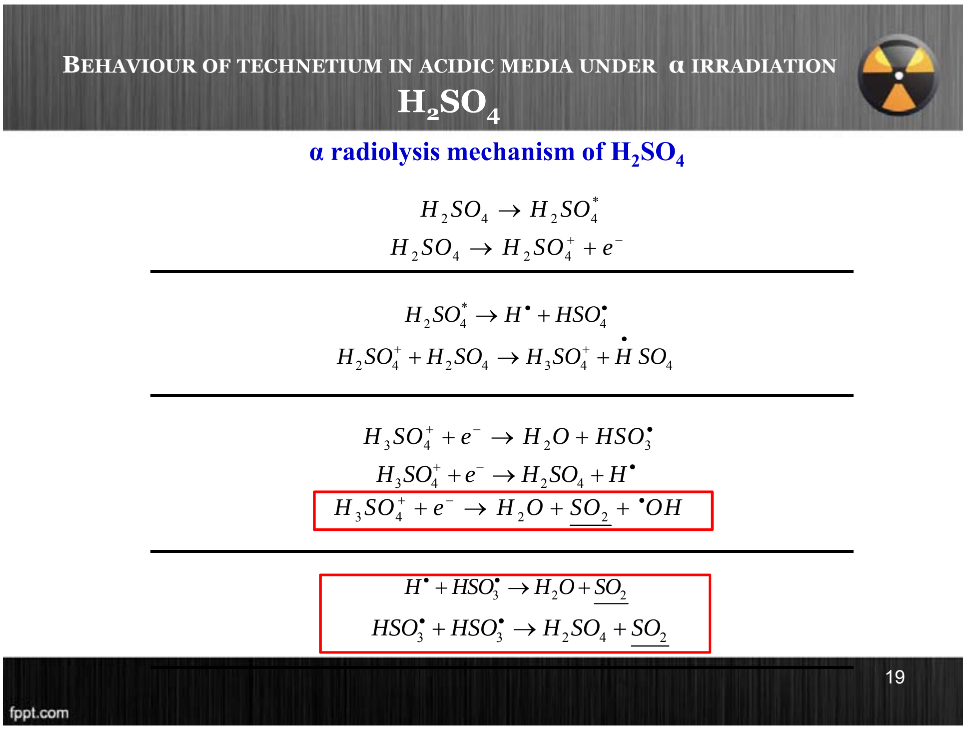


BEHAVIOUR OF TECHNETIUM IN ACIDIC MEDIA UNDER α IRRADIATION

H_2SO_4

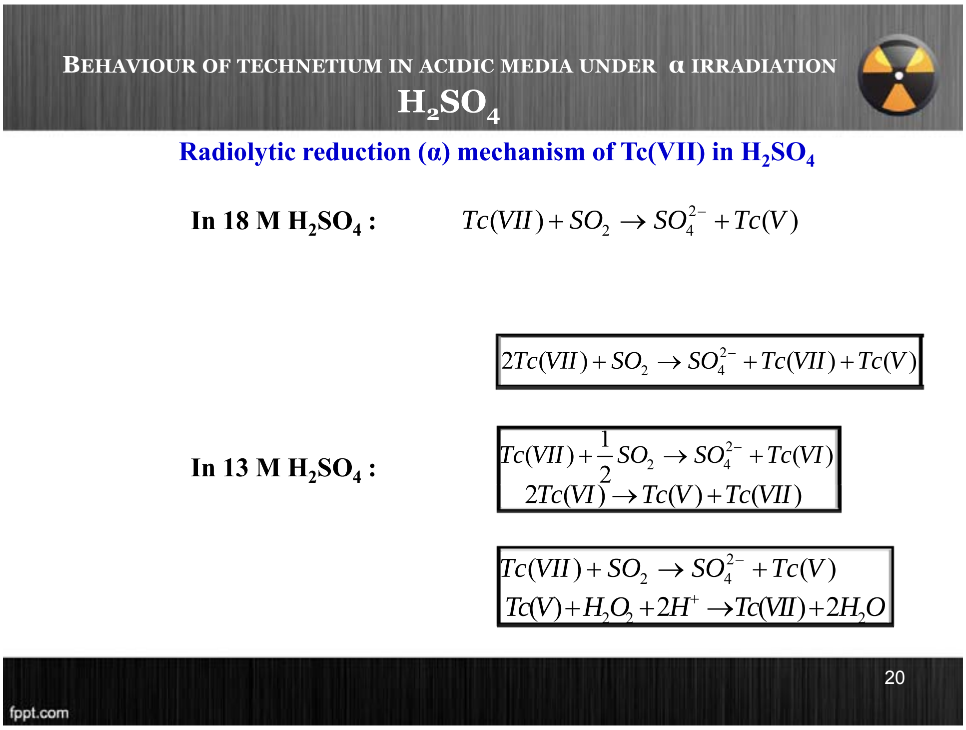
α radiolysis mechanism of H_2SO_4

$$H_2SO_4 \rightarrow H_2SO_4^*$$
$$H_2SO_4 \rightarrow H_2SO_4^+ + e^-$$

$$H_2SO_4^* \rightarrow H^\bullet + HSO_4^\bullet$$
$$H_2SO_4^+ + H_2SO_4 \rightarrow H_3SO_4^+ + \dot{H}SO_4$$

$$H_3SO_4^+ + e^- \rightarrow H_2O + HSO_3^\bullet$$
$$H_3SO_4^+ + e^- \rightarrow H_2SO_4 + H^\bullet$$
$$\boxed{H_3SO_4^+ + e^- \rightarrow H_2O + \underline{SO_2} + {}^\bullet OH}$$

$$\boxed{\begin{array}{c} H^\bullet + HSO_3^\bullet \rightarrow H_2O + \underline{SO_2} \\ HSO_3^\bullet + HSO_3^\bullet \rightarrow H_2SO_4 + \underline{SO_2} \end{array}}$$



BEHAVIOUR OF TECHNETIUM IN ACIDIC MEDIA UNDER α IRRADIATION

H_2SO_4

Radiolytic reduction (α) mechanism of Tc(VII) in H_2SO_4

In 18 M H_2SO_4 : $Tc(VII) + SO_2 \rightarrow SO_4^{2-} + Tc(V)$

$$\boxed{2Tc(VII) + SO_2 \rightarrow SO_4^{2-} + Tc(VII) + Tc(V)}$$

In 13 M H_2SO_4 :

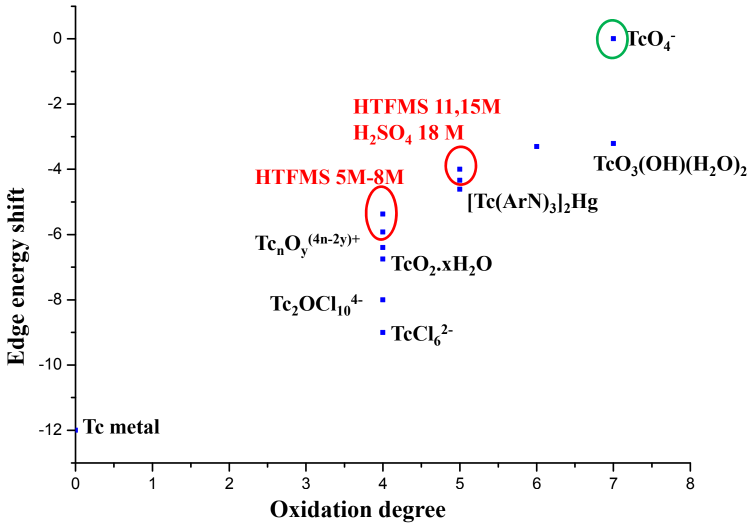
$$\boxed{\begin{array}{c} Tc(VII) + \frac{1}{2}SO_2 \rightarrow SO_4^{2-} + Tc(VI) \\ 2Tc(VI) \rightarrow Tc(V) + Tc(VII) \end{array}}$$

$$\boxed{\begin{array}{c} Tc(VII) + SO_2 \rightarrow SO_4^{2-} + Tc(V) \\ Tc(V) + H_2O_2 + 2H^+ \rightarrow Tc(VII) + 2H_2O \end{array}}$$

PRESENTATION PLAN

- BEHAVIOUR OF TECHNETIUM IN TRIFLIC ACID MEDIA IN THE ABSENCE OF EXTERNAL IRRADIATION
- BEHAVIOUR OF TECHNETIUM IN ACIDIC MEDIA UNDER α IRRADIATION
  - CF_3SO_3H
  - H_2SO_4
- SPECIATION OF TECHNETIUM BY X-RAY ABSORPTION SPECTROSCOPY (XANES/EXAFS)
  - CF_3SO_3H
  - H_2SO_4

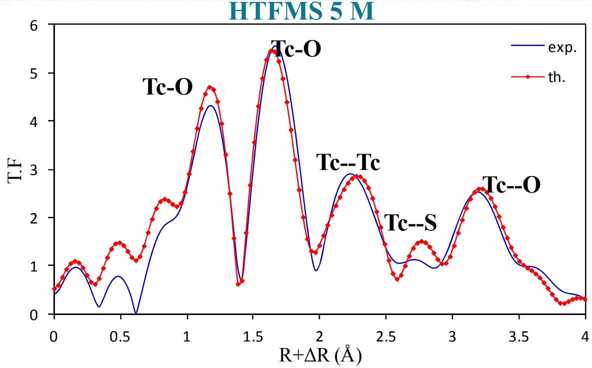
XANES analysis



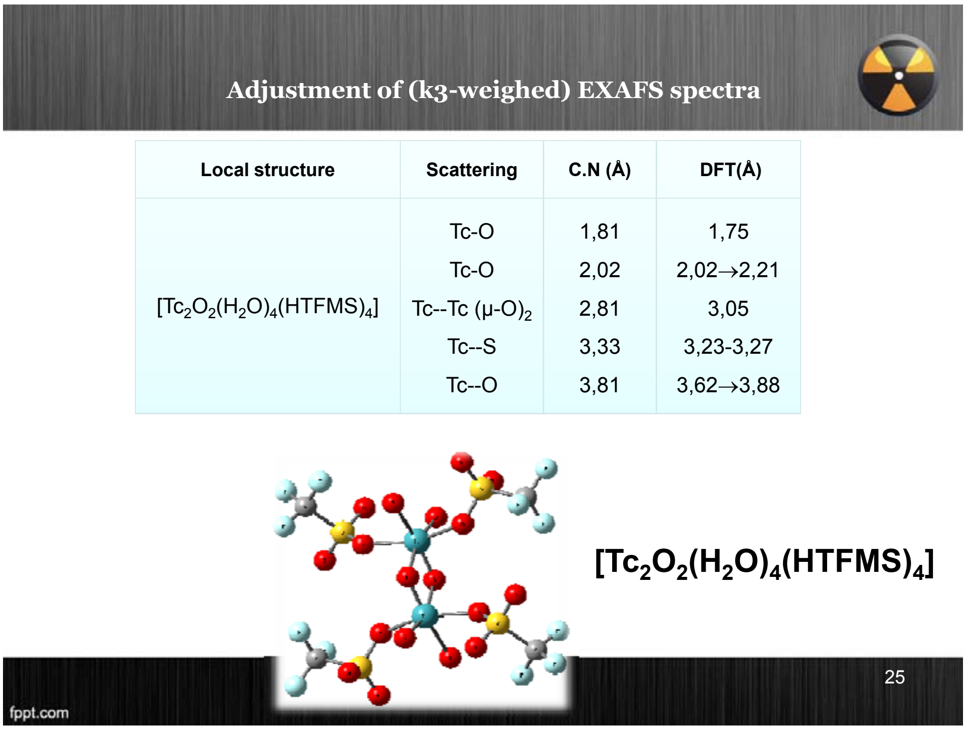
XANES analysis

Medium	Oxidation degree	Energy shift (eV)
H_2SO_4 (1 M) TcO_4^- (Reference)	VII	0
HTFMS 11,15 M non irradiated ($TcO_3(OH)(H_2O)_2$)	VII	-3,21
$TcO_2.xH_2O$	IV	-6,75
$Tc_nO_y^{(4n-2y)+}$	IV	-6,4
HTFMS 5 M	**IV**	**-5,92**
HTFMS 7 M	**IV**	**-5,37**
HTFMS 8 M	**IV**	**-5,37**
$[Tc(ArN)_3]_2Hg$	V	-4,61
HTFMS 9M	**IV-V**	**-4,06**
HTFMS 11,15 M	**V**	**-4,34**
H_2SO_4 13 M	**V –VII mixture**	**-3,3**
H_2SO_4 18 M	**V**	**-4**

Adjustment of (k3-weighed) EXAFS spectra



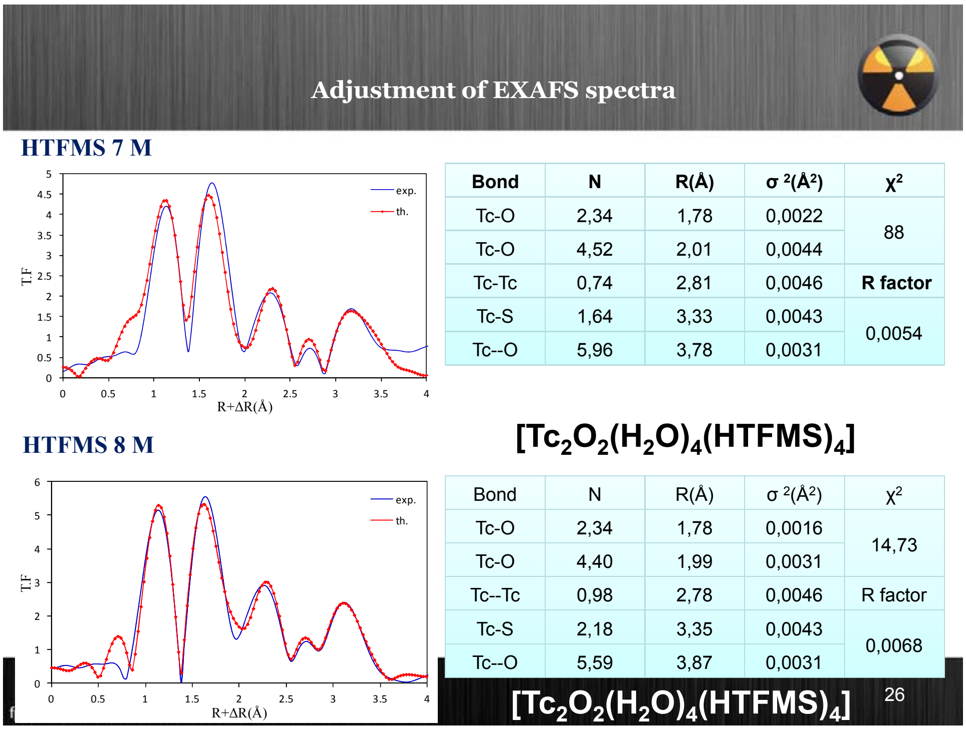
Bond	N	R(Å)	σ ²(Å²)	χ²
Tc-O	2,29	1,81	0,0023	15,44
Tc-O	4,34	2,02	0,0047	
Tc--Tc (µ-O)$_2$	0,87	2,81	0,0046	**R factor**
Tc - - S	2,17	3,33	0,0044	0,0009
Tc - - O	6,23	3,81	0,003	



Adjustment of (k3-weighed) EXAFS spectra

Local structure	Scattering	C.N (Å)	DFT(Å)
[$Tc_2O_2(H_2O)_4(HTFMS)_4$]	Tc-O	1,81	1,75
	Tc-O	2,02	2,02→2,21
	Tc--Tc (μ-O)$_2$	2,81	3,05
	Tc--S	3,33	3,23-3,27
	Tc--O	3,81	3,62→3,88

[$Tc_2O_2(H_2O)_4(HTFMS)_4$]



Adjustment of EXAFS spectra

HTFMS 7 M

Bond	N	R(Å)	σ^2(Å^2)	χ^2
Tc-O	2,34	1,78	0,0022	88
Tc-O	4,52	2,01	0,0044	
Tc-Tc	0,74	2,81	0,0046	**R factor**
Tc-S	1,64	3,33	0,0043	0,0054
Tc--O	5,96	3,78	0,0031	

[$Tc_2O_2(H_2O)_4(HTFMS)_4$]

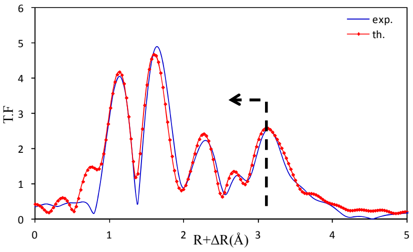
HTFMS 8 M

Bond	N	R(Å)	σ^2(Å^2)	χ^2
Tc-O	2,34	1,78	0,0016	14,73
Tc-O	4,40	1,99	0,0031	
Tc--Tc	0,98	2,78	0,0046	R factor
Tc-S	2,18	3,35	0,0043	0,0068
Tc--O	5,59	3,87	0,0031	

[$Tc_2O_2(H_2O)_4(HTFMS)_4$]

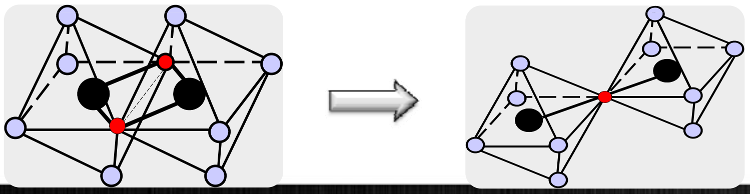
Adjustment of EXAFS spectra

HTFMS 9 M



Bond	N	R(Å)	σ ²(Å²)	χ²
Tc-O	2,06	1,79	0,0016	70,76
Tc-O	4,02	2,01	0,0034	
Tc-Tc	0,91	2,81	0,0046	**R factor**
Tc-S	3,28	3,38	0,0044	
Tc—Tc	2,23	3,62	0,0011	0,0048
Tc—O	6,47	3,92	0,0031	

Linearization of Tc(μ-O)$_2$Tc structure

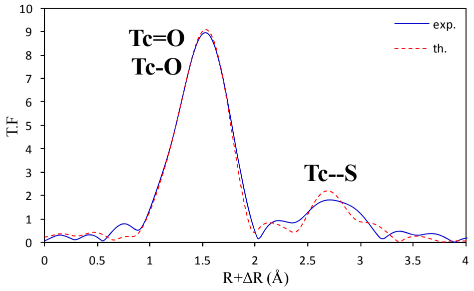


Tc(μ-O)$_2$Tc (2,81 Å)

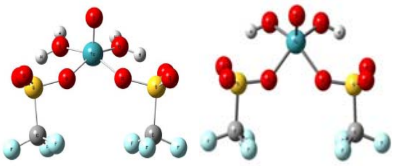
Tc-O-Tc (3,62 Å)

Adjustment of EXAFS spectra

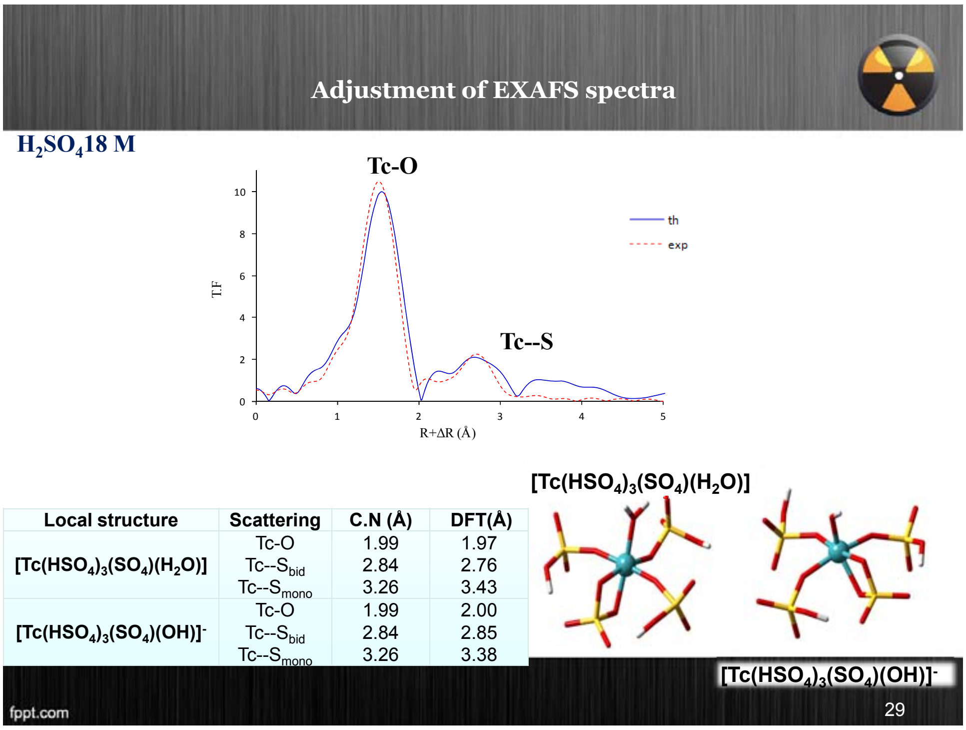
HTFMS 11,15 M



Local structure	Scattering	C.N (Å)	DFT(Å)
[OTc$^{(V)}$(F$_3$CSO$_3$)$_2$(H$_2$O)$_2$]$^+$	Tc=O	1,61	1,65
	Tc-O	2,02	1,92→2,03
	Tc--S	3,24	3,37
[OTc$^{(V)}$(F$_3$CSO$_3$)$_2$(OH)$_2$]$^-$	Tc=O	1,59	1,67
	Tc-O	2,01	1,93→2,09
	Tc--S	3,25	3,38



[OTc(F$_3$CSO$_3$)$_2$(H$_2$O)$_2$]$^+$ **[OTc(F$_3$CSO$_3$)$_2$(OH)$_2$]$^-$**



Adjustment of EXAFS spectra

$H_2SO_4$18 M

Local structure	Scattering	C.N (Å)	DFT(Å)
$[Tc(HSO_4)_3(SO_4)(H_2O)]$	Tc-O	1.99	1.97
	Tc--S_{bid}	2.84	2.76
	Tc--S_{mono}	3.26	3.43
$[Tc(HSO_4)_3(SO_4)(OH)]^-$	Tc-O	1.99	2.00
	Tc--S_{bid}	2.84	2.85
	Tc--S_{mono}	3.26	3.38

$[Tc(HSO_4)_3(SO_4)(H_2O)]$

$[Tc(HSO_4)_3(SO_4)(OH)]^-$

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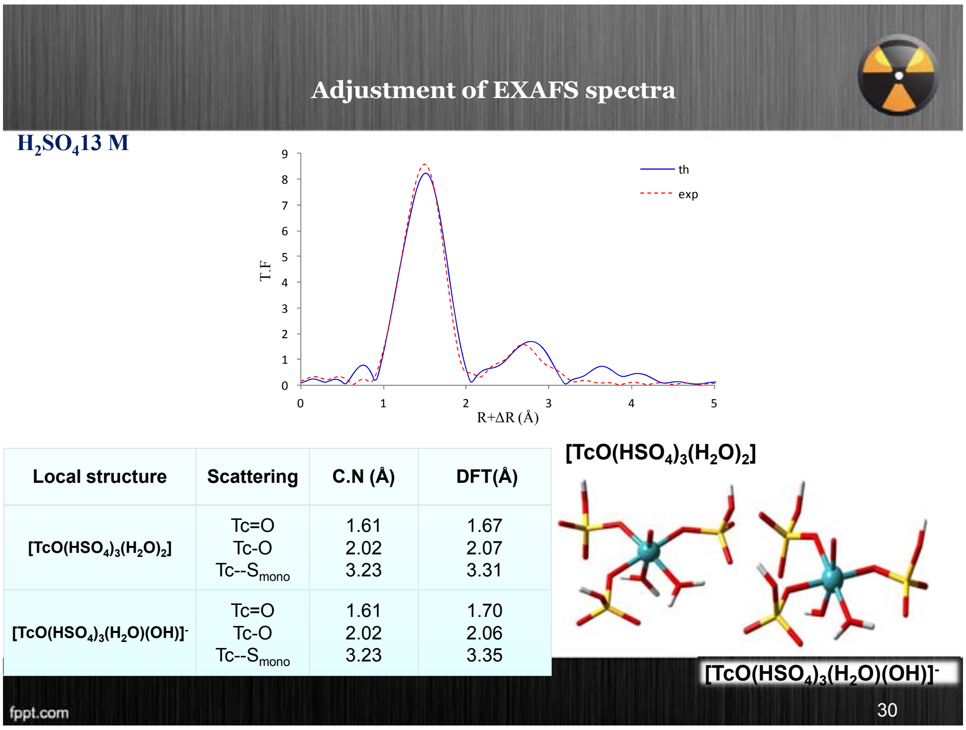

Adjustment of EXAFS spectra

$H_2SO_4$13 M

Local structure	Scattering	C.N (Å)	DFT(Å)
$[TcO(HSO_4)_3(H_2O)_2]$	Tc=O Tc-O Tc--S_{mono}	1.61 2.02 3.23	1.67 2.07 3.31
$[TcO(HSO_4)_3(H_2O)(OH)]^-$	Tc=O Tc-O Tc--S_{mono}	1.61 2.02 3.23	1.70 2.06 3.35

$[TcO(HSO_4)_3(H_2O)_2]$

$[TcO(HSO_4)_3(H_2O)(OH)]^-$

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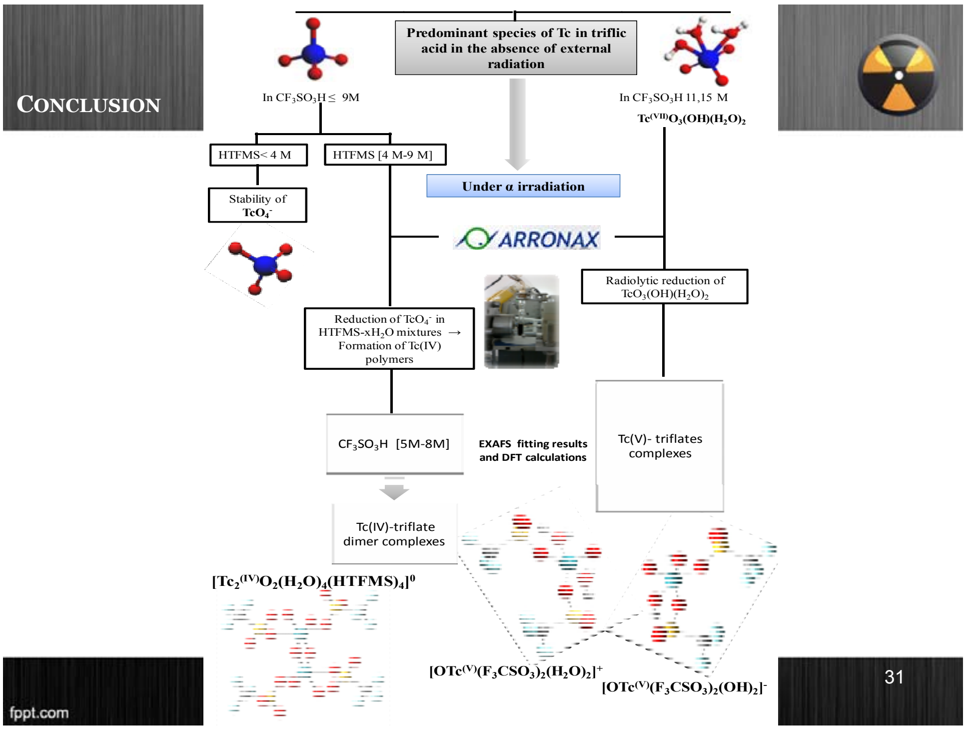

CONCLUSION

Predominant species of Tc in triflic acid in the absence of external radiation

In $CF_3SO_3H \leq$ 9M

In CF_3SO_3H 11,15 M

$Tc^{(VII)}O_3(OH)(H_2O)_2$

HTFMS< 4 M

HTFMS [4 M-9 M]

Stability of **TcO_4^-**

Under α irradiation

ARRONAX

Radiolytic reduction of $TcO_3(OH)(H_2O)_2$

Reduction of TcO_4^- in HTFMS-xH_2O mixtures → Formation of Tc(IV) polymers

CF_3SO_3H [5M-8M]

EXAFS fitting results and DFT calculations

Tc(V)- triflates complexes

Tc(IV)-triflate dimer complexes

$[Tc_2^{(IV)}O_2(H_2O)_4(HTFMS)_4]^0$

$[OTc^{(V)}(F_3CSO_3)_2(H_2O)_2]^+$

$[OTc^{(V)}(F_3CSO_3)_2(OH)_2]^-$

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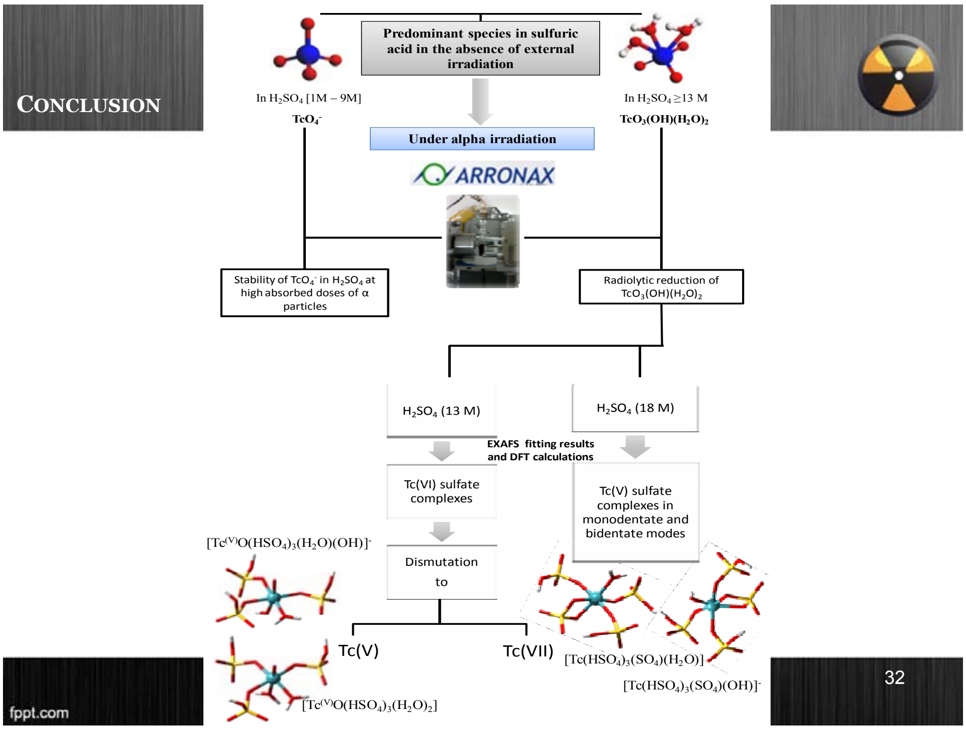

CONCLUSION

Predominant species in sulfuric acid in the absence of external irradiation

In H_2SO_4 [1M – 9M]

TcO_4^-

In $H_2SO_4 \geq$13 M

$TcO_3(OH)(H_2O)_2$

Under alpha irradiation

ARRONAX

Stability of TcO_4^- in H_2SO_4 at high absorbed doses of α particles

Radiolytic reduction of $TcO_3(OH)(H_2O)_2$

H_2SO_4 (13 M)

H_2SO_4 (18 M)

EXAFS fitting results and DFT calculations

Tc(VI) sulfate complexes

Tc(V) sulfate complexes in monodentate and bidentate modes

$[Tc^{(V)}O(HSO_4)_3(H_2O)(OH)]^-$

Dismutation to

Tc(V)

Tc(VII)

$[Tc(HSO_4)_3(SO_4)(H_2O)]$

$[Tc(HSO_4)_3(SO_4)(OH)]^-$

$[Tc^{(V)}O(HSO_4)_3(H_2O)_2]$

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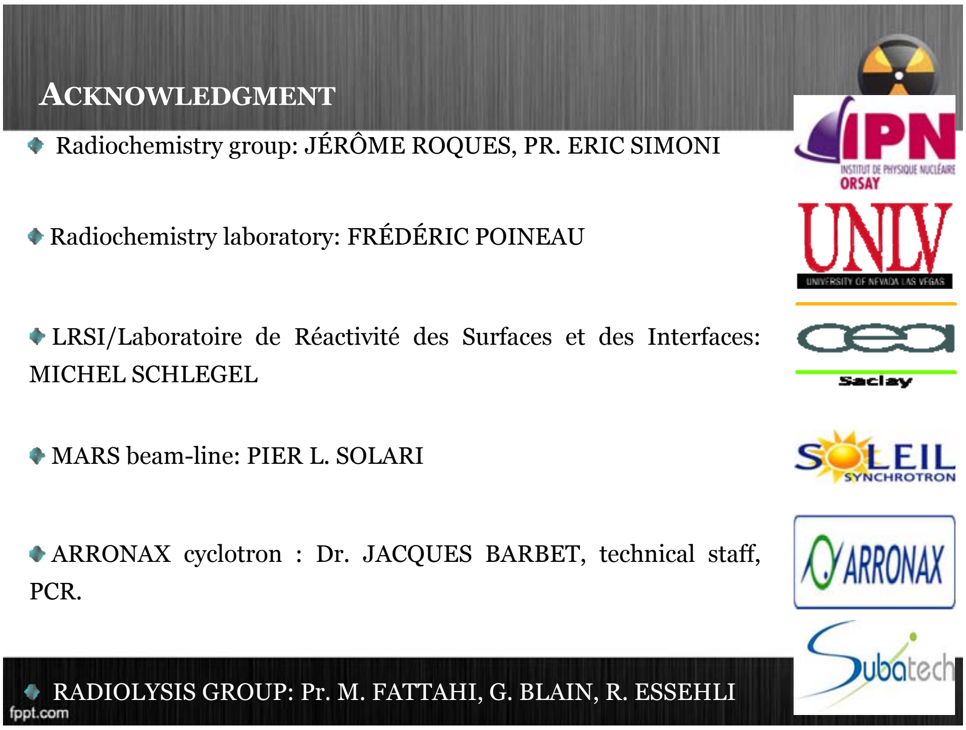

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- ARRONAX cyclotron : Dr. JACQUES BARBET, technical staff, PCR.
- RADIOLYSIS GROUP: Pr. M. FATTAHI, G. BLAIN, R. ESSEHLI

Study induced oxidation/reduction of Tc in carbonate media by α and γ radiolysis

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Technetium is a radioelement with a long half life time of 211000 years that present considerable interest in various contexts like nuclear medicine, reprocessing and storage of nuclear fuel. Understanding the chemistry of this transient element is essential for optimizing the extraction of fission products in reprocessing of used nuclear fuel [1]. Another reason that makes Tc study important is, the mobility of Tc based on its oxidation state. In fact, some species of technetium considered very mobile hence knowing its chemistry is important [2]. The aim of this study is using α and γ radiolysis for initiating and controlling the oxidation/reduction mechanism of Tc and its analogous (Mn and Re) in highly concentrated carbonate media. This study emphasize using one part of ARRONAX cyclotron which provide α high energy beam (E_α = 67 MeV, TEL = 22,7 keV.µm^{-1}) and secondly using γ irradiator at the same site in order to cover a wide range of LET for this oxidation/reduction experiments under irradiation. In first step of this work, electrochemistry experiments were performed in different Mn and carbonate concentration under controlled atmosphere to obtain optimum experimental conditions for electro-reduction. Second experiment was study the speciation of Mn by radiolysis that consist two parts; first, reduction of Mn(VII) and second, oxidation of Mn(II), each part was performed under α and γ irradiation. Spectra from in-situ UV-Vis spectrophotometer as a species monitoring tool, show the same characterizing spectrum as it was observed by electrochemical reduction. Reduction of Mn(VII) as a function of absorbed dose, shows that the reduction rate of γ radiolysis is 6 times higher than α radiolysis even the dose rate of α radiolysis is 1000 times more than γ one (Gγ(-Mn(VII)) = 1,54 × 10^{-7} mol.J^{-1}, Gα(-Mn(VII)) = 2,76 × 10^{-8} mol.J^{-1}, γ dose rate = 2,75 ± 0,40 Gy.min^{-1}, α dose rate = 3700 Gy.min^{-1}) that indicate the mechanism of reduction of Mn is radical not molecular one. Moreover the H_2 yield was measured and it is higher in case of αirradiation(Gγ(H_2) = 2,61 × 10^{-8} mol.J^{1} et Gα(H_2) = 5,4 × 10^{-8} mol.j^{-1}). The H_2 yield of soul carbonate is higher than Mn reducing system which means that some radical species, especially hydrogen radical participating in reduction of Mn(VII) or in intermediate reactions (Gγ(H_2) = 2,89 × 10^{-8} mol.J^{-1} et Gα(H_2) = 5,73 × 10^{-8} mol.J^{-1}). Also at the end of each radiolysis experiment, it observed that there is colloid precipitation of Mn_xCO_y that is quantifying by EPR, XRD, XPS and ATR-IR as a complementary data and identifying different oxidation state under irradiation. In next step, the same protocol (electrochemistry and radiolysis) was performed on Tc and Tc(IV) and (III) was observed. The products of oxidation/reduction of Tc will be characterized by using EXAFS as complimentary of ab initio DFT simulation. At the end, pulse radiolysis coupled with UV-Vis spectrophotometer in situ can provide the information about transient species (<1µs) for both solutions of Mn and Tc.

[1]. Nosco, D.L., Beaty-Nosco, J.A., 1999. Chemistry of technetium radiopharmaceuticals 1: Chemistry behind the development of technetium-99m compounds to determine kidney function. Coord. Chem. Rev. 184, 91-123.

[2]. Jenkinson, S.B., McCubbin, D., Kennedy, P.H.W., Dewar, A., Bonfield, R., Leonard, K.S., 2013. An estimate of the inventory of technetium-99 in the sub-tidal sediments of the Irish Sea.Journal of Environmental Radioactivity.

Study induced oxidation/reduction of M (Tc, Re & Mn) in carbonate media by α and γ irradiation

Ph.D (2nd year)

Mohammad GHALEI

Director: Massoud FATTAHI

Co-director: Johan VANDENBORRE

2012-2015

Overview

Introduction

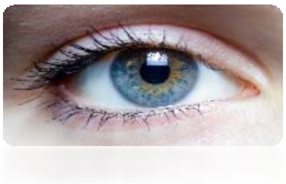
- Why Tc?
- Objectives
- Why Mn and Re

Results M

- Electrochemistry
- γ radiolysis
- α radiolysis

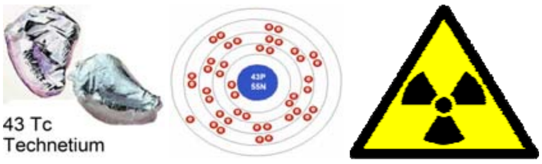
perspective

- EPR
- Pulse radiolysis
- EXAFS/DFT



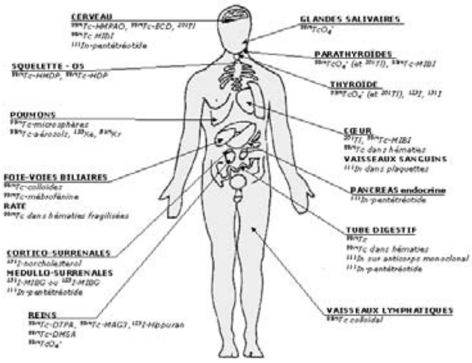
Introduction

- ❖ Why Tc?
- ❖ Objectives
- ❖ Why Mn et Re



Technetium was named technikos, a greek word that means «artificial». Technetium can not be find naturally in earth crust and it was the first element which was produced artificially .

^{99}Tc is ß emitter ($E_{max} = 294$ keV, $T_{1/2} = 2 \times 10^5$ years)



90 % of medical diagnostics exams (^{99m}Tc)

$$\mathrm{Tc(VII)} \xrightarrow[\text{complexation}]{\text{reduction}} \mathrm{Tc(V),\ Tc(IV),\ Tc(III),\ Tc(I)}$$

Beside high solubility of Tc in water, it shows high mobility based on its speciation that cause easy absorption by environment

Stabilize Tc by induced chemical reactions by radiolysis and changing oxidation state

Working on non-radioactive elements with close chemical properties of Tc

REDOX Potential (V)

Group VII

25
Mn
Manganese
54.938

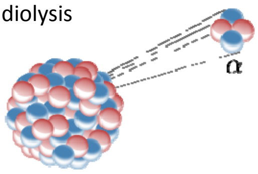
43
Tc 4.7
Technetium
98.907

75
Re
Rhenium
186.207

Electrochemistry

γ radiolysis

α radiolysis



Résultats Mn

- Electrochemistry
- γ radiolysis
- α radiolysis

Electrochemistry Mn

$[Mn]_{initial} = 5.10^{-4}$ M

pH= 10-11

1st experiment: air, $[CO_3^{2-}]$= 1M & $[HCO_3^{-}]$= 0,1M
⬇
Transparent solution and precipitate after 72h

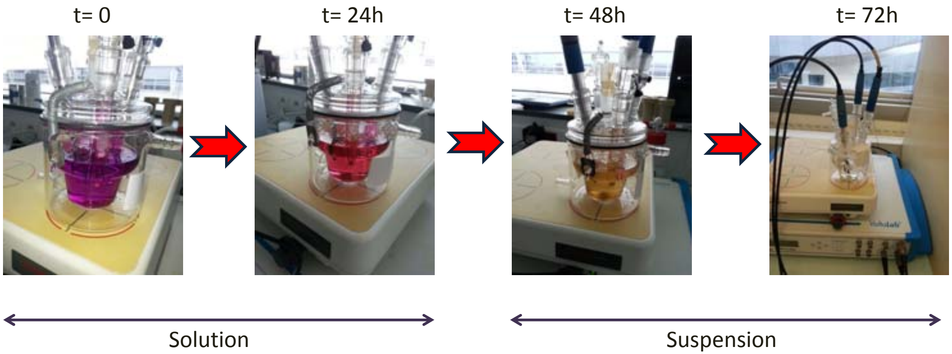
2nd experiment: air, $[CO_3^{2-}]$= 2M & $[HCO_3^{-}]$= 0,2M
⬇
Red solution after 24h

3rd experiment: Ar, $[CO_3^{2-}]$= 2M & $[HCO_3^{-}]$= 0,2M
⬇
Transparent solution and precipitate after 72h

4th experiment: Ar, $[CO_3^{2-}]$= 5M & $[HCO_3^{-}]$= 0,5M
⬇
Transparent solution and precipitate after 72h

Best Condition

Electrochemistry of Mn

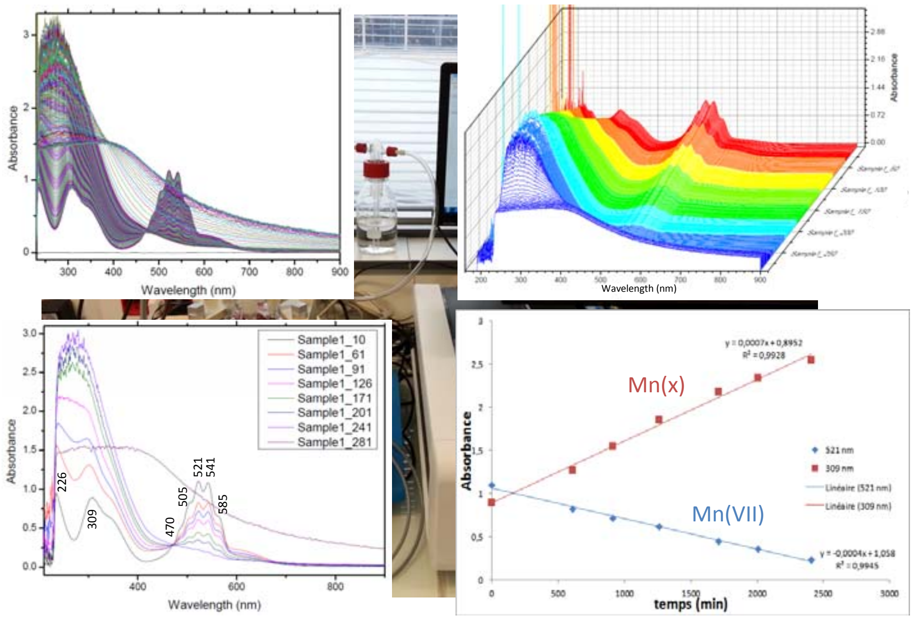


No spectrum after filtration

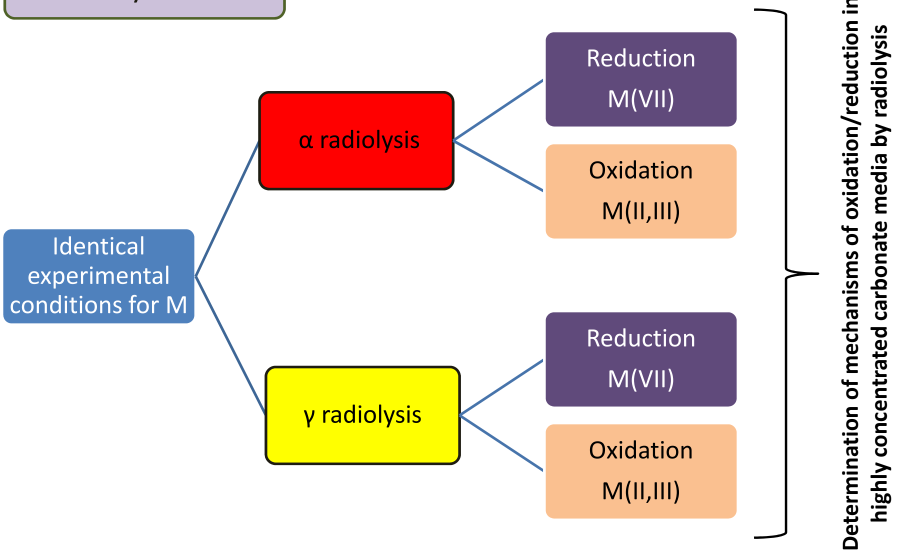
Electrochemistry Mn

Reduction of Mn(VII)

Colloids of Mn(x)



Radiolysis of M



Identical experimental conditions for M

α radiolysis

- Reduction M(VII)
- Oxidation M(II,III)

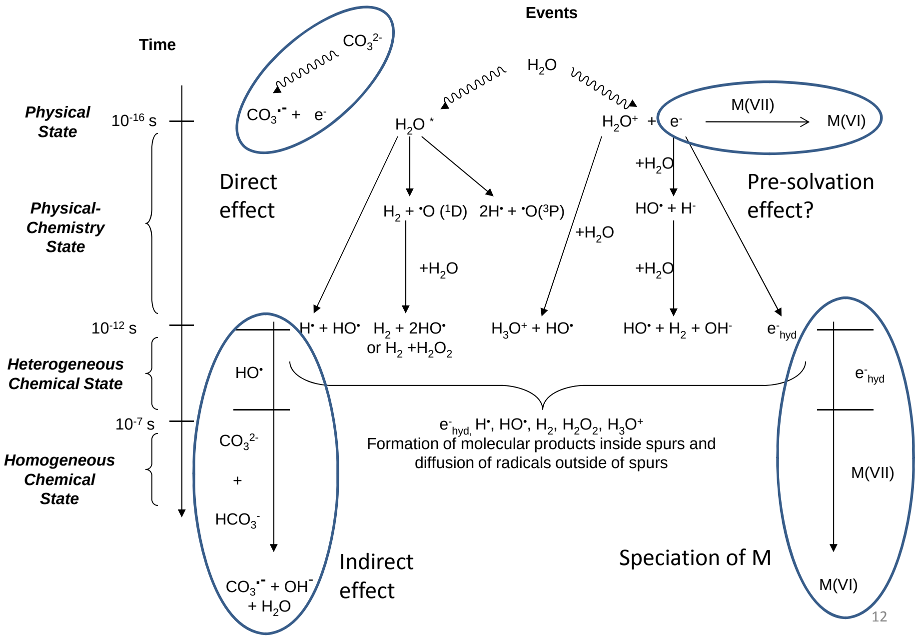
γ radiolysis

- Reduction M(VII)
- Oxidation M(II,III)

Determination of mechanisms of oxidation/reduction in highly concentrated carbonate media by radiolysis

Ar, $[CO_3^{2-}]$= 5M & $[HCO_3^-]$= 0,5M
$[Mn]_{initial}$ = 5.10^{-4} M

Radiolysis : decomposition of materials under irradiation



$HO^{\bullet}$ → Oxidant $HO^{\bullet} + M^{n+} \longrightarrow M^{n+1}$

$H^{\bullet}$ et $e^{-}_{(s)}$ → Reducter $e^{-}_{(s)} + M^{n+} \longrightarrow M^{n-1}$

- Adding scavenger for choosing interested media

Redox potential effect

Oxidant :

$$e_{aq}^{-} + N_2O \longrightarrow N_2 + O^{\bullet -}$$

Reducer:

$$^{\bullet}OH/H^{\bullet} + HCO_2^{-} \longrightarrow H_2O/H_2 + CO_2^{\bullet -}$$

Adding propanol for deactivating $HO^{\bullet}$

$$e_{aq}^{-} + RX \longrightarrow R^{\bullet} + X^{-}$$

Carbonate:

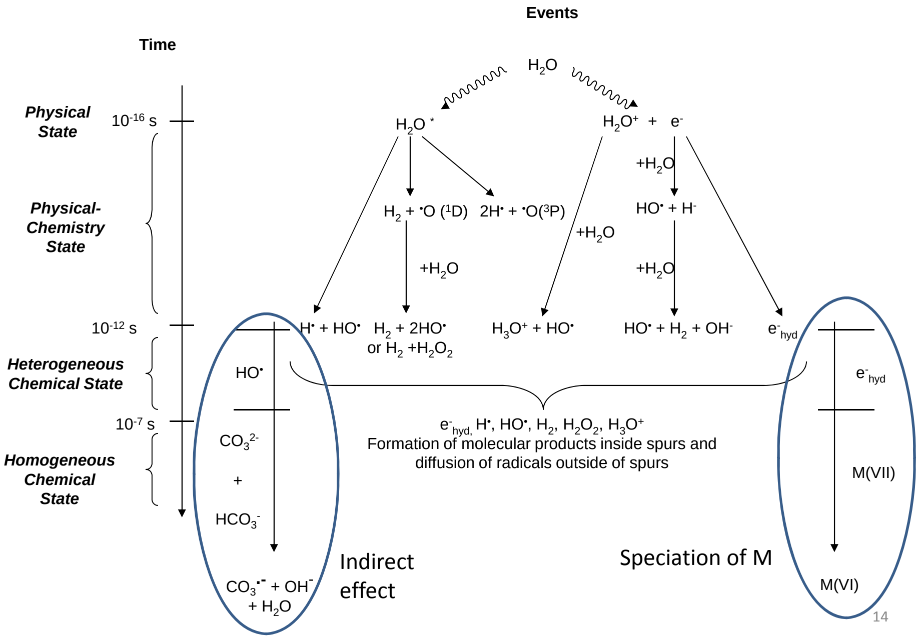
$$\bullet OH + CO_3^{2-} \rightarrow \bullet CO_3^{-} + OH^{-}$$ K = 3.9 . 10^{8} $M^{-1}.s^{-1}$

$$\bullet OH + HCO_3^{-} \rightarrow \bullet CO_3^{-} + H_2O$$ K = 8.5 . 10^{6} $M^{-1}.s^{-1}$

$CO_3^{\bullet -}$ → Oxidant

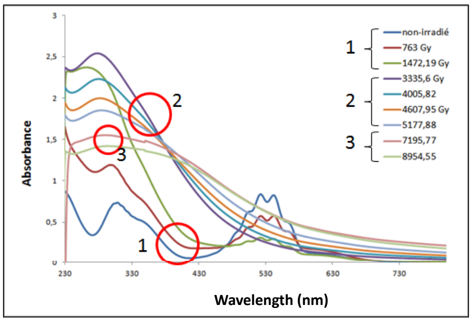
$H^{\bullet}$ et $e^{-}_{(s)}$ → Reducer

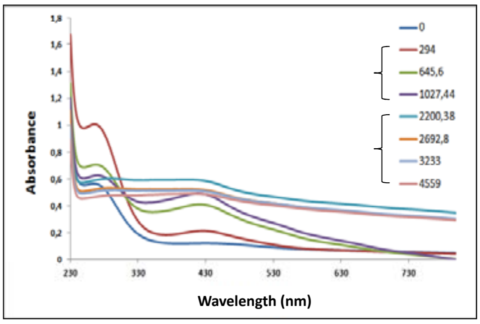
Radiolysis : decomposition of materials under irradiation

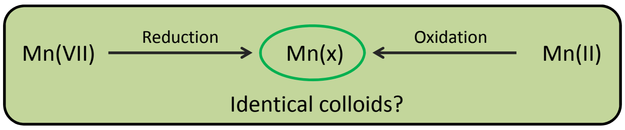


γ radiolysis

Irradiation conditions
Time: 2h-48h
Dose rate: 3Gy.min^{-1}
Cs source







$$Mn(VII) \xrightarrow{\text{Reduction}} \boxed{Mn(x)} \xleftarrow{\text{Oxidation}} Mn(II)$$

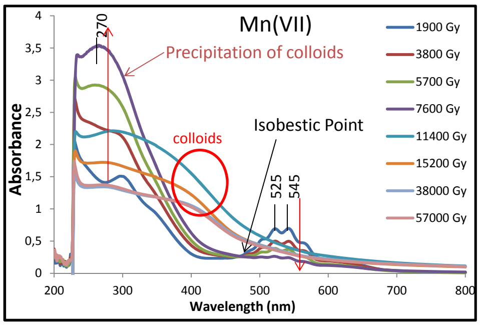
Identical colloids?

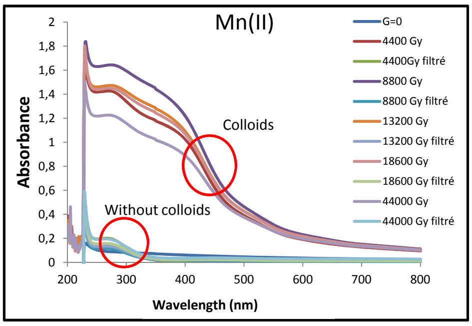
α radiolysis (1/2)

Cyclotron Arronax
α beam provider at high energy
(E_α=67MeV, LET = 22,7 keV.µm^{-1})
Dose rate: 3800 Gy.min^{-1}
Time: 0,5min-15min

Casmate AX

Radiolyse α (2/2)



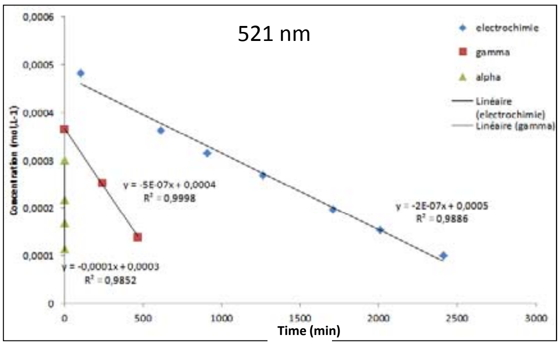


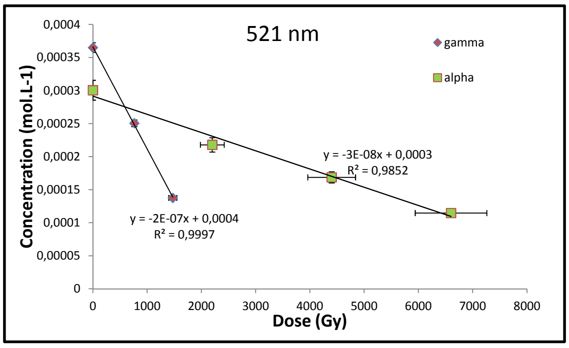
$$Mn(VII) \xrightarrow{Reduction} \boxed{Mn(x)} \xleftarrow{Oxidation} Mn(II)$$

- ➢ Identical colloids?
- ➢ Same structure for α and γ

Colloids precipitation of Mn(x) ?

G-[Mn(VII)]

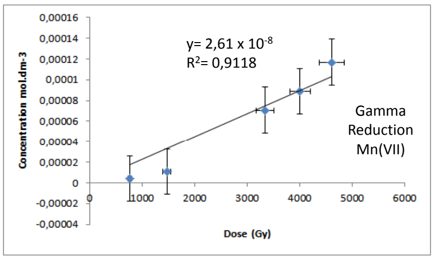


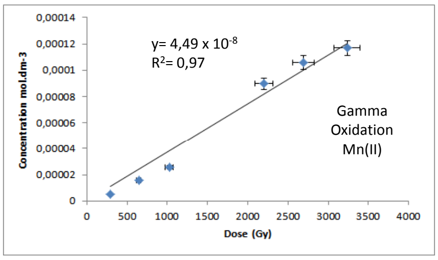


γ radiolysis is more efficient than α one so the mechanism is radical one

G(H_2)

$$Mn(VII) \xrightarrow{Reduction} Mn(x) \xleftarrow{Oxidation} Mn(II)$$



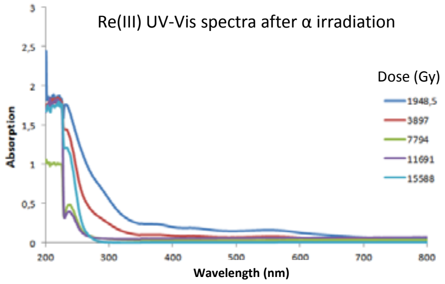


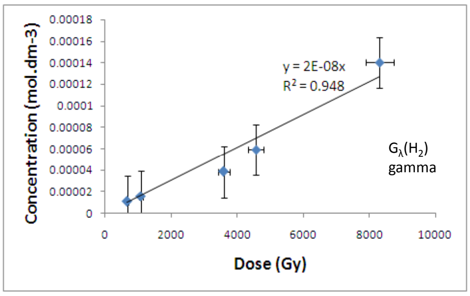
G(H_2) mol.J^{-1}	Carbonate	Reduction Mn(VII)	Oxidation Mn(II)	Ultra pure water
γ	$2{,}9 \times 10^{-8}$	$2{,}6 \times 10^{-8}$	$4{,}5 \times 10^{-8}$	$2{,}5 \times 10^{-8}$
α	$5{,}7 \times 10^{-8}$	$5{,}4 \times 10^{-8}$	$7{,}7 \times 10^{-8}$	$6{,}0 \times 10^{-8}$

1) Reduction = consummation of H_2 and oxidation = production of H_2 thus confirmation radical mechanism
2) In comparison to water, carbonate media has a small impact
3) Catalytic role of Mn(II) on production of H_2

F. Crumière, Etudes de l'effet des rayonnements ionisants sur l'eau : Rendements radiolytiques de l'hydrogène moléculaire, in: Ph.D., Université de Nantes, Nantes, 2012.

Re radiolysis





mol.L^{-1}.Gy^{-1}	Carbonate	Re(VII)	Re(II)
Gamma	$2{,}89 \times 10^{-8}$	$4{,}25 \times 10^{-8}$	$1{,}22 \times 10^{-8}$
Alpha	$5{,}73 \times 10^{-8}$	---------	$5{,}70 \times 10^{-8}$

Re radiolysis

As the e^-_{aq} and $H^\cdot$ can not reduce in presence of CO_3^{2-}

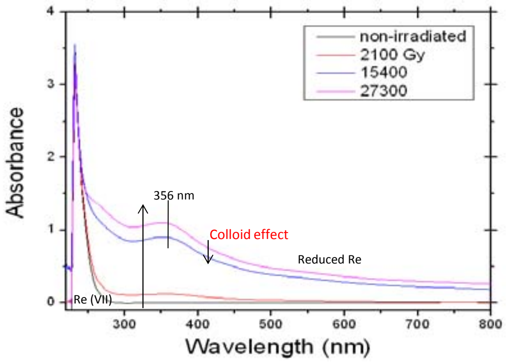
Solution

Adding formate

$$H_2O \xrightarrow{\alpha,\gamma,e^-} e_{aq}^-,\ H,\ OH,\ H_2,\ H_2O_2$$

$$OH + HCO_2^- \rightarrow H_2O + CO_2^{\bullet -} \quad 3.2 \times 10^9\ dm^3\ mol^{-1}\ s^{-1}$$

- Reducer
- Kinetic rate is 10 times higher than carbonate



Transparent Re(VII)

γ irradiation

Red-brownish solution

γ irradiation

Red-brownish solution
With very fine colloids

Conclusion Mn & Re

- Mn can be oxidized and reduced in the same media under irradiation
- The final product of Mn is oxo-carbonate complex
- The oxidation-reduction is radical
- The final product of Mn has resistance against extra oxidation/reduction
- Re can be just oxidize in carbonate media under irradiation
- For reduction of Re under irradiation, adding formate is necessary
- Final product of reduction of Re is oxidized in contact with air

Chemistry of Tc

Objective : Study chemistry and complexation of Tc in carbonate media

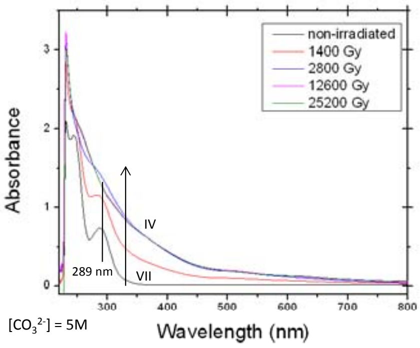
- ➢Polymeric or monomeric product ?!
- ➢Carbonate or oxo-carbonate complex ?!
- ➢Mechanism ?

Tools :

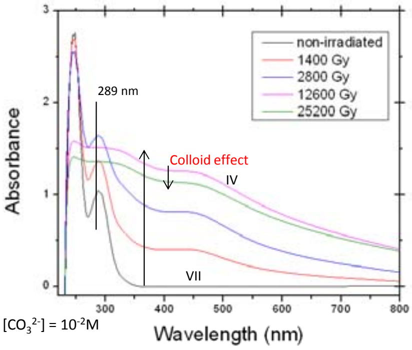
- ➢Electrochemistry
- ➢Radiolysis

Tc radiolysis

Can not be reduced in carbonate media so adding formate is necessary



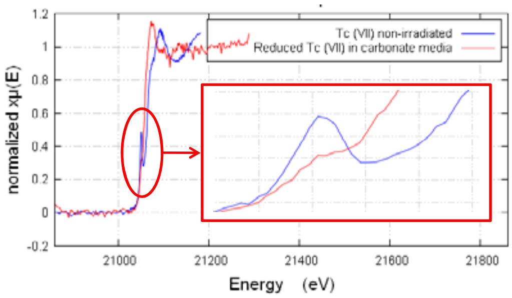
$[CO_3^{2-}]$ = 5M



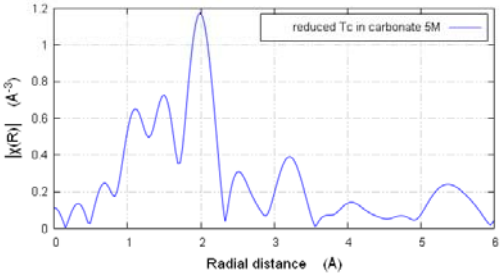
$[CO_3^{2-}]$ = 10^{-2}M

- ➢ In solution with $[CO_3^{2-}] < 1M$, TcO_2 will be dominant product
- ➢ The higher carbonate concentration, the more stable final product against re-oxidation

Tc radiolysis



- The final product has oxidation state of 4
- Re-confirmation that the higher carbonate concentration, the more stable against re-oxidation

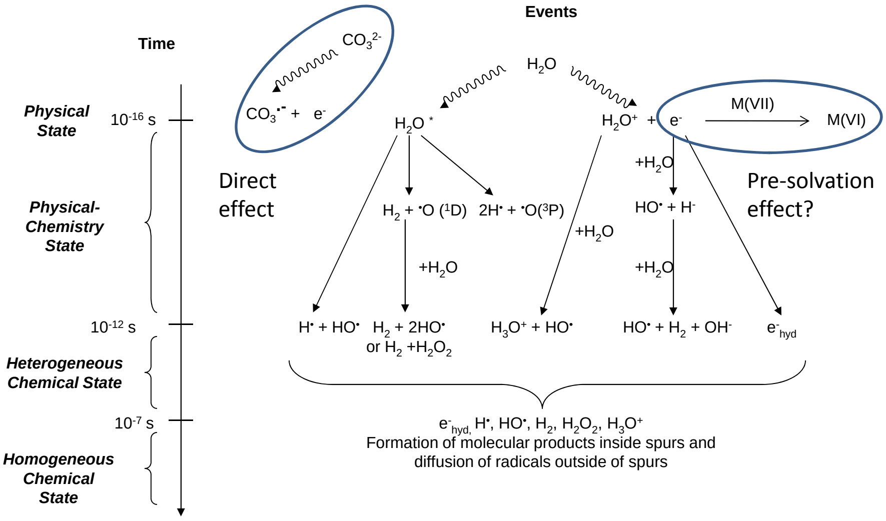


EXAFS spectrum

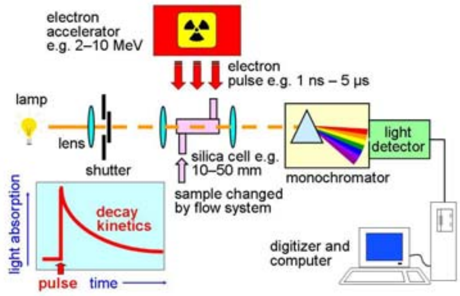
⬇

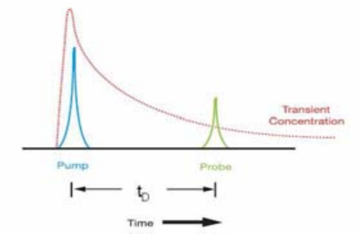
Interpreting to find molecular structure

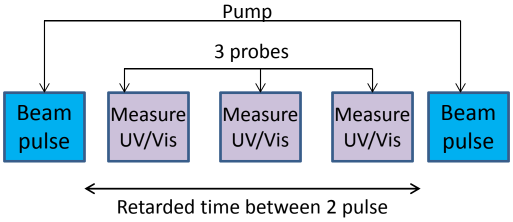
Radiolysis : decomposition of materials under irradiation



- **Electron pulse radiolysis, LCP , Orsay**
- **α pulse radiolysis, Cyclotron Arronax**






Pump

3 probes

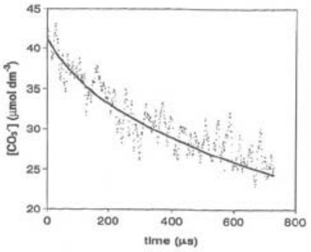
Beam pulse	Measure UV/Vis	Measure UV/Vis	Measure UV/Vis	Beam pulse

Retarded time between 2 pulse

Electron pulse radiolysis

$CO_2 + H_2O$	$HCO_3^- + H^+$	2.000×10^4
$HCO_3^- + H^+$	$CO_2 + H_2O$	5.000×10^{10}
HCO_3^-	$CO_3^{2-} + H^+$	2.000
$CO_3^{2-} + H^+$	HCO_3^-	5.000×10^{10}
$CO_2 + e^-_{aq}$	$CO_2^{\cdot-}$	7.700×10^9
$CO_3^{2-} + e^-_{aq}$	$CO_2^{\cdot-} + OH^- + OH^-$	3.900×10^5
$HCO_3^- + H^\cdot$	$CO_3^{\cdot-} + H_2$	4.400×10^4
$OH^\cdot + HCO_3^-$	$CO_3^{\cdot-} + H_2O$	8.500×10^6
$OH^\cdot + CO_3^{2-}$	$CO_3^{\cdot-} + OH^-$	3.900×10^8
$CO_3^{\cdot-} + CO_3^{\cdot-}$	$CO_4^{2-} + CO_2$	7.000×10^6
$CO_4^{2-} + H_2O$	$CO_2 + HO_2^- + OH^-$	2.000×10^{-1}
$CO_3^{\cdot-} + H_2O_2$	$CO_3^{2-} + HO_2^\cdot + H^+$	8.000×10^5
$CO_3^{\cdot-} + HO_2^-$	$CO_3^{2-} + O_2^{\cdot-} + H^+$	1.000×10^7
$CO_3^{\cdot-} + O_2^{\cdot-}$	$CO_3^{2-} + O_2$	6.005×10^8
$CO_3^{\cdot-} + CO_2^{\cdot-}$	$CO_3^{2-} + CO_2$	3.000×10^8
$CO_2^{\cdot-} + e^-_{aq}$	$HCOO^- + OH^-$	9.000×10^8
$CO_2^{\cdot-} + CO_2^{\cdot-}$	$C_2O_4^{2-}$	5.000×10^8
$CO_2^{\cdot-} + H_2O_2$	$CO_2 + OH^\cdot + OH^-$	6.000×10^5
$CO_2^{\cdot-} + O_2$	$CO_2 + O_2^{\cdot-}$	2.000×10^9
$CO_2^{\cdot-} + HCO_3^-$	$CO_3^{\cdot-} + HCOO^-$	2.000×10^3
$CO_3^{\cdot-} + HCOO^-$	$HCO_3^- + CO_2^{\cdot-}$	1.500×10^5
$OH^\cdot + HCOO^-$	$CO_2^{\cdot-} + H_2O$	3.200×10^9
$H^\cdot + HCOO^-$	$CO_2^{\cdot-} + H_2$	2.100×10^8
$e^-_{aq} + HCOO^-$	$CO_2^{\cdot-} - H^+ + H_2$	8.000×10^8
$OH^\cdot + C_2O_4^{2-}$	$CO_2^{\cdot-} + CO_2 + OH^-$	4.000×10^7

$[CO_3^{2-}] = 10^{-3}M$



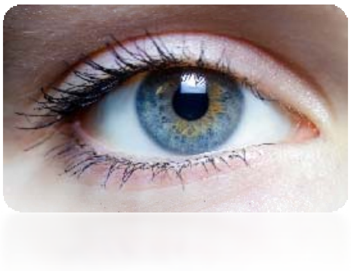
Carbonate radical decay with pulse radiolysis
$[CO_3^{2-}]$= 5 x 10^{-2}M , $[HCO_3^-]$= 7,5 x 10^{-4}M, sous N_2O

In the solution of $[CO_3^{2-}] = 5M$

- Direct effect
- The direct effect limit
- Mechanism: is it the same?
- Dependence of pH?
- Decay kinetic of carbonate
- Pre-solvated electron reaction ?!
- Study mechanism of speciation of Mn et Re

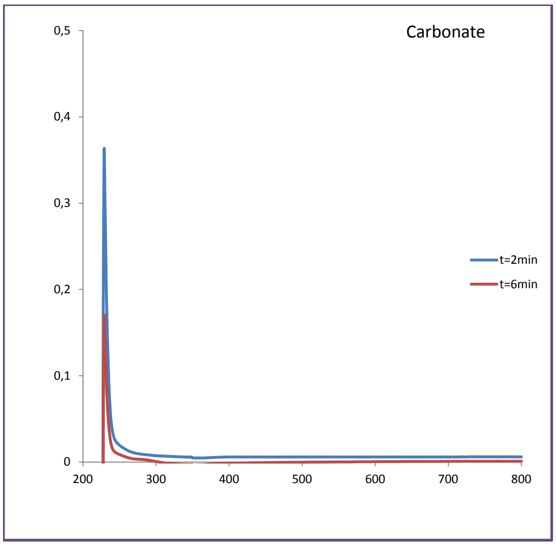
Trygve et al, *journal of nuclear materials* , 375 (2008) 331-339
Zhongli et al, *radio active waste managment and proposal*, 136 (2001) 231-240

Perspective



- Electrochemistry of Re
- H_2 yield for radiolysis of Tc
- Electron pulse radiolysis
- α pulse radiolysis carbonate
- characterization by EPR, EXAFS
- Speciation of M by EXAFS/ Simulation DFT

Thanks for your attention


Carbonate
0,5
0,4
0,3
0,2
0,1
0
200
300
400
500
600
700
800
t=2min
t=6min

Speciation of Technetium in Sulfuric Acid/Hydrogen Sulfide Solutions

Maryline Ferrier, Frederic Poineau, Jerome Roques, Alfred P. Satteleberger and Kenneth R. Czerwinski

Contact e-mail: ferrierm@unlv.nevada.edu

Chemical investigations of technetium are strongly coupled to nuclear fuel cycle and radiopharmaceuticals. The most readily available technetium isotope for chemistry studies is ^{99}Tc ($T_{1/2}$ = 2.13×10^5 years, β = 280 keV) which is produced during the fission of ^{235}U via the ^{99}Mo decay with a fission yield of nearly 6%. The high production rate and the long half-life make technetium an element of concern in waste management.

Despite its important role in radiopharmaceuticals and the nuclear fuel cycle, the fundamental chemistry of technetium is not as well developed as that of the neighboring transitions metals; one of the most striking examples is the sulfide chemistry. Only one binary sulfide (TcS_2) has been unambiguously characterized. Ditechnetiumheptasulfide (Tc_2S_7) has also been reported but its exact structure, speciation and composition is unclear but has been proposed as immobilization process for technetium in environment.[1,2,3]

Tc_2S_7 is obtained by the reaction between pertechnetate and hydrogen sulfide in an acidic solution (0.5 to 5 M HCl or H_2SO_4). Previous works analyzed the solid but the exact nature of the precipitate is controversy and the stoichiometry Tc_3S_{10} has been mentioned.[1] The speciation of technetium in presence of sulfide in aqueous media is unknown and the mechanism of formation and dissolution of "Tc_2S_7" are unclear.

In the present work, the reaction between Tc (VII) and $H_2S_{(g)}$ in 12 M H_2SO_4 has been studied. This reaction produced a black solid and a brown supernate. The solid was analyzed by energy dispersive X-ray (EDX) and X-ray absorption fine structure (XAFS) spectroscopy and the results were consistent with the presence of Tc_2S_7. The speciation of technetium in the supernate was performed by UV/Visible and XAFS spectroscopy. Experiments showed that in 12 M H_2SO_4 an intermediate Tc(V) sulfate complex was formed. Analysis indicated that the final complex present in solution was a polymeric species with a Tc–O–Tc core coordinated to sulfate ligands. Density Functional Theory (DFT) calculations showed that the proposed complexes were stable and that the theoretical structure was in good agreement with XAFS data.

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[1] W.W. Lukens, J. J. Bucher, D. K. Shuh and N. M. Edelstein, *Environ. Sci. Technol.*, **2005**, 39, 8064-8070
[2] Y. Liu, J. Terry and S. Jurisson, *RadiochimActa*, **2007**, 95, 717-725
[3] S. Kunze, V. Neck, K. Gompper and Th. Fanghanel, *Radiochim. Acta*, **1996**, 74, 159-163

Speciation of Tc in 12 M H_2SO_4/ H_2S solution

Maryline Ferrier
UNLV Radiochemistry Ph.D. student

M. Ferrier, J. Roques, F. Poineau, A. P. Sattelberger, J. Unger and K. R. Czerwinski,
Eur. J. Inorg. Chem., 2046-2054, **2014**

8th International Symposium on Technetium and Rhenium

09-30-2014

Outline

- Introduction
  - Technetium
  - Technetium sulfides
  - Technetium in 12 M sulfuric acid
- Experimental
- Results and discussion
- Conclusion and Future work

Synthesis of technetium sulfides

Introduction

Introduction: Technetium

- Goals:

  - Investigation of waste form for long term disposal
    - Glass, Oxide, Metallic, Sulfide compounds
      - ReS_2 described has having lower solubility than ReO_2 [1]
  - Need to understand technetium sulfide chemistry
- Only 2 binary Tc sulfide compounds are known:
  - Tc_2S_7 and TcS_2 [2]
- Evidence of technetium oxysulfide
  - TcO_3S^-: reaction in MeCN between TcO_4^- and $[(CH_3)_3Si]_2S$ [3]

[1] Y. Xiong, and S. Wood, *Geochemical* Transactions, 3, 1-10, **2002**
[2] K. Schwochau, Technetium: Chemistry and Radiopharmaceutical Applications, Wiley-VCH: Weinheim, Germany, **2000**
[3] M. Ferrier et al., *Dalton Trans.*, 41(20), 6291-6298, **2012**

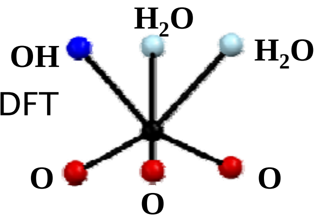
Introduction

- From literature:
  - TcO_4^- in 2-4 M H_2SO_4 + $H_2S_{(g)} \rightarrow T_2S_{7\ (s)}$
    - Solid is amorphous
      - EXAFS characterization
    - No analysis on the supernate
- What happens when you perform the reaction in 12 M H_2SO_4?

K. Schwochau, Technetium: Chemistry and Radiopharmaceutical Applications, Wiley-VCH: Weinheim, Germany, **2000**

Introduction

- Dissolution of $KTcO_4$ in H_2SO_4
  - For H_2SO_4 < 8 M: colorless TcO_4^- solution
  - For H_2SO_4 > 8 M: yellow solution
    - New band at 337 nm (new species)

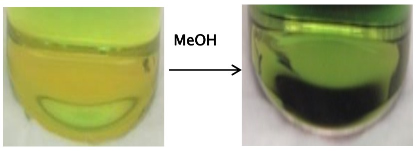


- After analyses: UV-Vis, NMR, EXAFS, DFT
  - Optimized structure: $Tc^{VII}O_3(H_2O)_2(OH)$
- What happens when you introduce a reducing agent in this solution?

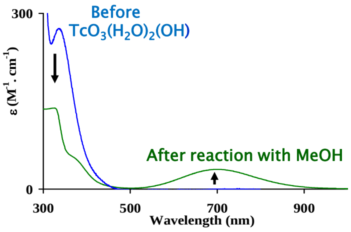
F. Poineau et al., *Dalton Transactions*, 39, 8616-8619, **2010**
F. Poineau et al., *Inorganica Chimica Acta*, 398, 147-150, **2013**

Introduction

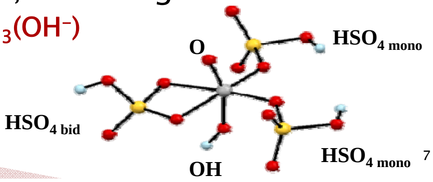
- Addition of MeOH
  - Obtained a green solution
    - New large band centered at 700 nm (new species)



Tc(+VII) in 13 M H_2SO_4 Tc(+V) in 13 M H_2SO_4



- After analyses: UV-Vis, EXAFS, DFT on green solution
  - Optimized structure: $Tc^{V}O(HSO_4)_3(OH^-)$



F. Poineau et al., *Dalton Transactions*, 2013, 42, 4348-4352

Experimental

Reaction with $H_2S_{(g)}$

$KTcO_4$ in
12 M H_2SO_4

RT, $H_2S_{(g)}$

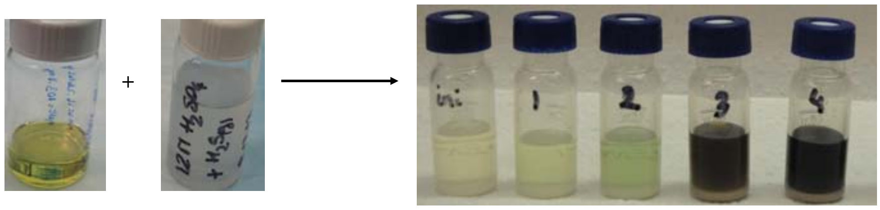
Supernate

Washes

Precipitate
Yield = 20%

- 100 mg $KTcO_4$ in 10 mL 12 M H_2SO_4 (yellow solution)
- Bubble $H_2S_{(g)}$ through the solution for 20 min.
- Remove the supernate
- Wash precipitates
  - Sulfuric acid, acetonitrile, diethyl ether, carbon disulfide

Reaction with $H_2S_{(aq)}$



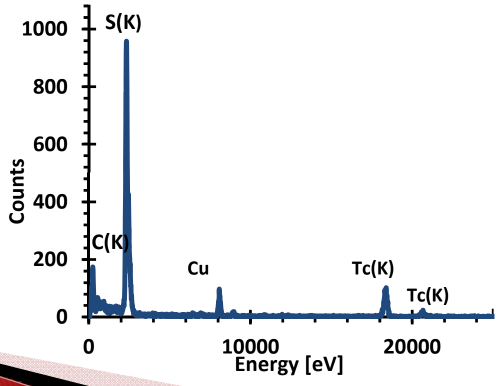
- 100 mg $KTcO_4$ in 5 mL 12 M H_2SO_4 (yellow solution)
- Bubble $H_2S_{(g)}$ in 12 M H_2SO_4 for 20 minutes
  - The solution went from colorless to cloudy

Samples	ini	1	2	3	4
$KTcO_4$ solution	200	200	200	200	200
12 M H_2SO_4 – $H_2S_{(aq)}$ solution	–	100	75	150	300
12 M H_2SO_4	800	700	725	650	500

Results and Discussions

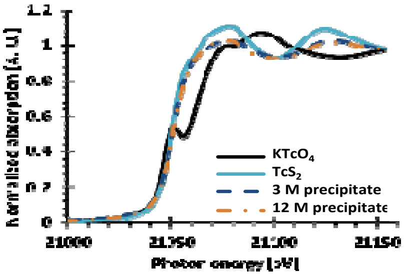
Precipitate – EDX analysis

- Spectrum exhibits peaks for Tc and S
  - No peak for O was observed
    - Complete reaction



Precipitate-XANES analysis

- Tc_2S_7
  - If we assume S in (-II) oxidation state
  - Tc should be in (+VII) oxidation state



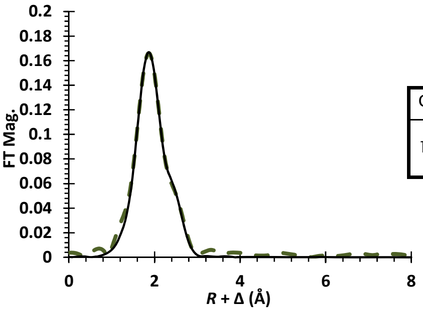
Compounds	Oxidation Sate	K-edge Shift
$KTcO_4$	VII	0
TcO_2 [1]	IV	- 6.95
TcS_2 [2]	IV	- 10.5
Tc_2S_7 [3]	IV	- 6.5
Tc_2S_7 [4]	IV or V/IV	- 8
Precipitates [this work]	-	- 9.9

- Tc_2S_7 not consistent with a +VII oxidation state but with a reduced state (probably +IV)
  - Possible mixture of S oxidation states

[1] I. Almahamid et al., *Inorg. Chem.*, 34(1), 193-198, **1995**
[2] M. Ferrier et al., *Dalton Trans.*, 42(44), 15540-15543, **2013**
[3] W. W. Lukens et al., *Environ. Sci. Technol.*, 39, 8064-8070, **2005**
[4] Y. Liu et al., *Radiochim. Acta*, 95, 717-725, **2007**

Precipitate-EXAFS analysis

- Use a model to try to fit the experimental data: TcS_2
  - Single scattering path: Tc - S at 2.297 Å
  - Single scattering path: Tc - Tc at 2.898 Å
- No parameter (CN, R, σ^2) fixed

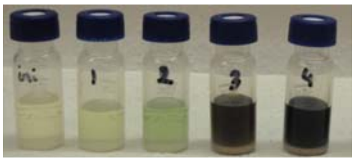


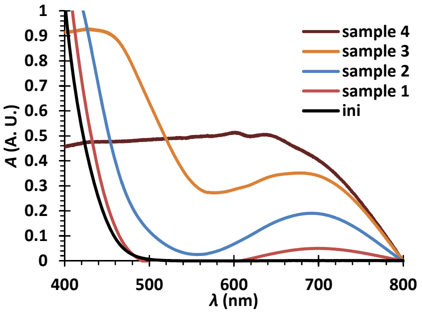
Compounds	Tc scattering	CN	R [Å]	σ^2 [Å^2]
12 M precipitate	Tc - S	6.8±1.4	2.37(2)	0.007
	Tc -Tc	2.0±0.4	2.78(3)	0.010

- The solid is similar to Tc_2S_7 and contains:
  - 7 Tc atoms at 2.37(2) Å
  - 2 S atoms at 2.78(3) Å

Solution–UV/Vis analysis

- Evaluate soluble species formation mechanism:

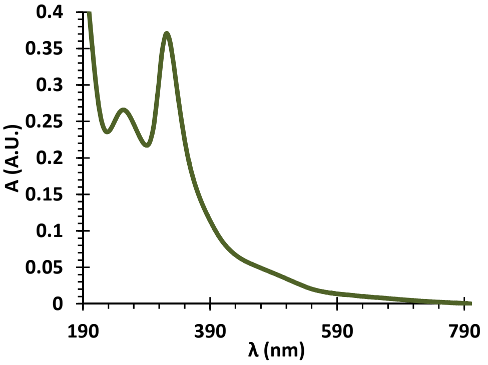




- Peak around 700 nm:
  - Signature peak of Tc (+V) green
  - Peak very stable over time

F. Poineau et al., *Dalton Transactions*, 2013, 42, 4348–4352

Supernate–UV/Vis analysis

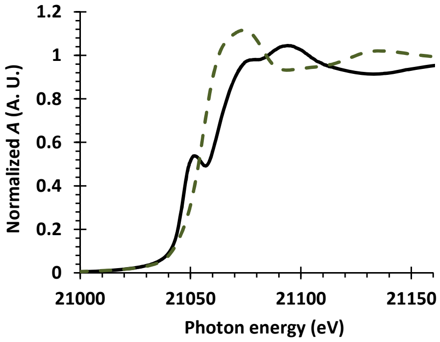


- Peak around 500 nm: signature of polymeric species like: Tc–O–Tc
- Peak at 323 nm: Probably due to $Tc_nO_y^{(4n-2y)+}$

L. Vichot et al., *Radiochim. Acta*, 2003, 91(5), 263–271
F. Poineau et al., *Radiochim. Acta*, 2006, 94, 291–299

Supernate–XANES analysis

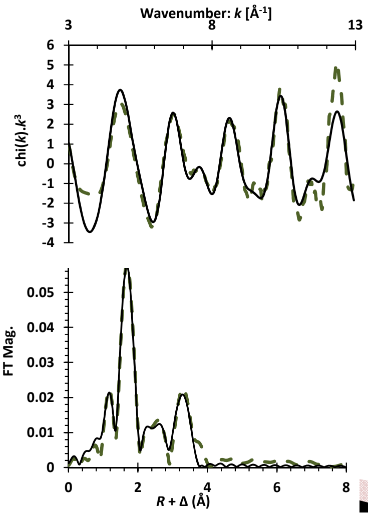
- The position of Tc K-edge = −7.5±0.3 eV



- Tc compound present in solution consistent with a reduced Tc species (probably +IV)

Supernate–EXAFS analysis

- Use a model: $Tc_2O(HSO_4)_4(H_2O)_2(OH)_2$
- **Parameter σ² fixed, CN and R allowed to vary**



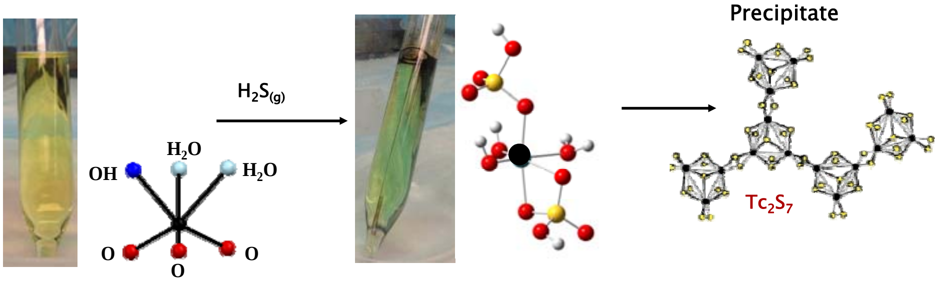
Compound	Tc scattering	CN	R [Å]	σ^2 [Å^2]
12 M supernate	Tc – O(–Tc)	1.3±0.3	1.81(2)	*0.002*
	Tc –O	3.8±0.8	2.03(2)	*0.004*
	Tc – S_{bid}	0.7±0.1	2.84(3)	*0.006*
	Tc – S_{mono}	1.7±0.2	3.16(3)	*0.009*
	Tc–O–Tc	0.7±0.3	3.62(4)	*0.008*

- Polymer Tc – O – Tc with
  - Monodentate sulfate ligand (1)
  - Bidentate sulfate ligand (1)
  - H_2O or OH ligands (0-1-2)

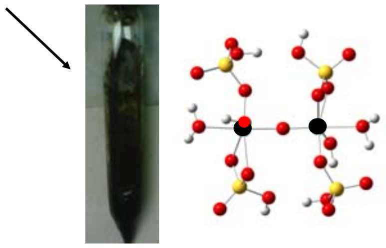
F. Poineau, P. F. Weck, B. P. Burton-Pye, I. Denden, E. Kim, W. Kerlin, K. E. German, M. Fattahi, L. Francesconi, A. P. Sattelberger, K. R. Czerwinski, *Dalton Trans.* 2013, *42*, 4348-4352.

Conclusions and Future Work

Conclusion



$KTcO_4$ in 12 M H_2SO_4



Supernate

- $TcO_3(H_2O)_2(OH)$ in solution (Tc +VII)
- Formation of intermediates (Tc +V)
- Precipitation of Tc_2S_7
- Presence in supernate
    - Tc – O – Tc polymer

Future Work

- Perform reaction at various H_2SO_4 molarity
  - See if still precipitation of Tc_2S_7
  - Study Tc speciation in solution
- Find different analyses possible for radioactive material in order to have a better understanding on the solids
  - EXAFS on S K-edge, Neutron diffraction, IR, Modeling

Acknowledgements

- Dr. Czerwinski, Dr. Poineau, Dr. Sattelberger
- Dr. Roques, Dr. Ma, Dr. Lee and Dr. Reihnart
- Julie Bertoia and Trevor Low
- Jeremy Unger
- Radiochemistry group at UNLV

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Questions

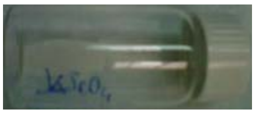
Starting Compound

NH_4TcO_4 with TcO_2

$\xrightarrow{120\ ^{0}C,\ KOH/H_2O_2/H_2O}$

$KTcO_4$

- 100 mg NH_4TcO_4/TcO_2 + 30 mg KOH
- 100 µL H_2O_2 and 3 mL H_2O
- Heat and stir for 40 min, reduce volume
- Cool down the solution: gives white precipitate
- Remove supernate
- Wash solid with isopropanol and then diethyl ether
- Dry at 80 °C overnight
- **95% yield $KTcO_4$**

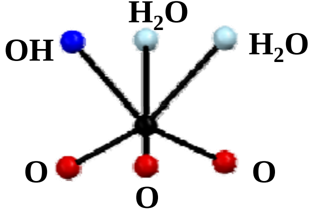


Pictures (top) courtesy to Dr. Poineau

Introduction

- Dissolution of $KTcO_4$ in H_2SO_4
  - For $H_2SO_4 < 8$ M: colorless TcO_4^- solution
  - For $H_2SO_4 > 8$ M: yellow solution
    - New band at 337 nm (new species)

- After analyses: UV-Vis, NMR, EXAFS, DFT
  - Optimized structure: $Tc^{VII}O_3(H_2O)_2(OH)$



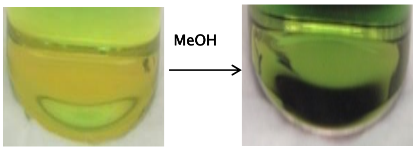
Distances [Å]	Tc=O	Tc–O(H)	Tc–O(H_2)
DFT	1.73	2.02	2.31
EXAFS	1.70(2)	2.07(2)	2.23(2)

- What happens when you introduce a reducing agent in this solution?

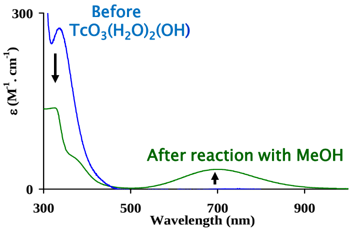
F. Poineau et al., *Dalton Transactions*, 39, 8616-8619, **2010**
F. Poineau et al., *Inorganica Chimica Acta*, 398, 147-150, **2013**

Introduction

- Addition of MeOH
  - Obtained a green solution
    - New large band centered at 700 nm (new species)

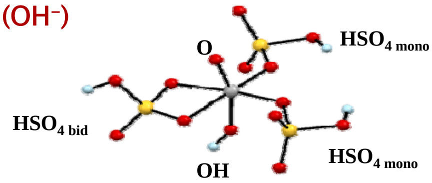


Tc(+VII) in 13 M H_2SO_4 Tc(+V) in 13 M H_2SO_4



- After analyses: UV-Vis, EXAFS, DFT on green solution
  - Optimized structure: $Tc^{V}O(HSO_4)_3(OH^-)$

Distances [Å]	Tc=O	Tc–O	Tc–S_{mono}	Tc–S_{bid}
DFT	1.69	2.08	3.35	2.92
EXAFS	1.65(2)	2.07(2)	3.30(3)	2.89(3)



F. Poineau et al., *Dalton Transactions*, **2013**, 42, 4348-4352

Electrochemical properties of technetium species in acidic media

Maciej Chotkowski, Faculty of Chemistry, University of Warsaw

Electrochemical properties of technetium species dissolved in aqueous acidic media have been examined using various "in situ" electrochemical methods, e.g. UV-Vis, EQCM. The results clearly show that the electrode matrix has a significant influence on the efficiency of TcO_4^- ions electroreduction.

Adsorption of technetate(VI) is the first step of pertechnetate ions electroreduction on a gold electrode.

The main and the most stable products of TcO_4^- ions electroreduction are dimeric oxotechnetium(III,IV) ions. These ions are much more resistant to oxidation than TcO^{2+} ions and even at potentials higher than 1V vs. SHE the rate of their oxidation is very slow.

The spectroelectrochemical measurements in Au/RVC-OTTLE system allowed determination of the standard redox potential for $[Tc(\mu\text{-}O)_2Tc]^{3+}/Tc(III)$ aqueous system which equals 0.255V.

Electrochemical properties of technetium species in acidic media

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8TH INTERNATIONAL SYMPOSIUM ON TECHNETIUM AND RHENIUM – SCIENCE AND UTILIZATION,

PORNICHET 29TH SEPT. – 03RD OCT. 2014

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overview

- ✓Technetium- general electrochemical properties
- ✓techniques
- ✓influence of surface, H_2SO_4 and TcO_4^- concentration on the electroreduction of TcO_4^- ions
- ✓influence of temperature on the electroreduction of TcO_4^- ions in H_2SO_4
- ✓extraction of technetium species with lower oxidation states from aqueous to organic phase
- ✓summary

general electrochemical properties of technetium

$E^0_{\mathrm{TcO2/TcO4-}} = 0.75\,\mathrm{V}$

$E^0_{\mathrm{TcO42-/TcO4-}} \sim -0.60\,\mathrm{V}$

$E^0_{\mathrm{Tc(V)/TcO4-}} = -0.60\,\mathrm{V}$

$E^0_{\mathrm{TcO(OH)2/TcO4-}} = 0.58\,\mathrm{V}$

$E^0_{\mathrm{H2O/O2}} = 1.23\,\mathrm{V}$

Oxidation state	**Mn**	**Tc**	**Re**
+VII	MnO_4^-	TcO_4^-	ReO_4^-
+VI	MnO_4^{2-} (b)	TcO_4^{2-}/ $HTcO_4^-$ (unstable a/b)	ReO_3 (a)
+V	MnO_4^{3-} (b)	Tc(V) (unstable b) but TcO^{3+} (a)	Re_2O_5 (a)

a: acidic; b: basic

$TcO_2{*}1{,}6H_2O \leftrightarrow TcO(OH)_2 + 0.6H_2O \qquad K = 10^{29,4}$

$TcO_4^- \rightarrow Tc(VI,V)(\text{disprop./electrored.}) \rightarrow TcO_4^- + Tc(IV) \rightarrow Tc(III)$

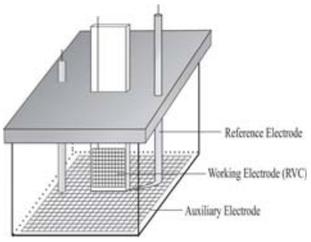
techniques

✓cyclic voltammetry (CV)

✓chronoamperometry (CA)

✓electrochemical quartz crystal microbalance (EQCM)

✓rotating ring disc electrode (Au-RRDE)

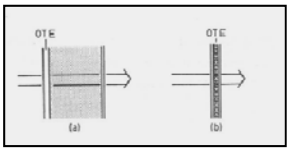


✓Spectroelectrochemistry

- optically transparent electrodes (Au-OTE):a

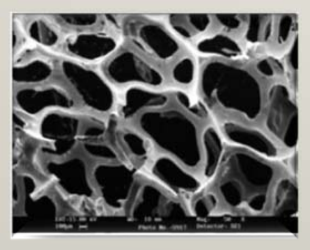
- optically transparent thin layer electrodes: b

(RVC-OTTLE; Au/RVC-OTTLE)



Reticulated Vitreous Carbon (RVC®)

Physical properties	Values	
	RVC	**GC**
Density [kg m^{-3}]	48	1650
Void volume [%]	90 - 97%	0
Bulk resistivity [Ω cm]	0.005	0.001
Thermal cunductivity [cal cm ^{0}C w 10^{-4} tor]	0.08-1200	0.01 – 0.02



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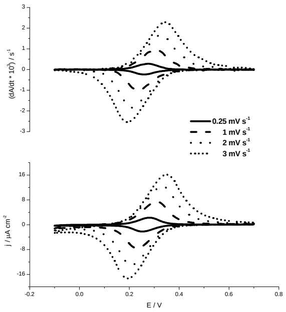
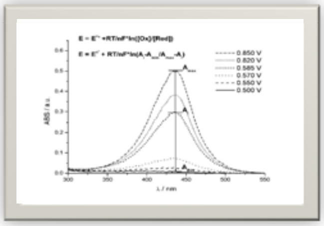
spectroelectrochemistry UV-Vis



Cyclic voltammogram and voltabsorbommogram
0.4 mM o-tolidine + 0.5 M CH_3COOH + 0.1 $HClO_4$
v = 0.2 mVs^{-1}, λ = 438 nm



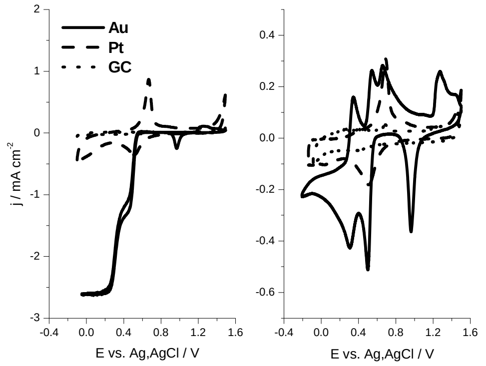
Spectroscopic signals recorded during chronoamperometric oxidation of 0.4 mM o-tolidine0.5 M CH_3COOH + 0.1 $HClO_4$

$$j = nFc\left(D\nu\frac{nF}{RT}\right)^{1/2} f(w,\xi)$$

$$\left(\frac{dA}{dt}\right) = \in c\left(D\nu\frac{nF}{RT}\right)^{1/2} f(w,\xi)$$

S. Zamponi, A. Czerwinski,
R. Marassi J. Electroanal. Chem.
266 (1989) 37

influence of surface on the electroreduction of TcO_4^- ions



Cyclic voltammograms of a Au, RVC and Pt electrodes recorded for Au, Pt and GC electrodes in $KTcO_4$ + 4M H_2SO_4, v = 2V min^{-1} left panel: hydrodynamic conditions; right panel: stationary conditions

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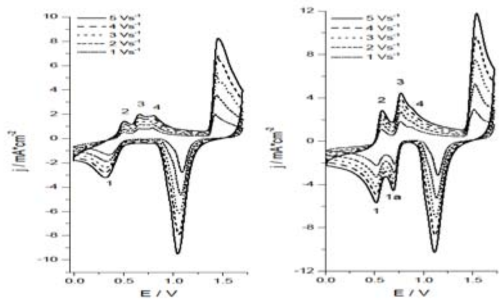
influence of H_2SO_4 concentration on the electroreduction of TcO_4^- ions

0.5M H_2SO_4 4M H_2SO_4



Electroreduction:

peak 1a Tc(VI) and Tc(V)

Peak 1 Tc(IV) and Tc(III)

Electrooxidation:

peak 2 Tc(IV)

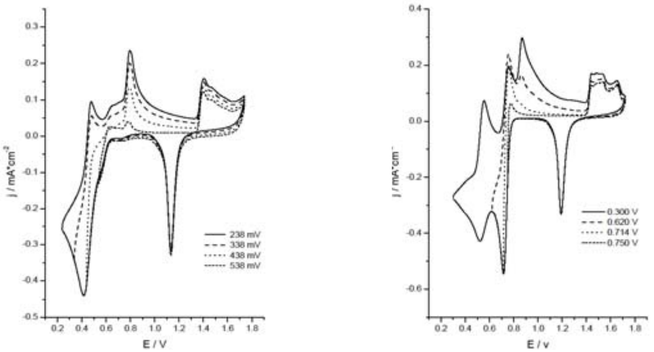
peak 3 Tc(VII)

peak 4 Tc(VII)

Cyclic voltammograms of a Au electrodes recorded for various scan rates in $KTcO_4$ + H_2SO_4.

influence of H_2SO_4 concentration on the electroreduction of TcO_4^- ions

0.5M H_2SO_4 4M H_2SO_4



Cyclic voltammograms of a Au electrodes recorded for various cathodic vertex potentials in $KTcO_4 + H_2SO_4$, $v = 0.05Vs^{-1}$

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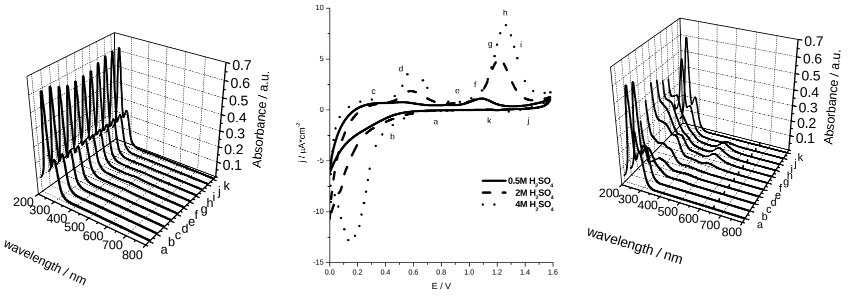
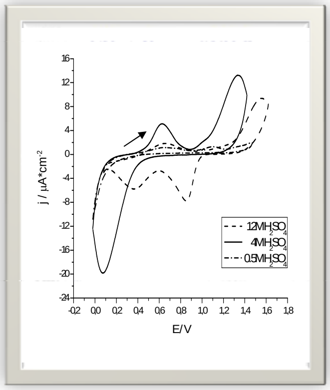
influence of H_2SO_4 concentration on the electroreduction of TcO_4^- ions

0.5M H_2SO_4 4M H_2SO_4

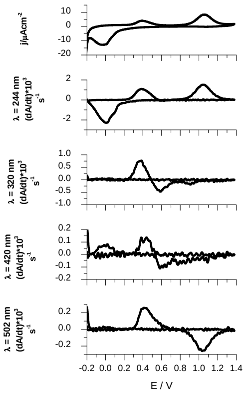


UV-Vis spectra and cyclic voltammogram of pertechnetates in 4M $H_2SO_4 + KTcO_4$, RVC-OTTLE

influence of H_2SO_4 concentration on the electroreduction o TcO_4^- ions on the carbon



Cyclic voltammograms of a RVC-OTTLE electrodes recorded for various concentrations of H_2SO_4, 1mM $KTcO_4$, v = 0.2 mVs^{-1}



Cyclic voltammogram and voltabsorbommograms recorded and calculated for RVC-OTTL electrode in 1 mM $KTcO_4$ + 4M H_2SO_4 v = 0.2 mVs^{-1}

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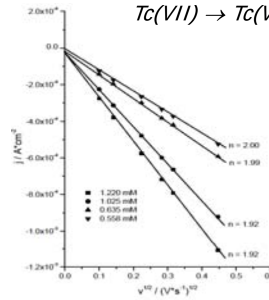
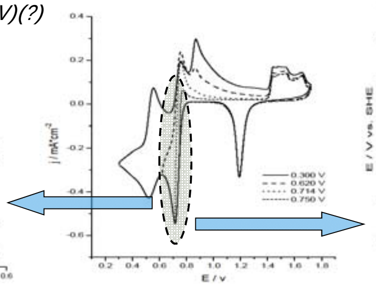
influence of TcO_4^- ions concentration on the electroreduction process in 4M H_2SO_4

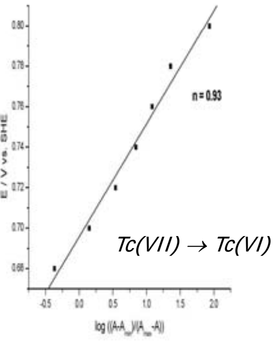


Tc(VII) → Tc(V)(?)

Peak current density as a function of square root of the scan rate recorded in 4M H_2SO_4 for different concentration of $KTcO_4$.



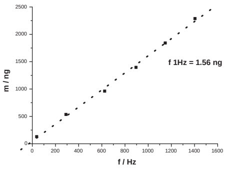
Cyclic voltammograms recorded in 4M H_2SO_4 + 1,19 mM $KTcO_4$ for different cathodic vertex potentials, v = 0.05 Vs^{-1}.



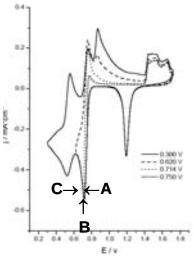
Tc(VII) → Tc(VI)

E vs. log ([Ox]/[Red]) plot. Spectroelectrochemical experiments recorded in 4M H_2SO_4 + 1,19 mM $KTcO_4$ Au-OTE

electrochemical microbalance study



Calibration of EQCM
c_{Cu2+} = 60.06 mmol/dm^3
c_{H2SO4} = 4 mol/dm^3



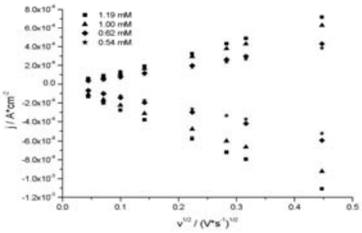
in 4M H2SO4 about 20% pertechnetates undissociated

E / V	Δ(M/z)
	4M H_2SO_4
A	0.74
B	0.69
C	0.71

Possible mechanism	Δ(M/z)
$H^+ + TcO_4^-{*}H_2O_{(ads)} + e^- \rightarrow HTcO_4^-{*}H_2O_{(ads)}$	**1**
$2H^+ + TcO_4^-{*}H_2O_{(ads)} + e^- \rightarrow TcO_3{*}H_2O_{(ads)} + H_2O$	-16
$HTcO_4{*}H_2O_{(ads)} + e^- \rightarrow HTcO_4^-{*}H_2O_{(ads)}$	0

---

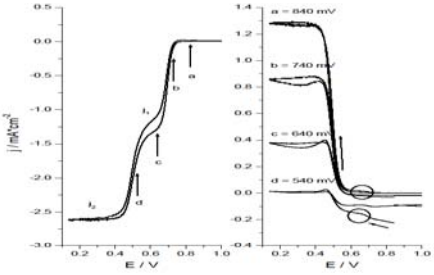
influence of TcO_4^- concentration on the electroreduction process



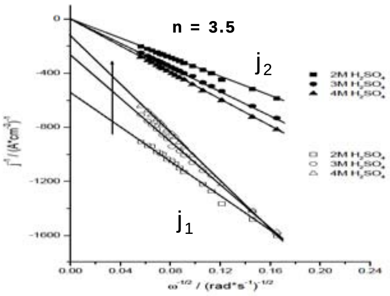
Peaks a and b currents as a functions of $v^{1/2}$ recorded in 4M H_2SO_4 for various concentrations of TcO_4^-, Au electrode,

Examinated mechanism	
ECE: A + e ↔ B; B ↔ C (rds); C + e ↔ D	**∂Ep/∂logv = 30; ∂Ep/∂c = 0**
DISP1: A + e ↔ B; B ↔ C (rds); B + C ↔ A + D	**∂Ep/∂logv = 30; ∂Ep/∂c = 0**
DISP2: A + e ↔ B; B ↔ C; B + C ↔ A + D (rds)	**∂Ep/∂logv = 20; ∂Ep/∂c = 20**

influence of H_2SO_4 concentration on the electroreduction of TcO_4^- ions



Left panel: cyclic voltammogram of a gold disc electrode of a RRDE assembly with rotation speed of 1600 rpm in 0.55mM $KTcO_4$ + 4M H_2SO_4, v = 2Vmin^{-1}. Right panel: ring electrode currents measured simultaneously to CV shown on the left panel for various constant potentials of the ring and indicated on the plot.



Reverse Levich plots for the limiting current of pertechnetate reduction current recorded at a gold electrode in various H_2SO_4 solutions, v = 2Vmin^{-1}.

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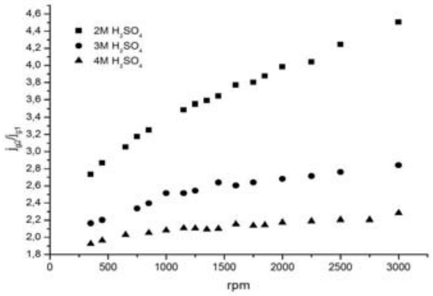
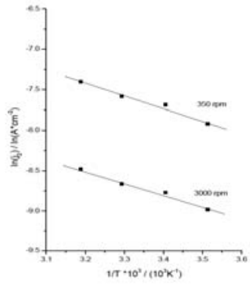
influence of H_2SO_4 concentration on the electroreduction of TcO_4^- ions

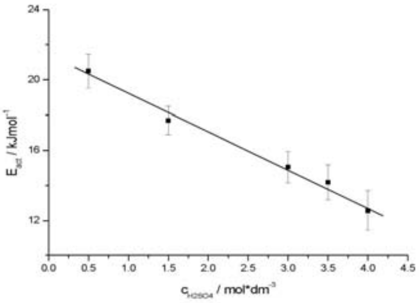


Reverse Levich plots for the limiting current of pertechnetate reduction current recorded at a gold electrode in various H_2SO_4 solutions, v = 2Vmin^{-1}.

influence of temperature, H_2SO_4 concentration on the electroreduction of TcO_4^- ions

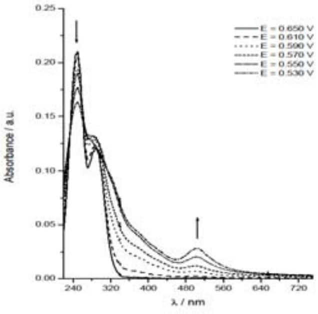


lnj **vs.** ***T*$^{-1}$** **plot for *j_2* limiting current of pertechnetates reduction current recorded on a gold electrode in $4H_2SO_4$ + 0.32 mM $KTcO_4$**

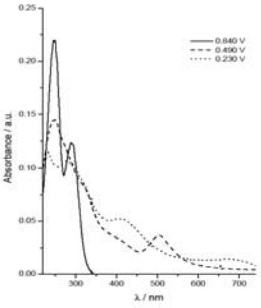


Calculated activation energy for *j_2* as a function of H_2SO_4 concentration in H_2SO_4 + 0.32 mM $KTcO_4$

spectroelectrochemistry of technetium in 4M H_2SO_4

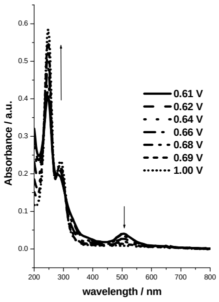


UV-Vis spectra recorded during chronoamperometric reduction of pertechnetates in 4M H_2SO_4 + 1.19mM $KTcO_4$, potential range 0.65V÷0.53V, Au-OTE

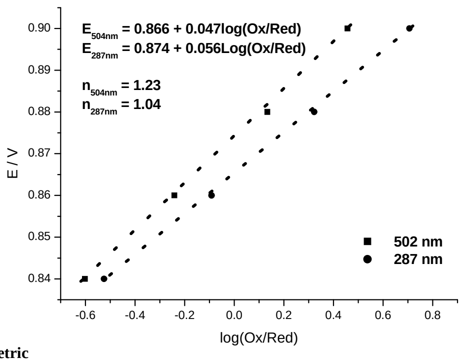


UV-Vis spectra of TcO_4^- (E= 0.84V), polymeric Tc(III,IV) (E = 0.49V) and Tc(IV) (E = 0.23V) recorded in 4M H_2SO_4 + 1.19mM $KTcO_4$ Au-OTE

spectroelectrochemistry of technetium in 4M H_2SO_4



UV-Vis spectra recorded during chronoamperometric oxidation of $[Tc_2O_2]^{3+}$ in 4M H_2SO_4 + $KTcO_4$, potential range 0.61V÷1V, Au-OTE, potentials vs. Ag,AgCl



E vs. log ([Ox]/[Red]) plot. Spectroelectrochemical experiments recorded in 4M H_2SO_4 + $KTcO_4$ RVC-OTTLE, potentials vs. SHE

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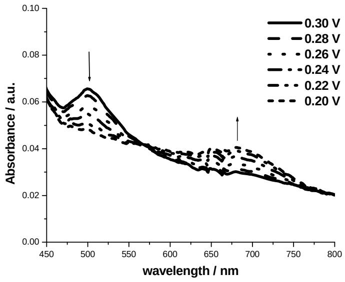
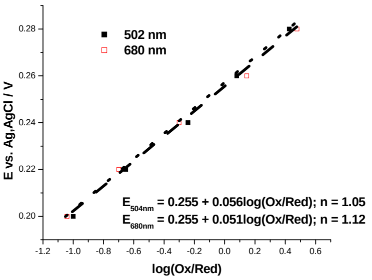
spectroelectrochemistry of technetium in 4M H_2SO_4



UV-Vis spectra recorded during chronoamperometric reduction of [Tc2O2]$^{3+}$ in 4M H_2SO_4 + $KTcO_4$, potential range 0.2V÷0.3V, Au/RVC-OTTLE



E vs. log ([Ox]/[Red]) plot. Spectroelectrochemical experiments recorded in 4M H_2SO_4 + $KTcO_4$ Au/RVC-OTTLE

summary

- ✓In hydrodynamic experiments the soluble, polymeric technetium(III,IV) species are generated. These species are formed during the process with rate controlled by diffusion as follows from the low value of activation energy.
- ✓The TcO^{2+}, Tc^{3+}/TcO^{+} and $[Tc_2O_2]^{3+}$ can be detected spectroscopically by the bands at 400, 440 and 502 nm respectively.
- ✓Extraction of Tc(III or IV) from 4M H_2SO_4 or 4M H_2SO_4/HNO_3 to organic phase is much lower than TcO_4^- ions
- ✓Tc(III and IV) species are not oxidized immediately by nitric acid

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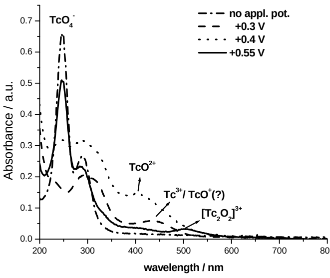
Thank You for Your Attention

extraction of Tc(III and IV) from H_2SO_4 and H_2SO_4/HNO_3 to kerosene /30% TBP



UV-Vis spectra recorded after chronoamperometric reduction of TcO_4^- in 4M H_2SO_4 at various applied potential, RVC-OTTLE

$V_{aq} = V_{org} = 2.1$ ml
t = 10 min
$c_{TcO4-} = 0.54$ mmol/dm^3
aq. phase : $c_{H2SO4} = 4$ mol/dm^3 (+ 0.1 cm$_3$ $HNO_{3(conc.)}$)
org. phase : kerosene + 30% TBP

Tc species	D_C	
	H_2SO_4	H_2SO_4/HNO_3
TcO_4^-	85.8	4.01
TcO^{2+}	0.18	0.84
Tc^{3+}/TcO^+	0.06	1.45
$[Tc_2O_2]^{3+}$	1.55	1.18

Distribution ratio of various Tc species

$$D_C = \frac{A_{org}}{A_{aq}}$$

---

summary

- ✓concentration of the sulfuric acid has a significant influence in the electrochemical reduction of pertechnate ions.

- ✓Tc species on lower oxidation states and generated during reduction of pertechnates are stabilized at higher concentrations of H_2SO_4.

- ✓The peak related to electroreduction of pertechnetates to Tc(VI,V) is much better developed in 4M H_2SO_4 as compared to 0.5M solution,

- ✓In the first step of pertechnetates reduction are generated adsorbed $HTcO_4^-$ on the surface of Au electrode

Maciej Chotkowski

Rhenium session :
Prof. Irina Troshkina and the session Chairman Fred Poineau

Aquatic chemistry and thermodynamics of Tc in dilute to concentrated saline systems

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Technetium–99 is a β–emitting fission product highly relevant for the safety assessment of waste repositories for radioactive waste disposal due to its significant inventory in spent nuclear fuel, long half-life ($t_{½}$ ~211.000 a) and redox sensitivity. Tc(VII) and Tc(IV) are the most stable redox states of Tc in the absence of any complexing ligands. Tc(VII) exists as highly soluble and mobile TcO_4^-pertechnetate anion under sub-oxic and oxidizing conditions, whereas Tc(IV) forms sparingly soluble hydrous oxide ($TcO_2 \cdot xH_2O$) under reducing conditions. For understanding Tc behaviour under repository relevant conditions, investigations focussing on redox state distribution,solubility and hydrolysis of Tc(IV) in dilute to concentrated NaCl, $MgCl_2$ and $CaCl_2$ solutions are required.

In the present study, the redox behavior of Tc(VII)/Tc(IV) was systematically investigated using various homogenous and heterogeneous reducing systems in dilute to concentrated NaCl and $MgCl_2$ solutions. Measured E_h and pH values were represented in *Pourbaix* diagrams calculated using thermodynamic data selected in the NEA–TDB [1] in order to assess Tc redox distribution in these systems. The thermodynamically calculated borderline for the Tc(VII)/Tc(IV) couple agrees well with the experimental data, indicating that E_h and pH are robust and reliable parameters for the prediction of Tc behavior in the absence of complexing ligands in the investigated aqueous systems. The study was complemented by advanced spectroscopy (EXAFS) to investigate the reduction/sorption mechanism of Tc on solid iron phases of special relevance for nuclear waste disposal.

Tc(IV) solubility was investigated in dilute to concentrated NaCl, $MgCl_2$ and $CaCl_2$ solutions in the presence of reducing chemicals. In the acidic pH range, a very significant increase in solubility (up to 4 orders of magnitude) is observed with increasing ionic strength for all considered salt systems. Thermodynamic analysisof this pH-region are on-going,taking into considerationhydrolysis species selectedby NEA–TDB [1] but also polymeric $Tc_nO_p^{(4n-2p)+}$ and/or $Tc_nO_pCl_m^{(4n-2p-m)-}$ species previously reported on the basis of spectroscopic observations[2]. In concentrated alkaline NaCl solutions, the same speciation as for diluted systems is retained (predominance of $TcO(OH)_3^-$), although a decrease in solubility compared to dilute systems takes place due to ion interaction processes. Changes in the aqueous speciation are observed in concentrated alkaline $MgCl_2$ and $CaCl_2$ brines, where the formation of ternary $Mg_3[TcO(OH)_5]^{3+}$ and $Ca_3[TcO(OH)_5]^{3+}$ species is proposed based on the slope analysis and model (SIT/Pitzer) calculations. These ternary Tc(IV) species aresimilar to those previously reported for actinides in analogous brine systems. XRD, SEM–EDS and chemical analysis confirm that $TcO_2 \cdot xH_2O(s)$ is the solid phase controlling the solubility of Tc(IV) in the saline systems at $pH_m \leq 10.5$. Unreported sharp XRD reflections from the Tc solid phases in 4.5 M $CaCl_2$ at $pH_m \geq 10.5$ hint towards a possible solid phase transformation of $TcO_2 \cdot xH_2O(s)$ into a so far unknown Ca–Tc–OHsolid. Chemical, thermodynamic and activity models (SIT, Pitzer) are derived for the system $Tc^{4+}–H^+–Na^+–Mg^{2+}–Ca^{2+}–OH^-–Cl^-–H_2O$ based upon the newly generated experimental solubility data and complement the current data selection of the OECD Nuclear Energy Agency (NEA–TDB)[1].

[1] Guillaumont, R., Fanghänel, T., Neck, V., Fuger, J., Palmer, D. A., Grenthe, I. and Rand, M. H., ed. OECD Nuclear Energy Agency. Vol. 5. North-Holland, Amsterdam, Elsevier, (2003).
[2] Vichot, L., Fattahi, M., Musikas, C. and Grambow, B., Radiochimica Acta, **91**, 263-271, (2003).

Aquatic chemistry and thermodynamics of Tc in dilute to concentrated saline systems

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Institute for Nuclear Waste Disposal, Karlsruhe Institute of Technology (KIT-INE), Germany

8th International Symposium on Technetium and
Rhenium: Science and Utilization
La Baule - Pornichet, France;
September 29th - October 3rd 2014

- **Introduction**
- **Experimental**
- **Redox behaviour of Tc(VII)/Tc(IV) in dilute to conc. NaCl and $MgCl_2$ solutions**
- **Solubility and hydrolysis of Tc(IV) in dilute to conc. NaCl, $MgCl_2$ and $CaCl_2$ solutions**
- **Summary and Outlook**

- **Introduction**
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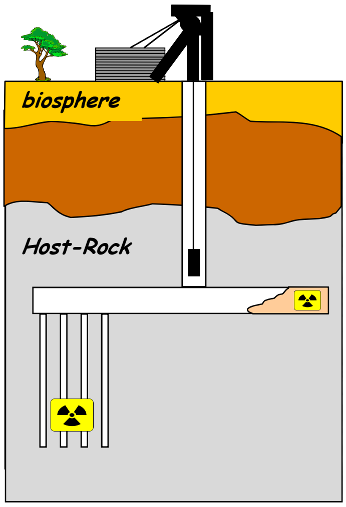
- Summary and Outlook

Introduction



Tc-99

⇩

Deep underground repositories

Host rock systems considered:
clay, crystalline (granite), salt

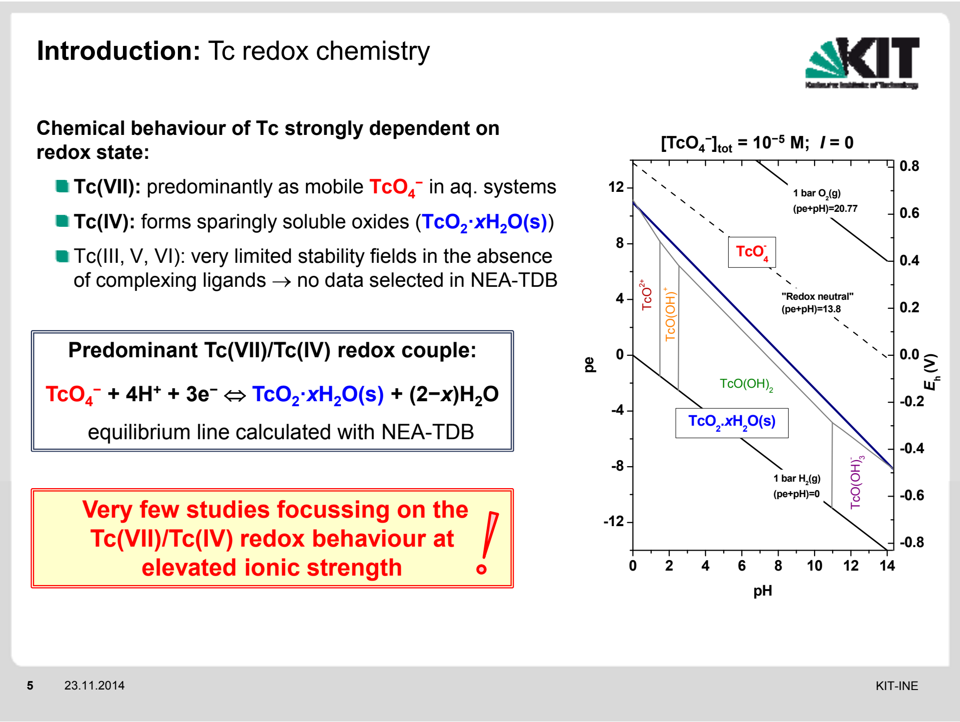
Relevant migration scenario caused by water intrusion into the repository:

→ **generation of aqueous systems**

Redox chemistry

Solubility and Hydrolysis

Sorption



Introduction: Tc redox chemistry

Chemical behaviour of Tc strongly dependent on redox state:

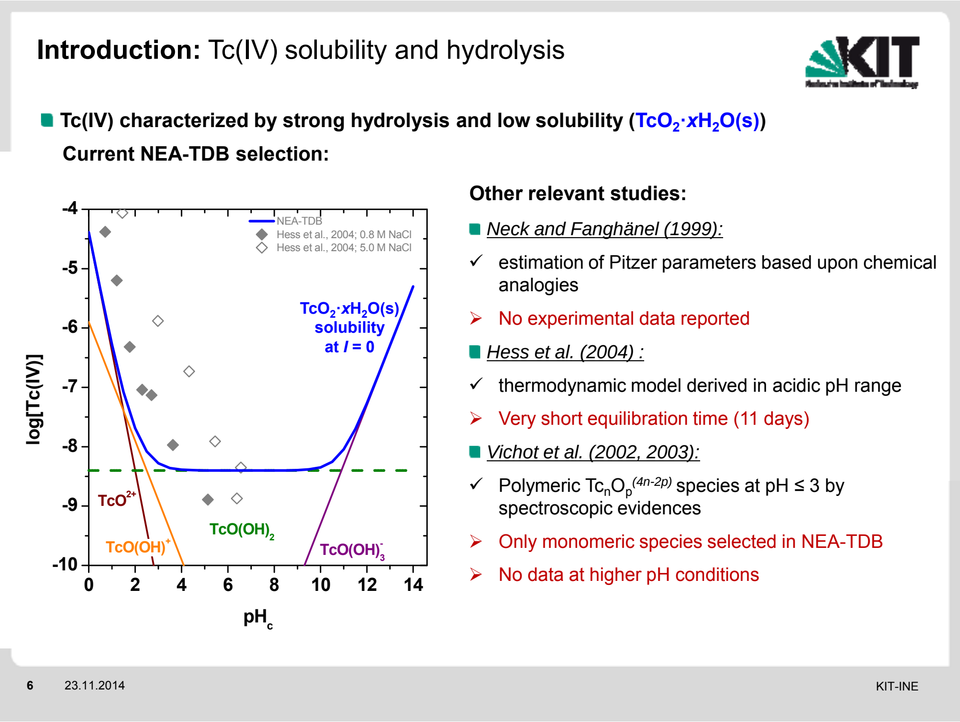
- **Tc(VII):** predominantly as mobile **TcO_4^-** in aq. systems
- **Tc(IV):** forms sparingly soluble oxides (**$TcO_2 \cdot xH_2O(s)$**)
- Tc(III, V, VI): very limited stability fields in the absence of complexing ligands → no data selected in NEA-TDB

Predominant Tc(VII)/Tc(IV) redox couple:

$$TcO_4^- + 4H^+ + 3e^- \Leftrightarrow TcO_2 \cdot xH_2O(s) + (2-x)H_2O$$

equilibrium line calculated with NEA-TDB

Very few studies focussing on the Tc(VII)/Tc(IV) redox behaviour at elevated ionic strength !



Introduction: Tc(IV) solubility and hydrolysis

- **Tc(IV) characterized by strong hydrolysis and low solubility ($TcO_2 \cdot xH_2O(s)$)**

Current NEA-TDB selection:

Other relevant studies:

- *Neck and Fanghänel (1999):*
  - ✓ estimation of Pitzer parameters based upon chemical analogies
  - ➢ No experimental data reported
- *Hess et al. (2004) :*
  - ✓ thermodynamic model derived in acidic pH range
  - ➢ Very short equilibration time (11 days)
- *Vichot et al. (2002, 2003):*
  - ✓ Polymeric $Tc_nO_p^{(4n-2p)}$ species at pH ≤ 3 by spectroscopic evidences
  - ➢ Only monomeric species selected in NEA-TDB
  - ➢ No data at higher pH conditions

Objectives

Part I. Redox studies

- Redox behaviour of Tc(VII)/Tc(IV) in dilute to concentrated NaCl and $MgCl_2$ solutions
- Evaluation of available thermodynamic and activity models (SIT, Pitzer)

Part II. Tc(IV) solubility studies

- Solubility of Tc(IV) in dilute to concentrated NaCl, $MgCl_2$ and $CaCl_2$ solutions
- Development of chemical, thermodynamic and activity models (SIT, Pitzer)

- Introduction
- **Experimental**
- Redox behaviour of Tc(VII)/Tc(IV) in dilute to conc. NaCl and $MgCl_2$ solutions
- Solubility and hydrolysis of Tc(IV) in dilute to conc. NaCl, $MgCl_2$ and $CaCl_2$ solutions
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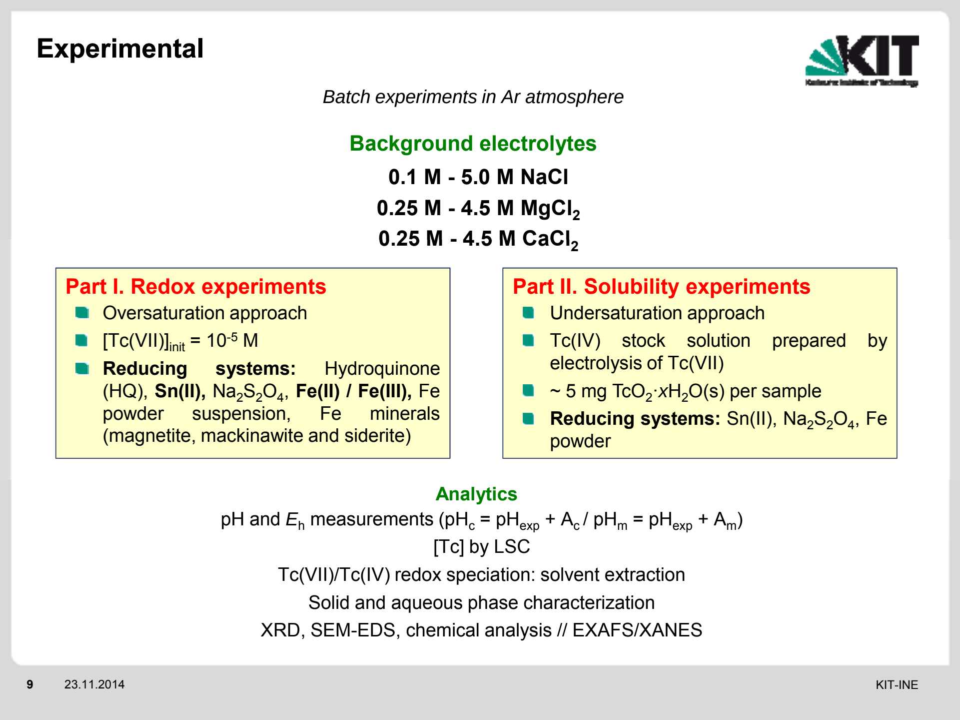


Experimental

Batch experiments in Ar atmosphere

Background electrolytes

0.1 M - 5.0 M NaCl
0.25 M - 4.5 M $MgCl_2$
0.25 M - 4.5 M $CaCl_2$

Part I. Redox experiments

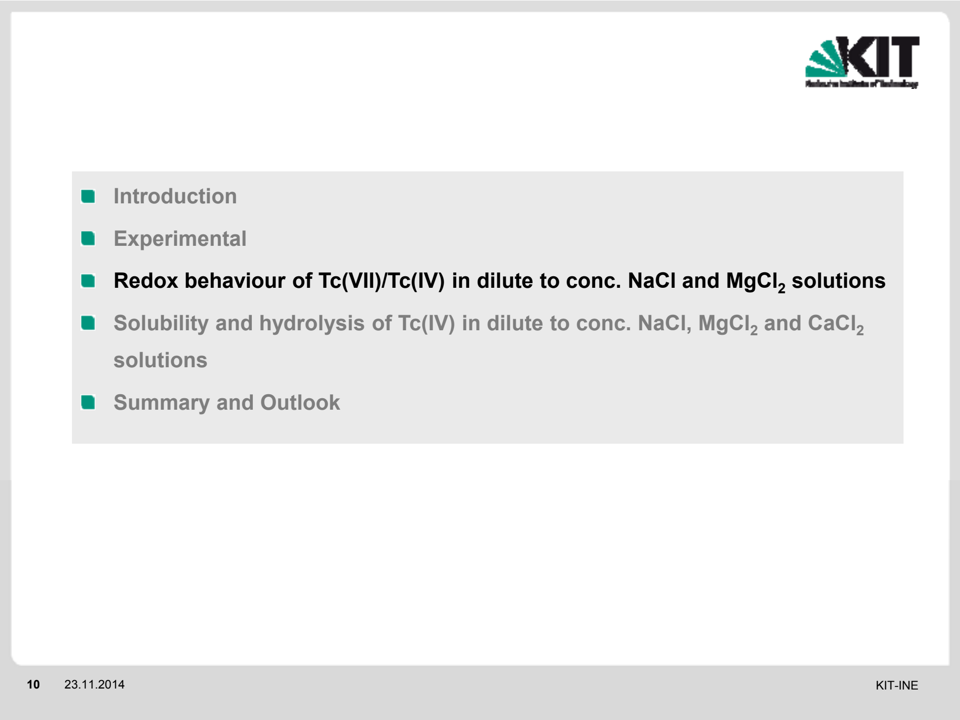
- Oversaturation approach
- $[Tc(VII)]_{init} = 10^{-5}$ M
- **Reducing systems:** Hydroquinone (HQ), **Sn(II),** $Na_2S_2O_4$, **Fe(II) / Fe(III),** Fe powder suspension, Fe minerals (magnetite, mackinawite and siderite)

Part II. Solubility experiments

- Undersaturation approach
- Tc(IV) stock solution prepared by electrolysis of Tc(VII)
- ~ 5 mg $TcO_2 \cdot xH_2O(s)$ per sample
- **Reducing systems:** Sn(II), $Na_2S_2O_4$, Fe powder

Analytics

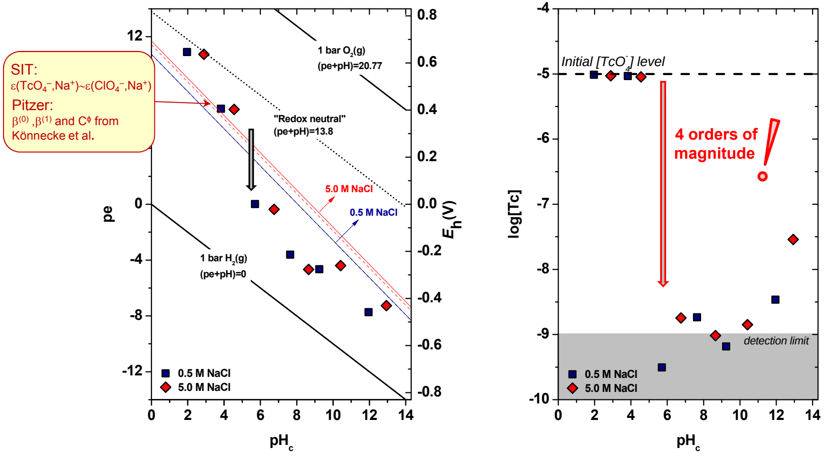
pH and E_h measurements ($pH_c = pH_{exp} + A_c$ / $pH_m = pH_{exp} + A_m$)
[Tc] by LSC
Tc(VII)/Tc(IV) redox speciation: solvent extraction
Solid and aqueous phase characterization
XRD, SEM-EDS, chemical analysis // EXAFS/XANES



Results and Discussion

Tc redox behavior in Fe(II)/Fe(III) systems: 0.5 and 5.0 M NaCl

$TcO_4^- + 4H^+ + 3e^- \Leftrightarrow TcO_2\cdot xH_2O(s) + (2-x)H_2O$

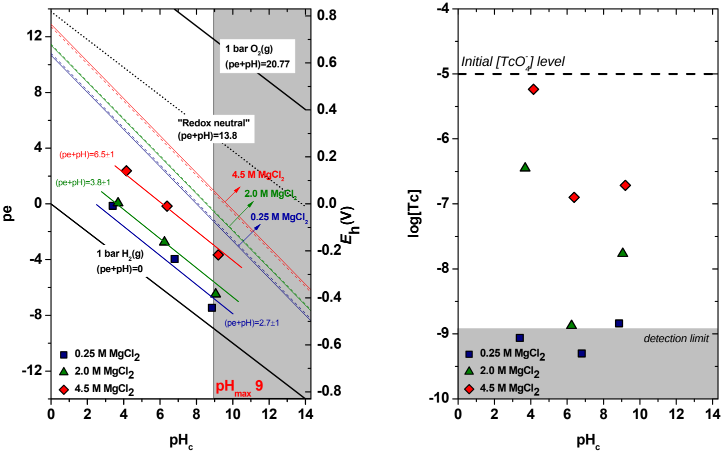

SIT: $\varepsilon(TcO_4^-,Na^+) \sim \varepsilon(ClO_4^-,Na^+)$
Pitzer: $\beta^{(0)}$, $\beta^{(1)}$ and C^{ϕ} from Könnecke et al.

- Drastic drop in $[Tc]_{aq}$ → Reduction of Tc(VII) to Tc(IV)
- Good agreement with thermodynamically calculated Tc(VII)/Tc(IV) borderline

Results and Discussion

Tc redox behavior in Sn(II) systems: 0.25, 2.0 and 4.5 M $MgCl_2$

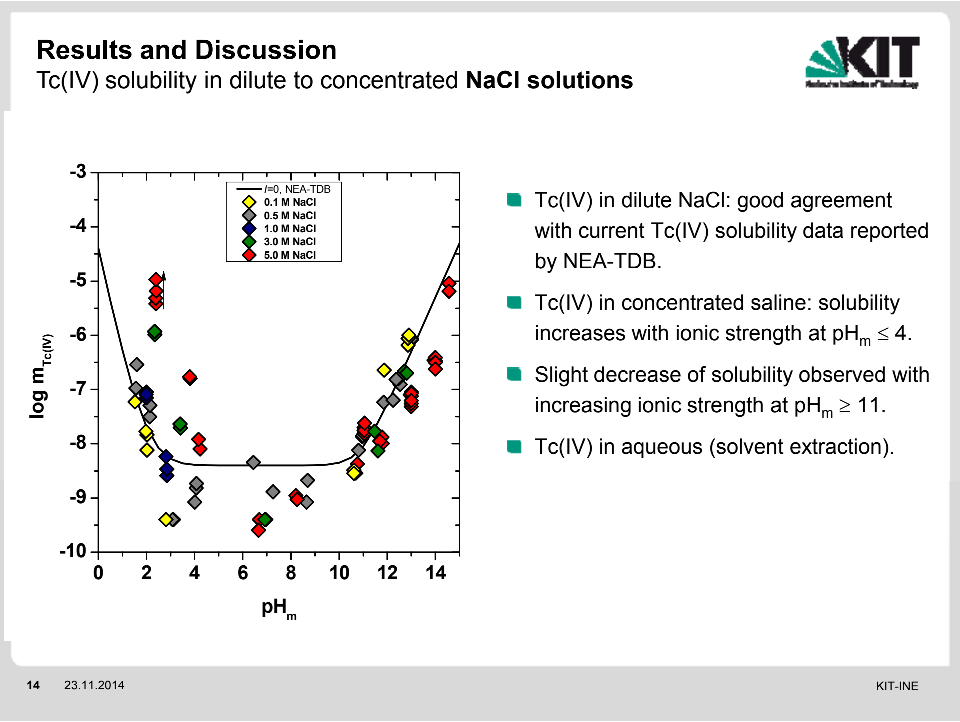
$TcO_4^- + 4H^+ + 3e^- \Leftrightarrow TcO_2\cdot xH_2O(s) + (2-x)H_2O$



- Strong *I* effect on both E_h and $[Tc]_{aq}$
- Redox distribution → high Tc concentration in 4.5 M MgCl? presence of Tc(VII) ?

→ Need of complete chemical/thermodynamic models in saline systems

- Introduction
- Experimental
- Redox behaviour of Tc(VII)/Tc(IV) in dilute to conc. NaCl and $MgCl_2$ solutions
- **Solubility and hydrolysis of Tc(IV) in dilute to conc. NaCl, $MgCl_2$ and $CaCl_2$ solutions**
- Summary and Outlook



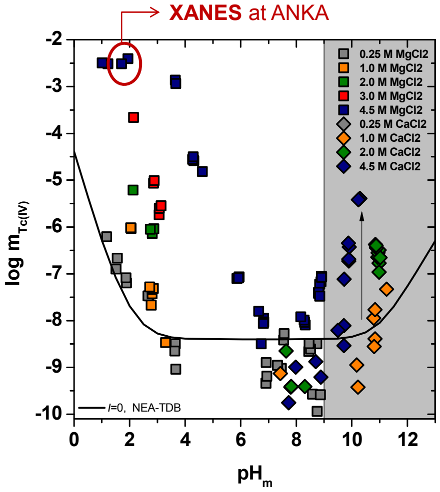
Results and Discussion

Tc(IV) solubility in dilute to concentrated **NaCl solutions**

- Tc(IV) in dilute NaCl: good agreement with current Tc(IV) solubility data reported by NEA-TDB.
- Tc(IV) in concentrated saline: solubility increases with ionic strength at $pH_m \leq 4$.
- Slight decrease of solubility observed with increasing ionic strength at $pH_m \geq 11$.
- Tc(IV) in aqueous (solvent extraction).

Results and Discussion

Tc(IV) solubility in dilute to concentrated **$MgCl_2$ and $CaCl_2$ solutions**



XANES at ANKA

- Tc(IV) in 0.25 M $MgCl_2$: analogous behaviour as for diluted NaCl.
- Systematic increase of solubility with ionic strength under acidic conditions ($pH_m \leq 6$).
- Solubility increase at pH_m ~9 ?
  - formation of Mg/Ca-Tc(IV)-OH species ?

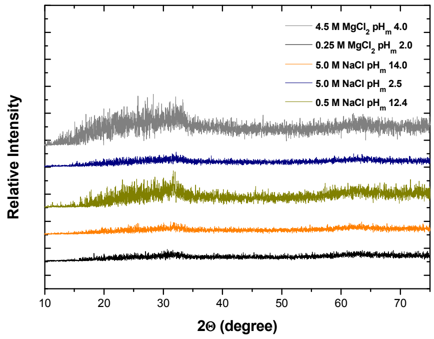
→ analogy with Ca-An(IV)-OH

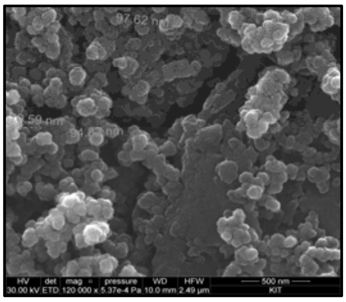
- Tc(IV) in aqueous (XANES)

Results and Discussion

Solid phase characterization in **NaCl, $MgCl_2$ and $CaCl_2$ systems**

- XRD ⟶ Broad spectra indicating amorphous solid phase
- SEM-EDS ⟶ Tc aggregates, no morphologic changes
- Chemical Analysis ⟶ Absence of Na, Mg and Ca in the solid phase ⟶ **$TcO_2 \cdot xH_2O$**
- Thermogravimetric analysis foreseen ⟶ Quantification of hydration waters (*x*)
- Solubility in very good agreement with calc. at *I* = 0 using NEA-TDB ⟶ **$TcO_2 \cdot 1.6H_2O$**

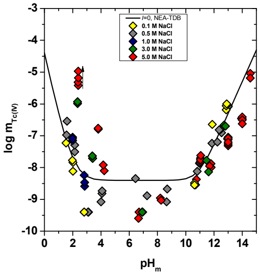




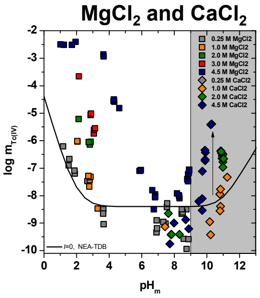
Results and Discussion

Model calculations for **Tc^{4+}–H^+–Na^+–Mg^{2+}–Ca^{2+}–OH^-–Cl^-–H_2O system**

NaCl



MgCl$_2$ and CaCl$_2$



Acidic pH region:

- Slope of -2 (log[Tc] *vs.* pH_m)
- Species evaluated:
  - **TcO^{2+}** [NEA-TDB]
  - **$Tc_nO_p^{(4n-2p)+}$** [Vichot et al. 2002, 2003]
  - **$Tc_nO_pCl_m^{(4n-2p-m)}$** (assess Cl-complexation)

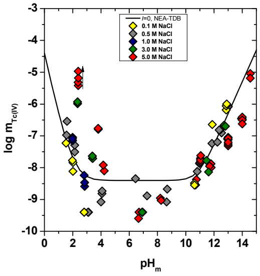
Weakly acidic to weakly alkaline pH region:

- pH-independent solubility behaviour
- Species evaluated:
  - **$TcO(OH)_2$ (aq)** [NEA-TDB]
  - **$Tc_nO_p(OH)_{4n-2p}$(aq)** → analogy with Zr(IV)??

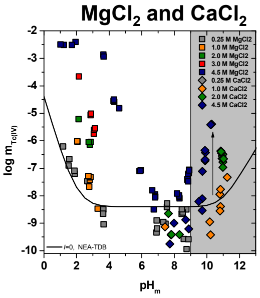
Results and Discussion

Model calculations for **Tc^{4+}–H^+–Na^+–Mg^{2+}–Ca^{2+}–OH^-–Cl^-–H_2O system**

NaCl



MgCl$_2$ and CaCl$_2$

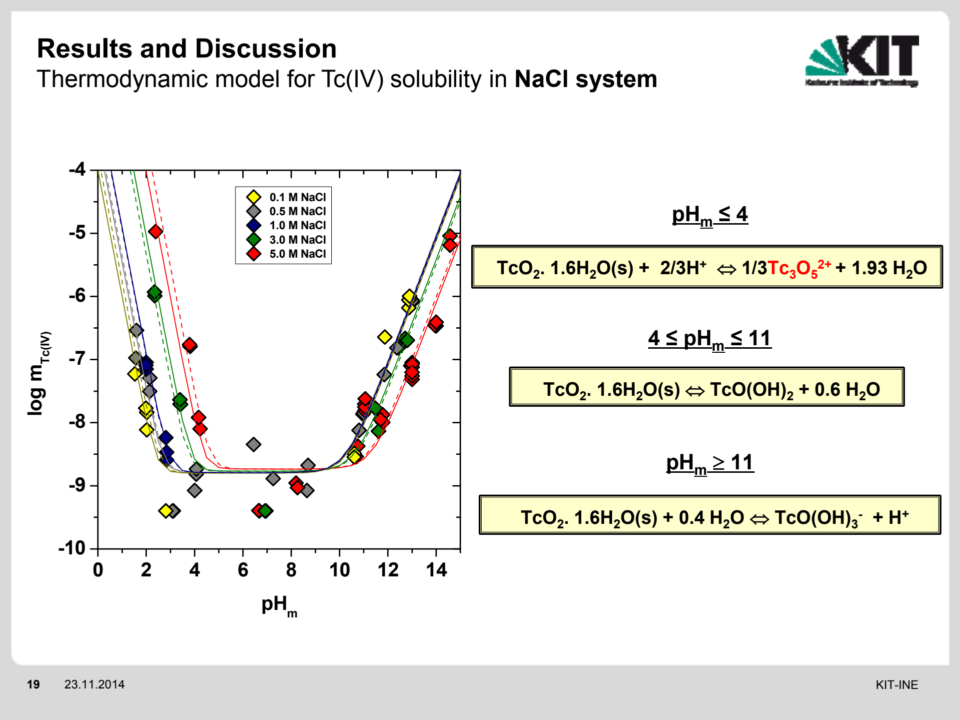


Alkaline pH region in NaCl system:

- Slope of +1 (log[Tc] *vs.* pH_m)
- Species evaluated:
  - **$TcO(OH)_3^-$** [NEA-TDB]

Alkaline pH region in MgCl$_2$ and CaCl$_2$ system:

- Slope of +3 (log[Tc] *vs.* pH_m)
- Species evaluated:
  - **Mg/Ca-Tc(IV)-OH** (Analogy with Ca-Zr(IV)-OH and Ca-An(IV)-OH species) [Altmaier et al. 2008, Fellhauer et al. 2010].



Results and Discussion

Thermodynamic model for Tc(IV) solubility in **NaCl system**

$pH_m \leq 4$

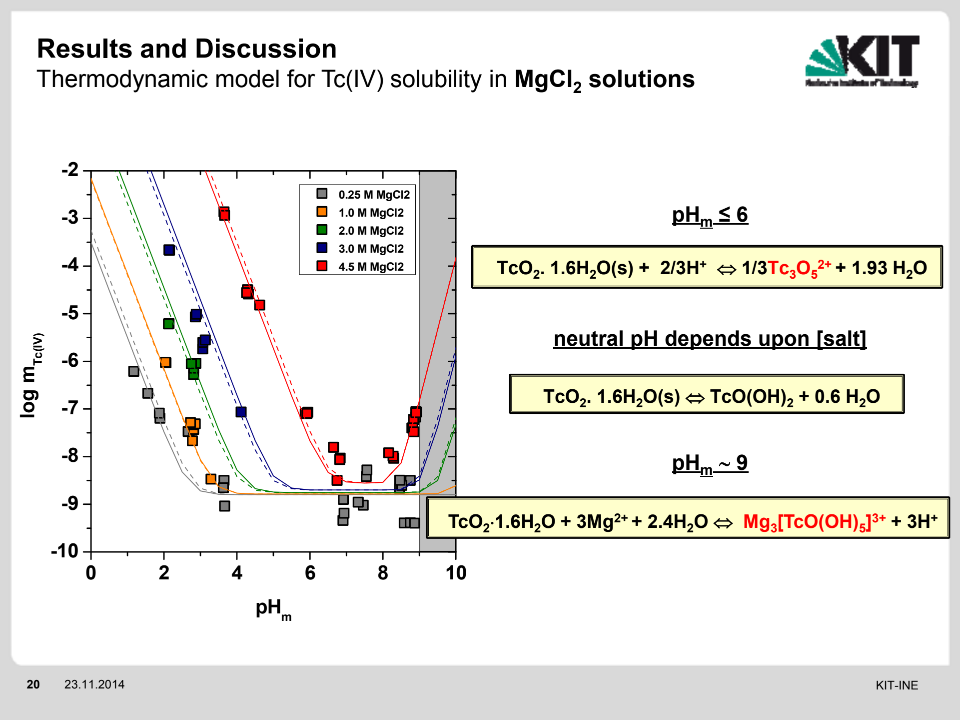
$TcO_2 .\ 1.6H_2O(s) + 2/3H^+ \Leftrightarrow 1/3Tc_3O_5^{2+} + 1.93\ H_2O$

$4 \leq pH_m \leq 11$

$TcO_2 .\ 1.6H_2O(s) \Leftrightarrow TcO(OH)_2 + 0.6\ H_2O$

$pH_m \geq 11$

$TcO_2 .\ 1.6H_2O(s) + 0.4\ H_2O \Leftrightarrow TcO(OH)_3^- + H^+$



Results and Discussion

Thermodynamic model for Tc(IV) solubility in **$MgCl_2$ solutions**

$pH_m \leq 6$

$TcO_2 .\ 1.6H_2O(s) + 2/3H^+ \Leftrightarrow 1/3Tc_3O_5^{2+} + 1.93\ H_2O$

neutral pH depends upon [salt]

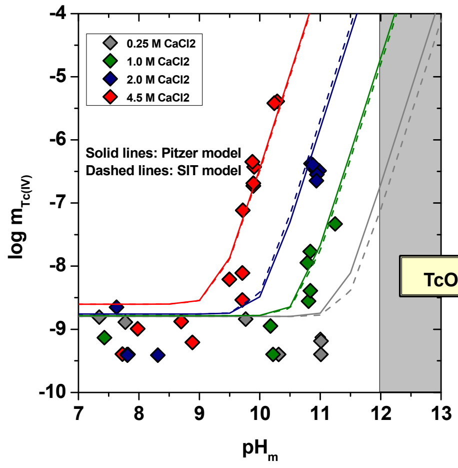
$TcO_2 .\ 1.6H_2O(s) \Leftrightarrow TcO(OH)_2 + 0.6\ H_2O$

$pH_m \sim 9$

$TcO_2 \cdot 1.6H_2O + 3Mg^{2+} + 2.4H_2O \Leftrightarrow Mg_3[TcO(OH)_5]^{3+} + 3H^+$

Results and Discussion

Thermodynamic model for Tc(IV) solubility in **$CaCl_2$ solutions**



Solid lines: Pitzer model
Dashed lines: SIT model

neutral pH depends upon [salt]

$TcO_2 \cdot 1.6H_2O(s) \Leftrightarrow TcO(OH)_2 + 0.6\ H_2O$

$pH_m \geq 9.5$

$TcO_2 \cdot 1.6H_2O + 3Ca^{2+} + 2.4H_2O \Leftrightarrow Ca_3[TcO(OH)_5]^{3+} + 3H^+$

Results and Discussion

Preliminary model for Tc(IV) solubility in
NaCl, $MgCl_2$ and $CaCl_2$ solutions

Chemical Reactions	**pH range**	**SIT**	**Pitzer**
		log*K°	**log*K°**
$TcO_2 \cdot 1.6H_2O(s) + 2/3H^+ \Leftrightarrow 1/3Tc_3O_5^{2+} + 1.93H_2O$	$pH_m \leq 4$	–1.49 ± 0.1	–1.56 ± 0.1
$TcO_2 \cdot 1.6H_2O(s) + \Leftrightarrow TcO(OH)_2(aq) + 0.6H_2O$	$4 \leq pH_m \leq 11$	–8.80 ± 0.5	–8.80 ± 0.5
$TcO_2 \cdot 1.6H_2O(s) + 0.4H_2O \Leftrightarrow TcO(OH)_3^- + H^+$	$pH_m \geq 11$	–19.26 ± 0.3	–19.32 ± 0.3
$TcO_2 \cdot 1.6H_2O(s) + 3Mg^{2+} + 2.4H_2O \Leftrightarrow Mg_3[TcO(OH)_5]^{3+} + 3H^+$	$pH_m \sim 9$	-40.00 ± 0.2	-39.87 ± 0.2
$TcO_2 \cdot 1.6H_2O(s) + 3Ca^{2+} + 2.4H_2O \Leftrightarrow Ca_3[TcO(OH)_5]^{3+} + 3H^+$	$pH_m \geq 9.5$	-41.47± 0.2	-41.00 ± 0.2

Species		**SIT**	**Pitzer**				
			Binary parameters			**Mixing parameters**	
i	***j***	ε_{ij}	$\beta^{(0)}$	$\beta^{(0)}$	$C^{(\Phi)}$	$\Theta_{ii'}$	$\Psi_{iji'}$
$Tc_3O_5^{2+}$	Cl^-	–0.33 ± 0.03	–0.34	1.6*	0.04	0	0
$TcO(OH)_3^-$	Na^+	0.1 ± 0.02	0.11	0.3*	0.04	0	0
$Mg_3[TcO(OH)_5]^{3+}$	Cl^-	-0.28 ± 0.05	0.12	4.3*	-0.02	0	0
$Ca_3[TcO(OH)_5]^{3+}$	Cl^-	-0.28 ± 0.05	0.12	4.3*	-0.02	0	0
$TcO(OH)_2$	$Na^+,Mg^{2+},Ca^{2+},Cl^-$	0			$\lambda_{ij} = 0$		

**fixed value for the corresponding charge type*

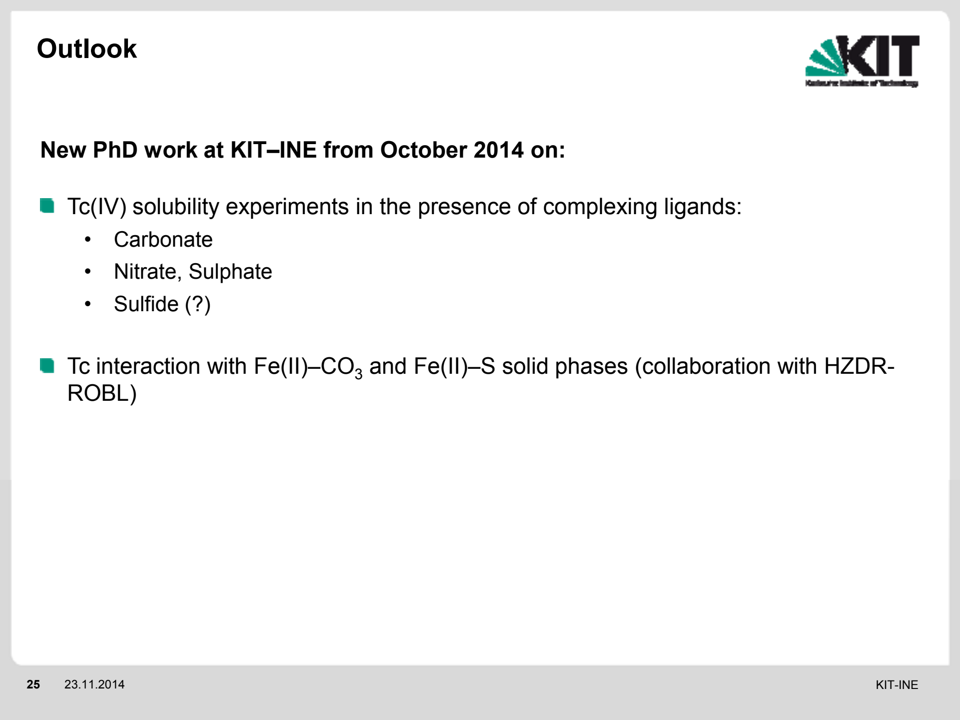
- Introduction
- Experimental
- Redox behaviour of Tc(VII)/Tc(IV) in dilute to conc. NaCl and $MgCl_2$ solutions
- Solubility and hydrolysis of Tc(IV) in dilute to conc. NaCl, $MgCl_2$ and $CaCl_2$ solutions
- **Summary and Outlook**

Summary

Very relevant effort undertaken to improve the knowledge of Tc redox chemistry, hydrolysis and solubility for PA purposes.

- **Tc(VII)/Tc(IV) redox behavior in dilute to concentrated NaCl and $MgCl_2$ solutions:**
  - → E_h and pH provide a sound basis for the assessment of Tc redox distribution, also at elevated ionic strength
  - → Thermodynamic and activity models available for Tc(VII)/Tc(IV) couple explain properly experimental data

- **Tc(IV) solubility in dilute to concentrated NaCl, $MgCl_2$ and $CaCl_2$ solutions:**
  - → Comprehensive chemical, thermodynamic and activity model derived for $Tc^{4+}–H^+–Na^+–Mg^{2+}–Ca^{2+}–OH^-–Cl^-–H_2O$ system
  - → New species proposed based on the newly generated solubility data, slope analysis and spectroscopic evidences in literature.

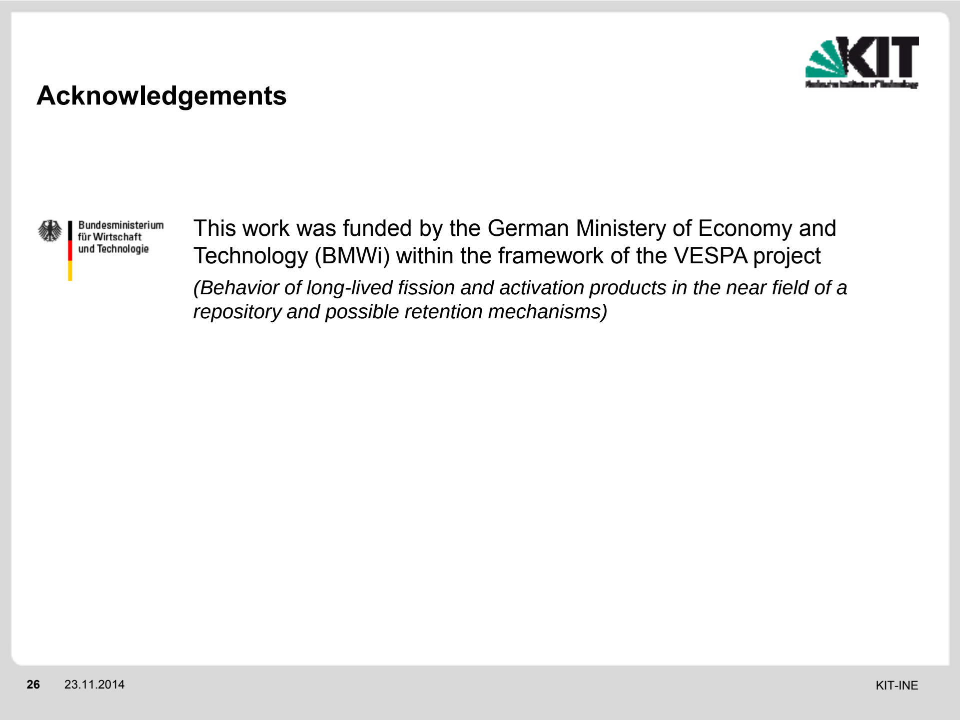


Outlook

New PhD work at KIT–INE from October 2014 on:

- Tc(IV) solubility experiments in the presence of complexing ligands:
  - Carbonate
  - Nitrate, Sulphate
  - Sulfide (?)

- Tc interaction with Fe(II)–CO_3 and Fe(II)–S solid phases (collaboration with HZDR-ROBL)



Acknowledgements

Bundesministerium
für Wirtschaft
und Technologie

This work was funded by the German Ministery of Economy and Technology (BMWi) within the framework of the VESPA project

(Behavior of long-lived fission and activation products in the near field of a repository and possible retention mechanisms)

Density and activity of perrhenic and pertechnetic acid aqueous solutions at 25°C

P. Moeyaert[a], L. Abiad[a], C. Sorel[a*], J.-F. Dufrêche[b], M. Miguirditchian[a] and P. Moisy[a]

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In the conditions of the spent nuclear fuel reprocessing, technetium is mostly present at the +7 oxidation state, which is the most stable oxidation state in solution, and forms pertechnetic acid $HTcO_4$.

In the solutions involved in the actinides separation processes (riched in cations and anions), it is not possible to make the approximation that activities are equal to concentrations. Stoichiometric activity coefficients in aqueous phase must be determined to take into account deviations from an ideal behaviour. To estimate the deviations from ideality whatever the solution theory used, binary data (variations of the osmotic coefficient, activity coefficient and density of the electrolyte in solution in the water) are needed. The knowledge of these data allows the prediction of various physico-chemical properties of solutions containing several electrolytes, and is required to model the thermodynamic behaviour of electrolytes in spent nuclear fuel.

Since perrhenic acid is an analogue of pertechnetic acid, binary data for $HReO_4$ at 25°C are first determined by direct water activity and osmolality measurements, by freeing ourselves from the constraint of gloves box environment. Thus, the validation of the experimental procedure on $HReO_4$ aqueous solutions allows carrying on the measurements in a confined volume for $HTcO_4$ binary solutions.

The variations of the osmotic coefficient of these acids in water are represented mathematically according to a model recommended by the National Institute of Standards and Technology and according to the specific interaction theory. The data are also used to evaluate the parameters of the standard three-parameters of Pitzer's ion-interaction model, along with the parameters of Archer's four-parameter extended ion-interaction model, to higher molalities than previously advised. Experimental thermodynamic data are well represented by these models. Density variations at 25°C are also established and used to express the activity coefficient values on both the molar and molal concentration scales.

$$\begin{tikzcd}
\begin{array}{c}\text{Exp data}\\ a_w \,\&\, \hat{m}\end{array} \arrow[r] & \phi = -\dfrac{\ln a_w}{\upsilon m M_{H2O}} \arrow[d, "\text{Fit}"] \\
\gamma = f(m) & \phi = f(m) \arrow[l, "\begin{array}{c}\text{Gibbs-Duheim}\\ \text{equation}\end{array}"']
\end{tikzcd}$$

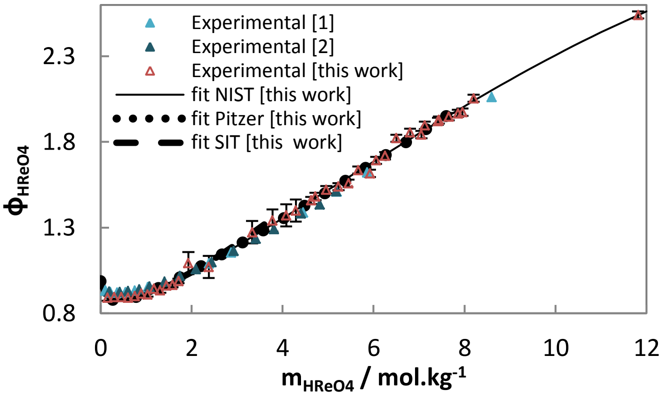

Figure 1: Experimental and calculated osmotic coefficient ϕ variation of binary $HReO_4$-H_2O solutions at 25°C with molal concentration.

1. O. D. Bonner, *J. Solut. Chem.*, 1982, **11**, 665-670.
2. G. E. Boyd, *Inorg. Chem.*, 1978, **17**, 1808-1810.

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DENSITY AND THERMODYNAMIC ACTIVITY OF PERRHENIC AND PERTECHNETIC ACID AQUEOUS SOLUTIONS AT 25°C

P. Moeyaert[a], L. Abiad[a], C. Sorel[a], M. Miguirditchian[a],
J.-F. Dufrêche[b], Ph. Moisy[a]

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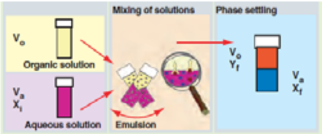
ISTR2014
La Baule, 30th september 2014

SOLVENT EXTRACTION MODELLING



Technetium in the spent fuel dissolution solution

- Tc = fission product
- Causes some problems (hydrazine destruction, U & Pu contamination)
- Measurements implemented in La Hague plant

Technetium SX equilibrium

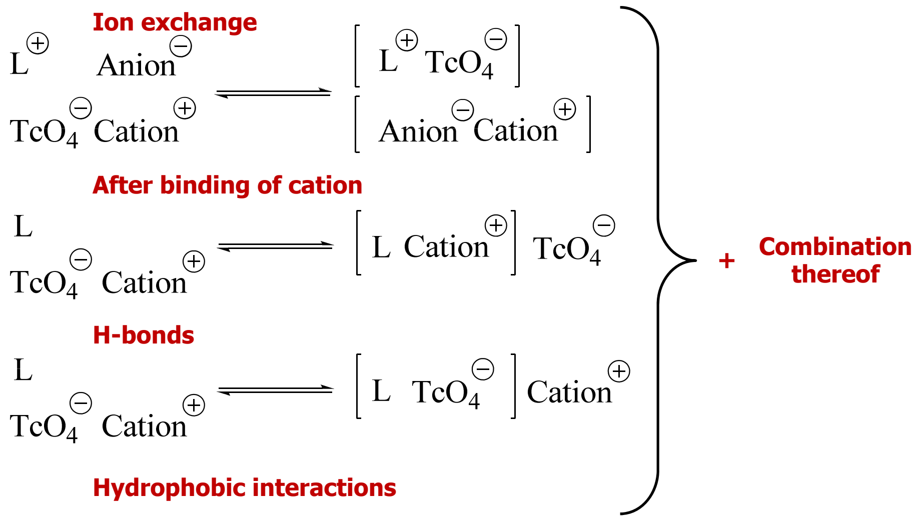
$$H^+ + TcO_4^- + pH_2O + x\overline{TBP} \leftrightharpoons \overline{HTcO_4(H_2O)_p(TBP)_x}$$
$$UO_2^{2+} + nTcO_4^- + (2-n)NO_3^- + x\overline{TBP} \leftrightharpoons \overline{UO_2(NO_3)_{2-n}(TcO_4)_nTBP_x}$$

Mass action law

$$K_{\overline{HTcO_4(H_2O)_p(TBP)_x}} = \frac{a_{\overline{HTcO_4(H_2O)_p(TBP)_x}}}{a_{HTcO_4}a_{H_2O}^{p}a_{\overline{TBP}}^{x}} = \frac{\left[\overline{HTcO_4(H_2O)_p(TBP)_x}\right]}{a_{H_2O}^{p}[HTcO_4]\gamma_{HTcO_4}\left[\overline{TBP}\right]^x}\frac{\gamma_{\overline{HTcO_4(H_2O)_p(TBP)_x}}}{\gamma_{\overline{TBP}}^{x}}$$

Issue: estimation of the activity coefficient

Prime mechanisms for binding of TcO_4^- and ReO_4^-



Ion exchange

$L^{\oplus}$ $Anion^{\ominus}$ + $TcO_4^{\ominus}$ $Cation^{\oplus}$ $\rightleftharpoons$ $[L^{\oplus}\ TcO_4^{\ominus}]$ + $[Anion^{\ominus}\ Cation^{\oplus}]$

After binding of cation

L + $TcO_4^{\ominus}$ $Cation^{\oplus}$ $\rightleftharpoons$ $[L\ Cation^{\oplus}]$ $TcO_4^{\ominus}$

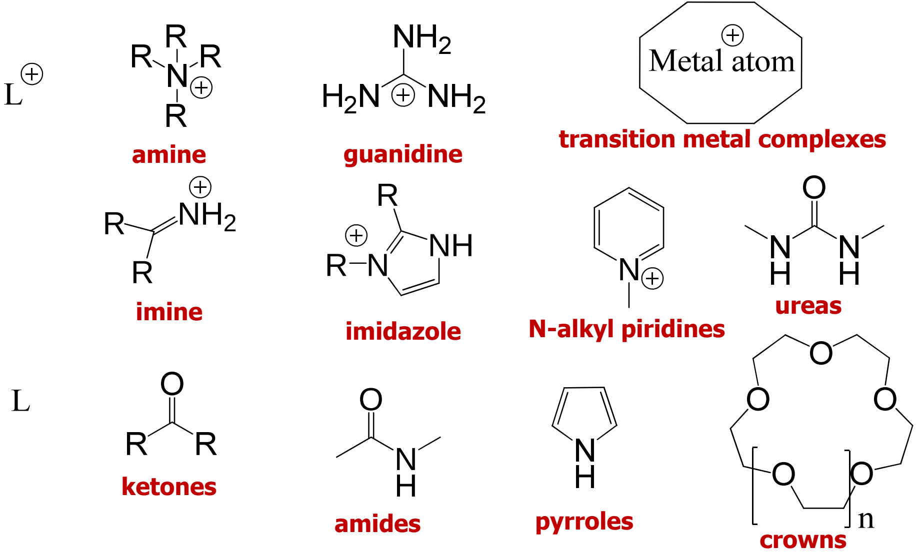
H-bonds

L + $TcO_4^{\ominus}$ $Cation^{\oplus}$ $\rightleftharpoons$ $[L\ TcO_4^{\ominus}]$ $Cation^{\oplus}$

Hydrophobic interactions

+ Combination thereof

Typical organic moieties for TcO_4^- binding



amine

guanidine

transition metal complexes

imine

imidazole

N-alkyl piridines

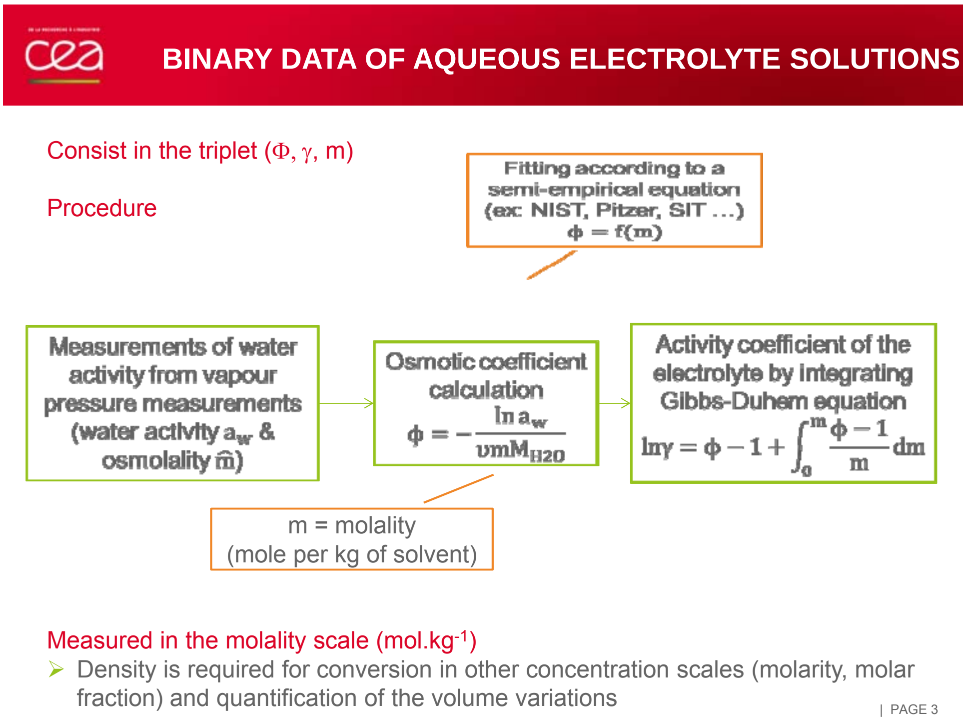
ureas

ketones

amides

pyrroles

crowns



BINARY DATA OF AQUEOUS ELECTROLYTE SOLUTIONS

Consist in the triplet (Φ, γ, m)

Procedure

Fitting according to a semi-empirical equation (ex: NIST, Pitzer, SIT …) $\phi = f(m)$

Measurements of water activity from vapour pressure measurements (water activity a_w & osmolality $\hat{m}$)

Osmotic coefficient calculation

$$\phi = -\frac{\ln a_w}{\upsilon m M_{H2O}}$$

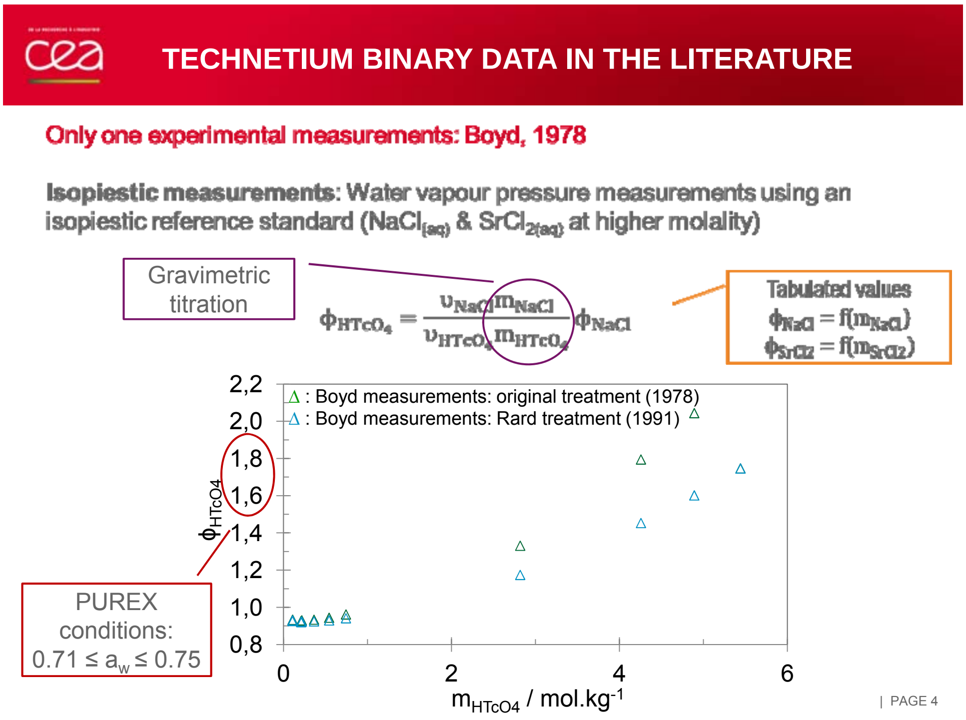
Activity coefficient of the electrolyte by integrating Gibbs-Duhem equation

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

m = molality
(mole per kg of solvent)

Measured in the molality scale (mol.kg^{-1})

- Density is required for conversion in other concentration scales (molarity, molar fraction) and quantification of the volume variations



TECHNETIUM BINARY DATA IN THE LITERATURE

Only one experimental measurements: Boyd, 1978

Isopiestic measurements: Water vapour pressure measurements using an isopiestic reference standard ($NaCl_{(aq)}$ & $SrCl_{2(aq)}$ at higher molality)

Gravimetric titration

$$\phi_{HTcO_4} = \frac{\upsilon_{NaCl} m_{NaCl}}{\upsilon_{HTcO_4} m_{HTcO_4}} \phi_{NaCl}$$

Tabulated values
$\phi_{NaCl} = f(m_{NaCl})$
$\phi_{SrCl2} = f(m_{SrCl2})$

△ : Boyd measurements: original treatment (1978)
△ : Boyd measurements: Rard treatment (1991)

PUREX conditions:
$0.71 \leq a_w \leq 0.75$

HREO$_4$ AS A SIMULANT FOR HTCO$_4$

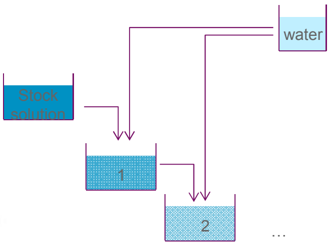
Validation of the experimental procedure on a simulant

- $HReO_4$: Re = non-radioactive analogue for Tc
- Outline:
  - → 1st part: activity of $HReO_4$ solutions
  - → 2nd part: activity of $HTcO_4$ solutions

HREO$_4$ PREPARATION & MEASUREMENTS

Preparation of the acid

- $HReO_4$ stock solution:
  - → Alfa Aesar
  - → m = 11.82 mol.kg^{-1}
- Cascading mass dilutions (11.82 to 0.15 mol.kg^{-1})



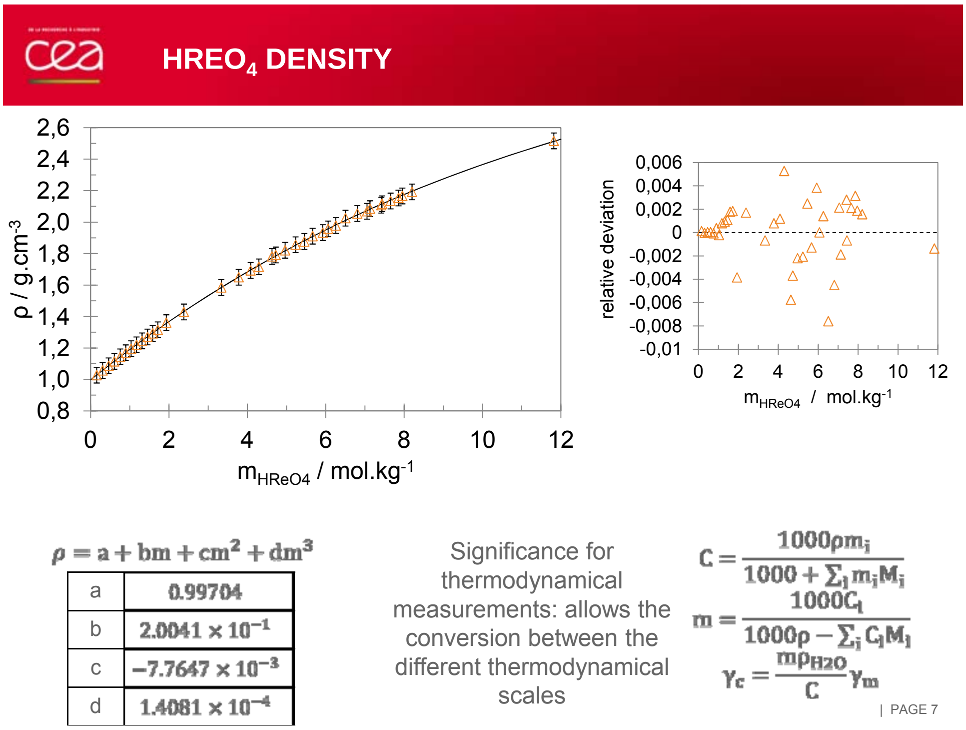
Measurement of density

Anton-Paar DMA 55 density meter

Measurement of activity

- $0.60 \leq a_w \leq 0.94$ range:
  - → More concentrated solutions
  - → Novasina AW-center water activity meter

- $0.94 \leq a_w \leq 0.995$ range:
  - → More dilute solutions
  - → Wescor Vapro dew-point osmometer
  - → Osmolality ($\tilde{m}$) measurements



HREO$_4$ DENSITY

$$\rho = a + bm + cm^2 + dm^3$$

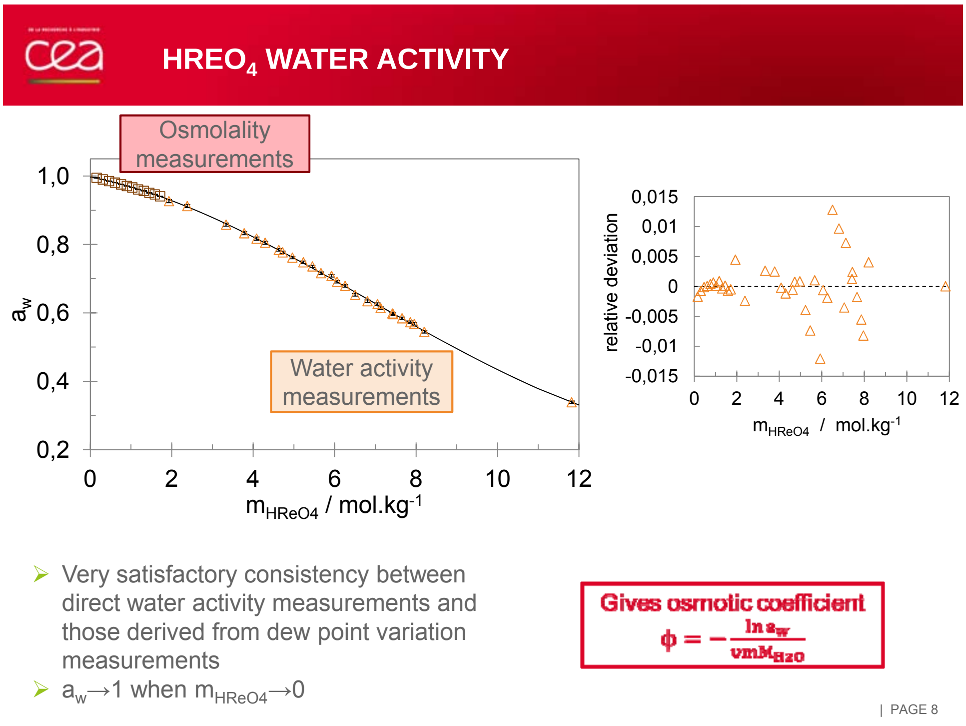
a	0.99704
b	2.0041×10^{-1}
c	-7.7647×10^{-3}
d	1.4081×10^{-4}

Significance for thermodynamical measurements: allows the conversion between the different thermodynamical scales

$$C = \frac{1000\rho m_i}{1000 + \sum_j m_j M_j}$$

$$m = \frac{1000C_i}{1000\rho - \sum_j C_j M_j}$$

$$\gamma_c = \frac{m\rho_{H2O}}{C}\gamma_m$$



HREO$_4$ WATER ACTIVITY

Osmolality measurements

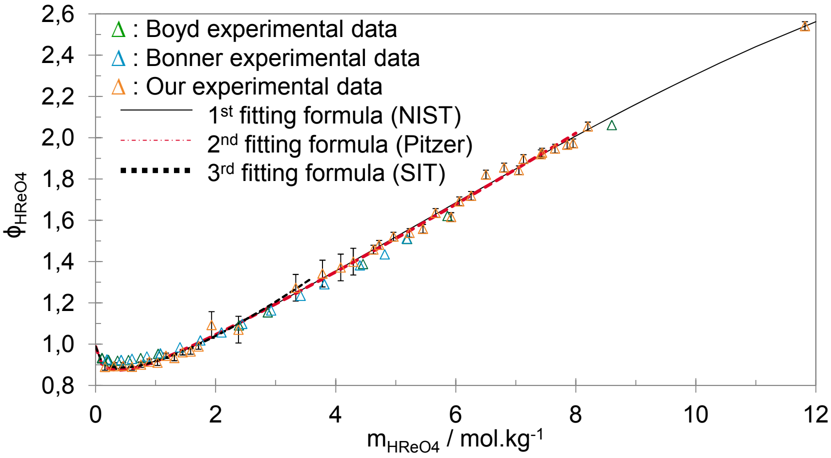
Water activity measurements

- Very satisfactory consistency between direct water activity measurements and those derived from dew point variation measurements
- $a_w \rightarrow 1$ when $m_{HReO4} \rightarrow 0$

Gives osmotic coefficient

$$\phi = -\frac{\ln a_w}{\nu m M_{H2O}}$$

$HREO_4$ OSMOTIC COEFFICIENT FIT



- Good agreement between Boyd, Bonner and the present experimental data
- Wider concentration range (especially above 6 $mol.kg^{-1}$)
- Good quality of the fits

Validation of the experimental procedure
⇒ Allows carrying on the measurements in a confined volume for $HTcO_4$ binary solutions

$HTCO_4$ PREPARATION & MEASUREMENTS

Preparation of the binary electrolyte $HTcO_4$

- $HTcO_4$ concentrated solution:
  - → From the mixed powder: NH_4TcO_4 + small amount of TcO_2
  - → + dissolution in NH_3 + heating → white powder of NH_4TcO_4
  - → + water + KOH + heating → $KTcO_4$
  - → + strong-acid cation exchanger (Dowex) → $HTcO_4$

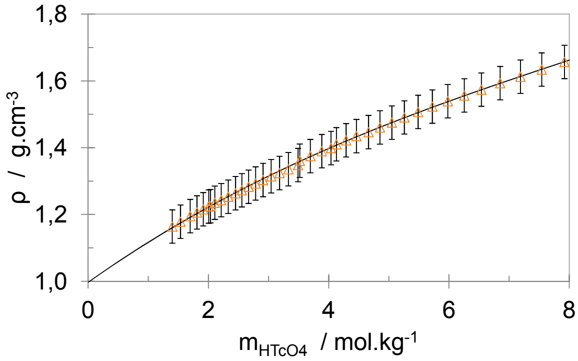
⇒ colourless binary $HTcO_4$-H_2O mother solution
⇒ m = 8.32 $mol.kg^{-1}$

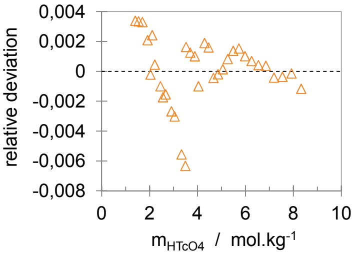
- Cascading mass dilutions

Measurements

- Density and water activity (similar methods as $HReO_4$)

$HTCO_4$ DENSITY

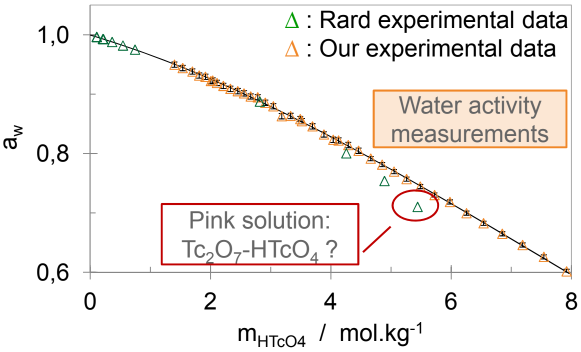




$$\rho = a + bm + cm^2 + dm^3$$

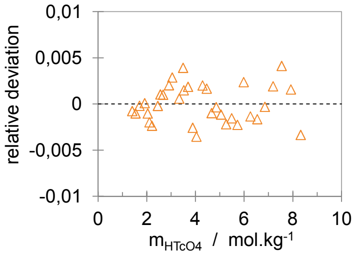
a	0.99704
b	1.2731×10^{-1}
c	-8.0687×10^{-3}
d	3.1841×10^{-4}

$HTCO_4$ WATER ACTIVITY



Water activity measurements

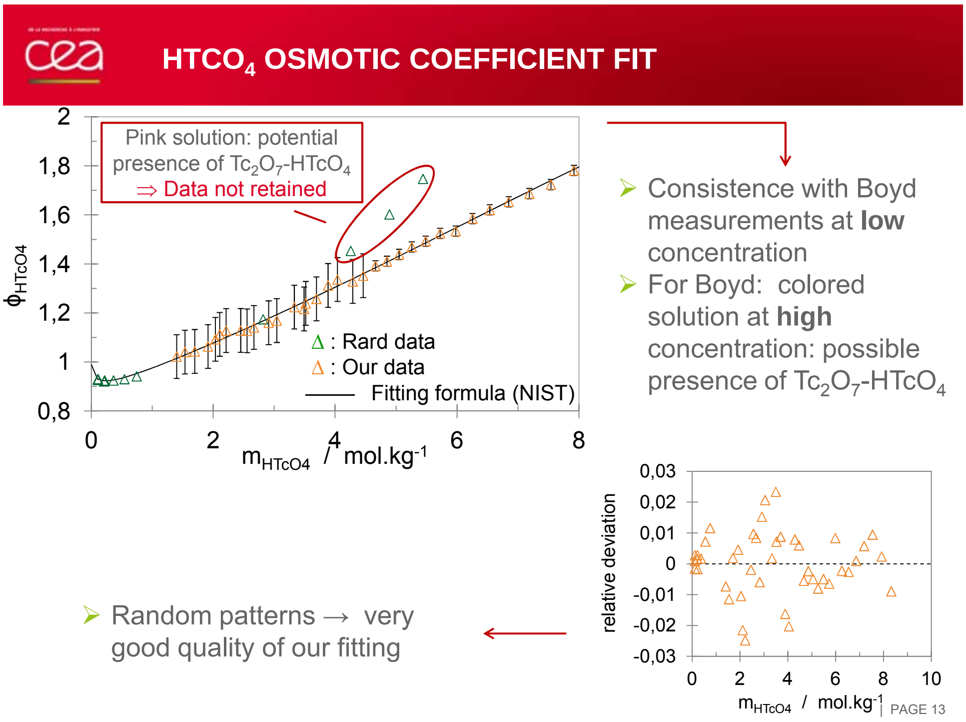
Pink solution: Tc_2O_7-$HTcO_4$?



$$a_w = a + bm + cm^2 + dm^3$$

a	0.99936
b	-2.9753×10^{-2}
c	-3.9270×10^{-3}
d	1.6733×10^{-4}

G. E. Boyd, *Inorg. Chem.*, 1978, **17**, 1808-1810.

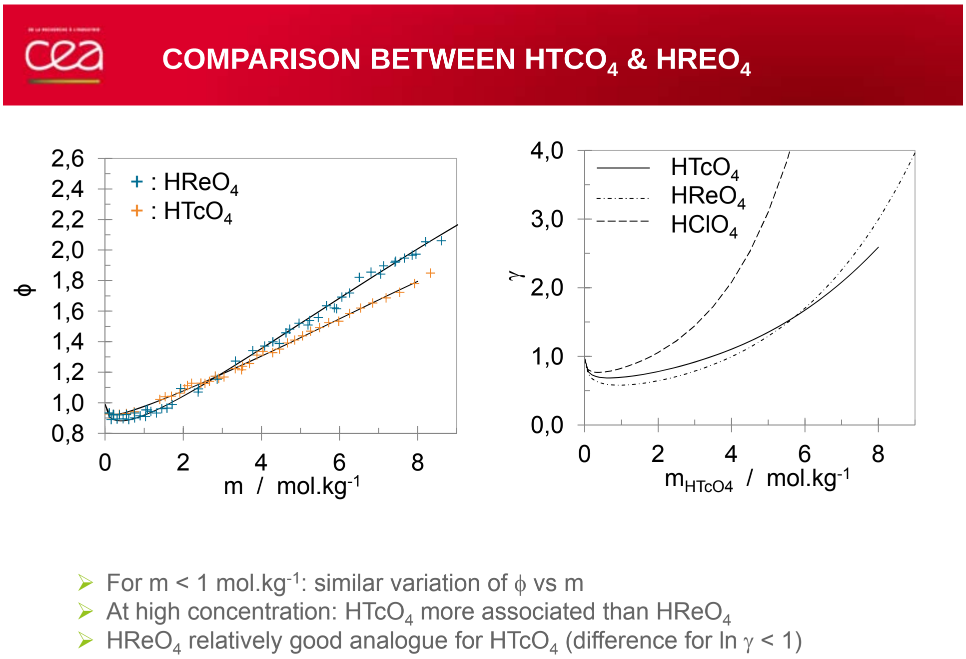


HTCO$_4$ OSMOTIC COEFFICIENT FIT

Pink solution: potential presence of Tc_2O_7-$HTcO_4$
⇒ Data not retained

- Consistence with Boyd measurements at **low** concentration
- For Boyd: colored solution at **high** concentration: possible presence of Tc_2O_7-$HTcO_4$

- Random patterns → very good quality of our fitting



COMPARISON BETWEEN HTCO$_4$ & HREO$_4$

- For m < 1 mol.kg^{-1}: similar variation of ϕ vs m
- At high concentration: $HTcO_4$ more associated than $HReO_4$
- $HReO_4$ relatively good analogue for $HTcO_4$ (difference for ln γ < 1)

CONCLUSION & OUTLOOK

Conclusion

- Measurements of density and activity coefficients for $HReO_4$ & $HTcO_4$
  - → Very **good agreement** between this work and previous studies
  - → Boyd's values for $HTcO_4$ at high concentration **probably wrong** (presence of Tc_2O_7 ?)
  - → Very **good quality** of the fitted formula (NIST, Pitzer) up to 8 mol.kg^{-1} ($HTcO_4$) and 12 mol.kg^{-1} ($HReO_4$)

Outlook

- Improvement in the description of aqueous Tc solutions for chemical engineering (separation processes: technetium models for PUREX or new separation processes)
- Improvement in the thermodynamic knowledge for $HReO_4$ (hydrometallurgy…)
- Measurements of thermodynamic data (association constant), hydrated size (BIMSA or MSA treatments)
- Measurements for mixture electrolytes (validity of mixing rules: ZSR, etc ?)

Aknowledgements

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Dr. Christian Sorel
Pr. Jean-François Dufrêche
Dr. Lidwine Abiad
Pr. Philippe Moisy
Dr. Manuel Miguirditchian
Pr. Pierre Turq

THANK YOU FOR YOUR ATTENTION

Commissariat à l'énergie atomique et aux énergies alternatives
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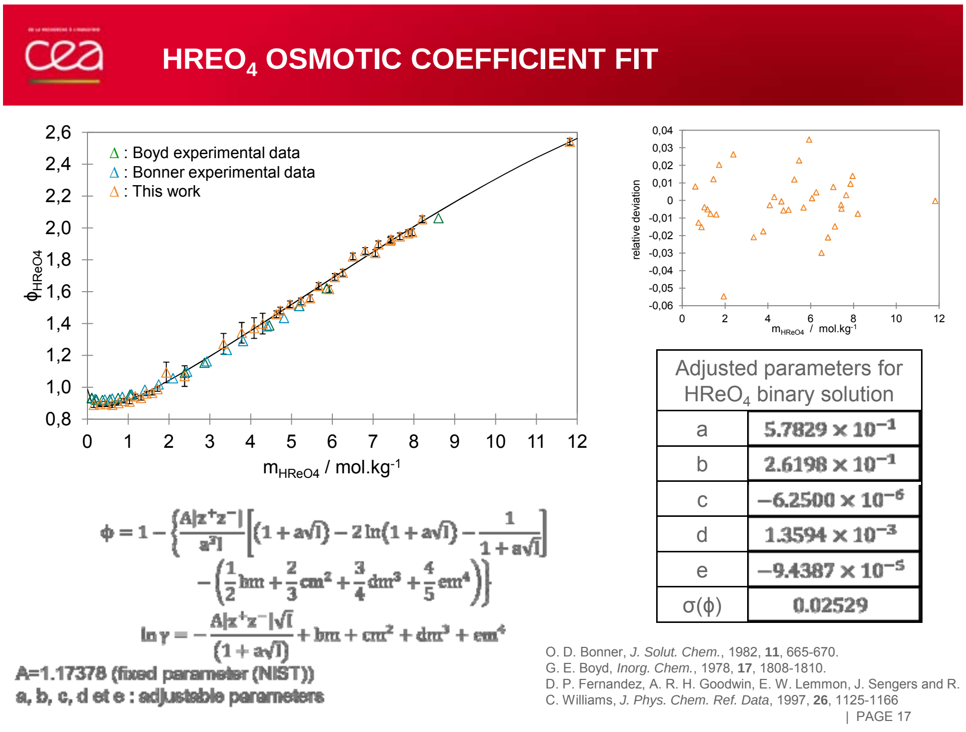
Direction de l'énergie nucléaire
Département de radiochimie des procédés
Service de modélisation et de chimie des procédés de séparation



HREO$_4$ OSMOTIC COEFFICIENT FIT

$$\phi = 1 - \left\{\frac{A|z^+z^-|}{a^3 I}\left[\left(1+a\sqrt{I}\right) - 2\ln\left(1+a\sqrt{I}\right) - \frac{1}{1+a\sqrt{I}}\right] - \left(\frac{1}{2}bm + \frac{2}{3}cm^2 + \frac{3}{4}dm^3 + \frac{4}{5}em^4\right)\right\}$$

$$\ln\gamma = -\frac{A|z^+z^-|\sqrt{I}}{\left(1+a\sqrt{I}\right)} + bm + cm^2 + dm^3 + em^4$$

A=1.17378 (fixed parameter (NIST))
a, b, c, d et e : adjustable parameters

Adjusted parameters for HReO$_4$ binary solution	
a	5.7829×10^{-1}
b	2.6198×10^{-1}
c	-6.2500×10^{-6}
d	1.3594×10^{-3}
e	-9.4387×10^{-5}
σ(ϕ)	0.02529

O. D. Bonner, *J. Solut. Chem.*, 1982, **11**, 665-670.
G. E. Boyd, *Inorg. Chem.*, 1978, **17**, 1808-1810.
D. P. Fernandez, A. R. H. Goodwin, E. W. Lemmon, J. Sengers and R. C. Williams, *J. Phys. Chem. Ref. Data*, 1997, **26**, 1125-1166

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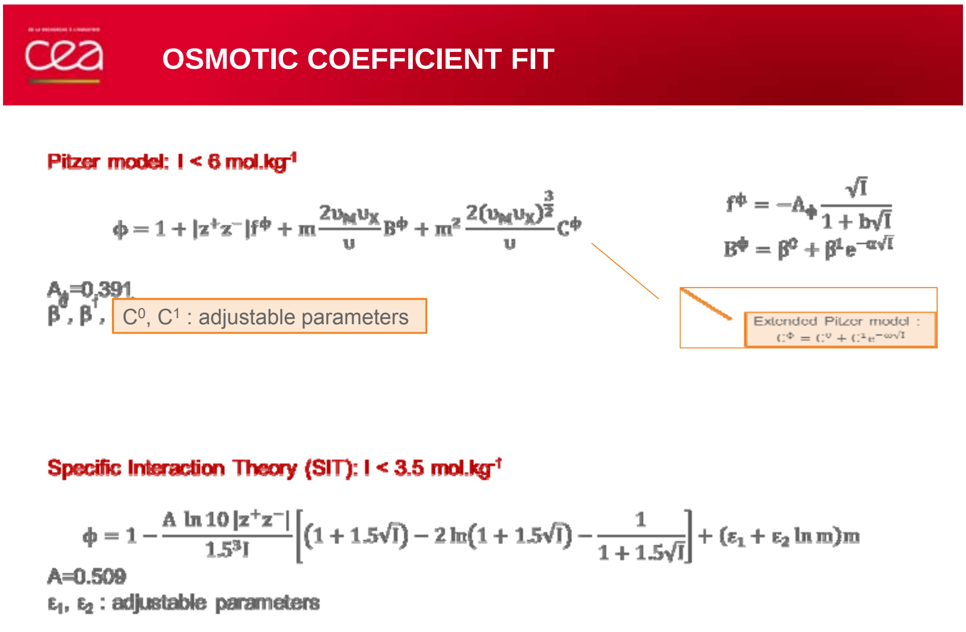

OSMOTIC COEFFICIENT FIT

Pitzer model: I < 6 mol.kg^{-1}

$$\phi = 1 + |z^+z^-|f^\phi + m\frac{2\upsilon_M\upsilon_X}{\upsilon}B^\phi + m^2\frac{2(\upsilon_M\upsilon_X)^{\frac{3}{2}}}{\upsilon}C^\phi$$

$$f^\phi = -A_\phi\frac{\sqrt{I}}{1+b\sqrt{I}}$$
$$B^\phi = \beta^0 + \beta^1 e^{-\alpha\sqrt{I}}$$

A_ϕ=0,391
β^0, β^1, C^0, C^1 : adjustable parameters

Extended Pitzer model :
$C^\phi = C^0 + C^1 e^{-\omega\sqrt{I}}$

Specific Interaction Theory (SIT): I < 3.5 mol.kg^{-1}

$$\phi = 1 - \frac{A\ \ln 10\,|z^+z^-|}{1.5^3 I}\left[\left(1+1.5\sqrt{I}\right) - 2\ln\left(1+1.5\sqrt{I}\right) - \frac{1}{1+1.5\sqrt{I}}\right] + (\varepsilon_1 + \varepsilon_2\ln m)m$$

A=0.509
ε_1, ε_2 : adjustable parameters

Comparative study of several supramolecular TcO_4^- and ReO_4^- receptors for applications in sensors and radiopharmaceuticals

K.E. German[1,2], Ya.A. Obruchnikova [1,2,3], G.V. Kolesnikov,
G.A. Kirakosyan[1,2,4] , I.G. Tananaev[1,5], B.F. Myasoedov[1]
1 – Frumkin Institute of Physical Chemistry and Electrochemistry RAS, Moscow, Russia
2 – Moscow Medical Institute REAVIZ, Moscow Russia
3 – Mendeleev Russian Chemical Technology University, Moscow, Russia
4 – Kurnakov IGIC RAS, Moscow, Russia; 5 – PO Mayak, Ozersk, Russia

TcO_4^- и ReO_4^- are extensively used in nuclear medicine and many other industries. Most of its radiopharmaceuticals are modified for usage in different deceases after chemical reduction of these metal(VII) anions to lower oxidation state. But the question of the species direct modification trough binding to organic cations of special design is of high interest. It is difficult to bind hydrophobic TcO_4^- и ReO_4^-. But not impossible. The best binding was achieved in case of quaternary phosphonium and vinilpyridinium anion-exchange resins. The K_d were reported as high as 10^6 ml/g. Also very high binding was achieved on TPPB in Sellafield for purification of alkali radwastes. Probably the most efficient receptor for TcO_4^- known was reported in [1].

This work is to sum up the available literature and our proper data for recently developed approach of template synthesis in course of new receptor design and synthesis. It was rational to reduce macrobicycle cavity to macrocyclic and consider the rigid macrocyclic receptors as promising binding centers while trying the supramolecular interactions as the rout for template synthesis of macrocycles.

As demonstrated in [2] the dendrimers are efficient but not selective.

So, we proposed the derivatives of triphenylguanidinium cation for binding TcO_4^- и ReO_4^- oxoanions. The results will be reported for the complex stability constants and considered in comparison with those obtained earlier.

The work was supported by the grant 45P for fundamental researches by Presidium of Russian Academy of Sciences.

1. Antipin I.S., Solovieva S.E., Stoikov I.I., Vershinina I.S., Pribylova G.A., Tananaev I.G., Myasoedov B.F. // Russ.Chem.Bull., Int. Ed. – 2004.
2. Stephan H., Spies H., Johannsen B., Klein L., Vögtle F. // Chem.Comm. – 1999.

ISTR 2014
8th International Symposium on Technetium and Rhenium
Pornichet LA BAULE, France
29th September - 3rd October 2014

Comparative study of several supramolecular TcO_4^- and ReO_4^- receptors for applications in sensors and radiopharmaceuticals

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1 – Frumkin Institute of Physical Chemistry and Electrochemistry RAS, Moscow, Russia
2 – Moscow Medical Institute REAVIZ, Moscow Russia
3 – Mendeleev Russian Chemical Technology University, Moscow, Russia
4 – Kurnakov IGIC RAS, Moscow, Russia; 5 – PO Mayak, Ozersk, Russia

Problem of Tc binding is urgent
TcO_4^- is the most stable form

- **Nuclear fuel cycle**:

high yields, more then 800 g per 1 t ^{235}U
facilitates reductant decomposition during treatment
forms precipitates

TcO_4^- needs to be extracted before treatment

- **Ecology**:

^{99}Tc ($E_{\beta-}$= 293.8 keV, $\lambda_{1/2}$ = 2.13×10^5 years)
TcO_4^- salts are poorly fixed with natural minerals
$NaTcO_4$ solubility in water — 11.3 M

Concentration control is necessary

TcO_4^- и ReO_4^- are extensively used in nuclear medicine

- ^{99m}Tc (E_γ = 141.0 keV, $\lambda_{1/2}$ = 6 h)

Diagnostic application

80% from 30 mln. injections yearly

- ^{188}Re ($E_{\beta-}$= 763.9 keV, $\lambda_{1/2}$ = 17 h)

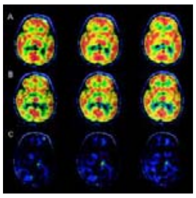
Therapeutic application

- **W**hat is common for both nuclides:

are produced as MO_4^- (M = Tc, Re)

then reduced with $SnCl_2$, $NaBH_4$

injected as M(III)−(V) complexes



It is difficult to bind hydrophobic TcO_4^- и ReO_4^-

Anion	ΔH^0_{hydr} kJ/mol*	R_{H2O}, nm	S_{ion}, Å^2	Q/S×10^2, Å^{-2}
$H_2PO_4^-$	-522	0.20	50.3	2.0
H_3CCOO^-	-425	0.16	33.0	3.0
Cl^-	-367	0.18	41.2	2.4
NO_3^-	-312	0.18	40.3	2.5
I^-	-291	0.22	60.8	1.6
ClO_4^-	-246	0.25	78.5	1.3
ReO_4^-	-244	0.26	85.0	1.2
TcO_4^-**	-247	0.25	78.5	1.3
MnO_4^-	-250	0.24	72.4	1.4

Increase

- hydrophobicity
- size

Decrease

- surface charge density

R_{H20} – ionic radius in water
S_{ion} – surface of an ion
Q/S – surface charge density of an ion

* ΔH^0_{hydr} и R_{H2O} obtained experimentally. Other data is calculated.

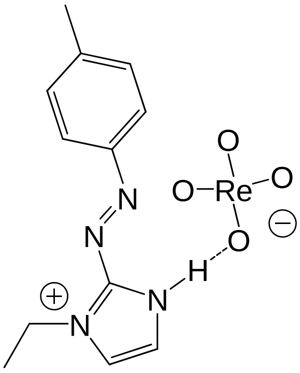
** for TcO_4^- data was produced by linear interpolation in the row: MnO_4^- - TcO_4^- - ReO_4^-.

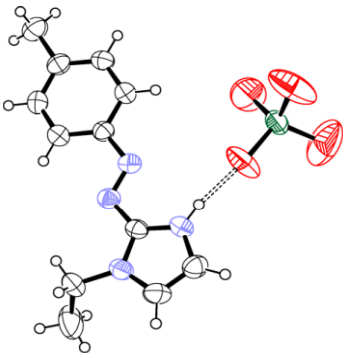
Known methods for measuring binding of TcO_4^- with organic receptors

- **E**xtraction – the most popular method
- **U**V-Vis – easy to get, but Tc and Re are UV active
- ^{1}H-NMR
  ^{99}Tc-NMR – precise, but concentration must be higher then in objects of interest
- **X**-ray – luck is needed

Some important examples of smaller receptors

- **Positive charge from N-alkyl imidazole**
- **Acidic N-H from imidazole**

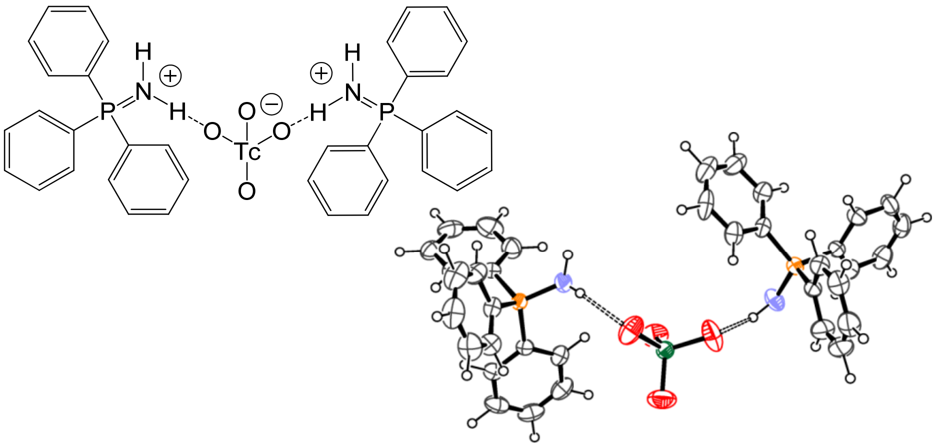




Ray U., Mostafa G., Lu T., Sinha C. Hydrogen bonded perrhenate-azoimidazoles. // Cryst.Eng. – 2002.
Ray U., Chand B., Dasmahapatra A., Mostafa G., Lu T., Sinha C. // Inorg.Chem.Commun. – 2003.

Some important examples of smaller receptors

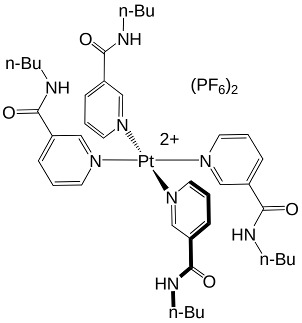
- **Positive charge from protonated imine**
- **Acidic N-H from protonated imine**

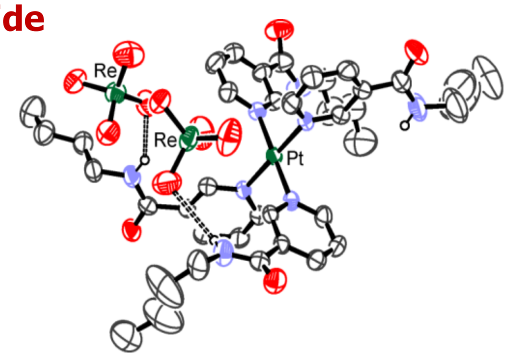


Eble B., Berning D., Barnes C.L., Katti K.V., Jurisson S. // J.Chem.Cryst. – 1999.

Some important examples of smaller receptors

- **Positive charge on metal**
- **Acidic N-H from amide**



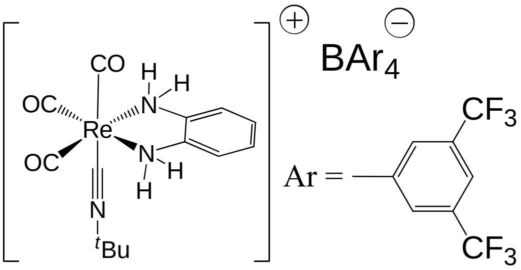


K_a ^{1}H-NMR in MeCN	HSO_4^-	$CF_3SO_3^-$	H_3CCOO^-	NO_3^-	ReO_4^-
	149	129	230 (1:1) 491 (1:2)	526 (1:1) 132 (1:2)	150

Bondy C.R., Gale P.A., Loeb S.J. // Chem.Comm. – 2001.

Some important examples of smaller receptors

- **Positive charge**
- **Acidic N-H from**



K_a ^{1}H-NMR in MeCN	HSO_4^-	Cl^-	Br^-	NO_3^-	ClO_4^-	ReO_4^-
	19	77	48	26	18	24

Nieto S., Pérez J., Riera L., Riera V., Miguel D. // New J.Chem. – 2006.

Known compounds for TcO_4^- and ReO_4^- binding

Holman et al., JACS, 1996

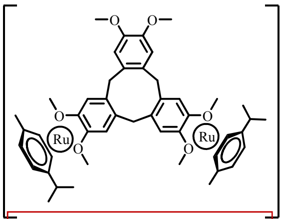
Antipin et al., Russ.Chem.Bull., 2004

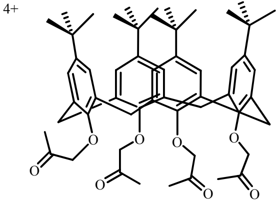
Beer et al., Chem.Comm., 1999

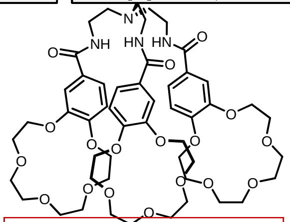
Extraction 0.9% NaCl in H_2O into $MeNO_2$ **88%** TcO_4^-

Extraction 1M NaOH in H_2O into dichloroethane **100%** TcO_4^- aqueous 1M HNO_3 into dichloroethane **80%** TcO_4^-

^{1}H NMR CDCl3 $K(ReO_4^-) = 40\ M^{-1}$
$K(ReO_4^-) = 840\ M^{-1}(+Na^+)$
Extraction aqueous NaOH, pH 11 into CH_2Cl_2 **70%** TcO_4^-



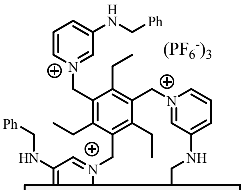


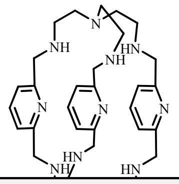


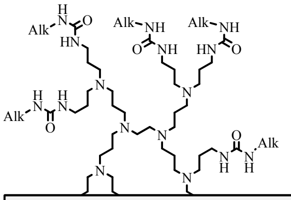
Steed et al., JACS, 2003

Wichmann et al., J.Chem.Soc.Dalton Trans., 2003

Vögtle et al., Chem.Comm, 1999







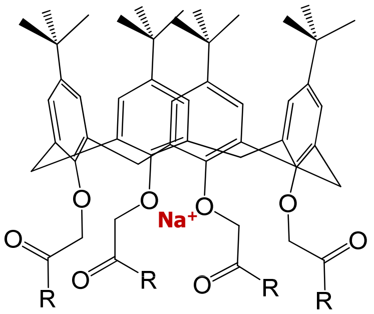
^{1}H NMR MeCN $K(ReO_4^-) =$ **112** M^{-1}

Extraction HEPES/NaOH, pH 7.4 into $CHCl_3$ **10%** TcO4−

Extraction HEPES/NaOH, pH 7.4 into $CHCl_3$ **50%** TcO4−

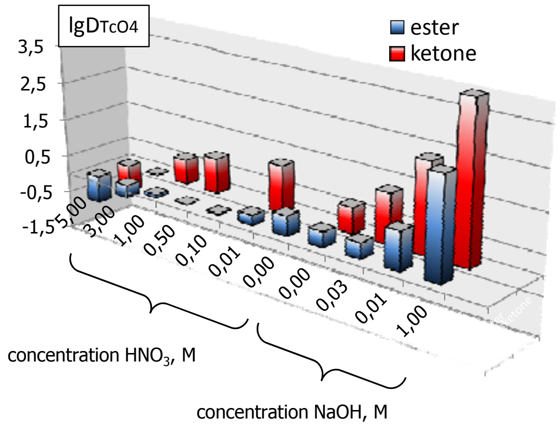
Very efficient ketone receptor for TcO_4^- (from NaOH)

- **Na^+ goes inside the moiety and pulls TcO_4^-**



ester: R=OC_2H_5

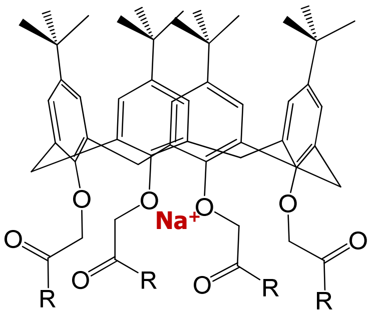
ketone: R=CH_3



Antipin I.S., Solovieva S.E., Stoikov I.I., Vershinina I.S., Pribylova G.A., Tananaev I.G., Myasoedov B.F. // Russ.Chem.Bull., Int. Ed. – 2004.

Very efficient ketone receptor for TcO_4^- (from NaOH)

- **Na^+ goes inside the moiety and pulls TcO_4^-**
- **Presence of NO_3^- influences slightly on extraction efficiency**



ester: R=OC_2H_5

ketone: R=CH_3

1M NaOH – **1M** $NaNO_3$

ester: D_{TcO4} = 142
ketone: D_{TcO4} = 118

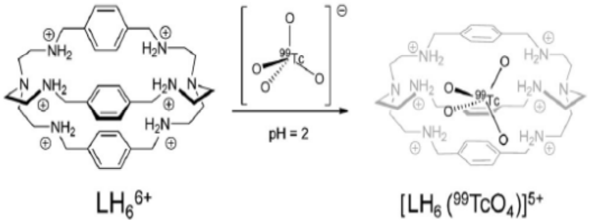
Low suppression

1M NaOH – **2M** $NaNO_3$

ester: D_{TcO4} = 102
ketone: D_{TcO4} = 108

Antipin I.S., Solovieva S.E., Stoikov I.I., Vershinina I.S., Pribylova G.A., Tananaev I.G., Myasoedov B.F. // Russ.Chem.Bull., Int. Ed. – 2004.

$^{99}TcO_4^-$: Selective Recognition and Trapping in Aqueous Solution



LH_6^{6+} interacts with $^{99}TcO_4^-$ in aqueous solution (pH 2.0).

This interaction leads to a 1:1 adduct, with the anion included in the cavity of the receptor.

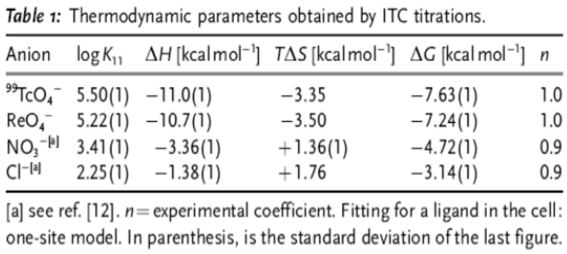
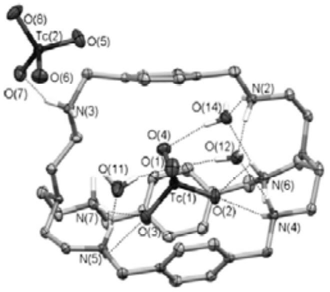


Table 1: Thermodynamic parameters obtained by ITC titrations.

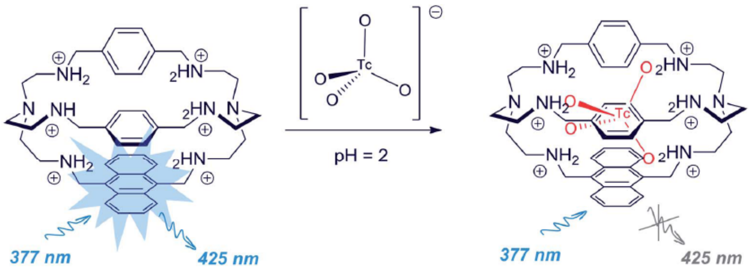
Anion	$\log K_{11}$	ΔH [kcal mol^{-1}]	$T\Delta S$ [kcal mol^{-1}]	ΔG [kcal mol^{-1}]	n
$^{99}TcO_4^-$	5.50(1)	−11.0(1)	−3.35	−7.63(1)	1.0
ReO_4^-	5.22(1)	−10.7(1)	−3.50	−7.24(1)	1.0
NO_3^-[a]	3.41(1)	−3.36(1)	+1.36(1)	−4.72(1)	0.9
Cl^-[a]	2.25(1)	−1.38(1)	+1.76	−3.14(1)	0.9

[a] see ref. [12]. n = experimental coefficient. Fitting for a ligand in the cell: one-site model. In parenthesis, is the standard deviation of the last figure.

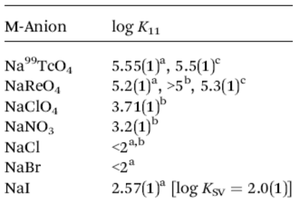


Work by R. Alberto, G. Bergamaschi, H. Braband, Th. Fox, V. Amendola. Angewandte Communications. Int. Ed. 2012, 51, 9772 –9776.

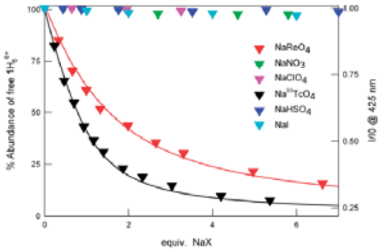
Fluorescent sensing of ^{99}Tc pertechnetate in water



The formation of an inclusion complex with $^{99}Tc(Re)O_4^-$ is accompanied by the quenching of the fluorescence of $1H_6^{6+}$.



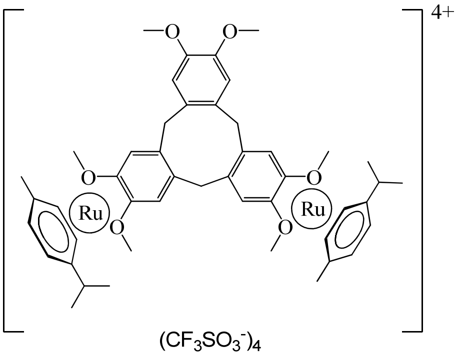
M-Anion	$\log K_{11}$
$Na^{99}TcO_4$	$5.55(1)^a$, $5.5(1)^c$
$NaReO_4$	$5.2(1)^a$, $>5^b$, $5.3(1)^c$
$NaClO_4$	$3.71(1)^b$
$NaNO_3$	$3.2(1)^b$
NaCl	$<2^{a,b}$
NaBr	$<2^a$
NaI	$2.57(1)^a$ [$\log K_{SV} = 2.0(1)$]



V. Amendola, G. Bergamaschi, M. Boiocchi, R. Alberto, H. Braband Chem. Sci., 2014, 5, 1820–1826

Hydrophobic cavitand with positively charged fragments

- **4^+ charge from two ruthenium atoms**
- **Hydrophobic cavity**



$(CF_3SO_3^-)_4$

Extraction	TcO_4^-	ReO_4^-
0.9% NaCl in H_2O	12%	29%
$MeNO_2$	**88%**	**71%**

20 eq.: Cl^-, HSO_4^-, NO_3^-

No suppression

20 eq.: ClO_4^-

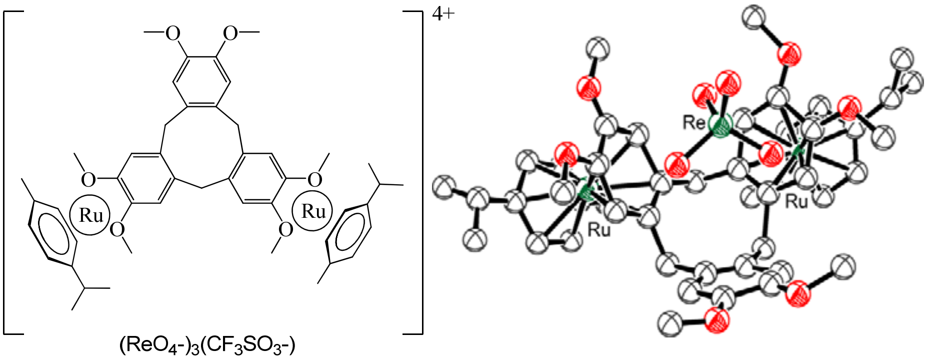
Extraction	TcO_4^-	ReO_4^-
0.9% NaCl in H_2O	---	94%
$MeNO_2$	---	**6%**

TcO_4^- > ReO_4^- > ClO_4^- >> NO_3^- > SO_4^{2-} > Cl^-

Holman K.T., Halihan M.M., Jurisson S.S., Atwood J.L., Burkhalter R.S., Mitchell A.R., Steed J.W. // J.Am.Chem.Soc. – 1996.

Hydrophobic cavitand with positively charged fragments

- **4^+ charge from two ruthenium atoms**
- **Coordination due to hydrophobic cavity and π interactions**

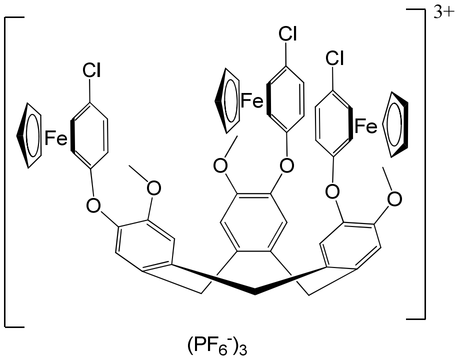


$(ReO_4^-)_3(CF_3SO_3^-)$

Holman K.T., Halihan M.M., Jurisson S.S., Atwood J.L., Burkhalter R.S., Mitchell A.R., Steed J.W. // J.Am.Chem.Soc. – 1996.

Hydrophobic cavitand with positively charged fragments

- **3^+ charge from three iron atoms**
- **More uniform charge distribution**
- **The same hydrophobicity**



Extraction	**TcO_4^-**	**ReO_4^-**
0.9% NaCl in H_2O	**< 10%**	**< 10%**
$MeNO_2$	**> 90%**	**> 90%**

20 eq.: Cl^-, HSO_4^-, NO_3^-

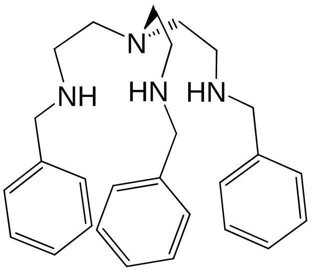
No suppression

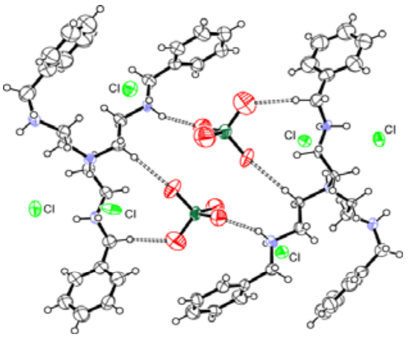
This receptor is more efficient and more selective than Ru-based predecessor

Gawenis J.A., Holman K.T., Atwood J.L., Jurisson S.S. // Inorg.Chem. – 2002.

C_3-symmetric ligands bind ReO_4^- after protonation

- **Protonation makes the receptor more rigid**
- **ReO_4^- coordinates with amino NH- and benzylic CH-groups**





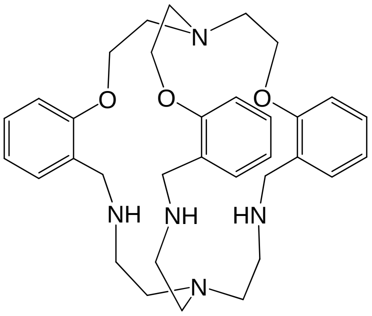
L•$(HReO_4)(HCl)_3$

Extraction	**TcO_4^-**	**ReO_4^-**
H_2O, pH 5.5	**18%**	**24%**
$CHCl_3$	**82%**	**76%**

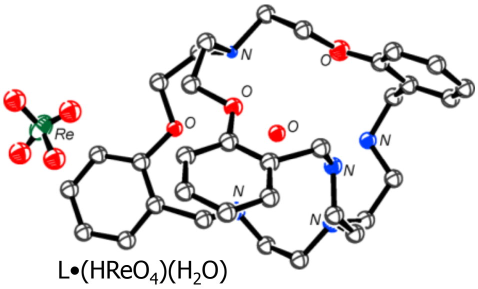
Antonioli B., Gloe K., Gloe K., Goretzki G., Grotjahn M., Heßke H., Langer M., Lindoy L.F., Mills A.M., Söhnel T. // Z.Anorg.Allg.Chem. – 2004.

C_3-symmetric macrobicycles bind ReO_4^- outside cavity

- **Protonation of receptor is important for strong binding**
- **ReO_4^- coordinates outside the cavity**



Extraction	**TcO_4^-**	**ReO_4^-**
H_2O, pH 7.4	**18%**	**24%**
$CHCl_3$	**82%**	**76%**

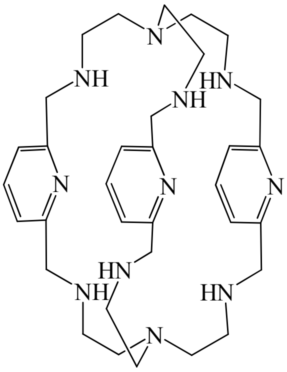


L•$(HReO_4)(H_2O)$

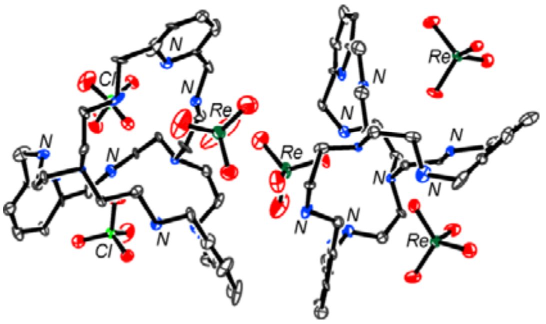
Stephan H., Gloe K., Kraus W., Spies H., Johannsen B., Wichmann K., Chand D.K., Bharadwaj P.K., Muller U., Muller W.M., Vogtle F. In «Fundamentals and applications of anion separations». Ed. by Singh R.P., Moyer B.A. Kluwer: New York; 2004.

C_3-symmetric macrobicycles bind ReO_4^- outside cavity

- **Larger cavity still does not allow TcO_4^- to go inside**
- **More hydrophilic ligand extracts worse**



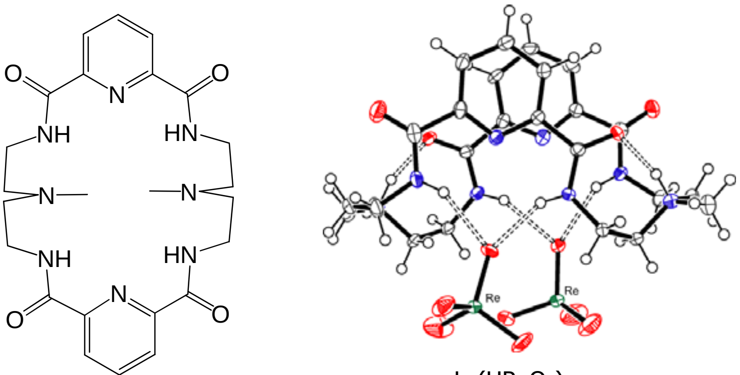
Extraction	**TcO_4^-**	**ReO_4^-**
H_2O, pH 7.4	86%	90%
$CHCl_3$	14%	10%



$[L•(HMO_4)_3]_2(H_2O)_3$, M=Cl, Re

It is rational to reduce macrobicycle cavity to macrocyclic

- **Amino groups are protonated but…**
- **Amides coordinate ReO_4^-**

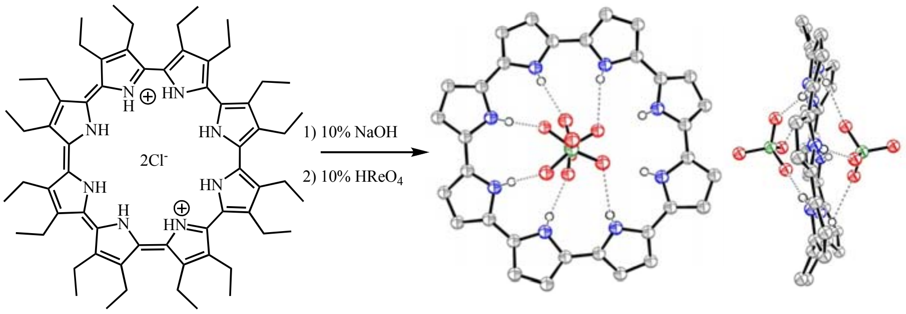


$L•(HReO_4)_2$

Ghosh S., Roehm B., Begum R.A., Kut J., Hossain Md.A., Day V.W., Bowman-James K. // Inorg.Chem. – 2007.

Rigid macrocyclic receptors are promising

- **Two positive charges, three H-bonds for each ReO_4^-**
- **Rigid planar macrocyclic core**



$\log K_a$ ^{1}H-NMR in MeCN	$H_2PO_4^-$	HSO_4^-	OAc^-	NO_3^-	I^-	ReO_4^-	TcO_4^-
	9.7	6.5	6.7	9.8	**5.0**	**5.9**	**6.0**

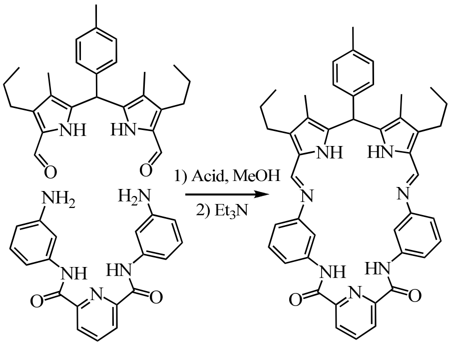
Seidel D., Lynch V., Sessler J.L. // Angew.Chem.Int.Ed. – 2002.
Kolesnikov G. PhD Thesis. 2011.

Yes, all these marcocycles do work perfectly, but how we can get'm?

SUPRAMOLECULAR INTERACTIONS AS THE ROUT FOR TEMPLATE SYNTHESIS OF MACROCYCLES

$HReO_4$ as a good template for macrocycle synthesis

- **Chloride is small and volatile, anything suits**
- **ReO_4^- is highly complementary to the rigid macrocyclic core**



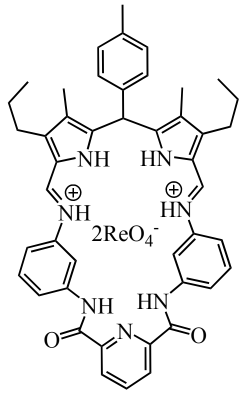
	Product	
Acid-template	**[1+1]**	**[2+2]**
H_3PO_4	+	+
H_2SO_4	+	+
HCl	+	−
$HReO_4$	+	−

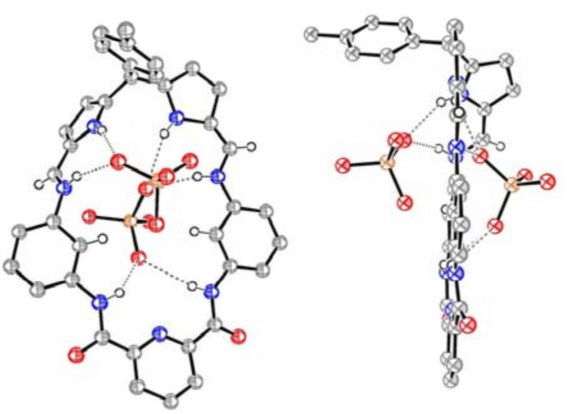
log**K_a** UV in DMSO	**$H_2PO_4^-$**	**HSO_4^-**	**Cl^-**	**NO_3^-**	**I^-**	**ReO_4^-**	**TcO_4^-**
	3.7	3.8	3.9	3.0	**5.3**	**4.8**	**5.1**

Kolesnikov G.V., German K.E, Kirakosyan G., Tananaev I.G., Ustynyuk Yu.A., Khrustalev V.N., Katayev E.A. // Org.Biomol.Chem. - 2011.

$HReO_4$ as a good template for macrocycle synthesis

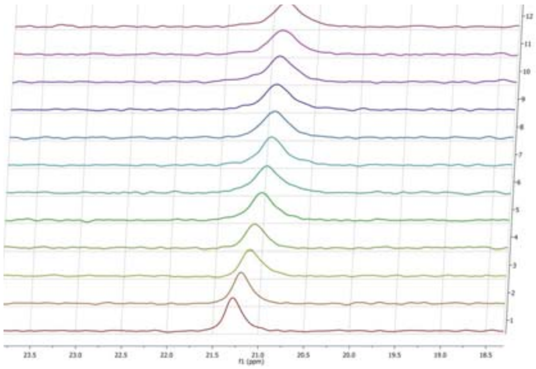
- **Two positive charges due to protonated imine fragments**
- **Pyrrolic and amide H-bonds bind each ReO_4^-**





Kolesnikov G.V., German K.E, Kirakosyan G., Tananaev I.G., Ustynyuk Yu.A., Khrustalev V.N., Katayev E.A. // Org.Biomol.Chem. - 2011.

^{99}Tc-NMR titration, Bu_4N^+ $^{99}TcO_4^-$ in $CDCl_3$



^{99}Tc-NMR strengths

- Clear signal
- Good correlation with UV

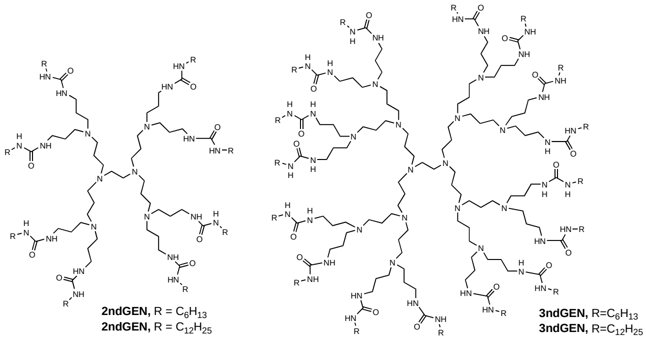
	^{99}Tc ЯМР, $CDCl_3$	**UV, dichloroethane**
Imine-amide macrocycle	log($\boldsymbol{\beta}_{11}$) = 3.2	log($\boldsymbol{\beta}_{11}$) = 5.1
Cyclo[8]pyrrole·2(HCl)	log($\boldsymbol{\beta}_{12}$) = 3.8	log($\boldsymbol{\beta}_{12}$) **=** 6.0

Kolesnikov G.V., German K.E, Kirakosyan G., Tananaev I.G., Ustynyuk Yu.A., Khrustalev V.N., Katayev E.A. // Org.Biomol.Chem. - 2011.

Dendrimers are efficient but not selective

- **Larger dendrimer and lower pH, lead to better extraction**

pH	Anion	2ndGEN-C_6H_{13}	2ndGEN-$C_{12}H_{25}$	3ndGEN-C_6H_{13}	2ndGEN-$C_{12}H_{25}$
7.4	ReO_4^-	38%	36%	**84%**	**74%**
	TcO_4^-	48%	46%	**90%**	**83%**
5.4	ReO_4^-	**92%**	**91%**	98%	97%
	TcO_4^-	**96%**	**95%**	99%	99%



2ndGEN, R = C_6H_{13}
2ndGEN, R = $C_{12}H_{25}$

3ndGEN, R=C_6H_{13}
3ndGEN, R=$C_{12}H_{25}$

Stephan H., Spies H., Johannsen B., Klein L., Vögtle F. // Chem.Comm. – 1999.

Solubility* of some TcO_4^- salts in H_2O

- **More hydrophobic cation produces less soluble salt with TcO_4^-**

$^{99}TcO_4$ Na	11.3	Cl (NBu_4)	20.53
$^{99}TcO_4$ (NMe_4)	0.14	Br (NBu_4)	21.48
$^{99}TcO_4$ (NBu_4)	4×10^{-3}	I (NBu_4)	7×10^{-2}
$^{99}TcO_4$ (**TPG**)	**4×10^{-3}**		
$^{99}TcO_4$ ($NHept_4$)	**1×10^{-5}**		

TPG = triphenylguanidinium

*the concentration is given in mol/L

Rard J.A., Rand M.H., Anderegg G., Wanner H. Chemical thermodynamics Vol. 3. Chemical thermodynamics of Technetium. Sandino M.C.A., Osthols E., Eds.; Elsevier, 1999.

Some important rules for hunting the TcO_4^- and ReO_4^-

Receptor property		*Binding*	*Selectivity*
Bigger size	=>	better	better
More (+) charge	=>	better	worse
More hydrophobic cavity	=>	better	better
Excess of H-bond groups	=>	better	worse
Harder to synthesize	=>	usually better	

Thank you for your attention!

THE CHEMISTRY OF TECHNETIUM CHLORIDES

Alfred Sattelberger

Argonne National Laboratory. Argonne, IL USA

Almost every element in the periodic table has well-defined halide chemistry. Technetium, the first radioelement, is a notable exception. Prior to 2008, only 3 binary halides of technetium had been reported, viz., TcF_6, TcF_5 and $TcCl_4$.

These compounds were prepared almost 60 years ago from the reactions of the metal with elemental fluorine or chlorine.

Since 2008, we have synthesized and characterized 4 new binary chlorides. The new chlorides can be binned into one of three categories:

(1) those that have a molybdenum and/or ruthenium analogue,

(2) those that have a rhenium analogue, and

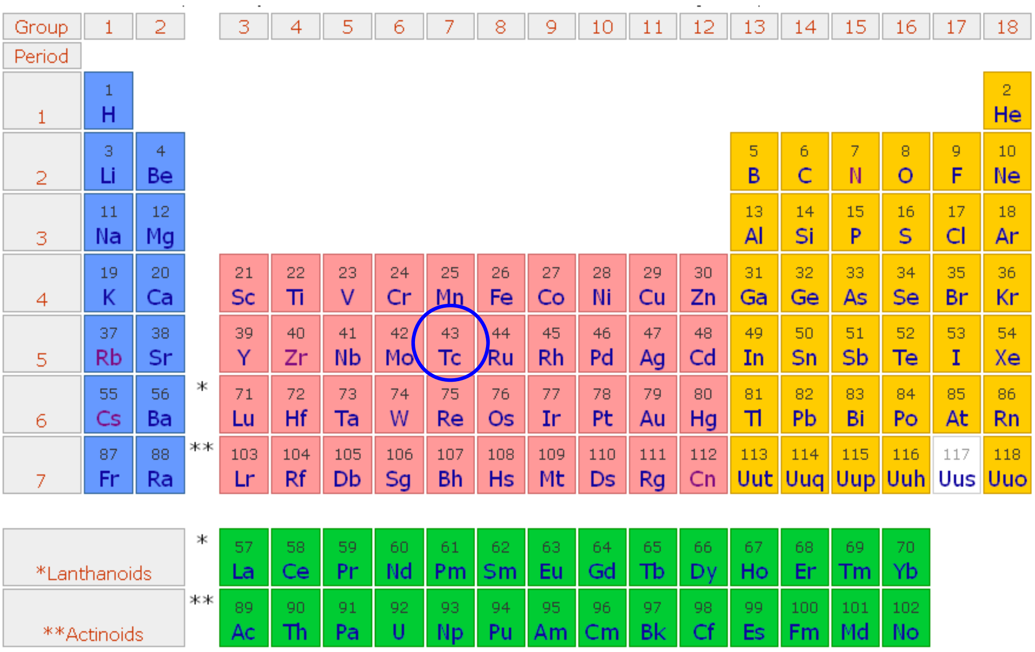
(3) those for which no analogues with neighboring elements currently exist. The synthetic routes to the new halides and their relationship to molecular technetium systems will be described. Solid-state structures, thermal stabilities, and selected aqueous and non-aqueous chemistry will be discussed. The synthesis of new chloride starting materials opens up exciting new opportunities for exploring the synthetic and mechanistic chemistry of low-valent technetium, as well as the possibility of new applications for the nuclear fuel cycle.

The Chemistry of Technetium Chlorides

ISTR-2014

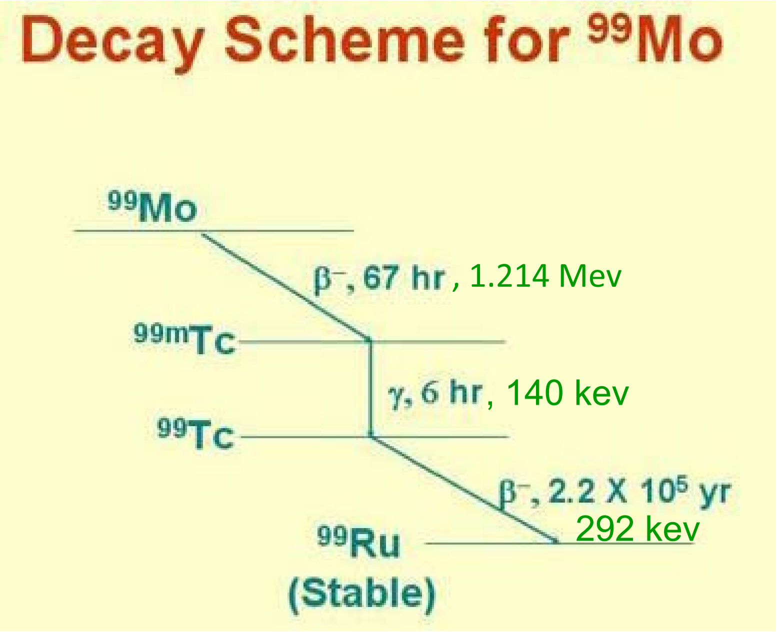
Al Sattelberger
Argonne National Laboratory
Argonne, IL USA

October 1, 2014



Group	1	2		3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
Period																			
1	1 H																		2 He
2	3 Li	4 Be												5 B	6 C	7 N	8 O	9 F	10 Ne
3	11 Na	12 Mg												13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
4	19 K	20 Ca		21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
5	37 Rb	38 Sr		39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
6	55 Cs	56 Ba	*	71 Lu	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
7	87 Fr	88 Ra	**	103 Lr	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Uut	114 Uuq	115 Uup	116 Uuh	117 Uus	118 Uuo
*Lanthanoids			*	57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb		
**Actinoids			**	89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No		

^{99}Tc $t_{1/2}$ = 2.12 x 10^5 y; ~6% of the fission yield of ^{235}U (via ^{99}Mo)
A 1000 MW$_e$ LW reactor produces ~25 g ^{99}Tc per day



***At least* 3 reasons to study Tc chemistry:**
(1) It's central position amongst the transition elements
(2) Nuclear medicine
(3) Nuclear waste forms

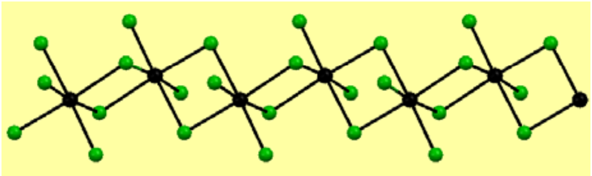
"… As one dramatic contrast, thirteen binary halides have been reported for rhenium, but only three are known and well characterized for technetium, i.e., TcF_6, TcF_5, and $TcCl_4$.[4] Other binary halides, new coordination compounds and organometallics will surely be discovered in the future but the pace of discovery is limited by the small number of operational technetium laboratories. …"

F. Poineau, B. L. Scott, and A.P. Sattelberger, COMCIII, 2007

Binary Halides

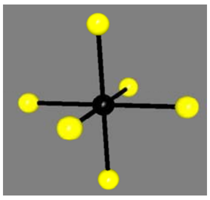
- **Transition metal binary halides MX_n (X = halide, and n = 1-7)**
- **More than two hundred are known (e.g., 13 for Re)**
- **Only three Tc binary halides, *viz.*, $TcCl_4$, TcF_5 and TcF_6, known prior to 2008**

$TcCl_4$: Tc + xs Cl_2 $\xrightarrow{\Delta}$ $TcCl_4$ ($ReCl_5$)



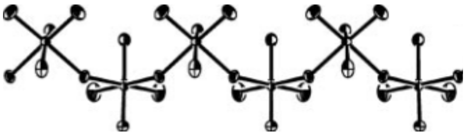
Infinite chains of edge-sharing $TcCl_6$ octahedra (1957)

TcF_6: Tc + xs F_2 $\xrightarrow{\Delta}$ TcF_6

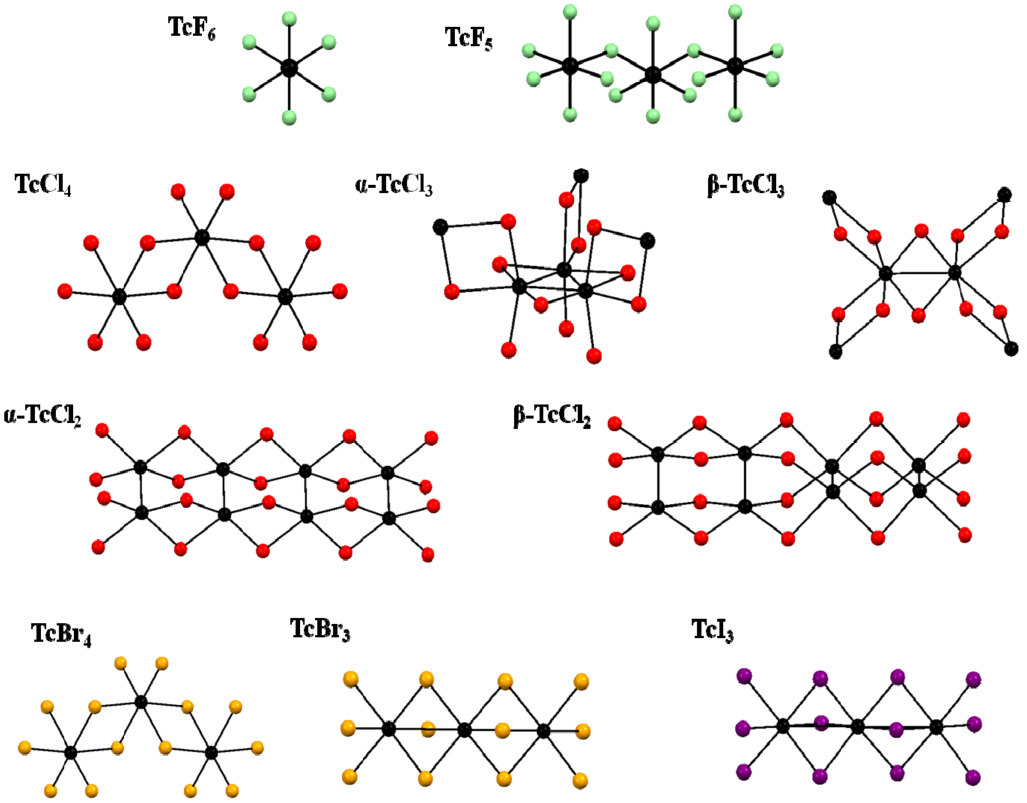


Molecular TcF_6 (1961)

TcF_5: Tc + N_2/F_2 $\xrightarrow{\Delta}$ TcF_5



Chains of TcF_6 octahedra (1963)



F. Poineau, et al., *Accts. Chem. Res.*, **2014**, *47*, 624-632

Experimental Approach - I

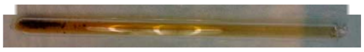
Stoichiometric reactions between the halogen and Tc metal at elevated temperature

Sealed tube reactions (Tc:X - 1:2, 1:3, 1:4+) have not been reported for Tc

Tc metal
in glass or
quartz tube

- Connected to Schlenk line
- Back-filled with Cl_2 or Br_2
- Reactants frozen in LN_2
- Flame-sealed under vacuum

Tc and Br_2



Tc and Cl_2

Tube furnace reactions
- Temperatures: 300-450°C
- Reaction times: 6-48 h

Technetium Dioxide and Tc Metal

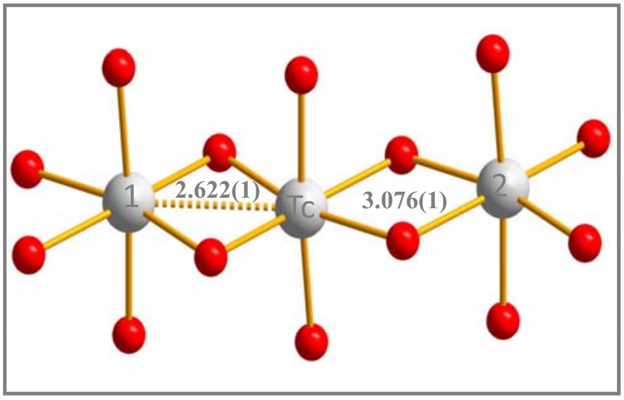
NH_4TcO_4

T = 750°C

Ar

TcO_2

Characterization by NPD



$$TcO_2 + H_2 \text{ (6\% in Ar) } \xrightarrow{1000^{o}C} Tc + 2\,H_2O$$

E. Rodriguez, et al., *J. Am. Chem. Soc.* **2007**, *129*, 10244-10248

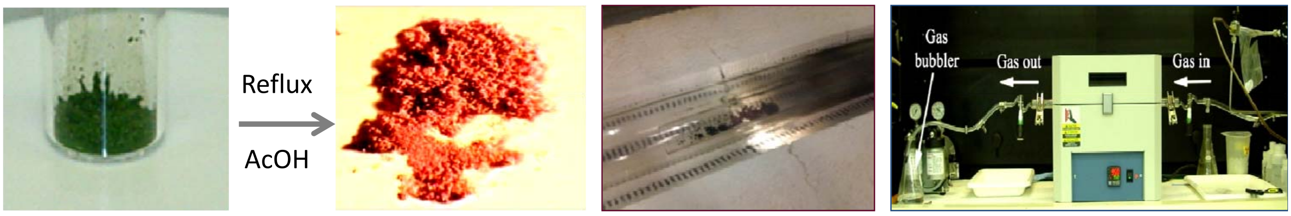
Experimental Approach - II

Reaction between a preformed M-M bonded dimer and HX(g)

Molybdenum: $Mo_2(OAc)_4 \rightarrow \beta\text{-}MoX_2$; Rhenium: $Re_2(OAc)_4X_2 \rightarrow Re_3X_9$

G. Wilkinson, R. E. McCarley, R. A. Walton and coworkers

Not reported for $Tc_2(OAc)_4X_2$ (X = Cl, Br)

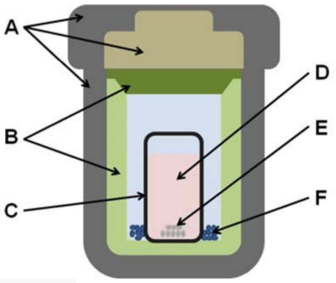


$(n\text{-}Bu_4N)_2Tc_2Cl_8$ ⟶ $Tc_2(OAc)_4Cl_2$ ⟶ Load in quartz boat ⟶ Flowing HX(g), T = 100-400°C

30-40% 40%

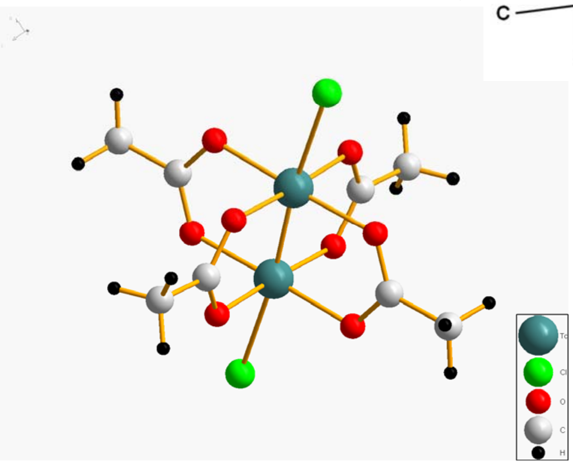
Alternative Synthesis of $Tc_2(O_2CCH_3)_4Cl_2$

$$KTcO_4 + 2{:}1\ HC_2H_3O_2{:}HCl(aq) \xrightarrow[210\ ^{\circ}C,\ 12\ hr]{36\ atm\ H_2}$$



Key Bond Distances:

- Tc-Tc = 2.1758(3) Å
- Tc-Cl = 2.5078(4) Å
- Tc-O = 2.021 Å (av)

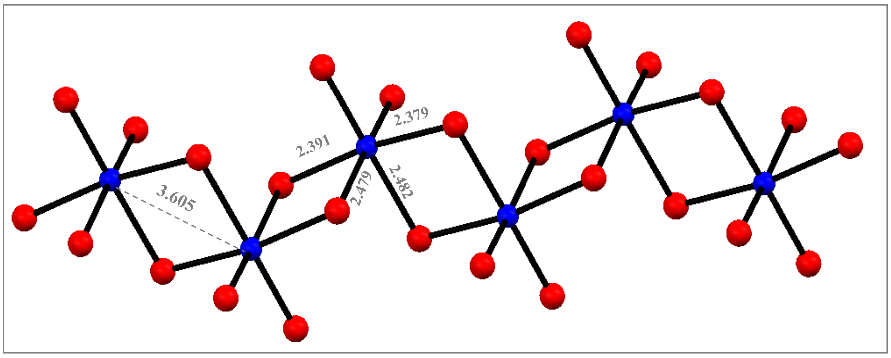


Red-orange crystals, 80%

(1) L. I. Zaitseva, A. S. Kotel'nikova and A. A. Reszvov, *Russ. J. Inorg. Chem.* **1980**, *25*, 1449
(2) W. M. Kerlin, et al., *Polyhedron* **2013**, *58*, 115-119

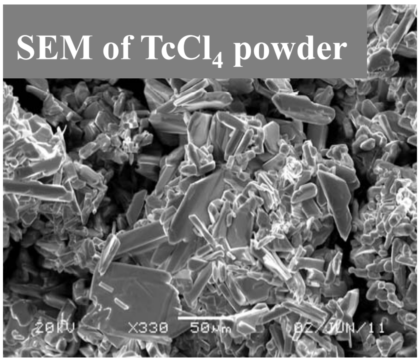
Technetium Tetrachloride

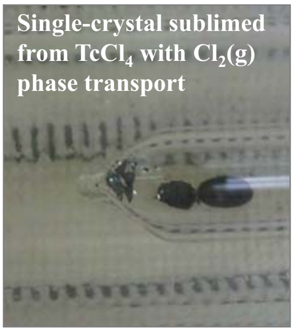
Tc metal plus Cl_2 (1:3) sealed tube at 450 °C for 14 h



Extended chains of distorted edge-sharing $TcCl_6$ octahedra - orthorhombic *Pbca* space group

Paramagnetic
μ_{eff} = 3.76 B.M.

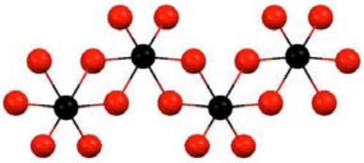

SEM of $TcCl_4$ powder


Single-crystal sublimed from $TcCl_4$ with Cl_2(g) phase transport

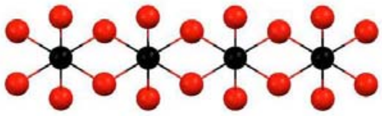
E. V. Johnstone, et al., *Inorg Chem.* **2012**, *51*, 8462-8467

Transition Metal Tetrachloride Structure Types

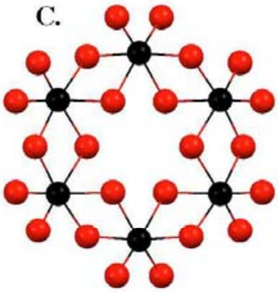
A.


Zr, Hf, Tc, Pt

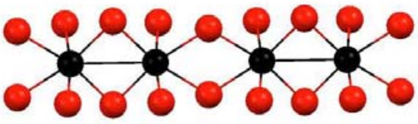
B.


Os

C.


β-Mo

D.


Nb, Ta, α-Mo, W

E.


Re

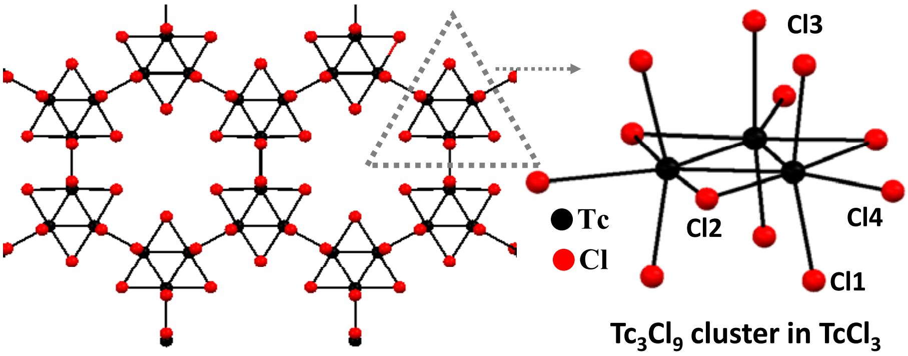
Technetium Trichloride

Reaction between $Tc_2(OAc)_4Cl_2$ and HCl(g) at 300^oC

Formation of $TcCl_3$ occurs in two steps:

$Tc_2(OAc)_4Cl_2$ | $Tc_2Cl_4(OAc)_2$: Green | $TcCl_3$: Black

$TcCl_3$: Infinite layers of Tc_3Cl_9 bridged by Cl ligands



Tc_3Cl_9 cluster in $TcCl_3$

Tc_3Cl_9 C_{3v} symmetry
7-coordinate Tc
Tc=Tc 2.444(1) Å

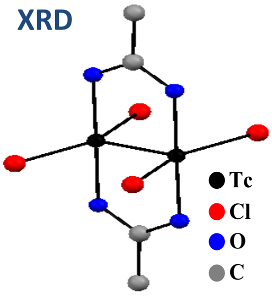
4 types of Cl
Tc-C1_1 = 2.237(2) Å
Tc-C$1_{2,3}$ = 2.373(2) Å
Tc-C1_4 = 2.585(2) Å

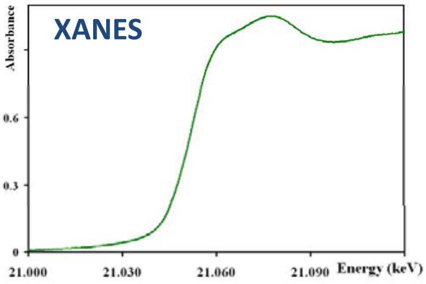
- $TcCl_3$ crystallizes with the "$ReCl_3$" structure-type
- Calculations confirm $TcCl_3$ stability with "$ReCl_3$" structure-type

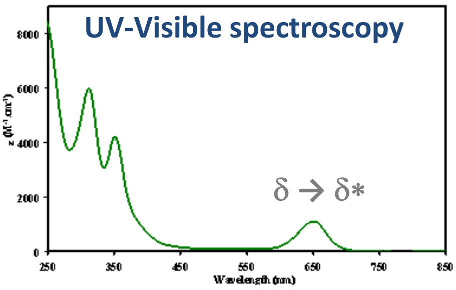
---

Characterization of $Tc_2Cl_4(OAc)_2$

XRD







Tc-Tc = 2.150(2) Å
· Tc-Tc quadruple bond

Edge at 21052 eV
· Trivalent Tc

Band at 650 nm
· δ → δ* transition

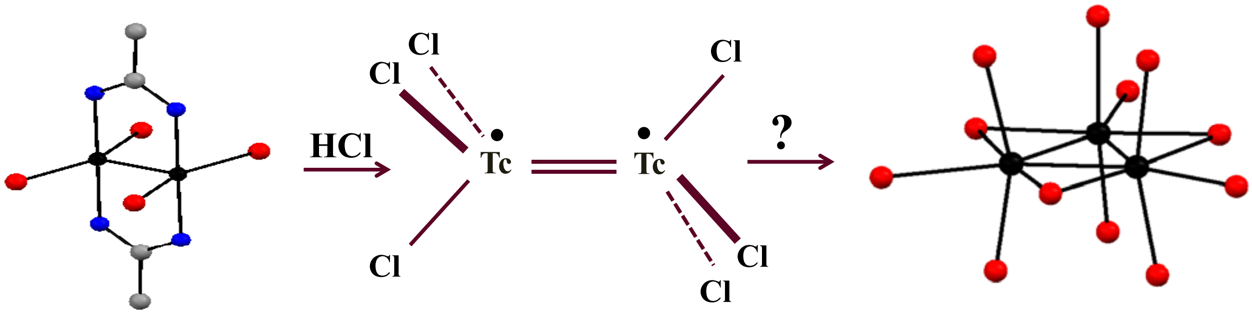
(n-Bu_4N)$_2Tc_2Cl_8$
· Tc-Tc = 2.151(4) Å

(n-Bu_4N)$_2Tc_2Cl_8$
· Edge at 21052 eV

(n-Bu_4N)$_2Tc_2Cl_8$
· δ → δ* at 675 nm

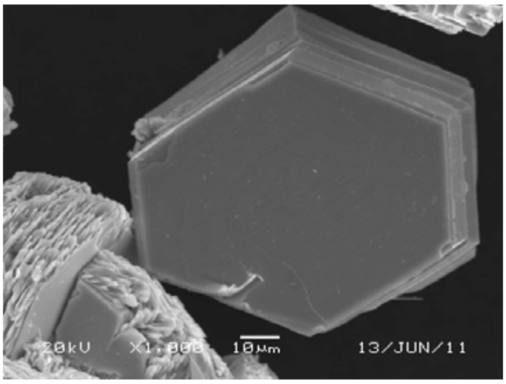
F. Poineau, et al., *Polyhedron*, **2014**, *70*, 144-147

Formation of Tc_3Cl_9



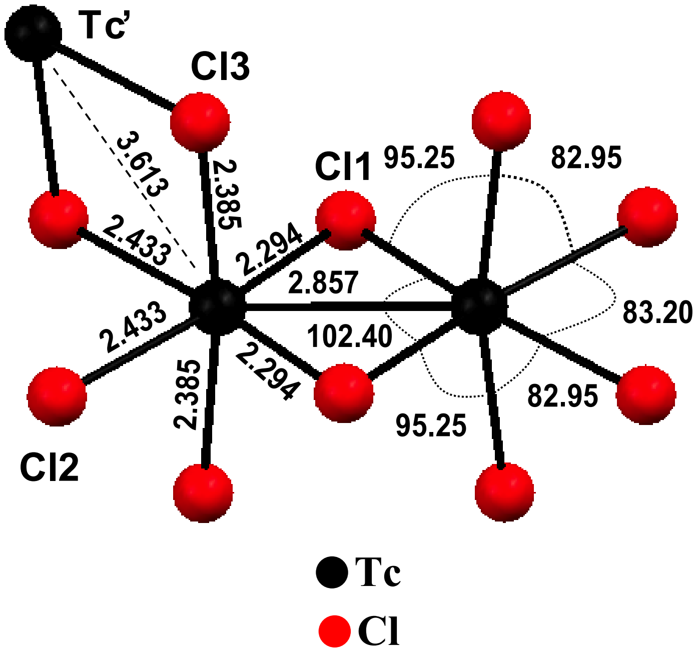
Technetium Trichloride

Reaction between Tc metal and 1.5 Cl_2 in sealed tube at 450°C for 24 hrs



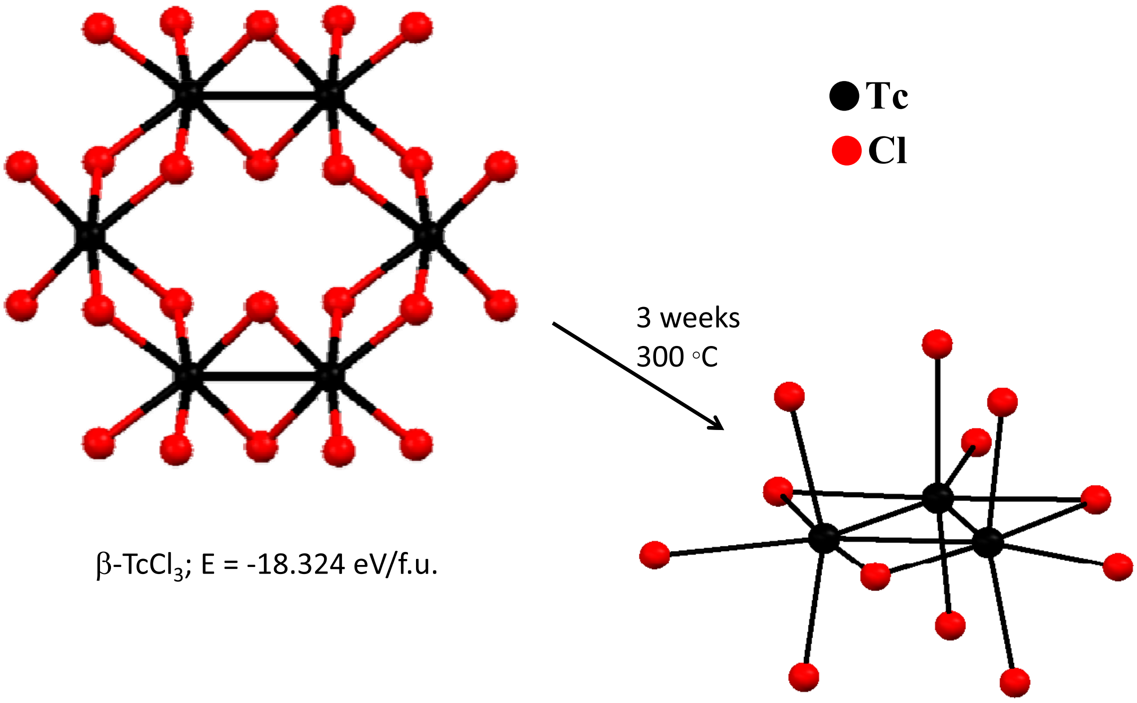
Resublimed crystals of $TcCl_3$

Dist. (Å)	$MoCl_3$	$TcCl_3$	$RuCl_3$
M-M	2.757(3)	2.857(1)	3.44(1)
M···M	3.714(3)	3.613(2)	3.45(1)
ΔMM	0.957(4)	0.756(2)	0.01(1)



F. Poineau, et al., *Inorg. Chem.* **2012**, *51*, 4915-17

Interconversion of $TcCl_3$ Polymorphs

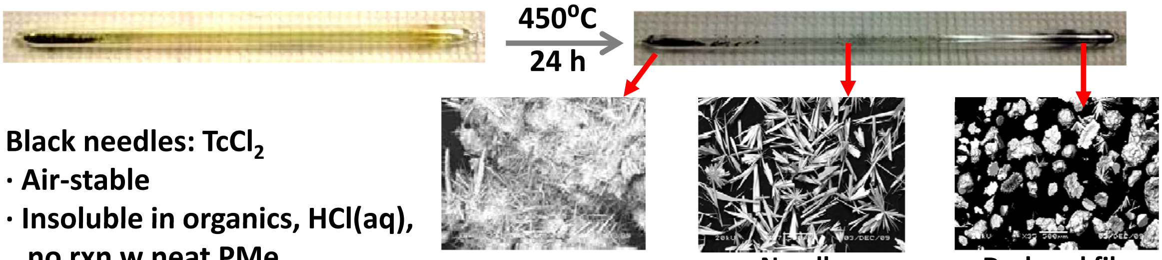


β-$TcCl_3$; E = -18.324 eV/f.u.

α-$TcCl_3$; E = -18.743 eV/f.u.

Technetium Dichloride

Reaction between Tc metal and Cl_2 in sealed tube (Tc:Cl ~ 1:2)

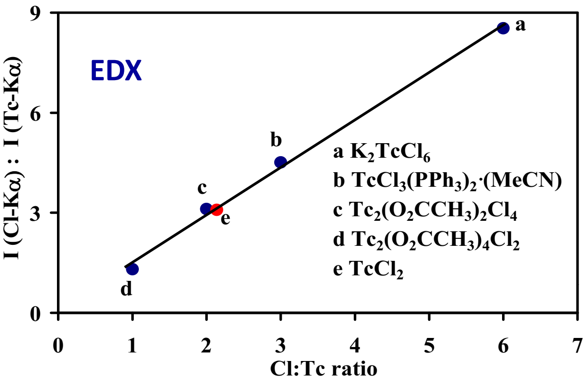


Needles + metal

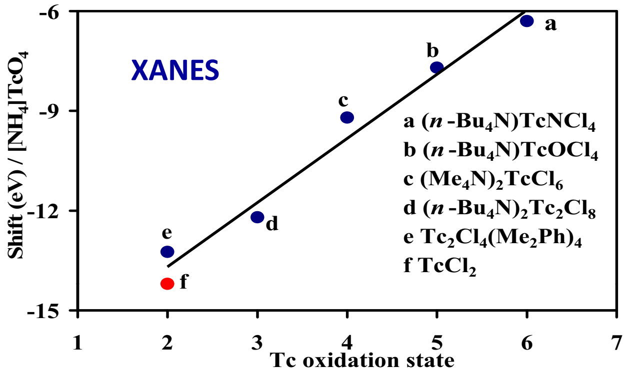
Needles

Dark-red film

Black needles: $TcCl_2$
- Air-stable
- Insoluble in organics, HCl(aq), no rxn w neat PMe_3



Correlation [Cl:Tc] ratio (1 to 6) *w* [Intensity Cl-K_α: Intensity Tc-K_α]

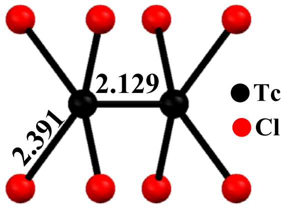


Correlation Tc oxidation state (1 to 6) *w* Tc absorption K-edge (eV/NH_4TcO_4)

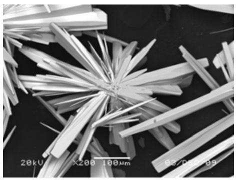
Characterization of $TcCl_2$ by single crystal XRD

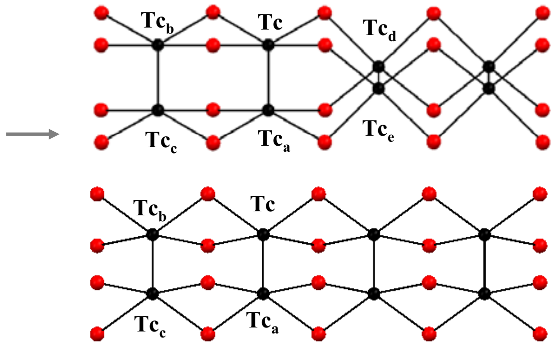
$TcCl_2$: Infinite chains of face-sharing Tc_2Cl_8 rectangular prisms

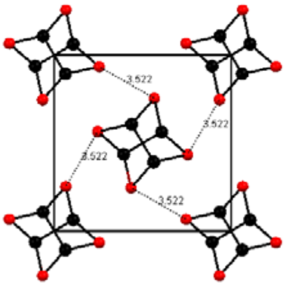
- $[Tc_2Cl_8]$ eclipsed geometry (Tc-Tc = 2.129 Å)
- Tc≡Tc triple bond
- Natural bond orbital (NBO) occupancy: 5.3



$[Tc_2Cl_8]$ unit





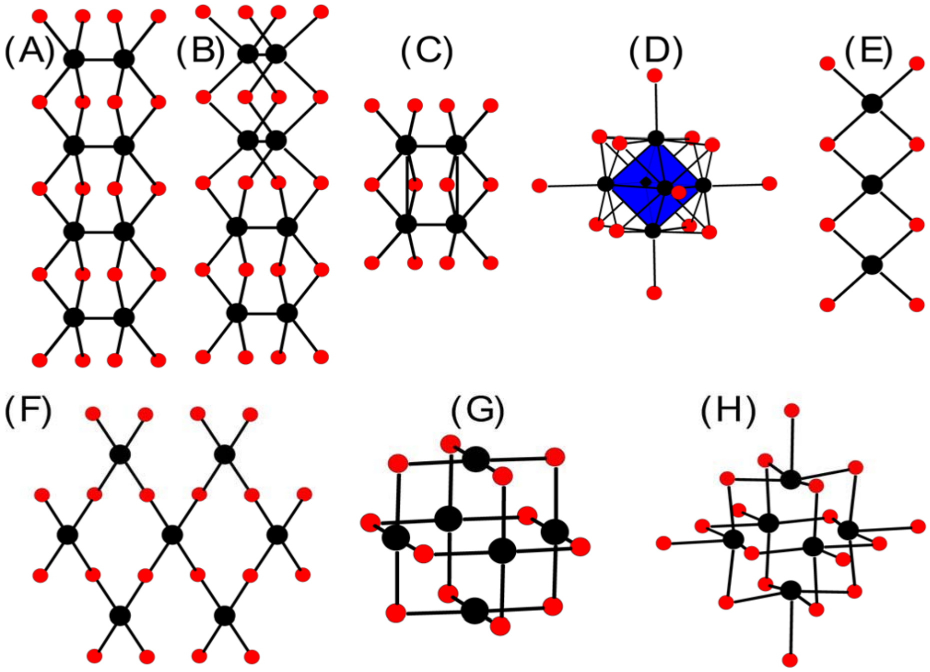


$TcCl_2$ chains in the cell

- $TcCl_2$ exhibits a new binary halide structure type
- Highest bond multiplicity reported for a binary halide

C. D. Malliakas, et al., *J. Am. Chem. Soc.* **2013**, *135*, 15955-15962

Transition Metal Dichlorides



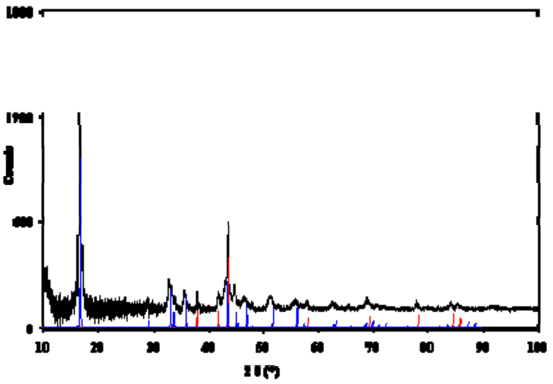
(A) α-$TcCl_2$; (B) β-$TcCl_2$; (C) β-$MoCl_2$; (D) α-$MoCl_2$, α-WCl_2; (E) α-$PtCl_2$, α-$PdCl_2$, δ-$PdCl_2$; (F) γ-$PdCl_2$; (G) β-$PdCl_2$, β-$PtCl_2$; (H) $ZrCl_2$

Comparison with Neighboring Elements

Gaps in the Periodic Table

$MoCl_2$	$TcCl_2$	Ru: ?	Rh: ?	$PdCl_2$
WCl_2	Re: ?	Os: ?	Ir: ?	$PtCl_2$

1:1 reactions between Cl_2 and metal (Re, Ru, Mo) at 450°C



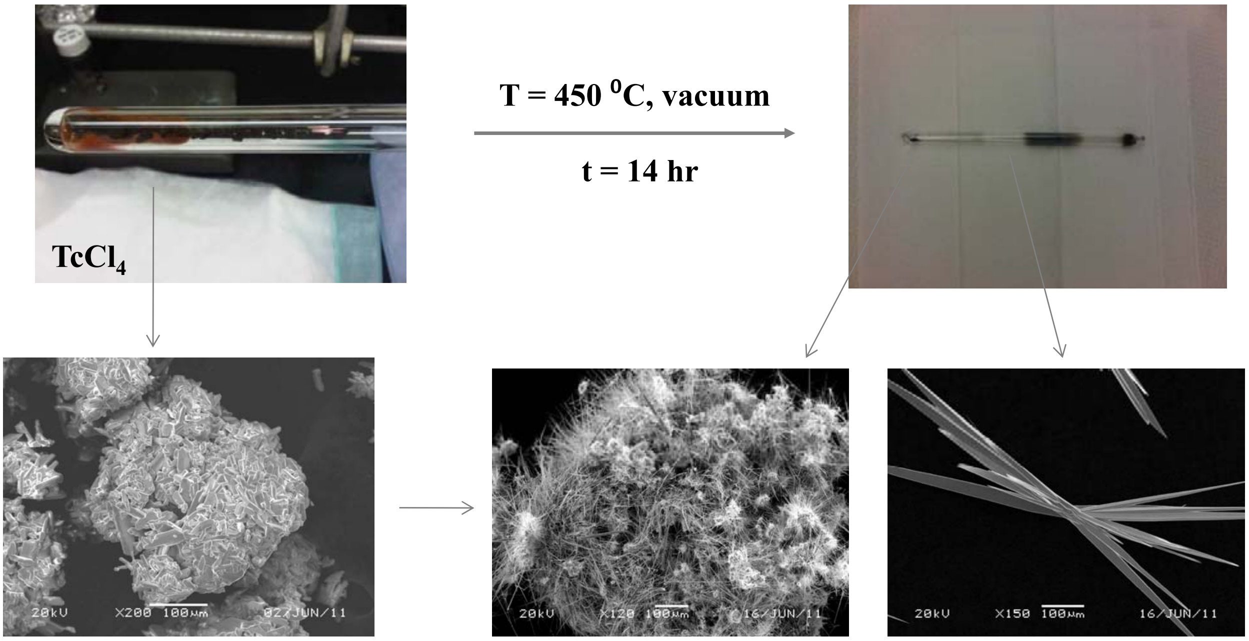
$Re + Cl_2 \rightarrow ReCl_5 + Re$
$Ru + Cl_2 \rightarrow RuCl_3 + Ru$
$Mo + Cl_2 \rightarrow MoCl_3 + Mo$

Powder pattern after reaction of Ru metal with Cl_2 at 450°C
Simulated XRD pattern of: $RuCl_3$ (in blue) and Ru metal (in red)

Technetium appears to exhibit unique behavior

- **Stochiometric reaction or decomposition of $TcCl_4$ or $TcCl_3$?**

Decomposition of $TcCl_4$ to $TcCl_2$



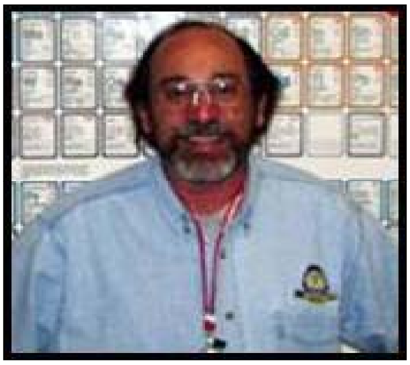
$TcCl_4$ powder **$TcCl_2$ powder** **$TcCl_2$ single crystals**

Confirmed by XRD

E. V. Johnstone, et al., *Inorg Chem.* **2012**, *51*, 8462-8467

Technetium Synthesis Group

Acknowledgments



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- Eunja Kim
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- Mercouri Kanatzidis

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Synthesis and Characterization of Binary Technetium Bromides and Iodides

Erik Johnstone[1,2], Frederic Poineau[2], Paul M. Forster[2], Alfred P. Sattelberger[2,3], and Kenneth R. Czerwinski[2]

[1] Institute of Resource Ecology, Helmholtz-Zentrum Dresden-Rossendorf, Dresden, Germany.
[2] Department of Chemistry, University of Nevada Las Vegas, Las Vegas, NV, USA.
[3] Energy Engineering and Systems Analysis Directorate, Argonne National Laboratory, Lemont, IL, USA.

Technetium (Z = 43) is the lightest element on the periodic table with no stable isotopes. It is produced in nuclear fuels as a primary fission product in ~6% yield, and yet many of the fundamental facets of transition metal chemistry have not been explored for technetium. An example of this is was the deficiency of the binary technetium halide chemistry prior to 2008, which consisted of only three known compounds (i.e., TcF_6, TcF_5, and $TcCl_4$) that did not include any bromine or iodine derivatives. In this work the synthesis of novel binary technetium bromides and iodides was explored in the solid state and their chemistries investigated by means of thermal stability, solubility, and physical properties studies. Furthermore, these compounds were characterized using various physicochemical methods including single-crystal and powder X-ray diffraction (XRD), IR spectroscopy, X-ray absorption fine structure (XAFS), and elemental analysis to determine structural and compositional properties.

Solid-State Investigations of the Heavier Binary Technetium Halides: Synthesis and Characterization

Erik V. Johnstone[1], Frederic Poineau[2], Thomas Hartmann[2], Paul M. Forster[1], Kenneth R. Czerwinski[2], and Alfred P. Sattelberger[2,3]

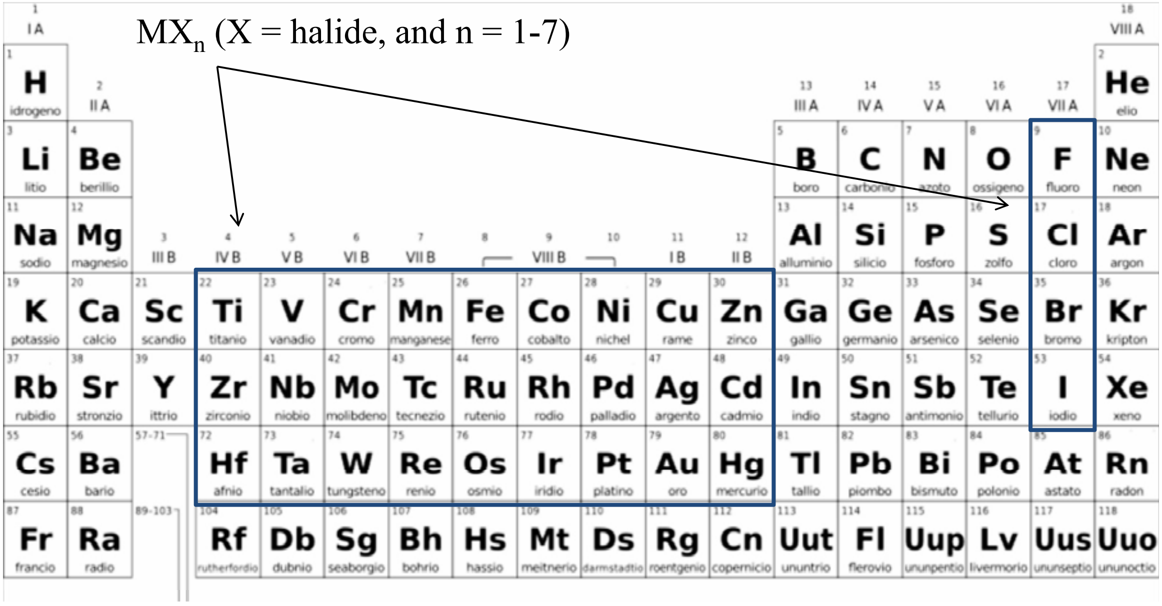
[1] Helmholtz-Zentrum Dresden Rossendorf, Dresden, Germany
[2] Department of Chemistry, University of Nevada Las Vegas, Las Vegas, NV
[3] Energy Engineering and Systems Analysis Directorate, Argonne National Laboratory, Argonne, IL

International Symposium on Technetium and Rhenium 2014
Pornichet, France

Outline

- I. Introduction
  - Binary Transition Metal Halides
  - Binary Technetium Halides
- II. Experimental
  - Methods
  - Tc Bromides
  - Tc Iodide
- III. Conclusions
- IV. Future Work
- V. Acknowledgements

Transition Metal Binary Halides


MX_n (X = halide, and n = 1-7)

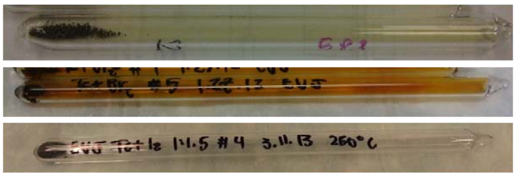
More than 200 are known

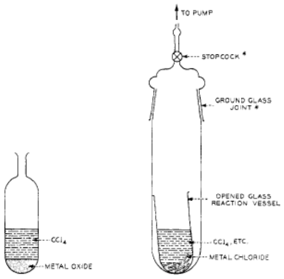
Applications as inorganic precusors, catalysts, and materials

Cotton, F. A. *Advanced Inorganic Chemistry*, 6th ed.; John Wiley and Sons: New York, **1999**.

Transition Metal Binary Halides

Synthetic Methods





Structure-types

Molecular				Infinite Chain			Layered	Cluster	
Monomeric	Dimeric	Trimeric	Tetrameric	Corner-sharing	Edge-sharing	Face-sharing		Trinuclear	Hexanuclear
MF_6, M = Mo, W, Tc, Re, Ru, Os, Ir, Pt	M_2Cl_{10}, M = Nb, Ta, Mo, W, Re	$((RuF_5)_3)$	$((MF_5)_4)$, M = Nb, Ta, Mo, Ru, Os	MF_5, M = Tc, Re	MCl_4, M = Zr, Hf, Nb, Ta, Mo, W, Tc, Os, Pt; MBr_4, M = Tc, Os, Pt	MBr_3, M = Mo, Ru; MI_3, M = Zr, Hf, Nb, Mo, Ru, Os	α-MCl_3 M = Mo, Ru; β-$MoCl_4$	Re_3X_9, M_3X_8, M = Nb, Ta	M_6X_{12}, M = Mo, W; M_6X_{14}, M = Nb, Ta; M_6X_{15}, M = Nb, Ta

Canterford, J. H.; Colton, R. *Halides of the Second and Third Row Transition Metals*; John Wiley and Sons: New York, **1968**.

Transition Metal Binary Halides

Technetium → Only 3 known prior to 2008: TcF_6 (1961), TcF_5 (1963), and $TcCl_4$ (1957)

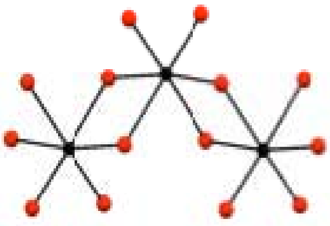
1) $Tc + xs\ Cl_2(g) \rightarrow TcCl_4$

$$Tc_2O_7(s) + 7\ CCl_4(l) \rightarrow 2\ TcCl_4(s) + 7\ COCl_2(g) + Cl_2(g)$$

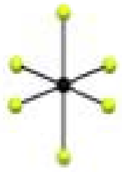
2) $Tc + xs\ F_2(g) \rightarrow TcF_6$

3) $Tc + xs\ F_2/N_2(g) \rightarrow TcF_5$

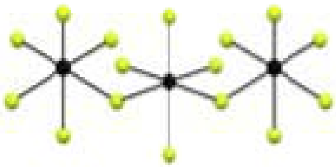
$$I_2(s) + 10\ TcF_6(s) \leftrightarrow 10\ TcF_5(s) + 2\ IF_5(s)$$



$TcCl_4$



TcF_6



TcF_5

Colton, R. *Nature*, **1962**, *193*, 872.

Edwards, A. J.; Hugill, D.; Peacock, R. D. *Nature*. **1963**, *200*, 672.
Selig, H.; Chernick, C. L.; Malm, J. G. *J. Inorg. Nucl. Chem*. **1961**, *19*, 377.

Transition Metal Binary Halides

Technetium → With additions of $TcBr_4$, $TcBr_3$, α/β-$TcCl_3$, and α/β-$TcCl_2$ there are 9 known

Rhenium → 15 reported binary halides

Oxidation state	Fluorides	Chlorides	Bromides	Iodides
I	-	-	-	ReI
II	-	α/β-$TcCl_2$	-	ReI_2
III	-	α/β-$TcCl_3$, Re_3Cl_9	$TcBr_3$, Re_3Br_9	Re_3l_9
IV	ReF_4	$TcCl_4$, $ReCl_4$	$TcBr_4$, $ReBr_4$	ReI_4
V	TcF_5, ReF_5	$ReCl_5$	$ReBr_5$	-
VI	TcF_6, ReF_6	$ReCl_6$	-	-
VII	ReF_7	-	-	-

Synthesis and Characterization of Technetium Bromides and Iodides

Research Questions

1. How can binary technetium bromides and iodides be prepared?

2. What structural and physical properties of these materials will be observed?

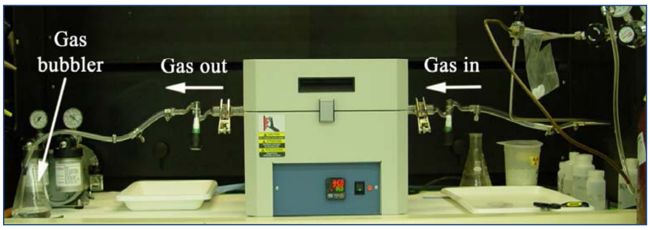
1. How will these compounds compare with similar ones of neighboring elements?

Binary Transition Metal Chlorides, Bromides, Iodides

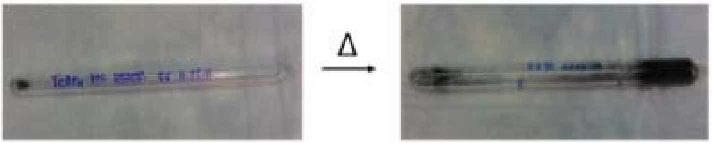
Preparative Methods:

1) Reaction of the elements, i.e., $M + X_2 \rightarrow MX_n$ (X = Cl, Br, I)

2) Reaction of molecular dimer and flowing HX(g), i.e., $M_2(O_2CCH_3)_4Cl_2 + HX(g)$ (X = Cl, Br, I)

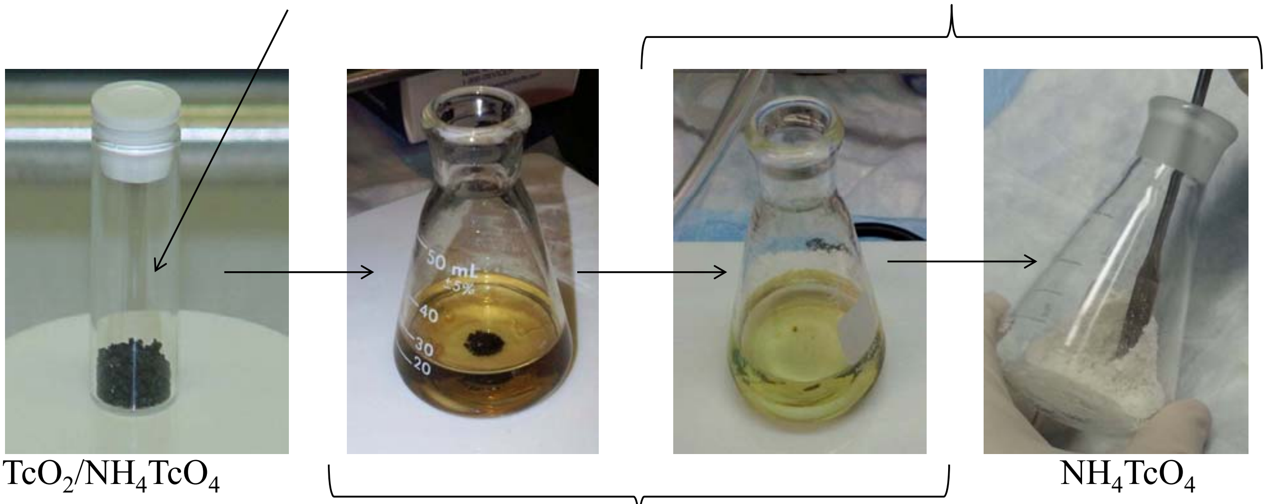


3) Thermal decompositions under vacuum, i.e., $MX_n \rightarrow MX_{n-y} + X_2$



Preparation of Precursors

Purification of ammonium pertechnetate



Impure ORNL Starting Material

Precipitation and Isolation under Ar(g) flux

TcO_2/NH_4TcO_4

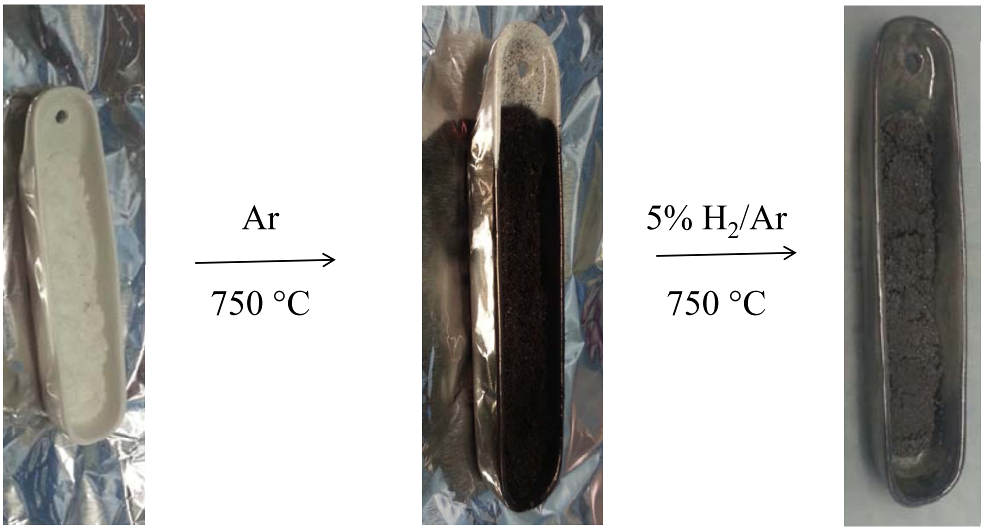
NH_4TcO_4

Dissolution/Oxidation in $H_2O/NH_4OH/H_2O_2$

Preparation of Precursors

Synthesis of Technetium Metal

1) $NH_4TcO_4 \rightarrow TcO_2 + 2\ H_2O + \frac{1}{2}\ N_2$
2) $TcO_2 + H_2 \rightarrow Tc + 2\ H_2O$



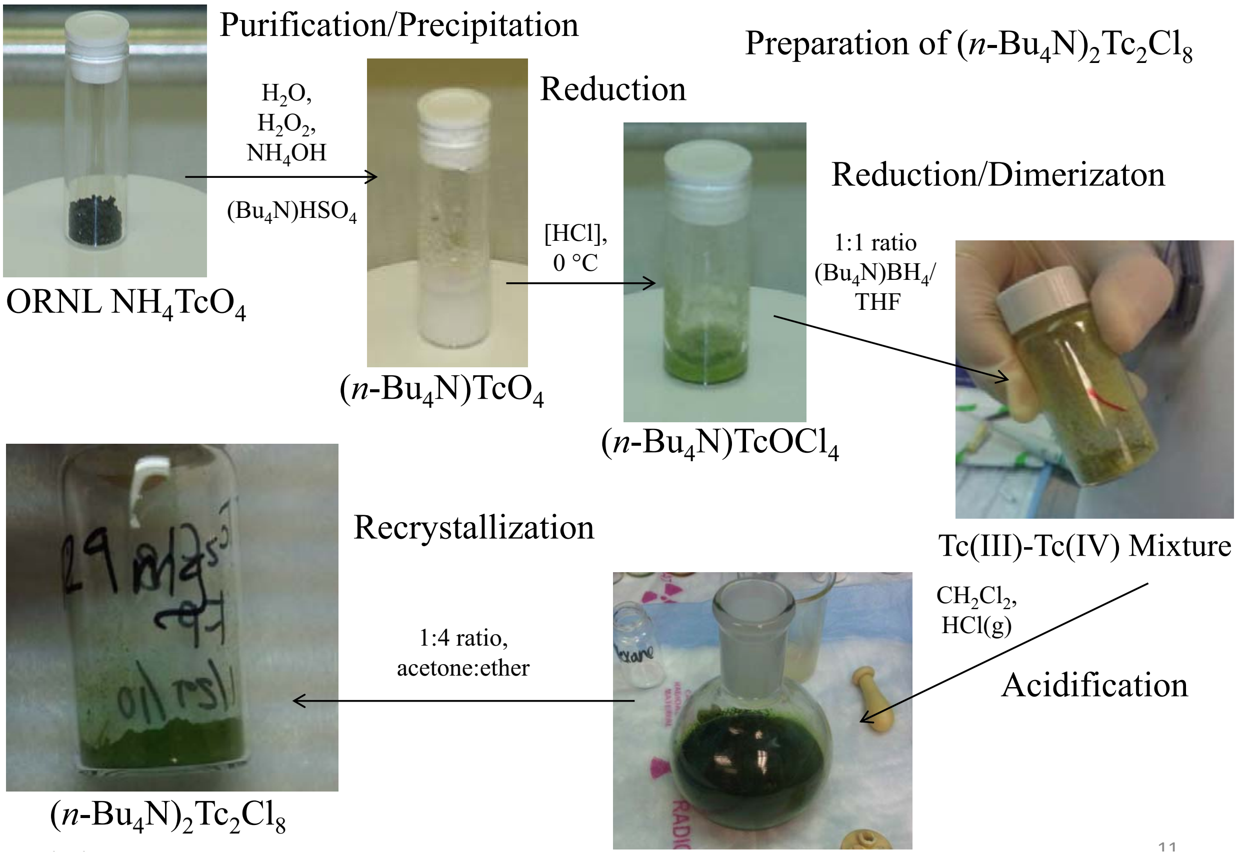
$$NH_4TcO_4 \xrightarrow[750\ °C]{Ar} TcO_2 \xrightarrow[750\ °C]{5\%\ H_2/Ar} \text{Tc Metal}$$

NH_4TcO_4

TcO_2

Tc Metal

Preparation of Precursors



Purification/Precipitation

Preparation of $(n\text{-}Bu_4N)_2Tc_2Cl_8$

H_2O, H_2O_2, NH_4OH

$(Bu_4N)HSO_4$

ORNL NH_4TcO_4

Reduction

[HCl], 0 °C

$(n\text{-}Bu_4N)TcO_4$

Reduction/Dimerizaton

1:1 ratio $(Bu_4N)BH_4$/ THF

$(n\text{-}Bu_4N)TcOCl_4$

Tc(III)-Tc(IV) Mixture

CH_2Cl_2, HCl(g)

Acidification

Recrystallization

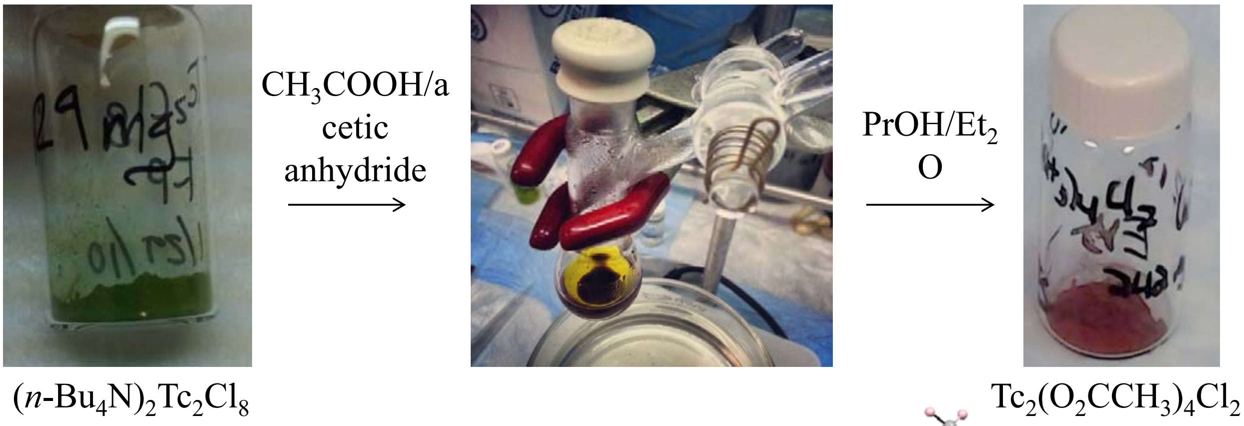
1:4 ratio, acetone:ether

$(n\text{-}Bu_4N)_2Tc_2Cl_8$

Preparation of Precursors

Synthesis of Bis(μ-tetraaceate)dichloride ditechnetate

$(n\text{-}Bu_4N)_2Tc_2Cl_8 + 4\ CH_3COOH \rightarrow Tc_2(O_2CCH_3)_4Cl_2 + 2\ (n\text{-}Bu_4N)Cl + 4\ HCl$

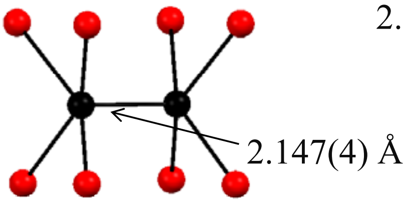


CH_3COOH/acetic anhydride

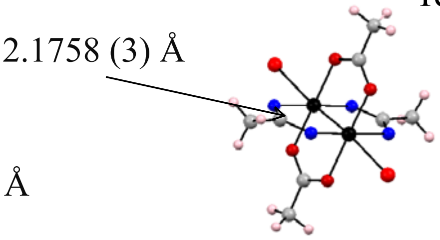
PrOH/Et_2O

$(n\text{-}Bu_4N)_2Tc_2Cl_8$

$Tc_2(O_2CCH_3)_4Cl_2$



Cotton, F. A.; Bratton, W. K. *J. Am. Chem. Soc.* **1965**, *87*, 921.

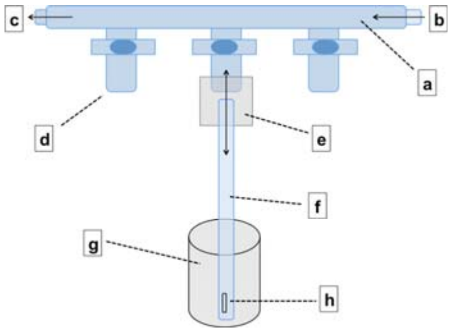


Kerlin, W. M, et. al. *Polyhedron*. **2013**, *58*, 115-119.

Binary Technetium Bromides

Synthesis of $TcBr_4$

Schlenk line sealed tube sealing



$$Tc + 2\ Br_2 \rightarrow TcBr_4$$

Tc metal

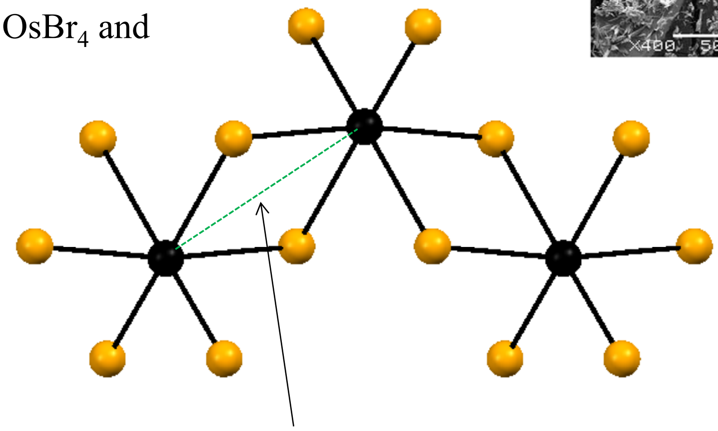
$$\xrightarrow[T = 400\ ºC]{Br_2\ 1:4}$$

$TcBr_4$

Binary Technetium Bromides

Structure of $TcBr_4$

- Orthorhomic space group *Pbca*
- $TcCl_4$ structure-type: infinite zig-zag chains of edge-sharing $TcBr_6$ octahedra
- Isomorphous to $OsBr_4$ and $PtBr_4$

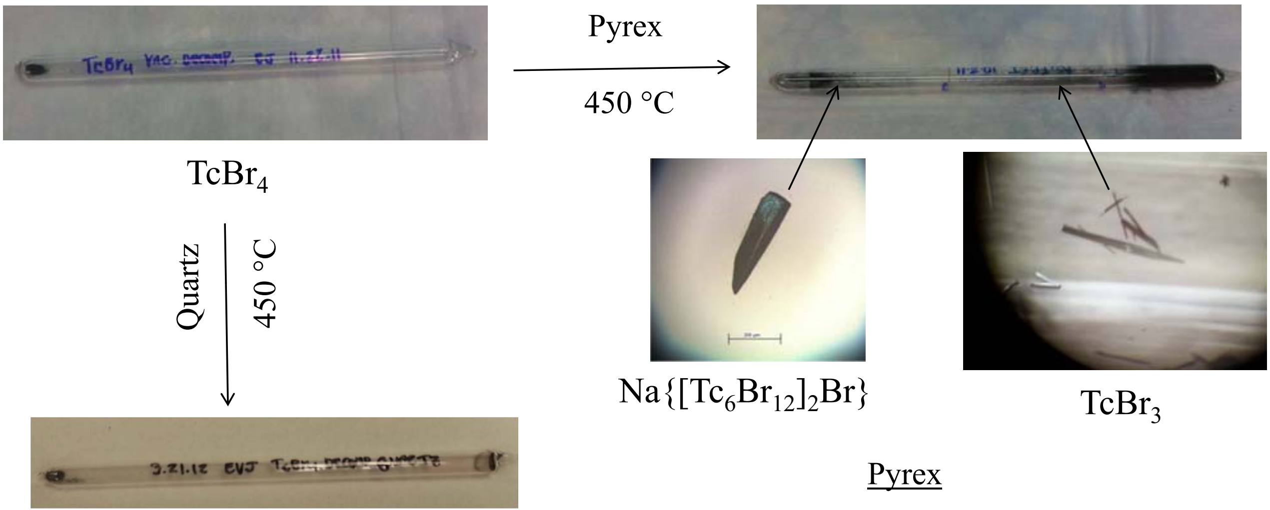


Tc-Tc separation = 3.791 Å

Poineau, F. et. al. *J. Am. Chem. Soc.* **2009**, *131*, 910-911.

Binary Technetium Bromides

Thermal decomposition of $TcBr_4$



Pyrex

450 °C

$TcBr_4$

Quartz

450 °C

$Na\{[Tc_6Br_{12}]_2Br\}$

$TcBr_3$

Tc Metal

Pyrex

SiO_2 83.34%, B_2O_3 11.19%, Na_2O 4.08%, Al_2O_3 1.33%, K_2O 0.04%.

Johnstone, E. V. et. al. , A. P. *Inorg. Chem.* **2013**, *52(10)*, 5660-5662.

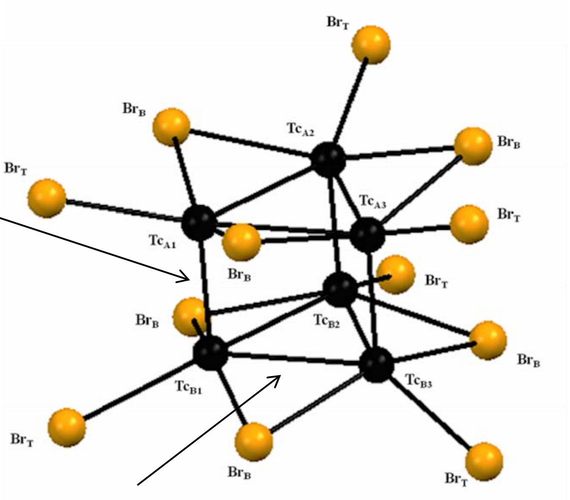
Binary Technetium Bromides

Structure of $Na\{[Tc_6Br_{12}]_2Br\}$

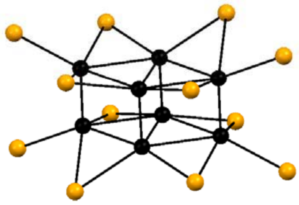
Tc-Tc separation ~ 2.1735 Å

Magic cluster electron count (Wheeler and Hoffmann) of 30:

$\sigma^{12}\pi^{10}\delta^{4}\delta^{*4}$



Tc-Tc separation ~ 2.6879 Å



Compound	Tc_A–Tc_A	Tc_A–Tc_B	Tc–Br_T	Tc–Br_B
$Na\{[Tc_6Br_{12}]_2Br\}$	**2.6845(5)**	**2.1735(5)**	**2.4966(8)**	**2.4738(7)**
$(Et_4N)_2\{[Tc_6Br_{12}]Br_2\}^b$	**2.66(2)**	**2.188(5)**	**2.50(1)**	**2.49(1)**
Tc_6Br_{12}	*2.720*	*2.173*	*2.479*	*2.494*

Johnstone, E. V. et. al. , A. P. *Inorg. Chem.* **2013**, *52(10)*, 5660-5662.

Binary Technetium Bromides

Synthesis of $TcBr_3$

I.

$$Tc + 3/2\ Br_2 \rightarrow TcBr_3$$

Tc metal

$$\xrightarrow[T = 400\ ^{\circ}C]{Br_2\ 1:3}$$

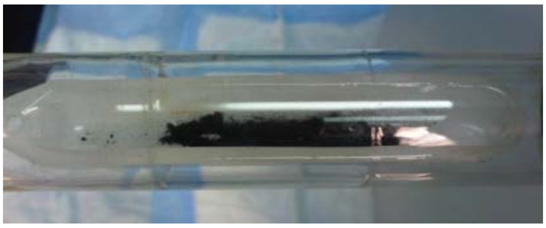
$TcBr_3$

II.

$$Tc_2(O_2CCH_3)_4Cl_2 + 6\ HBr\ (g) \rightarrow 2\ TcBr_3 + 4\ CH_3COOH + 2HCl$$

$Tc_2(O_2CCH_3)_4Cl_2$

$$\xrightarrow[150\ \text{and}\ 300\ ^{\circ}C]{HBr(g)}$$



$TcBr_3$

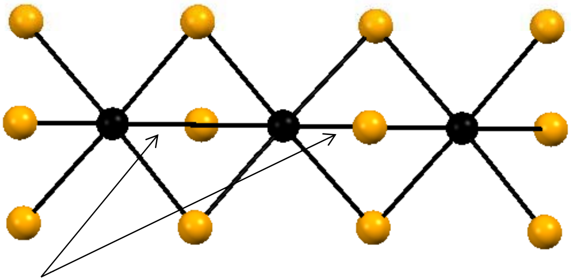
Poineau, F. et. al. *J. Am. Chem. Soc.* **2009**, *131*, 910-911.

Binary Technetium Bromides

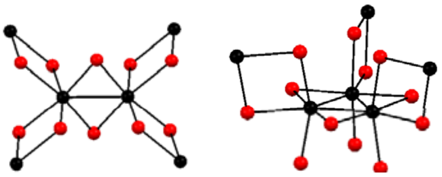
Structure of $TcBr_3$

- Distorted TiI_3 structure-type: infinite chains of face–sharing $TcBr_6$ octahedra
- Regular alternation of short and long Tc-Tc distances is observed
  - Shorter separations are consistent with the presence of Tc-Tc bonding
- Isomorphous with $RuBr_3$ and $MoBr_3$

Image (x35) of needles and clusters 10 to 100 µm



Tc-Tc separations = 3.1434 Å and 2.8283 Å

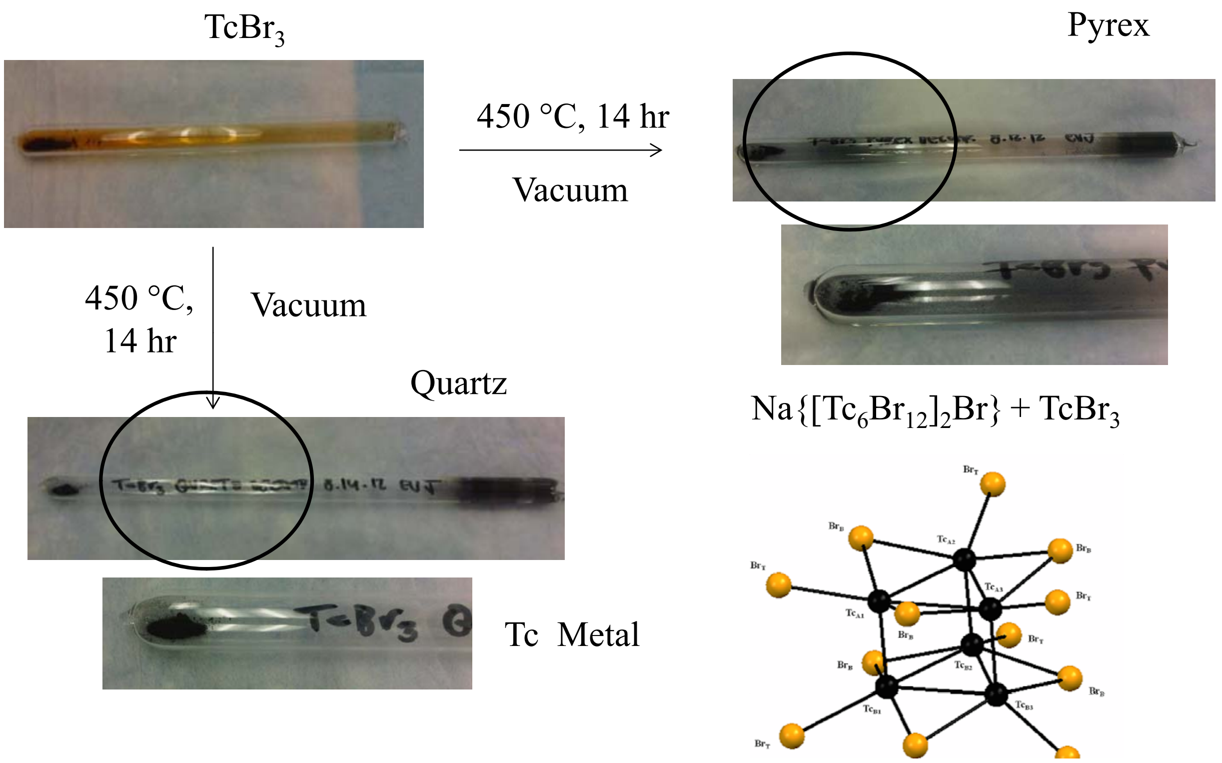


Poineau, F. et. al. *J. Am. Chem. Soc.* **2009**, *131*, 910-911.

Lin, J.; Miller, G. J. *Inorg. Chem.* **1993**, *32*, 1476-1487.

Binary Technetium Bromides

Thermal decomposition of $TcBr_3$



$TcBr_3$

450 °C, 14 hr

Vacuum

Pyrex

450 °C, 14 hr

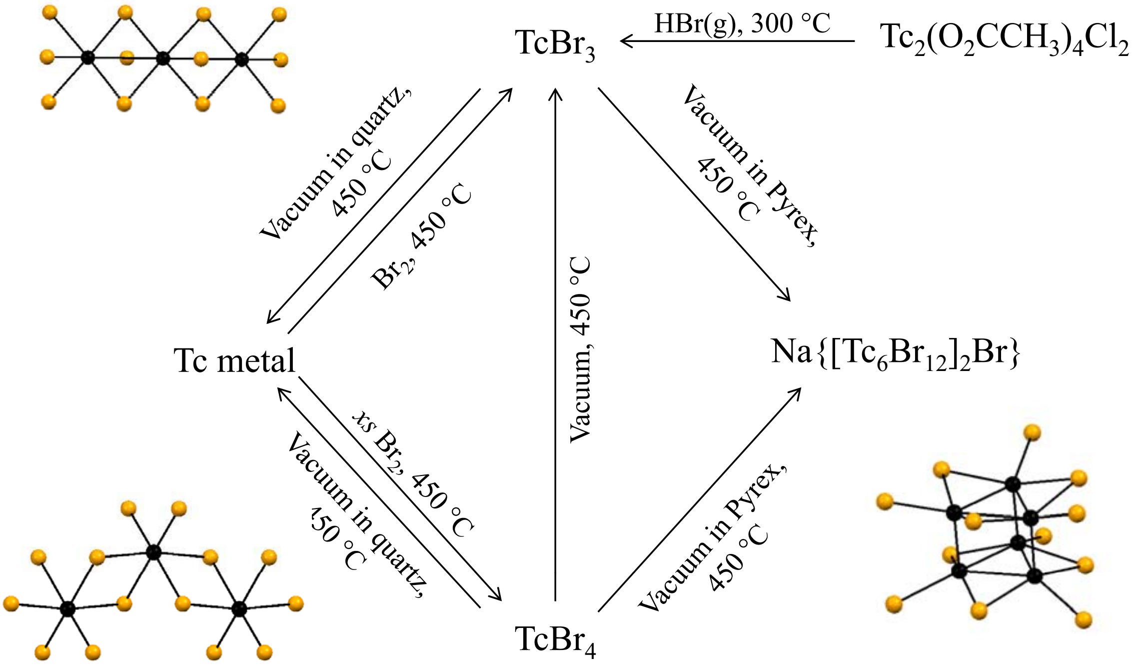
Vacuum

Quartz

Tc Metal

$Na\{[Tc_6Br_{12}]_2Br\} + TcBr_3$

Binary Technetium Bromides



$TcBr_3$ ← HBr(g), 300 °C ← $Tc_2(O_2CCH_3)_4Cl_2$

$TcBr_3$ → Vacuum in quartz, 450 °C → Tc metal

Tc metal → Br_2, 450 °C → $TcBr_3$

$TcBr_3$ → Vacuum in Pyrex, 450 °C → $Na\{[Tc_6Br_{12}]_2Br\}$

$TcBr_4$ → Vacuum, 450 °C → $TcBr_3$

Tc metal → xs Br_2, 450 °C → $TcBr_4$

$TcBr_4$ → Vacuum in quartz, 450 °C → Tc metal

$TcBr_4$ → Vacuum in Pyrex, 450 °C → $Na\{[Tc_6Br_{12}]_2Br\}$

Binary Technetium Iodide

Synthesis of TcI_3

I.

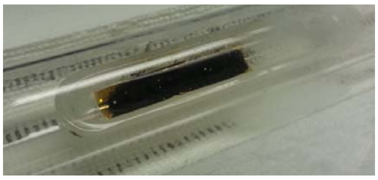
$$Tc + 3/2\ I_2 \rightarrow TcI_3$$

$$\xrightarrow[\text{Tc:I 1:3}]{\text{250-400 °C, 2 wks}}$$

II.

$$Tc_2(O_2CCH_3)_4Cl_2 + 6\ HI\ (g) \rightarrow 2\ TcI_3 + 4\ CH_3COOH + 2HCl$$

$$\xrightarrow[\text{150 and 300 °C}]{\text{HI(g)}}$$

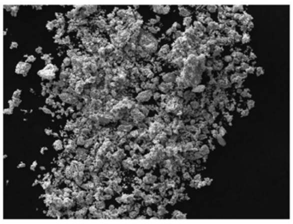


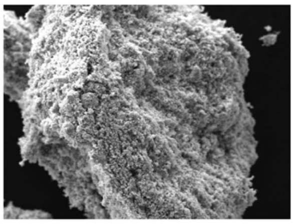
Johnstone, E. V., et. al. *Inorg. Chem.* **2013**, *52(24)*, 14309-14316.

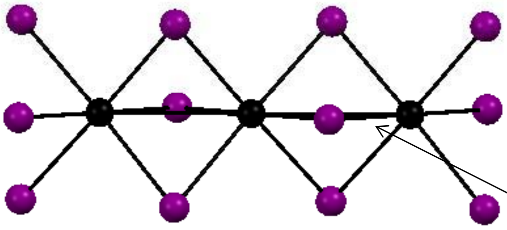
Binary Technetium Iodide

Structure of TcI_3

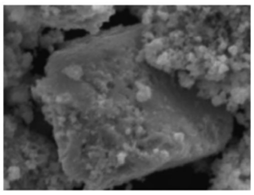
- Distorted TiI_3 structure-type: infinite chains of face–sharing TcI_6 octahedra
- Isomorphous with RuI_3 and MoI_3







Tc-Tc separation = 3.10(3) Å



Johnstone, E. V., et. al. *Inorg. Chem.* **2013**, *52(24)*, 14309-14316.

Binary Technetium Iodide

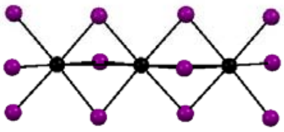
Thermal decomposition of TcI_3

TcI_3

$\xrightarrow[\text{Vacuum}]{450\ °C,\ 24\ \text{hrs}}$

Tc Metal

$$\text{Tc metal} \underset{\text{Vacuum, 450 °C}}{\overset{I_2,\ 300\ °C}{\rightleftarrows}} TcI_3 \xleftarrow{\text{HI(g), 300 °C}} Tc_2(O_2CCH_3)_4Cl_2$$



Johnstone, E. V., et. al. *Inorg. Chem.* **2013**, *52(24)*, 14309-14316.

Future Work

We have only scratched the surface of the binary technetium halides.

What other synthetic routes can be investigated?

How can we begin to better study these reaction mechanisms?

How can these be used for other Tc chemistry?

How can these serve for potential materials in industry and applications?

Acknowledgements

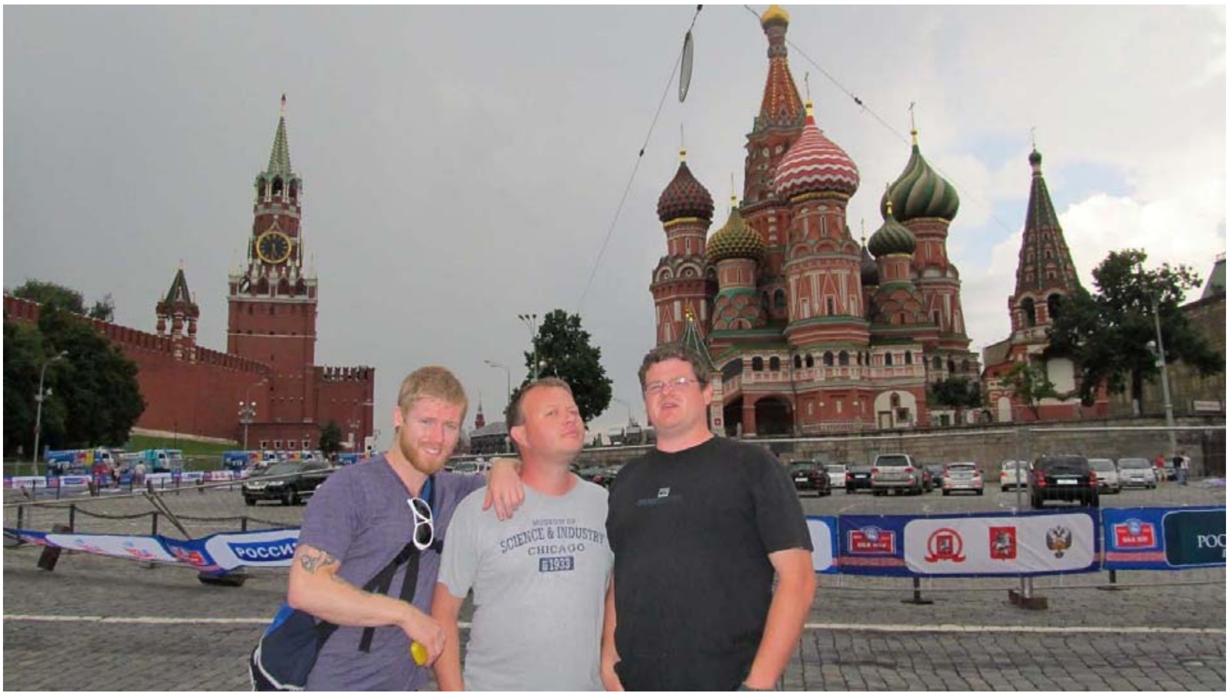
UNLV Radiochemistry Department

Technetium Synthesis Group

Dr. Ken Czerwinski, Dr. Alfred Sattelberger, and Dr. Frederic Poineau
Romina Farmand, Jenna Starkey, Jeremy Hilgar
Tom O'Dou, Julie Bertoia, and Trevor Low for Radiation Safety

SISGR-Fundamental Chemistry of Technetium-99 Incorporated into Metal Oxide, Phosphate and Sulfide: Toward Stabilization of Low-Valent Technetium
Contract No. 47824B Basic Energy Sciences, DOE

Questions



ISTR 2011 Moscow, Russia

DINUCLEAR TECHNETIUM COMPLEXES WITH MULTIPLE METAL-METAL BONDS

Poineau F.*, Forster P.M.*, Todorova T.K.**, Johnstone E.V.*, Kerlin W.M.*, Gagliardi L.***, Czerwinski K.R.*, Sattelberger A.P.****

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***Department of Chemistry and Supercomputing Institute, University of Minnesota, Minneapolis, MN 55455, USA
****Energy Engineering and Systems Analysis Directorate, Argonne National Laboratory, Argonne, IL 60439, USA

Transition metal complexes with multiple metal-metal bonds exhibit interesting catalytic and biological properties. One element whose metal-metal bond chemistry has been poorly studied is technetium. Currently, only 25 technetium complexes with multiple metal-metal bond complexes are structurally characterized. The nature of metal-metal bonding in these complexes, as well as the influence of ligands on the bonding in the Tc_2^{n+} unit (n = 6, 5, 4) are not well understood. In order to better understand the influence of ligands on the Tc-Tc bonding, a study of the solid state and electronic structure of dinuclear complexes with the Tc_2^{n+} unit (n= 6, 5, 4) has been performed. The dinuclear technetium complexes $(n\text{-}Bu_4N)_2Tc_2X_8$, $Tc_2(O_2CCH_3)_4X_2$, $Tc_2(O_2CCH_3)_2Cl_4$, cesium salts of $Tc_2X_8^{3-}$, and $Tc_2X_4(PMe_3)_4$ (X = Cl, Br) were synthesized; their molecular electronic structure, as well as the electronic absorption were studied by a number of physical and computational techniques. The structure and bonding in these systems has been investigated using multiconfigurational quantum calculations. For all these complexes, the calculated geometries are in very good agreement with the one determined experimentally. Bond order analysis demonstrates that all these complexes exhibit a total bond order of ~3. Analysis of individual effective bond order components shows that these complexes have similar σ components while the strength of the π components follow the order $Tc_2X_4(PMe_3)_4 > Tc_2X_8^{3-} > Tc_2(O_2CCH_3)_2Cl_4 > Tc_2X_8^{2-}$. Calculations indicate the δ components to be the weakest bond in $Tc_2X_8^{n-}$ (n = 2, 3) and $Tc_2(O_2CCH_3)_2Cl_4$. Further analysis on $Tc_2X_8^{3-}$ and $Tc_2X_4(PMe_3)_4$ (X = Cl, Br) indicates that the electronic structure of the Tc_2^{5+} and Tc_2^{4+} units is insensitive to the nature of the coordinating ligands.

UNLV

Dinuclear Technetium Complexes with Multiple Metal-Metal Bonds

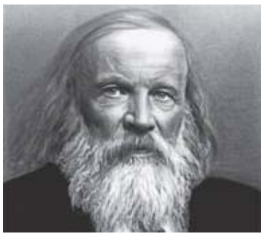
<u>Frederic Poineau</u>[1], Paul M. Forster[1], Tanya K. Todorova[2], Eric V. Johnstone[3], William M. Kerlin[1], Laura Gagliardi[4], Kenneth R. Czerwinski[1] and Alfred P. Sattelberger[5]

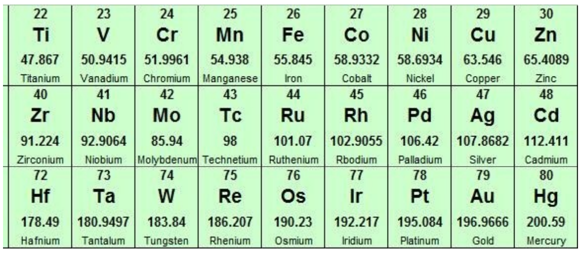
[1] Department of Chemistry, University of Nevada Las Vegas, Las Vegas, NV 89154
[2] Laboratory for Computational Molecular Design, Ecole Polytechnique Fédérale de Lausanne, Lausanne, CH-1015
[3] Institute of Resource Ecology, Helmholtz-Zentrum Dresden-Rossendorf, Dresden, Germany
[4] Department of Chemistry and Supercomputing Institute, University of Minnesota, Minneapolis, MN 55455
[5] Energy Engineering and Systems Analysis Directorate, Argonne National Laboratory, Argonne, IL 60439

Technetium

Element 43, Group 7- second row transition metal

- 1869: Predicted by D. Mendeleev

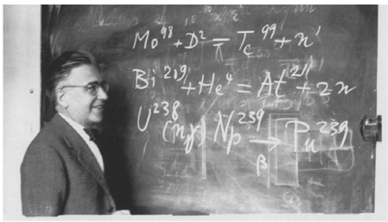




22 **Ti** 47.867 Titanium	23 **V** 50.9415 Vanadium	24 **Cr** 51.9961 Chromium	25 **Mn** 54.938 Manganese	26 **Fe** 55.845 Iron	27 **Co** 58.9332 Cobalt	28 **Ni** 58.6934 Nickel	29 **Cu** 63.546 Copper	30 **Zn** 65.4089 Zinc
40 **Zr** 91.224 Zirconium	41 **Nb** 92.9064 Niobium	42 **Mo** 85.94 Molybdenum	43 **Tc** 98 Technetium	44 **Ru** 101.07 Ruthenium	45 **Rh** 102.9055 Rbodium	46 **Pd** 106.42 Palladium	47 **Ag** 107.8682 Silver	48 **Cd** 112.411 Cadmium
72 **Hf** 178.49 Hafnium	73 **Ta** 180.9497 Tantalum	74 **W** 183.84 Tungsten	75 **Re** 186.207 Rhenium	76 **Os** 190.23 Osmium	77 **Ir** 192.217 Iridium	78 **Pt** 195.084 Platinum	79 **Au** 196.9666 Gold	80 **Hg** 200.59 Mercury

- 1934: Predicted to have no stable isotope (Mattauch rule)

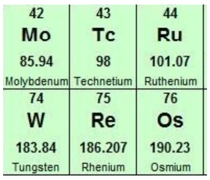
- 1937: Discovered by E. Segre and C. Perrier



Irradiation of molybdenum plate at Berkeley cyclotron

Technetium chemistry

Electronic structure: [Kr]$4d^5 5s^2$, 9 oxidation states (+7 to -1)



42 Mo 85.94 Molybdenum	43 Tc 98 Technetium	44 Ru 101.07 Ruthenium
74 W 183.84 Tungsten	75 Re 186.207 Rhenium	76 Os 190.23 Osmium

Tc and Re share similar electronic structure

- ➢ Similar coordination complexes

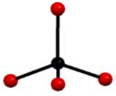
Binary halides

MF_5

Metal-metal bonded dimers

$M_2Cl_8^{2-}$

Heptavalent complexes



MO_4^-

- ➢ Tc coordination chemistry less developed than Re (as of 2008)

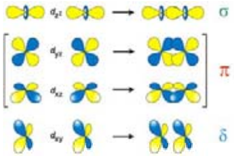
	Binary halides	Metal-metal bonded dimers	Heptavalent complexes
Tc	3	27	30
Re	15	500	150

Understand fundamental chemistry of Tc

- ➢ Improve nuclear fuel cycle applications
- ➢ Development of new imaging agents

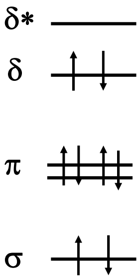
Metal-metal bonded dimers: M_2^{n+} units coordinated to ligands

In the M_2^{n+}: d orbitals can overlap and form σ, π and δ bonds



Technetium: Tc_2^{6+}, Tc_2^{5+} and Tc_2^{4+} unit

For Tc_2^{6+}

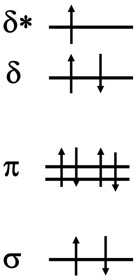


$Tc_2Br_8^{2-}$

quadruple bond

5 compounds

For Tc_2^{5+}

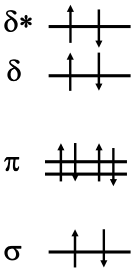


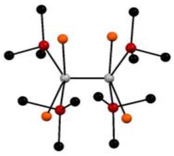
$Tc_2Br_8^{3-}$

Bond order of 3.5

14 compounds

For Tc_2^{4+}





$Tc_2Br_4(PMe_3)_4$

electron-rich triple bond

8 compounds

❖Synthetic and coordination chemistry not well developed

No organometallic dinuclear complexes known

Preparation of $Tc_2Cl_8^{2-}$ complicated (5 days, yield ~ 30 %)

❖Relation between structure and bonding not well understood

It can be expected than complexes with high B.O will have short metal-metal separation

$Mo_2(SO_4)_4^{4-}$: B.O = 4, Mo-Mo ~ 2.11 Å | $Mo_2(SO_4)_4^{3-}$: B.O = 3.5, Mo-Mo ~ 2.17 Å

❖ Technetium complexes with high B.O have long metal-metal separation

$Tc_2Cl_8^{2-}$: B.O = 4, Tc-Tc ~2.16 Å | $Tc_2Cl_8^{3-}$: B.O = 3.5, Tc-Tc ~ 2.12 Å

Goal: Expand the chemistry of dinuclear Tc complexes

- **Prepare new compounds**
- **Study of structure, bonding and spectroscopic properties**

Study of complexes with Tc_2^{6+} unit: $(TBA)_2Tc_2X_8$, $Tc_2(OAc)_4Cl_2$, $Tc_2(OAc)_2Cl_4$
Tc_2^{5+} unit: $Cs_{2+x}H_3O_{(1-x)}Tc_2Br_8$

Outline

I. Preparation of dinuclear Tc complexes

II. Crystallographic Structure

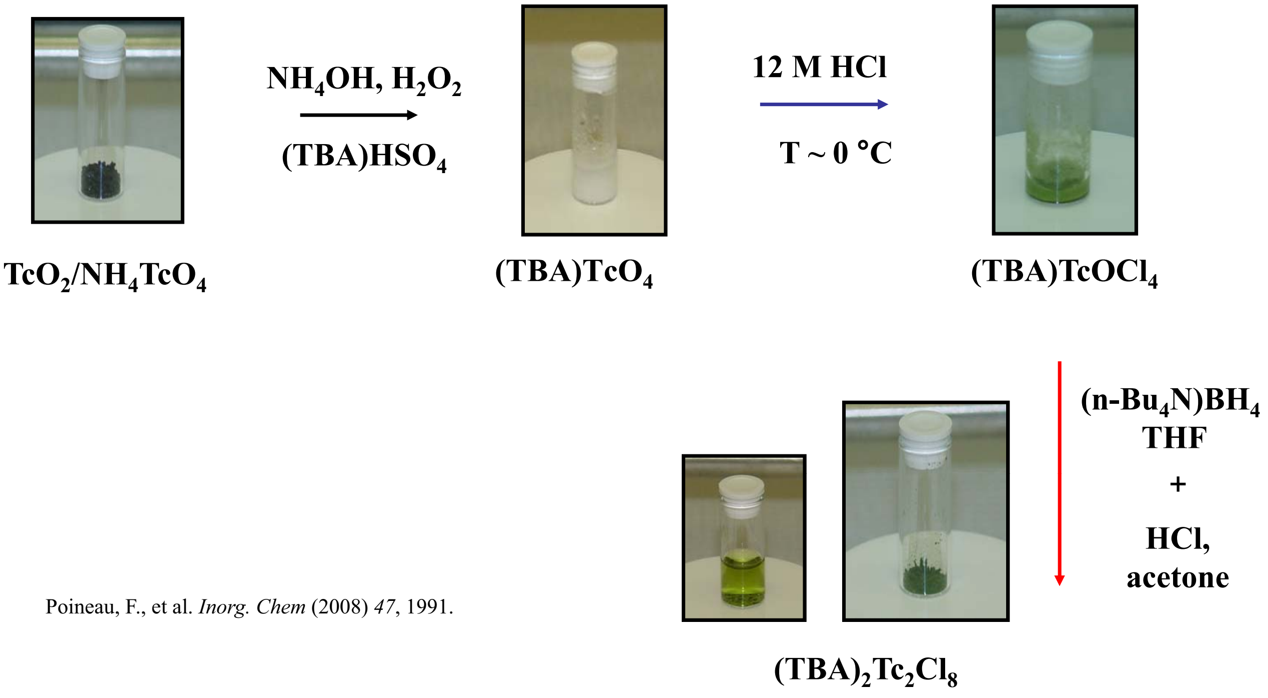
III. Electronic Structure and Spectroscopy

IV. Summary

I. Preparation of dinuclear Tc complexes

Preparation of $Tc_2Cl_8^{2-}$

Successive reductions: Tc(VII) → Tc(V) → Tc(III)



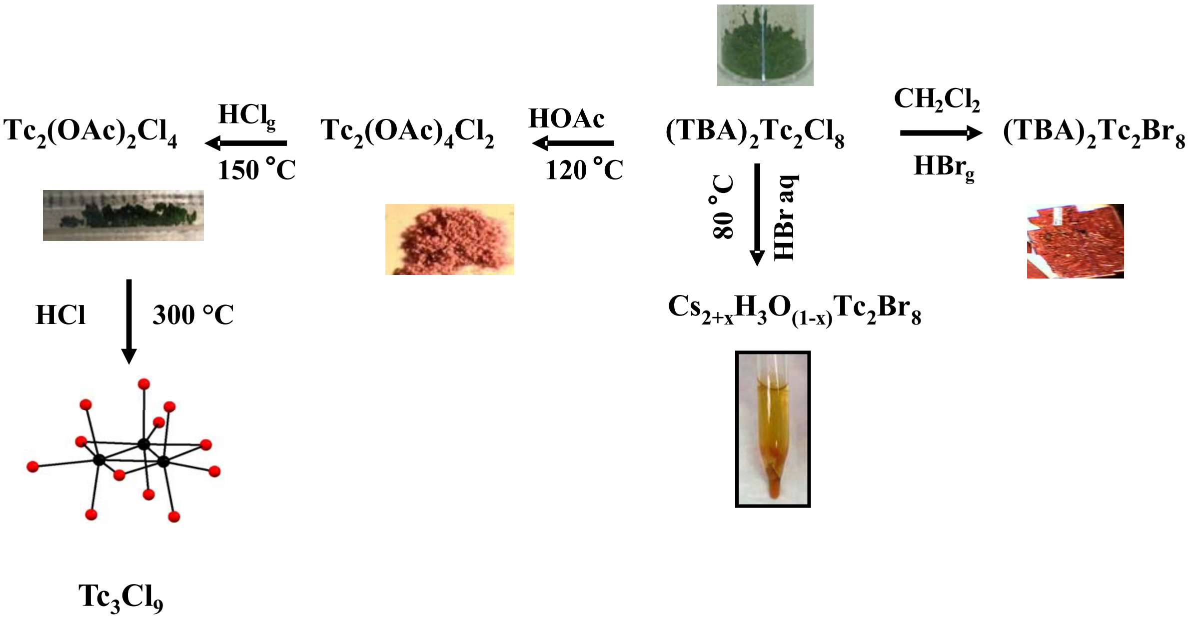
TcO_2/NH_4TcO_4 $\xrightarrow[(TBA)HSO_4]{NH_4OH,\ H_2O_2}$ **$(TBA)TcO_4$** $\xrightarrow[T \sim 0\ °C]{12\ M\ HCl}$ **$(TBA)TcOCl_4$**

$(n\text{-}Bu_4N)BH_4$
THF
+
HCl,
acetone

$(TBA)_2Tc_2Cl_8$

Poineau, F., et al. *Inorg. Chem* (2008) *47*, 1991.

Preparation of complexes with Tc_2^{6+} and Tc_2^{5+} units



$$Tc_2(OAc)_2Cl_4 \xleftarrow[150\ ^\circ C]{HCl_g} Tc_2(OAc)_4Cl_2 \xleftarrow[120\ ^\circ C]{HOAc} (TBA)_2Tc_2Cl_8 \xrightarrow[HBr_g]{CH_2Cl_2} (TBA)_2Tc_2Br_8$$

$$(TBA)_2Tc_2Cl_8 \xrightarrow[80\ ^\circ C]{HBr\ aq} Cs_{2+x}H_3O_{(1-x)}Tc_2Br_8$$

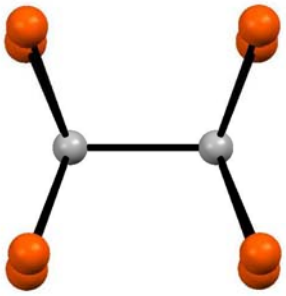
$$Tc_2(OAc)_2Cl_4 \xrightarrow[300\ ^\circ C]{HCl} Tc_3Cl_9$$

Reaction mechanisms from $(TBA)_2Tc_2Cl_8$ to Tc_3Cl_9 mimic the one of Re

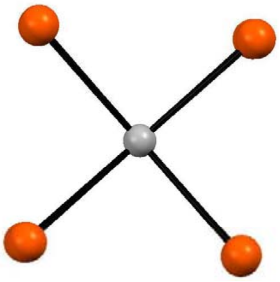
II. Crystallographic Structure

$Tc_2X_8^{2-}$

Crystallization from acetone / ether for single crystal XRD
→ Formation of an acetone solvate: $(TBA)_2Tc_2X_8 \cdot 4[(CH_3)_2CO]$



$Tc_2X_8^{2-}$



Eclipsed TcX_4 units

Anions	Tc-Tc (Å)	<Tc-Tc-X> (°)
$Tc_2Br_8^{2-}$	2.1625(9)	105.01(3)
$Tc_2Cl_8^{2-}$	2.1560(3)	103.92(2)

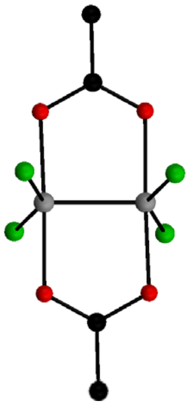
- **Steric effect induced by bromide in $Tc_2Br_8^{2-}$ ion**

  Increase of Tc-Tc separation and Tc-Tc-X angle

Poineau, F., et al. *Dalton Trans.* (2009) *30*, 5954.

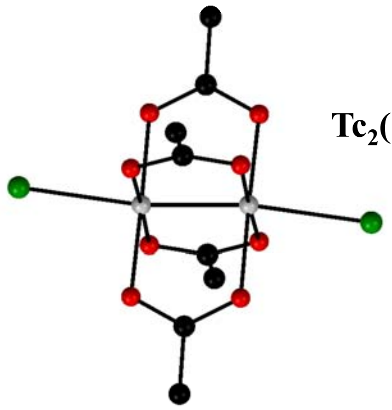
$Tc_2(OAc)_2Cl_4$ and $Tc_2(OAc)_4Cl_2$

$Tc_2(OAc)_2Cl_4$



Poineau, F., et al. *J. Am. Chem. Soc.* (2010) *132*, 15864.

$Tc_2(OAc)_4Cl_2$



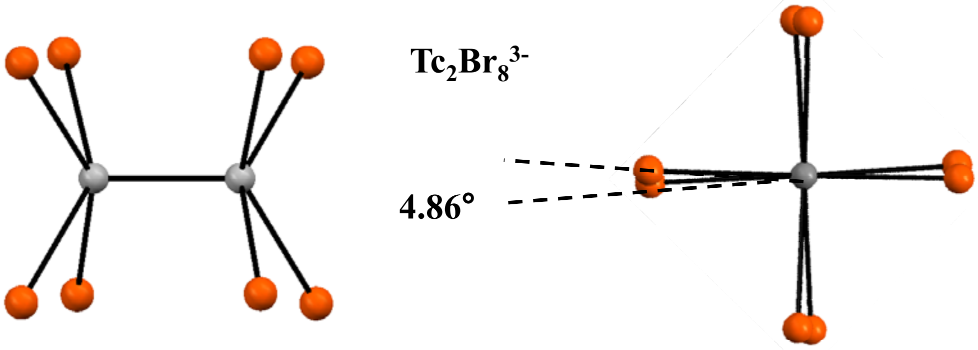
Kerlin, W., et al. *Polyhedron* (2013) *58*, 115.

Compounds	Tc-Tc (Å)	Tc-X (Å)
$Tc_2(OAc)_4Cl_2$	2.176(1)	2.508(4)
$Tc_2(OAc)_2Cl_4$	2.150(1)	2.312

Decrease of Tc-Tc from $Tc_2(OAc)_4Cl_2$ to $Tc_2(OAc)_2Cl_4$
influence of axial Cl ligand on Tc-Tc separation

$Tc_2X_8^{3-}$

Crystallization in concentrated HBr for single crystal XRD
→ Formation of hydrate: $[Cs_{(2+x)}][H_3O_{(1-x)}]Tc_2Br_8\cdot 4.6H_2O$ (x = 0.221)



Anion	Tc-Tc (Å)	<Tc-Tc-X> (°)
$Tc_2Br_8^{3-}$	2.1265(9)	106.07(3)
*$Tc_2Cl_8^{3-}$	2.117(4)	104.82(7)

- **Steric effect induced by bromide in $Tc_2Br_8^{3-}$**

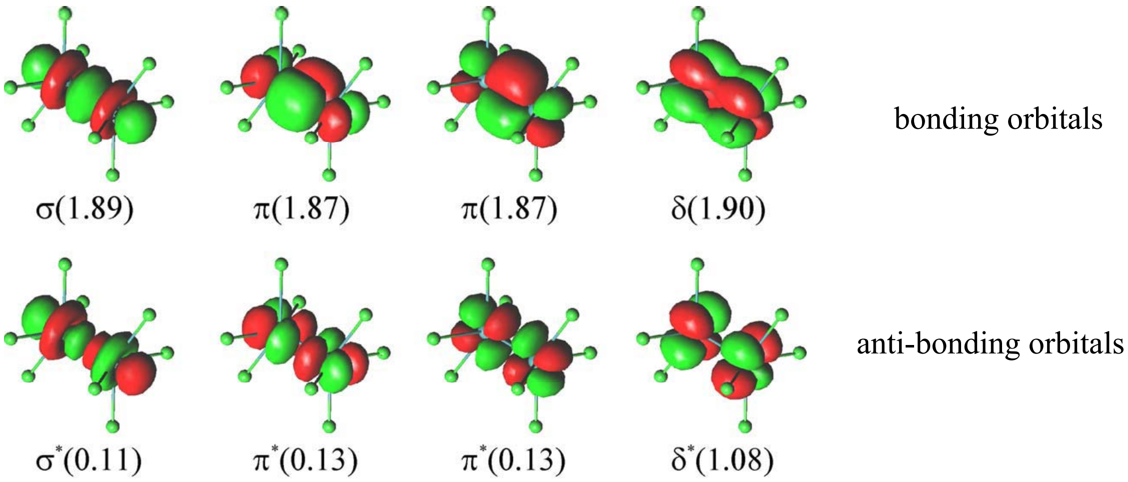
Internal rotation angle in $Tc_2Br_8^{3-}$ (4.86 °)
d(Tc-Tc) in $Tc_2Br_8^{3-}$ is ~ 0.04 Å shorter than in $Tc_2Br_8^{2-}$

* Cotton, F. A., et al. *Inorg. Chem.* (1975) *14*, 2032. Poineau, F., et al. *Dalton Trans.* (2012) *41*, 2869.

III. Electronic Structure and Spectroscopy

Tc-Tc bonding quantified in terms of effective bond order (EBO): $(\eta_b-\eta_a)/(\eta_b+\eta_a)$

η_b: occupation number for the Tc-Tc bonding orbital
η_a: occupation number for the Tc-Tc antibonding orbital



Active orbitals and their occupation numbers for $Tc_2X_8^{3-}$ (X = Cl, Br)

	Tc-Tc (Å)	E. B. O			Total B.O
		σ	π	δ	
$Tc_2(OAc)_4Cl_2$	**2.176(1)**	**0.90**	**1.63**	**0.55**	**3.08**
$Tc_2Br_8^{2-}$	**2.1625(9)**	**0.88**	**1.69**	**0.50**	**3.07**
$Tc_2Cl_8^{2-}$	**2.1560(3)**	**0.88**	**1.68**	**0.47**	**3.03**
$Tc_2(OAc)_2Cl_4$	**2.150(1)**	**0.90**	**1.71**	**0.59**	**3.20**
$Tc_2Br_8^{3-}$	**2.1265(9)**	**0.89**	**1.74**	**0.41**	**3.04**
$Tc_2Cl_8^{3-}$	**2.117(4)**	**0.89**	**1.74**	**0.41**	**3.04**

- **Total bond order in $Tc_2X_8^{n-}$ are similar (~3)**

Changing electronic structure $\sigma^2\pi^4\delta^2$ to $\sigma^2\pi^4\delta^2\delta^*$ has a negligible effect on the total bond order

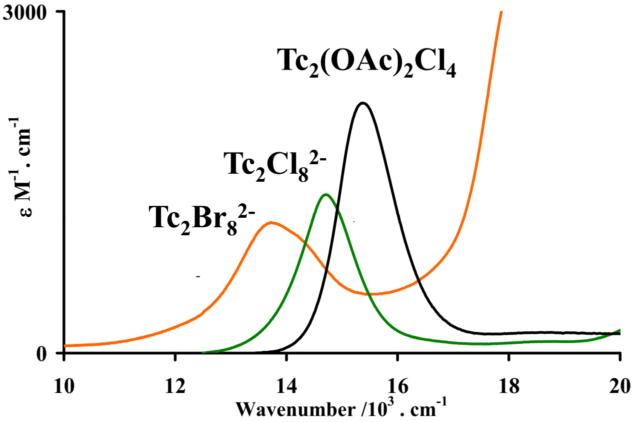
- **Strength of bonding follow order: $\pi > \sigma > \delta$**

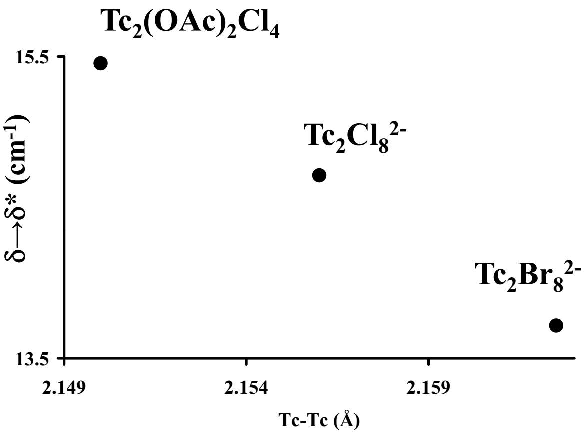
σ bond: similar strength
π bond: stronger bond → Tc-Tc separation correlated to the strength of π bond
δ bond: weaker bond → internal rotation angle in $Tc_2X_8^{3-}$

Poineau, F., et al. *Dalton Trans.* (2012) *41*, 2869.

Spectroscopic study on $Tc_2X_8^{2-}$ and $Tc_2(OAc)_2Cl_4$

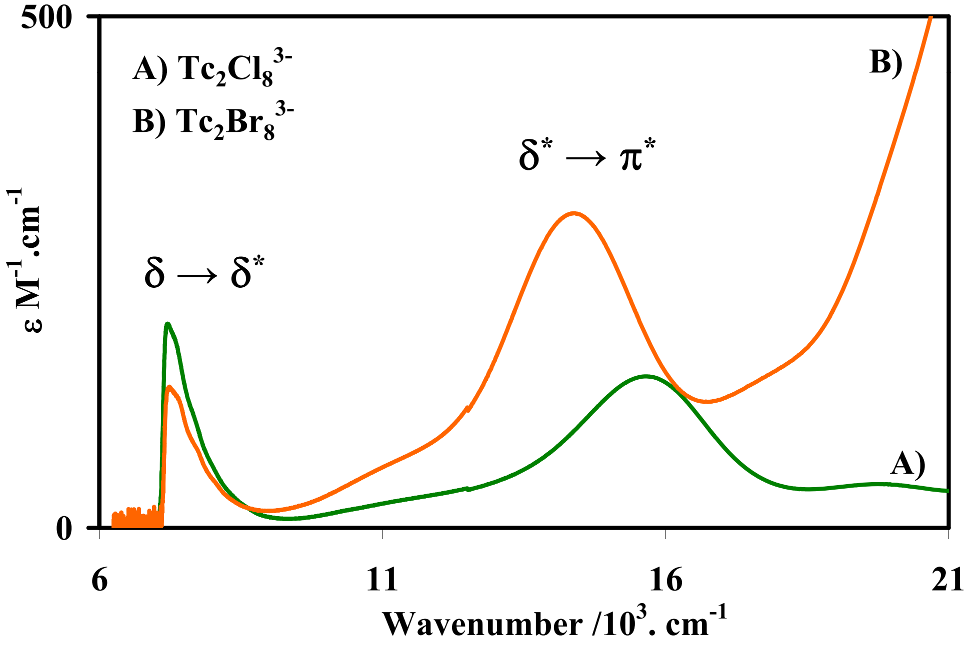
Attribution of transition based on quantum calculations


δ → δ* transition



- **Effect of the Tc-Tc separation on the position of δ → δ* transition**

Spectroscopic study on $Tc_2X_8^{3-}$



UV-visible spectra of $Tc_2X_8^{3-}$ in concentrated HX (X= Cl, Br)

IV. Summary

- **Technetium dinuclear complexes with multiple Tc-Tc bonds**

Four complexes characterized: $(TBA)_2Tc_2X_8$, $Tc_2(OAc)_4Cl_2$, $Tc_2(OAc)_2Cl_4$, $Cs_{2+x}(H_3O)_{1-x}Tc_2Br_8$
Mimic the Re reaction: $M_2Cl_8^{2-} \rightarrow M_2(OAc)_4Cl_2 \rightarrow M_2(OAc)_2Cl_4 \rightarrow M_3Cl_9$

- **d(Tc-Tc) in Tc_2^{6+} unit is sensitive to the position and nature of ligand**

Bromide *vs* chlorine: steric effect
Axial *vs* equatorial: trans-effect

- **Complexes with Tc_2^{6+} units have longer d(Tc-Tc) that those with Tc_2^{5+} units**

Tc-Tc separation correlated to the strength of π bond
Strength of bonding follow order: $\pi > \sigma > \delta$

- **Effect of the Tc-Tc separation on the position of the $\delta \rightarrow \delta^*$ transition**

Acknowledgments

Julie Bertoia and Trevor Low
Radiation protection and laboratory management

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Questions

Radiochemistry Program at the University of Nevada Las Vegas

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Polynuclear Technetium Iodides Compounds with Multiple Metal-metal Bonds

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A new solvothermal synthesis route for the preparation of Technetium extended metals atoms chains (EMAC) and clustershave been developed.Technetium EMAC ($Tc_2(\mu\text{-}O_2CCH_3)_4I$) and Tc-iodide clusters($K[Tc_8I_{13}]$ and Tc_5I_{13}) were prepared form the reaction of potassium pertechnetate with glacial acetic acid plus either hydroiodic acid or iodide salts under *in-situ* hydrogen production by sodium borohydride at various temperatures yields . These compounds were characterized by single crystal X-ray diffraction and their structures will be presented. In the solvothermal reaction the oxidation state of the Tc atoms in the reaction productsis also dependent on temperature and pH of the starting solutions and will be explained in extensive detail. Magnetic susceptibility measurements have been conducted and will presented. These complexes mightfound in applications in the nuclear industry (waste forms) and in the radiopharmaceuticals industry as imaging agents.

Keywords: technetium carboxylates; metal-metal bonds; metal-halogen bond; hydro/solvo-thermal reactions; polymers; characterization(SC-XRD).

Polynuclear Technetium Iodides Compounds with Multiple Metal-metal Bonds

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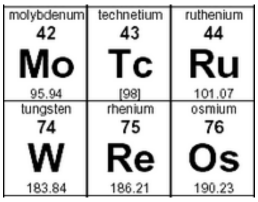
University of Nevada Las Vegas, Radiochemistry
8th International Symposium on Technetium & Rhenium 2014
Pornichet La Baule, France Oct. 1st 2014

Overview

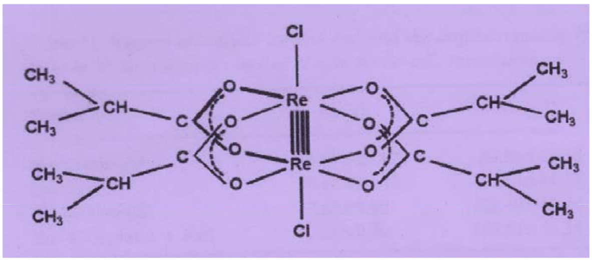
- Introduction
- Experimental Methods
- Results
- Conclusion
- Future Studies

Pharmaceuticals Applications

- Dichlorotetra-μ-Isobutyratodirhenium(III)
  - Re-Re metal-metal bond
- Stabilizing red blood cells
- Anti-tumor/cancer properties
  - Seen High Effectiveness in
    - Sarcoma S-180
    - Leukemia P-388
    - Melanoma B-16

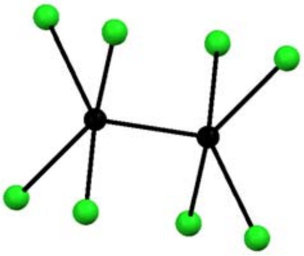


molybdenum 42 Mo 95.94	technetium 43 Tc [98]	ruthenium 44 Ru 101.07
tungsten 74 W 183.84	rhenium 75 Re 186.21	osmium 76 Os 190.23

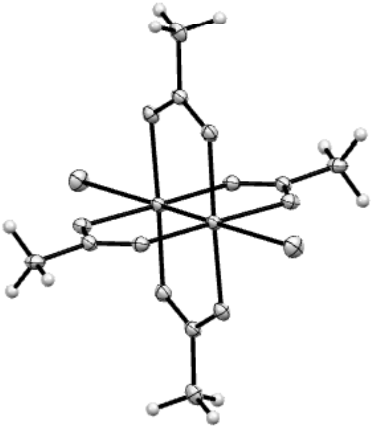


Shtemenko, N., P. Collery, and A. Shtemenko, *Anticancer Research* 27: 2487-2492 (**2007**)

Technetium Metal-Metal dimers



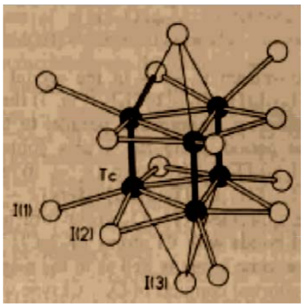
- Quadruple Metal-Metal dimers
  - Cotton, A. 1964, $Re_2Cl_8^{-2}$
  - Cotton, A. 1977, $Tc_2(O_2CMe_3)_4Cl_2$
  - Cotton, A. 1981, $Tc_2Cl_8^{-2}$
- Known Tc compounds of Acetate Dimers
  - Tc_2^{+6} core
    - $Tc_2(\mu\text{-}O_2CCH_3)_4X_2$ (X= Cl, Br)
    - $Tc_2(\mu\text{-}O_2CCH_3)_2Cl_2 \cdot (dma)_2$
    - $Tc_2(\mu\text{-}O_2CCH_3)_2Cl_2 \cdot (H_2O)_2$
    - $Tc_2(\mu\text{-}O_2CCH_3)_4(TcO_4)_2$
  - Tc_2^{+5} core
    - $Tc_2(\mu\text{-}O_2CCH_3)_4X$ (X= Cl, Br)
    - $K[Tc_2(\mu\text{-}O_2CCH_3)_4Cl_2]$

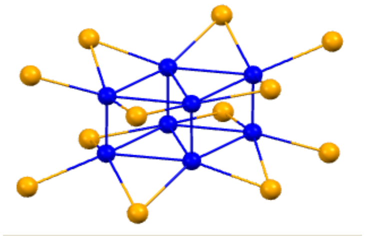


F. A. Cotton, C. A. Murillo, R. A. Walton (Eds), Springer, New York **2005** A.P. Sattelberger, in Multiple Bonds between Metal Atoms, Chapter 7, 3rd Ed.,

Polynuclear Halide Clusters: (~10 structures)

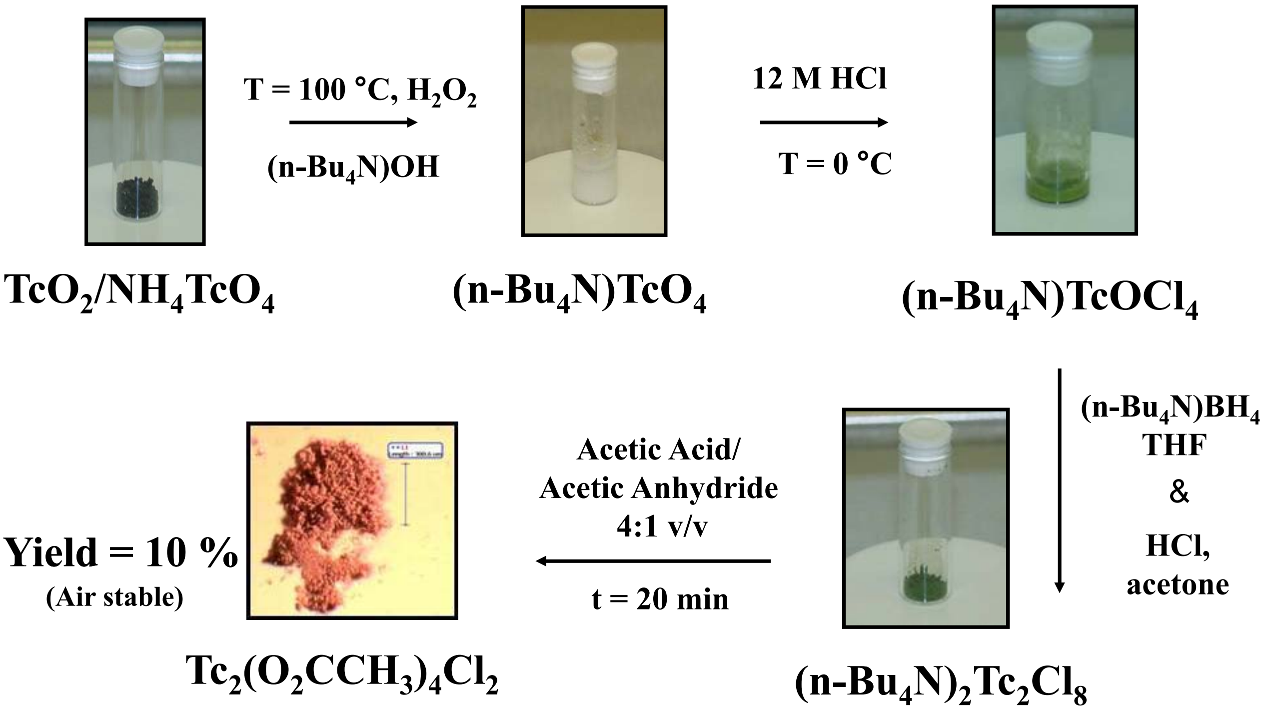
- Tc -Chloro, -Bromo
  - Hexa
    - $[Tc_6(\mu\text{-}Cl)_6Cl_6]^{2-}$, $\{[Tc_6(\mu\text{-}Cl)_6Cl_6]\ Cl_2\}^{3-}$
    - $\{[Tc_6(\mu\text{-}Br)_6Br_6]_2Br\}^{-}$, $\{[Tc_6(\mu\text{-}Br)_6Br_6]Br_2\}^{2-}$, $\{[Tc_6(\mu\text{-}Br)_6Br_6]\ Br_2\}^{3-}$
  - Octa
    - $[H(H_2O)_2]\{[Tc_8(\mu\text{-}Br)_8Br_4]Br\}$, $[H(H_2O)_2]_2\{[Tc_8(\mu\text{-}Br)_8Br_4]Br_2\}$
    - $\{[Tc_8(\mu\text{-}Br)_8Br_4]Br\}\cdot 2H_2O$
- Tc- Iodo
  - $\{[Tc_6(\mu\text{-}I)_6I_6]I_2\}^{3-}$
  - $\{[Tc_8(\mu\text{-}Br)_4(\mu\text{-}I)_4Br_2I_2]I_2\}^{2-}$





Experimental Method

Conventional Preparation: $Tc_2(O_2CCH_3)_4Cl_2$



TcO_2/NH_4TcO_4 $\xrightarrow[(n\text{-}Bu_4N)OH]{T = 100\ °C,\ H_2O_2}$ $(n\text{-}Bu_4N)TcO_4$ $\xrightarrow[T = 0\ °C]{12\ M\ HCl}$ $(n\text{-}Bu_4N)TcOCl_4$

$(n\text{-}Bu_4N)TcOCl_4$ $\xrightarrow[\text{HCl, acetone}]{(n\text{-}Bu_4N)BH_4\ \text{THF}\ \&}$ $(n\text{-}Bu_4N)_2Tc_2Cl_8$

$(n\text{-}Bu_4N)_2Tc_2Cl_8$ $\xrightarrow[t = 20\ min]{\text{Acetic Acid/Acetic Anhydride 4:1 v/v}}$ $Tc_2(O_2CCH_3)_4Cl_2$

Yield = 10 %
(Air stable)

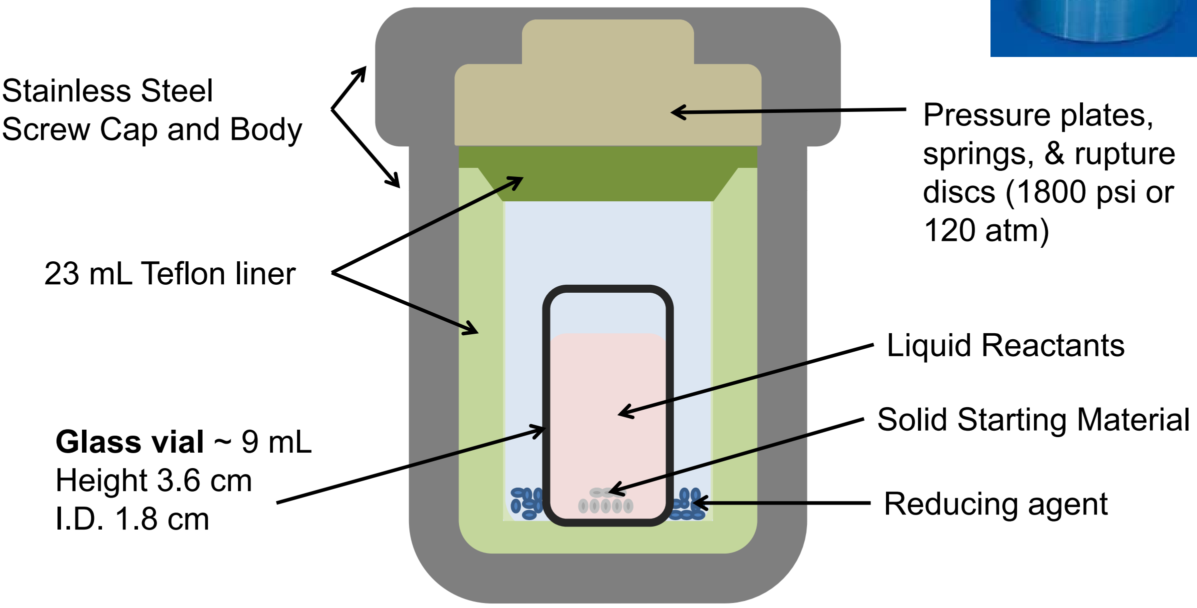
Autoclave Systems: Our Tools

Parr 5500 Series High Pressure Controlled Atmosphere Autoclave

- Max. Temp. 350 °C
- Max. Pressure
  - 200 atm
- Volume
  - 300 mL
- Atmosphere
  - Inert
  - Reducing

Parr 4749 Autoclave

Experimental Setup



Stainless Steel
Screw Cap and Body

Pressure plates, springs, & rupture discs (1800 psi or 120 atm)

23 mL Teflon liner

Liquid Reactants

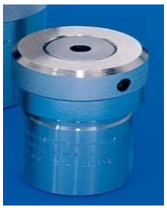
Solid Starting Material

Glass vial ~ 9 mL
Height 3.6 cm
I.D. 1.8 cm

Reducing agent

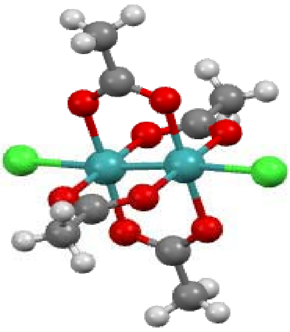
Two Synthesis Routes: $Tc_2(\mu\text{-}O_2CCH_3)_4Cl_2$

$$^{*}KTcO_4 + 2{:}1\ HC_2H_3O_2{:}HCl \xrightarrow[210\ ^{\circ}C,\ 12\ hr]{36\ atm\ H_2}$$

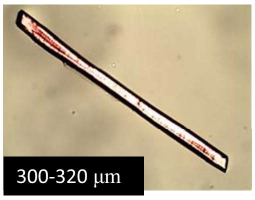


$$KTcO_4 + 2{:}1\ HC_2H_3O_2{:}HCl + NaBH_4 \xrightarrow[210\ ^{\circ}C,\ 72\ hr]{\sim 70\ atm}$$

$$NaBH_{4(s)} + 2\ H_2O_{(g)} \rightarrow NaBO_{2(s)} + \mathbf{4\ H_{2(g)}}$$

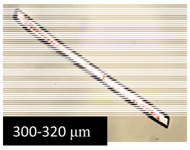


Monoclinic: $P2_1/n$



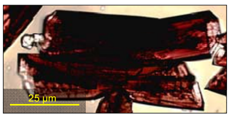
Yield: 70%

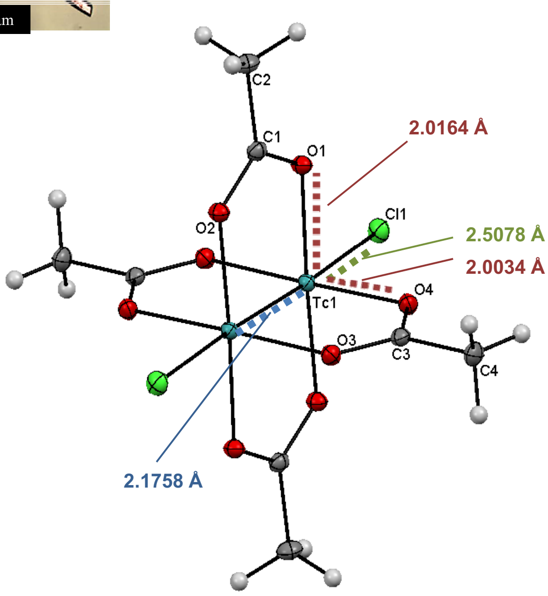
- L. I. Zaitseva, A.S. Kotel'nikova and A.A. Reszvov, *Russ. J. Inorg. Chem.* 1980, **25**, 1449
- W.M. Kerlin, et.al. Polyhedron, 2013, **58**, 115-119

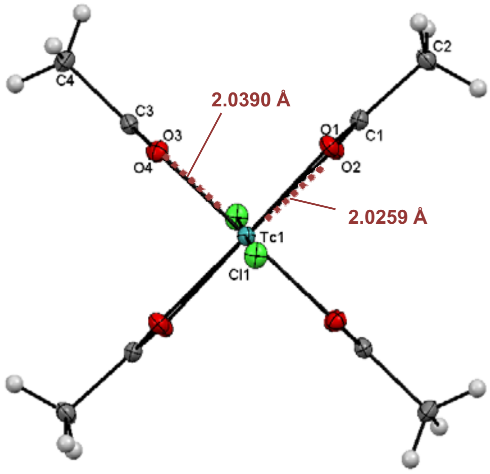


$Tc_2(\mu\text{-}O_2CCH_3)_4Cl_2$

$Tc_2(\mu\text{-}O_2CCH_3)_4Br_2$







Compound	d M-M	d M-X	d M-O	M-M-X	O-M-O
$Tc_2(\mu\text{-}O_2CCH_3)_4Cl_2$	2.1758(3)	2.5078(4)	2.0211(12)	171.903(13)	90.63(4)
$Tc_2(\mu\text{-}O_2CCH_3)_4Br_2$	2.1764(3)	2.6554(3)	2.0189(14)	173.564(12)	90.65(6)
$Tc_2(\mu\text{-}O_2CC(CH_3)_3)_4Cl_2$	2.192(2)	2.408(4)	2.032(4)	180.00	90.67(11)
$Re_2(\mu\text{-}O_2CCH_3)_4Cl_2$	2.224(4)	2.5213(4)	2.0181(14)	176.519(5)	90.074(5)

Synthesis: $Tc_2(\mu\text{-}O_2CCH_3)_4\text{-}\eta\text{-}O_2CCH_3$

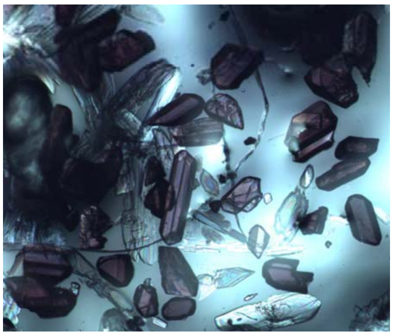
- $KTcO_4 + HC_2H_3O_2 + KF + NaBH_4 \longrightarrow Tc_2(\mu\text{-}O\cancel{_2C}CH_3)_4F_2$
- $KTcO_4 + HC_2H_3O_2 + NaBH_4 \longrightarrow Tc_2(\mu\text{-}O_2CCH_3)_5$
    - Final Pressure at 210 °C approx. 70 atm, 72 hrs.
        - Synthesis at temperature between 120 – 210 °C

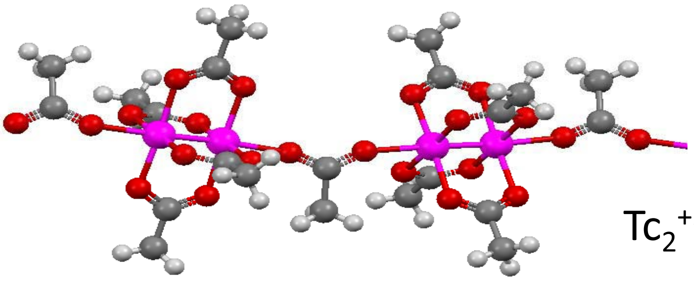
Yield: 73%

XRD, Single Crystal

- Space Group: Monoclinic Cc
- Unit Cell: a= 13.0686(4) b= 8.3444(3) c= 15.0232(5)

$\alpha = \gamma = 90^\circ$ $\beta = 106.19^\circ$ $V = 1573.2$ Å^3

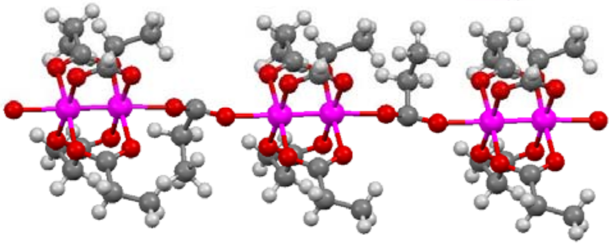




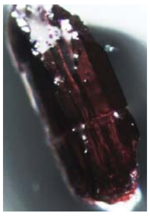
Tc_2^{+5} core

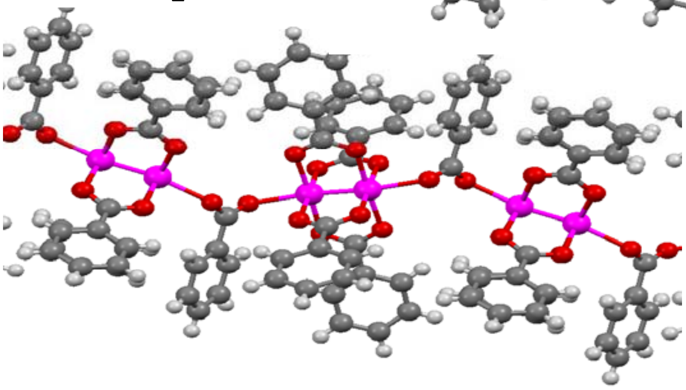
Reactions with Other Carboxylic Acids?

- $KTcO_4$ + Carboxylic acid + $NaBH_4$ $\longrightarrow$ $Tc_2(oL)_5$
  - Propionic acid
    - $CH_3CH_2CO_2H$
  - Benzoic acid
    - $C_6H_5CO_2H$



Tc_2^{+5} cores





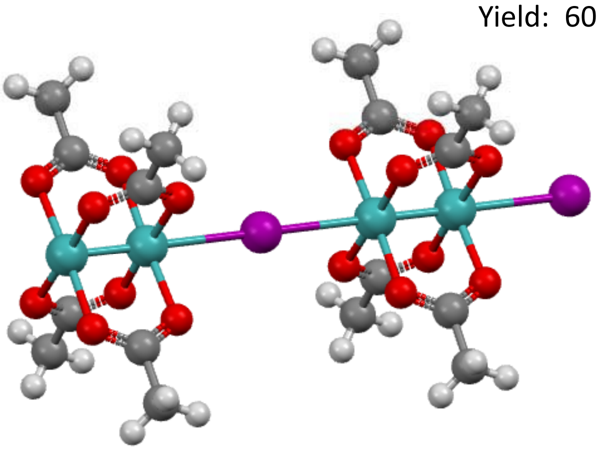
Yield: < 40%

Synthesis: $Tc_2(\mu\text{-}O_2CCH_3)_4I$

$KTcO_4 + NaI + HC_2H_3O_2 + NaBH_4 \longrightarrow Tc_2(\mu\text{-}O_2CCH_3)_4I$

- Conditions
  - 2:1 ratio NaI: TcO_4^-
  - 120 ºC for 72 hrs

Yield: 60%



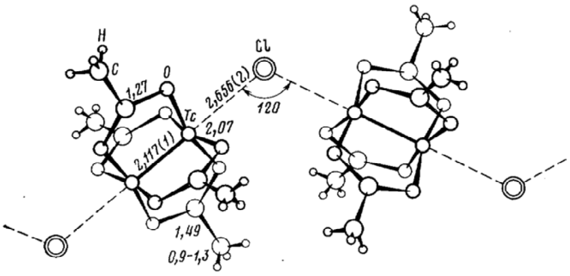
$Tc_2(\mu\text{-}O_2CCH_3)_4Cl$
Kozmin P. A., et. al., 1981
$Tc_2(\mu\text{-}O_2CCH_3)_4Br$
Kozmin P. A., et. al., 1983

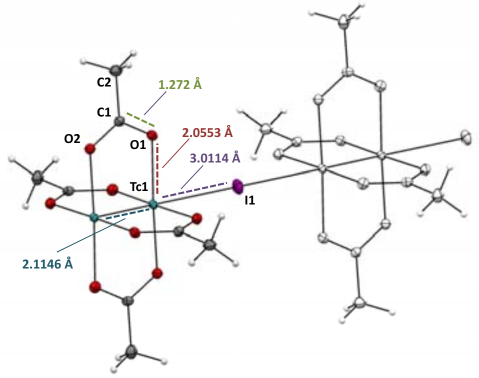
Synthesis from $K_3Tc_2X_8$

Space Group: Monoclinic C2/m
Unit Cell: a= 7.2002(8) b= 14.5629(17) c= 7.1549(8)
α= γ =90° β=110.89° V= 700.91 $Å^3$

Comparison Halide Polymer Linkage Tc_2^{+5} core, Bond Order 3.5

	Tc-Tc (Å)	Tc-O(eq)(Å)	Tc-L(ax) (Å)	Reference
†$Tc_2(\mu\text{-}O_2CCH_3)_4$ η-Cl Chloro	2.117 (1)	2.066 (5)	2.656 (1)	Kozmin et. al. 1981
‡$Tc_2(\mu\text{-}O_2CCH_3)_4$ η-Br Bromo	2.112 (1)	2.060 (4)	2.843 (1)	Kozmin et. al. 1983
$Tc_2(\mu\text{-}O_2CCH_3)_4$ η-I Iodo	2.1146 (4)	2.0553 (13)	3.0114 (3)	Kerlin et. al. 2014 This Work



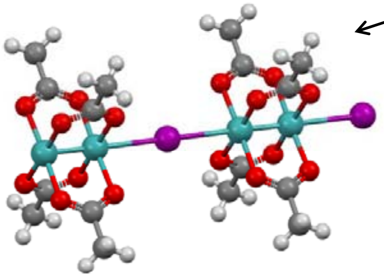


† P.A Koz'min, T.B. Larina, and M.D. Suraazhskaya, *Koord. Khim*. **1981**, 7, 1719.
‡ P.A Koz'min, T.B. Larina, and M.D. Suraazhskaya, *Koord. Khim*. **1983**, 9, 1114.
W. M. Kerlin, F. Poineau, P. M. Forster, K. R. Czerwinski, and A. P. Sattelberger, Inorg. Chim. Acta, 2014. DOI: 10.1016/j.ica.2014.09.024

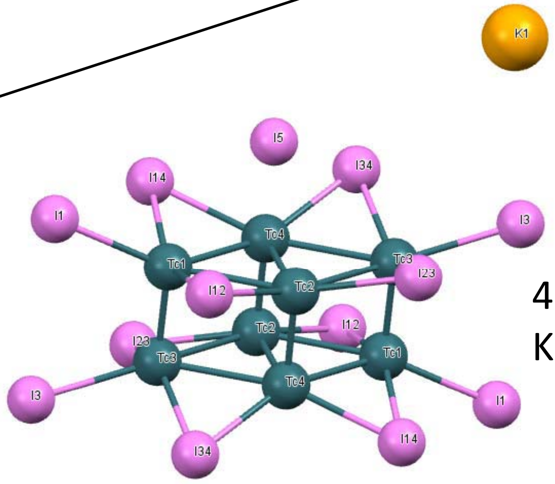
Synthesis: $M[Tc_8I_{12}]I$ M = Na, K

$$KTcO_4 + KI + HI + \text{ex. } HC_2H_3O_2 + NaBH_4 \xrightarrow[\text{200 °C, 72 hr}]{\text{~ 70 atm}}$$

- 1:2:2 ratio $KTcO_4$: KI : HI
- $NaBH_{4(s)} + 2\ H_2O_{(g)} \rightarrow NaBO_{2(s)} + $ **$4\ H_{2(g)}$**



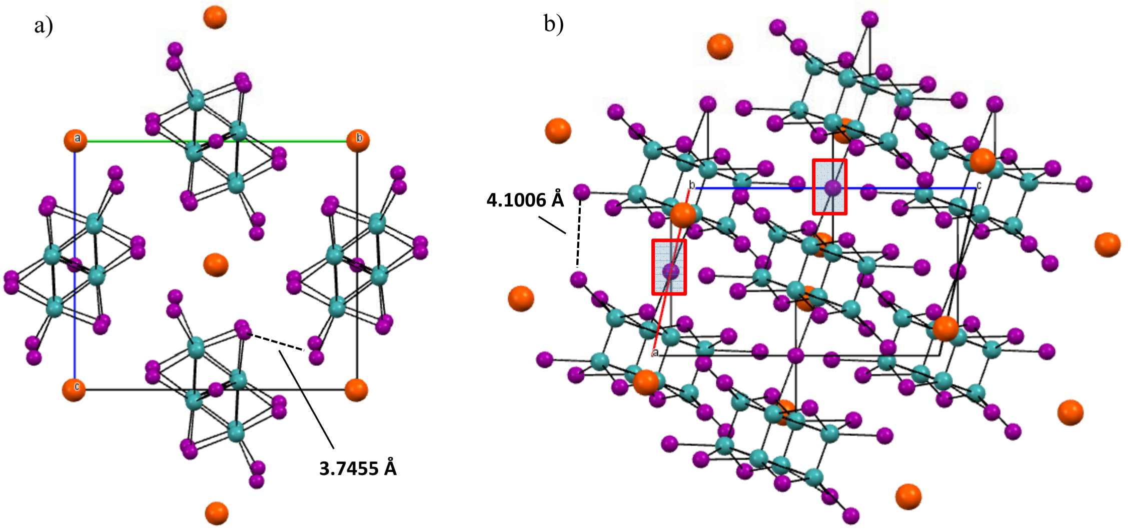
60% $Tc_2(\mu\text{-}O_2CCH_3)_4I$



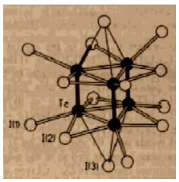
40% $K[Tc_8I_{12}]I$

$K[Tc_8(\mu\text{-}I)_8I_4]I$

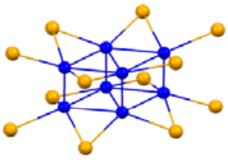
Potassium – Orange
Technetium – Turquoise
Iodine – Purple



Monoclinic $P2_1/n$
a = 8.0018(5) Å, b = 14.5125(10) Å, c = 13.1948(9) Å
β = 102.3090(10)º



Hexa- Octanuclear Tc Clusters



	Tc-Tc	$Tc\text{-}X_{term}$	$Tc\text{-}X_{Bri}$	$Tc\text{-}X_{cap}$	Reference
$K[Tc_8(\mu\text{-}I)_8I_4]I$	2.164/3/, 2.5308(8), 2.72/3/	2.731/12/	2.68/3/	3.187/53/	This Work Kerlin, et al. 2014
$[FeCp_2]_3\{Tc_6(\mu\text{-}I)_6I_6]I_2\}$	2.18(1), 2.67(1)	2.71(1)	2.61/2/	3.26(2)	Grigoriev 1993
$[H(H_2O)_2]\{[Tc_8(\mu\text{-}Br)_8Br_4]Br\}$	2.155/3/, 2.531/2/ 2.70/2/	2.53/2/	2.51/2/	2.99/7/	Koz'min et al. 1982 Kryuchkov, et al. 1986
$[H(H_2O)_2]_2\{[Tc_8(\mu\text{-}Br)_8Br_4]Br_2\}$	2.152/9/, 2.520/9/ 2.69(1)	2.52/1/	2.52/1/	2.90/2/	Koz'min et al. 1982 Spitzin et al. 1988
$[Tc_8(\mu\text{-}Br)_8Br_4]Br\cdot 2H_2O$	2.146(2), 2.521(2) 2.69/2/	2.509/8/	2.50/2/	3.00/7/	Kryuchkov, et al. 1986

W. Kerlin, F. Poineau, P. Forster, K. R. Czerwinski, A. P. Sattelberger, *Inorg. Chimi, Acta*, **2014.**
M. S. Grigoriev, S. V. Kryuchkov, *Radiochim. Acta* **1993**, *63*, 187.
P. A. Koz'min, M. D. Surazhskaya, T. B. Larina, *Dokl. Phys. Chem.* **1982**, *265*, 656.
S. V. Kryuchkov, A. F. Kuzina, V. I. Spitsyn, *Dokl. Chem.* **1986**, *287*, 1400.
V. I. Spitzin, S. V. Kryuchkov, M. S. Grigoriev, A. F. Kuzina, *Z. Anorg. Allg. Chem.* **1988**, *563*, 136.
S. V. Kryuchkov, M. S. Grigoriev, A. F. Kuzina, B. F. Gulev, V. I. Spitsyn, *Dokl. Chem.* **1986**, *288*, 172.

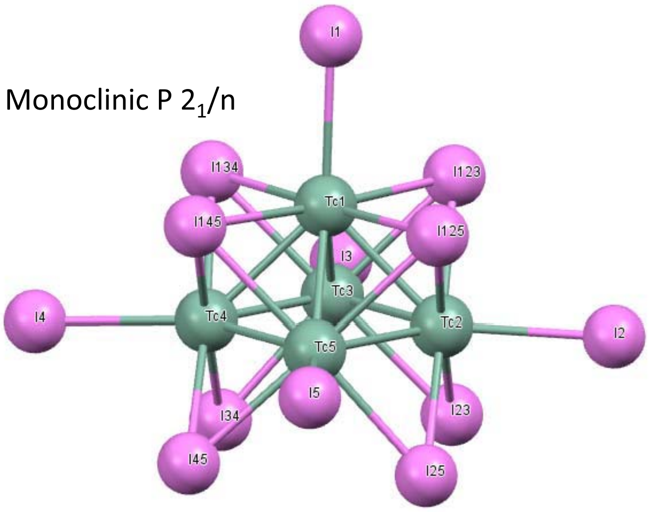
Synthesis: Tc_5I_{13}

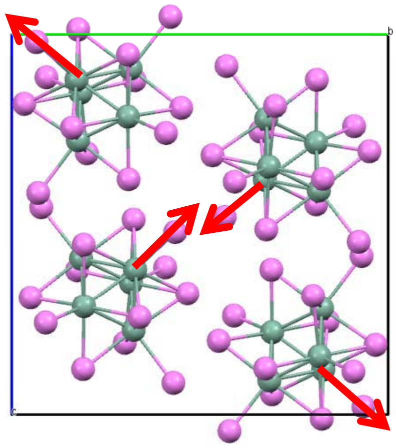
$$* \ MTcO_4 + \text{ex. } HI + H_2 \xrightarrow[140 - 150\ °C,\ 5\ hr]{\sim 30\ atm} (TcI_2 \cdot 0.5\ H_2O)_n$$

M = H, K, NH_4

$$KTcO_4 + \text{ex. } HI + NaBH_4 \xrightarrow[200\ °C,\ 72\ hr]{\sim 70\ atm} Tc_5I_{13} + Tc^0$$

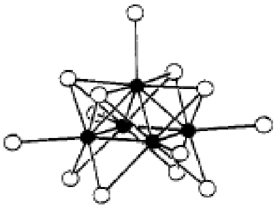
Monoclinic P 2_1/n




View along a-axis

* Kryuchkov, Koz'min. *Doklady Akademii Nauk*, **1982**, 266, p.127

Penta-nuclear Clusters

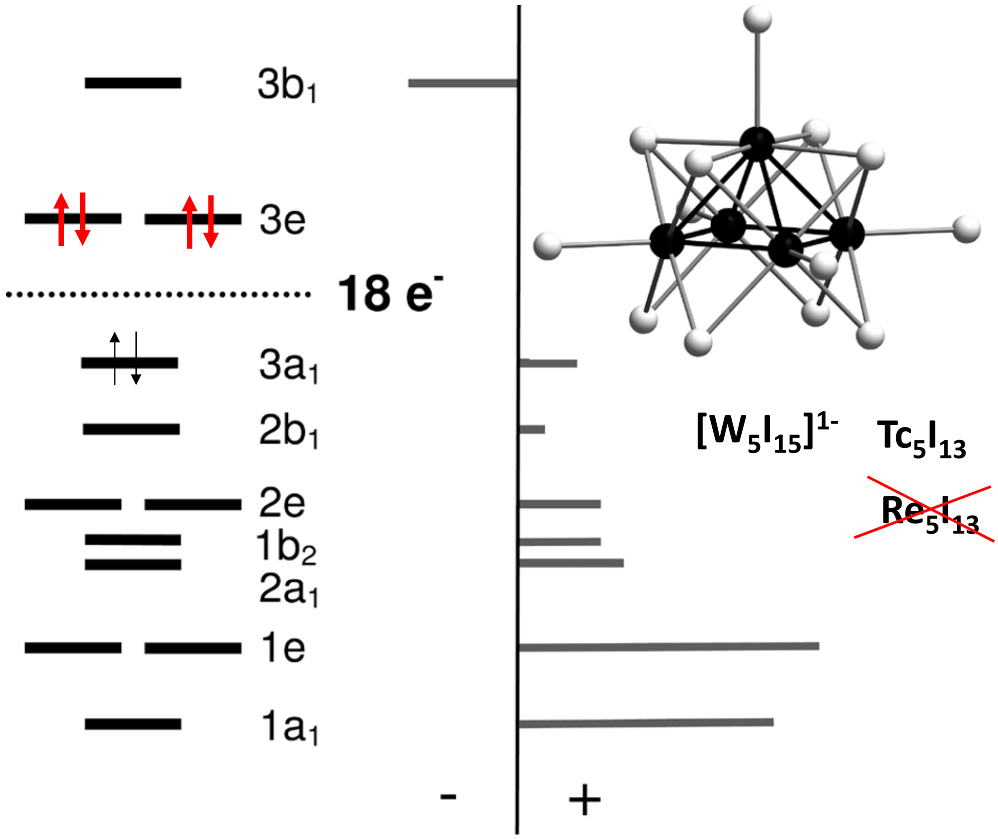


$[Mo_5Cl_{13}]^{2-}$
$[W_5I_{13}]^{1-}$
$[Tc_5I_{13}]$

	M-M	$Tc-X_{term}$	$Tc-X_{Bri}$	Reference
$(Tc_5I_8)I_5$	2.6470 – 2.6662(8)	2.7268 – 2.7670(8)	2.6851 – 2.7571(8)	This Work
$[Mo_5Cl_8)Cl_5]^{2-}$	2.602 – 2.563(3)	2.418 – 2.440	2.434 – 2.473	Jödden et al. 1975
$[(W_5I_8)I_5]^-$	2.673 – 2.692 (1)	2.763 – 2.843 (2)	2.741 – 2.788(2)	Franolic et al. 1995
$\{[Tc_6(\mu\text{-}I)_6I_6]I_2\}^{3-}$	2.18(1), 2.67(1)	2.71(1)	2.61/2/	Grigoriev et al. 1993
$K[Tc_8(\mu\text{-}I)_8I_4]I$	2.164/3/,2.5308(8), 2.72/3/	2.731/12/	2.68/3/	This Work Kerlin, et al. 2014

K. Jödden, H. Schnering, H. Schäfer. *Angew. Chem., Int. Ed. Engl*. **1975**, 14, 570.
J. Franolic, J. Long, R. Holm. *J. Am. Chem. Soc.* **1995**, 117, 8139-8153.

M. S. Grigoriev, S. V. Kryuchkov, *Radiochim. Acta* **1993**, *63*, 187.
W. Kerlin, F. Poineau, P. Forster, K. R. Czerwinski, A. P. Sattelberger, *Inorg. Chimi, Acta*, **2014.**



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Conclusions

- New one-step synthesis route to Tc dimer species
  - In-situ hydrogen production from sodium borohydride
- Synthesize three new Tc-I species
  - $Tc_2(\mu\text{-}O_2CCH_3)_4I$
  - $K[Tc_8(\mu\text{-}I)_8I_4]I$
  - $Tc_5(\mu\text{-}I)_8I_5$
- Controlled hydrothermal reduction of $KTcO_4$ in acetic acid/MI (M = Na, K, H) for preferred product

Future Studies

- Uv-Vis spectrum of $Tc_2(\mu\text{-}O_2CCH_3)_4X$ core
  - Low temperature KBr pellet to observe δ - δ^* transition or other methods
- Computational Calculations
  - Magnetic Susceptibility
- What about?
  - $Tc_2(\mu\text{-}O_2CCH_3)_4F_2$
  - $Tc_2(\mu\text{-}O_2CCH_3)_4I_2$

Acknowledgements

- Ken Czerwinski, Paul Forster, Al Sattelberger, Frederic Poineau, Christos Malliakas
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  - Trevor Low, Julie Bertoia

- SISGR-Fundamental Chemistry of Technetium-99 Incorporated into Metal Oxide, Phosphate and Sulfide: Toward Stabilization of Low-Valent Technetium Contract No. 47824B Basic Energy Sciences, DOE

Thank you for your attention
Questions

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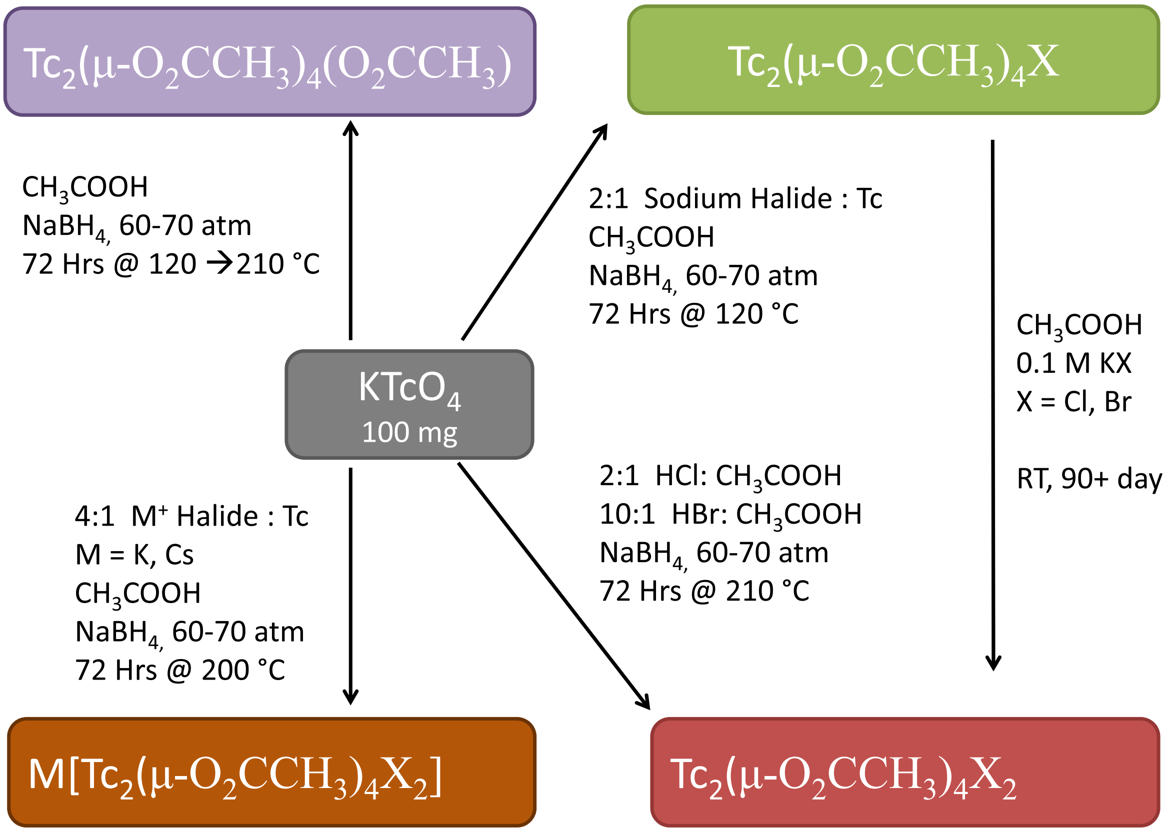


$Tc_2(\mu\text{-}O_2CCH_3)_4(O_2CCH_3)$

$Tc_2(\mu\text{-}O_2CCH_3)_4X$

CH_3COOH
$NaBH_{4,}$ 60-70 atm
72 Hrs @ 120 →210 °C

2:1 Sodium Halide : Tc
CH_3COOH
$NaBH_{4,}$ 60-70 atm
72 Hrs @ 120 °C

CH_3COOH
0.1 M KX
X = Cl, Br

RT, 90+ days

$KTcO_4$
100 mg

2:1 HCl: CH_3COOH
10:1 HBr: CH_3COOH
$NaBH_{4,}$ 60-70 atm
72 Hrs @ 210 °C

4:1 M^+ Halide : Tc
M = K, Cs
CH_3COOH
$NaBH_{4,}$ 60-70 atm
72 Hrs @ 200 °C

$M[Tc_2(\mu\text{-}O_2CCH_3)_4X_2]$

$Tc_2(\mu\text{-}O_2CCH_3)_4X_2$

Synthesis: $M[Tc_2(\mu\text{-}O_2CCH_3)_4X_2]$

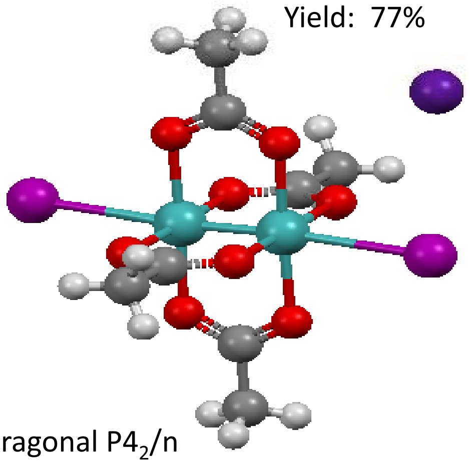
M = K, Cs X= Br, I

$$KTcO_4 + CsI + HC_2H_3O_2 + NaBH_4 \rightarrow Cs[Tc_2(\mu\text{-}O_2CCH_3)_4I_2]$$

- Conditions
  - 4:1 ratio CsI: TcO_4^-
  - 200 °C for 72 hrs

$K[Tc_2(\mu\text{-}O_2CCH_3)_4Cl_2]$
Spitsyn., et. al., 1980
Kozmin P. A., et. al., 1982

Synthesis from $K_3Tc_2Cl_8$



Yield: 77%

Space Group: Tetragonal $P4_2/n$
Unit Cell: a= 12.614(7) b= 12.614(7) c= 11.661(6)
V= 1855.36 Å^3

Comparing dihalide alkali salt Tc_2^{+5} core, Bond Order 3.5

	Tc-Tc (Å)	**Tc-O(eq)(Å)**	**Tc-L(ax) (Å)**	**Reference**
†K[$Tc_2(\mu\text{-}O_2CCH_3)_4Cl_2$] Chloro anion	2.126 (5)	2.071 (3)	2.589 (1)	Kozmin et. al. 1982
K[$Tc_2(\mu\text{-}O_2CCH_3)_4Br_2$] Bromo anion	2.1274 (3)	2.064 (13)	2.7467 (2)	This work
Cs[$Tc_2(\mu\text{-}O_2CCH_3)_4Br_2$] Bromo anion	2.1298 (3)	2.065 (13)	2.7453 (3)	This Work
Cs[$Tc_2(\mu\text{-}O_2CCH_3)_4I_2$] Iodo anion	2.1275 (3)	2.065 (13)	2.9813 (3)	This work
ǂ$Tc_2(\mu\text{-}O_2CCH_3)_4Cl_2$ $Tc_2(\mu\text{-}O_2CCH_3)_4Br_2$	2.1758 (3) 2.1763 (3)	2.0211 (12) 2.0223 (14)	2.5078 (4) 2.6555 (3)	Kerlin et. al. 2013 This work

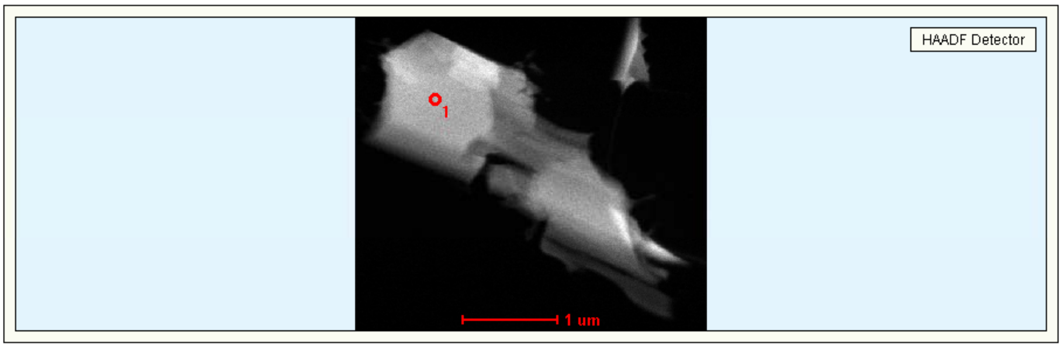
†P.A Koz'man, T.B. Larina, and M.D. Suraazhskaya, *Koord. Khim*. **1982**, 8, 851.

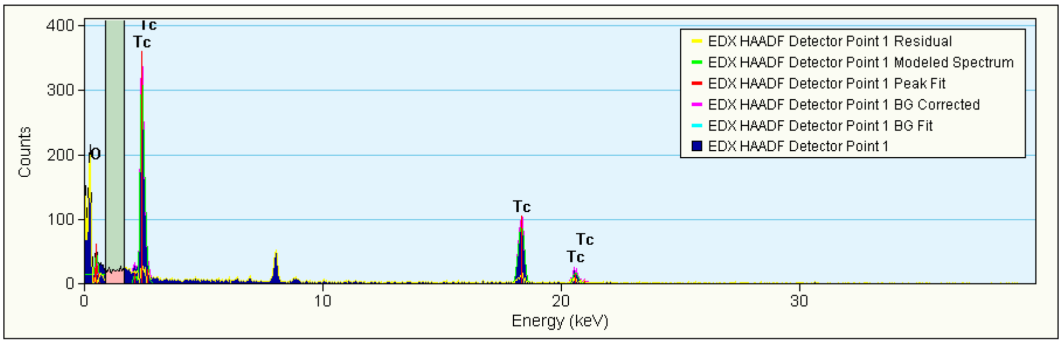
‡ P.A Koz'man, T.B. Larina, and M.D. Suraazhskaya, *Koord. Khim*. **1981**, 7, 1719. ‡ P.A Koz'man, T.B. Larina, and M.D. Suraazhskaya, *Koord. Khim*. **1983**, 9, 1114.

ǂ W.M. Kerlin, F. Poineua, P. Forster, K. R. Czerwinski, A. P. Sattelberger, Polyhedron, **2013,** 58, 115.

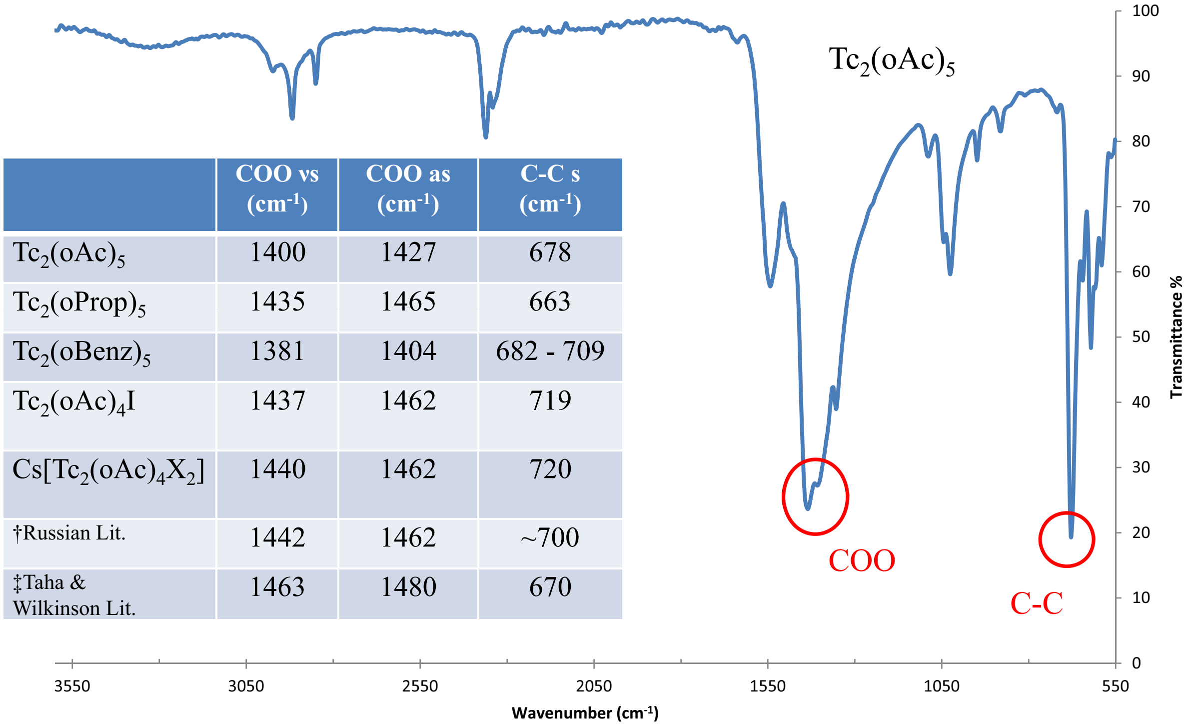
TEM-EDX of Crystalline Product

- Fluoride not present in sample



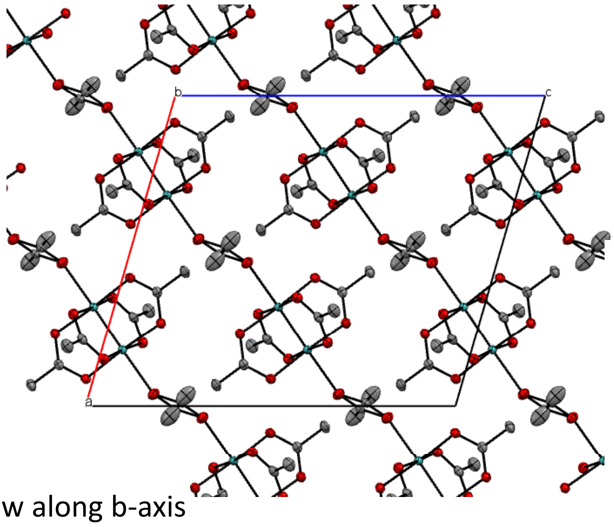


Carboxylate IR Frequencies



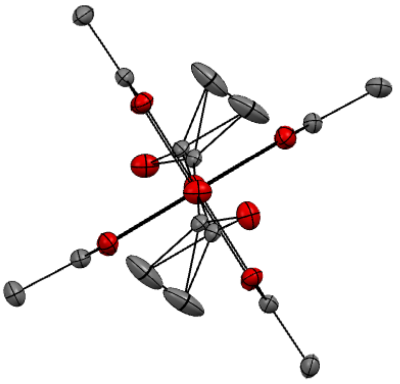
	COO vs (cm^{-1})	COO as (cm^{-1})	C-C s (cm^{-1})
$Tc_2(oAc)_5$	1400	1427	678
$Tc_2(oProp)_5$	1435	1465	663
$Tc_2(oBenz)_5$	1381	1404	682 - 709
$Tc_2(oAc)_4I$	1437	1462	719
$Cs[Tc_2(oAc)_4X_2]$	1440	1462	720
†Russian Lit.	1442	1462	~700
‡Taha & Wilkinson Lit.	1463	1480	670

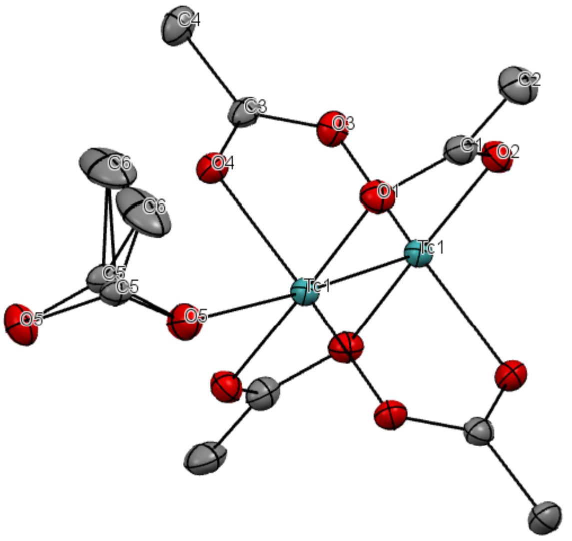
†V.I. Spitsyn, B. Baierl, S.V. Kryuchkov, A.F. Kuzina, and M. Varen, *Dokl. Akad. Nauk*. **1981**, 256, 608
‡F. Taha and G. Wilkinson. J. Chem. Soc. 5406 (**1963**)



View along b-axis

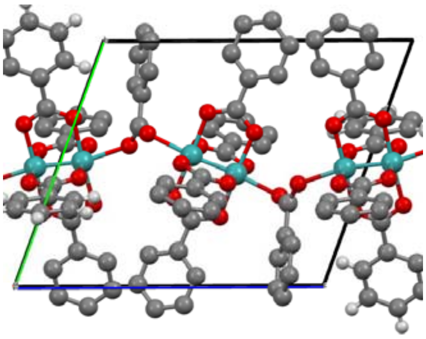
$Tc_2(\mu\text{-}O_2CCH_3)_4\text{-}\eta\text{-}O_2CCH_3$

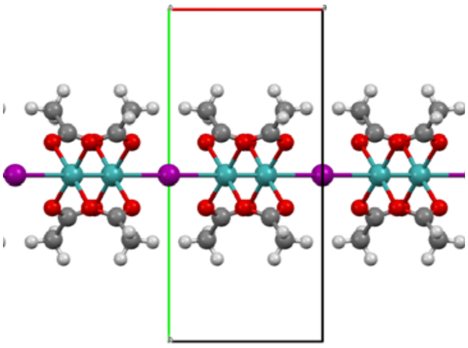




Tc-Tc-O = 176.65(3) °

Single Crystal –XRD Polymeric Chains





- $Tc_2(\mu\text{-}O_2CCH_3)_4\text{-}\eta\text{-}O_2CCH_3$
  - Monoclinic Cc
- $Tc_2(\mu\text{-}O_2CCH_2CH_3)_4\text{-}\eta\text{-}O_2CCH_2CH_3$
  - Orthorhombic $P2_12_12_1$
- $Tc_2(\mu\text{-}O_2CC_6H_5)_4\text{-}\eta\text{-}O_2CC_6H_5$
  - Triclinic P-1
- † $Tc_2(\mu\text{-}O_2CCH_3)_4\text{-}\eta\text{-}Cl$
  - Monoclinic C2/c Tc-Cl-Tc : 120ºC
- ‡ $Tc_2(\mu\text{-}O_2CCH_3)_4\text{-}\eta\text{-}Br$
  - Monoclinic C2/m Tc-Br-Tc : 180ºC
- $Tc_2(\mu\text{-}O_2CCH_3)_4\text{-}\eta\text{-}I$
  - Monoclinic C2/m Tc-I-Tc: 180ºC

†P.A Koz'man, T.B. Larina, and M.D. Suraazhskaya, *Koord. Khim*. **1981**, 7, 1719.
‡ P.A Koz'man, T.B. Larina, and M.D. Suraazhskaya, *Koord. Khim*. **1983**, 9, 1114.

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$Cs[Tc_2(\mu\text{-}O_2CCH_3)_4I_2]$ Iodo anion	2.1275 (3)	2.065 (13)	2.9813 (3)	This work
ǂ$Tc_2(\mu\text{-}O_2CCH_3)_4Cl_2$ $Tc_2(\mu\text{-}O_2CCH_3)_4Br_2$	2.1758 (3) 2.1763 (3)	2.0211 (12) 2.0223 (14)	2.5078 (4) 2.6555 (3)	Kerlin et. al. 2013 This work

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‡ P.A Koz'man, T.B. Larina, and M.D. Suraazhskaya, *Koord. Khim*. **1981**, 7, 1719. ‡ P.A Koz'man, T.B. Larina, and M.D. Suraazhskaya, *Koord. Khim*. **1983**, 9, 1114.
ǂ W.M. Kerlin, F. Poineua, P. Forster, K. R. Czerwinski, A. P. Sattelberger, Polyhedron, **2013,** 58, 115.

In-Situ Study Of Minor And Major Phase Formation And Transformation In Tc Bearing Mineral Analogues with Carbonate Starting Components.

We have recently embarked on studies of the structure and magnetic properties of technetium oxides including $SrTcO_3$, $CaTcO_3$, $PbTcO_3$ and Co_2TcO_4 the majority of which were first reported by Muller et al in 1964. Our typical method of synthesis involves calcination of $NH_4[TcO_4]$ with the associated nitrates in an argon atmosphere at 700°C and then subsequent sintering at 1000°C. Recently in a discussion with collaborators we were told that they had produced Sr_2TcO_4 which is an analogue of the superconductor Sr_2RuO_4 at 500°C, a temperature well below the normal calcination temperature for these materials. The implications of this could be quite significant for the nuclear industry in the formation of Tcbearing materials. Un-separated nuclear waste when stored can reach temperatures of several hundred degrees due to radiogenic heating. This implies that minor phases could be formed in the presence of other fission products if Tc is freely available in waste-forms or if precursor materials are left to for a period before calcination. More importantly, it is also a possible pathway to novel Tc compounds produced at lower temperatures. We will report on the formation of various Tc mineral analogues starting from TcO_2 and carbonates and examine their stability at temperatures up to 1000 °C via Synchrotron XRD. The powder diffraction beamline at the Australian Synchrotron provides ample incident beam flux that allows us to use very small amounts of sample and so reduce the amount of radiation being dealt with to more than manageable levels. Additionally this strategy allows us to heat the sample in a sealed quartz capillary and also minimise the amount of waste that would be produced by heating several Tc containing compounds (each of which would weigh at least a gram each) to various temperatures and then examining them via laboratory XRD. Another advantage of Synchrotron XRD is that it enables us to determine the technetium and *A*-cation positions accurately which will then enable us to calculate the oxygen distances. The Tc to O distances are important due to the fact that Tc is tetrahedrally coordinated in some of these materials which is then related to the magnetic and other properties.

Australian Government

ansto

In-Situ Study Of Minor And Major Phase Formation And Transformation In Tc Bearing Mineral Analogues

Gordon Thorogood, Brendan Kennedy, Emily Reynolds,
Massey De Los Reyes and Helen Brand

First What is ANSTO

- Australian Nuclear Science and Technology Organisation.
- Started as the Australian Atomic Energy Commission (AAEC), in 1952, Lucas Heights site in 1958.
- Had two reactors HIFAR and MOATA.
- We almost built a nuclear power plant but it was abandoned due to cost in 1971.
- OPAL opened in 2007.
- Over 1000 employees, 40km SW of Sydney, 70 hectare campus.

First What is ANSTO

- One of our main activities is medical radioisotopes.
- 10,000 doses of nuclear medicine to 224 hospitals and clinics in Australia, per week.

Background of these Tc compounds

- Studies on the technetium oxides $SrTcO_3$, $CaTcO_3$, $PbTcO_3$ and Co_2TcO_4 first reported by Muller et al in 1964.
- We've recently become interested in the properties of these materials.

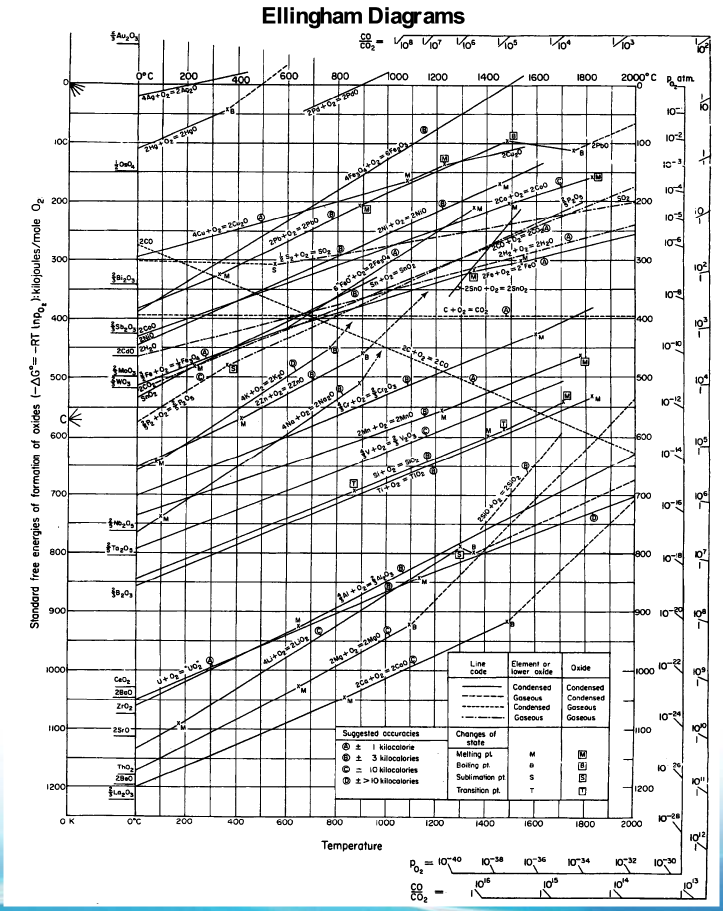
Compound Synthesis

- Our current standard method involves calcination of $NH_4[TcO_4]$ with nitrates in an argon atmosphere at 700° C and then sintering at 1000° C.
- We want to avoid temperatures above 1250° C due to Tc oxidising to 7+.
- What lead to this line of investigation was we have been trying to make $CdTcO_3$ via oxides as UNLV group without success (enough for neutron diffraction that is).

Our challenges

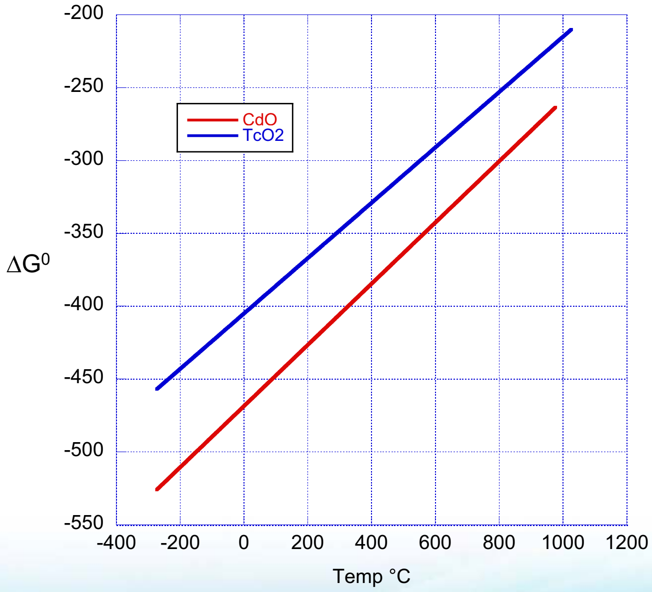
Some insight is required

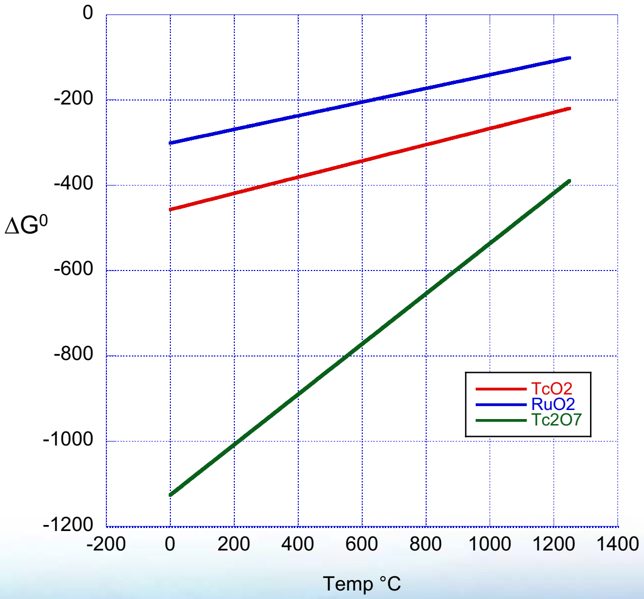
- At the Atalante 2012 conference Thomas Hartman reported that Sr_2TcO_4 which is an analogue of the superconductor Sr_2RuO_4 forms at 500° C.
- It's well below the normal calcination temperature for these materials.
- The implications of this could be quite significant. Is this phase A_2TcO_4 occurring in a lot of materials.



As per Wikipedia:
An Ellingham diagram is a graph showing the temperature dependence of the stability for compounds. This analysis is usually used to evaluate the ease of reduction of metal oxides and sulphides.
The Ellingham diagram plots the Gibbs free energy, reaction as a function of temperature

Make Your Own Ellingham Diagram





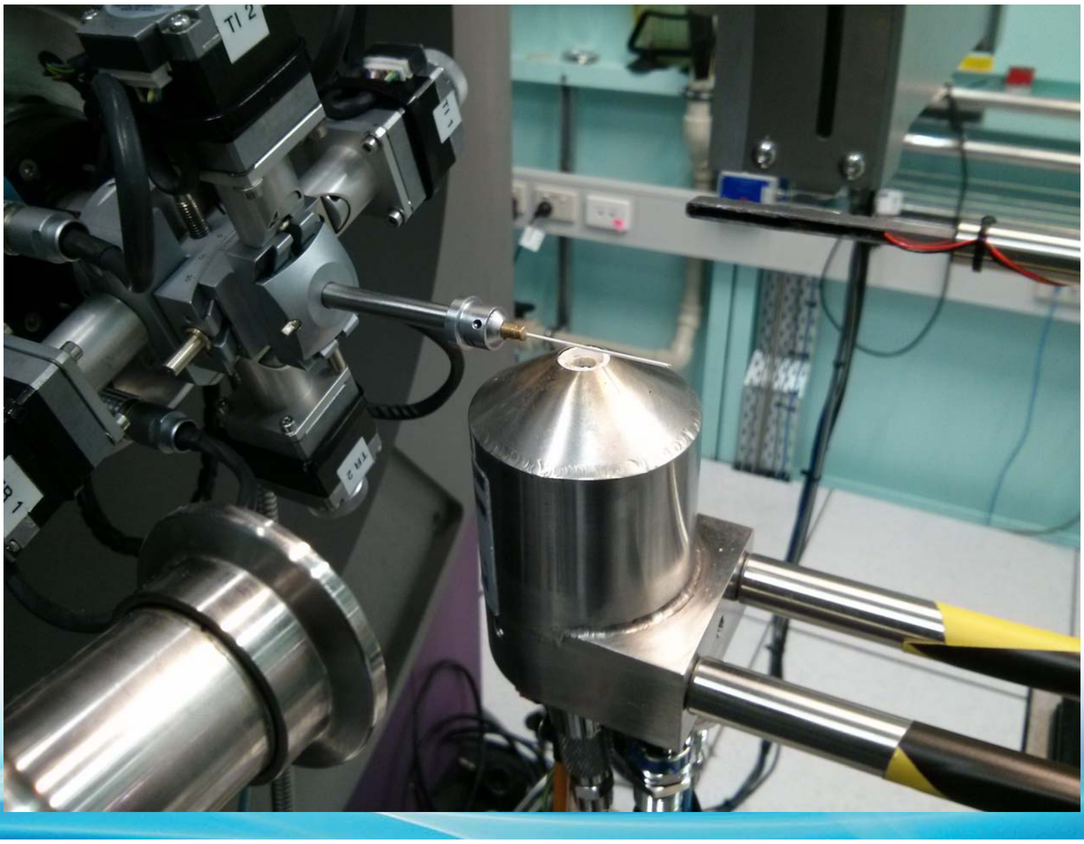
Something Might be Wrong With Our Furnace

- Ellingham diagram tells us we can make $CdTcO_3$ via oxides but we can't.
- So we either have a higher partial pressure of oxygen in our Argon or our thermocouple is reading incorrectly in the furnace.
- Solution in-situ XRD to see at what temp certain phases form.
- Problem it's Tc. Place it in sealed quartz capillaries and do the expt at the Synchrotron.
- Lets start with something simple.

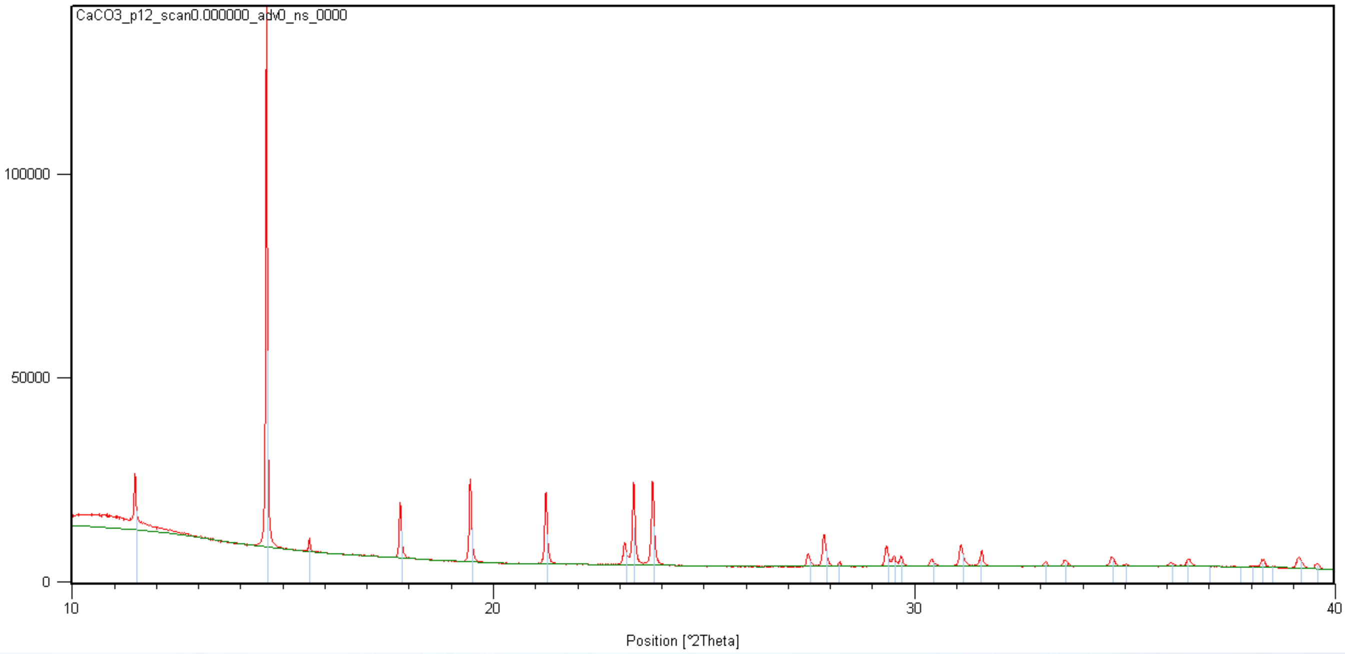
Australian Synchrotron Setup

Australian Synchrotron Setup

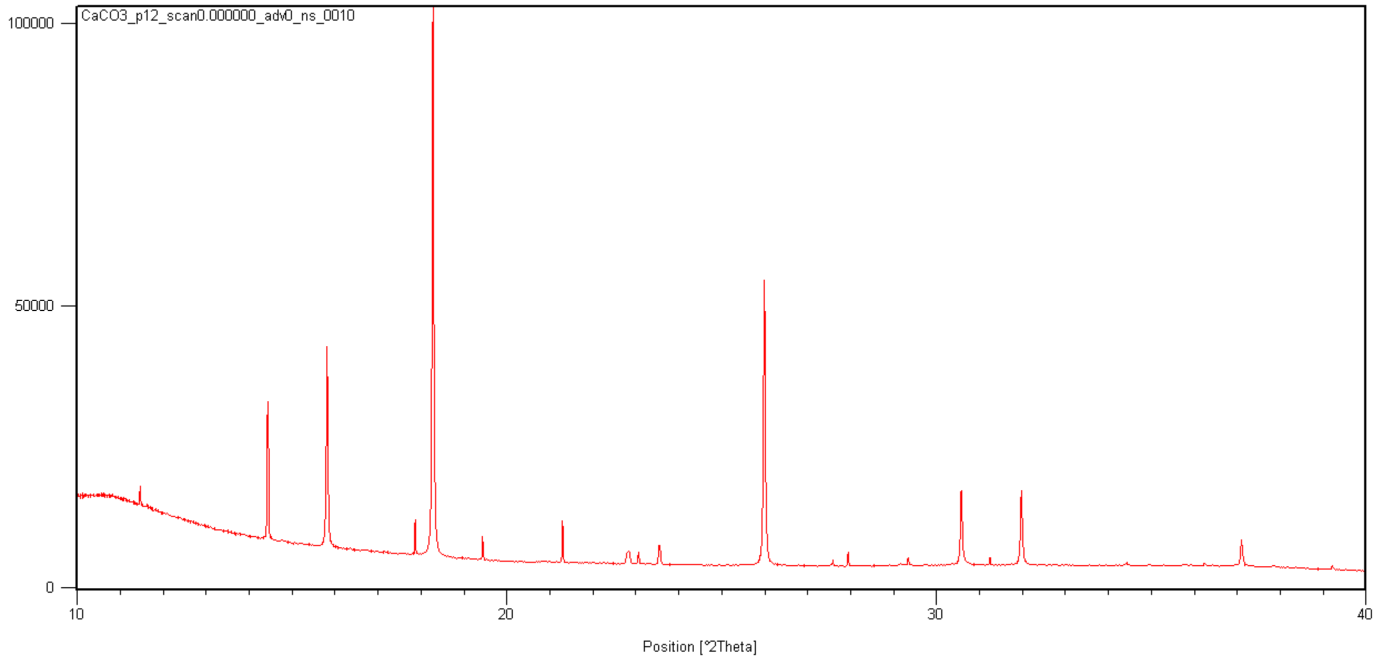
Australian Synchrotron Setup



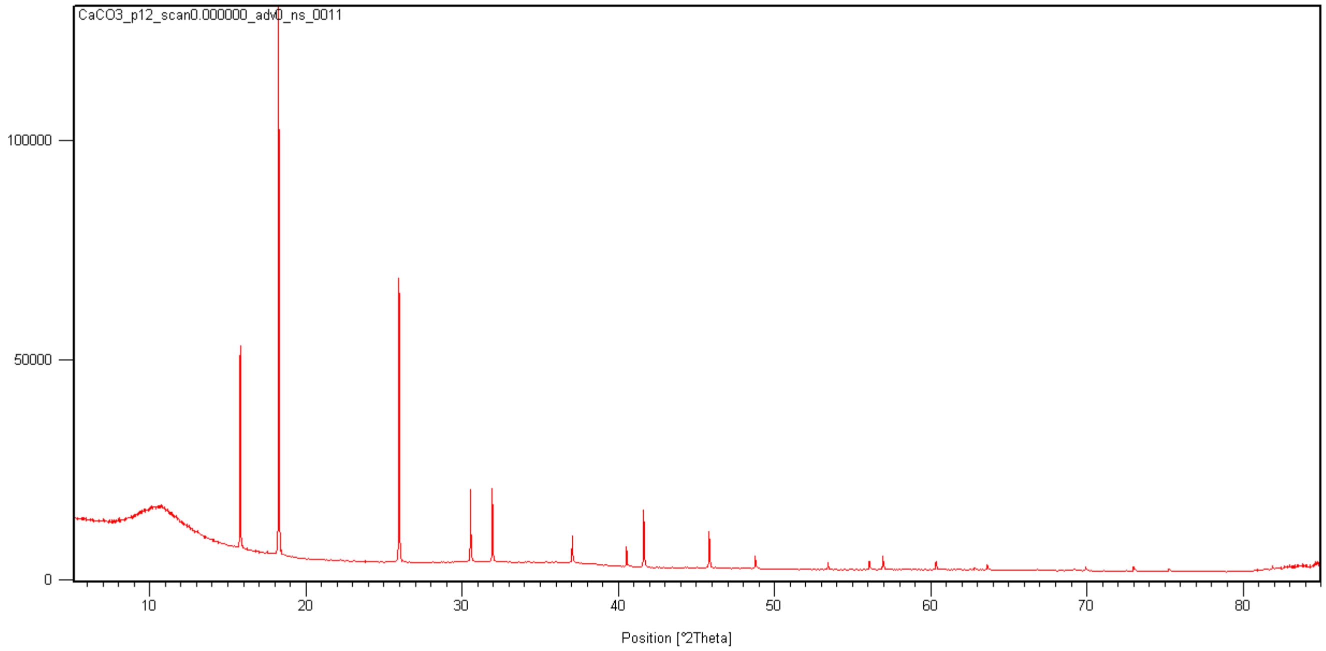
$CaCO_3$ (Calcite) 25° C, Decomp check



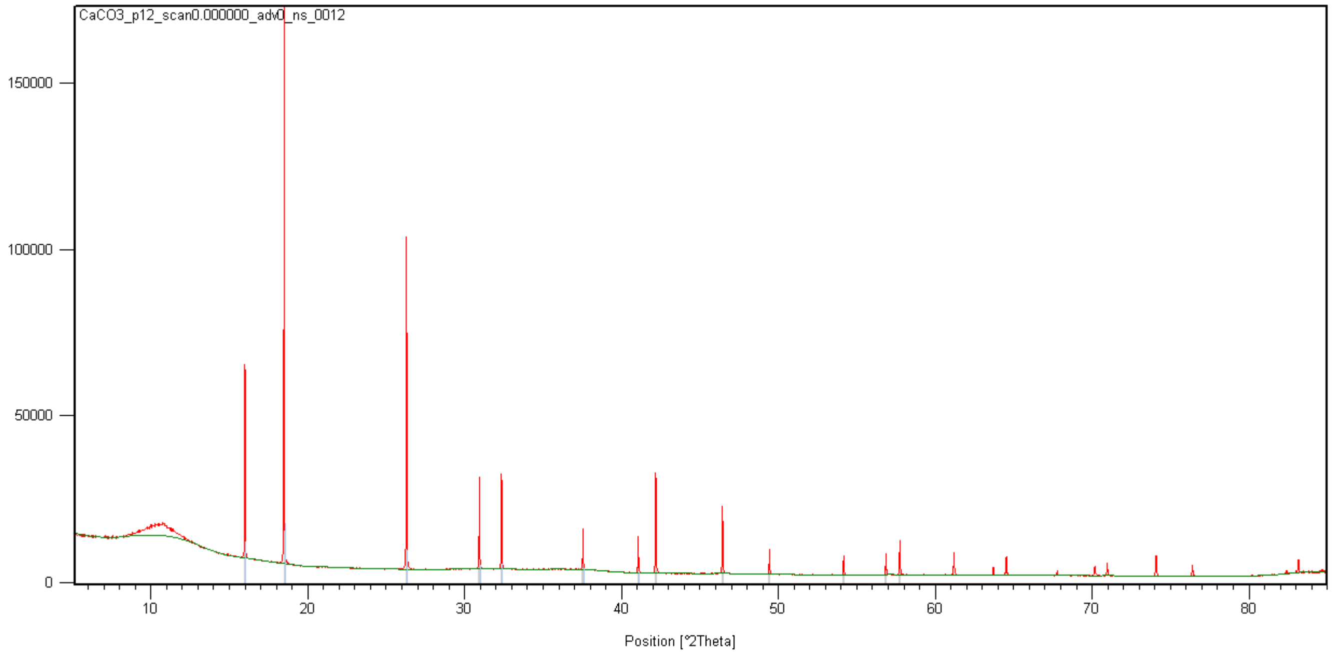
$CaCO_3$ 900° C



$CaCO_3$ 1000° C



CaO 25° C cooled



Role of partial pressure of CO_2

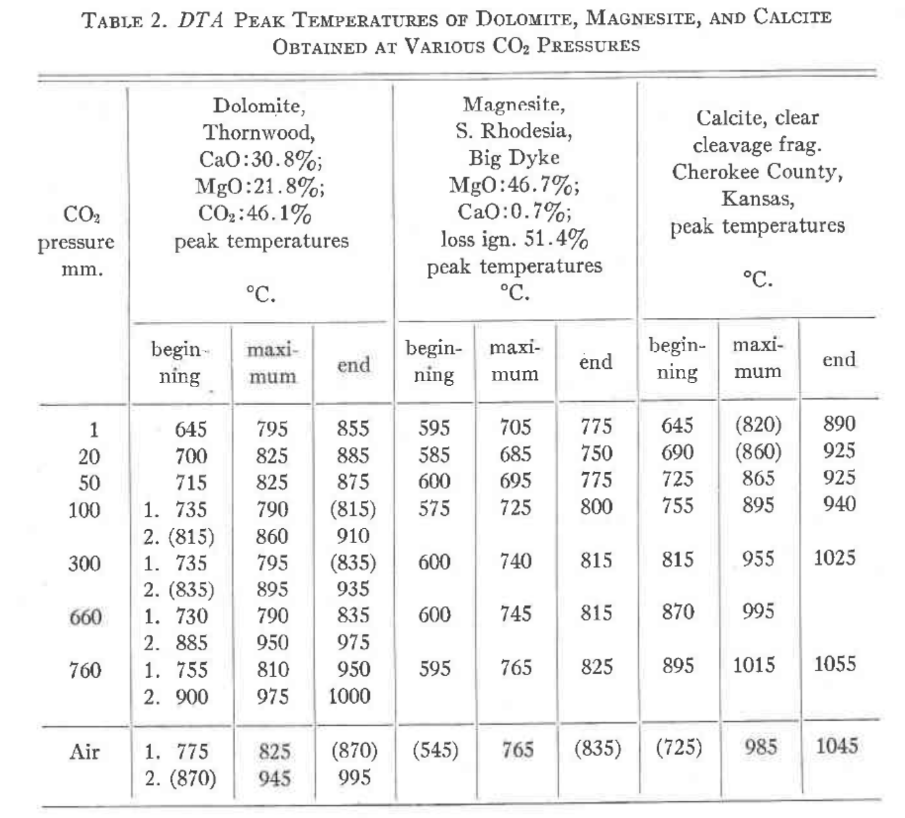


TABLE 2. *DTA* PEAK TEMPERATURES OF DOLOMITE, MAGNESITE, AND CALCITE OBTAINED AT VARIOUS CO_2 PRESSURES

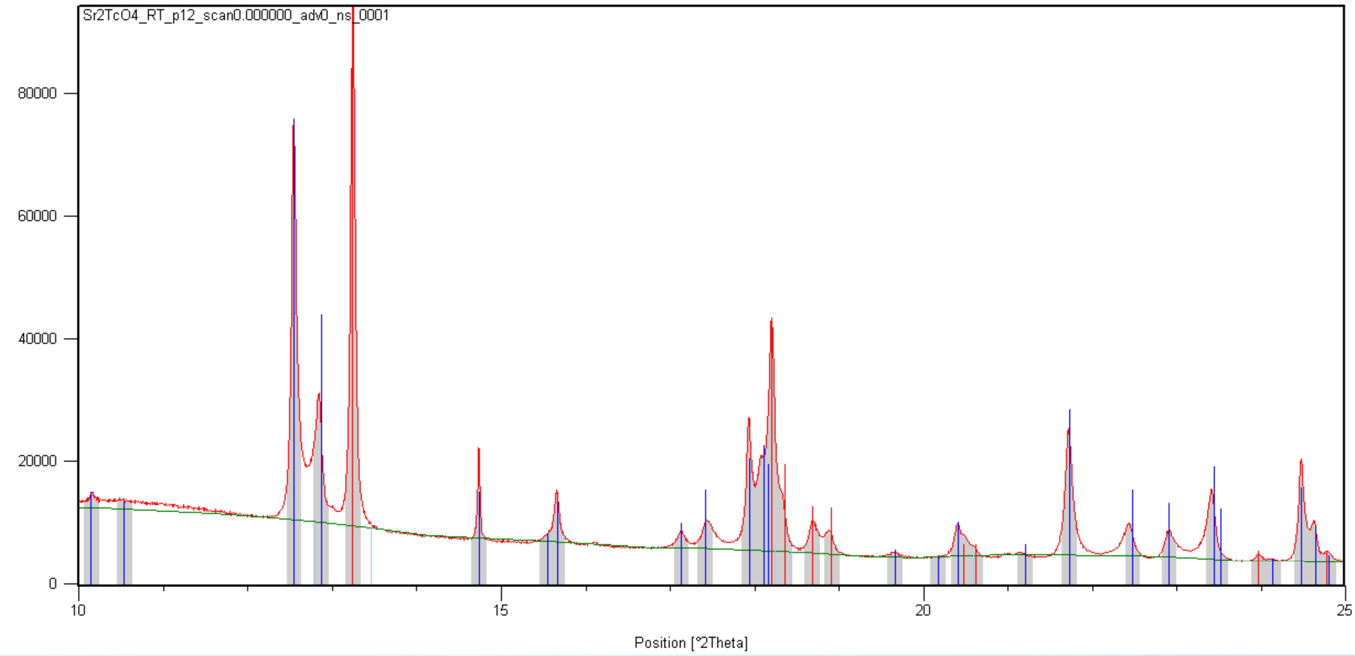
CO_2 pressure mm.	Dolomite, Thornwood, CaO:30.8%; MgO:21.8%; CO_2:46.1% peak temperatures °C.			Magnesite, S. Rhodesia, Big Dyke MgO:46.7%; CaO:0.7%; loss ign. 51.4% peak temperatures °C.			Calcite, clear cleavage frag. Cherokee County, Kansas, peak temperatures °C.		
	beginning	maximum	end	beginning	maximum	end	beginning	maximum	end
1	645	795	855	595	705	775	645	(820)	890
20	700	825	885	585	685	750	690	(860)	925
50	715	825	875	600	695	775	725	865	925
100	1. 735	790	(815)	575	725	800	755	895	940
	2. (815)	860	910						
300	1. 735	795	(835)	600	740	815	815	955	1025
	2. (835)	895	935						
660	1. 730	790	835	600	745	815	870	995	
	2. 885	950	975						
760	1. 755	810	950	595	765	825	895	1015	1055
	2. 900	975	1000						
Air	1. 775	825	(870)	(545)	765	(835)	(725)	985	1045
	2. (870)	945	995						

Robert. A. W. Haul et.al 1951

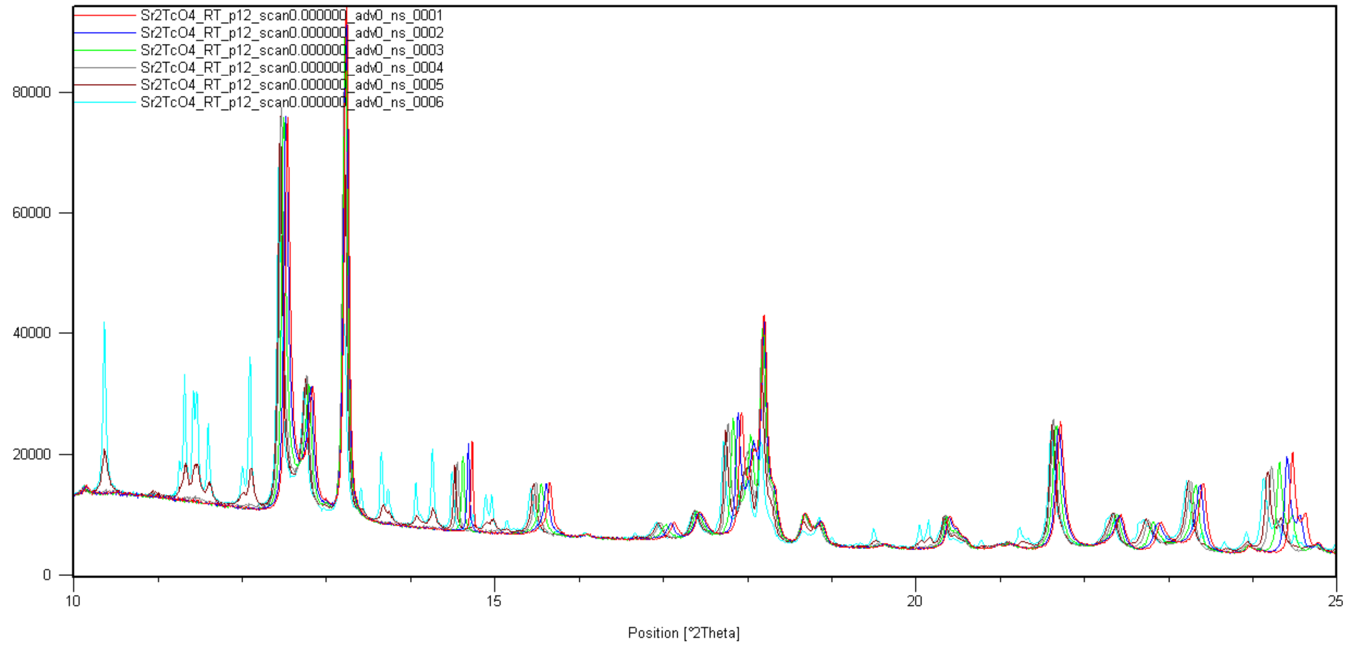
So How About Those Pesky A_2TcO_4's?

- We decided to go with what we know.
- As we have experience of $SrTcO_3$ we thought try Sr_2TcO_4, seeing Thomas had made it.
- Next a little further from what we know, we have experience with $CaTcO_3$ so Ca_2TcO_4.

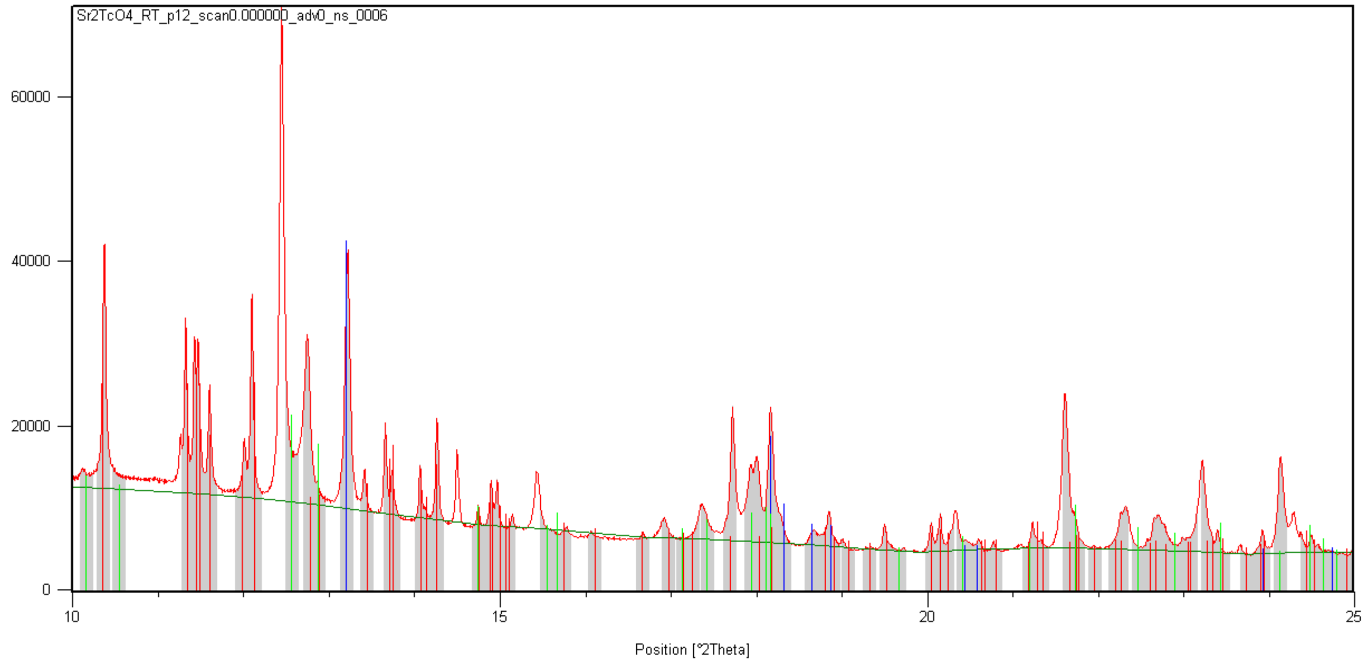
Sr_2TcO_4



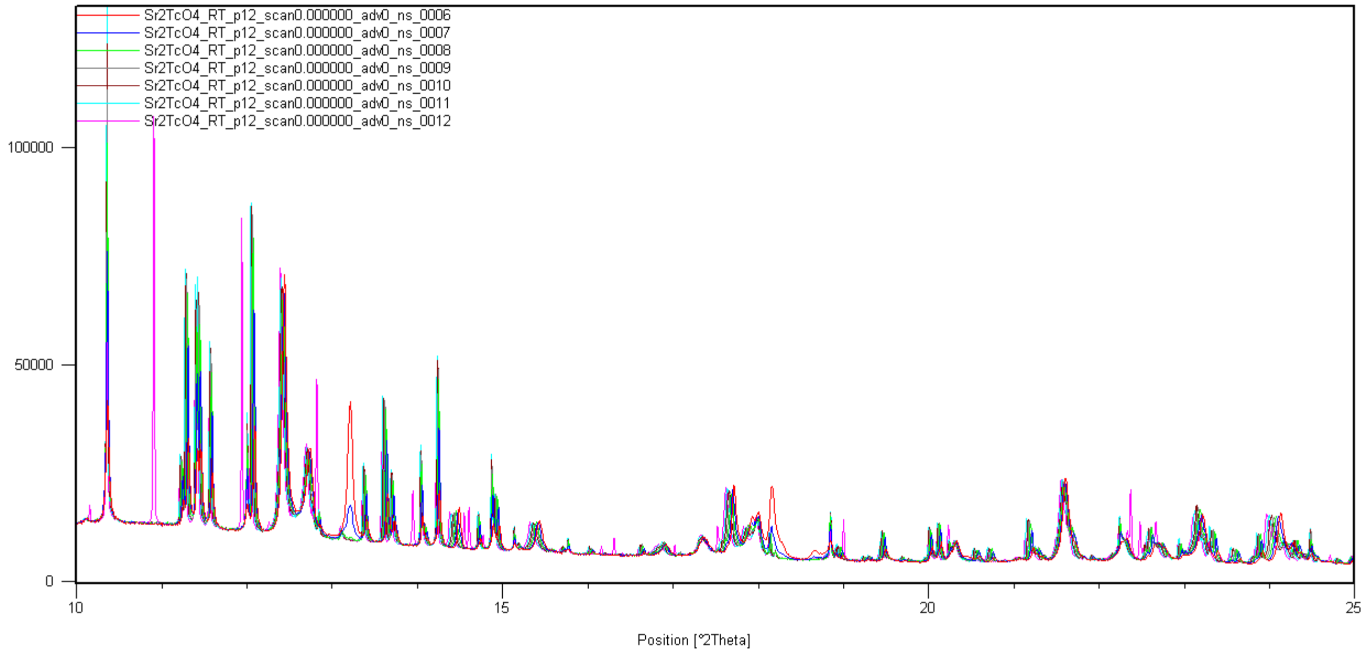
Sr_2TcO_4



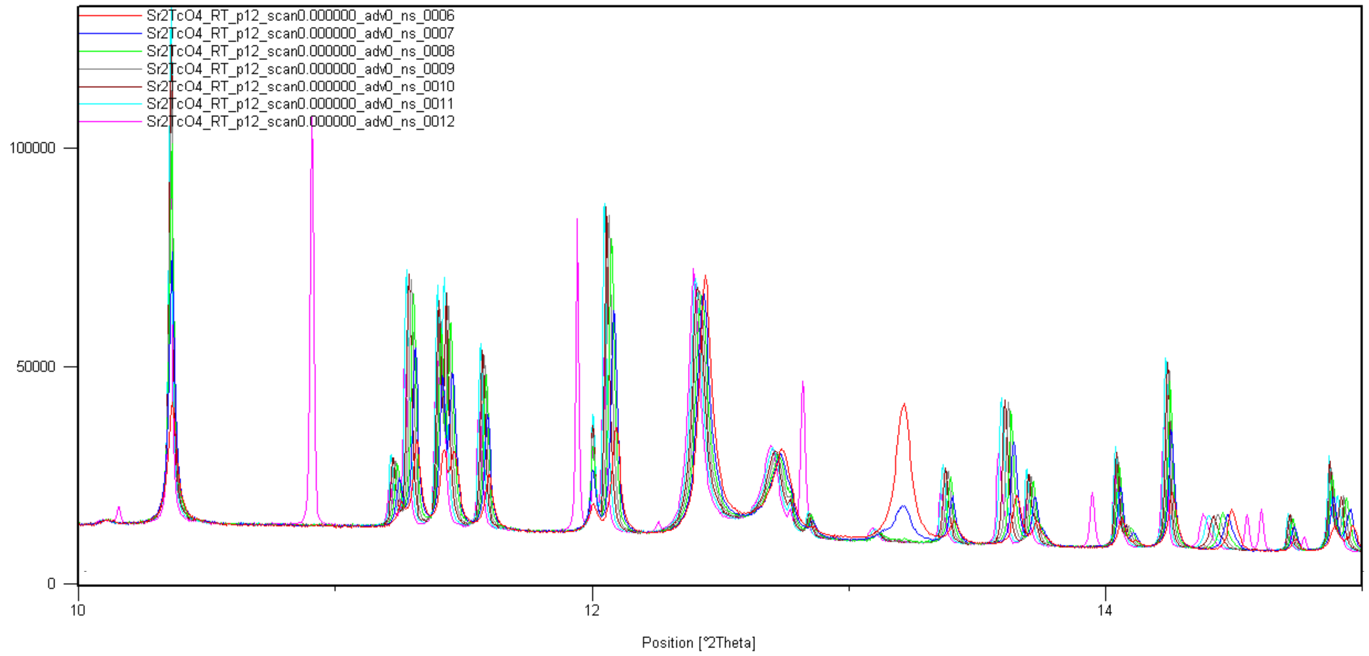
Sr_2TcO_4



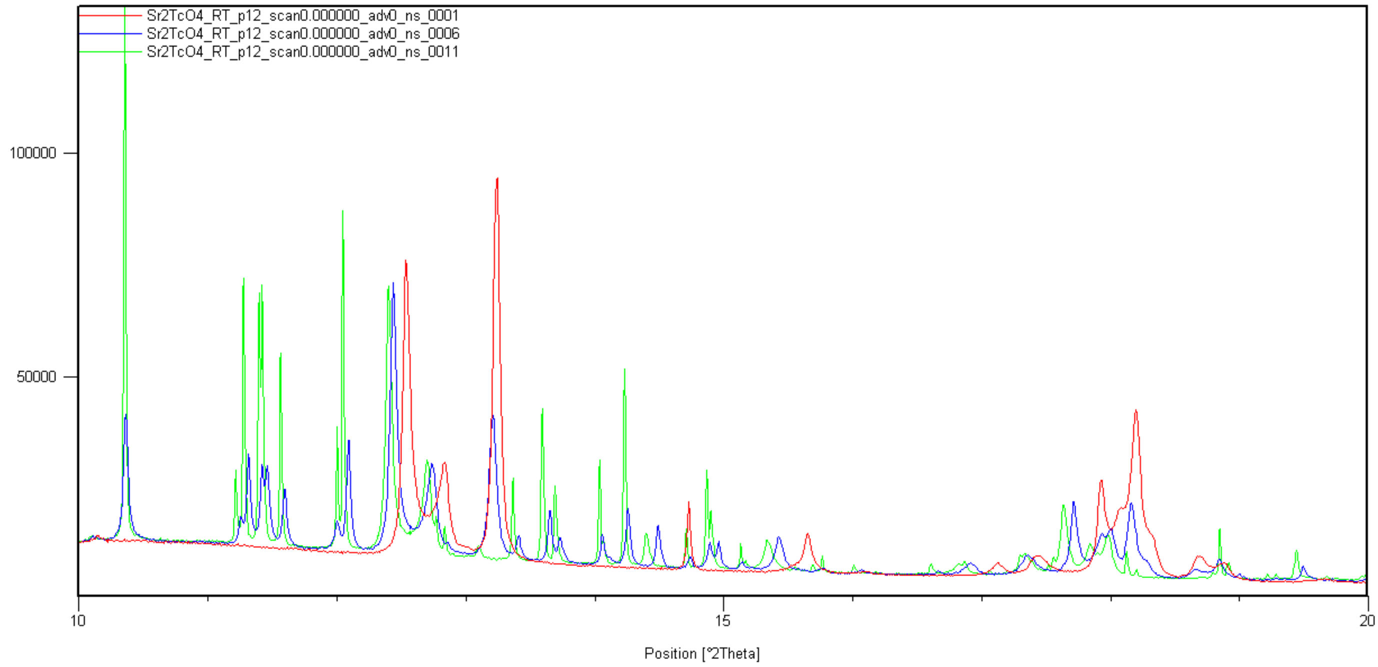
Sr_2TcO_4



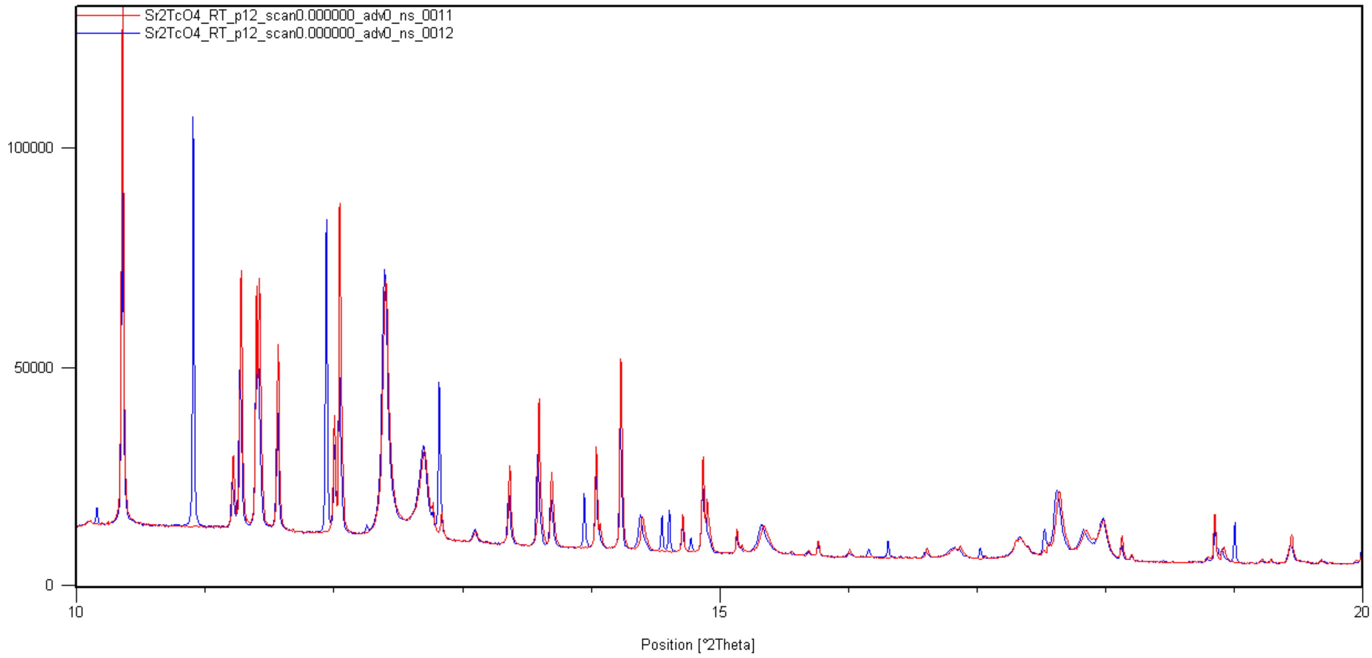
Sr_2TcO_4



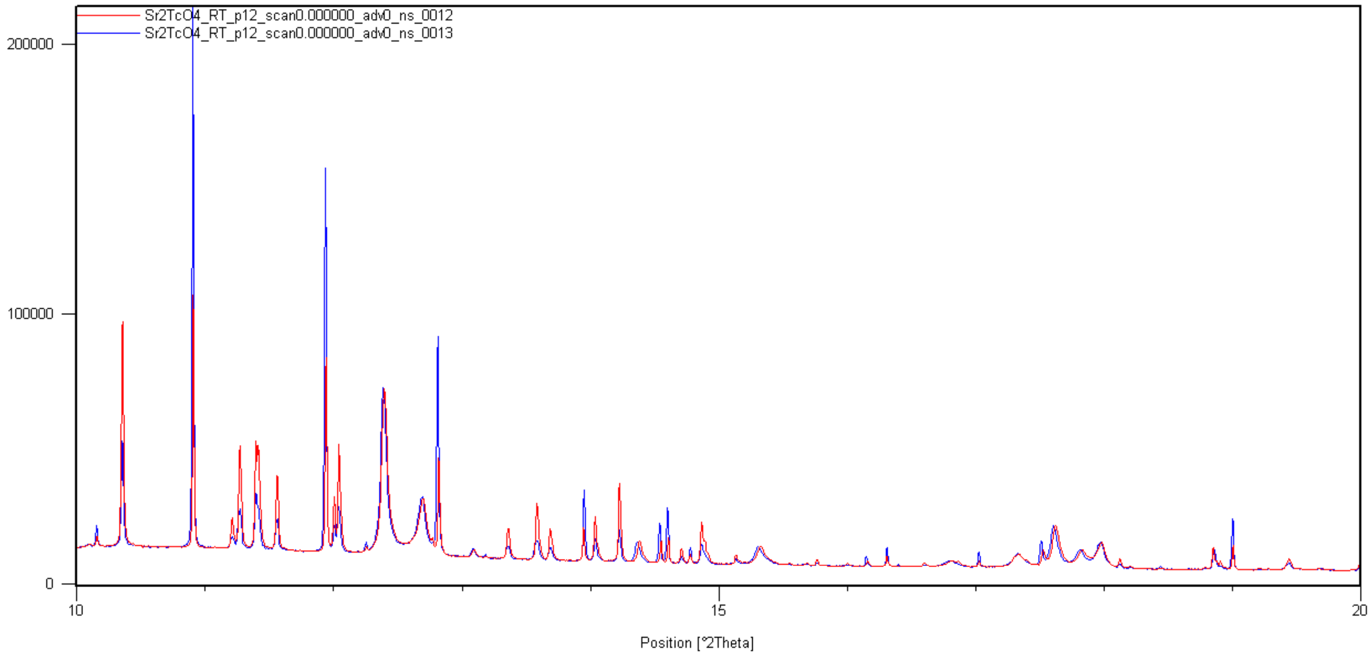
Sr_2TcO_4



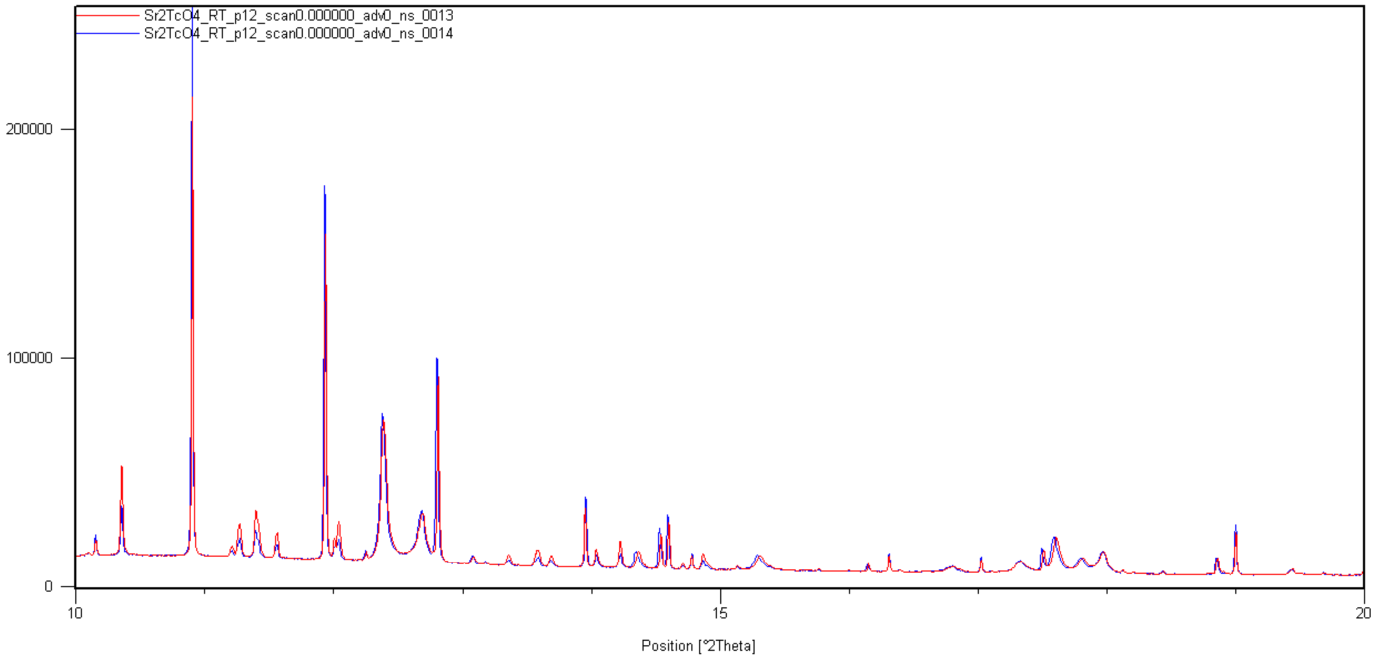
Sr_2TcO_4



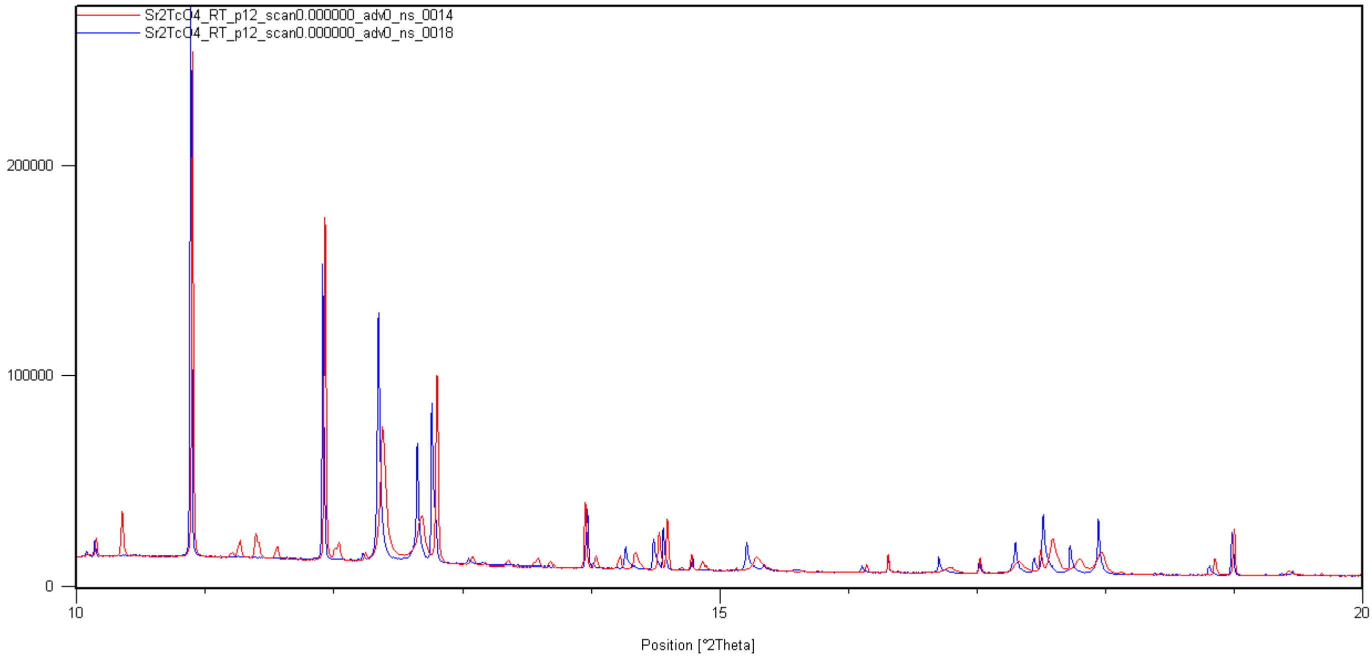
Sr_2TcO_4



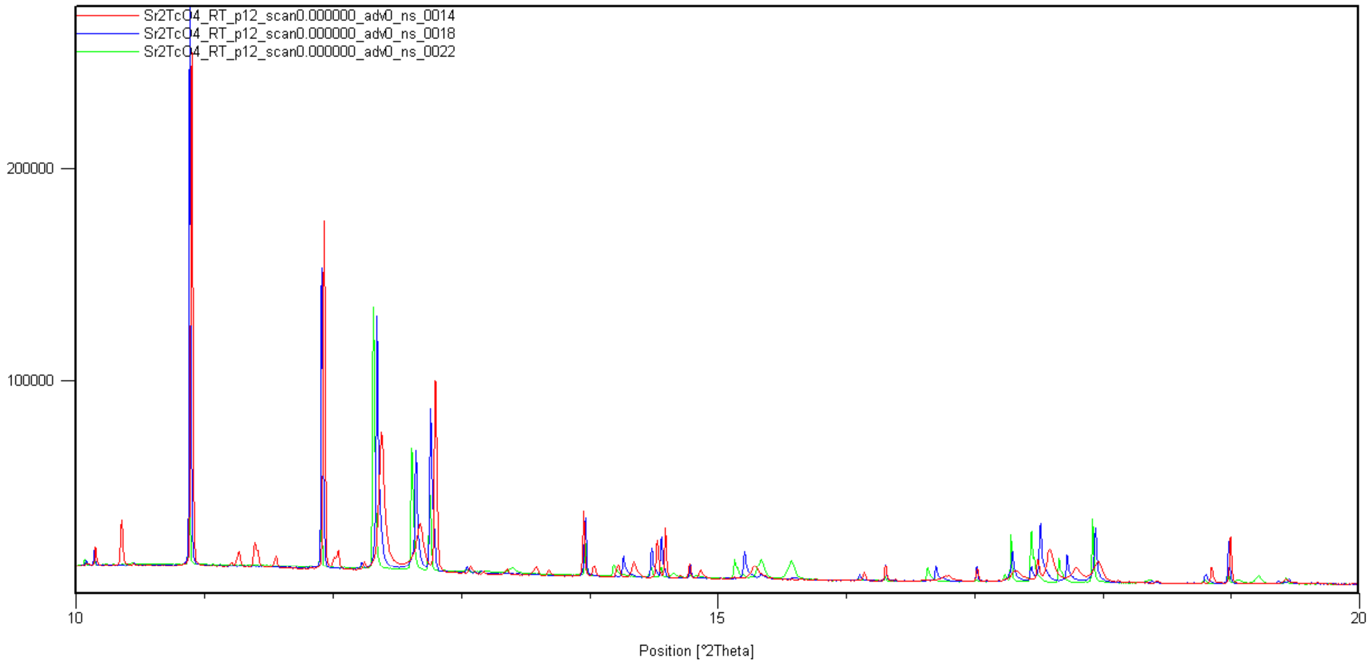
Sr_2TcO_4



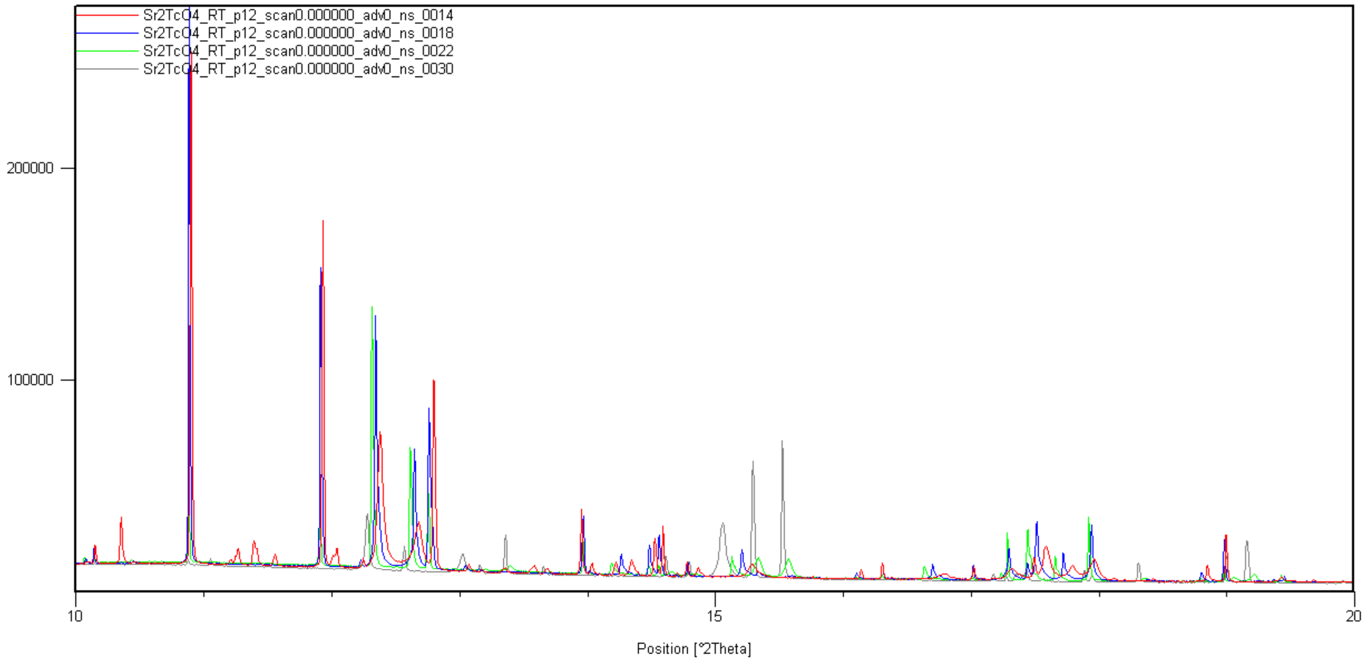
Sr_2TcO_4



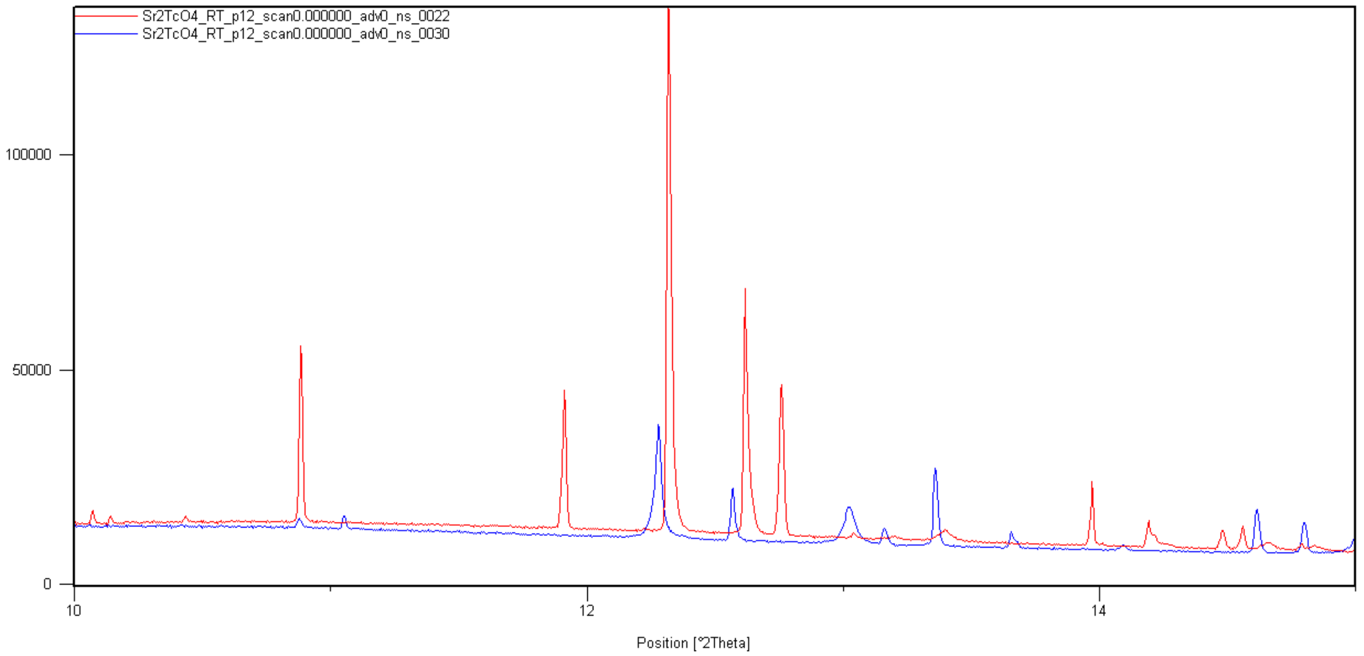
Sr_2TcO_4



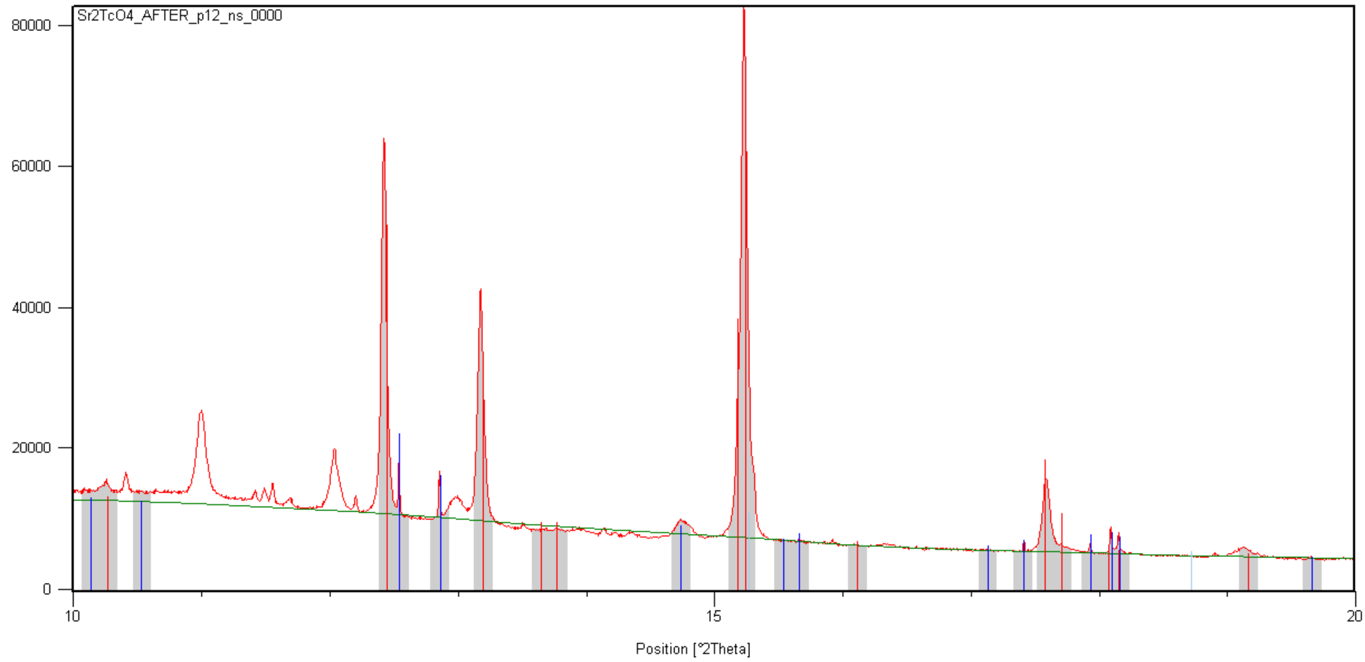
Sr_2TcO_4



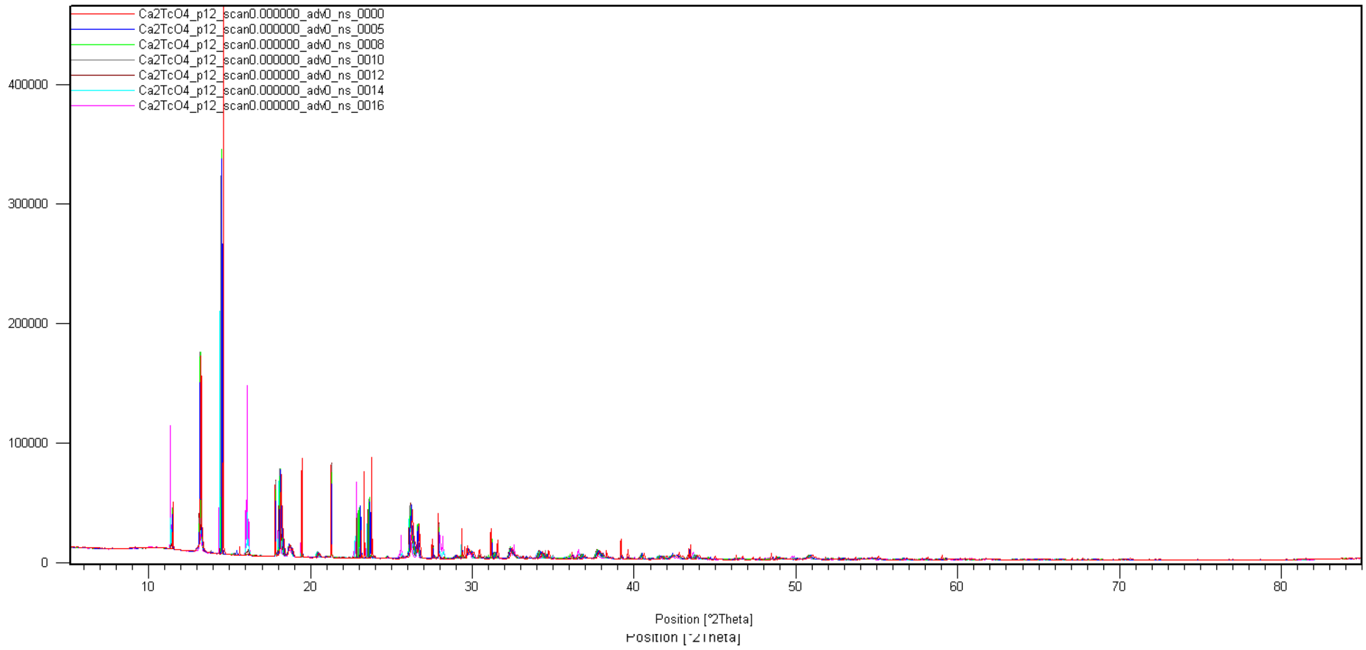
Sr_2TcO_4



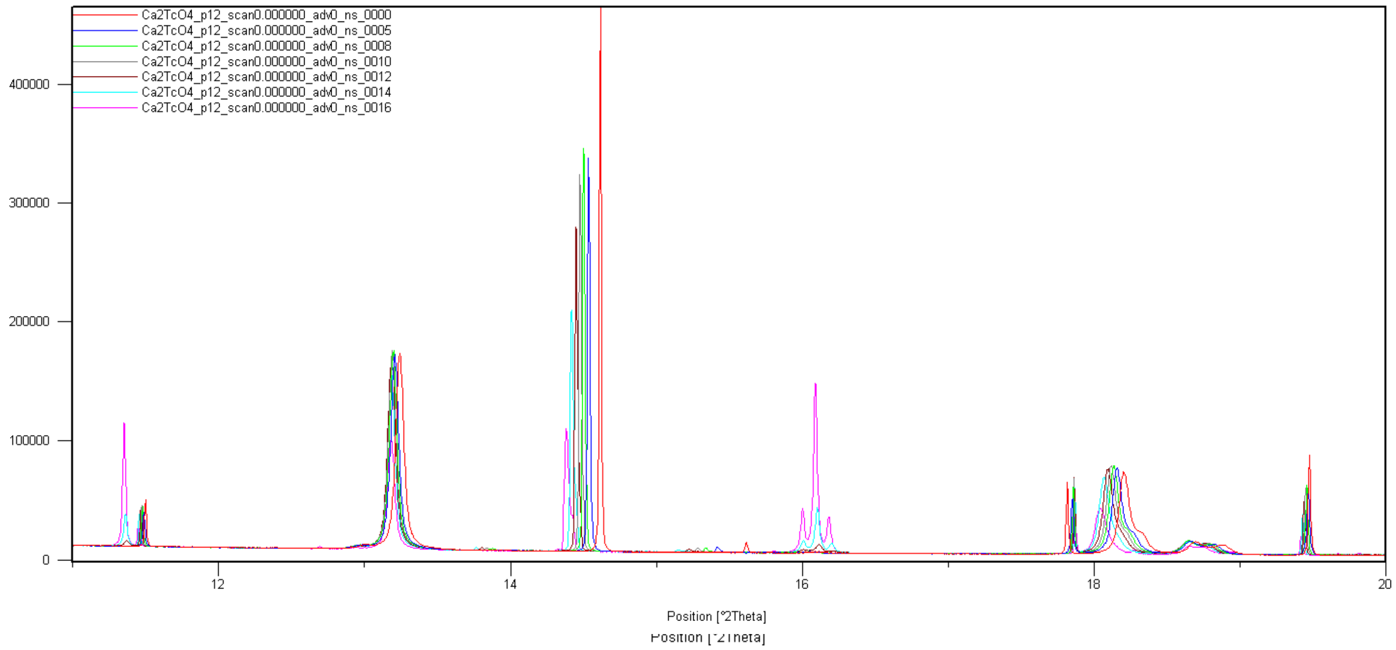
Sr_2TcO_4 after heating ???



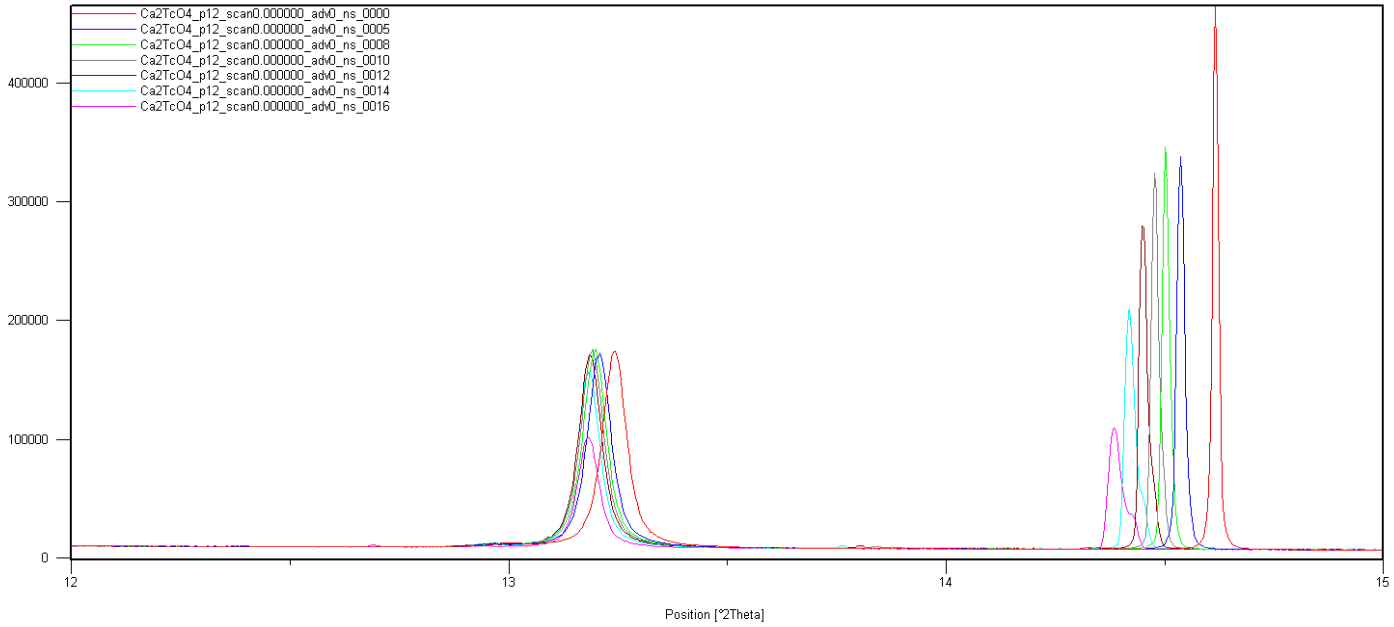
One Step Up Ca_2TcO_4



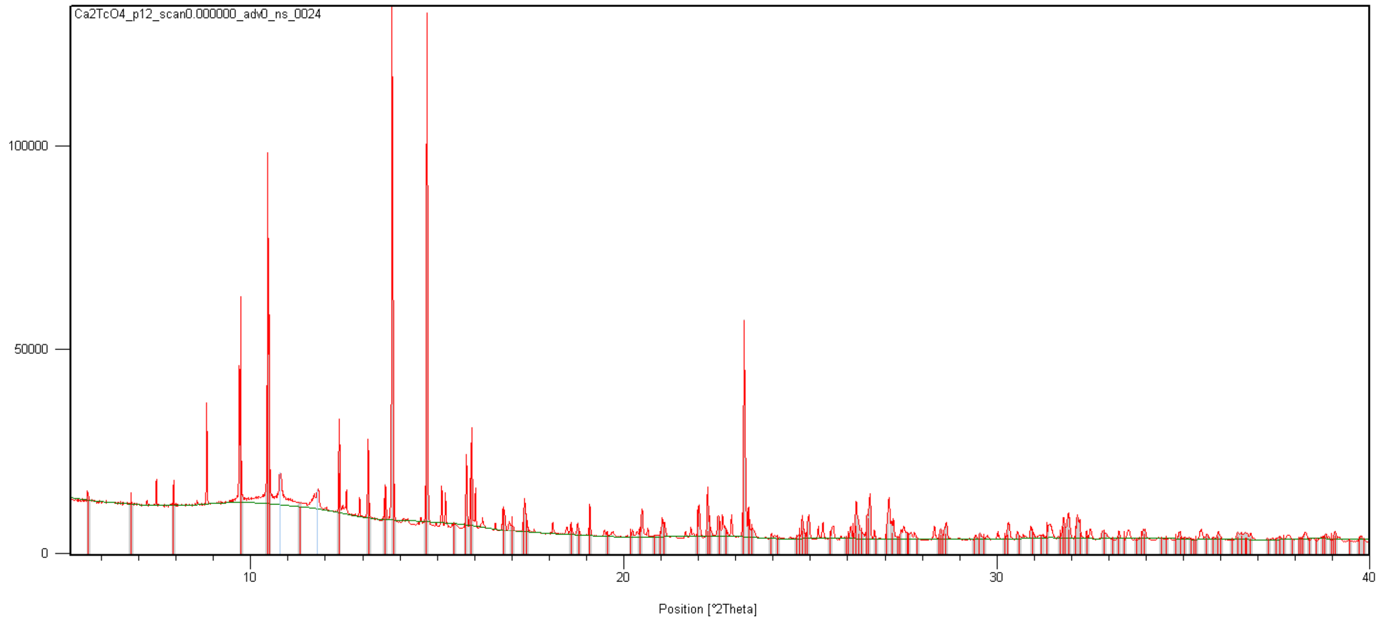
Zoom in a Little, Ca_2TcO_4



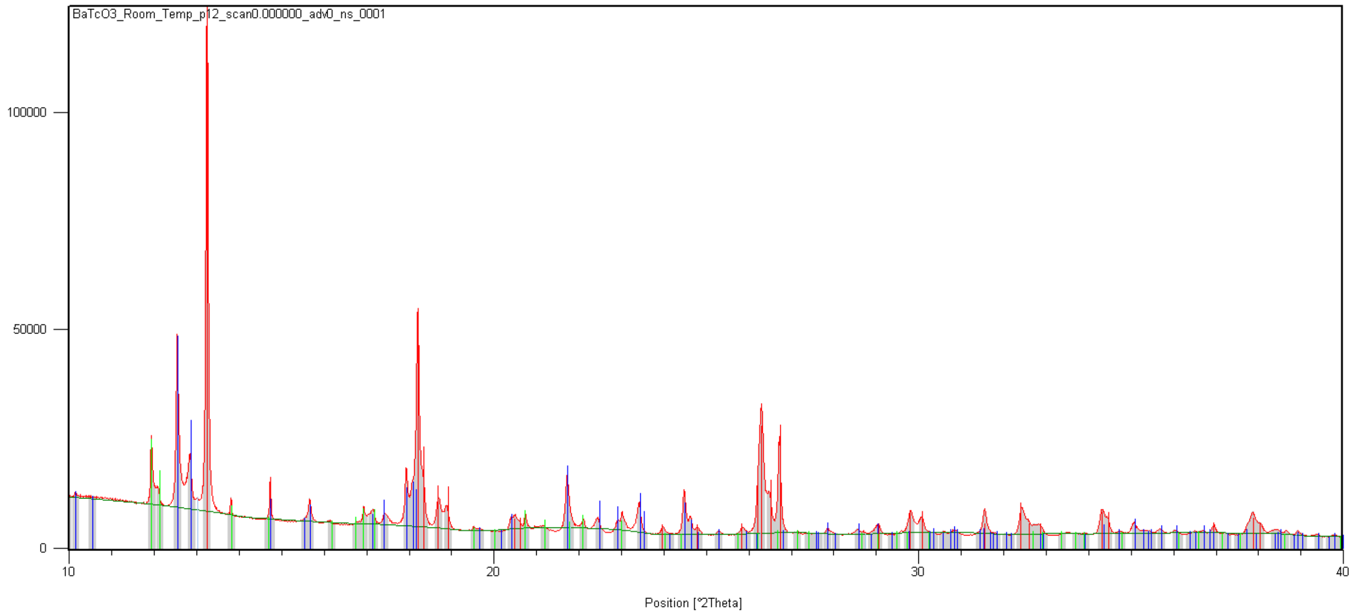
A Closer Look Again, Ca_2TcO_4



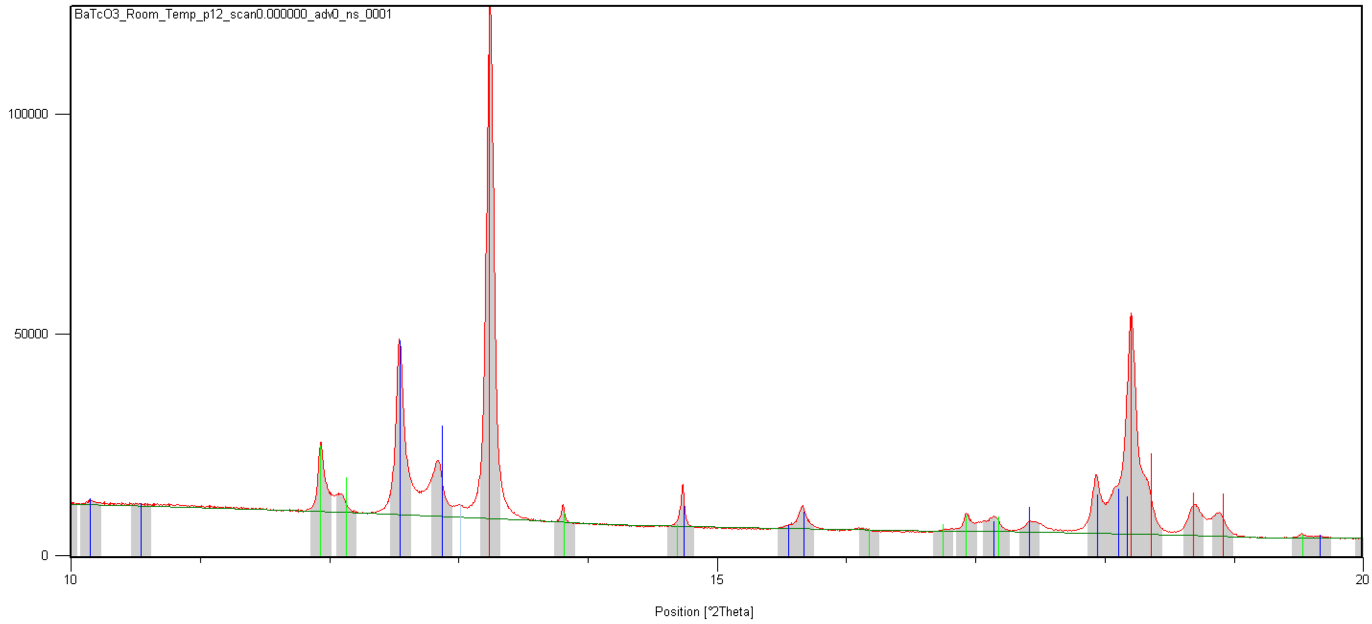
After 1000C Close to $Ca_5Re_3O_{14.74}$ Ca_2TcO_4



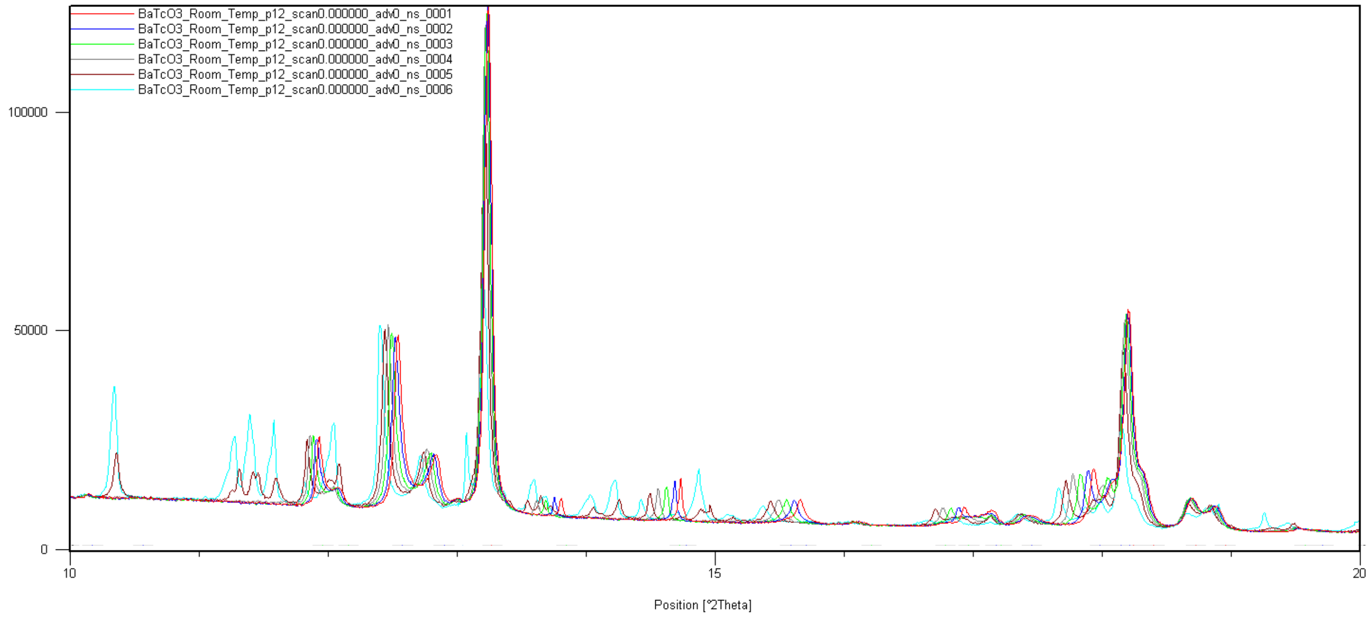
Lets Go Further $Sr_{0.9}Ba_{0.1}TcO_3$



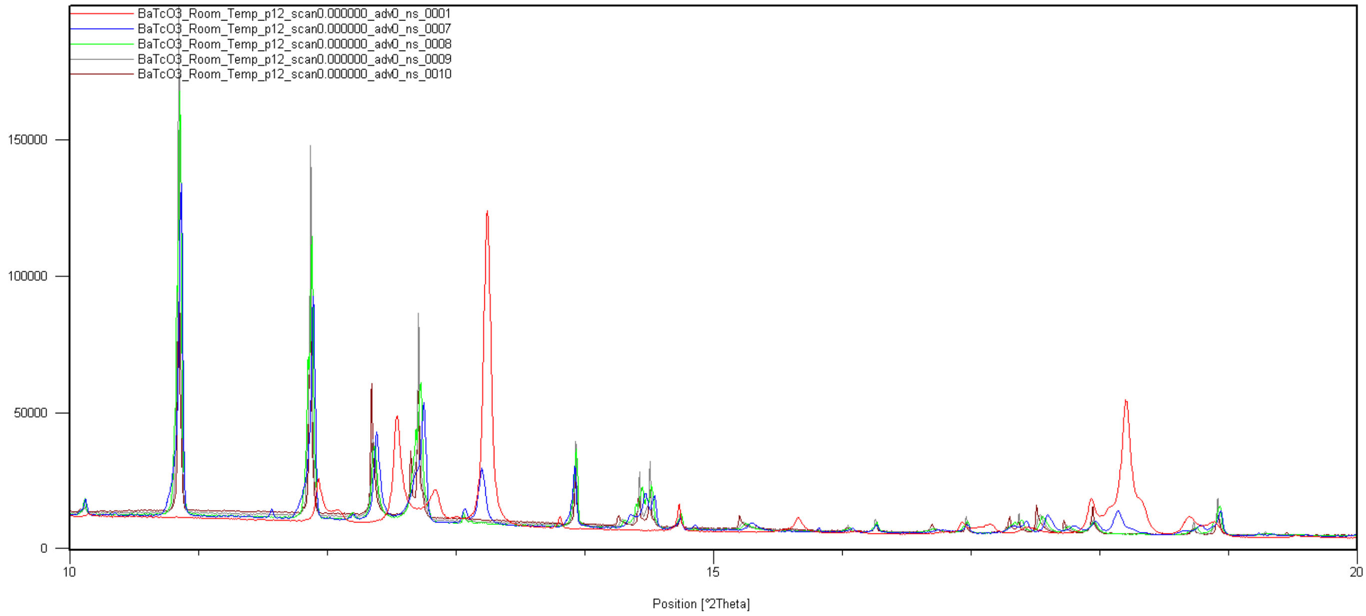
$Sr_xBa_{1-x}TcO_3$ ($Sr_{0.9}Ba_{0.1}TcO_3$)



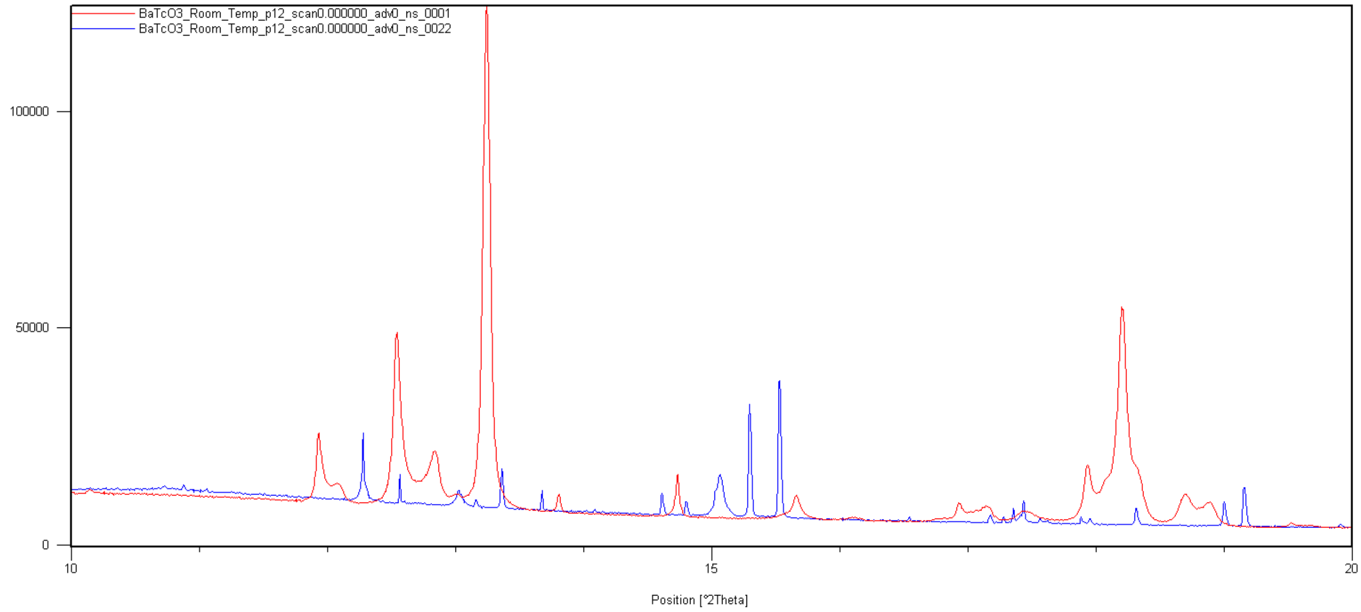
$Sr_xBa_{1-x}TcO_3$ ($Sr_{0.9}Ba_{0.1}TcO_3$)



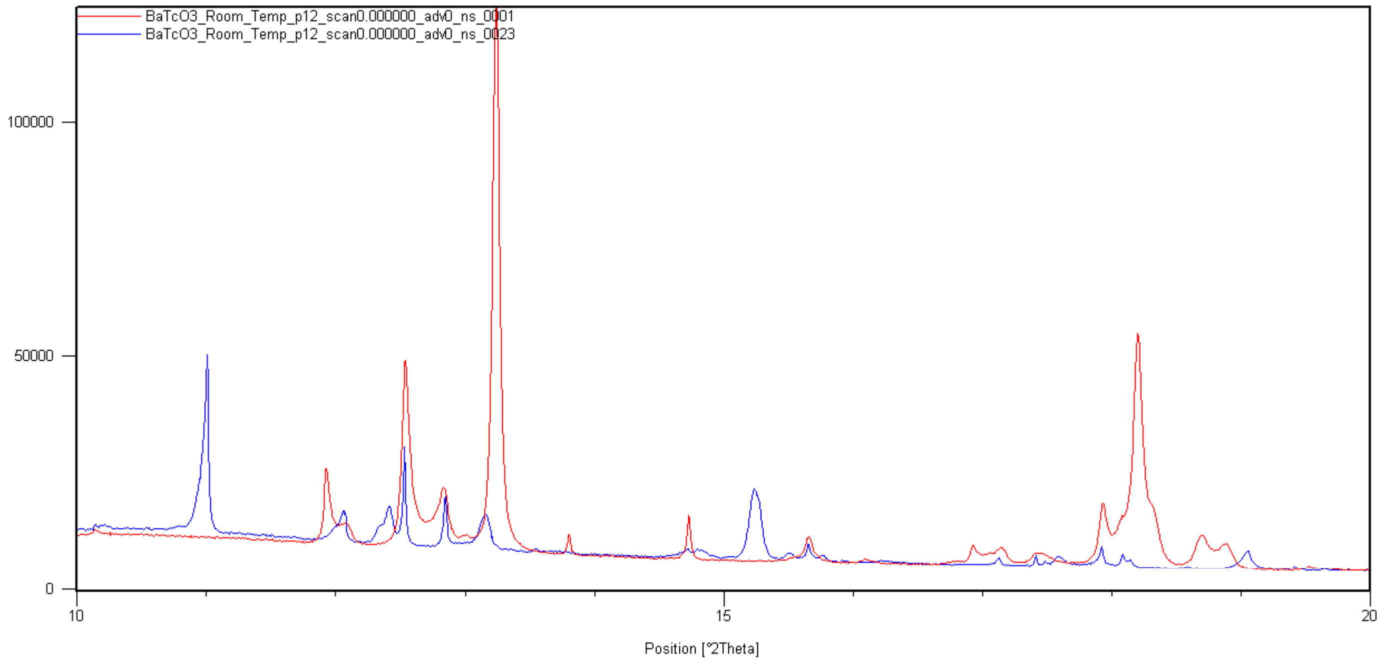
$Sr_xBa_{1-x}TcO_3$ ($Sr_{0.9}Ba_{0.1}TcO_3$)



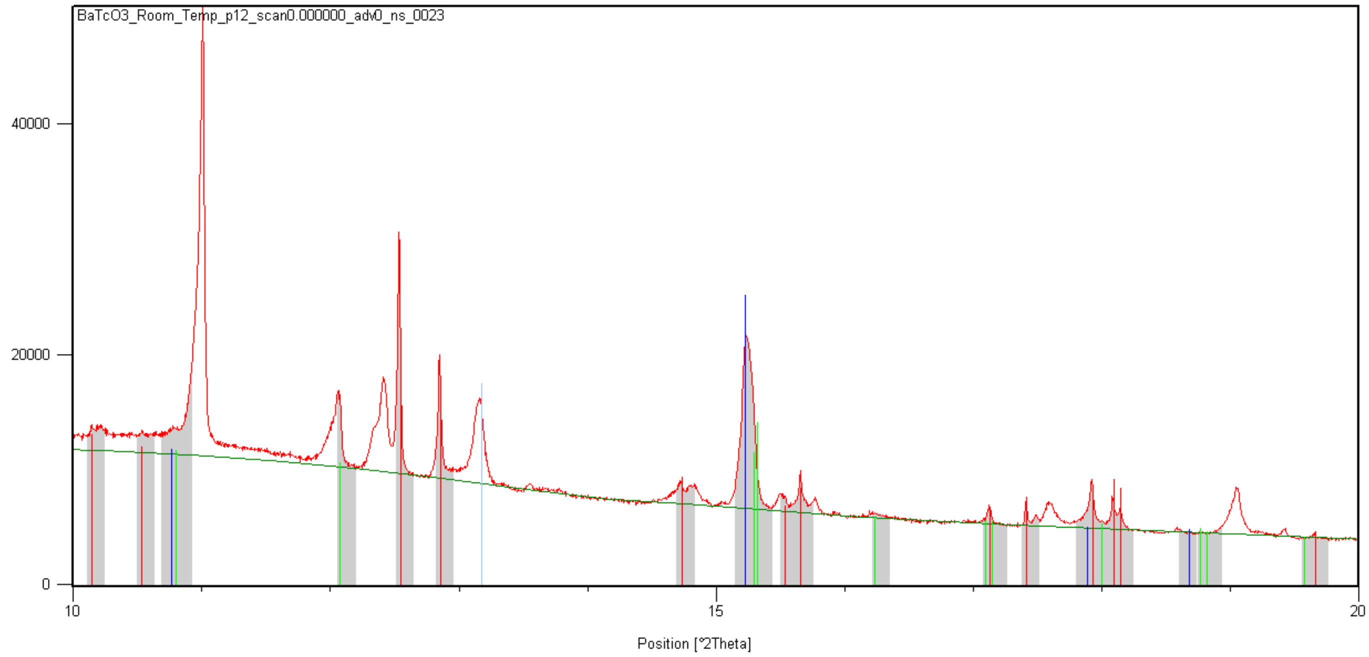
$Sr_xBa_{1-x}TcO_3$ ($Sr_{0.9}Ba_{0.1}TcO_3$)



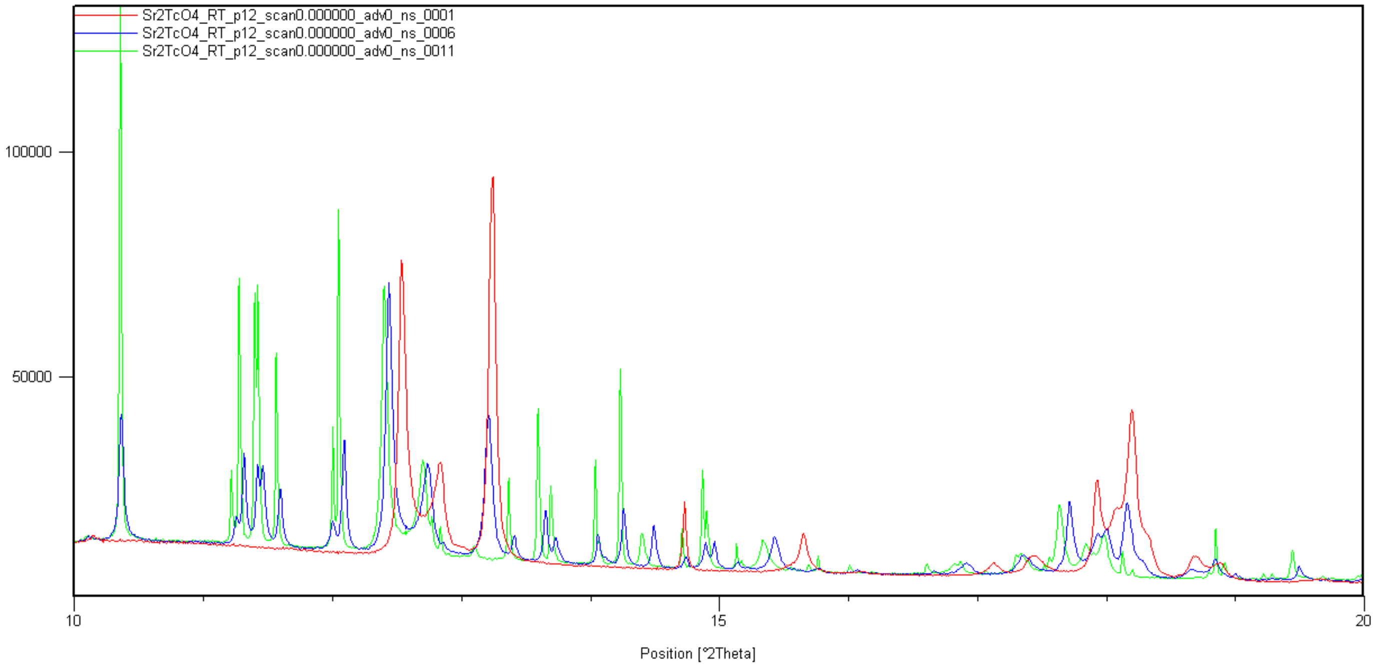
$Sr_xBa_{1-x}TcO_3$ ($Sr_{0.9}Ba_{0.1}TcO_3$)



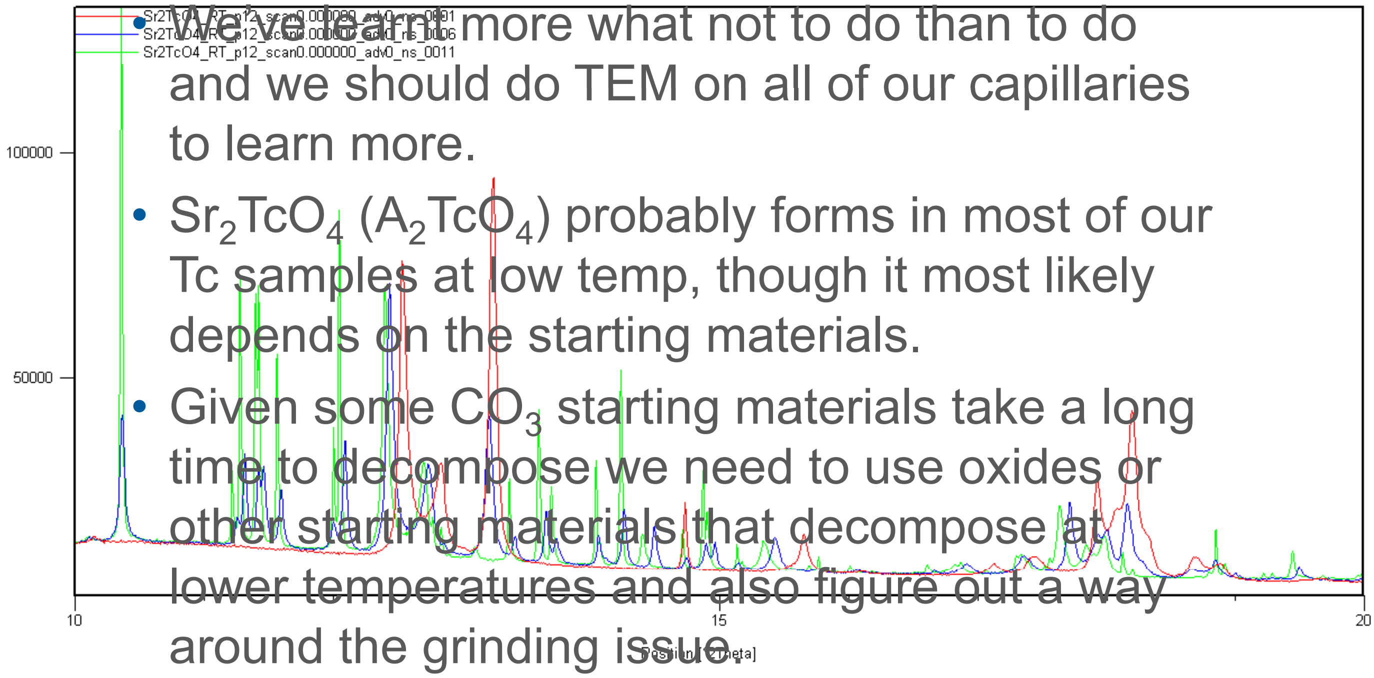
$Sr_xBa_{1-x}TcO_3$ ($Sr_{0.9}Ba_{0.1}TcO_3$)



Conclusions / Further Work



Conclusions / Further Work



- We've learnt more what not to do than to do and we should do TEM on all of our capillaries to learn more.
- Sr_2TcO_4 (A_2TcO_4) probably forms in most of our Tc samples at low temp, though it most likely depends on the starting materials.
- Given some CO_3 starting materials take a long time to decompose we need to use oxides or other starting materials that decompose at lower temperatures and also figure out a way around the grinding issue.

Australian Government

ansto

Thanks to the people in the Actinides suite for helping to make the samples and at the Australian Synchrotron for letting me bring my Tc samples along.

Gordon Thorogood announcing Sydney, Australia as the site for the next ISTR2017

Spectroscopic and Photophysical Properties of Tetracyanidonitridorhenium(V) and –technetium(V) Complexes

Takashi Yoshimura,[1]Hayato Ikeda,[2]Akitaka Ito,[3]Eri Sakuda,[3] Noboru Kitamura,[3]
Tsutomu Takayama,[4] Tsutomu Sekine,[5]and Atsushi Shinohara[2]

[1]Radioisotope Research Center, Osaka University, Suita, Japan, [2]Department of Chemistry, Graduate School of Science, Osaka University, Toyonaka, Japan, [3]Department of Chemical Sciences and Engineering, Graduate School of Chemical Sciences and Engineering, Hokkaido University, Sapporo, Japan, [4]Department of Chemistry, Daido University, Nagoya, Japan, [5]Center for Advancement of Higher Education, Tohoku University, Sendai, Japan

Among the Group 7 metal ions, a very small number of technetium complexes have been reported to show photoluminescence. In coordination compounds, molecular sensing can be done based on the color change of a complex through changes in the coordination environments and/or direct interaction of the metal ion with a molecule to be sensed. In contrast, molecular sensing based on the vapochromic luminescence through a ligand substitution reaction and the coordination number of a metal ion in the solid state has been rarely reported.We report photoluminescent properties of novel six-coordinate nitridoRe(V) and Tc(V) complexes and their five-coordinate square pyramidal complexes without an axial ligand.

All of the five-coordinate square pyramidal and six-coordinate distorted octahedral complexes showed photoluminescence in the solid state at room temperature. The emission spectra and photophysical data of the five-coordinate $[ReN(CN)_4]^{2-}$ were significantly different from those of the relevant six-coordinate complexes.The present study demonstrated for the first time that the nitridoTc(V) complex showed luminescence in the solid phase at room temperature. Vapochromic luminescence between the bi-stable five- and six-coordinate Re complexes with the VOCs (MeOH, EtOH, acetone, or MeCN) and between the six-coordinate complexes was investigated. We found unique reversible coordination and elimination of a VOC at the axial site of the Re complex in the solid state that gave rise to changes in the emission maximum wavelength, demonstrating photoluminescence switching and sensing of VOC by the present Re(V) complexes at room temperature.Upon exposure of MeOH vapor to the five-coordinate Tc complex, the emission spectrum changed to that of the MeOH coordinate complex. The coordinating MeOH molecule can be removed by vacuum.The emission band shapes of the five-coordinate Tc complex remained unchanged even upon exposure of acetone vapor. The emission spectrum of MeOH coordinate Tc complex changed to that of the five-coordinate complex by exposure to acetone vapor. This suggests that the coordinating MeOH molecule in the Tc complex was eliminated under acetone vapor atmosphere, but acetone was not incorporated and did not coordinate at the axial site in the Tc complex.

[1] H. Ikeda, T. Yoshimura, A. Ito, E. Sakuda, N. Kitamura, T. Takayama, T. Sekine, A. Shinohara, *Inorg. Chem.*2012, *51*, 12065.

[2] H. Ikeda, A. Ito, E. Sakuda, N. Kitamura, T. Takayama, T. Sekine, A. Shinohara, T. Yoshimura, *Inorg. Chem.*2013, *52*, 6319.

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Tsutomu Takayama, Tsutomu Sekine, Atsushi Shinohara

Osaka Univ., Hokkaido Univ., Daido Univ., Tohoku Univ.

Contents

- Synthesis, spectroscopic, and photophysical properties of tetracyanidonitridorhenium(V) and –technetium(V) complexes

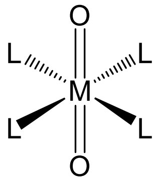
  $[MN(CN)_4L]^{2-}$ (M = Re, Tc; L = MeOH, EtOH, acetone
  MeCN, pyridine)

  $[MN(CN)_4]^{2-}$

- Vapochromic luminescence between five- and six-coordinate complexes and between six-coordinate complexes

- Control of the photoemissive excited state characteristic by the N-heteroaromatic ligand

Photoluminescent technetium complexes

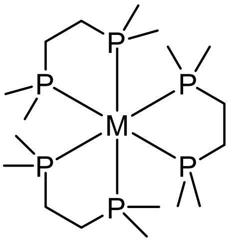


[MO$_2$L$_4$]

L	λ_{em} / nm	
	M = Re	M = Tc
CN	575	675
py	610	679
pic	618	733

* solid state

A. S. Del Negro *et al.*, *J. Am. Chem. Soc.* **127**, 14978–14979 (2005).

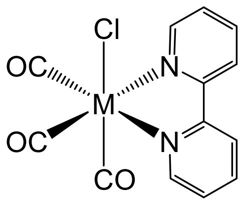


[M(dmpe)$_3$]$^{2+}$

L	λ_{em} / nm
Tc	660
Re	600

* MeCN solution

A. S. Del Negro *et al.*, *J. Am. Chem. Soc.* **128**, 16494–16495 (2005).

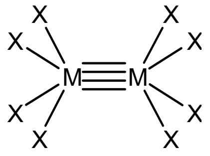


[MCl(bpy)(CO)$_3$]

L	λ_{em} / nm
Tc	570–580
Re	580

* DMF solution

P. Kurz *et al.*, *Eur. J. Inorg. Chem.*, 2966-2974 (2006).



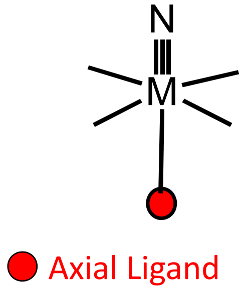
[M$_2$X$_8$]$^{2-}$

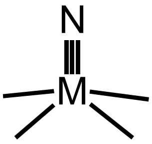
M	λ_{em} / nm	
	X = Cl	X = Br
Tc	ca. 750	686
Re	ca. 750	716

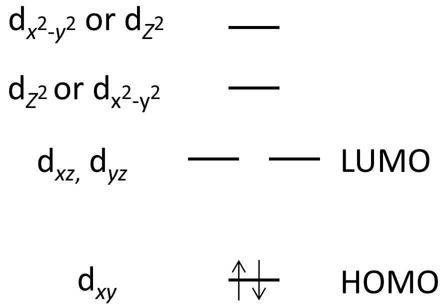
* Tc: solid state
Re: CH$_2$Cl$_2$ solution

Tc: B. N. Briggs *et al.*, *Dalton Trans.*, 11322–11324 (2010).
Re: V. M. Miskowski *et al.*, *Inorg. Chem.* **18**, 86–89 (1979).

d^2 nitridometal complex







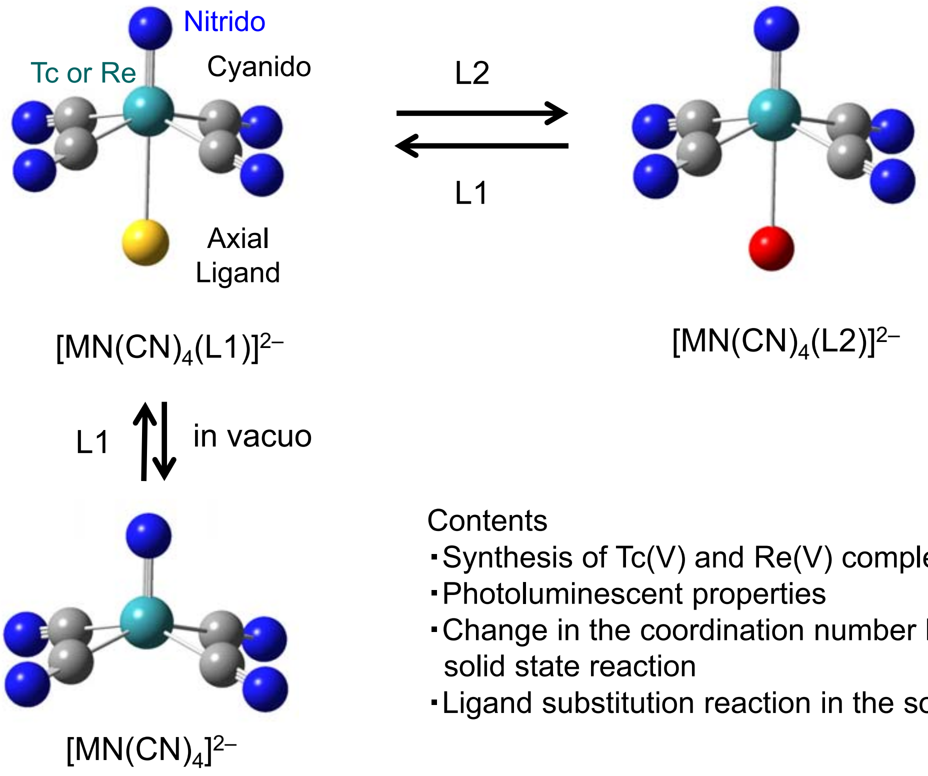
Photoluminescence of nitridorhenium(V) complexes

Emission maximum wavelength (λ_{em}) 480 ~ 800 nm
Emission lifetime (τ_{em}) 0.05 ~ 20 µs
Emission quantum yield (Φ_{em}) 10^{-5} ~ 0.06 (in solution、298 K)

The origin of the photoluminescence
Excited $^3[d_{xy}{}^1,(d_{xz}d_{yz})^1]$ with contribution of nitrido ligand
→ $^3[d_{xy}{}^1,(d_{xz}d_{yz})^1]$

V. W.-W. Yam, et al. *J. C. S. Dalton Trans.*, 1125 (1996)

Present study



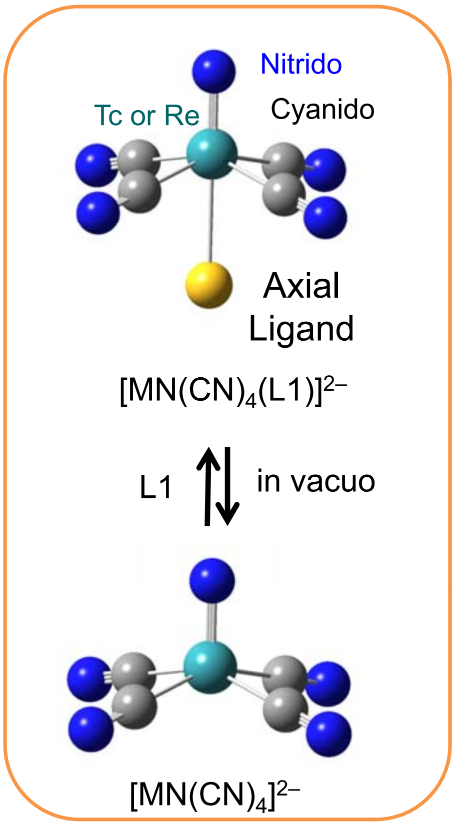
$[MN(CN)_4(L1)]^{2-}$

$[MN(CN)_4(L2)]^{2-}$

$[MN(CN)_4]^{2-}$

Contents
- Synthesis of Tc(V) and Re(V) complexes
- Photoluminescent properties
- Change in the coordination number by the solid state reaction
- Ligand substitution reaction in the solid state

Present study



$[MN(CN)_4(L1)]^{2-}$

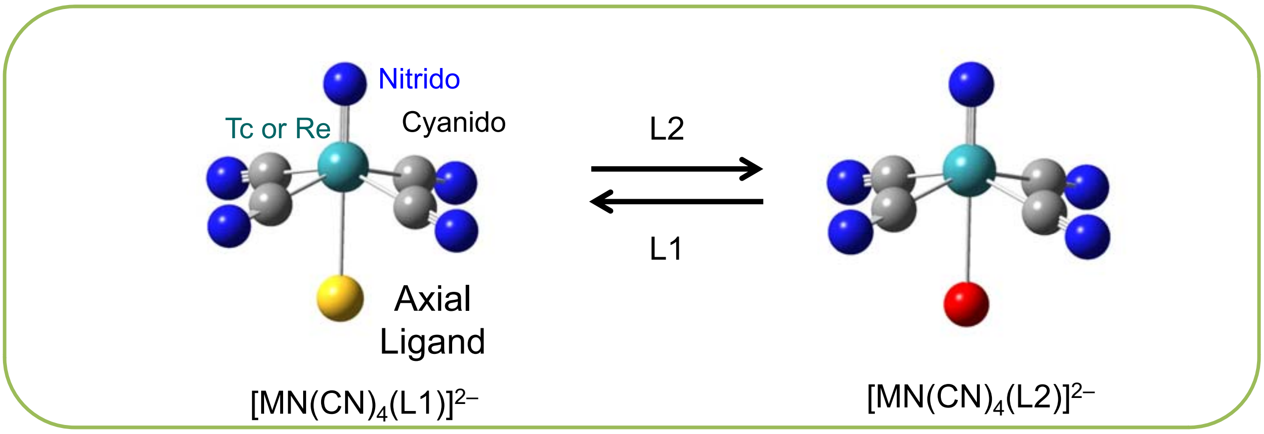
$[MN(CN)_4]^{2-}$

Vapochromic luminescence
by change in the coordination number
between five- and six-coordinate
in the solid state

Contents
- Synthesis of Tc(V) and Re(V) complexes
- Photoluminescent properties
- Change in the coordination number by the solid state reaction
- Ligand substitution reaction in the solid state

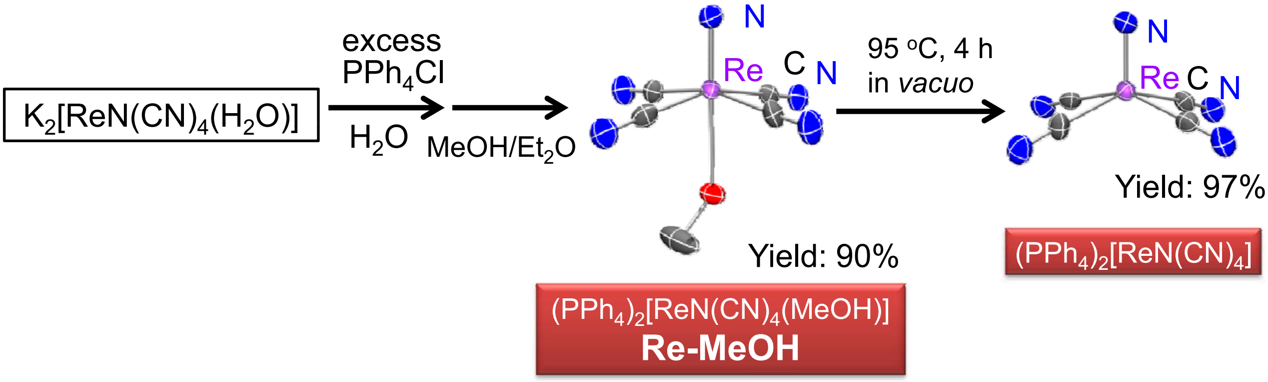
Present study

Vapochromic luminescence by ligand substitution reaction between six-coordinate complexes in the solid state



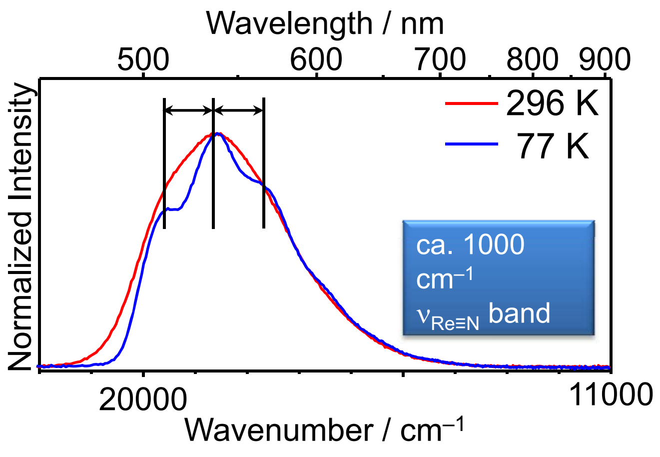
Contents
- Synthesis of Tc(V) and Re(V) complexes
- Photoluminescent properties
- Change in the coordination number by the solid state reaction
- Ligand substitution reaction in the solid state

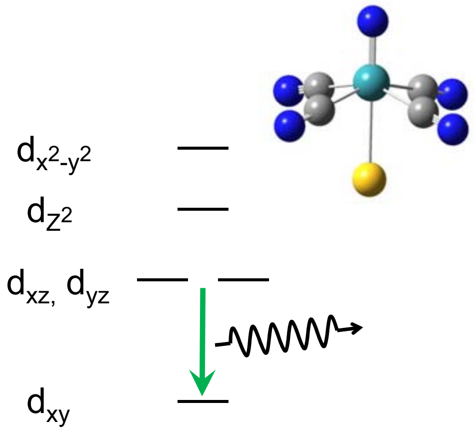
Synthesis of the Re(V) and Tc(V) complexes



	Re(V)	Tc(V)
Six-coordinate	$[ReN(CN)_4(MeOH)]^{2-}$	$[TcN(CN)_4(MeOH)]^{2-}$
	$[ReN(CN)_4(EtOH)]^{2-}$	$[TcN(CN)_4(pyridine)]^{2-}$
	$[ReN(CN)_4(acetone)]^{2-}$	
	$[ReN(CN)_4(MeCN)]^{2-}$	
	$[ReN(CN)_4(pyridine)]^{2-}$	
Five-coordinate	$[ReN(CN)_4]^{2-}$	$[TcN(CN)_4]^{2-}$

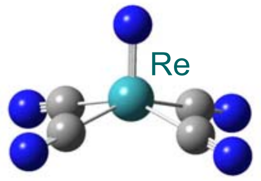
Photoluminescence of six-coordinate Re(V) in the solid state

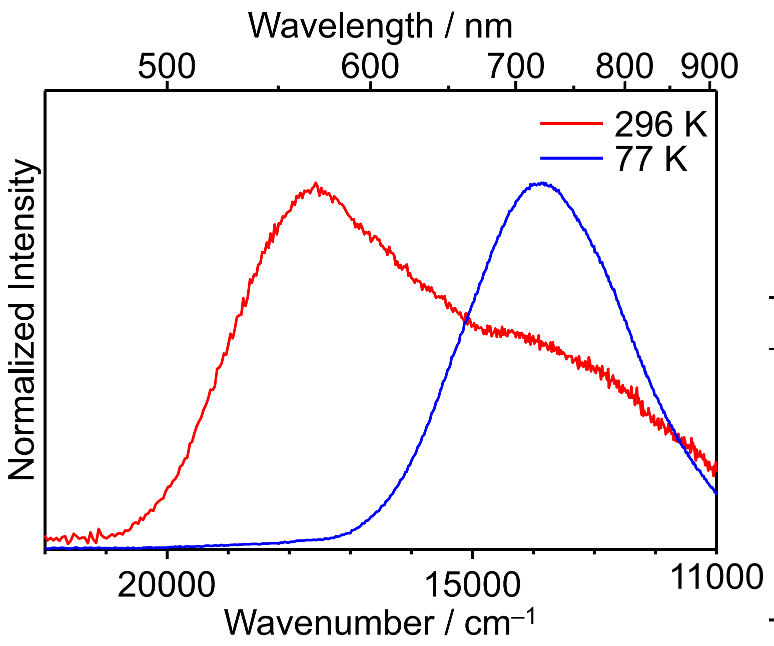




	λ_{em} / nm		τ_{em} / µs		Φ_{em}
	296 K	77 K	296 K	77 K	296 K
Re-MeOH	527	496, 523, 552	0.41, 2.2, 11	77	0.13
Re-EtOH	548	493, 520, 541, 551	5.5, 18	4.9, 55	< 0.01
Re-acetone	533	505, 531, 560	21	109	0.34
Re-MeCN	545	551	2.0	166	0.02
Re-pyridine	539	513, 539, 569, 604	45	100	0.93

Photoluminescence of five-coordinate Re(V) in the solid state

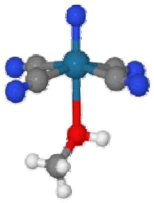




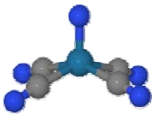
$(PPh_4)_2[ReN(CN)_4]$

	296 K	77 K
λ_{em} / nm	569 720(sh)	721
τ_{em} / µs	0.35 1.2 7.6	0.29 3.3 14
Φ_{em}	< 0.01	—

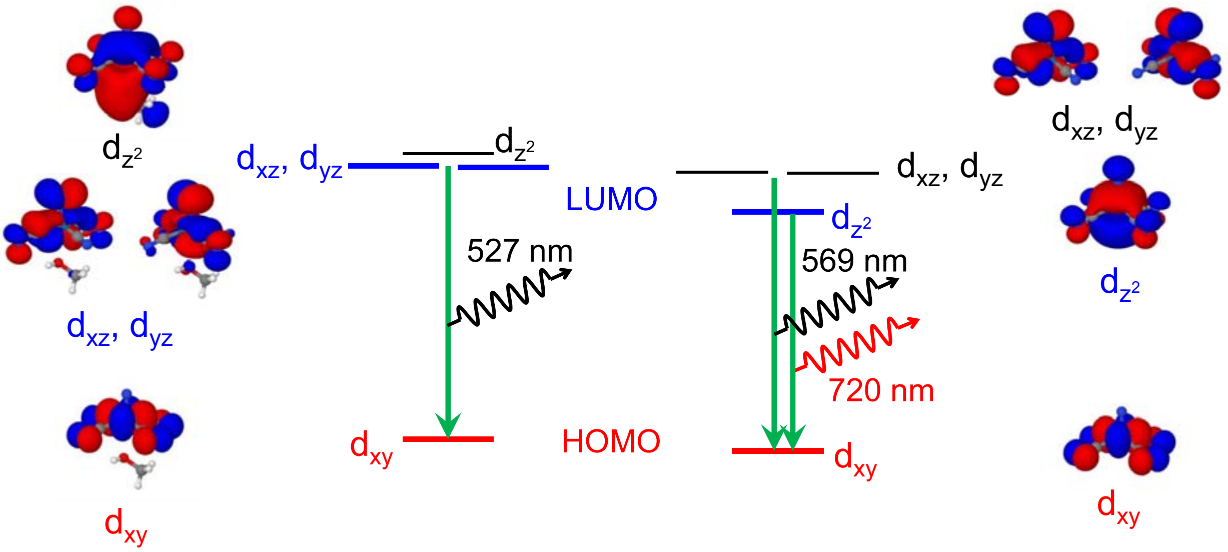
DFT calculations of six- and five-coordinate Re(V) complexes



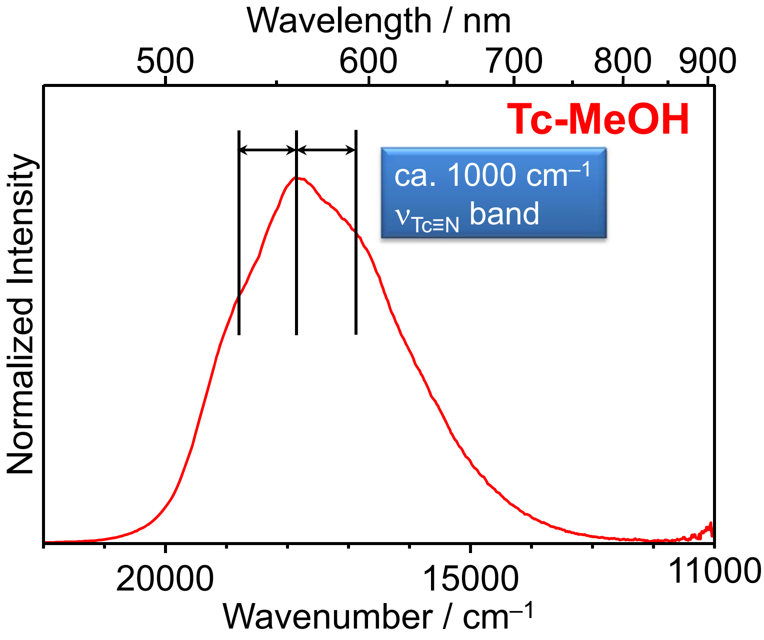
$[ReN(CN)_4(MeOH)]^{2-}$

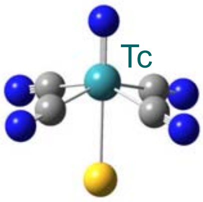


$[ReN(CN)_4]^{2-}$



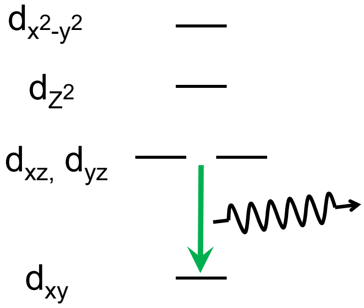
Photoluminescence of six-coordinate Tc(V) in the solid state



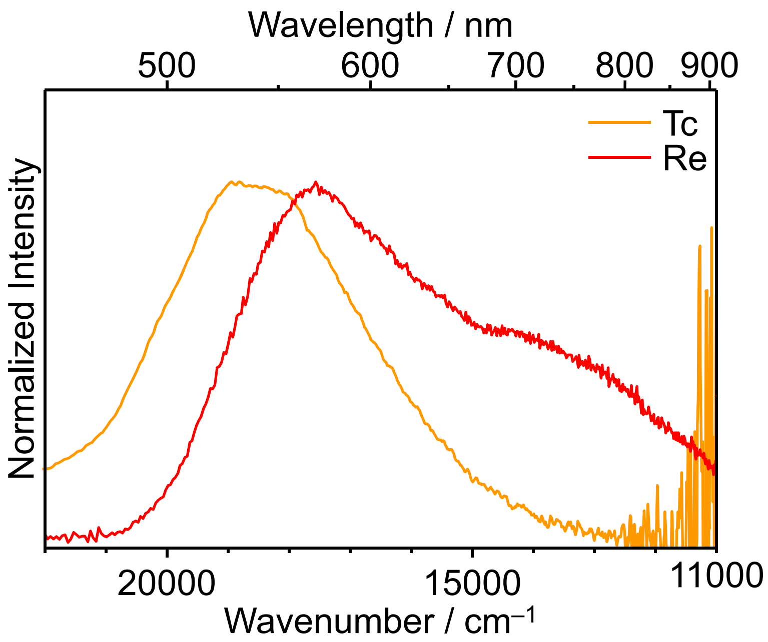


Complexes	λ_{em} / nm
Tc-MeOH	559
Tc-py	576

Emissive excited state
$^3[d_{xy}{}^1,(d_{xz},d_{yz})^1]$

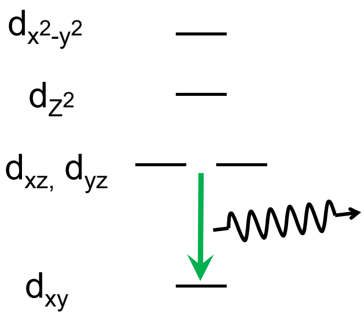


Emission spectrum of five-coordinate technetium complex (296 K)



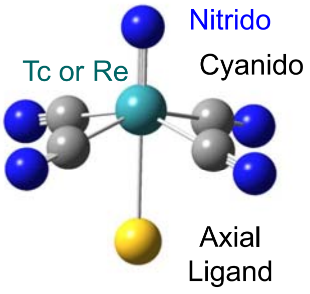
Spectroscopic and photophysical data of $(PPh_4)_2[MN(CN)_4]$ (M = Tc, Re)

	Tc	Re
λ_{em} / nm	528 556 (sh)	569 720(sh)
τ_{em} / µs	—	0.35 1.2 7.6
Φ_{em}	—	< 0.01

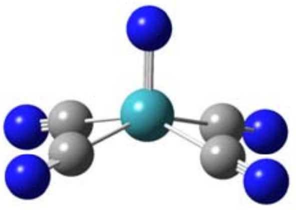


Emissive excited state
$^3[d_{xy}{}^1,(d_{xz},d_{yz})^1]$

Summary 1



$[MN(CN)_4(L1)]^{2-}$



$[MN(CN)_4]^{2-}$

The first nitridotechnetium(V) complexes showing photoluminescence

Photoemissive excited state $^3[d_{xy}{}^1,(d_{xz},d_{yz})^1]$

The nitridorhenium(V) complexes

Photoemissive excited state

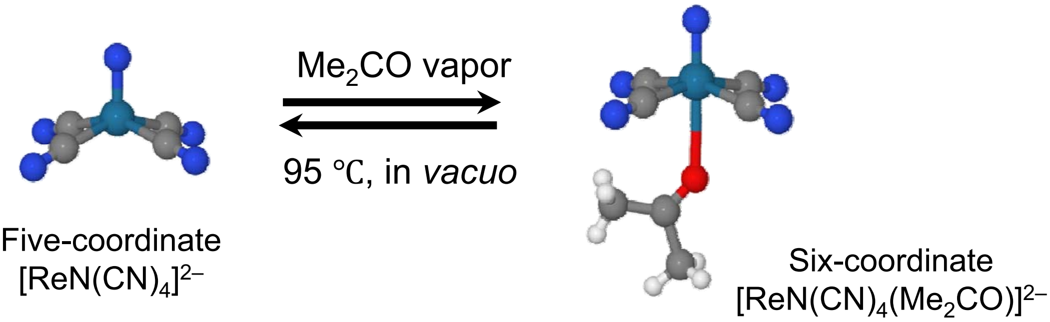
The six-coordinate complex $^3[d_{xy}{}^1,(d_{xz},d_{yz})^1]$

The pyridine coordinate Re(V) complex Φ_{em} = 0.93

The five-coordinate complex

The excited state character is different from that of the six-coordinate complex

Vapochromic luminescece by change in coordination number between five- and six-coordinate rhenium complexes in the solid state

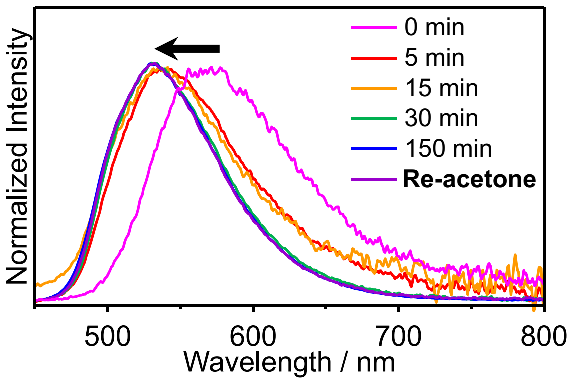


Me$_2$CO vapor

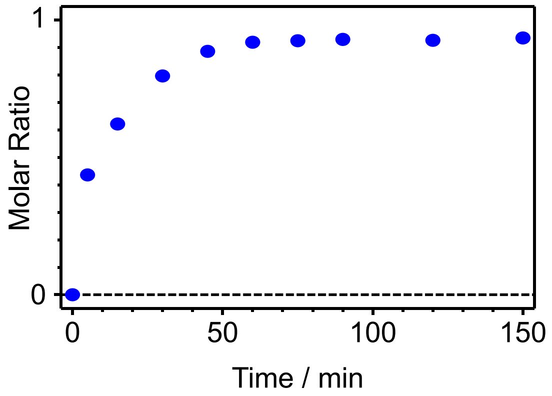
95 ℃, in *vacuo*

Five-coordinate
[ReN(CN)$_4$]$^{2–}$

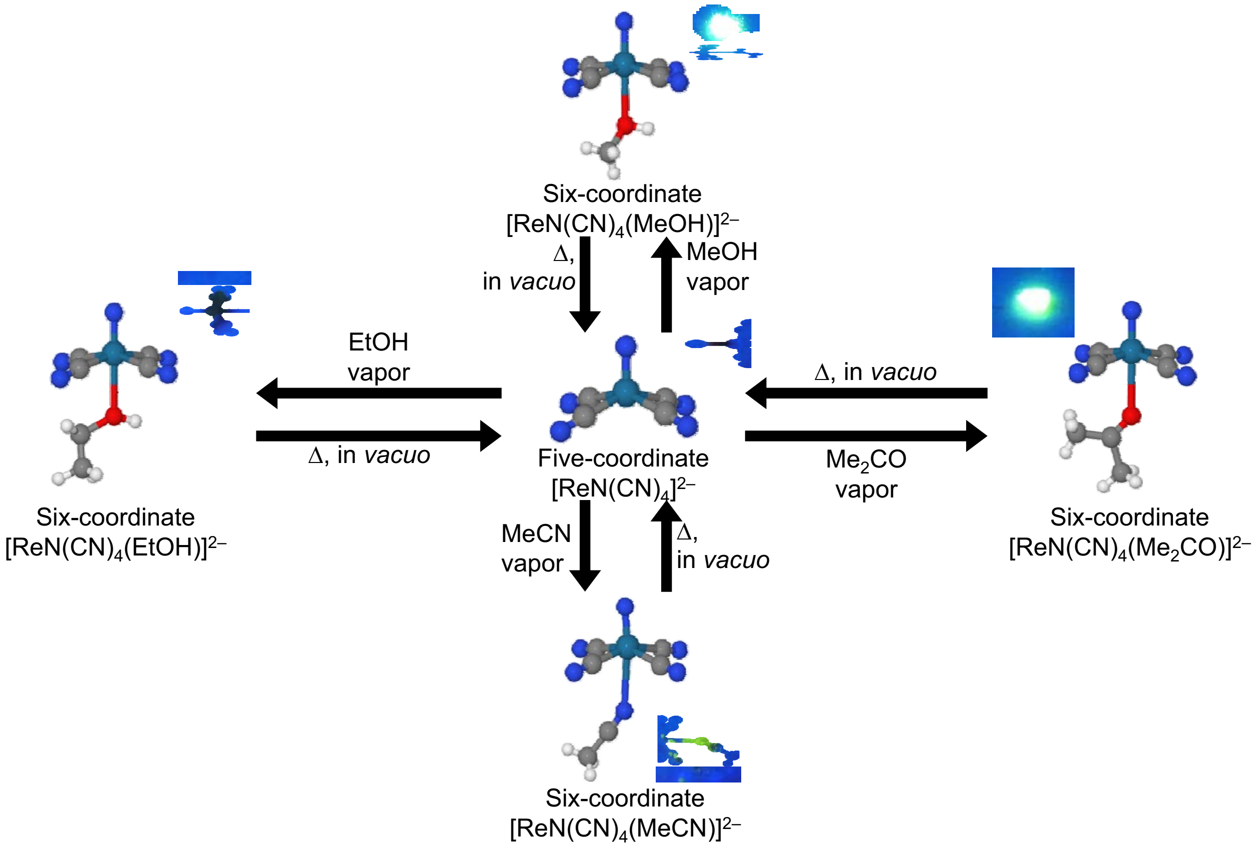
Six-coordinate
[ReN(CN)$_4$(Me$_2$CO)]$^{2–}$



Emission spectral change by exposure time of acetone vapor to [ReN(CN)$_4$]$^{2-}$ in the solid state.



Plot of the molar ratio of acetone with the Re complex against exposure time of acetone vapor



Six-coordinate
[ReN(CN)$_4$(MeOH)]$^{2–}$

Δ,
in *vacuo*

MeOH
vapor

EtOH
vapor

Δ, in *vacuo*

Five-coordinate
[ReN(CN)$_4$]$^{2–}$

Δ, in *vacuo*

Me$_2$CO
vapor

Six-coordinate
[ReN(CN)$_4$(EtOH)]$^{2–}$

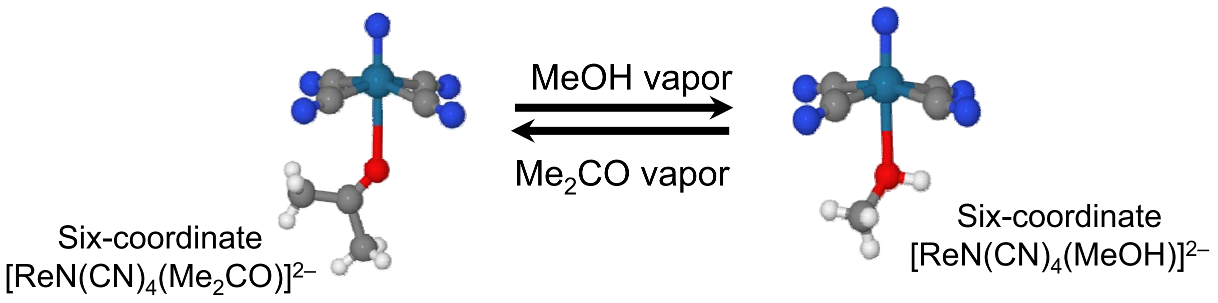
Six-coordinate
[ReN(CN)$_4$(Me$_2$CO)]$^{2–}$

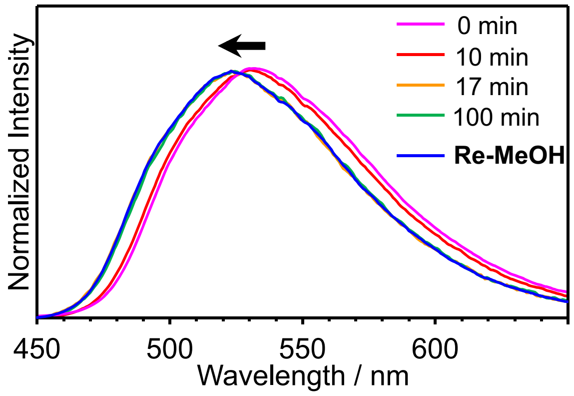
MeCN
vapor

Δ,
in *vacuo*

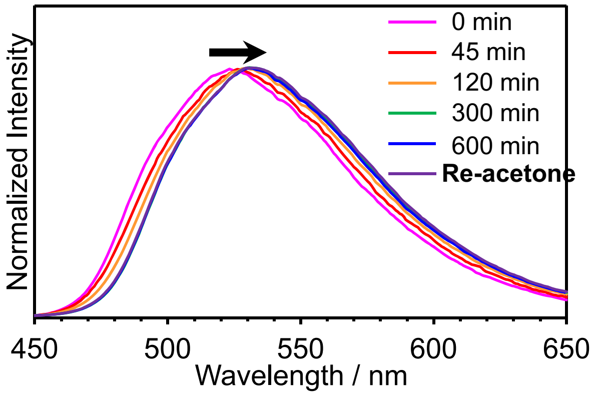
Six-coordinate
[ReN(CN)$_4$(MeCN)]$^{2–}$

Ligand substitution between six-coordinate Re(V) complexes in the solid state



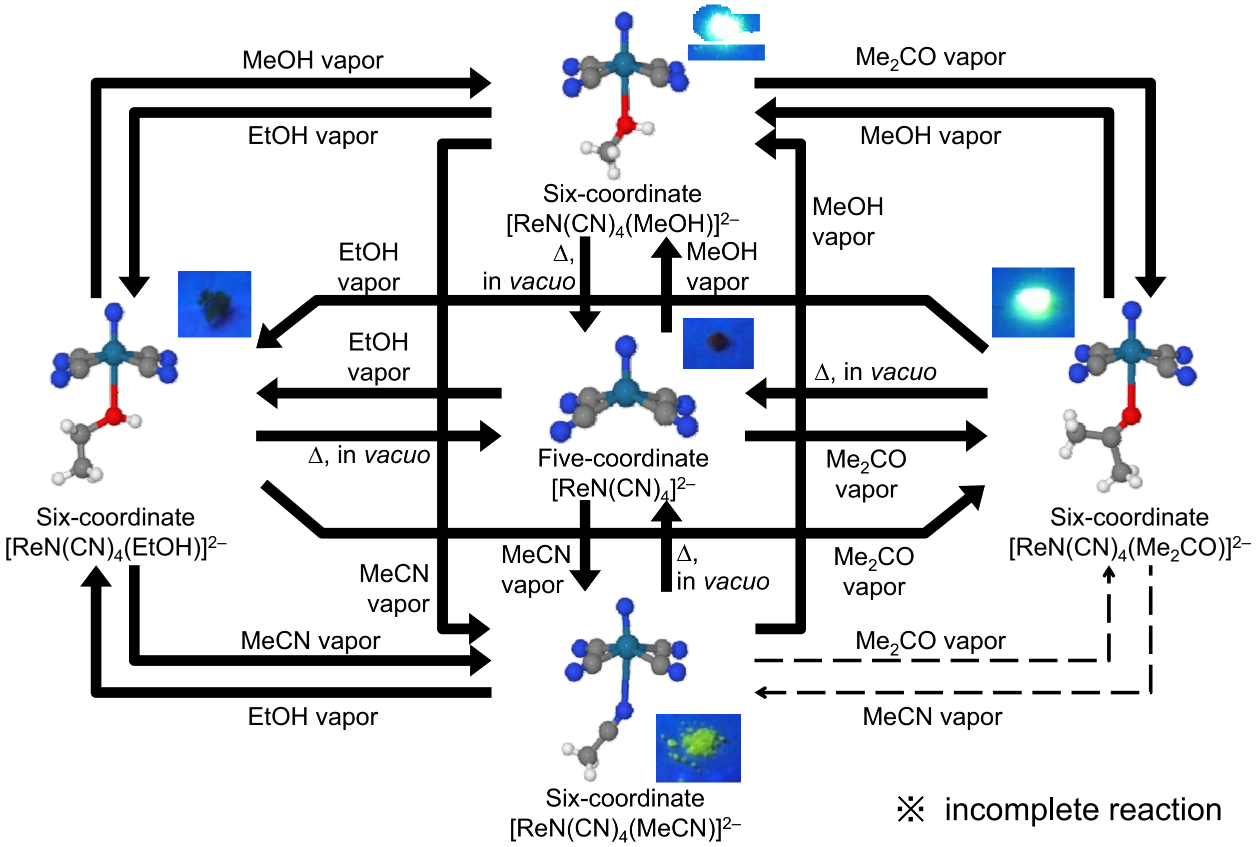


Emission spectral change by exposure time of MeOH vapor to $[ReN(CN)_4(acetone)]^{2-}$ in the solid state.

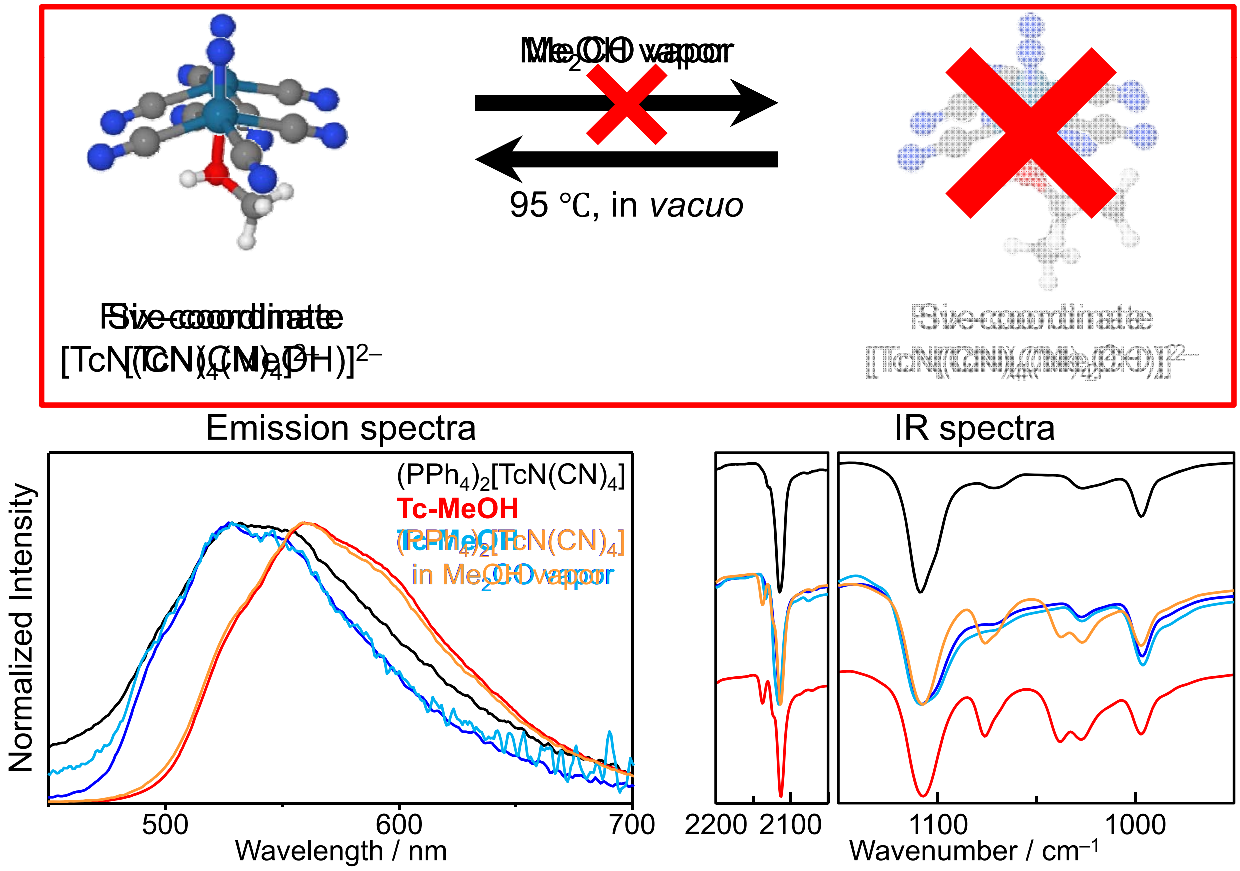


Emission spectral change by exposure time of acetone vapor to $[ReN(CN)_4(MeOH)]^{2-}$ in the solid state.

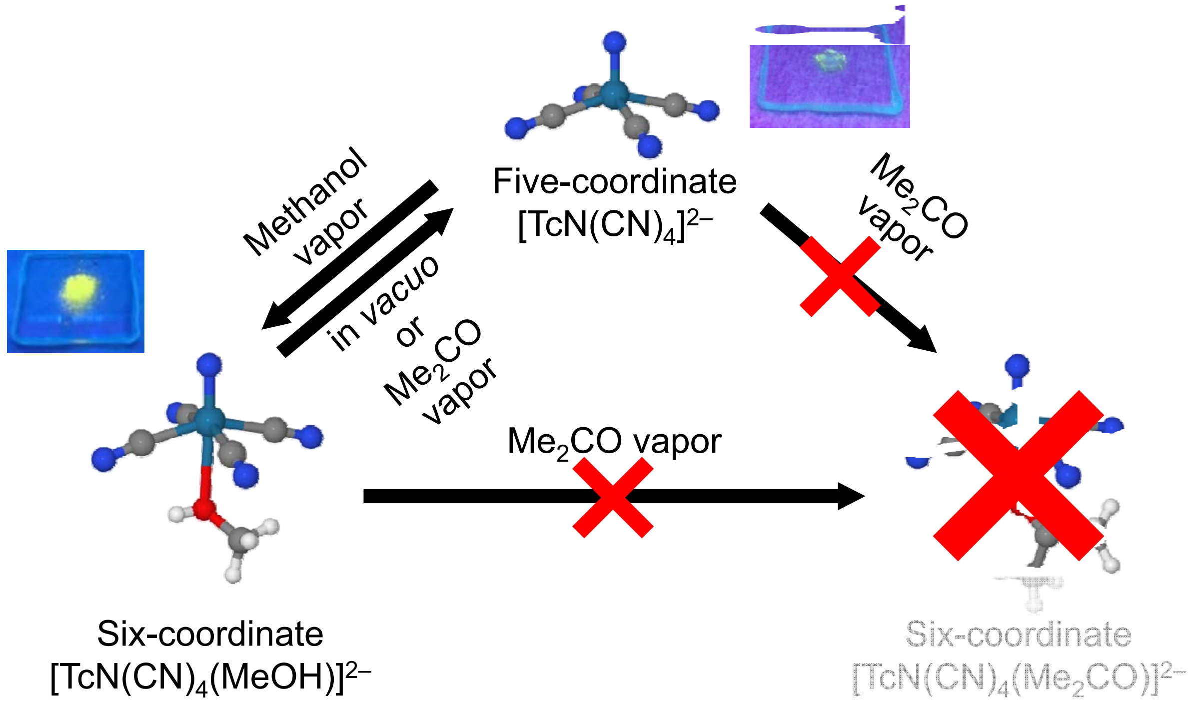
Vapochromic luminescence of Re(V) complexes



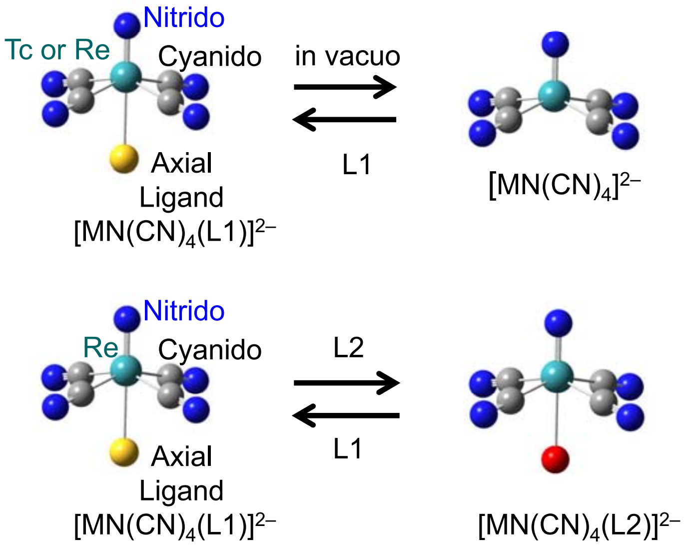
Vapochromic luminescence of Tc(V) complexes



Vapochromic luminescence of Tc(V) complexes



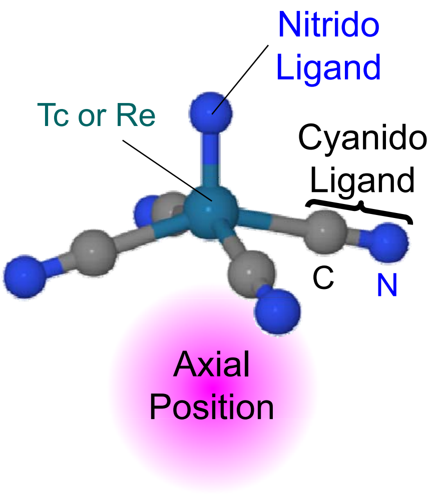
Summary2

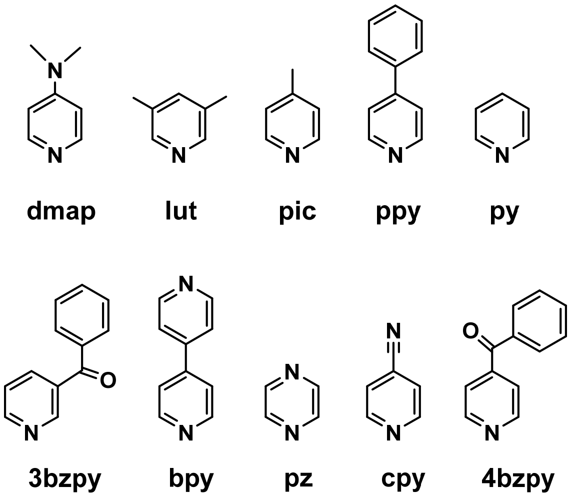


Reversible photoluminescence switching
between six- and five-coordinate complexes
between six-coordinate complexes
in the solid state

H. Ikeda, T. Yoshimura, et al. *Inorg. Chem.* **2012**, *51*, 12065

This study



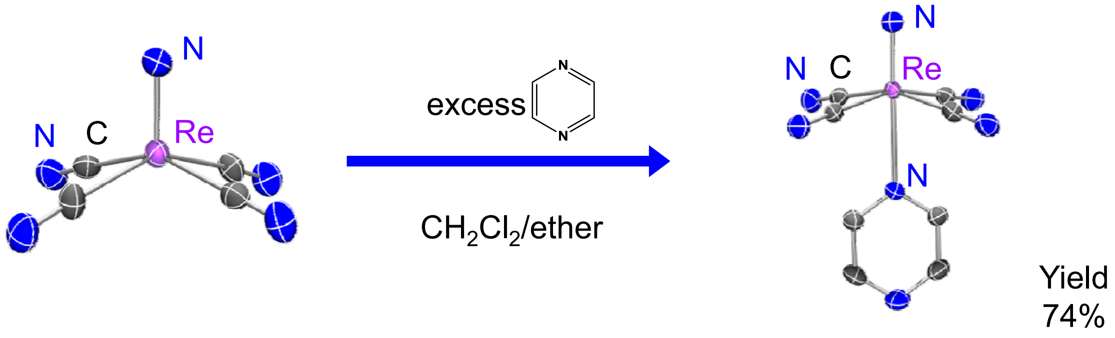


M = Re, L = dmap, lut, pic, ppy, py,
3bzpy, bpy, pz, cpy, and 4bzpy

M = Tc, L = dmap, lut, pic, py, pz, and cpy

Control of the photoemissive excited state characteristic
by the N-heteroaromatic ligand

Synthesis of the complexes

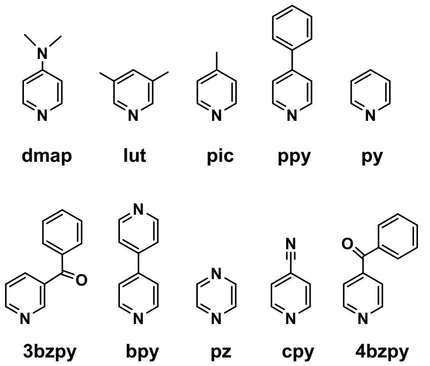


excess

CH_2Cl_2/ether

Yield
74%

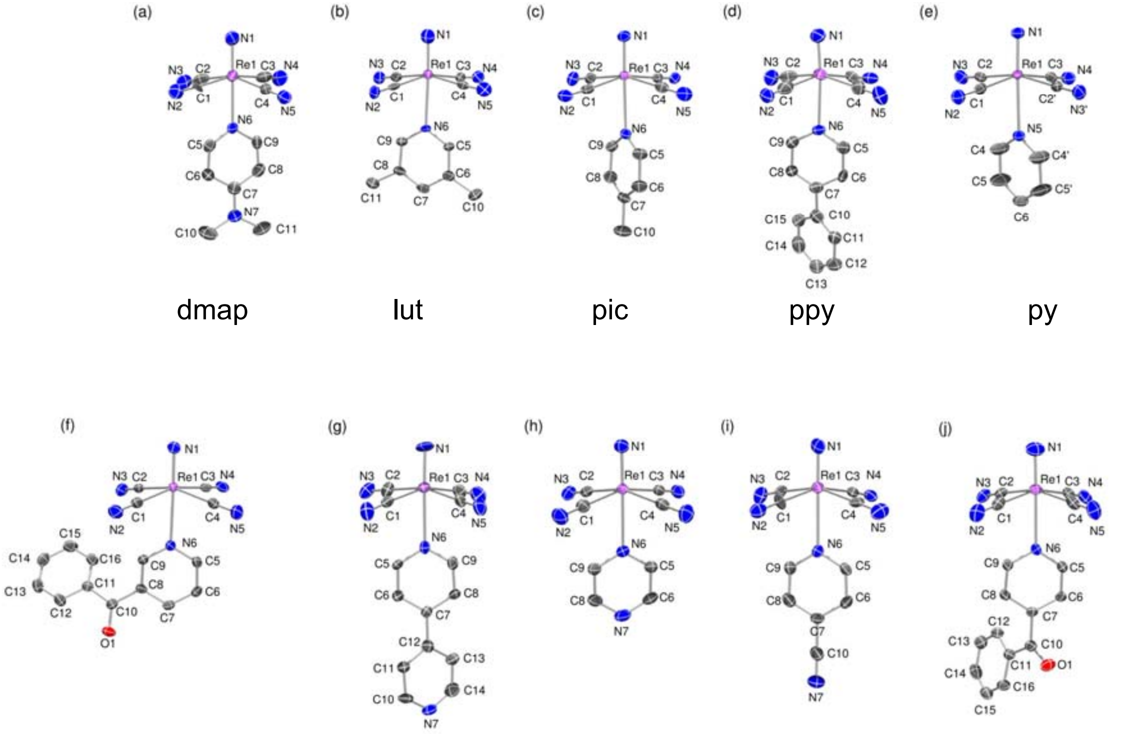
$(PPh_4)_2[ReN(CN)_4(pz)]$
Re-pz



M = Re, L = dmap, lut, pic, ppy, py,
3bzpy, bpy, pz, cpy, and 4bzpy

M = Tc, L = dmap, lut, pic, py, pz, and cpy

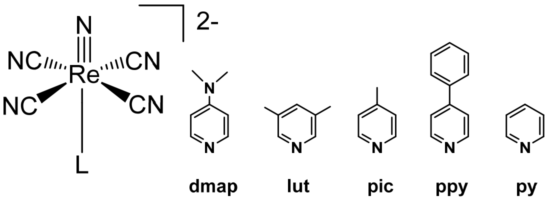
X-ray structures (Re complexes)

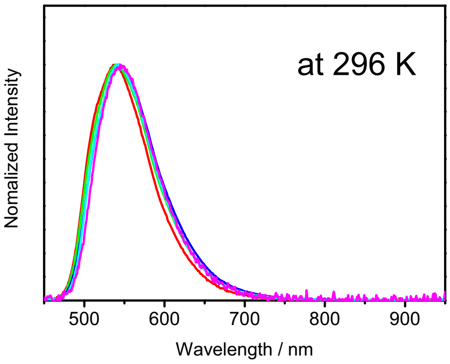


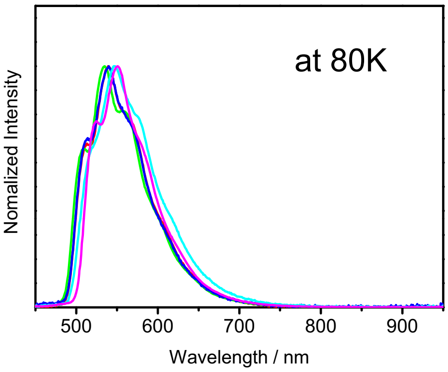
dmap lut pic ppy py

3-bzpy bpy pz cpy 4bzpy

Emission spectra in the solid state



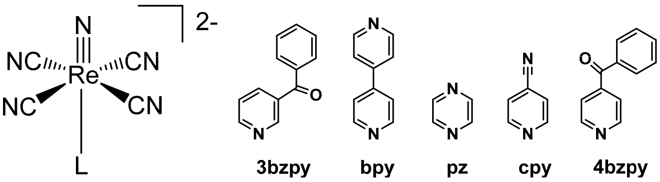


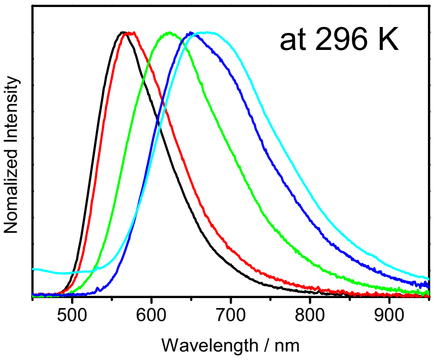


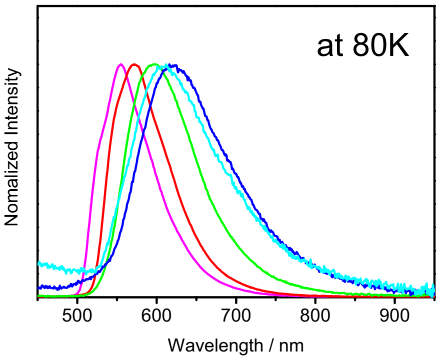
L	λ_{em}/nm	Φ_{em}	τ_{em} /μs (%)
dmap	539	0.79	36(70), 10 (30)
lut	544	0.39	26
pic	544	0.79	44
ppy	545	0.71	40
py	539	0.93	45

L	λ_{em}/nm	τ_{em} /μs
dmap	535	75
lut	540	111
pic	547	142
ppy	551	106
py	539	100

Emission spectra in the solid state



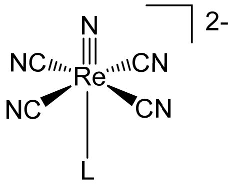


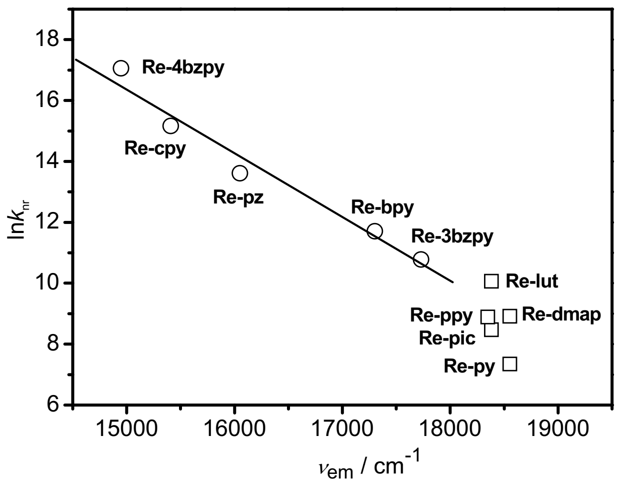


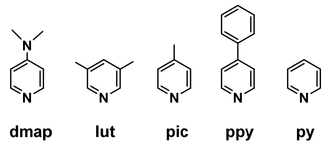
L	λ_{em}/nm	Φ_{em}	τ_{em} /μs (%)
3bzpy	564	0.36	13.3
bpy	578	0.18	9.7 (59), 2.5 (41)
pz	623	0.05	2.7 (19), 0.80 (81)
cpy	649	0.01	0.65 (26), 0.12 (74)
4bzpy	669	< 0.01	0.20 (5), 0.03 (95)

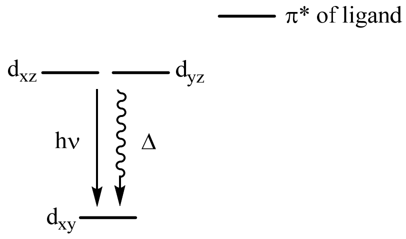
L	λ_{em}/nm	τ_{em} /ms
3bzpy	555	64
bpy	572	68 (62), 31 (38)
pz	597	53 (77), 25 (23)
cpy	616	5.0 (3), 1.2 (97)
4bzpy	612	4.2 (12), 0.95 (88)

Energy gap plot

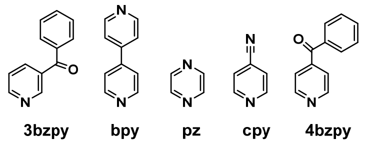


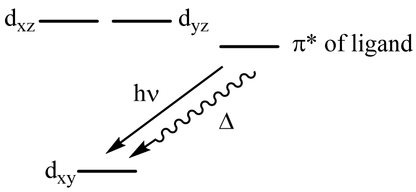






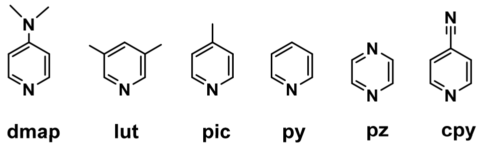
Emissive excited state
$^3[d_{xy}{}^1,(d_{xz},d_{yz})^1]$

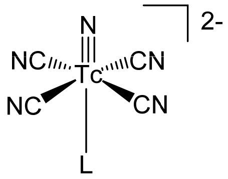


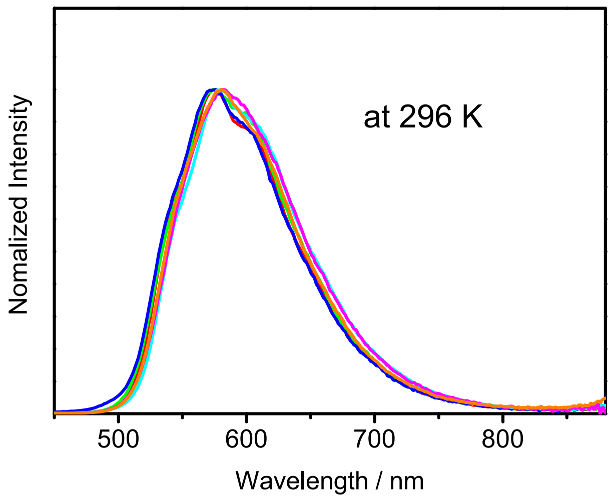


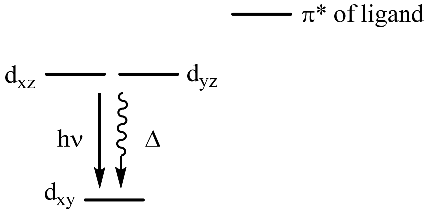
Emissive excited state
^{3}MLCT(L = N-heterocycle)

Emission spectra in the solid state





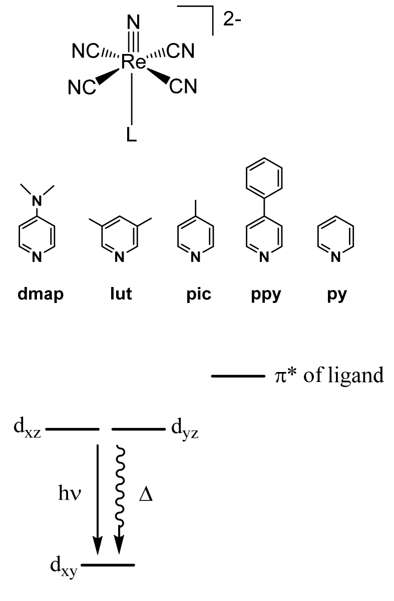




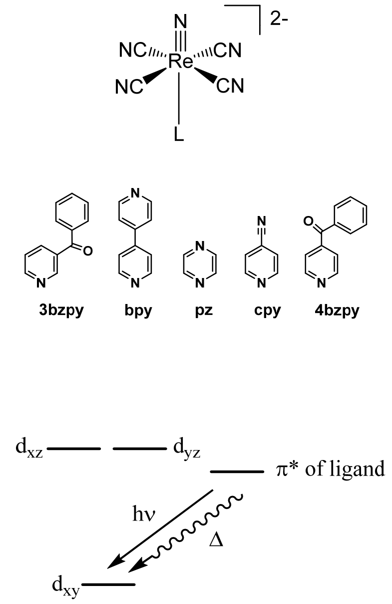
L	dmap	lut	pic	py	pz	cpy
λ_{em}/nm	574	576	580	576	581	580

Emissive excited state
$^3[d_{xy}{}^1,(d_{xz},d_{yz})^1]$

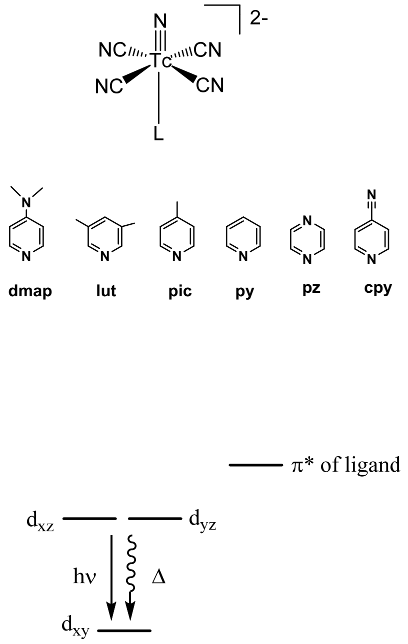
Summary 3



$^3[d_{xy}^1,(d_{xz},d_{yz})^1]$



^{3}MLCT
(L = N-heterocycle)



$^3[d_{xy}^1,(d_{xz},d_{yz})^1]$

Yoshimura, et al., *Inorg. Chem.* **2013**, *52*, 6319

Educational Opportunities Within the UNLV Radiochemistry PhD Program

Wendee Johns, Program Manager

The Radiochemistry Ph.D. program at UNLV was founded as a joint program by the Department of Chemistry and the Health Physics Department in 2004. It is a student-driven, research intensive program that stresses the fundamental aspects of radiochemistry science. Its curriculum consists of a series of core courses that are complemented by elective classes offered by several different colleges, making it a truly interdisciplinary program. The program offersvarious research opportunities to undergraduate and graduate students, providing them with unique training and educational opportunities. In particular, it allows students to gain hands-on experience in handling, manipulating and detecting unsealed radioactive material early in their career. UNLV has the resources and capabilities to perform novel experiments that aid in exploring, understanding and utilizing the fundamental properties of radioisotopes. Given Nevada's unique relationship with nuclear activities, UNLV has emerged as a premier location for studying the chemistry of the actinides, technetium and other radionuclides.

The curriculum and research provide a comprehensive and interdisciplinary examination of topics and experiences necessary to produce graduates who are ready to secure employment and participate in radiochemistry research.The program has over 1500 square feet of radiochemistry laboratories capable of handling a range of activities. These facilities contain a host of experimental equipment for use in research including radionuclide counting facilities, spectroscopy, microscopy and x-ray diffraction. Student opportunities in research and education are expanded through interactions with national and international collaborators. The program focuses on student development in the areas of technical competency, communication skills, analytical and critical thinking skills and expertise in the field of radiochemistry.The student experience at UNLV’s Radiochemistry program is further enhanced by collaboration with the Department of Energy sponsored Radiochemistry Fuel Cycle Summer School. This program, hosted by UNLV since 2010, provides UNLV PhD students with the unique experience of mentoring undergraduate students in radiochemistry research that is relevant to their thesis pursuits.Department of Energy researchers and staff scientists from national laboratories hold seminars and lecture series as part of the program which further expands education opportunities for UNLV students.A Ph.D. degree from UNLV in the field of radiochemistry, provides a wide variety of career opportunities performing forefront research in areas as diverse as radiochemistry, nuclear chemistry, materials research, renewable energy studies, nuclear forensics, and environmental studies to name a few.

ISTR 2014
La Baule – Pornichet, France
29th sept. – 3rd oct. 2014

Educational opportunities within the

UNLV RADIOCHEMISTRY PHD PROGRAM

Wendee Johns, Program Manager

wendee.johns@unlv.edu

OVERVIEW

- **PROGRAM**
  - LOCATION
  - RESEARCH TEAM
  - AREAS OF INTEREST
- **STUDENT DEVELOPMENT**
  - COURSE REQUIREMENTS
  - TRAINING
  - COLLABORATIONS
- **WHAT DOES THIS MEAN FOR YOU?**

INTERDISCIPLINARY PROGRAM

- **DEPARTMENT OF CHEMISTRY**
  - KENNETH CZERWINSKI, PHD
  - FREDERIC POINEAU, PHD
  - DAVID HATCHETT, PHD
  - PAUL FORSTER, PHD
- **DEPARTMENT OF HEALTH PHYSICS**
  - RALF SUDOWE, PHD
  - GARY CEREFICE, PHD
- **DEPARTMENT OF ENGINEERING**
  - THOMAS HARTMANN, PHD

UNLV

RESEARCH TEAM

- **FACULTY**
  - Chemistry, Health Physics, Engineering
- **ASSOCIATE FACULTY/RESEARCH FACULTY**
  - Physics, Mechanical Engineering
- **26 GRADUATE STUDENTS**
  - 18 grant funded students
  - 5 on fellowship at UNLV
  - 3 on Fellowship at National Labs
- **2 LABORATORY MANAGEMENT PERSONNEL**
  - Technical Quality Assurance Manager
  - Laboratory Manager

UNLV

Radioanalytical Separations

Front Row: Lucas Boron-Brenner, Ralf Sudowe, Julia Nell, Audrey Roman
Back Row: Rebecca Springs, Derek McLain, Jaimie Daum, Sherry Faye, Jeff Rolfes

UNLV

Actinide-Lanthanide Subgroup

Front Row: Dan Koury, Jacquelyn Dorhout
Second Row: Ken Czerwinski, Saadi Nazal, Eunja Kim, Keri Campbell
Back Row: AJ Swift, Daniel Rego, Marc Fitzgerald, Nicholas Wozniak

UNLV

Technetium Subgroup

Front Row: Bradley Childs, Ken Czerwinski, Thomas Hartmann, Kyle Childs, Romina Farmand

Back Row: William Kerlin, Erik Johnstone, Frederic Poineau, Vanessa Sanders, Maryline Ferrier

UNLV

RADCHEM PHD PROGRAM: Focus on Student Development

- Provide Students with Interesting and Important Research
- Analytical and Critical Thinking Skills
- Academic Driven Research Direction
- Strong Collaborations
- Noted Researchers
- Technical Competency
- Communication Skills
- Expertise in the field of Radiochemistry

Pathway to the PhD

- Required Coursework
  - 4 core courses
    - Introduction to Radiochemistry
    - Applied Nuclear Physics
    - Radiation Detection
    - Radiation Physics and Instrumentation Laboratory
  - Maintain a B or better average
  - Additional 48 Credits of Instructor Approved Coursework

- Weekly Seminar
  - 20 minute Presentation to Peers / Instructors
  - Safety, Equipment, Labs

The Road Continues…

- Selection of Research Project
- Committee Selection
- 2 Part Oral Exam on Research and Outside Topic
- Advance to Candidacy
- Conduct Research for Thesis
- Form their thesis committee

UNLV

…and Continues

Culminating in a Written Thesis and Oral Defense

UNLV

Interactions With Researchers Outside UNLV

- Research opportunities at DOE laboratories
  - Summer Internships at LANL, PNNL
- Conference Presentations
  - ACS, ANS, ACA, UITI, Marc IX
  - ISTR, Atalante, APSORC, CHE 8
- Fellowships
  - 2 Livermore Scholars, 4 Nuclear Forensics Graduate Fellows, 2 NEUP-IUP Fellows
- Publications

UNLV

COLLABORATORS
US DEPT OF ENERGY

- Argonne National Laboratory
  - Tc coordination chemistry
- Los Alamos National Laboratory
  - Actinide oxide aging for forensics
  - Tc-U Separations
  - Technetium waste forms
  - Nuclear Forensics Summer School
    - 1st school at UNLV in summer 2010

- NSTec
  - Nuclear Forensics
  - Environmental Pu chemistry

UNLV

COLLABORATORS

US DEPT OF ENERGY

- Idaho National Laboratory
  - Fuel cycle separations and nuclear fuels
- Pacific Northwest National Laboratory
  - Microscopy of tank waste solids and Tc waste forms
  - NMR of Tc
  - Actinide separations and spectroscopy
- Lawrence Berkeley National Laboratory
  - Characterization of Tc compounds
- Livermore National Laboratory
  - Nuclear forensics
  - Heavy element chemistry

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UNIVERSITY COLLABORATIONS

- Nuclear Science and Security Consortium
  - Coordinated by UC-Berkeley NE
- NSF-IGERT
  - Hunter College, University of Missouri

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UNDERGRADUATE SUMMER SCHOOLS

- FUEL CYCLE SUMMER SCHOOL
  - Department of Energy – Nuclear Energy
  - 2010 – 2014
  - 12 Students
  - US Citizens Only

- NUCLEAR FORENSICS SUMMER SCHOOL
  - US Dept of Homeland Security - DNDO
  - Regional Program
  - Hosted by UNLV 2011 and 2014

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STUDENT INTERNSHIPS

- Typically 3-6 months depending on institution
- UNLV Assistance with Visa Application Process
- UNLV Assistance with Coordinating Housing

- ANSTO
- Chimie Paris Tech
- University of Nantes
- Universite de Savoie

UNLV

WHAT DOES THIS MEAN FOR YOU?

- Opportunity for Student Interaction Through Internships
- Highly Motivated Students
- Need to Fulfill Internship Requirements for Degree
- Interested in Our Research
- Ability to Secure Funding Through Scholarships and Fellowships

- Email to: Wendee.Johns@UNLV.edu

Thank You

Questions?


POW
To
ONWARD
GLORIOUS HEROES OF
RADIOCHEMISTRY!
ISLAND
of
STABILITY
USS Radchem
RFCSS

Rhenium Complexes of Benzothiazoles as Models for the Diagnosis of Alzheimer`s Disease

T.I.A. Gerber*, X. Schoultz

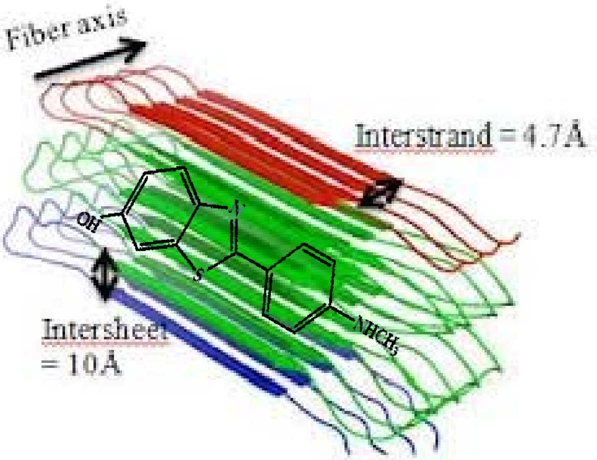
Nelson Mandela University

South Africa

Alzheimer`s Disease

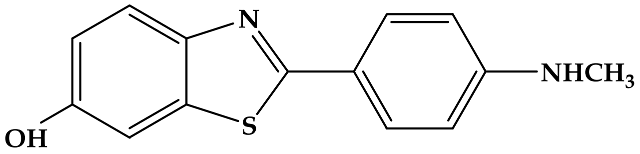
- AD major cause of dementia
- Neurodegenerative disorder leading to synaptic failure and neutronal death
- Pathological feature is presence of extracellular senile plaques in the brain
- Plaques consist of insoluble peptide called *amyloid-β (Aβ)*
- Diagnostic imaging agents targeting *Aβ* important in diagnosis, treatment and monitoring of patients
- *Aβ* fibrils have a cross-β-sheet structure, held together by H-bonding, π-π stacking and electrostatic interactions
- Orientation of sheets generates small channels and pockets to which aromatic molecules can intercalate and bind via π-π.

β-Strands running perpendicular to the fiber axis



International Year of Crystallography

Benzothiazoles (bt)



- Bt`s show some selectivity to Aβ fibrils and plaques

- Rigid aromatic systems that enter channels or hydrophobic pockets and bind via π-π interactions

- Prerequisites: - ability to cross the BBB
  - small lipophilic agents/tracers
  - excellent brain uptake
  - fast washout from normal brain

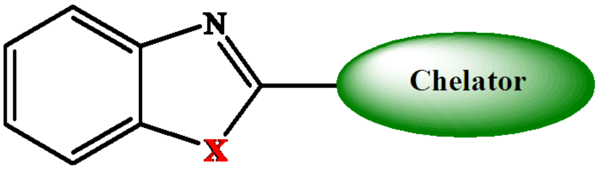
- Pittsburgh Compound –B most well-characterized agent for Aβ plaques

J. Neuro Sci, 2007, **27**, 10365.

Heterocyclics

- **Benzothiazole (X = S)**

  Alzheimer's disease

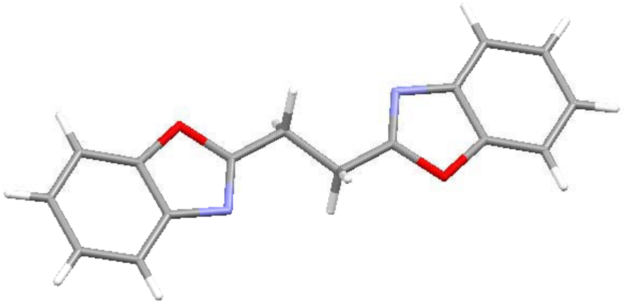


- **Benzoxazole (X = O)**

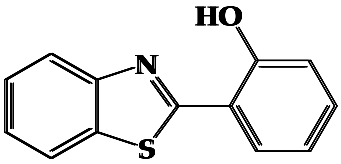
  Antimicrobial

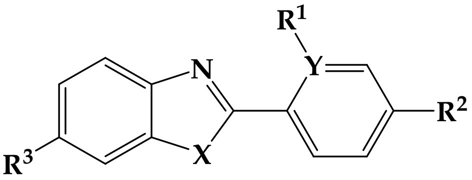
- **Benzimidazole (X = NH)**

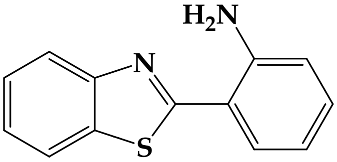
  Anti-tumour

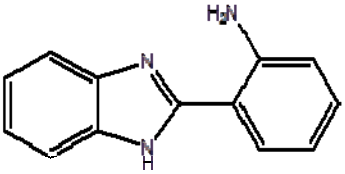


Analogous Bidentate Ligands

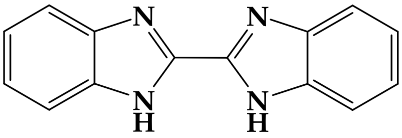




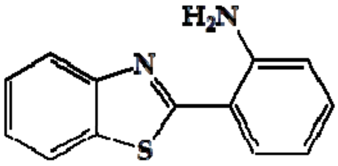


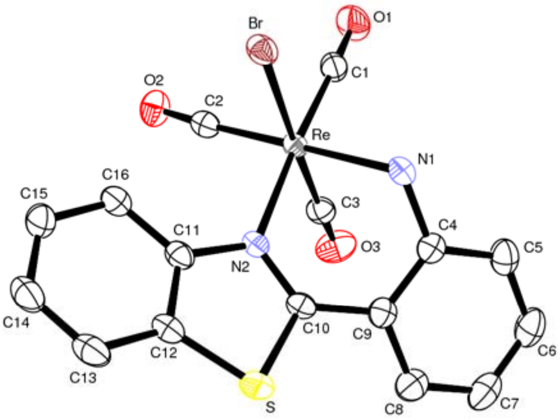


	X	*Y*	*R^1*	*R^2*	*R^3*
Pittsburgh Compound B	**S**	**C**	**H**	**$NHCH_3$**	**OH**
Hhpd	**S**	**C**	**O**	**H**	**H**
Habt	**S**	**C**	**NH_2**	**H**	**H**
H_2pab	**NH**	**C**	**NH_2**	**H**	**H**
bibzimH$_2$	**N**	**-**	**-**	**-**	**H**



$[Re(CO)_5Br]$

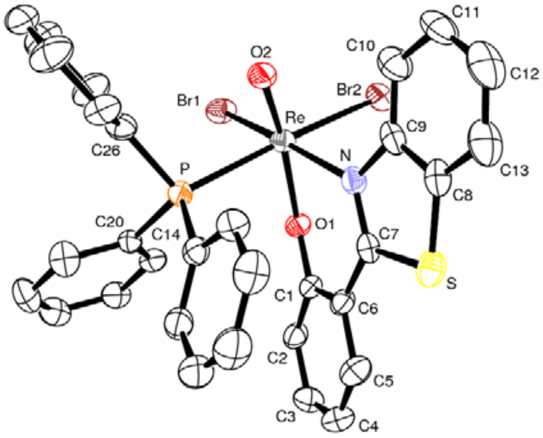


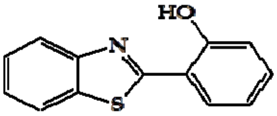


Re-N(1)H_2 = 2.227(3) Å
Re-N(2) = 2.227(2) Å

I. Booysen, T. I.A. Gerber, P. Mayer, Inorganic Chimica Acta, 2010, 363, 1292-1296.

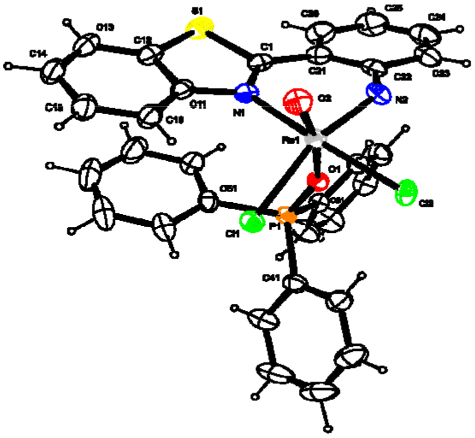
Hhpd versus Habt

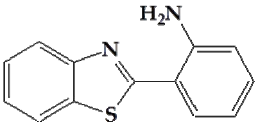




[ReOBr$_3$(PPh$_3$)$_2$]

Re-N = 2.180(7) Å
Re-O(1) = 1.949(5) Å

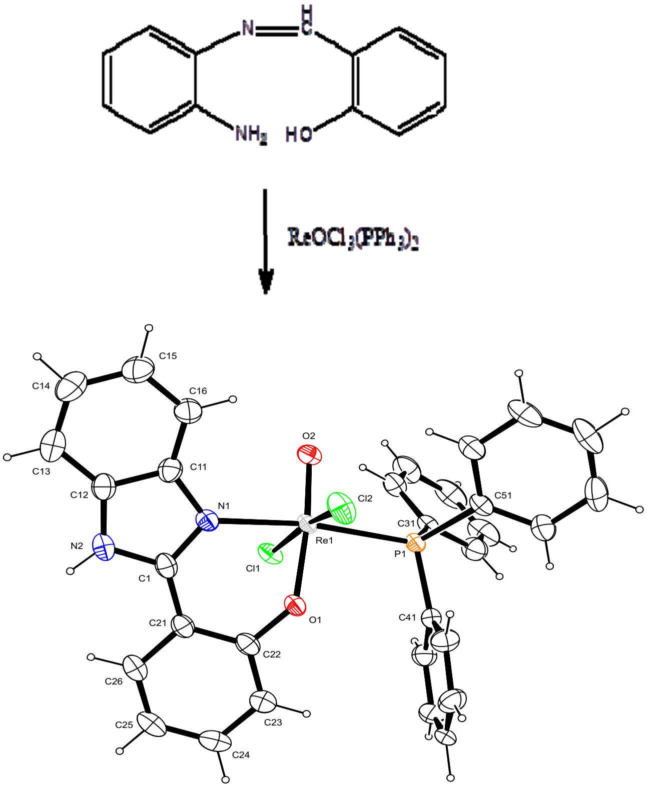




[ReOCl$_3$(PPh$_3$)$_2$]

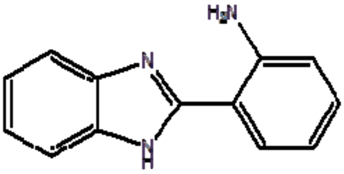
Re-N(2)H = 1.952(2) Å
Re-N(1) = 2.143(2) Å

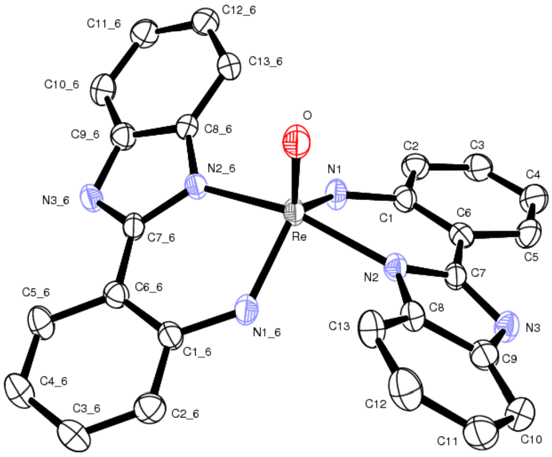
Trans-dichloro



Re-O(2) = 1.691(3) Å
Re-O(1) = 1.934(3) Å
Cl(1)-Re-Cl(2) = 170.37(4)°

With *trans*-$[ReO_2(py)_4]^+$ in Ethanol

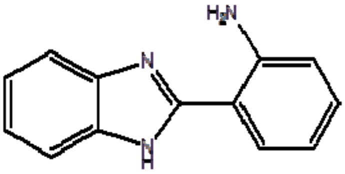


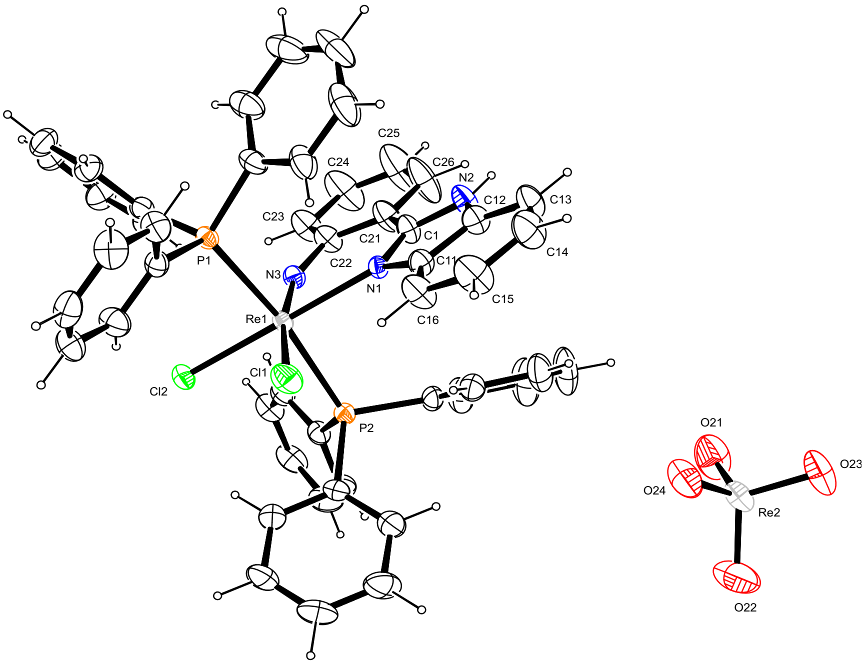


- tbp
- Re-N(1)H = 1.947(4) Å
- Re-N(2) = 2.060(4) Å
- N(2)-Re-N(2a) = 160.7(1)°
- N(1)-Re-N(1a) = 120.6(2)°
- N(1)-Re-N(2) = 85.6(2)°

I. Booysen, T. I.A. Gerber, P. Mayer, Journal of Coordination Chemistry, 2008, 61, 1525 – 1531.

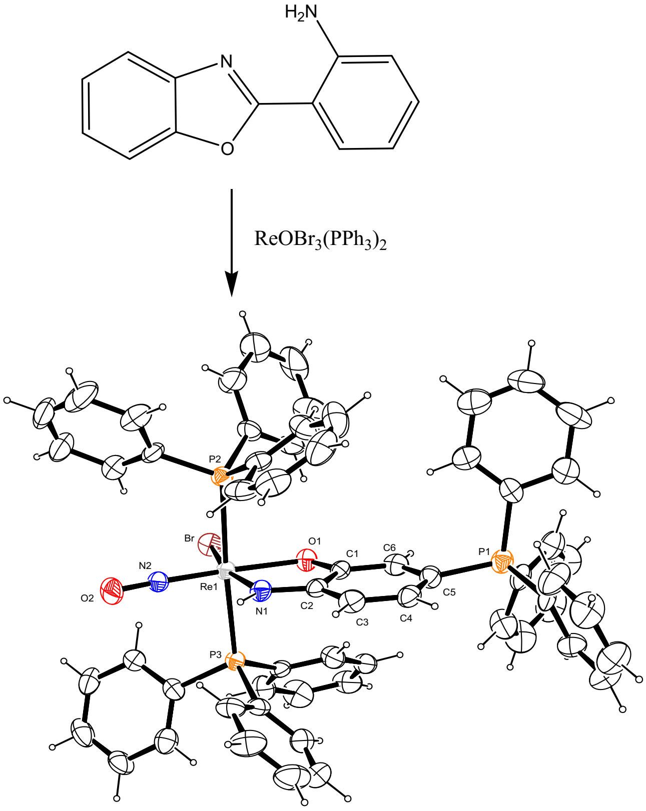
With $[ReOCl_3(PPh_3)_2]$ in Ethanol





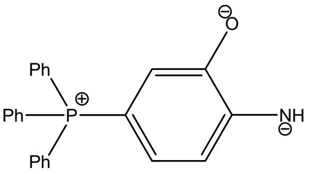
Re-N(1) = 2.248(5) Å
Re-N(3) = 1.740(5) Å [Re=N-]
N(1)-Re-N(3) = 80.0(2)°

With $[ReOBr_3(PPh_3)_2]$ in Methanol

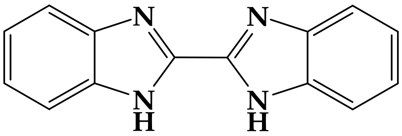


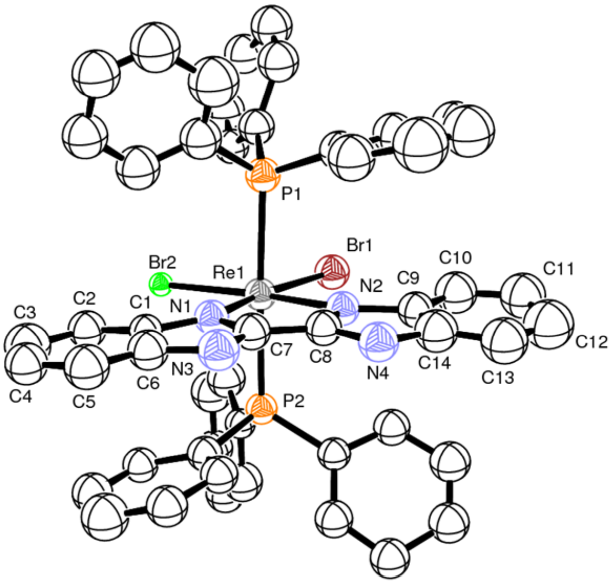
$[Re^{II}(NO)BrL(PPh_3)_2]^+ ReO_4^-$

Re-N(1) = 1.996(9) Å
Re-N(2) = 1.762(7) Å
Re-O(1) = 2.067(7) Å
N(2)-O(2) = 1.20(1) Å
P(1)-C(5) = 1.79(1) Å



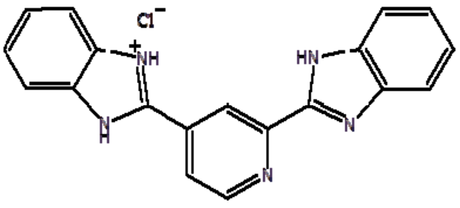
With $[ReOBr_3(PPh_3)_2]$ in Ethanol

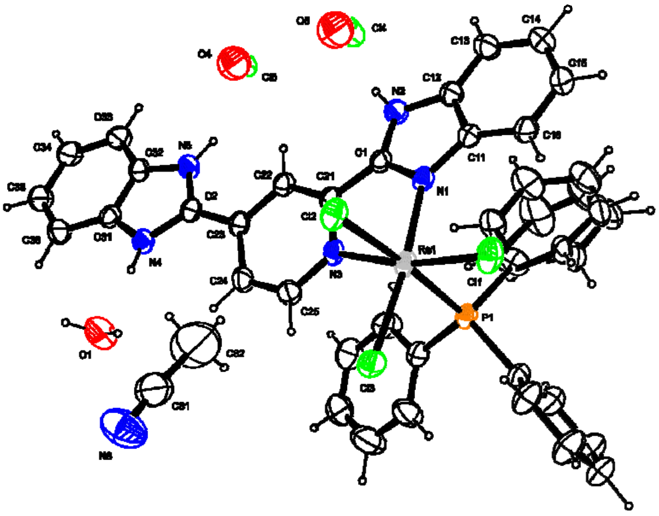




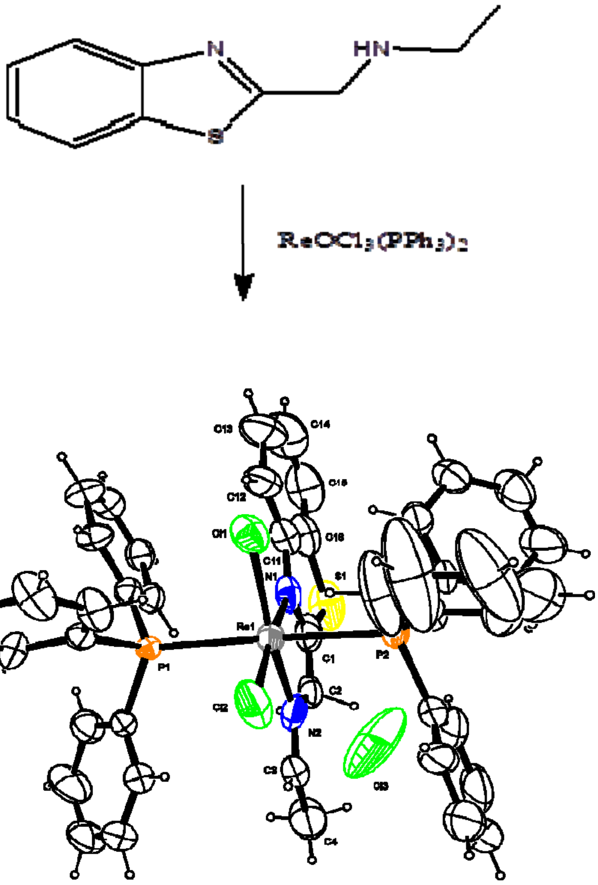
- Re(III)
- Re-N(1) = 2.134(5) Å
- Re-N(2) = 2.148(4) Å

With $[ReOCl_3(PPh_3)_2]$ in Acetonitrile

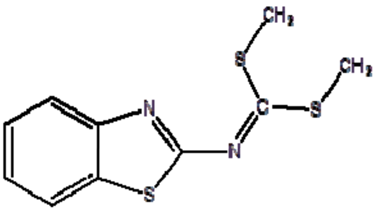


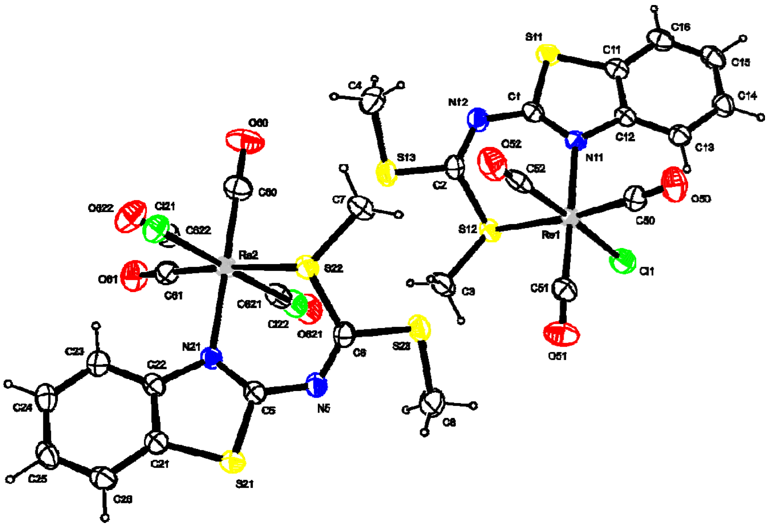


Re(III)
Re-N(1) = 2.089(2) Å
Re-N(3) = 2.079(2) Å



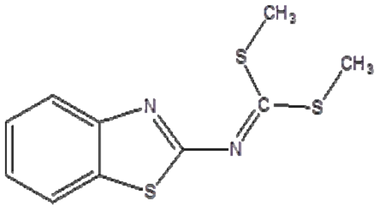
Re(III)
Re-N(1) = 2.149(9) Å
Re-N(2) = 2.09(1) Å
C(2)-N(2) = 1.42(2) Å
C(3)-N(2) = 1.293(18) Å

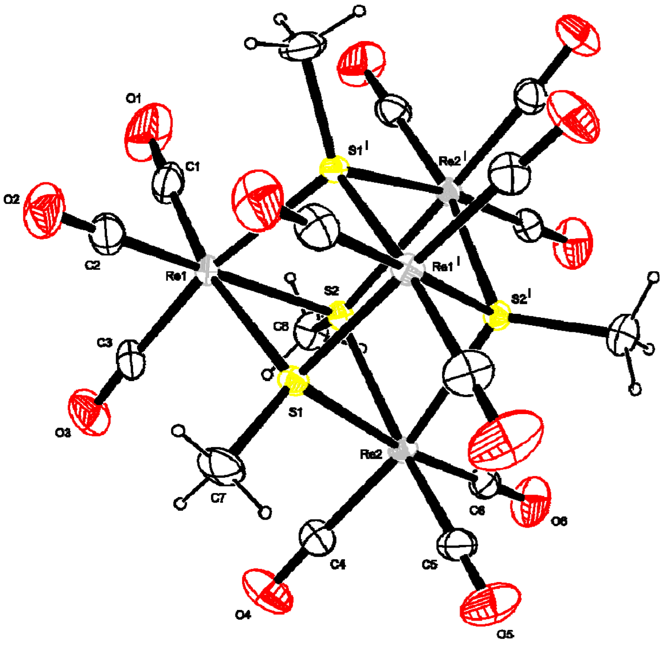




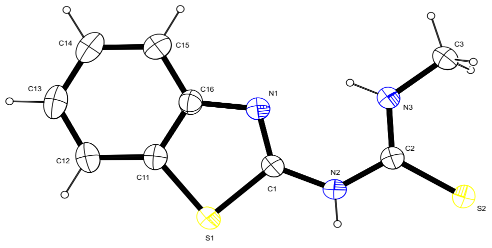
Re(1)-N(11) = 2.211(2) Å
Re(1)-S(12) = 2.512(1) Å
C(1)-N(11) = 1.313(4) Å
C(2)-N(12) = 1.276(3) Å

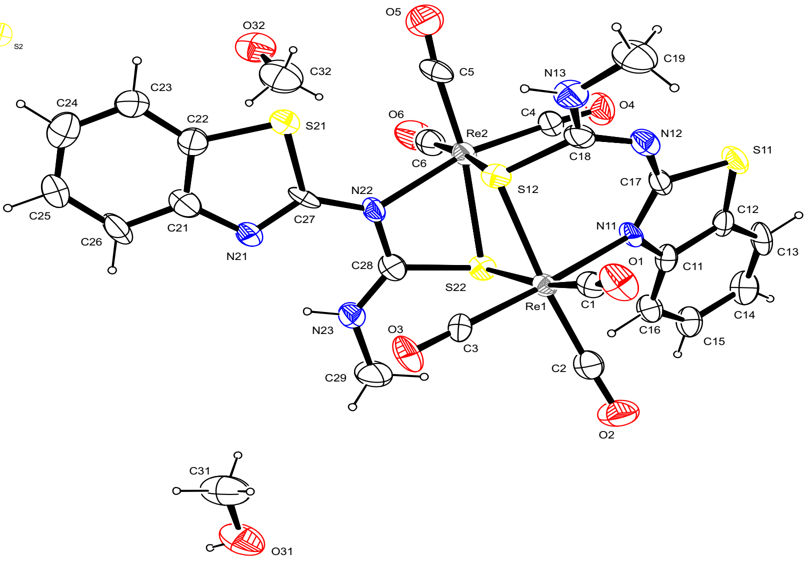
$[Re_4(CO)_{12}(MeS)_4]$



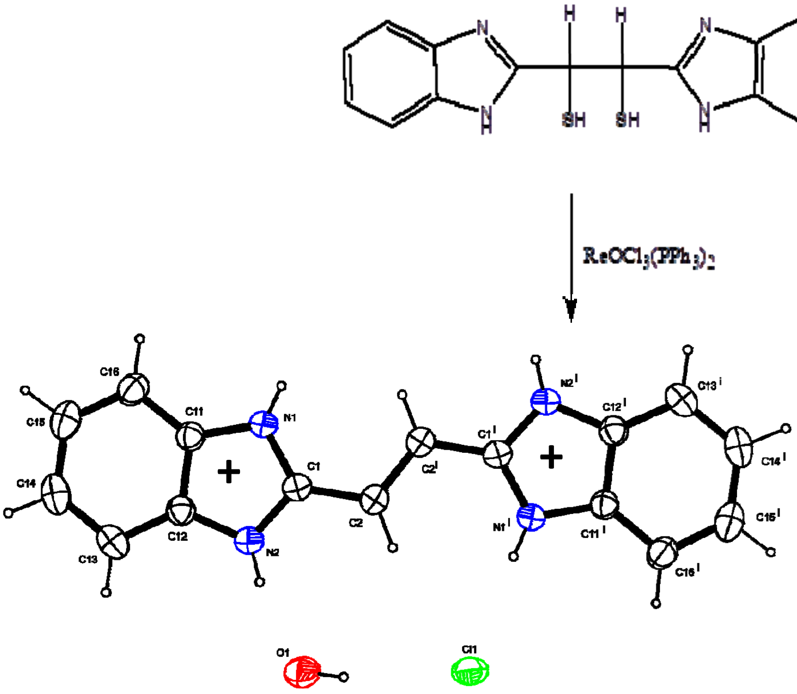


Re(1)-S(1) = 2.499(1) Å
Re(1)-S(2) = 2.489(1) Å
Re(2)-S(1) = 2.501(2) Å
Re(2)-S(1) = 2.511(1) Å
Re(1)-S(1)-Re(2) = 101.41(5)°





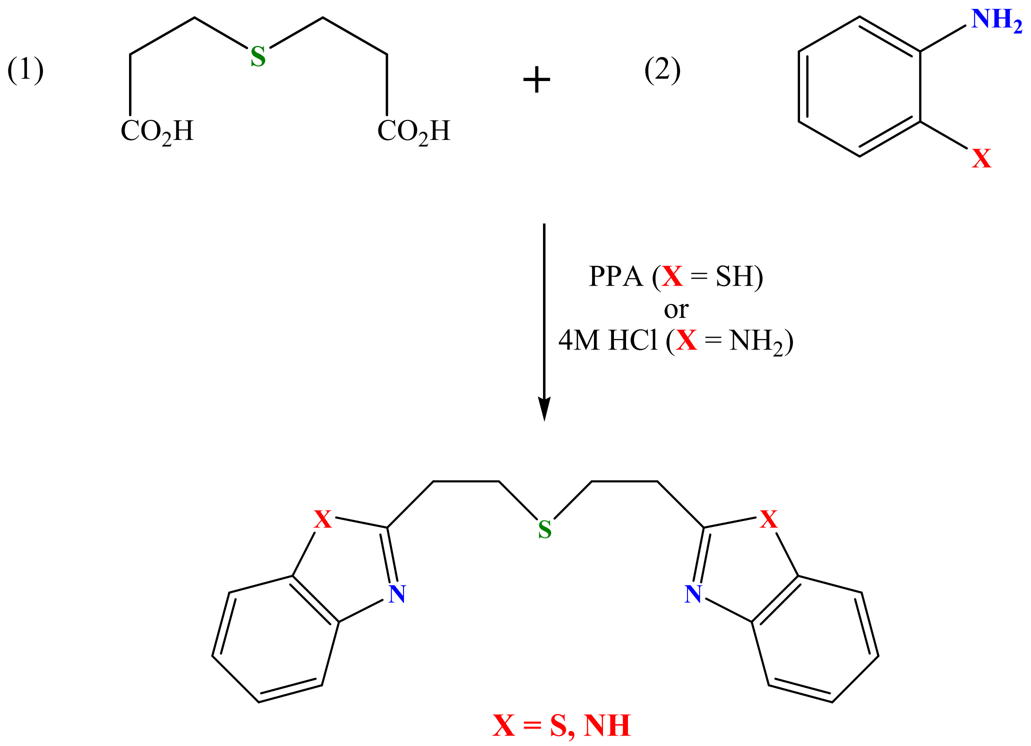
Re(1)-N(11) = 2.205(9) Å
Re(2)-N(22) = 2.192(9) Å
Re(1)-S(12) = 2.481(2) Å
Re(2)-S(12) = 2.516(2) Å
Re(1)-S(22) = 2.572(3) Å
Re(2)-S(22) = 2.550(2) Å
N(12)-C(18) = 1.296(16) Å



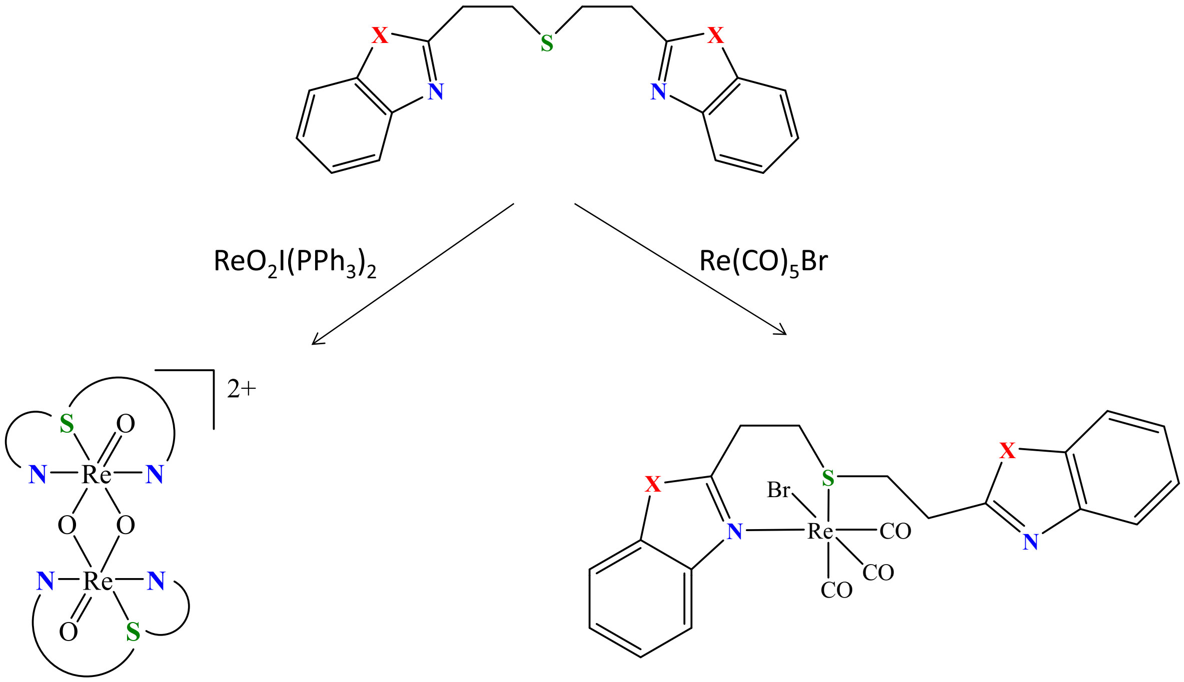
+ $Ph_3P=S$

C(2)-C(2a) = 1.378(2) Å

Synthesis of tridentate ligands



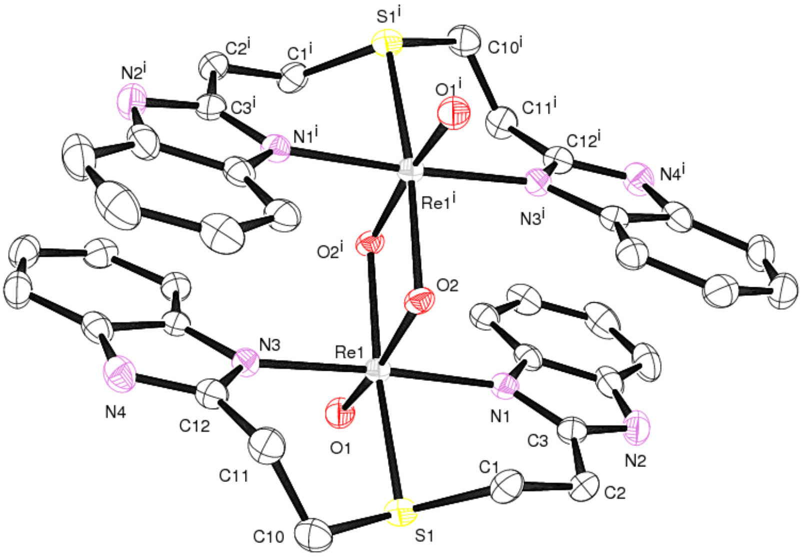
Synthesis of complexes



X = **NH**

X = **S**

Characterization



Re – O(1) = 1.712(2) Å

Re – O(2) = 1.859(2) Å

Re – $O(2^{i})$ = 2.109(3) Å

O(1) – Re – O(2) = 170.2(1)˚

N(1) – Re – S(1) = 85.62(9)˚

N(3) – Re – S(1) = 91.07(7)˚

***ν*(Re=O) = 942 cm^{-1}**

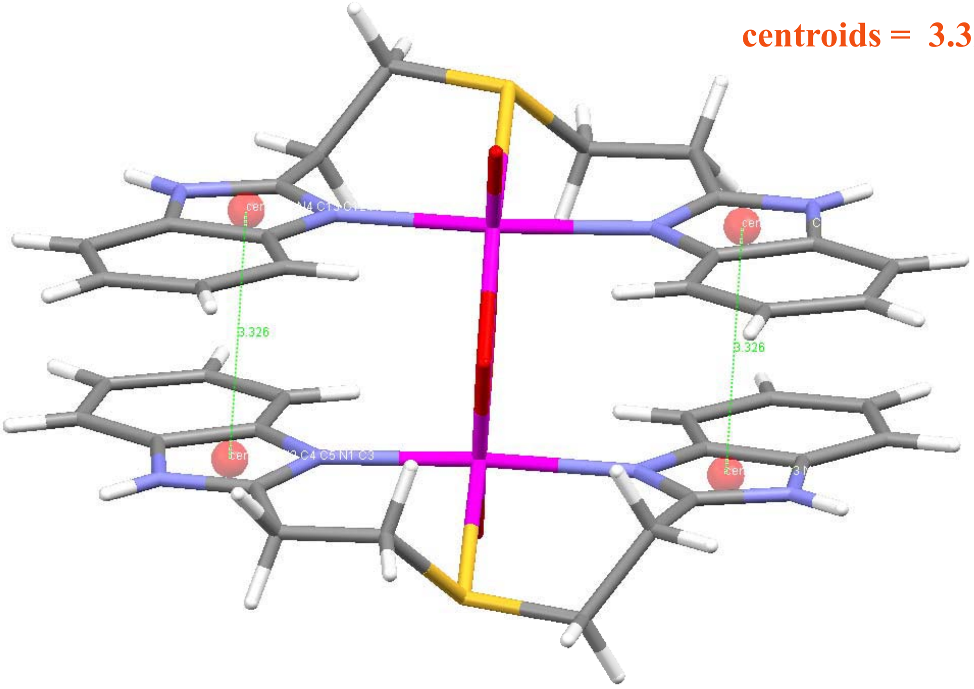
***ν*(Re-O-Re) = 694 cm^{-1}**

Conductivity (CH_3CN, 10^{-3}M): 256 ohm^{-1}cm^{2}mol^{-1}

1:2 electrolyte

π – π stacking

Distance between imidazole ring centroids = 3.326 Å



Rhenium complexes of benzothiazoles as models for the diagnosis of Alzheimer`s disease

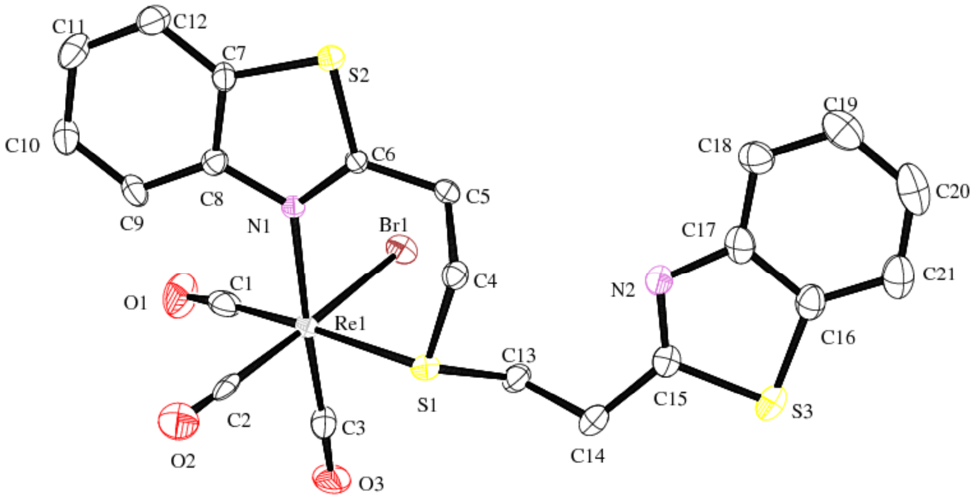
T.I.A. Gerber and X. Schoultz
Department of Chemistry, Nelson Mandela Metropolitan University, 6031 Port Elizabeth, South Africa

Rhenium complexes of benzothiazole derivatives may be of interest for the development of potential radiopharmaceuticals for radiotherapy and for the diagnosis of Alzheimer's disease. Benzothiazoles were found to be active against a range of breast carcinoma cell lines, and can provide information on amyloid deposits in AD patients.

Derivatives of 1,3-benzothiazoles have been synthesized and coordinated to rhenium. Bis-(benzothiazole) ligands containing the thioether bridge has been prepared and spectroscopically characterized. For example, bromopentacarbonylrhenium(I) reacted with bis(benzothiazol-2-ylethyl)sulfide (bbt) to produce the *fac*-$[Re(CO)_3(bbt)Br]$ complex. The ligand acts as a neutral bidentate chelate with one of the benzothiazole units remaining uncoordinated. The bis(benzothiazole) ligands has also been derivatized to include amino and hydroxyl groups which can potentially coordinate as tridentate chelating ligands to the metal centre. These novel rhenium-benzothiazole complexes may have significance in the development of technetium-99m analogues that could possibly be applied as a diagnostic tool for Alzheimer's disease.

This work was extended to include the corresponding benzoxazoles and benzimidazoles. These ligand systems have demonstrated interesting pharmacological activities and have recently been extensively studied for their anticancer activity. An *in vitro* biological evaluation of 2-substituted benzoxazoles showed that this class of ligands has anticancer/antineoplastic, anti-HIV-1 and antimicrobial activities. The broadening of the scope of the project to include novel rhenium-benzoxazole and benzimidazole complexes may lead to the development of a suitable radiopharmaceutical for the treatment of cancer. The synthesized complexes were fully characterized through the use of infra red and ^1H NMR spectroscopy, UV-Vis spectroscopy, conductivity measurements, cyclic voltammetry, X-ray structure determination and computational analysis.

Characterization



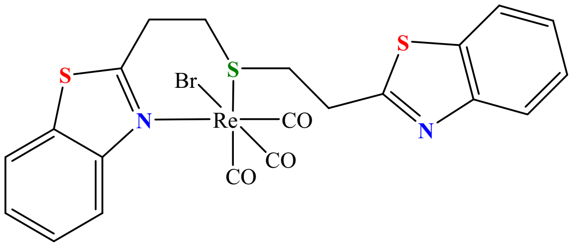
Re – N(1) = 2.222(3) Å

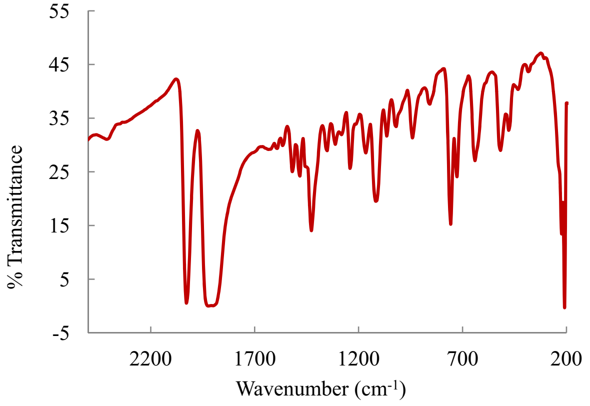
Re – S(1) = 2.4907(11) Å

Re – CO = 1.896(5) – 1.960(5) Å

N(1) – Re – S(1) = 88.66(9)˚

Spectroscopic Characterization

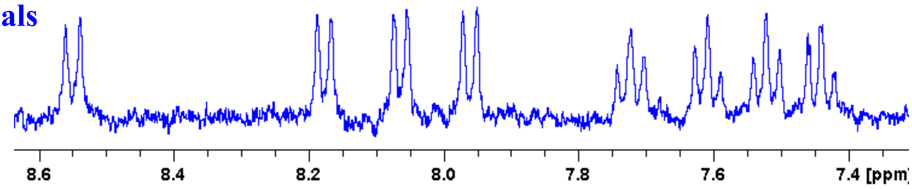




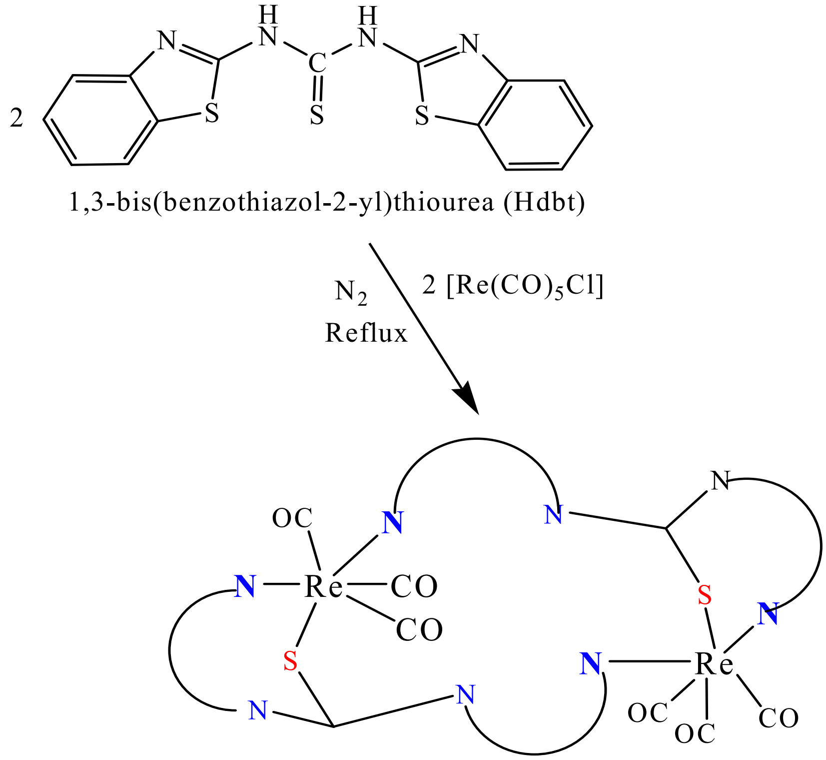
- ν(C=N) = 1519 cm^{-1}
- ν(Re-N) = 482 cm^{-1}
- $\nu(\mathrm{CO})_{fac}$ = 2024, 1933, 1891cm^{-1}

Eight one-proton signals

- 4 doublets
- 4 triplets

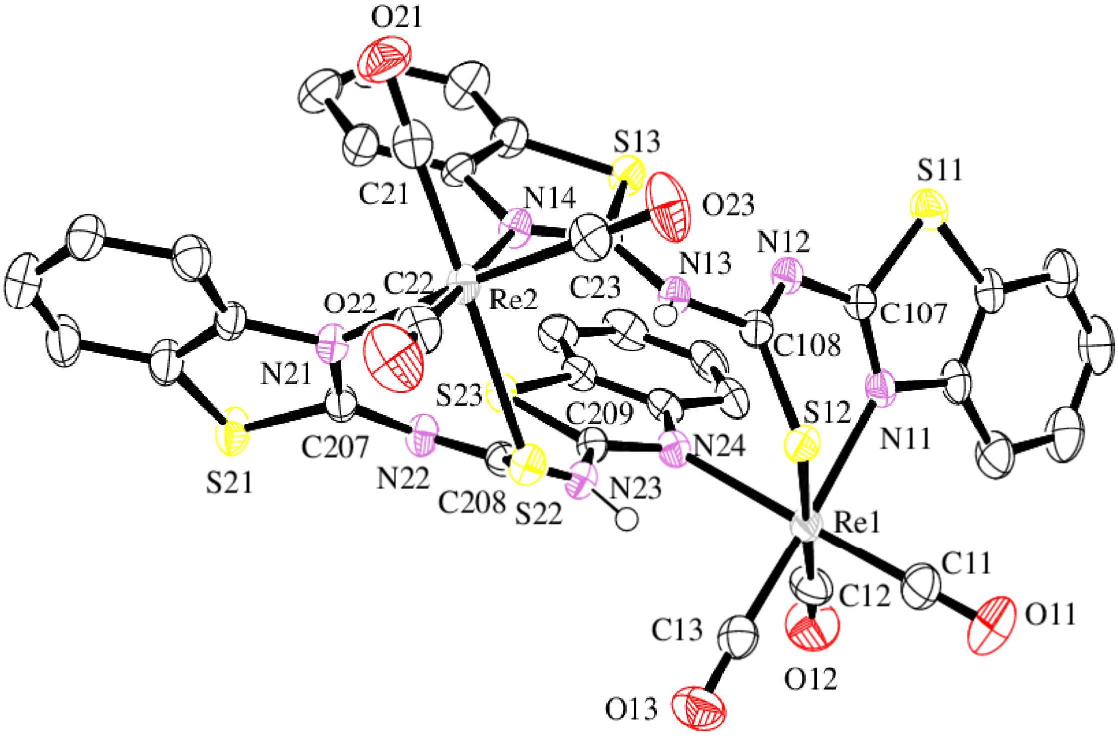


Synthesis



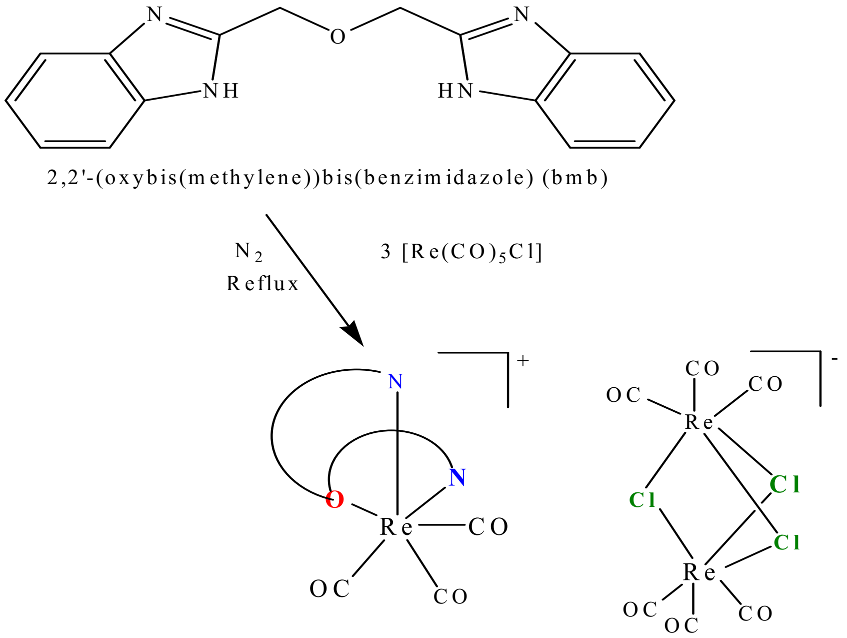
(μ-dbt)$_2$[Re(CO)$_3$]$_2$

Crystal structure

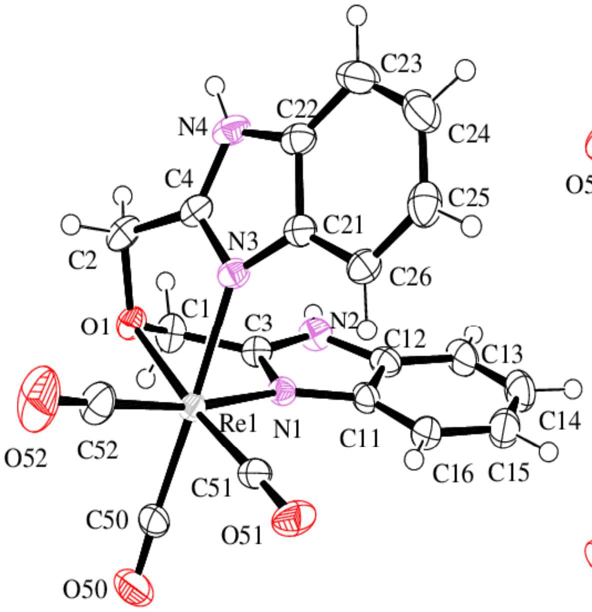


K. Potgieter, P. Mayer, T.I.A Gerber, *Aust. J. Chem.*, 2010, 63, 1382

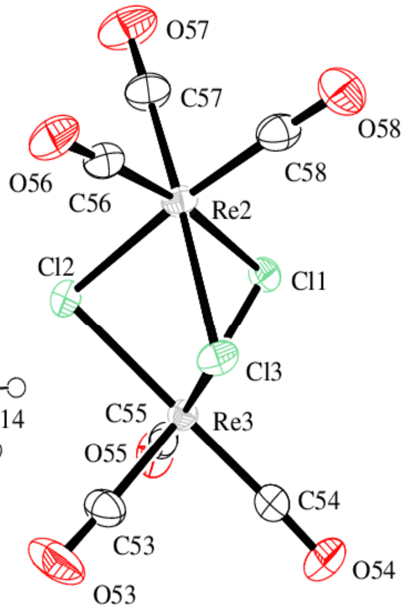
Synthesis of complex



Crystal structure

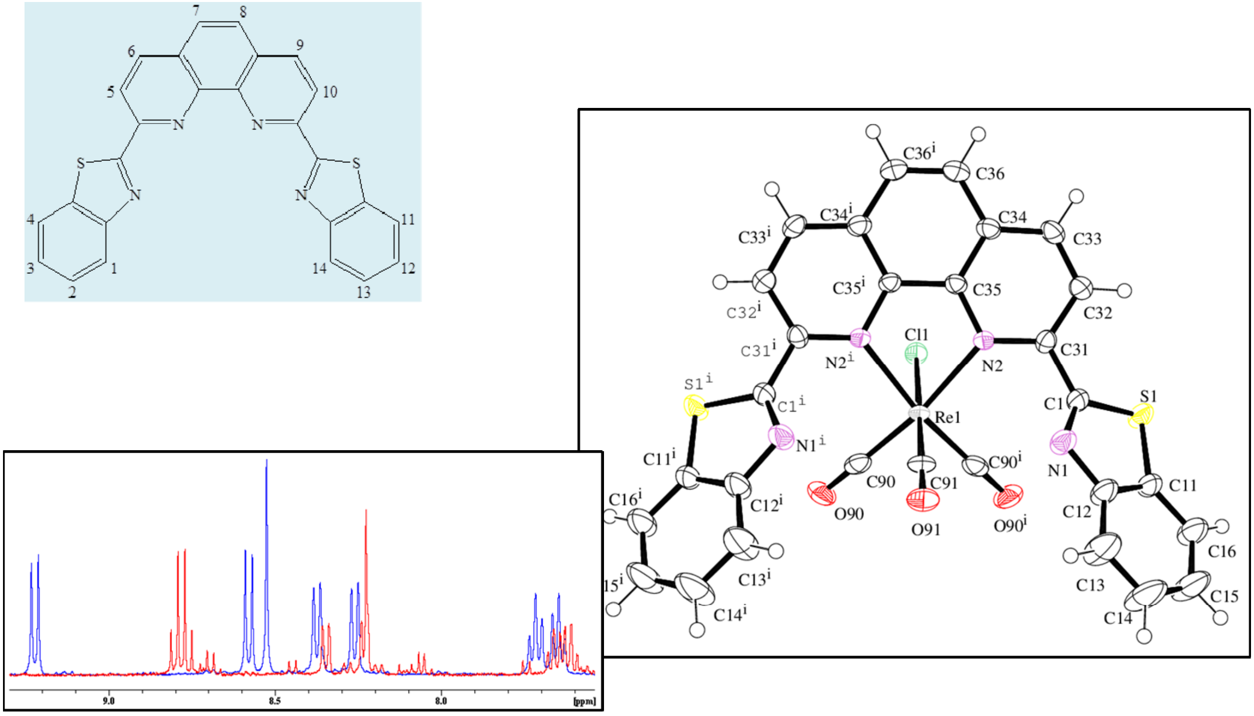


[Re(bmb)(CO)$_3$]$^+$



[Re$_2$Cl$_3$(CO)$_6$]$^-$

$Re(CO)_5Cl$



- Cl(1)-Re-C(91) = 179.3(2)° lies in a σ_v mirror plane

Acknowledgements

- NMMU
- National Research Foundation
- Ntembi Consortium
- Dr Peter Mayer
- Dr Eric Hosten
- You, for your interest, patience and time!

Beaches

Addo National Park

Nitrosyltechnetium Complexes with Various *P,N* Ligands

Janine Ackermann[1*], Adelheid Hagenbach[1], Ulrich Abram[1]
Freie Universität Berlin - Germany
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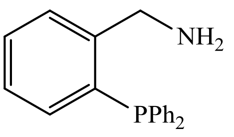
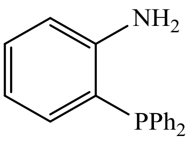
The coordination chemistry of rhenium and particularly technetium nitrosyls can be regarded as widely unexplored. This is surprising with regard to the fact that rhenium compounds frequently possess remarkable catalytic properties and compounds of the metastable, gamma-emitting technetium nuclide ^{99m}Tc ($t_{1/2}$ = 6 h) with the metal in low oxidation states found application in diagnostic nuclear medicine.



H_2L1



H_2L2

$(NBu_4)[Tc(NO)Cl_4(MeOH)]$ is a suitable starting material for the syntheses of Tc^{II} and Tc^{I} nitrosyl complexes.[1] Reactions with (2-aminomethylphenyl)diphenylphosphine, H_2L1, give different products depending on the conditions applied. The products involve technetium(I) and technetium(II) complexes, which contain the phosphineamine in various coordination modes and positions. Reactions in methanol form products such as the technetium(I) complexes $[Tc(NO)Cl_2(H_2L1\text{-}\kappa N,P)(H_2L1\text{-}\kappa N)]$ and $[Tc(NO)Cl_2(H_2L1\text{-}\kappa N,P)_2]^+$ or the technetium(II) compounds $[Tc(NO)Cl_3(H_2L1\text{-}\kappa N,P)]$ and $[Tc(NO)Cl_4(H_2L1\text{-}\kappa N)]^-$ (see Fig. 1). The products could be isolated in crystalline form and studied by X-ray diffraction.

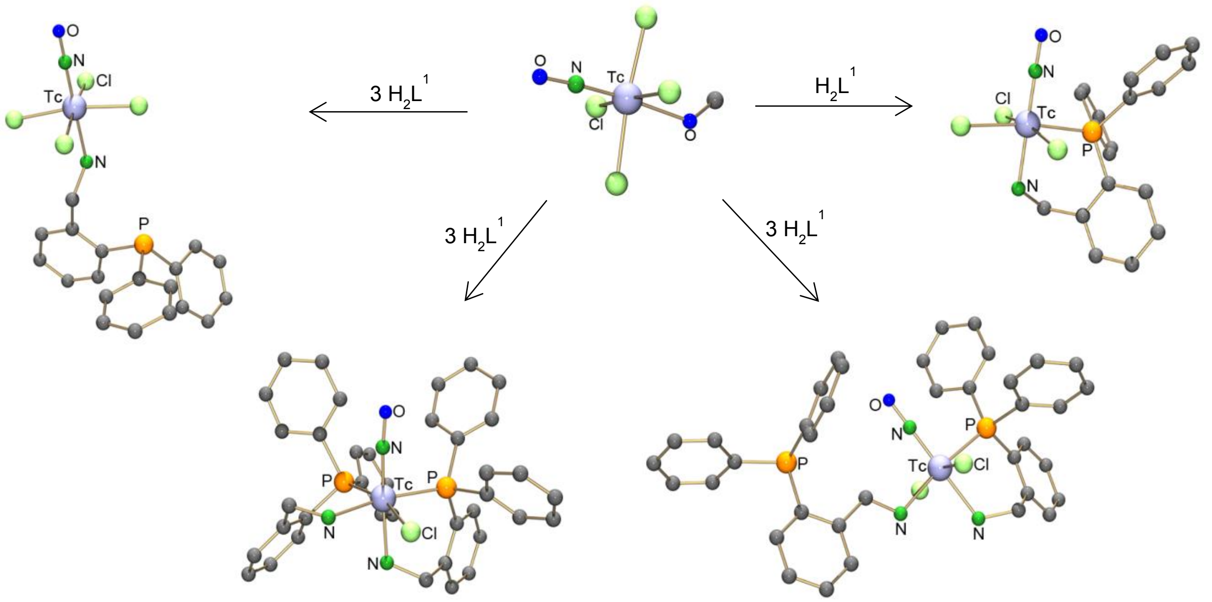


Fig. 1: Overview of the reactions with $(NBu_4)[Tc(NO)Cl_4(MeOH)]$ with H_2L1 in methanol.

Reactions of (2-aminophenyl)diphenylphosphine, H_2L2, with $(NBu_4)[Tc(NO)Cl_4(MeOH)]$ give the cationic technetium(I) chelate $[Tc(NO)Cl(H_2L2\text{-}\kappa N,P)_2]^+$ in two isomeric forms depending of the reaction conditions applied. Both products were studied spectroscopically and by single crystal X-ray crystallography.

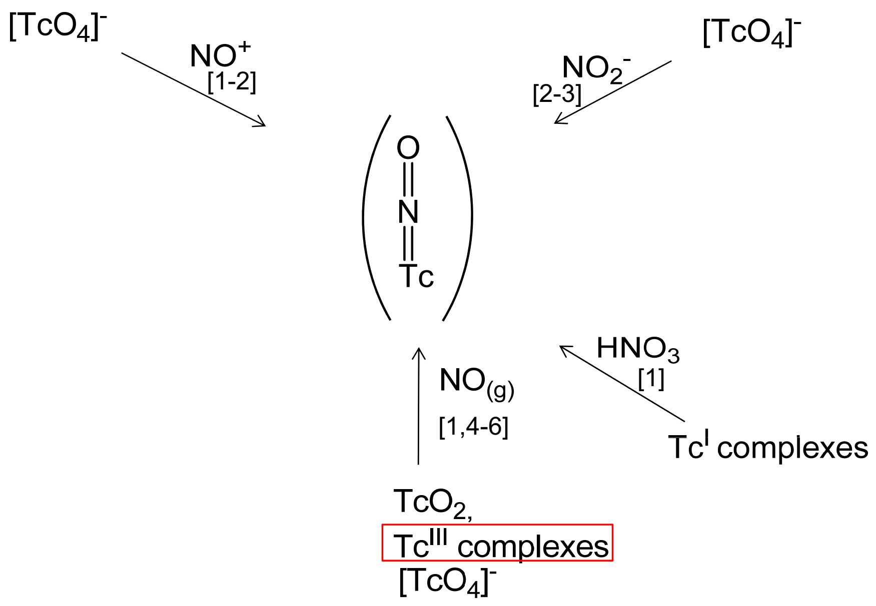
[1] Cheah, C. T.; Newman, J. L.; Nowotnik, D. P.; Thornback, J.R.; *Nucl. Med. Biol.* **1987**, *14*, 573.

Nitrosyltechnetium Complexes with Various *P*,*N* Ligands

Janine Ackermann
Institute of Chemistry and Biochemistry
Freie Universität Berlin

8th International Symposium on Technetium and Rhenium

Technetium Nitrosyls



$[TcO_4]^-$ $\xrightarrow{NO^+}$ [1-2]

$[TcO_4]^-$ $\xrightarrow{NO_2^-}$ [2-3]

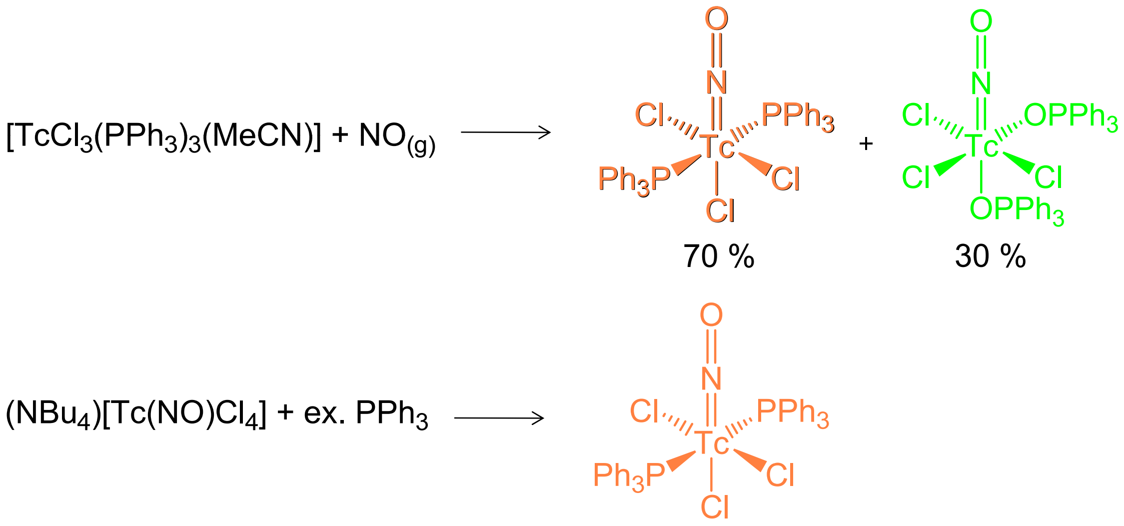
TcO_2, Tc^{III} complexes, $[TcO_4]^-$ $\xrightarrow{NO_{(g)}}$ [1,4-6]

Tc^{I} complexes $\xrightarrow{HNO_3}$ [1]

[1] K. E. Linder, A. Davison, J. C. Dewan, C. E. Costello, S. Maleknia, *Inorg. Chem.* **1986**, *25*, 2085., [2] R. Schibli, N. Marti, P. Maurer, B. Spingler, M. L. Lehaire, V. Gramlich, C. L. Barnes, *Inorg. Chem.* **2005**, *44*, 683., [3] D. Rattat, A. Verbruggen, H. Schmalle, H. Berke, R. Alberto, *Tetrahedron Letters.* **2004**, *45*, 4089., [4] Orvig, C.; Davison, A.; Jones, A. G. *J. Labelled Compd. Radiopharm.* **1981**, *18*, 148., [5] T. Nicholson, P. Müller, A. Davison, A. G. Jones, *Inorg. Chim. Acta* **2006**, *359*,1296., [6] R. M. Pearlstein, W. M. Davis, A. G. Jones, A. Davison, *Inorg. Chem.* **1989**, *28*, 3332.

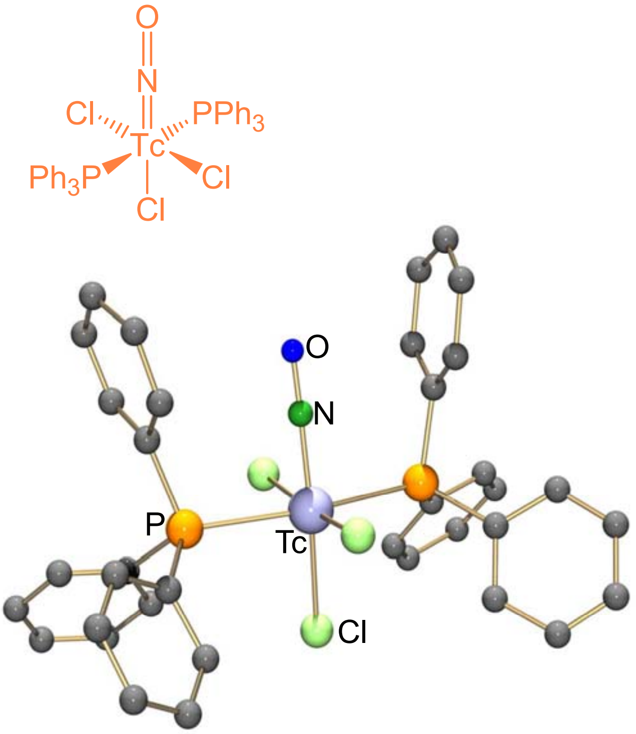
Synthese of Technetium Nitrosyls

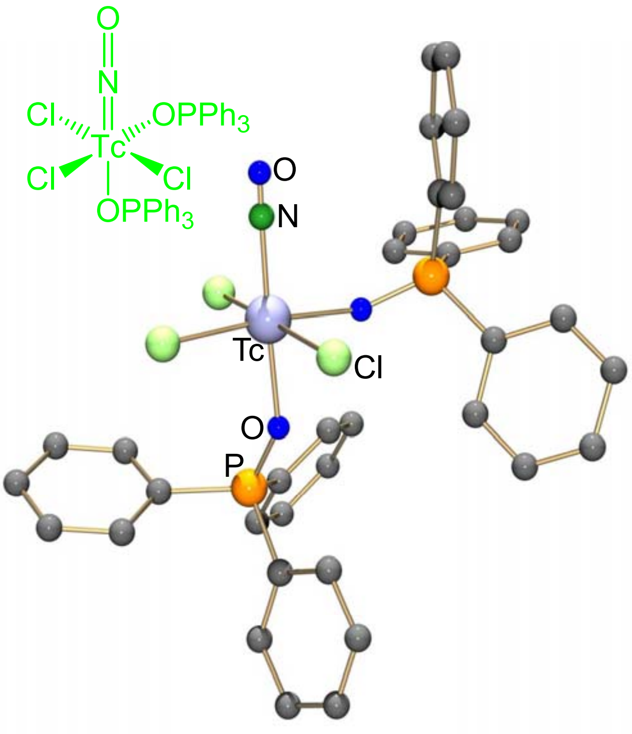
- starting from Tc(III) complexes with $NO_{(g)}$[5]



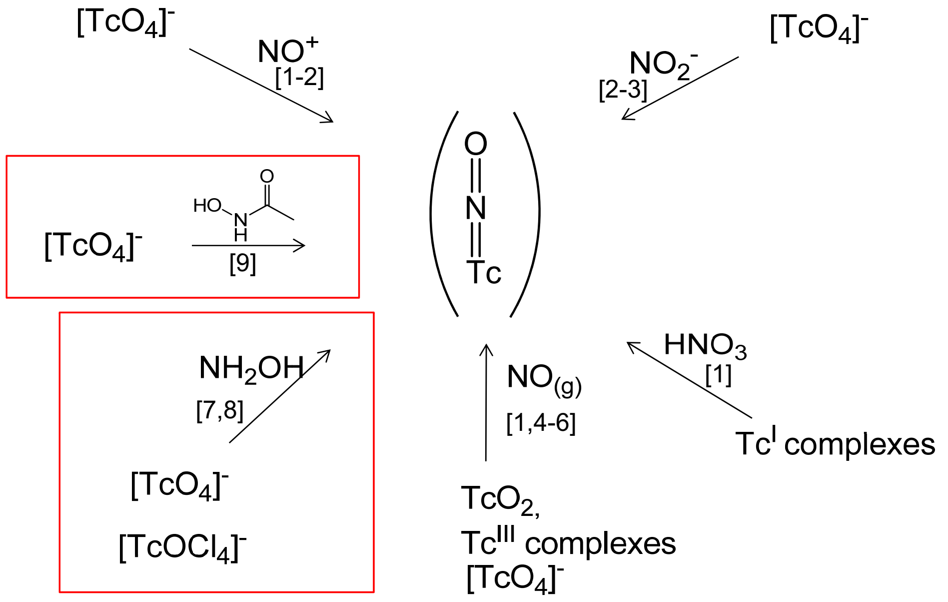
[5] T. Nicholson, P. Müller, A. Davison, A. G. Jones, *Inorg. Chim. Acta* **2006**, *359*,1296.

Synthese of Technetium Nitrosyls





Technetium Nitrosyls



$[TcO_4]^-$ $\xrightarrow[{[1\text{-}2]}]{NO^+}$

$[TcO_4]^-$ $\xrightarrow[{[2\text{-}3]}]{NO_2^-}$

$[TcO_4]^-$ $\xrightarrow[{[9]}]{}$

$(O{=}N{=}Tc)$

NH_2OH [7,8]

$[TcO_4]^-$

$[TcOCl_4]^-$

$NO_{(g)}$ [1,4-6]

TcO_2, Tc^{III} complexes $[TcO_4]^-$

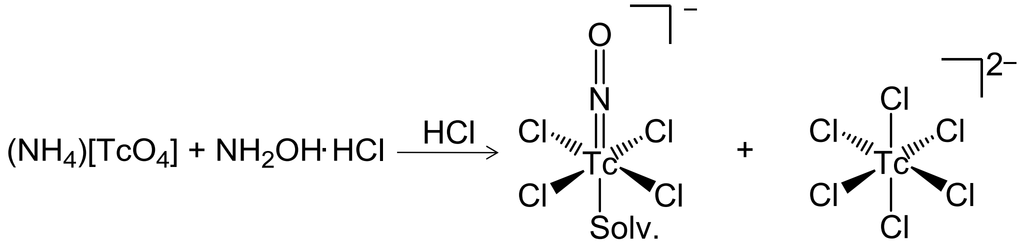
HNO_3 [1]

Tc^I complexes

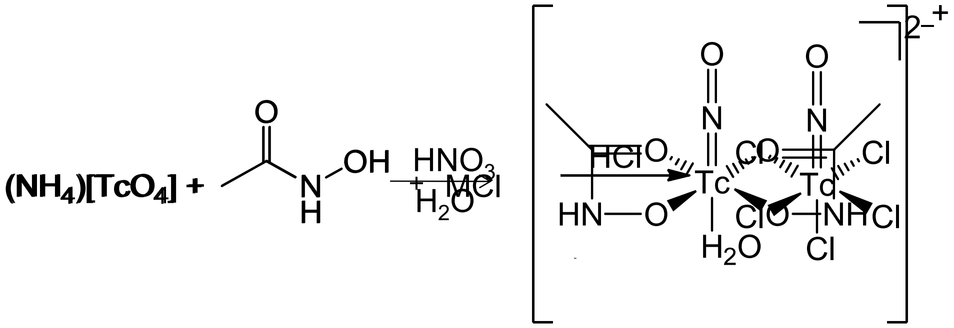
[1] K. E. Linder, A. Davison, J. C. Dewan, C. E. Costello, S. Maleknia, *Inorg. Chem.* **1986**, *25*, 2085., [2] R. Schibli, N. Marti, P. Maurer, B. Spingler, M. L. Lehaire, V. Gramlich, C. L. Barnes, *Inorg. Chem.* **2005**, *44*, 683., [3] D. Rattat, A. Verbruggen, H. Schmalle, H. Berke, R. Alberto, *Tetrahedron Letters.* **2004**, *45*, 4089., [4] Orvig, C.; Davison, A.; Jones, A. G. *J. Labelled Compd. Radiopharm.* **1981**, *18*, 148., [5] T. Nicholson, P. Müller, A. Davison, A. G. Jones, *Inorg. Chim. Acta* **2006**, *359*,1296., [6] R. M. Pearlstein, W. M. Davis, A. G. Jones, A. Davison, *Inorg. Chem.* **1989**, *28*, 3332., [7] C.T. Cheah, J.L. Newman, D.P. Nowotnik, J.R. Thornback, *Nucl. Med. Biol.* **1987**, *14*, 573., [8] T. Nicholson, P. Müller, A. Davison, A. G. Jones, *Inorg. Chim. Acta* **2006**, *359*, 1296. [9] C. S Gong, W. W. Lukens, F. Poineau, K. R. Czerwinski, *Inorg. Chem.* **2008**, *47*, 6674.

Syntheses of Technetium Nitrosyls

- reduction of pertechnetate with hydroxylamine hydrochloride

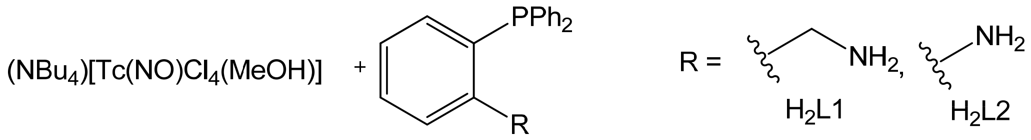


- reduction of pertechnetate with acetohydroxamic acid

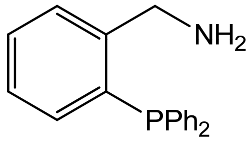


[9] C. S Gong, W. W. Lukens, F. Poineau, K. R. Czerwinski, *Inorg. Chem.* **2008**, *47*, 6674. [10] S. M. Balasekaran, J. Spandl, A. Hagenbach, K. Köhler, M. Drees, U. Abram, *Inorg. Chem.* **2014**, *53*, 5117.

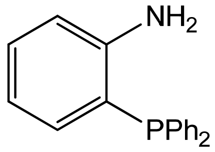
P, *N* – ligand systems



- able to stabilize transition metals in high and low oxidation states
- ligand systems with two donor center
- “soft” phosphorus and “hard” amine
- amine group acts either as neutral or negatively charged by deprotonation → obtaining cationic complexes

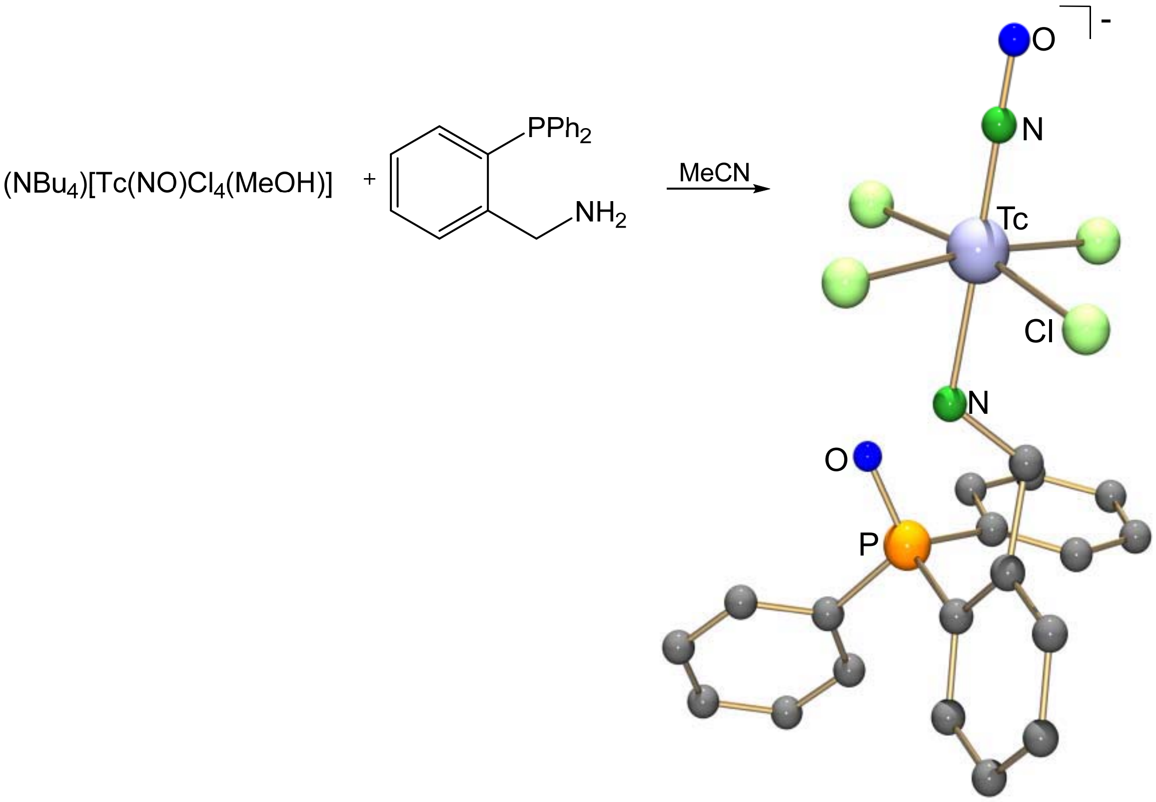


H_2L1



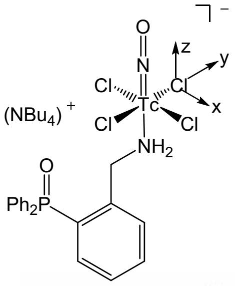
H_2L2

$(NBu_4)[Tc(NO)Cl_4(H_2L1\text{-}\kappa N)]$

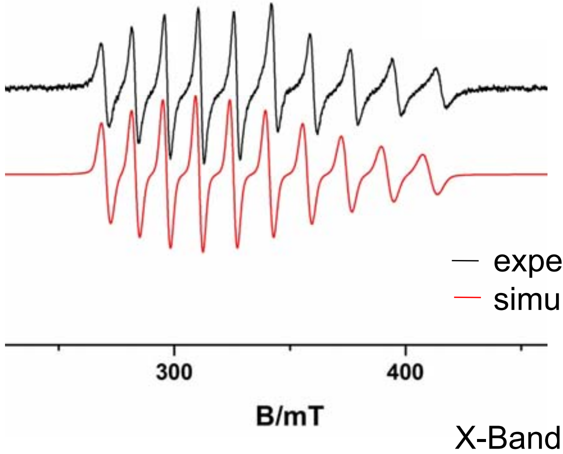


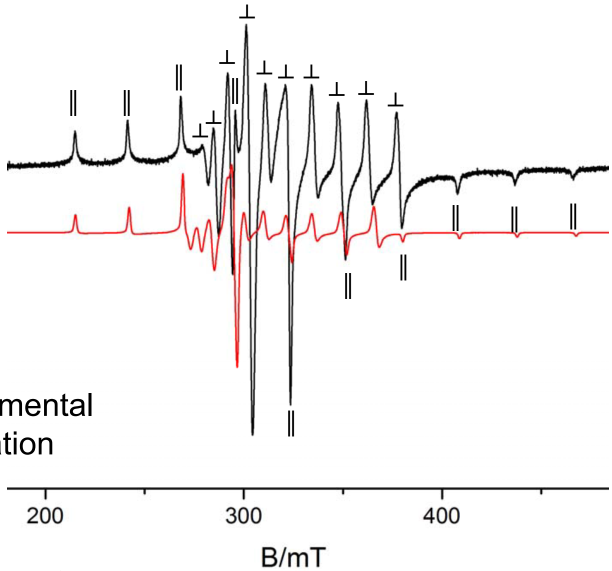
[12] J. Ackermann, A. Hagenbach, U. Abram, *Inorg. Chim. Acta* **2014**, *419*, 59.

EPR of $(NBu_4)[Tc(NO)Cl_4(H_2L1\text{-}\kappa N)]$



properties of $^{99}Tc(II)$
d^5-low spin
$S = 1/2$
$I = 9/2$





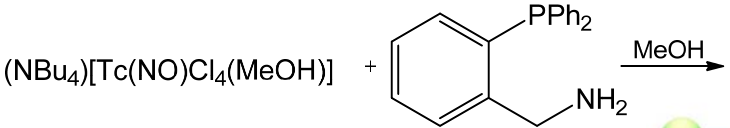
X-Band spectra

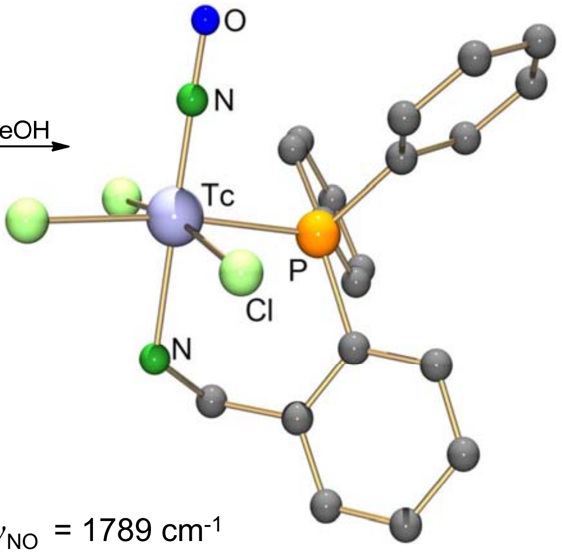
room temperature

frozen solution (77 K)

[12] J. Ackermann, A. Hagenbach, U. Abram, *Inorg. Chim. Acta* **2014**, *419*, 59.

$[Tc(NO)Cl_3(H_2L1\text{-}\kappa N,P)]$

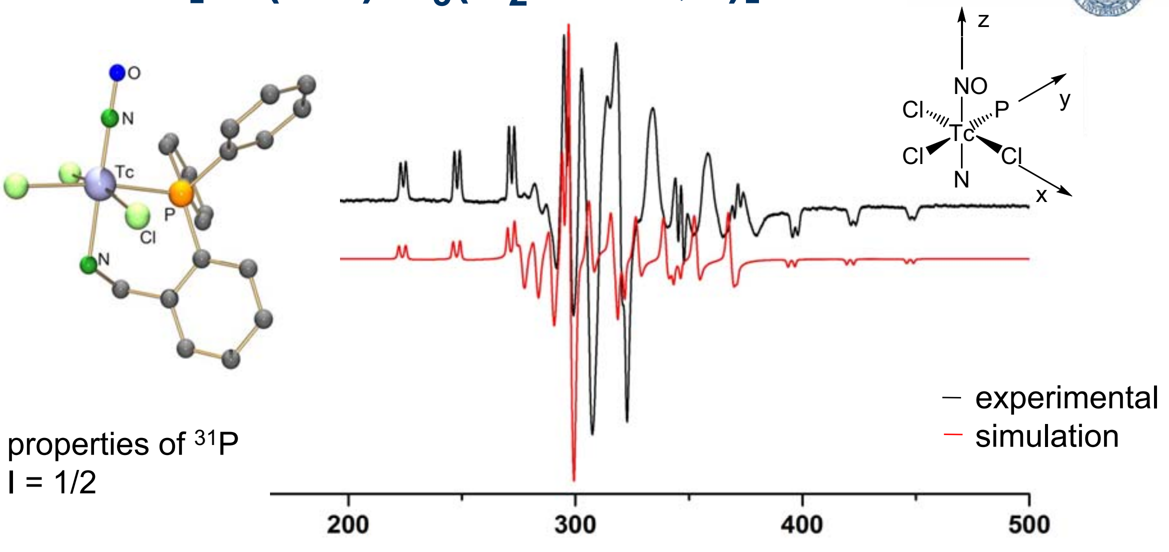




$\nu_{NO} = 1789\ cm^{-1}$

[12] J. Ackermann, A. Hagenbach, U. Abram, *Inorg. Chim. Acta* **2014**, *419*, 59.

EPR of [Tc(NO)Cl$_3$(H$_2$L1-κ*N*,*P*)]



— experimental
— simulation

properties of ^{31}P
I = 1/2

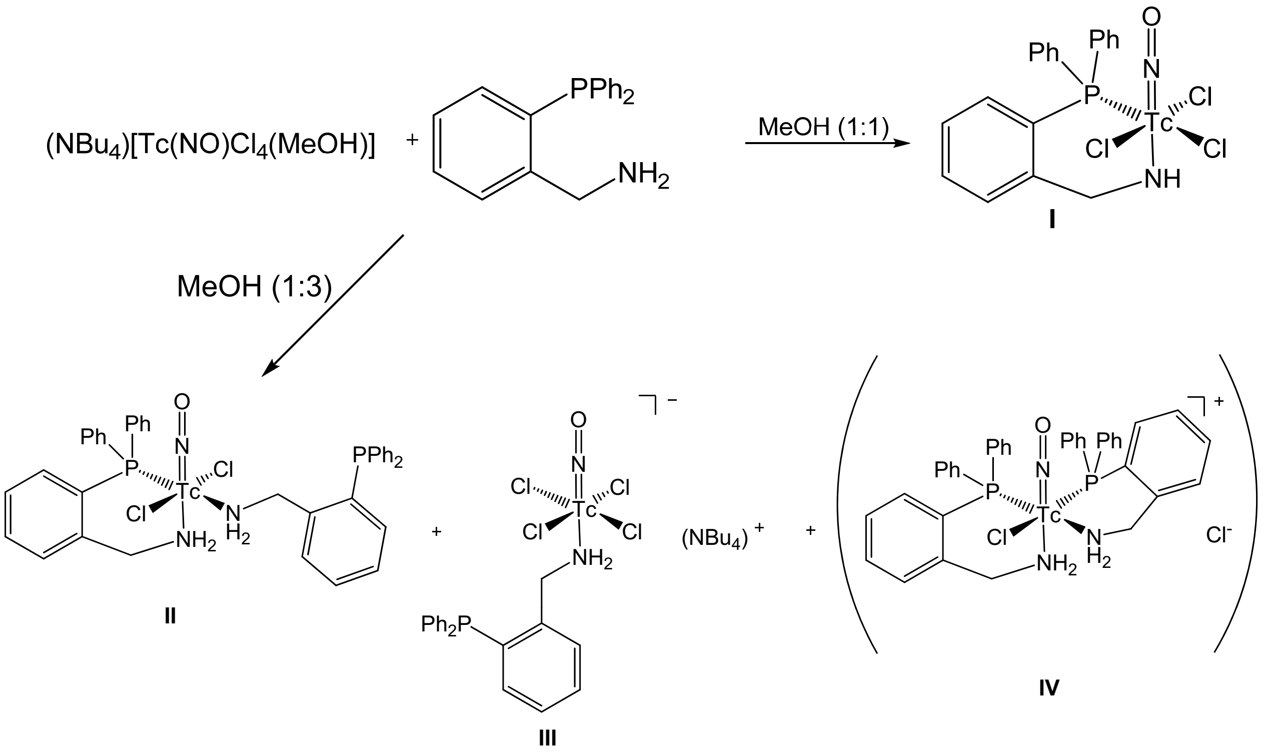
X-band spectrum of a frozen solution

	Solvent	$g_{\parallel}$	$g_{\perp}$	$A_{\parallel}^{Tc}$	$A_{\perp}^{Tc}$	$A_{\parallel}^{P}$
[Tc(NO)Cl$_4$(H$_2$L1-κ*N*)]$^-$	DMF	2.021	2.091	234.9	99.6	28.3
[Tc(NO)Cl$_3$(PPhMe$_2$)$_2$][12]	CHCl$_3$	2.045	2.049	214.8	89.2	23.6

coupling constants are given in 10^{-4} cm^{-1}

[12] J. Ackermann, A. Hagenbach, U. Abram, *Inorg. Chim. Acta* **2014**, *419*, 59. [13] R. Kirmse, B. Lorenz, K. Schmidt, *Polyhedron* **1983**, *2*, 935.

Reactions with H$_2$L1 in Methanol



I

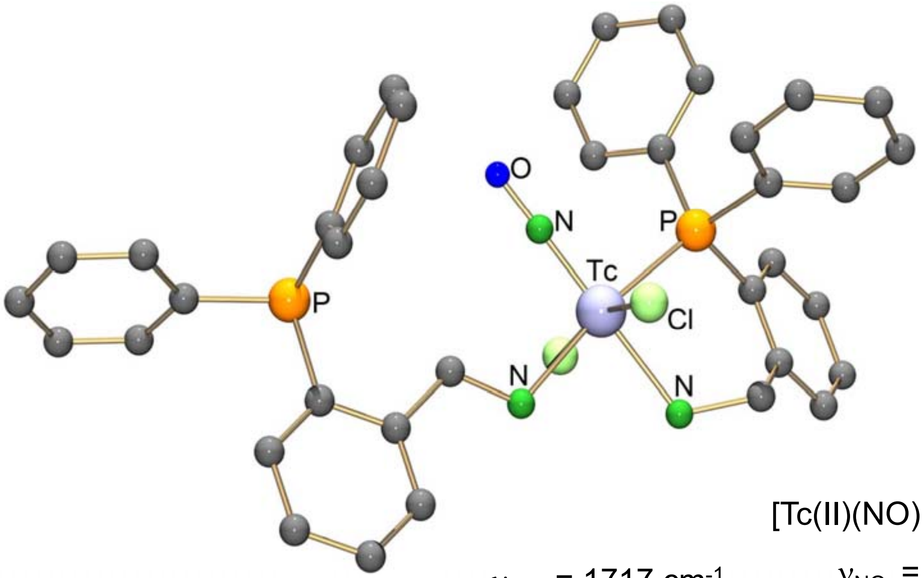
II

III

IV

[11] J. Ackermann, A. Hagenbach, U. Abram, *Inorg. Chim. Acta* **2014**, *419*, 59.

$[\mathrm{Tc(NO)Cl_2(H_2L1\text{-}\kappa}\mathit{N,P}\mathrm{)(H_2L1\text{-}\kappa}\mathit{N}\mathrm{)]}$



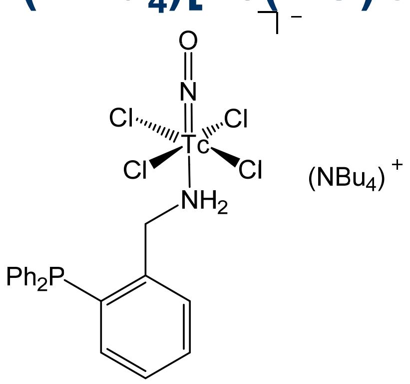
$[\mathrm{Tc(II)(NO)Cl_3(H_2L1\text{-}\kappa}\mathit{N,P}\mathrm{)]}$

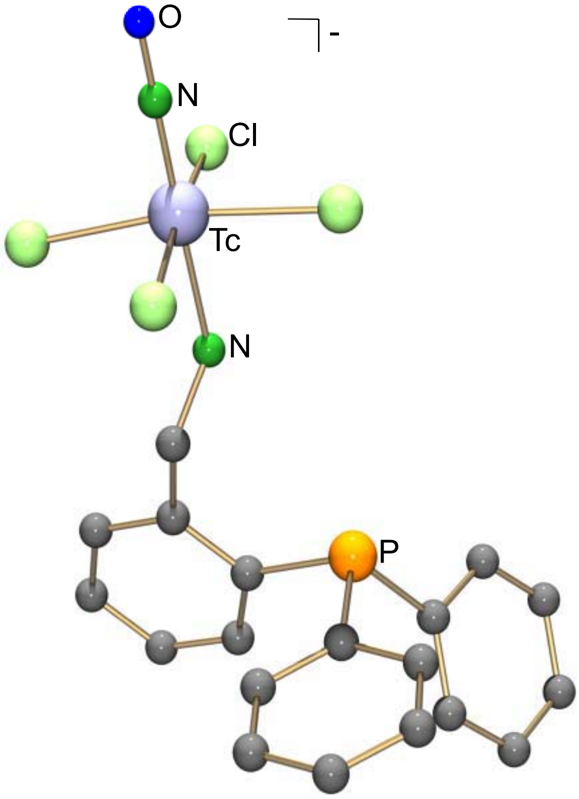
ν_{NO} = 1717 cm^{-1}

ν_{NO} = 1789 cm^{-1}

[12] J. Ackermann, A. Hagenbach, U. Abram, *Inorg. Chim. Acta* **2014**, *419*, 59.

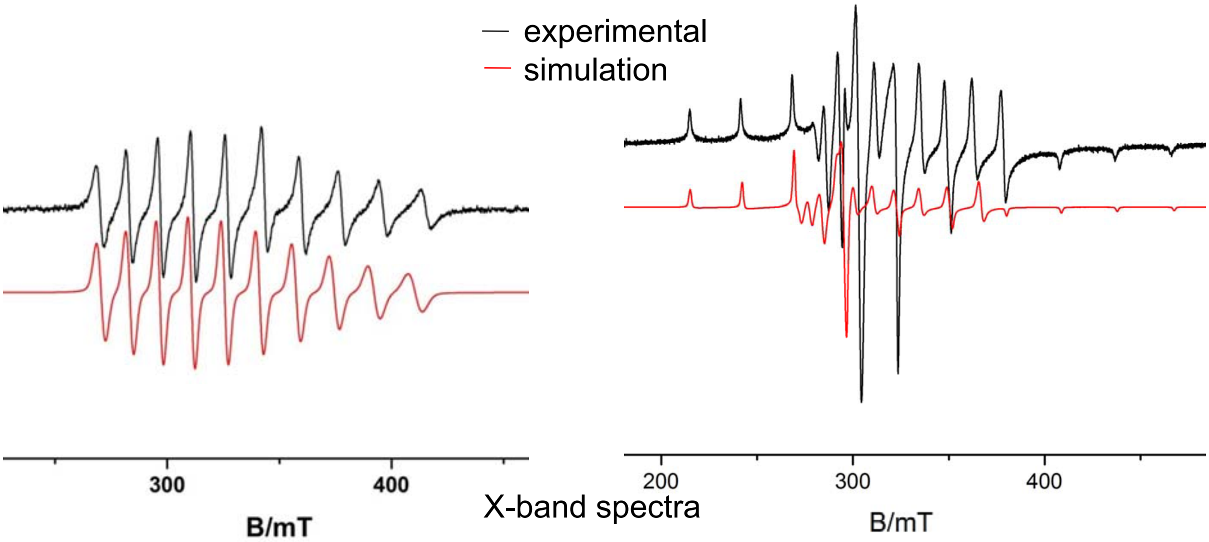
$\mathrm{(NBu_4)[Tc(NO)Cl_4(H_2L1\text{-}\kappa}\mathit{N}\mathrm{)]}$





[12] J. Ackermann, A. Hagenbach, U. Abram, *Inorg. Chim. Acta* **2014**, *419*, 59.

EPR of $(NBu_4)[Tc(NO)Cl_4(H_2L1\text{-}\kappa N)]$



room temperature

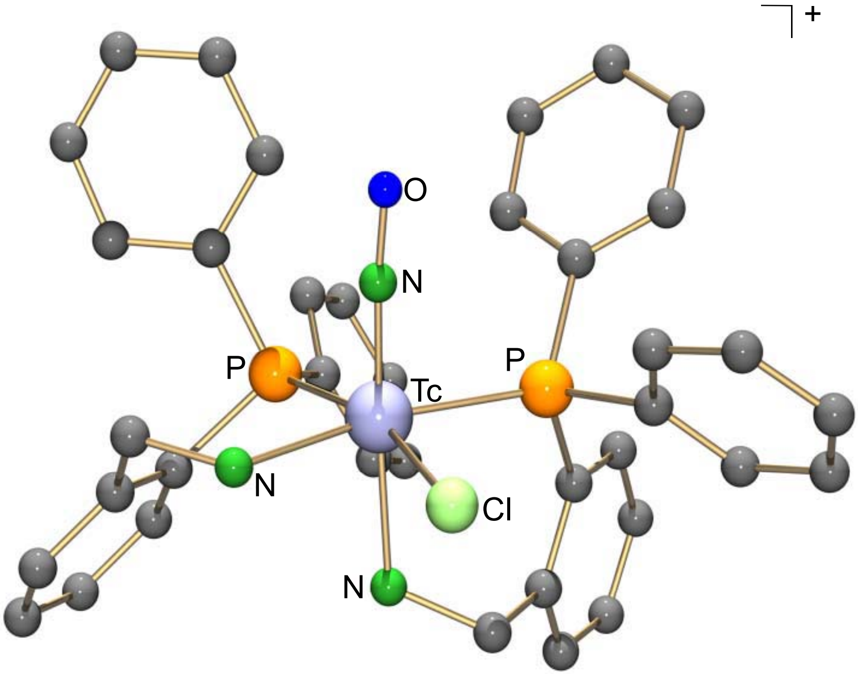
frozen solution (77 K)

Compound	Solvent	$g_{\parallel}$	$g_{\perp}$	$A_{\parallel}^{Tc}$	$A_{\perp}^{Tc}$	g_0	a_0^{Tc}
$[Tc(NO)Cl_4(H_2L1\text{-}kN)]^-$	CH_2Cl_2	1.989	2.083	258.9	105.2	2.037	151.8
$[Tc(NO)Cl_5]^{2-}$	CH_2Cl_2	1.985	2.037	259.8	111.0	2.029	157.6

coupling constants are given in 10^{-4} cm^{-1}

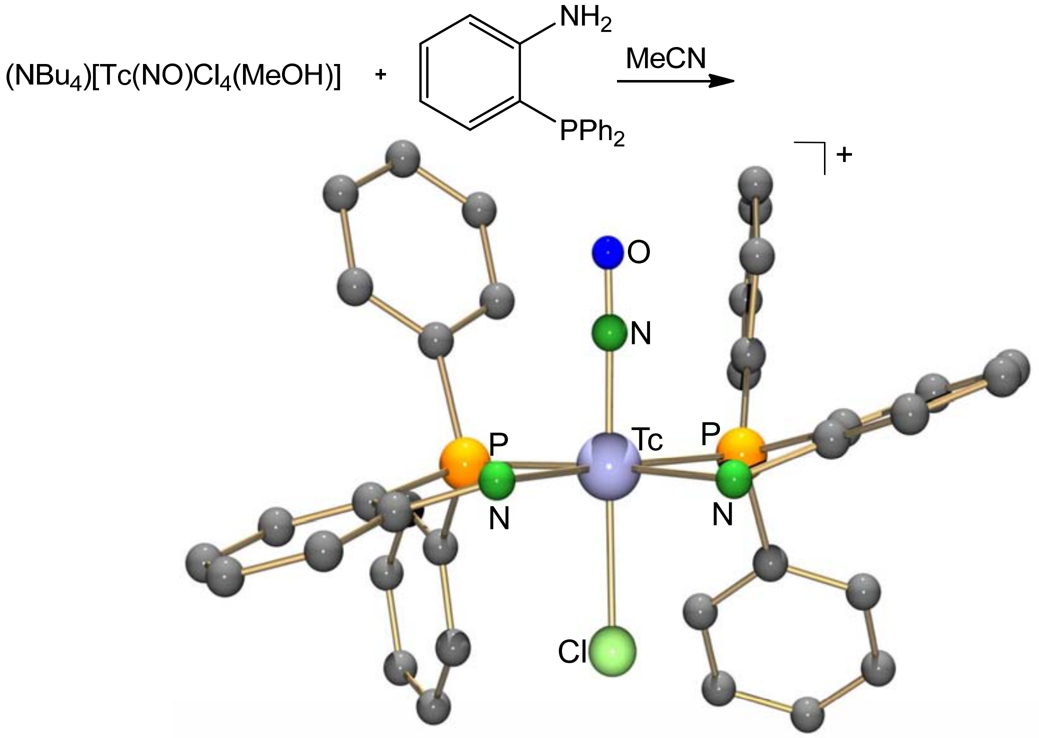
[12]J. Ackermann, A. Hagenbach, U. Abram, *Inorg. Chim. Acta* **2014**, *419*, 59., [13] G. C. Yang, M. W. Heitzmann, L. A. Ford, W. R. Benson, *Inorg. Chem.* **1982**, *21*, 3242.

$[Tc(NO)Cl(H_2L1\text{-}\kappa N,P)_2]$



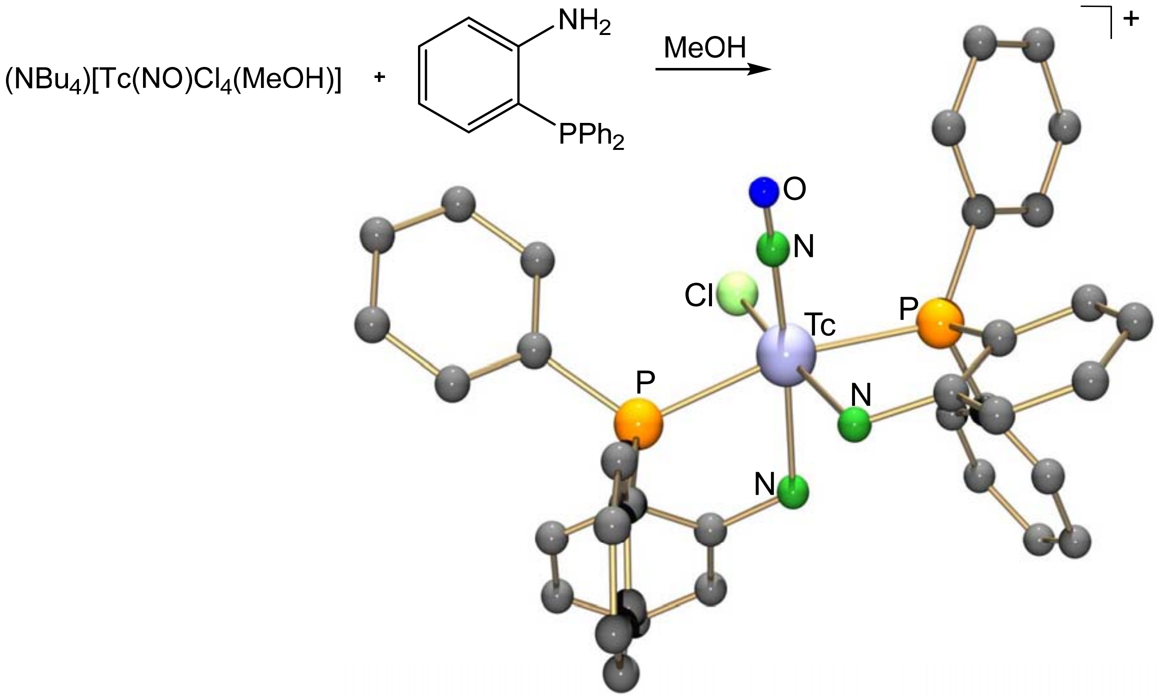
[12] J. Ackermann, A. Hagenbach, U. Abram, *Inorg. Chim. Acta* **2014**, *419*, 59.

$[Tc(NO)Cl\,(H_2L2\text{-}\kappa N,P)_2]$



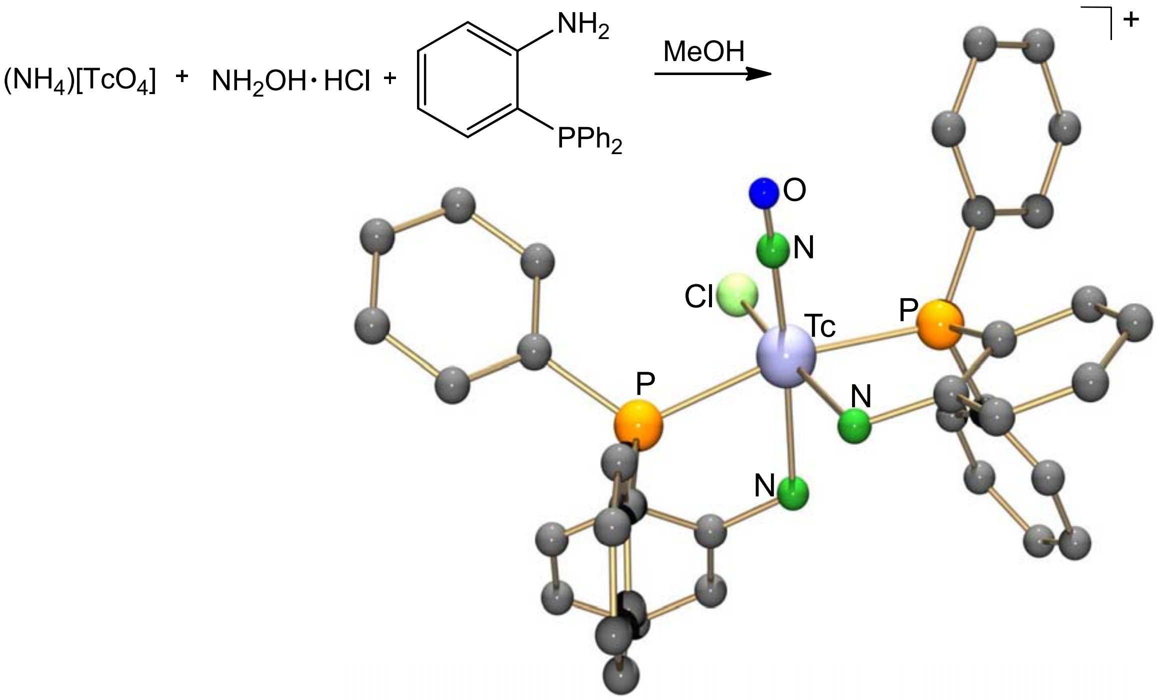
[14] J. Ackermann, A. Hagenbach, U. Abram, unpublished results.

$[Tc(NO)Cl\,(H_2L2\text{-}\kappa N,P)_2]$



[14] J. Ackermann, A. Hagenbach, U. Abram, unpublished results.

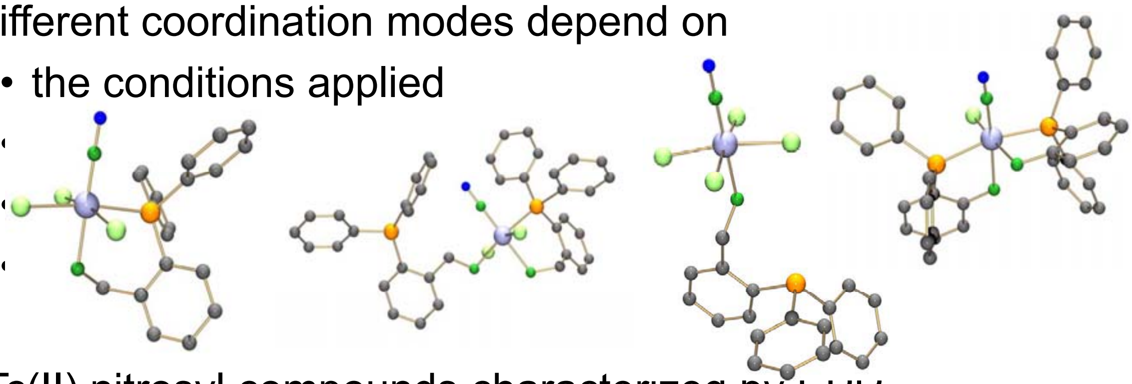
[Tc(NO)Cl (H$_2$L2-κ*N*,*P*)$_2$]



[14] J. Ackermann, A. Hagenbach, U. Abram, unpublished results.

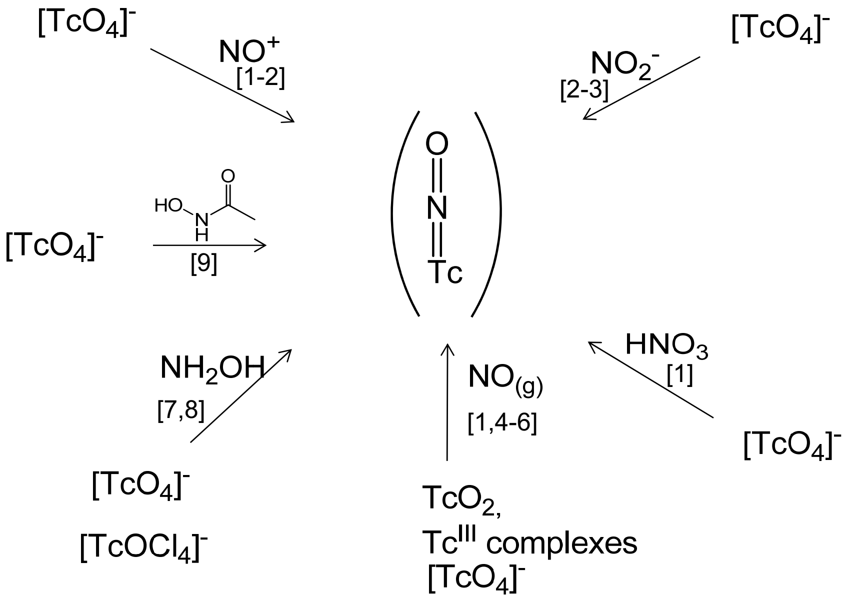
Summary

- Syntheses of new Tc(I) and Tc(II) nitrosyl complexes with *P*, *N* ligands
  - starting material: (NH$_4$)[TcO$_4$], (NBu$_4$)[Tc(NO)Cl$_4$]
- different coordination modes depend on
  - the conditions applied



- Tc(II) nitrosyl compounds characterized by EPR
  - superhyperfine coupling with phosphorus

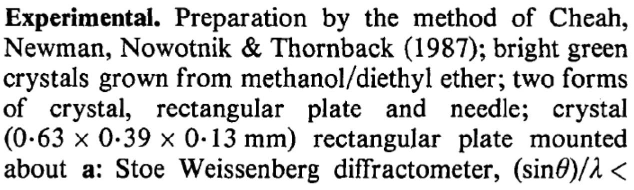
Technetium Nitrosyls



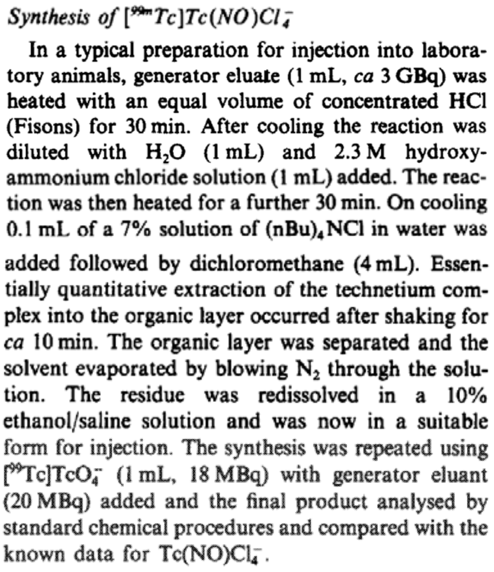
[1] K. E. Linder, A. Davison, J. C. Dewan, C. E. Costello, S. Maleknia, *Inorg. Chem.* **1986**, *25*, 2085., [2] R. Schibli, N. Marti, P. Maurer, B. Spingler, M. L. Lehaire, V. Gramlich, C. L. Barnes, *Inorg. Chem.* **2005**, *44*, 683., [3] D. Rattat, A. Verbruggen, H. Schmalle, H. Berke, R. Alberto, *Tetrahedron Letters.* **2004**, *45*, 4089., [4] Orvig, C.; Davison, A.; Jones, A. G. *J. Labelled Compd. Radiopharm.* **1981**, *18*, 148., [5] T. Nicholson, P. Müller, A. Davison, A. G. Jones, Inorg. Chim. Acta 2006, 359,1296., [6] R. M. Pearlstein, W. M. Davis, A. G. Jones, A. Davison, *Inorg. Chem.* **1989**, *28*, 3332., [7] C.T. Cheah, J.L. Newman, D.P. Nowotnik, J.R. Thornback, Nucl. Med. Biol. **1987**, *14*, 573., [8] T. Nicholson, P. Müller, A. Davison, A. G. Jones, *Inorg. Chim. Acta* **2006**, *359*, 1296. [9] [9] C. S Gong, W. W. Lukens, F. Poineau, K. R. Czerwinski, *Inorg. Chem.* **2008**, *47*, 6674.

$[Tc(NO)Cl_4]^-$ in literature

D.S. Brown, J.L. Newman, J.R. Thornback, A. Davison, Acta Crystallogr., Sect. C **1987**, *43*, 1692.


Experimental. Preparation by the method of Cheah, Newman, Nowotnik & Thornback (1987); bright green crystals grown from methanol/diethyl ether; two forms of crystal, rectangular plate and needle; crystal (0·63 × 0·39 × 0·13 mm) rectangular plate mounted about **a**: Stoe Weissenberg diffractometer, $(\sin\theta)/\lambda <$

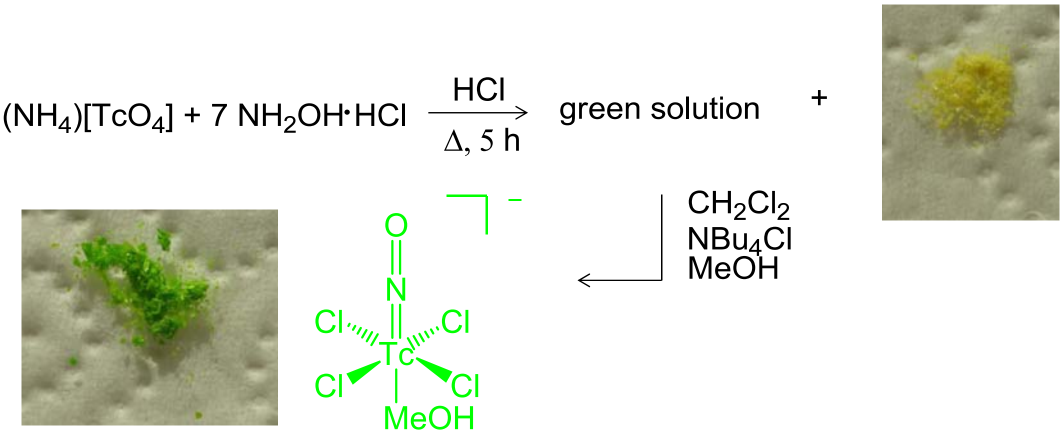
C.T. Cheah, J.L. Newman, D.P. Nowotnik, J.R. Thornback, Nucl. Med. Biol. **1987**, *14*, 573.


Synthesis of [^{99m}*Tc*]*Tc*(*NO*)*Cl*$_4^-$

In a typical preparation for injection into laboratory animals, generator eluate (1 mL, *ca* 3 GBq) was heated with an equal volume of concentrated HCl (Fisons) for 30 min. After cooling the reaction was diluted with H_2O (1 mL) and 2.3 M hydroxyammonium chloride solution (1 mL) added. The reaction was then heated for a further 30 min. On cooling 0.1 mL of a 7% solution of $(nBu)_4NCl$ in water was added followed by dichloromethane (4 mL). Essentially quantitative extraction of the technetium complex into the organic layer occurred after shaking for *ca* 10 min. The organic layer was separated and the solvent evaporated by blowing N_2 through the solution. The residue was redissolved in a 10% ethanol/saline solution and was now in a suitable form for injection. The synthesis was repeated using [^{99}Tc]TcO_4^- (1 mL, 18 MBq) with generator eluant (20 MBq) added and the final product analysed by standard chemical procedures and compared with the known data for $Tc(NO)Cl_4^-$.

Synthesis of $[Tc(NO)Cl_4(MeOH)]^-$

$$(NH_4)[TcO_4] + NH_2OH{\cdot}HCl \xrightarrow[\Delta]{HCl} [Tc(NO)Cl_5]^-$$

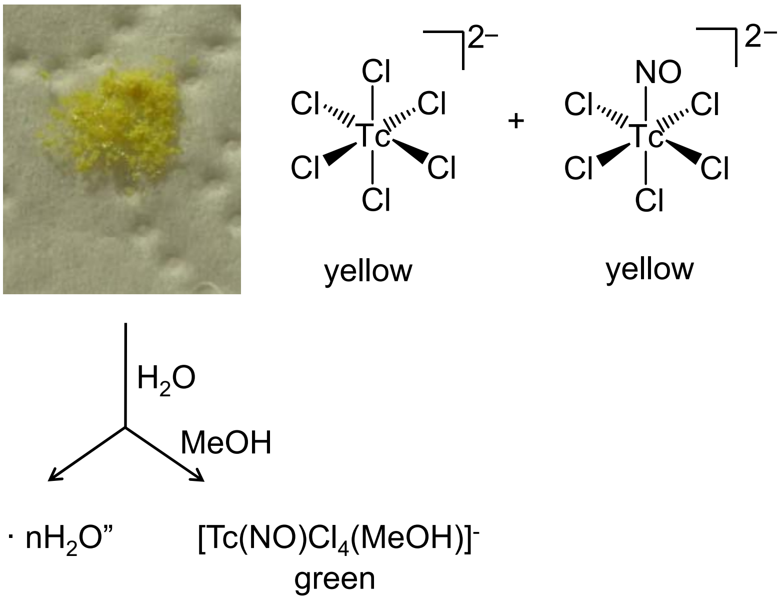


$$(NH_4)[TcO_4] + 7\ NH_2OH{\cdot}HCl \xrightarrow[\Delta,\ 5\ h]{HCl} \text{green solution} +$$

CH_2Cl_2
NBu_4Cl
MeOH

yield: 70 %

What about the yellow compound?



yellow

yellow

H_2O

MeOH

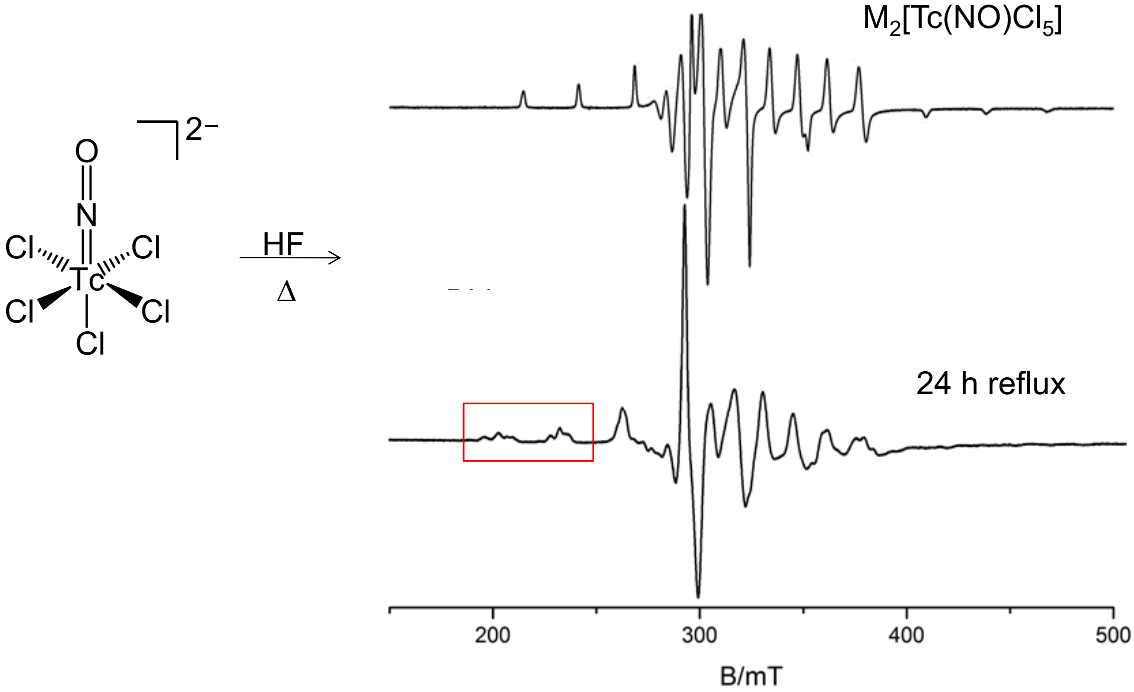
"$TcO_2 \cdot nH_2O$"

$[Tc(NO)Cl_4(MeOH)]^-$
green

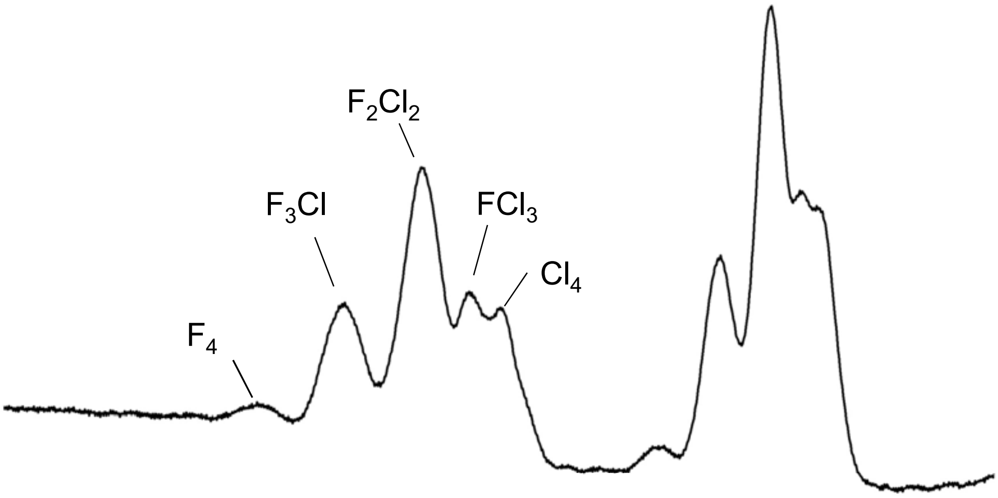
$$(AsPh_4)[Tc(NO)Br_4] + HCl \longrightarrow (AsPh_4)_2[Tc(NO)Cl_5]$$

[15] R. Kirmse, J. Stach, U. Abram, I. N. Marov, *Z. Anorg. Allg. Chem.* **1984**, *518*, 210.

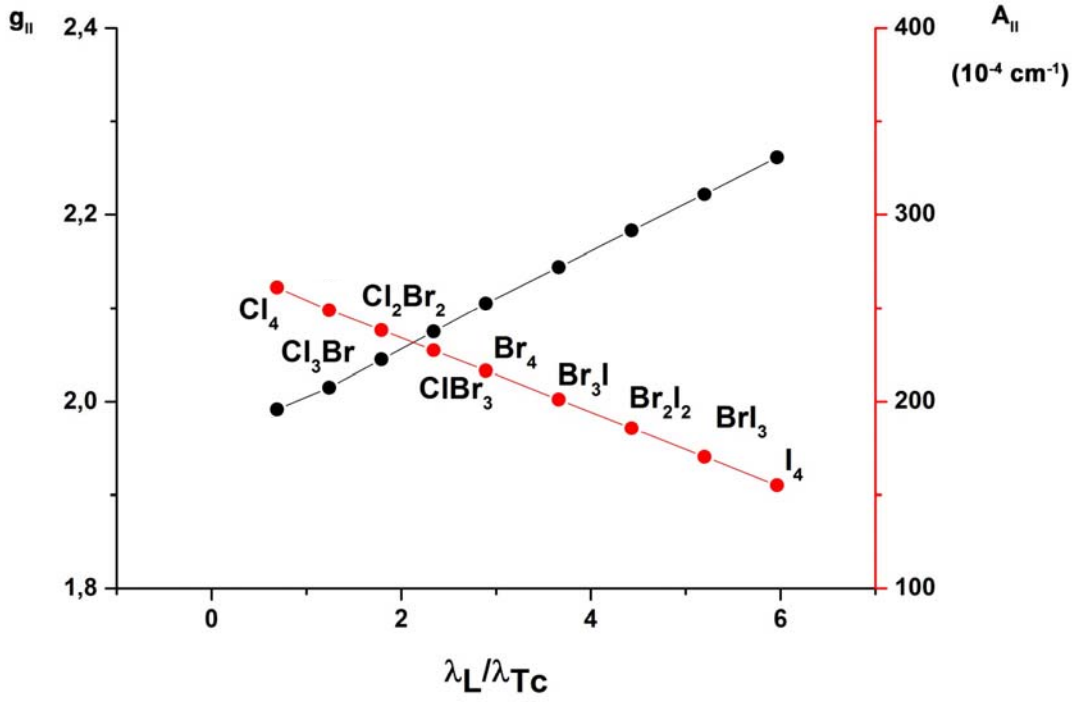
Ligand Exchange with HF



Ligand Exchange with HF

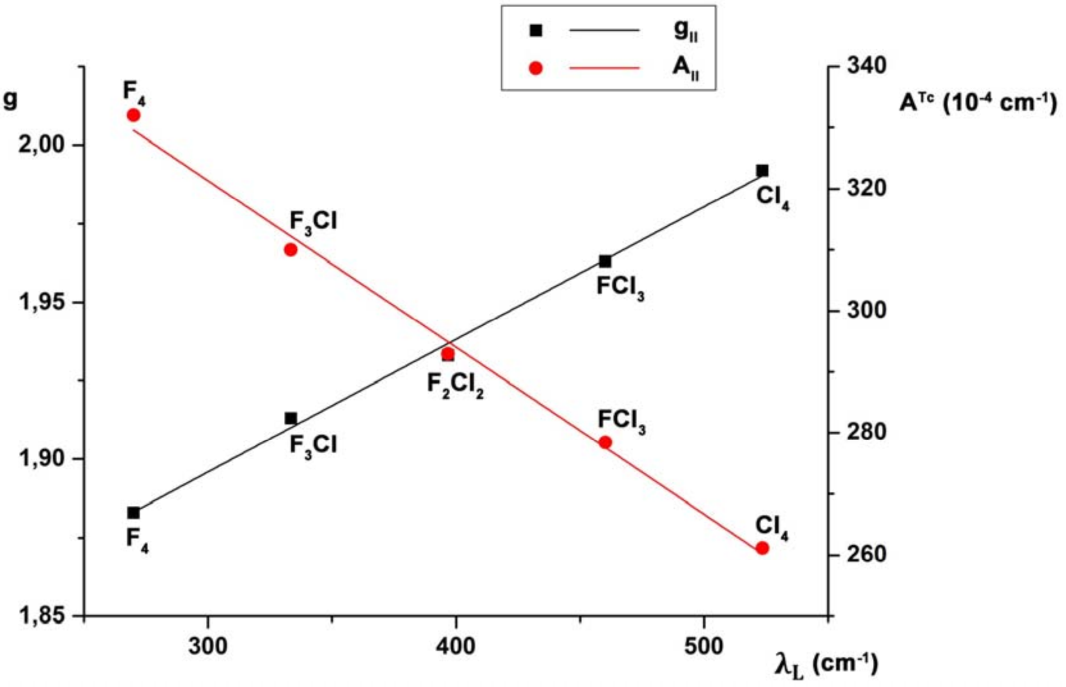


Linear Dependency



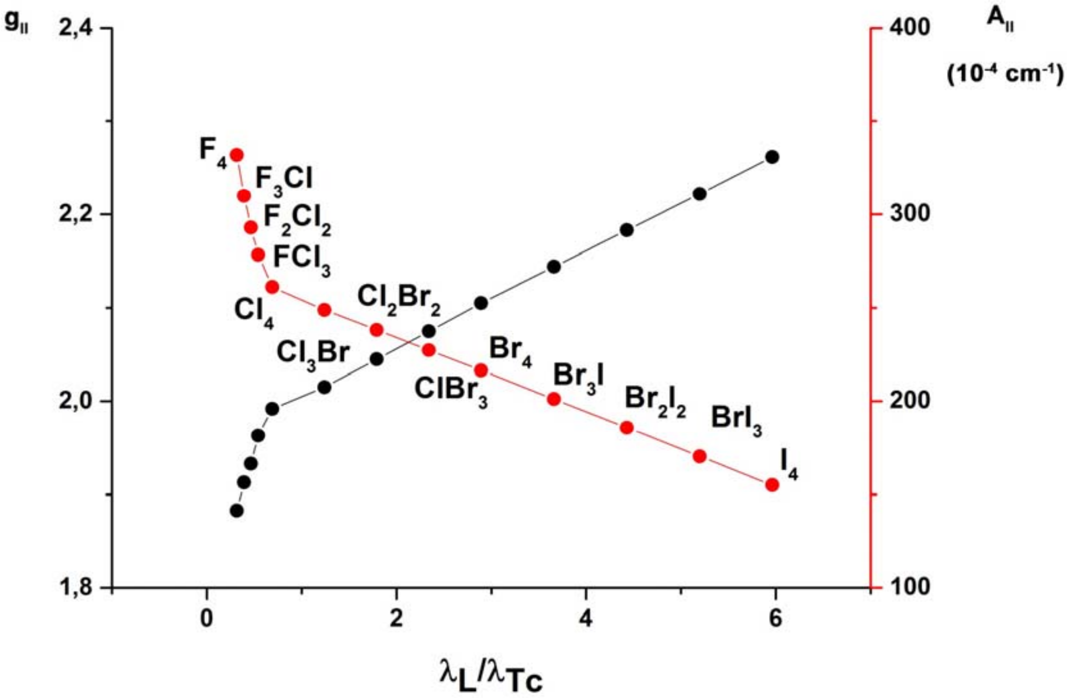
[16] R. Kirmse, U. Abram, *Z. Anorg. Allg. Chem.* **1989**, *573*, 63.

Linear Dependency



Thank you very much for your kind attention!

Linear Dependency



Fluorido Complexes of Low-valent Technetium

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The coordination chemistry of technetium with fluorido ligands is by far less explored than that with other halides. Almost all hitherto published reports on technetium fluorides focus on the higher oxidation states of the metal,[1] while the coordination chemistry of low-valent technetium compounds is almost unknown. Here we report synthesis, spectroscopic and structural characterization as well as reactions of novel nitridotechnetium(VI), nitrosyltechnetium(I) and -(II) fluorides together with a reinvestigation of hexafluoridotechnetate(IV). Representative compounds are shown in Fig. 1.

The nitrido complexes were synthesized either from nitridotechnetic(VI) acid or from pertechnetate by using reducing agent and have been isolated as cesium or tetraethylammonium salts. Various salts of hexafluoridotechnetate(IV) were prepared by a novel and improved synthesis and some of the critical issues of early publications such as the color, some spectroscopic properties, reactivity and structural features of this key compounds have been solved.[2]

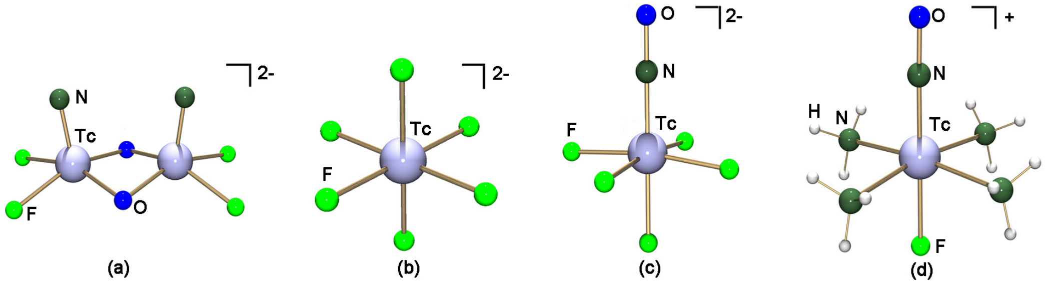


Fig. 1: Molecular anions of (a) $[Tc^{VI}_2N_2O_2F_4]^{2-}$ (b) $[Tc^{IV}F_6]^{2-}$ (c) $[Tc^{II}(NO)F_5]^{2-}$ (d) $[Tc^{I}(NO)(NH_3)_4F]^{+}$

Following a new preparative route for nitrosyltechnetium complexes,[3] pentafluoridonitrosyltechnetate(II) and *trans*-tetraamminefluoridonitrosyltechnetium(I) were prepared and characterized by spectroscopic and crystallographic methods.[4] Ligand exchange reactions of the nitrosylfluoridotechnetium complexes were studied.

References:

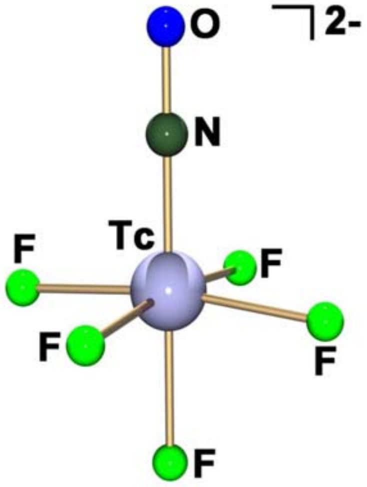
1. See references 5 to 13 of ref. 2 of this abstract.

2. S. M. Balasekaran, M. Molski, L. Spandl, A. Hagenbach, R. Alberto, U. Abram, *Inorg. Chem.* **2013**, 52, 7094.

3. C. -M. S. Gong, W. W. Lukens, F. Poineau, K. R. Czerwinski, *Inorg. Chem.* **2008**, 47, 6674.

4. S. M. Balasekaran, J. Spandl, A. Hagenbach, K. Köhler, M. Drees, U. Abram, *Inorg. Chem.* **2014**, 53, 5117.

Fluorido Complexes of Low-valent Technetium



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Institute of Chemistry and Biochemistry,
Freie Universität Berlin,
Berlin.

01-10-2014.

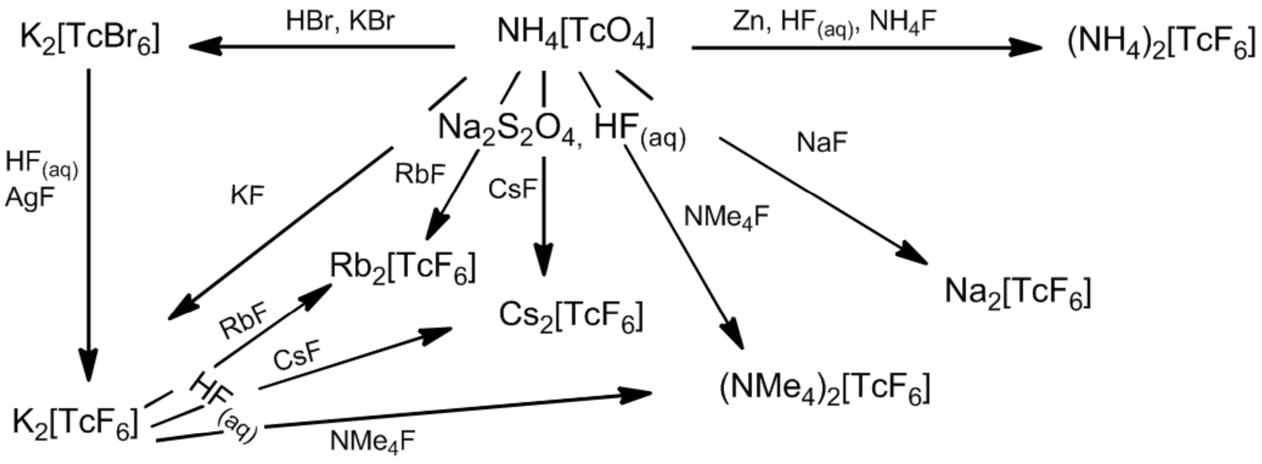
Introduction

- Technetium fluorides in the oxidation state VII-V are known.

Oxidation states	Fluorides	Oxidofluorides
VII	-	$TcOF_5$, TcO_2F_3, TcO_3F
VI	TcF_6	$TcOF_4$
V	TcF_5	-
IV	**$[TcF_6]^{2-}$**	**$[F_5TcOTcF_5]^{4-}$**
III	-	-
II	-	-
I	-	-

(1) Schwochau, K.; Herr, W. *Angew. Chem.* **1963**, *75*, 95; *Angew. Chem. Int, Edit.* **1963**, *2*, 97. (2) Schwochau, K. Z. *Naturforsch.* **1964**, *19a*, 1237. (3) Jorgensen, C. K.; Schwochau, K. Z. *Naturforsch.* **1965**, *20a*, 65. (4) Krasser, W.; Schwochau, K. Z. *Naturforsch.* **1970**, *25a*, 206. (5) Alberto, R.; Anderegg, G. *Polyhedron* **1985**, *6*, 1067.

Syntheses of $[TcF_6]^{2-}$



$K_2[TcBr_6]$ ← HBr, KBr ← $NH_4[TcO_4]$ → Zn, $HF_{(aq)}$, NH_4F → $(NH_4)_2[TcF_6]$

$Na_2S_2O_4$, $HF_{(aq)}$

$HF_{(aq)}$
AgF

KF

RbF

CsF

NaF

NMe_4F

$Rb_2[TcF_6]$

$Cs_2[TcF_6]$

$Na_2[TcF_6]$

$(NMe_4)_2[TcF_6]$

$K_2[TcF_6]$

RbF

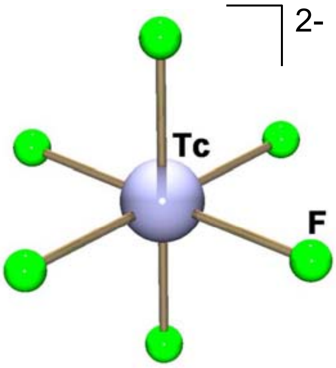
CsF

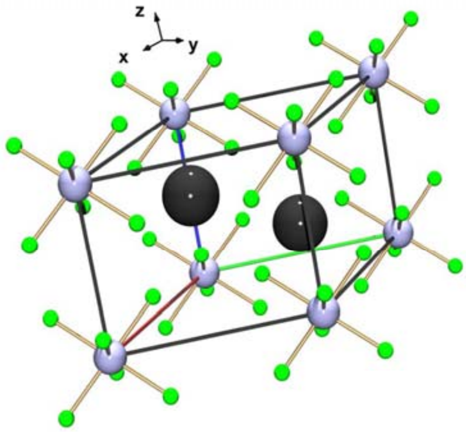
$HF_{(aq)}$

NMe_4F

Alberto, R.; Anderegg, G. *Polyhedron* **1985**, *6*, 1067.
Mariappan Balasekaran, S.; Molski, M.; Spandl, J.; Hagenbach, A.; Alberto, R.; Abram, U. *Inorg.Chem.* **2013**, *52*, 7094.

Structures of $[TcF_6]^{2-}$





	$(NH_4)_2[TcF_6]$	$Na_2[TcF_6]$	$K_2[TcF_6]$	$Rb_2[TcF_6]$	$Cs_2[TcF_6]$	$(NMe_4)_2[TcF_6]$
Tc–F / Å	1.922(6)	1.895(6)	1.928(1)	1.933(3)	1.935(5)	1.929(2)
F–Tc–F / °	87.7(2)	87.6(3)	86.93(5)	87.2(2)	87.8(2)	89.8(1)
	92.3(2)	92.4(3)	93.07(5)	92.8(2)	92.2(2)	90.2(1)
	180.0(4)	180.0(4)	180.0(1)	180.0(1)	180.0(1)	180.0(1)

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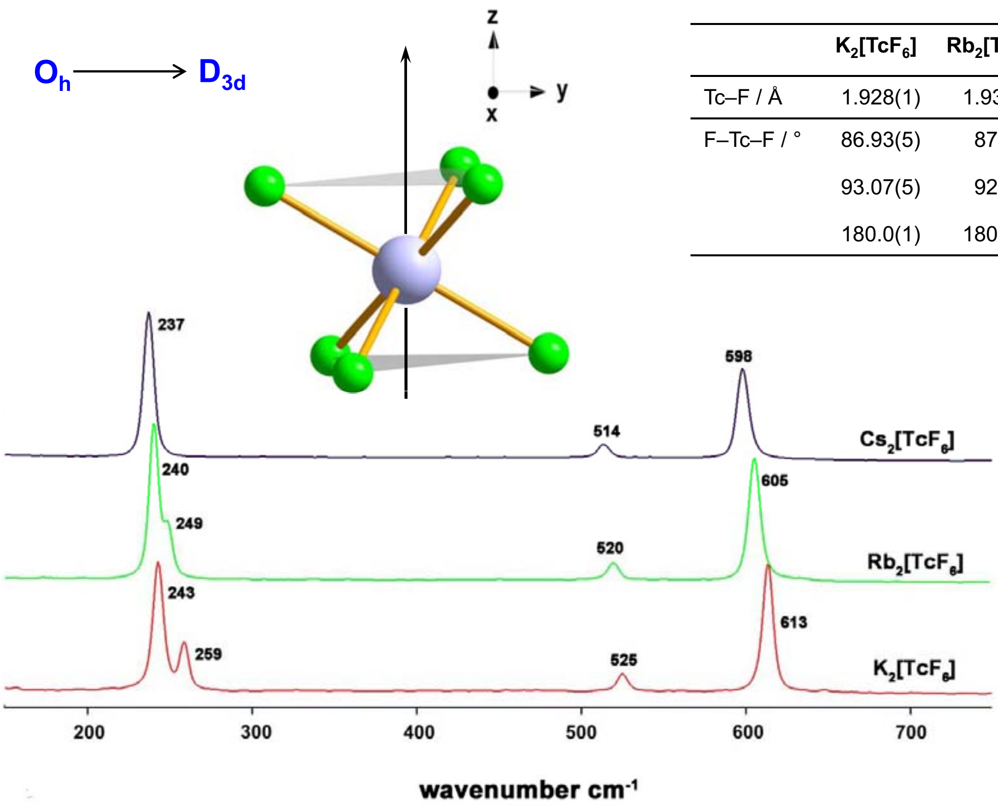
Structures of $[TcF_6]^{2-}$

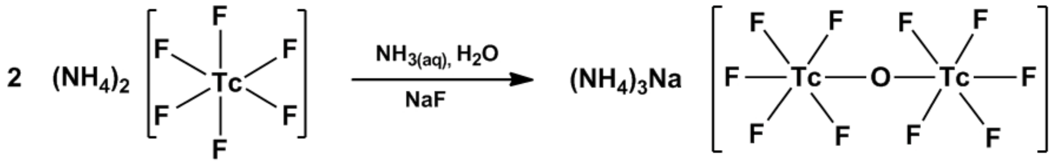


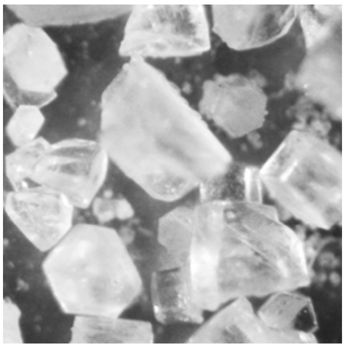
	$K_2[TcF_6]$	$Rb_2[TcF_6]$	$Cs_2[TcF_6]$
Tc–F / Å	1.928(1)	1.933(3)	1.935(5)
F–Tc–F / °	86.93(5)	87.2(2)	87.8(2)
	93.07(5)	92.8(2)	92.2(2)
	180.0(1)	180.0(1)	180.0(1)

Mariappan Balasekaran, S.; Molski, M.; Spandl, J.; Hagenbach, A.; Alberto, R.; Abram, U. *Inorg.Chem.* **2013**, *52*, 7094.

Reactivity of $[TcF_6]^{2-}$

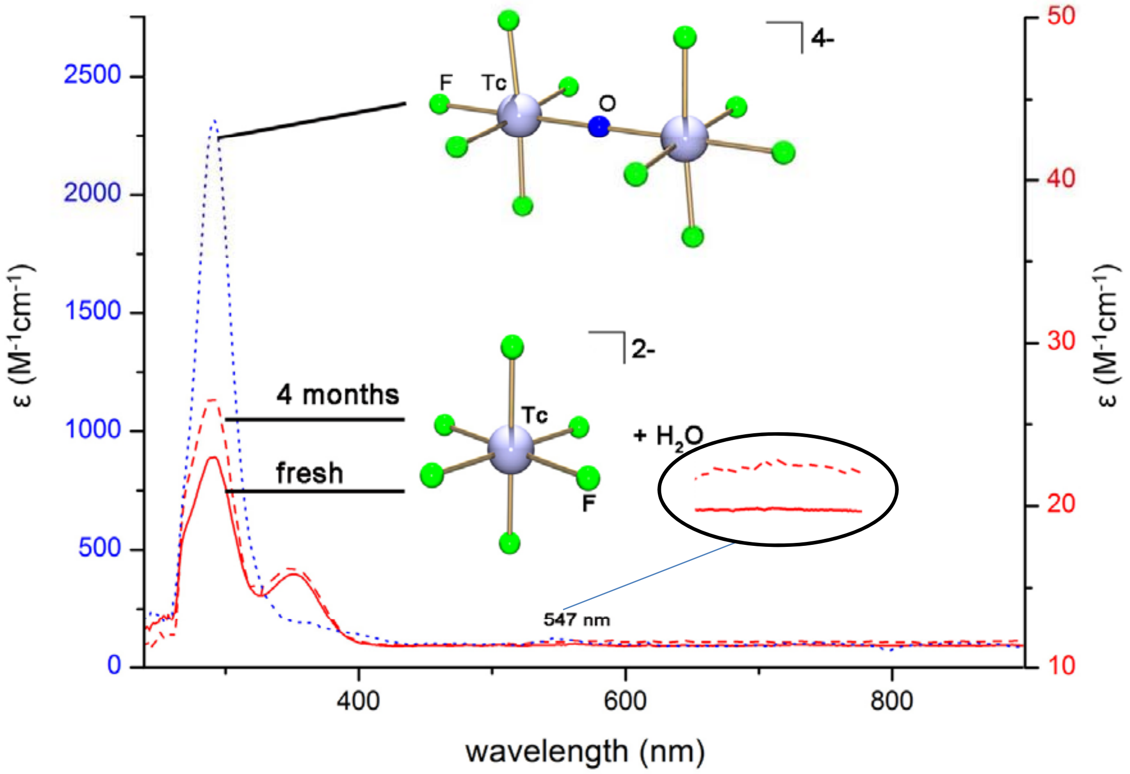
$[TcF_6]^{2-}$ is inert, did not react even with strong chelating ligands.





Mariappan Balasekaran, S.; Molski, M.; Spandl, J.; Hagenbach, A.; Alberto, R.; Abram, U. *Inorg.Chem.* **2013**, *52*, 7094.

Hydrolysis of $[TcF_6]^{2-}$



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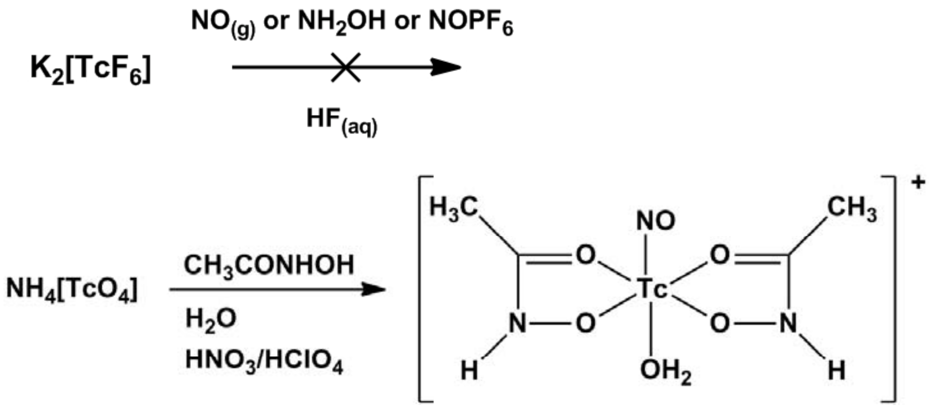
Reactivity of $[TcF_6]^{2-}$



Gong, C.-M. S.; Lukens, W. W.; Poineau, F.; Czerwinski, K. R. *Inorg. Chem.* **2008**, *47*, 6674.
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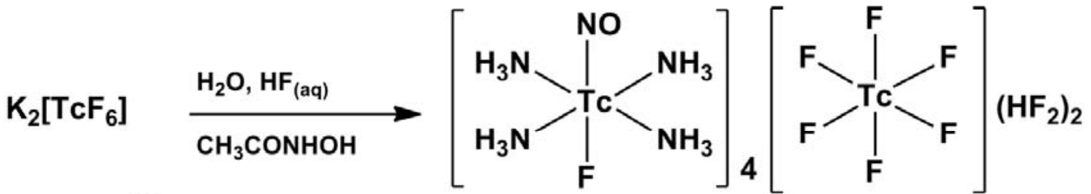
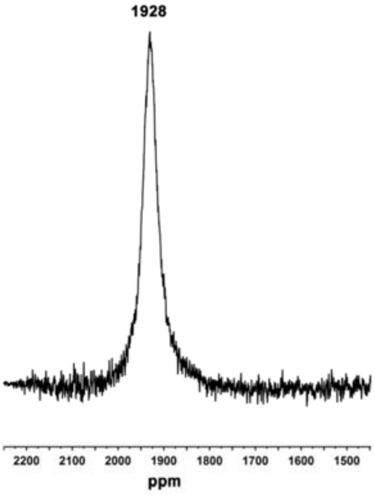
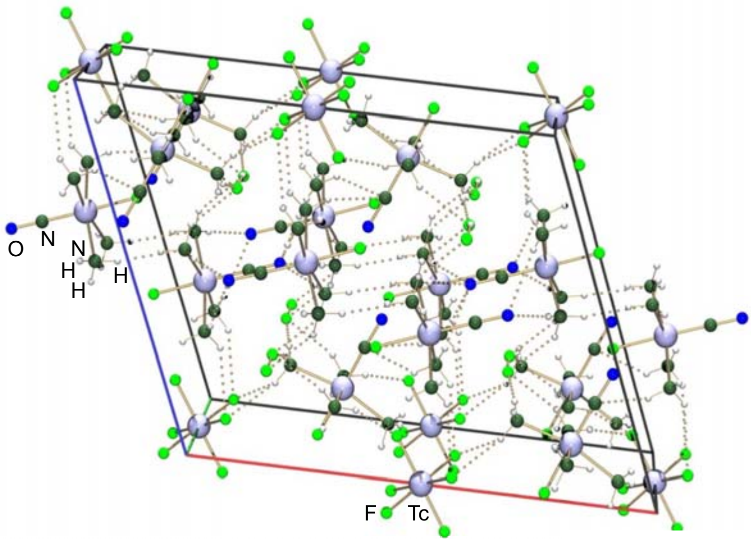
Reactivity of $[TcF_6]^{2-}$





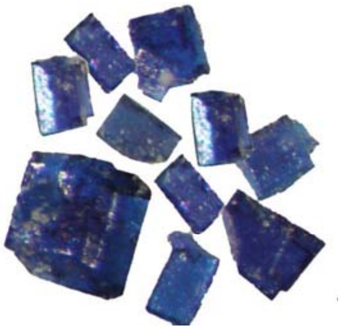
^{99}Tc NMR



Mariappan Balasekaran, S.; Molski, M.; Hagenbach, A.; Abram, U. *Z. Anorg. Allg. Chem.* **2013**, *639*, 672.

Technetium Nitrosyl Chemistry

$$NH_4[TcO_4] \xrightarrow[\text{MF (M = Rb-Cs) or } KPF_6]{HF_{(aq)}\text{, reflux, } CH_3CONHOH}$$



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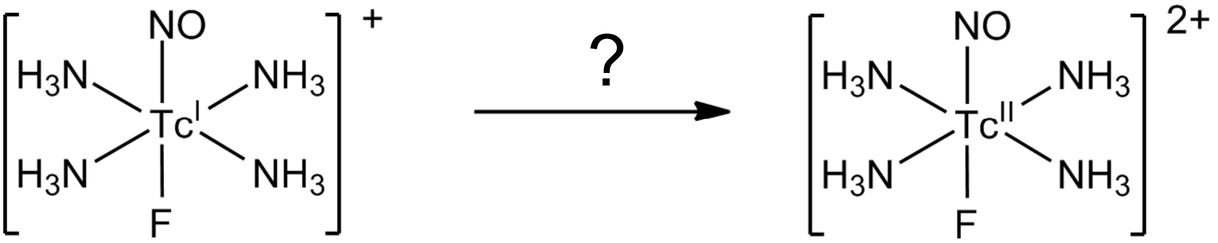
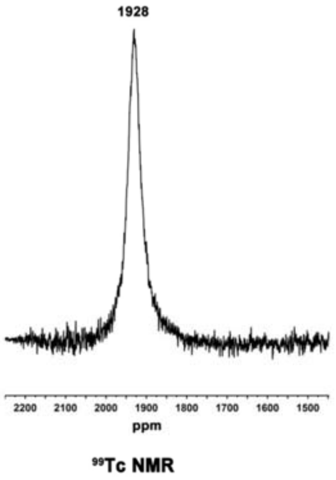
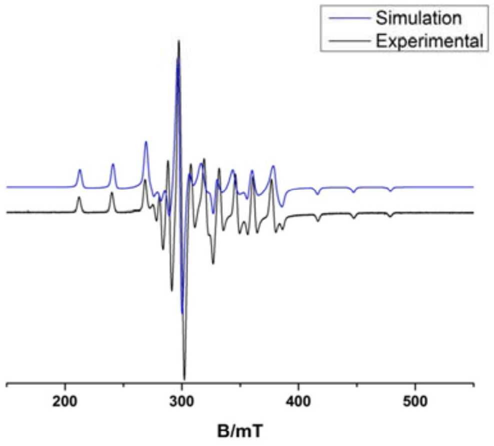
Technetium Nitrosyl Chemistry







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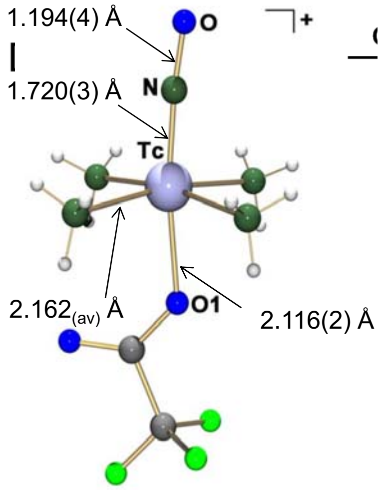
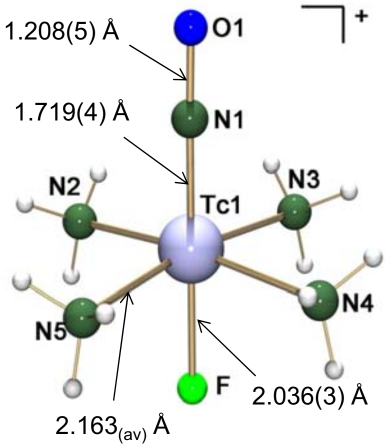
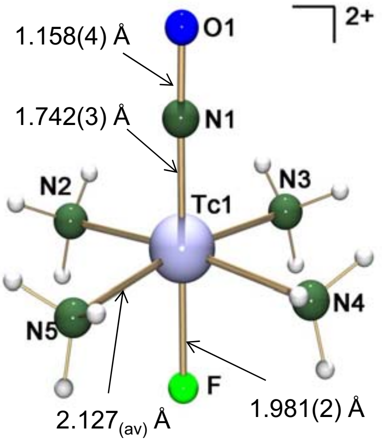
Technetium Nitrosyl Chemistry



trans- TFA-Tc$^{(I)}$NO



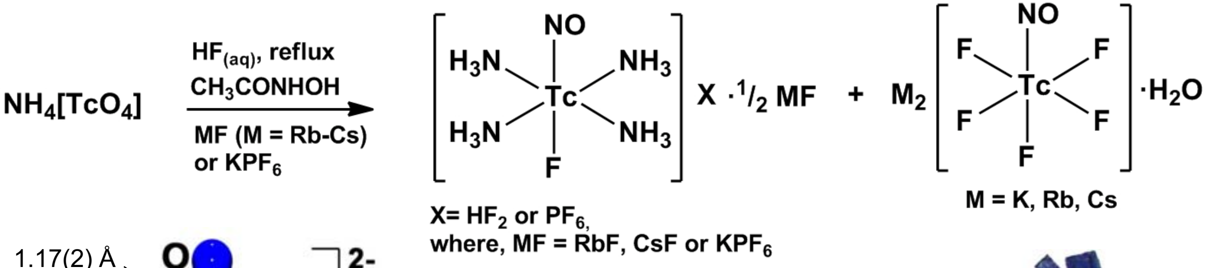
trans- F-Tc$^{(I)}$NO

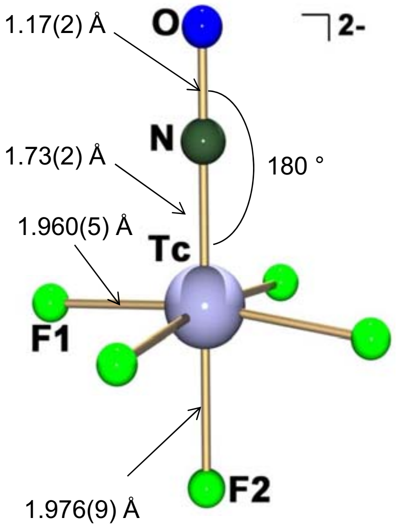


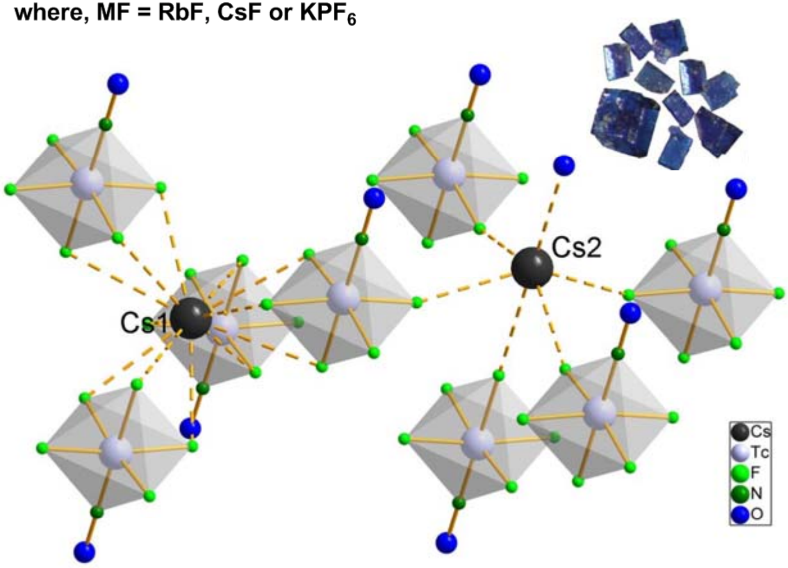
trans- F-Tc$^{(II)}$NO

***trans-* TFA-Tc$^{(I)}$NO**	***trans-* F-Tc$^{(I)}$NO**	***trans-* F-Tc$^{(II)}$NO**	
1670	**1650**	**1817**	IR, Frequency (cm^{-1})
2017	1931	-	NMR, Chemical Shift (ppm)
-	-	$g_{\|} = 1.959$; $g_{\perp} = 2.051$ $A_{\|} = 271.2$; $A_{\perp} = 112.4$	EPR, g and A(10^{-4}cm^{-1})

Technetium Nitrosyl Chemistry







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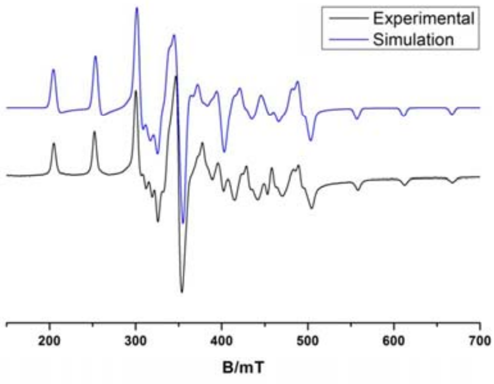
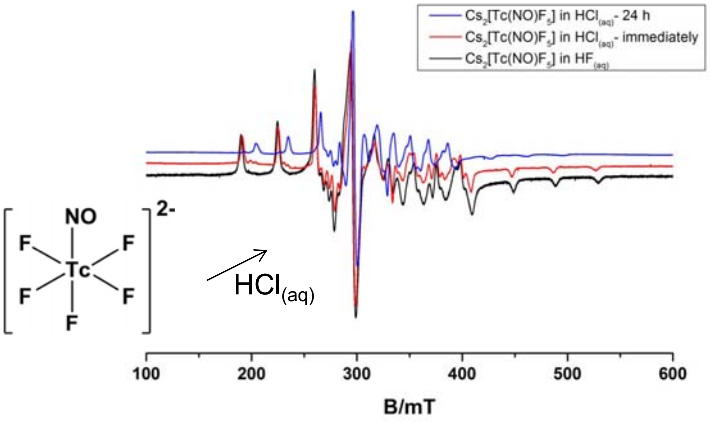
Technetium Nitrosyl Chemistry



Frozen Solution EPR in HF$_{(aq)}$

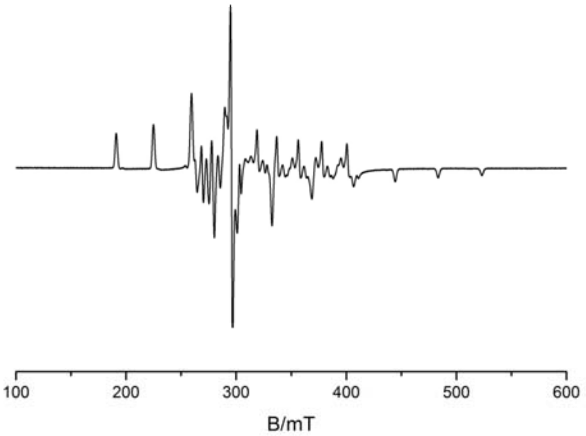


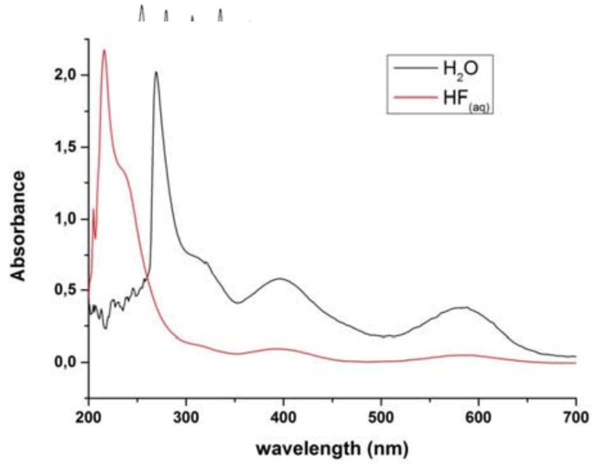
Anion	g∥	g⊥	A∥ 10^{-4} cm^{-1}	A⊥ 10^{-4} cm^{-1}	Reference
$[Tc(NO)F_5]^{2-}$	**1.883**	**2.019**	**332**	**144**	**(a)**
$[Tc(NO)Cl_5]^{2-}$	1.985	2.037	259.8	111	(b)
$[Tc(NO)Br_4]^{-}$	2.105	2.081	216.5	89.3	(c)
$[Tc(NO)I_4]^{-}$	2.262	2.144	155	73	(d)

[a] Mariappan Balasekaran, S.; Spandl, J.; Hagenbach, A.; Köhler, K.; Drees, M.; Abram, U. *Inorg.Chem.* **2014**, *53*, 5117.
[b] Yang, G. C.; Heitzmann, M. W.; Ford, L. A.; Benson, W. R. *Inorg. Chem.* **1982**, *21*, 3242.
[c] Kirmse, R.; Stach, J.; Lorenz, B.; Marov, I. N. *Z. Chem.* **1984**, *24*, 36.
[d] Kirmse, R.; Stach, J.; Abram, U. *Polyhedron.* **1985**, *4*, 1275.

Technetium Nitrosyl Chemistry

Freie Universität Berlin





Frozen solution EPR in CH_2Cl_2 at 77K

Solution EPR in CH_2Cl_2 at 77K

Technetium Nitrosyl Chemistry

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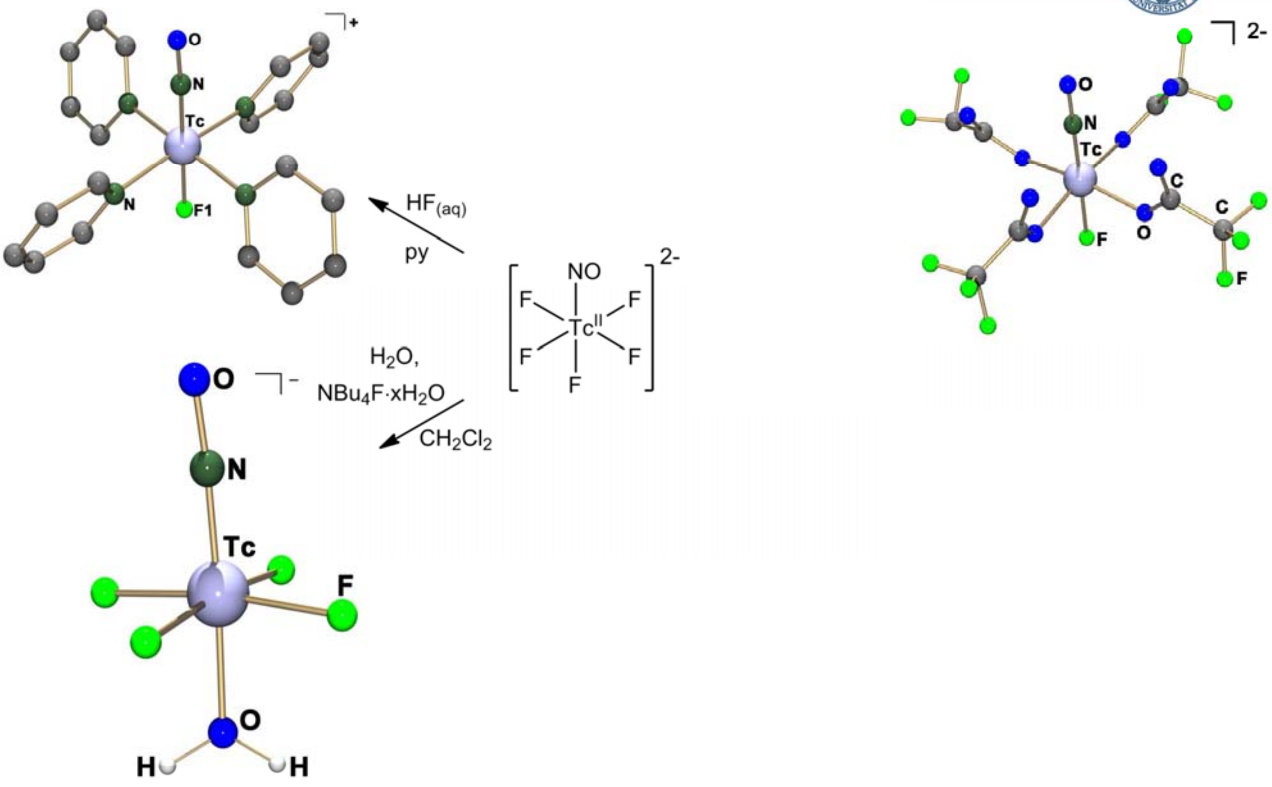
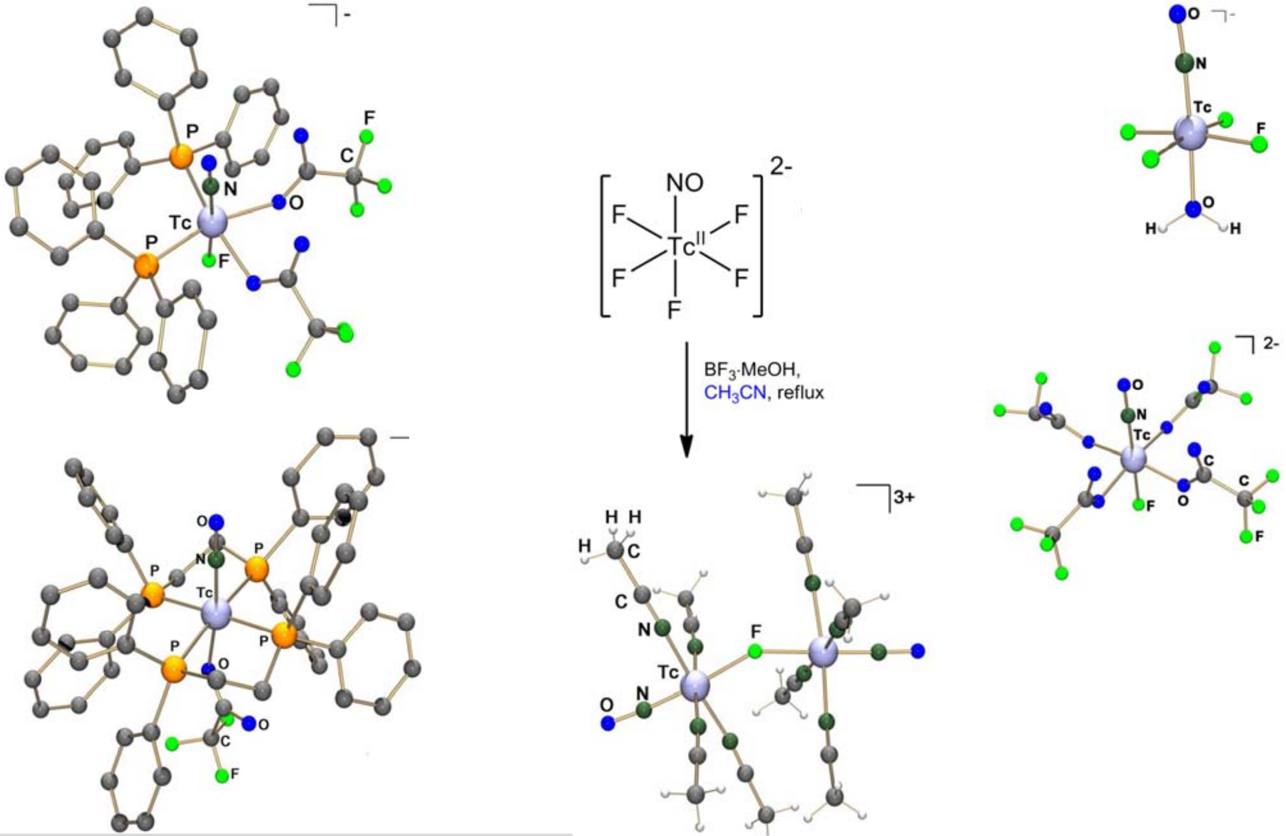
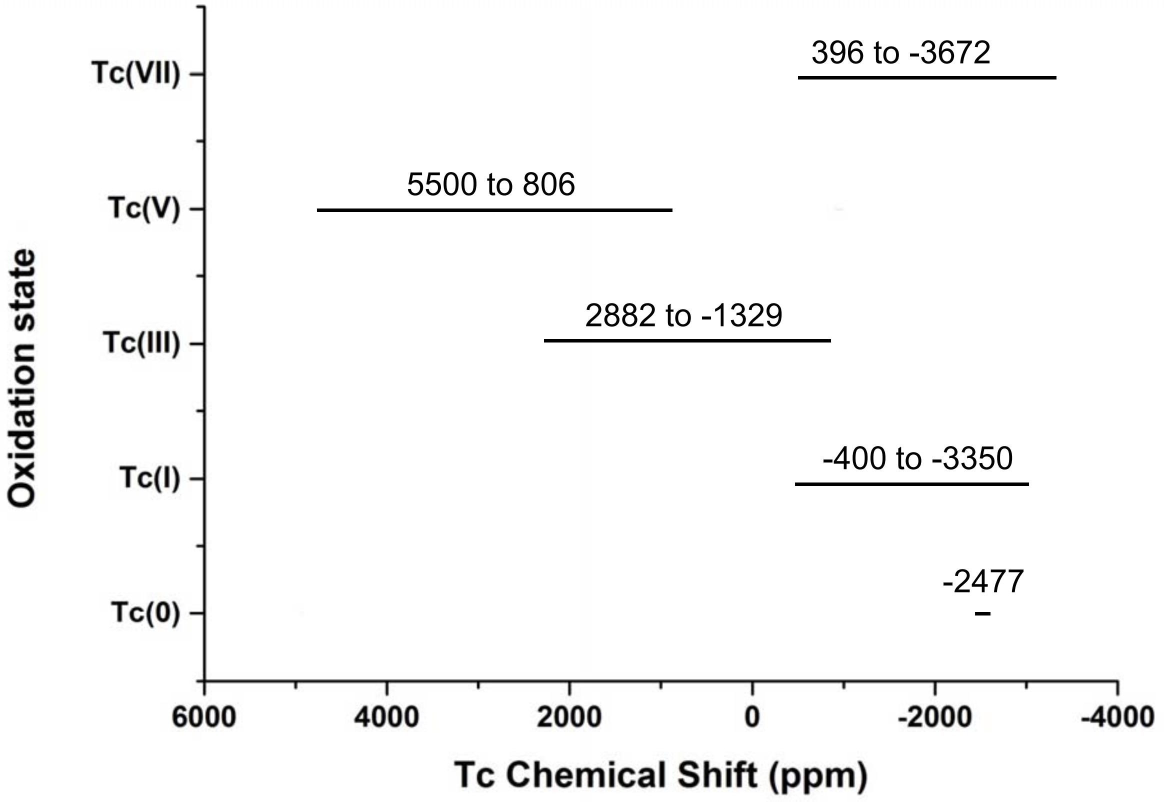


Technetium Nitrosyl Chemistry



Technetium Nitrosyl Chemistry



Summary

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- Fluorido Complexes of low-valent fluorido technetium complexes starting from Tc(IV), Tc(II) and Tc(I) compounds were synthesized.
- Tc(II) and Tc(I) compounds are stabilized with NO core.
- Low-valent Tc-F bonds are unexceptionally inert.
- Fluoride withdrawing agents facilitates ligand exchange reactions.

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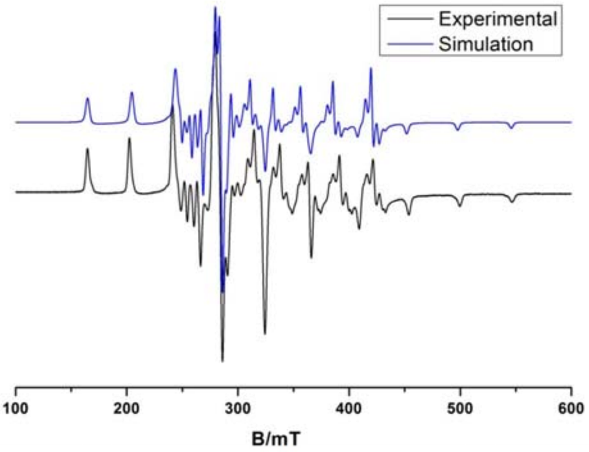
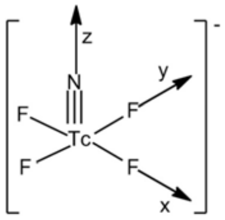
Thank you for your attention.

Nitridofluoridotechnetate(VI)

$$[TcN(OH)_3]_n + HF_{(aq)} \xrightarrow[- H_2O]{} H[TcNF_4]$$





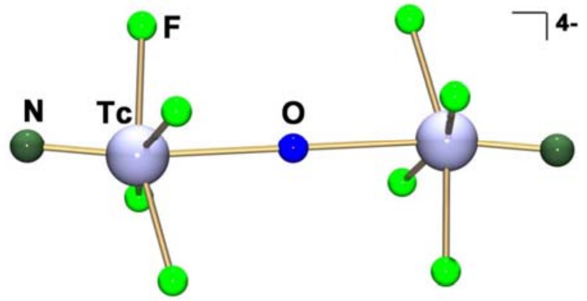
d^1 system
Electron spin: 1/2
Nuclear spin: 9/2

Anion	in	$g_{\parallel}$	$g_{\perp}$	$A_{\parallel}$ 10^{-4} cm^{-1}	$A_{\perp}$ 10^{-4} cm^{-1}	Ref
$[TcNF_4]^-$	**HF**	**1.916**	**2.004**	**378.4**	**171.0**	**This study**
$[TcNF_4]^-$	HF	1.895	1.990	376.5	179.0	(2)
$[TcNF_4]^-$	MeCN	1.895	1.987	367.0	175.0	(2)
$[TcNF_5]^{2-}$	MeCN	1.915	2.000	351.0	165.0	(2)

(1) Baldas, J.; Boas, J. F.; Bonnyman, J. *Aust. J. Chem.* **1989**, *42*, 639.

(2) Baldas, J.; Boas, J. F.; Ivanov, Z.; James, B. D. *Transition Met. Chem.* **1997**, *22*, 74.

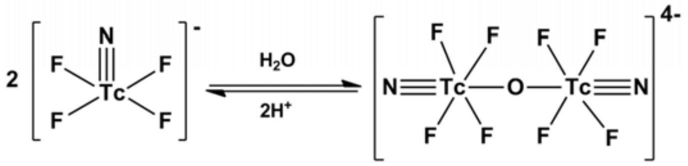
Nitridofluoridotechnetate(VI)

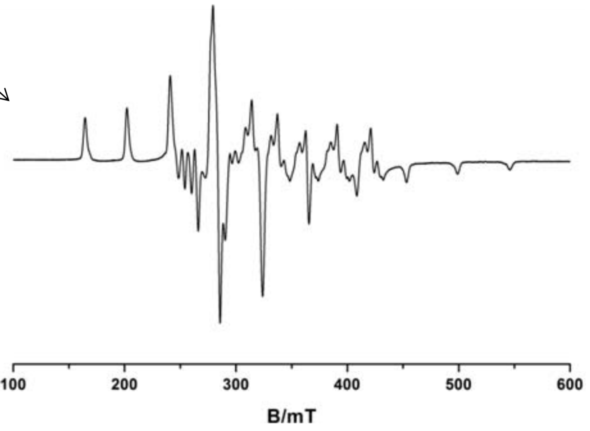


Solubility: H_2O, $HF_{(aq)}$

In H_2O : EPR silent

$HF_{(aq)}$

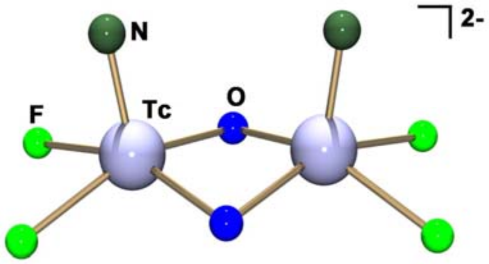


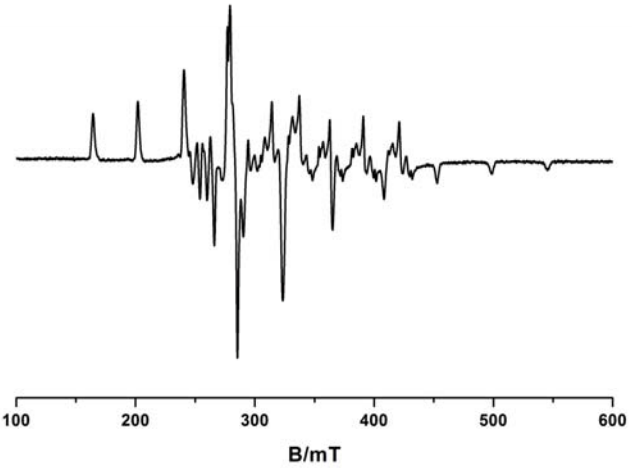


$[TcNF_4]^-$ in $HF_{(aq)}$

Nitridofluoridotechnetate(VI)

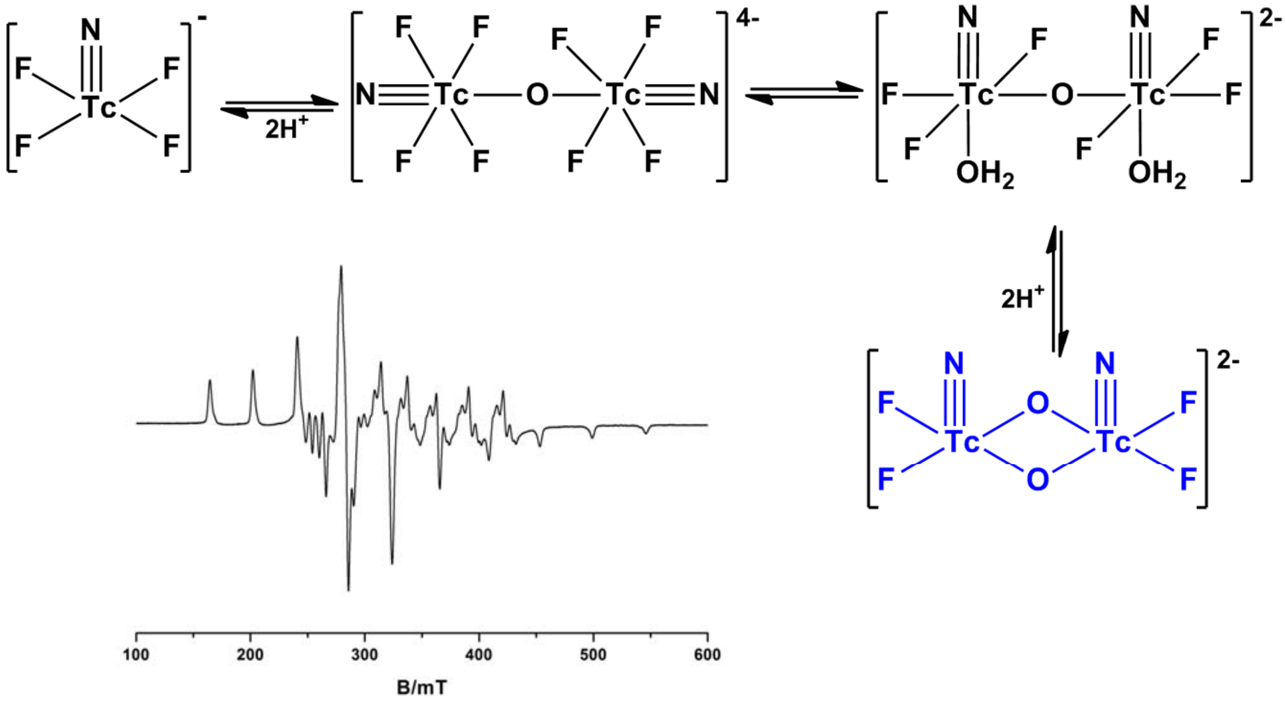
$$H[TcNF_4] \xrightarrow[HF_{(aq)}]{NEt_4F\cdot 3H_2O} (NEt_4)_3(NH_4)[Tc_4N_4F_8O_4]$$





in $HF_{(aq)}$

Nitridofluoridotechnetate(VI)



in $HF_{(aq)}$

Formation of nitrosyl-containing o-phenanthroline complex of iron in presence of TcO4- and HNO3.

Tatiana Boytsova, V.G.Khlopin Radium Institute

Previously, precipitation of technetium with o-phenanthroline complex of iron(II) (Ferroin nitrate) was suggested for technetium recovery from nitric acid solutions of the SNF reprocessing.This complex allows to precipitate 93±5% Tc from the solutions with the concentration of nitric acid up to 2M.[1]

The study of formed sediments by elemental analysis revealed the formation of compounds with a variable composition, which depends on the precipitation conditions.[2]

When the physicochemical properties of these compounds were studied, the band in the range of 1700 cm^{-1} was detected along with the band at 900 cm^{-1}, belonging to pretechnetate-ion, the band at 1385 cm^{-1} of nitrate-ion and the band at 3200-3600 cm^{-1}indicating the presence of crystallization water.

The IR spectrumwith the band at 1700 $cm^{-1}$was compared with the IR spectra of Ferroin nitrate, $KTcO_4$, and TcO_2, which probably could be formed during the incomplete pretechnetateion reduction. It was found that the band at 1700 cm^{-1} is absent in the IR spectra of these compounds.Basing on the datagiven in [3] it was supposed that this band at 1700 cm^{-1}belongs to the coordinated NO group.

For comparison,the precipitates were prepared by the pertechnetateion precipitation with Ferroinsulphate from the sulfuric acid solutions. The IR spectra of the precipitates formed under the above conditions alsodidn't containband at 1700 cm^{-1}.

It was found that under defined experimental conditions the presence of the mother solution in the course of dehydration is necessary to obtain the nitrosyl-containing complexes. The content of the mother solution was determined by elemental analysis and UV-VIS spectrophotometry. It was determined that along with nitric acid, pertechnetateion, oxidized o-phenanthroline complex of iron(III), this solution also contains the initial Ferroin nitrate.

Poorly soluble compounds of rhenium were prepared under the same experimental conditions by precipitation of perrhenateion from the solutions of nitric acid. The IR spectra of the resulting rhenium-containing complexes showed the absence of coordinated NO group. Hence, the nitrosyl-containing o-phenanthroline complexes of ironcan be formed only in the presence of pertechnetateion.

Additional data on the structure and composition of the nitrosyl-containing compounds obtained bypretechnetateion precipitation with Ferroin nitrate from the nitric acid solutions were obtained using single-crystal X-ray diffractometry and Mossbauer spectroscopy.

The mechanism of formation of the nitrosyl-containing iron complex in the presence of pertechnetateion and nitric acid solution is suggested.

1T.A. Boytsova, A.A. Murzin, V.A. Babain, The pertechnetate-ion precipitation in nitric acid solutions with o-phen complex of iron (II) nitrate., «Russian-nordic Symposium on radiochemistry», Abstracts, p. 5, http://rnsr.org/images/7%20boytsova.pdf

2BoytsovaT.A., MurzinA.A., Babain V.A., Lumpov A.A. 1,10-phenantroline complex of iron(II) nitrate: the challenging salt for the technetium precipitation from nitric acid solutions., 17th Radiochemical conference, MarianskeLazne, Czech Republic, 2014, p.305

3 Накамото К., Инфракрасные спектры неорганических и координационных соединений// Мир, М., 1966, с 41

The 8th International Symposium on Technetium and Rhenium: Science and Utilization.
September 29th - October 3rd 2014
La Baule - Pornichet, France.

Formation of nitrosyl-containing o-phenanthroline complex of iron in presence of TcO_4^- and HNO_3.

T.A. Boytsova, V.A. Babain, A.A. Lumpov, A.A. Murzin

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tboytsova@khlopin.ru

Introduction

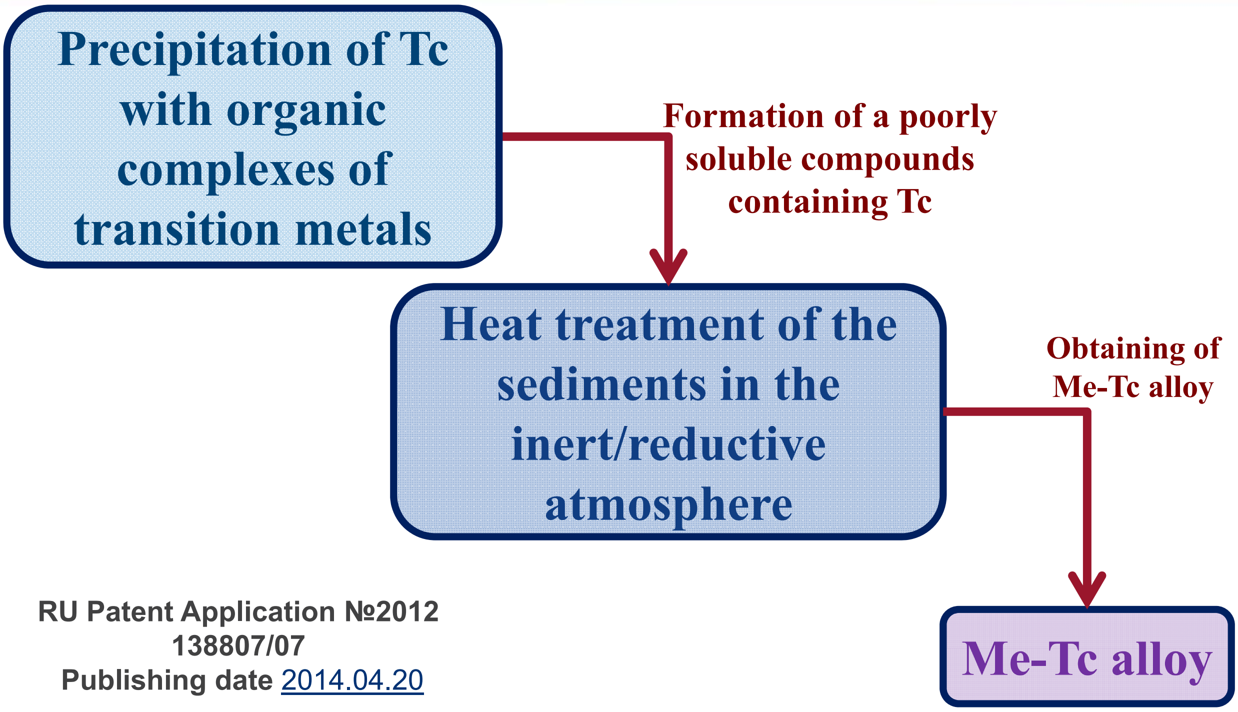
^{99}Tc is a synthetic long-lived radioactive isotope, the main source of which is a nuclear fuel irradiated with thermal neutrons. The ^{99}Tc yield is 1 kg ^{99}Tc from 1t of U.

In the spent nuclear fuel (SNF) reprocessing using different manufacturing flowsheets, technetium, partly distributes along the streams of major components, or can be outputted to the raffinate or individual stream. The presence of technetium in the streams of actinides affects their purity and thus the extra refining stages are required. Also, long half-life, chemical activity, and high environmental mobility of technetium compounds, present in the SNF solutions, directly indicate the necessity of safe technetium immobilization.

Earlier, to solve this problem, we proposed to precipitate Tc with organic complexes of transition metals[1].

1. Boytsova T A, Murzin A A, Babain V A, Shadrin A Yu, (2014) RU PATENT 2513724. 20.04.2014, Bull 11

The Scheme of the process



Precipitation of Tc with organic complexes of transition metals

Formation of a poorly soluble compounds containing Tc

Heat treatment of the sediments in the inert/reductive atmosphere

Obtaining of Me-Tc alloy

Me-Tc alloy

RU Patent Application №2012 138807/07
Publishing date 2014.04.20

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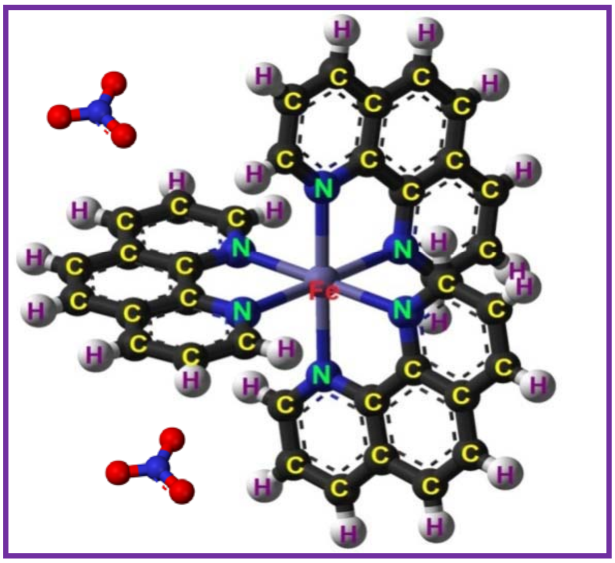
o-phenantroline complex of iron(II) – Ferroin nitrate – $Fe(phen)_3(NO_3)_2$



Maximum yield of Tc into the sediment:

93±5%

- The concentration of Tc 1 g/L in the initial solution

Boytsova T.A., Murzin A.A., Babain V.A., Lumpov A.A. 1,10-phenantroline complex of iron(II) nitrate: the challenging salt for the technetium precipitation from nitric acid solutions., 17th Radiochemical conference, Marianske Lazne, Czech Republic, 2014, p.305

The conditions of the Tc precipitation

- **Initial solution: 1 g/L Tc, 1 M HNO_3;**
- **Precipitant solution- Ferroin nitrate.**
- **Mole ratios Ferroin/Tc = 1/2, 1/1, 1.5/1**

Experiments at variable temperatures of the solutions

The temperature of the initial solutions, °C	The temperature of the precipitant solution, °C		
	15-20	45-50	65-70
15-20	+	+	+
45-50	-	+	-
65-70	-	-	+

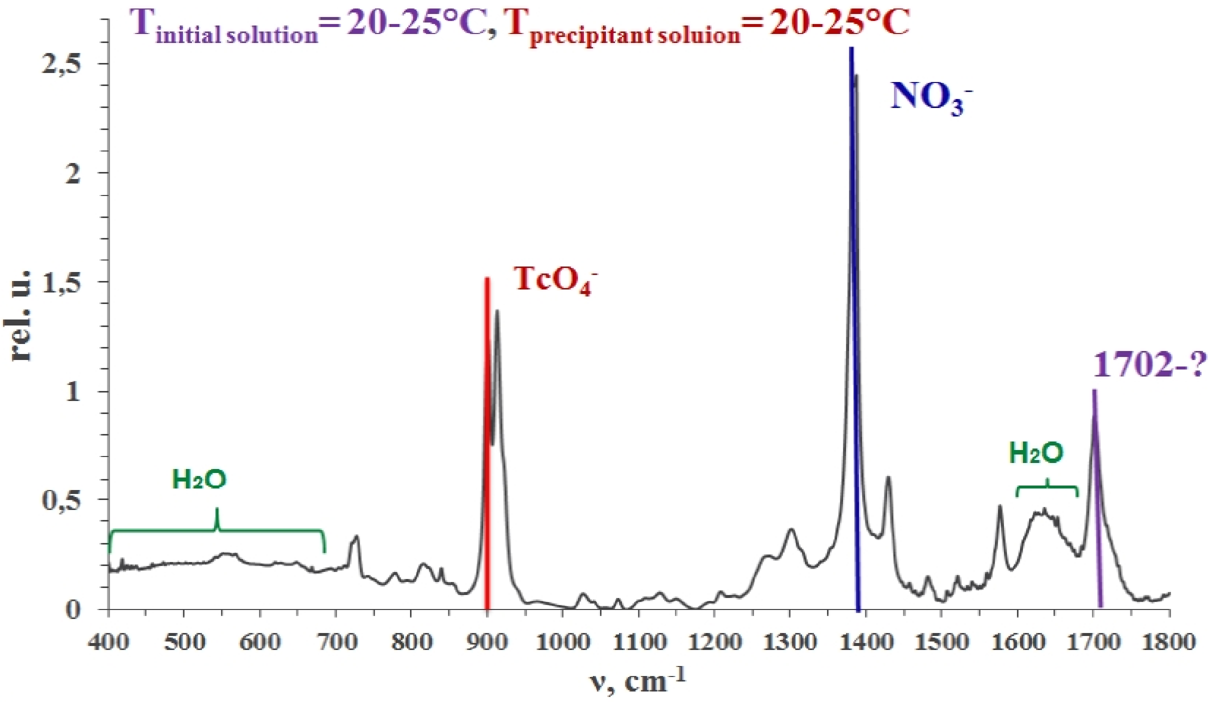
The main goal of this work was to study the composition and structure of the precipitating compounds and the possible mechanism of their formation.

Tc/Fe mole ratio in the sediments obtained in the solutions at variable temperatures

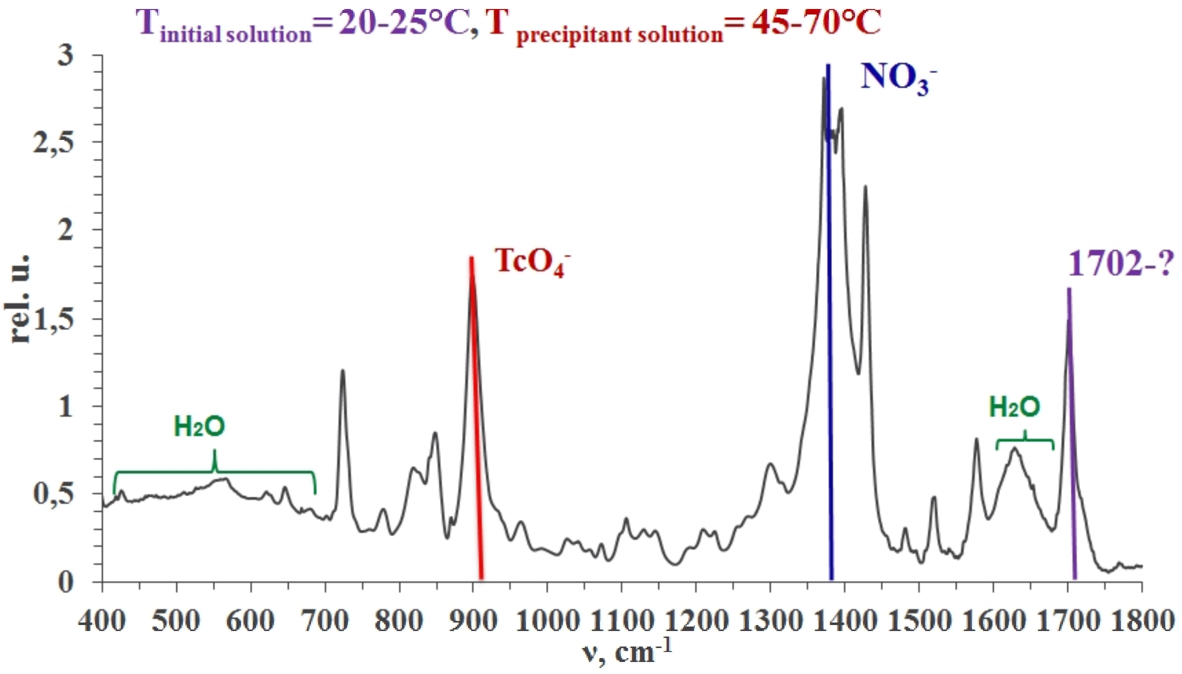
The temperature of the initial solutions, °C	The temperature of the precipitant solution, °C							
	15-20		45-50			65-70		
	Ferroin/Tc mole ratio							
	1/2	1/1	1/2	1/1	1.5/1	1/2	1/1	1.5/1
15-20	1.67±0.08	1.38±0.07	0.94±0.05	2.03±0.10	1.44±0.07	0.89±0.04	1.67±0.08	0.77±0.04
45-50	-	-	1.43±0.73	1.58±0.08	1.51±0.05	-	-	-
65-70	-	-	-	-	-	0.89±0.04	0.95±0.05	0.67±0.03

Fe(phen)$_3$(TcO$_4$)$_x$(NO$_3$)$_y$• nH$_2$O- ?

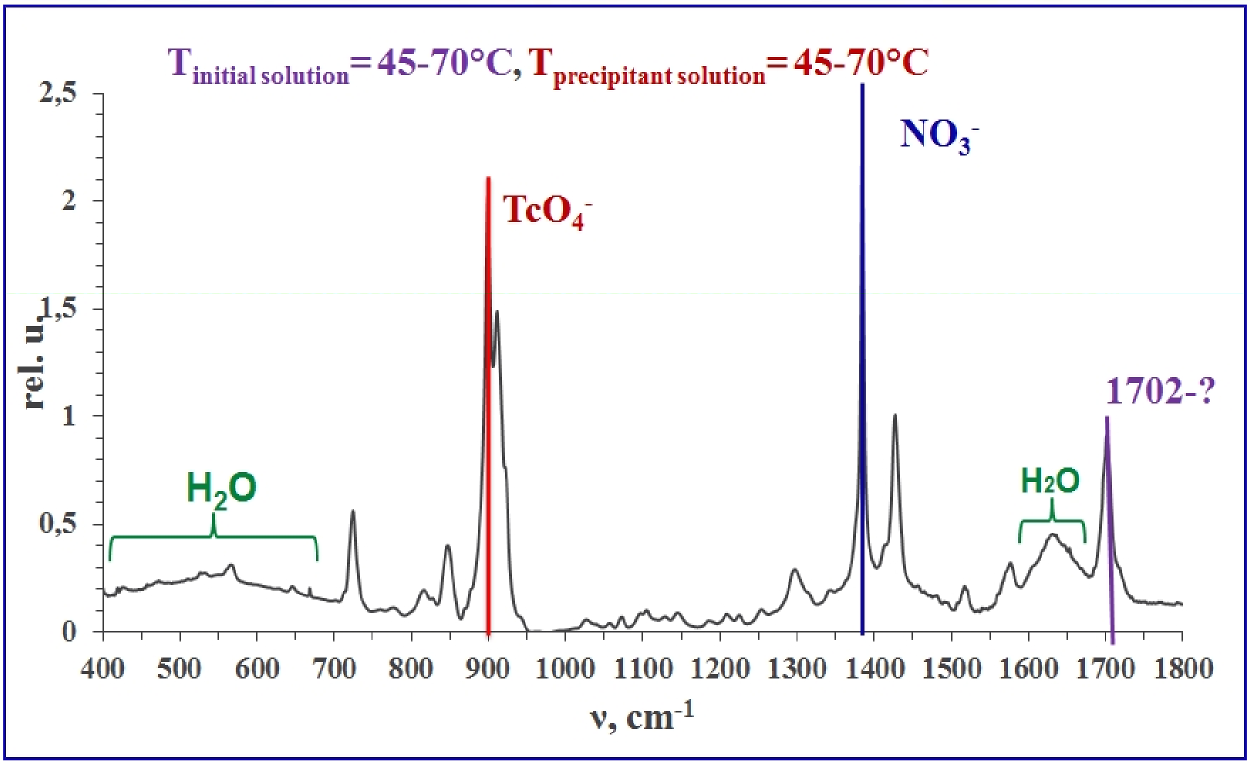
IR Spectrum of the sediment received from 1 M HNO_3 with Ferroin nitrate



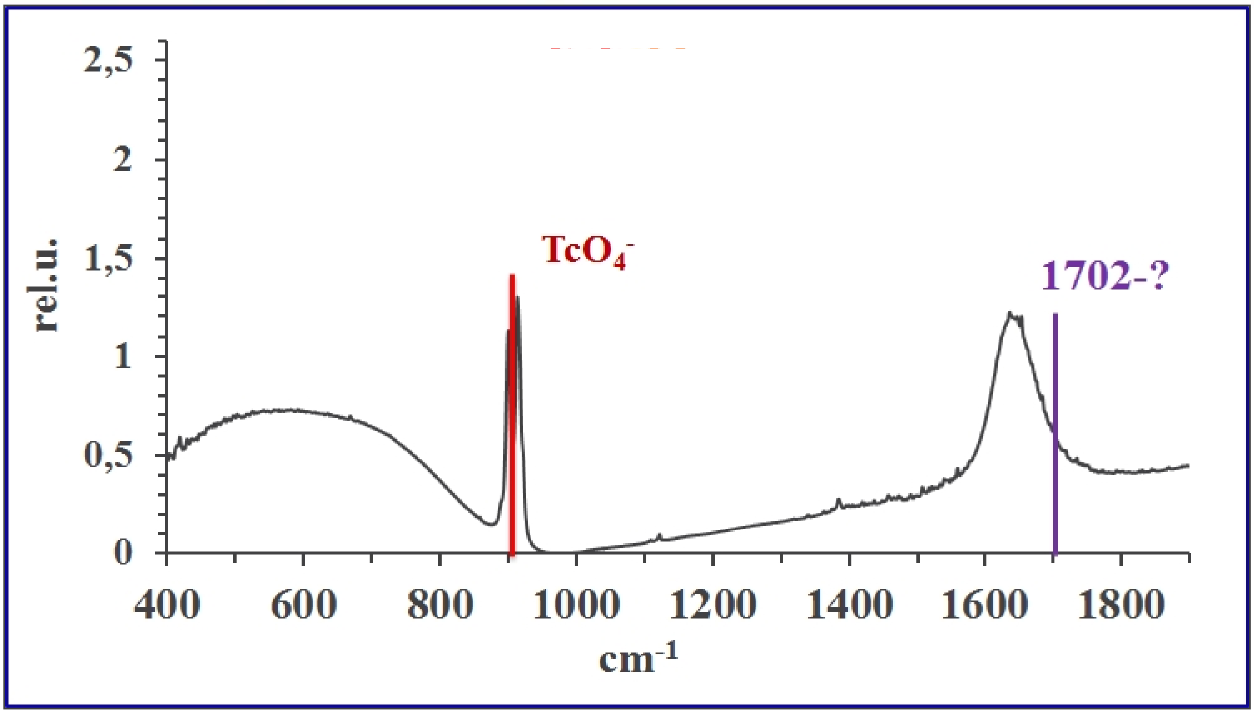
IR Spectrum of the sediment received from 1 M HNO_3 with Ferroin nitrate

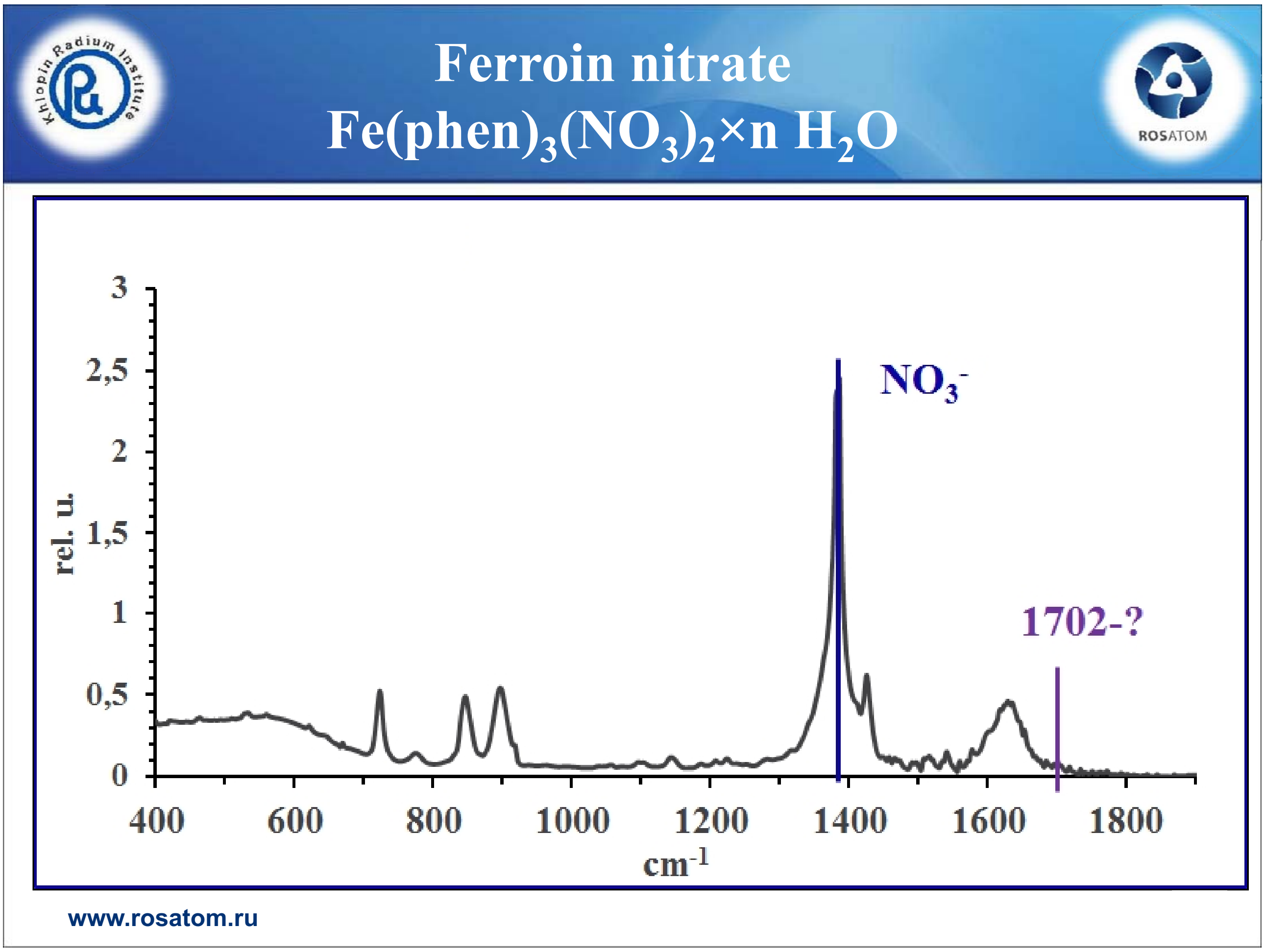


IR Spectrum of the sediment received from 1 M HNO_3 with Ferroin nitrate



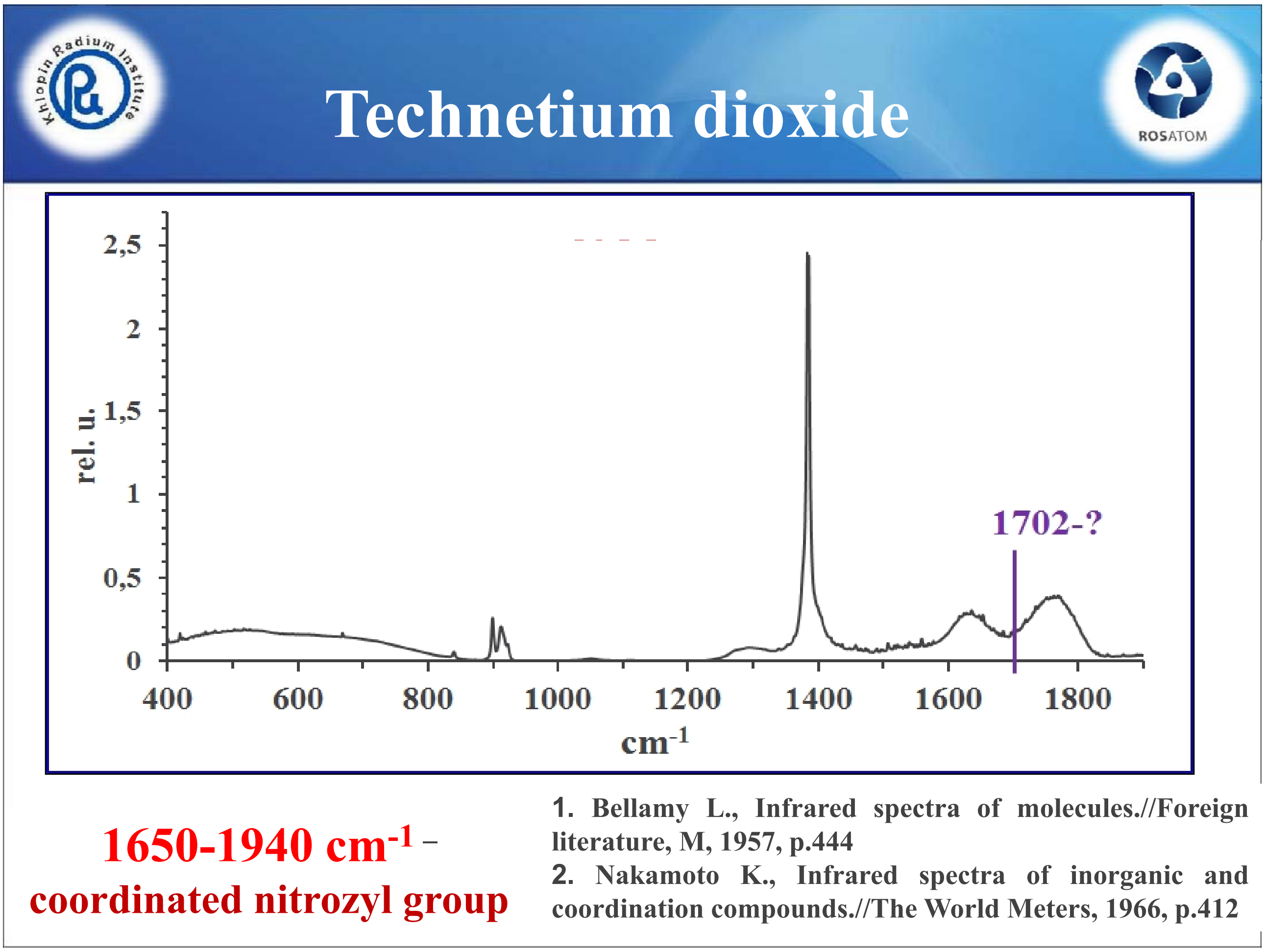
Potassium pertechnetate





Ferroin nitrate
$Fe(phen)_3(NO_3)_2 \times n\ H_2O$

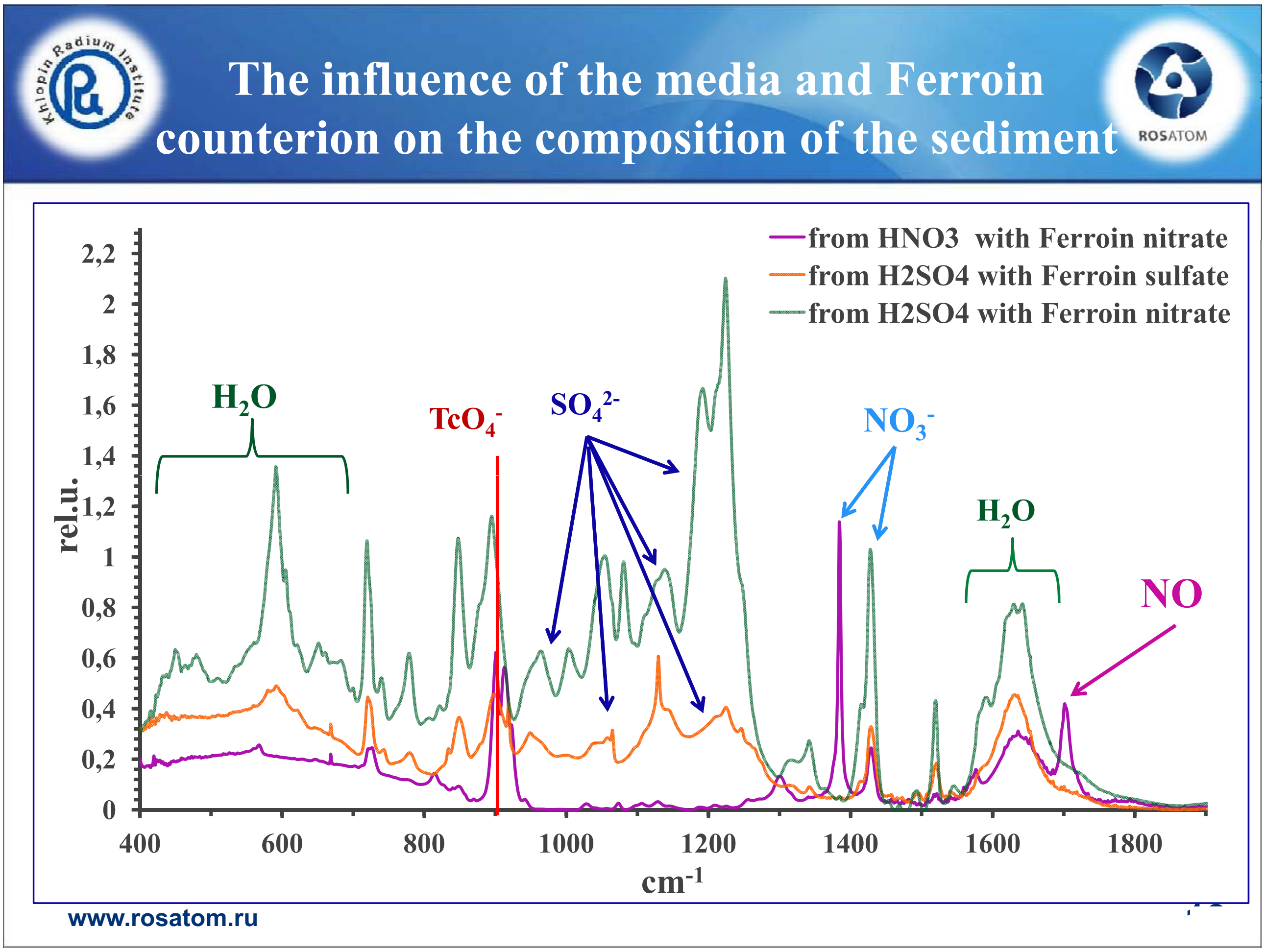
www.rosatom.ru



Technetium dioxide

1650-1940 cm^{-1} – coordinated nitrozyl group

1. Bellamy L., Infrared spectra of molecules.//Foreign literature, M, 1957, p.444
2. Nakamoto K., Infrared spectra of inorganic and coordination compounds.//The World Meters, 1966, p.412



The influence of the media and Ferroin counterion on the composition of the sediment

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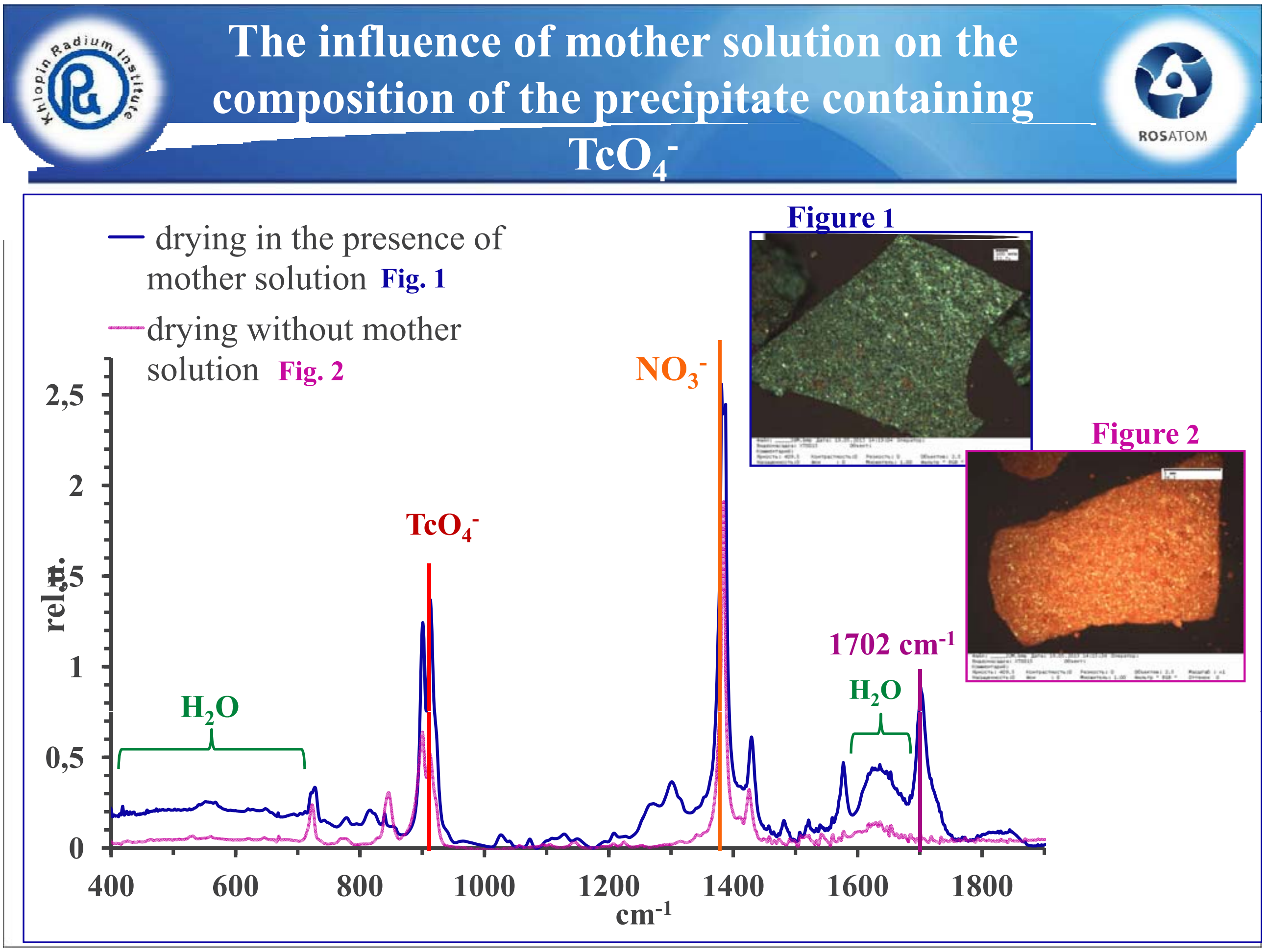
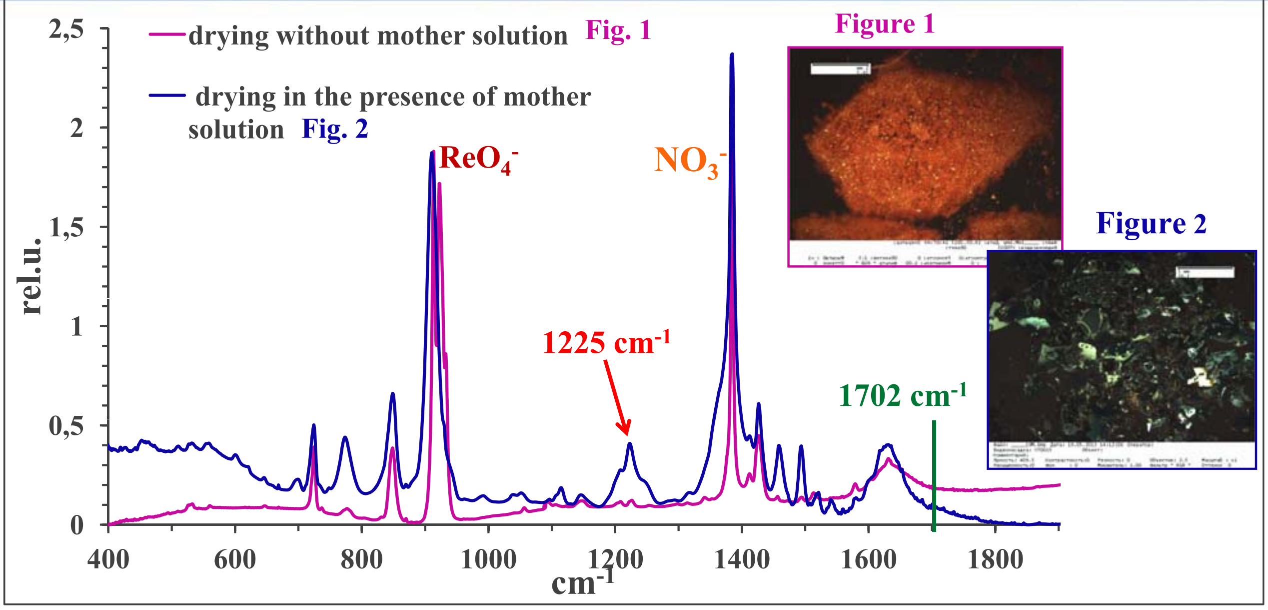


The influence of mother solution on the composition of the precipitate containing TcO_4^-

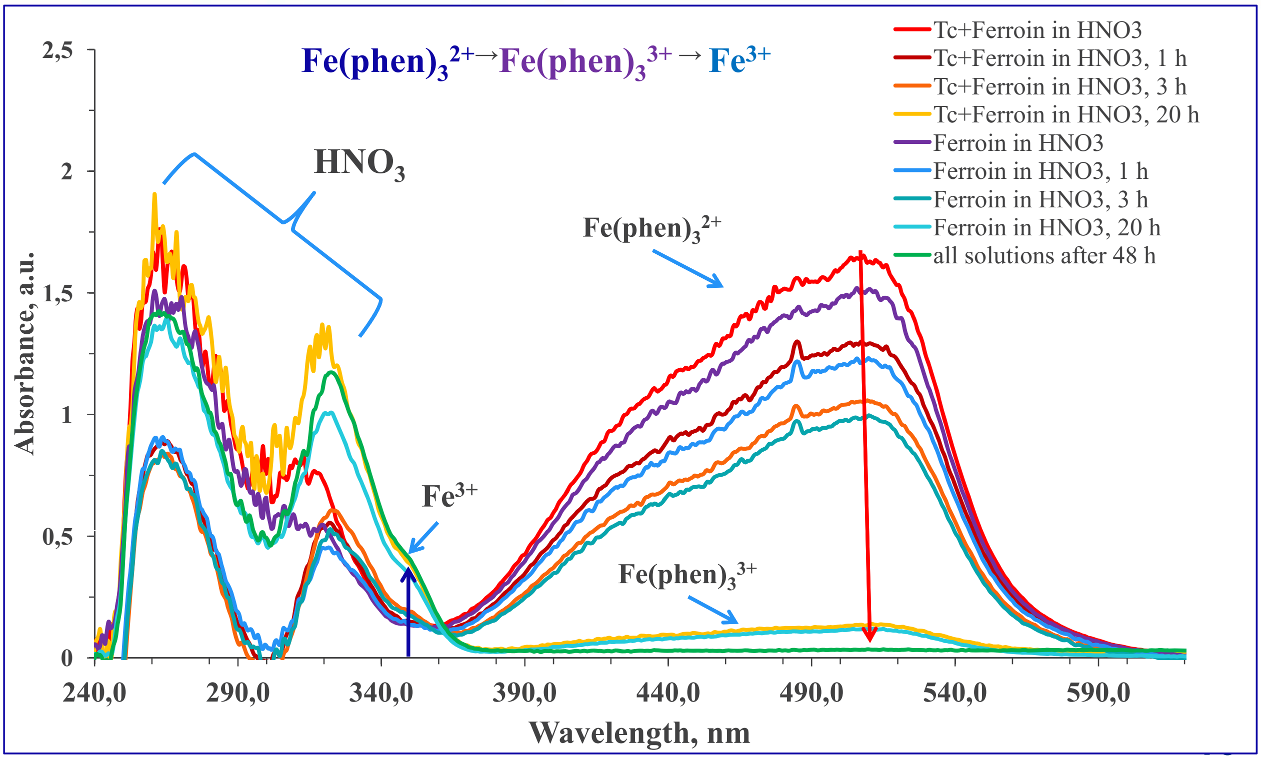
The influence of mother solution on the composition of the precipitate containing ReO_4^-



850 cm^{-1}, 1225 cm^{-1} – phenantroline oxide [1,2]

1. Dulnev P.G, Kruglova E.D., Donchenko P.A., Mycanov A.G., Manuil'skiy V.D., Vilnesov G.I., Boyko A.P., RU Patent 2106352.
2. Nageswara R. N., Ulrich K. Synthesis and characterization of *trans*-[Re(L-L)2O(OH)](ReO4)2 (L-L=2,2'-bipyridine, 4,4'-dimethyl-2,2'-bipyridine) and *trans*-[Re(L-L)2O2]ReO4 (L-L=1,10-phenantroline) complex. Polyhedron, Vol.11-13, 1992, pp.1615-1622

UV spectra of the solution after the precipitation of TcO_4^- with Ferroin nitrate from 1M HNO_3 in comparison with UV spectra of the solution of Ferroin nitrate in 1M HNO_3

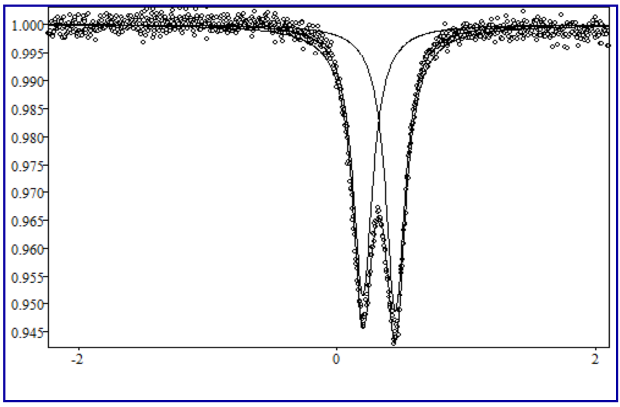


Mossbauer spectra of
$Fe(phen)_3(NO_3)_2$ and $Fe(phen)_3(TcO_4)_x(NO_3)_y$

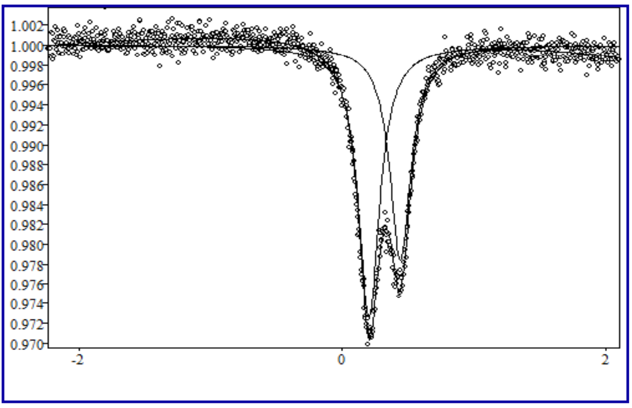
Chemical formula	Form 1			
	Isomer shift, mm/s	Quadropole spliting (Asymmetry parameter), mm/s	Breadth of the experimental line, mm/s	S, %
$Fe(phen)_3(NO_3)_2$	0.32	0.25 (0.94)	0.19	100
$Fe(phen)_3(TcO_4)_x(NO_3)_y$	0.32	0.24 (1.27)	0.19	100

S - the proportion of the corresponding lines in the experimental spectrum.

$Fe(phen)_3(NO_3)_2$

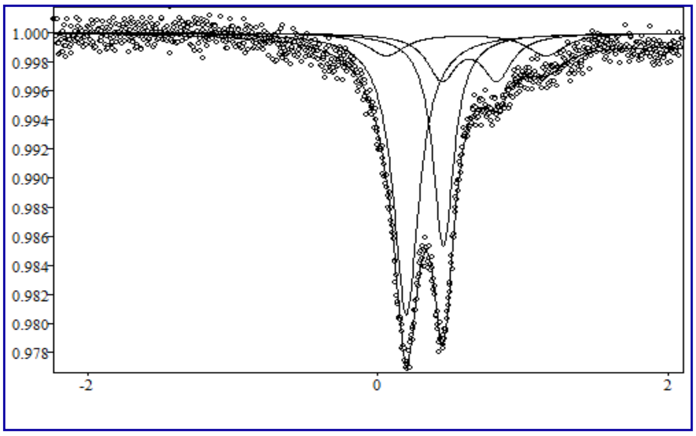


$Fe(phen)_3(TcO_4)_x(NO_3)_y$



Mossbauer spectrum of
$Fe(phen)_2(NO)_x(TcO_4)_y(NO_3)_z$

Chemical formula	Form 1				Form 2				Form 3			
	I.s., mm/s	Q.s. (A.p.), mm/s	G., mm/s	S, %	I.s., mm/s	Q.s. (A.p.), mm/s	G., mm/s	S, %	I.s., mm/s	Q.s. (A.p.), mm/s	G., mm/s	S, %
$Fe(phen)_3(NO_3)_2$	0.32	0.25 (0.94)	0.19	100								
$Fe(phen)_3(TcO_4)_x(NO_3)_y$	0.32	0.24 (1.27)	0.19	100								
$Fe(phen)_2(NO)_x(TcO_4)_y(NO_3)_z$	0.32	0.26 (1.32)	0.19	73	0.63	0.38	0.25	16	0.61	1.10	0.31	11



I.s.- Isomer shift;
Q.s.-Quadropole spliting;
A.p.- Asymmetry parameter;
G- Breadth of the experimental line;
S- the proportion of the corresponding bands in the experimental spectrum.

The scheme of the formation mechanism of nitrozyl containing complex

1. Precipitation.

$Fe(phen)_3^{2+} + TcO_4^- + HNO_3 \rightarrow Fe(phen)_3^{3+} + Fe(phen)_3(TcO_4)_x(NO_3)_{(2-x)}\cdot nH_2O + NO_x + H_2O$

2. Nitrozyl complex formation.(Drying with air in the presence of mother solution)

- $Fe^{II}(phen)_3(TcO_4)_x(NO_3)_{2-x}\cdot nH_2O + HNO_3 \rightarrow Fe(phen)_3^{3+} + TcO_3^-(TcO_4^{2-}) + NO_3^- + H_2O + Fe^{II}(phen)_3(TcO_4)_y(NO_3)_{2-y}\cdot nH_2O$
- $TcO_3^-\,(TcO_4^{2-}) + HNO_3 \rightarrow TcO_4^- + HNO_2$
- $Fe^{II}(phen)_3(TcO_4)_y(NO_3)_{2-y}\cdot nH_2O + HNO_2 \rightarrow Fe^{II}(phen)_3(TcO_4)_z(NO_3)_{2-z}\cdot nH_2O$ (partial dissolution is possible) $+ Fe^{II}(phen)_2(NO)_y(TcO_4)_k(NO_3)_{2-k}\cdot phen\cdot nH_2O + NO_x + H_2O$

CONCLUSIONS

- The poorly soluble compound containing Tc and nitrate ions ($Fe(phen)_3(TcO_4)_x(NO_3)_{(2-x)}\cdot nH_2O$) was formed at the first stage of the Tc precipitation with Ferroin nitrate. On the base of this compound stable Fe-Tc alloy could be obtained by the heat treatment in reductive or inert atmosphere.
- The pertecnetate-ions and nitric acid in presence of iron(II) complexes allowed to change the composition of this compound.
- Due to the catalytic properties of pertechnetate-ion in the presence of nitric acid and reductant on the base of the formed compound the nitrozyl complex of iron(II) ($Fe^{II}(phen)_2(NO)_y(TcO_4)_k(NO_3)_{2-k}\cdot phen\cdot nH_2O$) can be obtained.

A new method for rapid extraction of rhenium from raw vegetation with subsequent determination of the metal under field conditions

Ognyan Bozhkov* and Christina Tzvetkova

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*E- mail: bozhkov@svr.igic.bas.bg

It is known that the plant biosphere is a natural extractor and concentrator of Re from soils and waters. The authors of this paper developed a green technology for rhenium phytomining from the areas of Cu mines and Cu processing regions, where the Re is dispersed in soils and waters. For practical application of this technology with profit, is very important to find the places with Re concentrations of industrial importance in plants ($C_{Re} \geq 500$ g Re/t dry mass). This is established through regional studies on the rhenium distribution in the vegetation of a region. Field tests are suitable for this purpose.

The aim of the present study is to develop a simple and easy to apply in the field conditions procedure for Re extraction from raw vegetation, following by spot test determination of Re with N, N Dimethyldithiooxamide (DMDTO).

Previous investigations of the authors have shown indirectly that Re is accumulated in vacuoles of plant tissue as perrhenate ion. SEM analysis of vegetation with accumulated rhenium would prove directly rhenium location in the plant. For SEM analysis were prepared clover leaves with known Re content by immersing the clover stems in an aqueous Re solution with C_{Re}=1000μgRe/ml. The leaves were kept for 5 days in this solution and then removed from it. An accurately weighed quantity of clover was ashed and the Re was extracted from ash by an alkaline solution. In all cases, the content of rhenium in solutions was determined by catalytic method with DMDTO. The results of analysis showed that for 5 days the clover accumulate 1498 μg Re/ g raw mass, respectively 11261 μg Re/ g dry mass. These leaves were used in all further experiments. For SEM analysis the raw leaves of clover with Re were frozen with liquid nitrogen and dried in vacuum (0.120 mbars) at -50C^{o} with an Alpha- Crist Freeze-Dryer during 6 h. The lyophilized leaves were analyzed by SEM. The SEM pictures demonstrated that Re is accumulated in vacuoles of the plant. X-ray spectral microanalysis of freeze-dried clover leaves proved the existence of the element.

For full extraction of Re from raw vegetation is necessary to disrupted cell membrane of the vacuole and to leach Re as a ReO_4^- only by water. The authors have chosen the freezing of the raw leaves by liquid nitrogen, because in this process, the water in plants cells freezes and forms ice crystals that drill the cell membrane. Adding water to the frozen clover leads to its thawing and the resulting solution contains thawed plant and soluble components of the cell sap, including perrhenate ions. The plant mass was separated by filtration through filter paper and the filtrate was transferred into a measuring vessel and made up to volume with water. Determination of rhenium was done with an aliquot of this solution by semi-quantitative express spot test with DMDTO. The result showed that C_{Re}=1498 μg Re/ g raw mass, respectively 11261 μg Re/ g dry mass and are similar to those obtained by ashing.

As a result a simple rapid field test for Re determination in raw vegetation was developed. The method includes: a) freezing of raw mass with liquid nitrogen; b) water extraction of ReO_4^-; c) spot test determination of Re with DMDTO.

Acknowledgements: This work is supported by ESF (Grant BG051PO001-3.3.06-0050

A new method for rapid extraction of rhenium from raw vegetation with subsequent determination of the metal under field conditions

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GREEN TECHNOLOGY FOR RHENIUM PHYTOMINING

The method is based on the unique property of Re to accumulate and concentrate in green vegetation in amounts exceeding hundred and thousand times its natural occurrence.

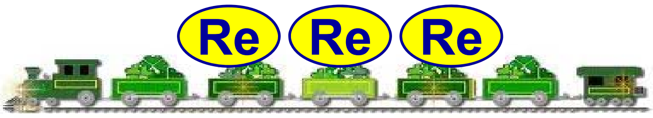
The technology includes following steps:

Regional investigation on the Re distribution in vegetation of Cu mining and Cu processing areas.

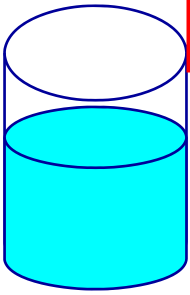
The regions with Re concentrations of industrial importance ($C_{Re} \geq 500$ g Re/t dry mass) are planted with Re hyperaccumulator, discovered by us, which is able to accumulate up to 46kg Re/t hay.

Harvesting the hyperaccumulator with Re.

Extraction of Re from hay and obtaining of perrhenate



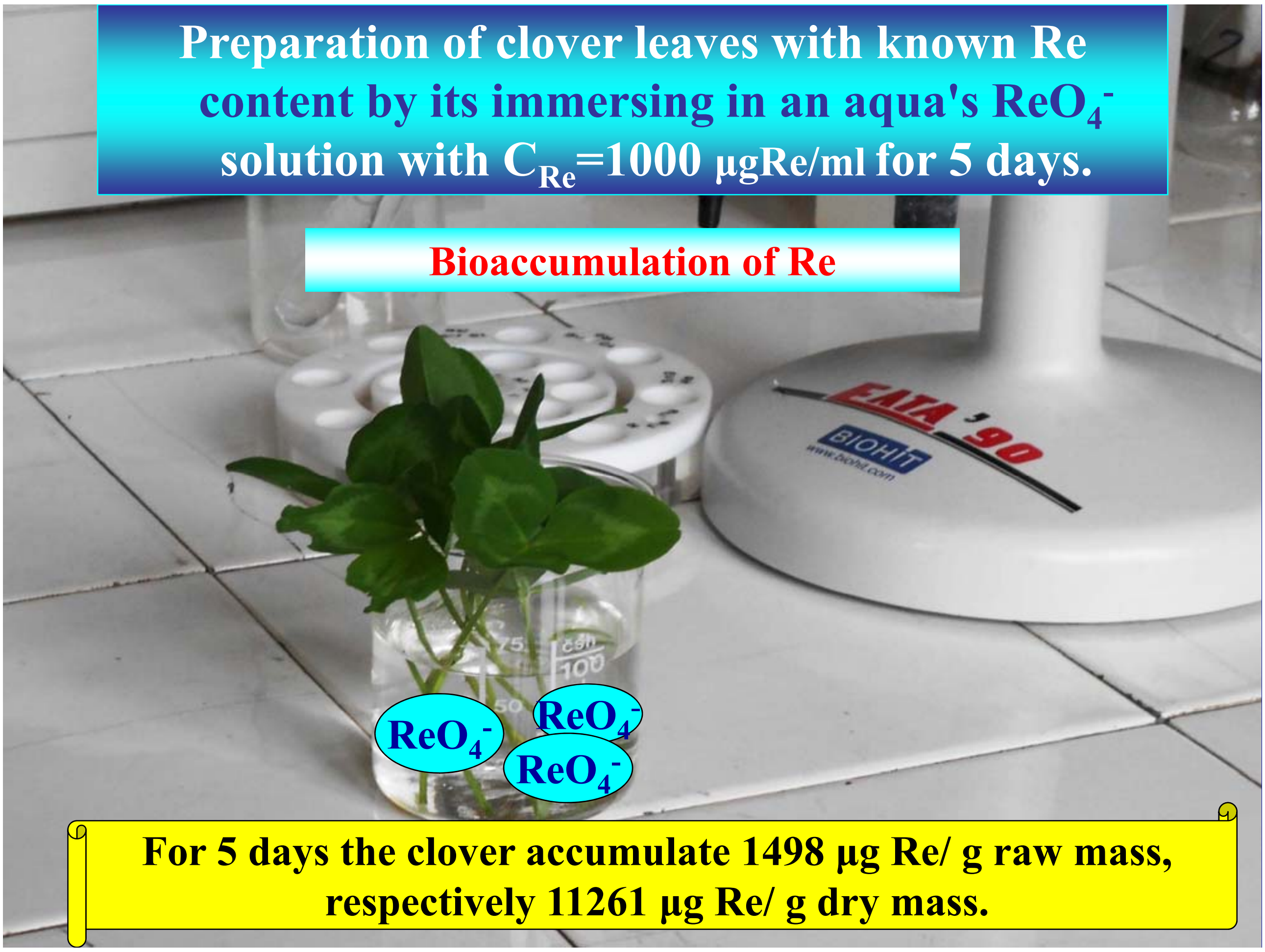
Environmental friendly extraction of Re from hay according our know how method



For practical application of this method with profit the most important is to find the places with Re concentrations of industrial importance in plants ($C_{Re} \geq 500$ g Re/t dry mass). This is established through regional studies on the rhenium distribution in the vegetation of areas of: open Cu pit mine, Cu bioleaching and processing of Cu concentrates. Field tests are suitable for this purpose.

For the development of a method for the rapid extraction of rhenium from raw plants is very important to know in which part of the cell is accumulated rhenium.

SEM analysis of vegetation with accumulated rhenium would prove directly rhenium location in the plant.



Preparation of clover leaves with known Re content by its immersing in an aqua's ReO_4^- solution with C_{Re}=1000 µgRe/ml for 5 days.

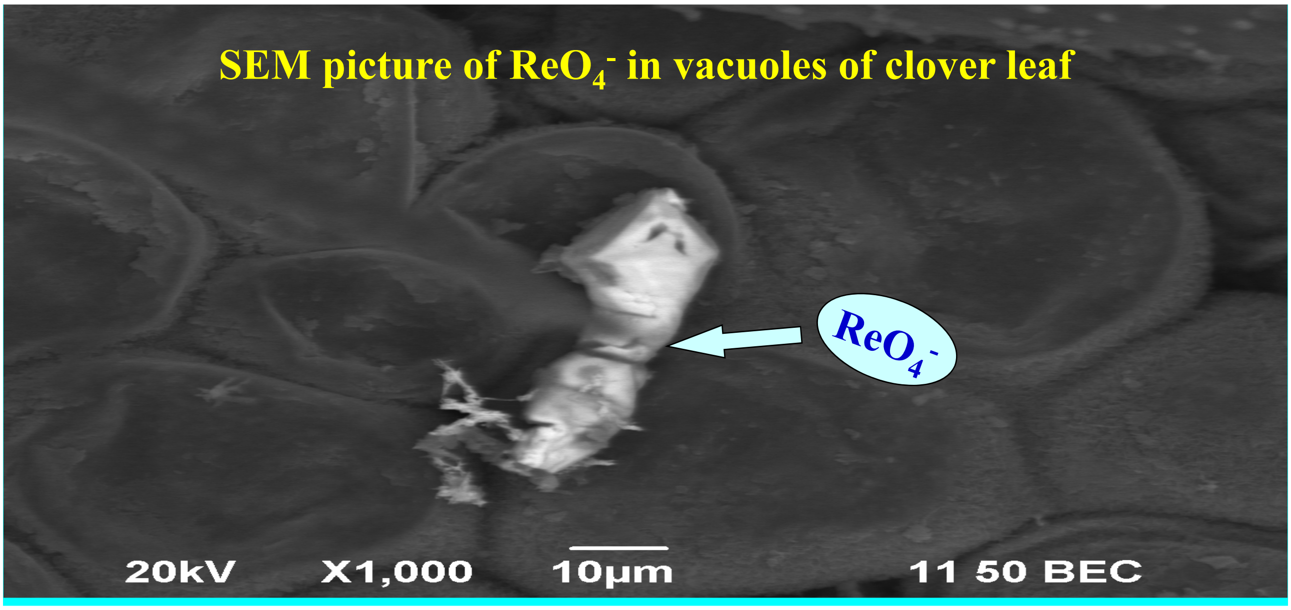
Bioaccumulation of Re

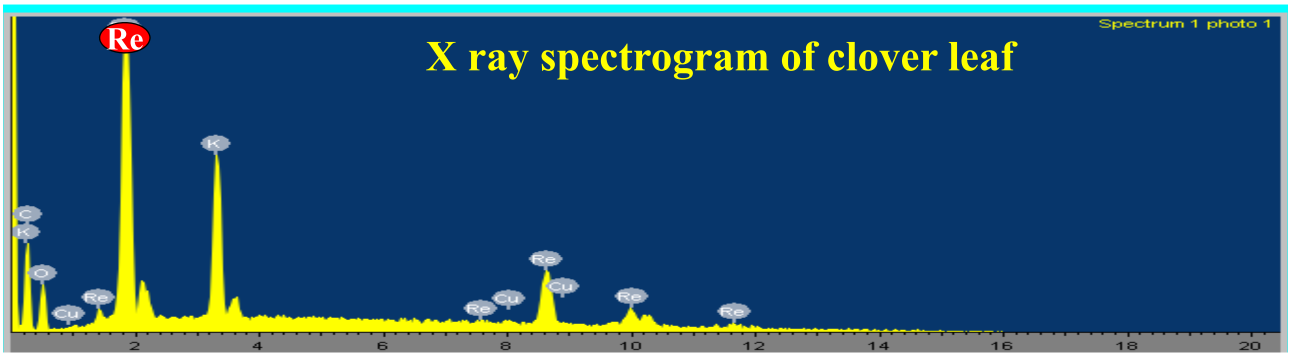
For 5 days the clover accumulate 1498 µg Re/ g raw mass, respectively 11261 µg Re/ g dry mass.

Preparation of clover leaves for SEM analysis by lyophylization

1. Freezing of clover with liquid nitrogen

2. Drying frozen clover in vacuum (0.120 mbars) at -50^{o} C with an Alpha- Crist Freeze-Dryer during 6 h.


SEM picture of ReO_4^- in vacuoles of clover leaf


X ray spectrogram of clover leaf

Results of X ray analysis

Element	App	Intensity	Weight %	Weight%	Atomic%
	Conc.	Corrn.		Sigma	
C K	8.06	0.6820	25.08	1.23	58.22
O K	3.03	0.4935	13.05	0.70	22.74
K K	7.43	0.9680	16.31	0.47	11.63
Cu K	0.88	0.9159	2.03	0.66	0.89
Re M	18.01	0.8786	43.52	1.00	6.52
Totals			100.00		

Conclusions

1. The SEM pictures demonstrated that Re is accumulated in vacuoles of the plant.

2. X-ray spectral microanalysis of freeze-dried clover leaves proved the existence of the element in vegetation.

3. For full extraction of Re from raw vegetation is necessary to disrupted cell membrane of the vacuole and to leach Re as a ReO_4^- only by water.

Experimental approach of authors for Re extraction from raw leaves.

1.The authors have chosen the freezing of the raw leaves by liquid nitrogen, because in this process, the water in plant cells freezes and forms ice crystals that drill the cell membrane.

2.Addition of water to the frozen clover leads to its thawing and the resulting solution contains thawed plant and soluble components of the cell sap of vacuoles, including perrhenate ions.

3. The plant mass was separated by filtration through filter paper and the filtrate was transferred into a measuring vessel and made up to volume with water.

Weighing and Freezing the clover leaves with Re

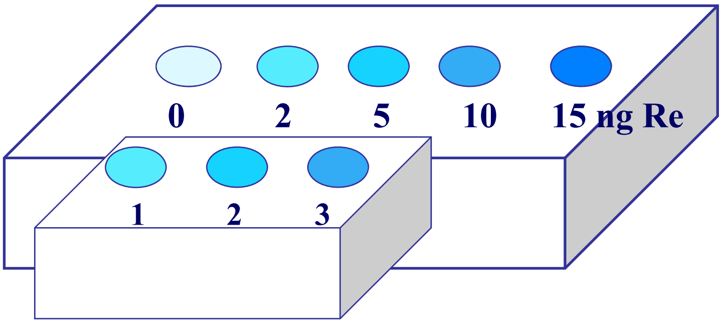
Field balance

Thermos with liquid nitrogen

Thawing of plant mass by addition of water and extraction of ReO_4^-

Separation of plant mass from leaching solution

Rapid spot test for Re determination with N’-N’ Dimethyldithiooxamide



Results: C_{Re}=1498 µg Re/ g raw mass, respectively 11261 µg Re/ g dry mass

Equipment that you need for performance of the field test

Acknowledgements: This work is supported by
ESF (Grant BG051PO001-3.3.06-0050

Thank you for your attention!

SORPTION SEPARATION OF RHENIUM AND ASSOCIATED COMPONENTS OF POLYMETALLIC RAW MATERIALS

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Among the non-traditional sources of rhenium raw materials, polymetallic uranium-containing ores are notable for complex composition and the presence of a number of valuable components − vanadium, molybdenum, rare earth elements [1, 2]. Complex processing of this raw material with relatively low content of associated metals includes operations of sorption using selective ion-exchange resins.

The aim of this investigation is to determine the conditions of sorption separation of rhenium, uranium and vanadium in sulfuric acid solutions, simulating the composition of productive solutions of underground leaching (ISL) of polymetallic ores.

As sorbents intended for uranium and rhenium recovery granular strong and weak base ion exchangers were used, produced by Federal State Unitary Enterprise Leader Research Institute of Chemical Technology (developer Balanovsky N.V.), Russian Federation and the company Purolite International Limited. In addition, to increase the rate of metals sorption fibrous nitrogen ion exchangers FIBAN (AK-22 and A-6) (Institute of Physical Organic Chemistry, Academy of Sciences of Belarus) were tested. Sorption has been carried out in static and dynamic conditions.

Determination of the parameters of sorption separation of rhenium and uranium was carried out at varying concentrations of natural fulvic acids (FA) present in ISL sulfuric acid solutions of polymetallic ores. Fulvic acid concentration was varied in the range 25 ÷ 300 mg/dm^3. Sorption of rhenium in the presence of fulvic acids by selected ion exchangers is almost unchanged. It was found out that rhenium selectivity of nitrogen-containing ion exchangers of different types and structures increases with increasing of fulvic acids concentration and the pH of the solution, and the greatest separation coefficients of rhenium and uranium (~ 50) are observed during the sorption by the macroporous weak base ion exchangers [3]. The separation factor of uranium and rhenium has a maximum (~ 50) by sorption from solutions containing 50 ÷ 100 mg FC /dm^3 [4].

Determination of the parameters of sorption separation of rhenium and vanadium was performed using fibrous ion exchangers FIBAN AK-22 and A-6. It was ascertained that the sorption rate of vanadium (V) present in the solution as decavanadate-ions of a large size is lower than the ion exchange rate of mobile perrhenate ion: the values of the effective diffusion coefficients, calculated with respect to half-sorption time, differ by an order that allows separate these elements under dynamic conditions [5].

References

1. A.A. Palant, I.D. Troshkina, A.M. Chekmarev. *Metallurgy of Rhenium*, Science: Moscow (2007). 298 p. (rus.).
2. *In-Situ Leaching of Ores*, Academy of Mining Sciences, Publishing House: Moscow (1998). 446 p. (rus.).
3. I.D. Troshkina., A.V. Shilayev, A.P. Grekhov. Sorption of Uranium and Rhenium in the Presence of Fulvic Acids. In: Abstract Book of the 2nd China-Japan Academic Symposium on Nuclear Fuel Cycle (ASNFC 2013). Shanghai. 2013, p. 36.
4. I.D. Troshkina, A.V. Shilyaev, E.V. Butorina et al. Method of rhenium recovery from uranium solutions. Pat. RF 2523892/02. C22B 61/00. Bulletin of inventions, Number 21. Date published 27.07.2014. (rus.).
5. Nway Shwan Oo, I.D. Troshkina, Aye Min, A.V. Shilyaev. *Russian Journal of Non-Ferrous Metals*. 2014**,** *55, № 3*, 242-246.

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SORPTION SEPARATION OF RHENIUM AND ASSOCIATED COMPONENTS OF POLYMETALLIC RAW MATERIALS

PROPERTIES OF RHENIUM

- Rhenium is present in the earth's crust at a **very low concentration – 0.7 ppm**

-**Melting point of rhenium – 3180 ℃** (the highest melting metal next to tungsten, 3380 ℃)

-Rhenium is **the only refractory metal** which **does not form carbides**

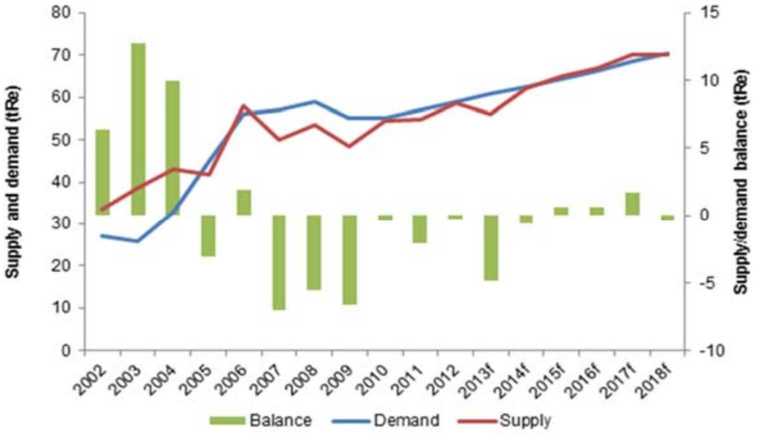
-Rhenium has **high specific gravity (21.4)** next only to Os, Ir, Pt

-Rhenium form compounds with valency -1,1, 2, **4**, 5, 6, **7**

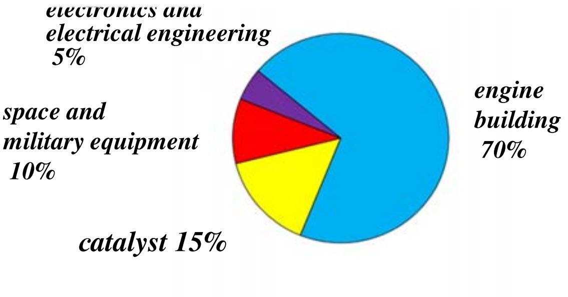
-Rhenium has a **hexagonal close-packed structure** and does not undergo a ductile-brittle transformation (in contrast to other refractory metals)

The dynamics of the rhenium global market

(www.roskill.com/reports/minor-and-light-metals/rhenium)



The annual consumption of Re in 2018 will reach 70 t



-**Superalloys** (W-Re, Mo-Re, Ni- Re) in aircraft engine industry
-**Reforming catalysts** in petroleum industry
- **Other application** (~10 %) (thermocouples, filaments of mass spectrographs, x-ray tube targets, contacts in electronic devices)
Price of rhenium* – ~ *3200 $/kg (2014)

RHENIUM RAW MATERIALS

Traditional:

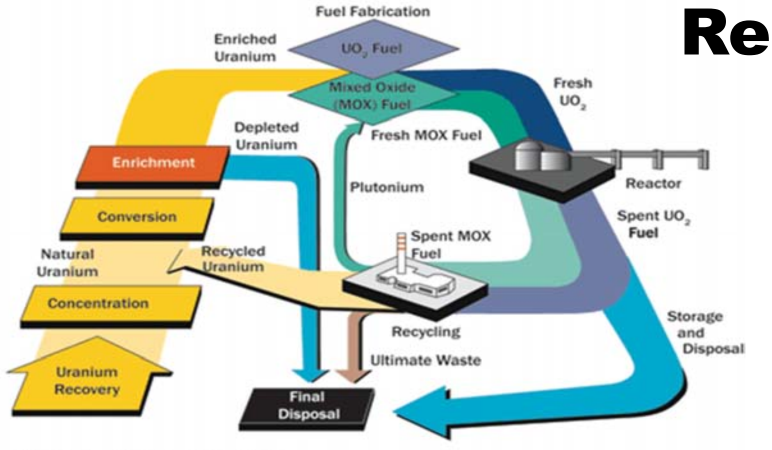
- **Molybdenum**-copper sulfide ores
- Cupper sulfide ores

The terms of the depletion of rhenium in molybdenum raw materials — 45-50 years

[Palant A.A., Troshkina I.D., Chekmarev A.M. Metallurgy of Rhenium. 2007 (rus.)]

Untraditional:

- **Uranium-contained ores;**
- Solutions of heap leaching of copper ores (USA);
- Fumaroles (*Kurile Islands, Iturup*, Russia);
- Carbonaseous sources (coal, oil shale);
- Mine water
- Spent Fuel *[**M. Ozawa**, et al. 7th Int. Symp. on Technetium and Rhenium - Science and Utilization: Book of Proceedings. July 4-8, 2011, Moscow, Russia (Eds. K.E. German, B.F. Myasoedov, G.E. Kodina, A. Ya. Maruk, I.D. Troshkina). Moscow: Publishing House GRANITSA, 2011. P. 107-111]*



Source: U.S. Nuclear Regulatory Commission

Re in U-ores

USA:
1969-1974, Falls City, Texas area by Susquehanna Corporation → Shattuck Chemical in Denver

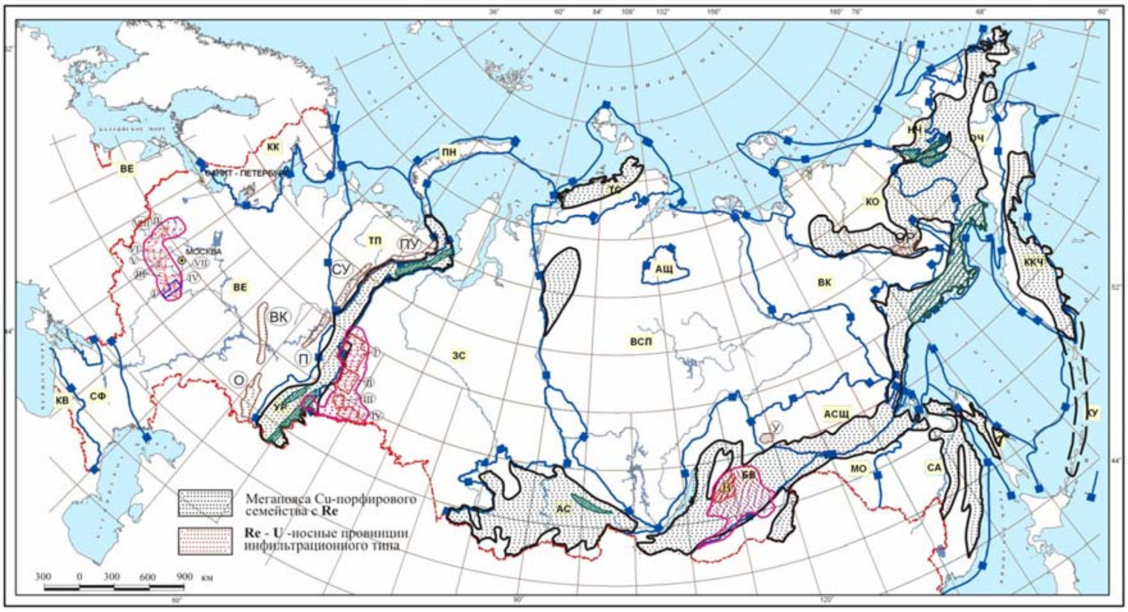
Former USSR:
1978, Central Asia, Bukinayskaya group, underground leaching

The content of rhenium in the uranium ores

Type of the deposit	*Deposit*	*Re, g/t*
Sedimentary	Colorado Plateau (Sun Valley)	0.5 –3.0
Stratum-infiltration	South Dakota	up to 50

Rhenium in the ore bodies found in forms: *oxide, sulphide and native*

Forecasting-metallogenic map of rhenium deposits of Russian Federation



(IMGRE, Russia, Kremenetsky A.A. and others, 2010)

LOWER CONCENTRATION LIMIT OF COST-EFFECTIVE PROCESSING

(In-Situ Leaching of Ores / N.P. Laverov *et.al.* M., 1998)

Element	Concentration limit, mg/l
Rhenium	**0.2**
Selenium	10
Molybdenum	10
Vanadium	40-50
Scandium	0.3
TR	10

Profitability of rhenium recovery – 540 %

(concentration of Re, mg/l:

Initial – 0.2, residual – 0.1)

The aim of this work

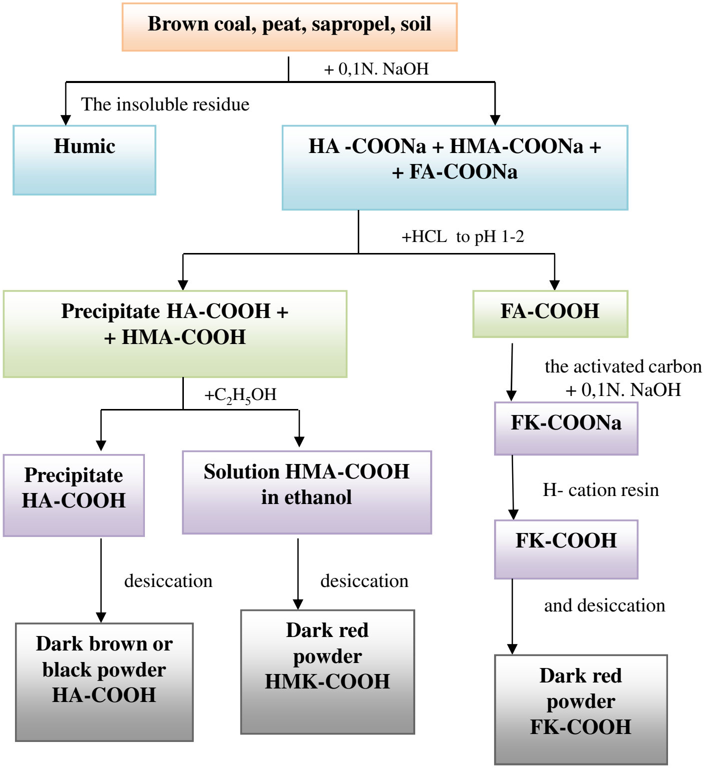
is to study of possibility **of increasing of rhenium selectivity** in the process of sorption of uranium and by-product from sulfuric acid solutions modeling solutions obtained in the uranium underground leaching

The work was carried out in two directions:

1) *the study of the influence of **fulvic acids** on the selectivity of rhenium sorption by anion resins from uranium-contained sulfuric acid solutions*

2) *the study of possibility of **kinetic separation** of rhenium and vanadium in the sorption by **fibrous** ionites*

THE ALLOCATION SCHEME OF FA


Brown coal, peat, sapropel, soil

+ 0,1N. NaOH

The insoluble residue

Humic

HA -COONa + HMA-COONa + + FA-COONa

+HCL to pH 1-2

Precipitate HA-COOH + + HMA-COOH

FA-COOH

+C_2H_5OH

the activated carbon + 0,1N. NaOH

Precipitate HA-COOH

Solution HMA-COOH in ethanol

FK-COONa

H- cation resin

FK-COOH

desiccation

desiccation

and desiccation

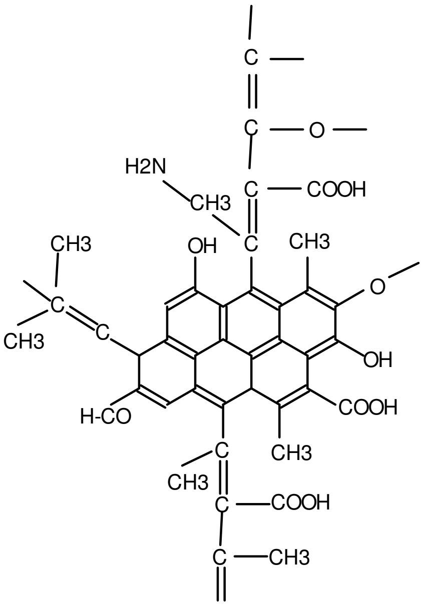
Dark brown or black powder HA-COOH

Dark red powder HMK-COOH

Dark red powder FK-COOH

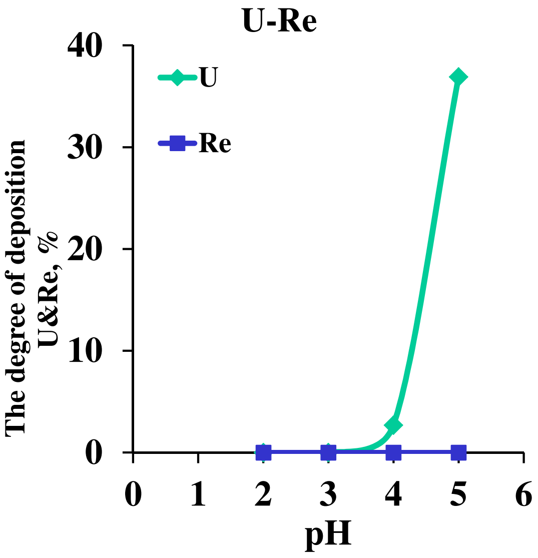
Orlov D.S., 1997 GOST 26213-91

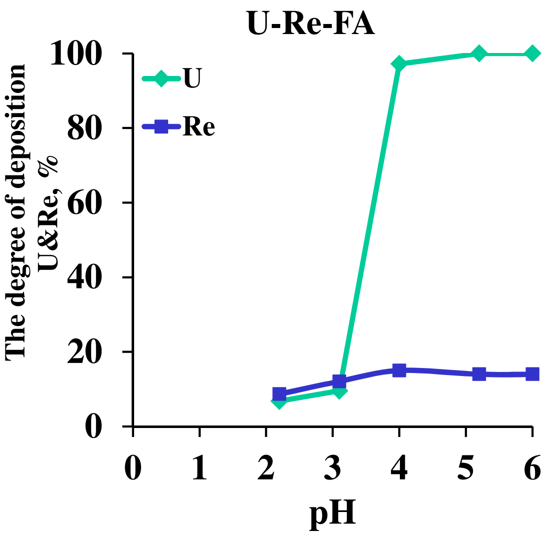
THE FRAGMENT OF FA



Slavinskaja G.V., Selemenev F.V., 2001

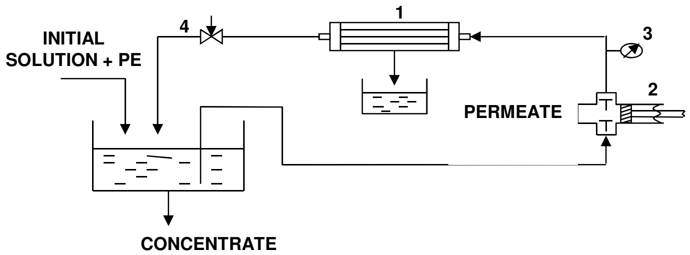
EFFECT OF pH OF MINERALIZED SOLUTIONS ON THE DEGREE OF DEPOSITION OF URANIUM AND RHENIUM IN THE PRESENCE OF FA





*Analysis of uranium and rhenium was carried out by *photocolorimetric method*

THE SCHEME OF ULTRAFILTRATION



THE SCHEME OF LABORATORY-SCALE INSTALLATION:
1 – MEMBRANE UNIT; 2 – PLUNGER PUMP; 3 – MANOMETER; 4 – VALVE

$$\varphi = \left(1 - \frac{C_p}{C_{Re}}\right)$$

φ – selectivity
C_p – concentration in the permeate, mg/l
C_{Re} – concentration in the feed solution, mg/l

CHARACTERISTICS OF THE ULTRAFILTRATION MODULE

Filtration surface, m^2	The membrane material	Ultrafilter sizes		The nominal intercepted molecular weight, amu
		diameter, mm	length, mm	
0,02	polysulfone	25	250	20000

ULTRAFILTRATION BEHAVIOR OF URANIUM AND RHENIUM IN SULFURIC ACID SOLUTIONS IN THE PRESENCE OF FA

Molecular weight of FA associates are from 300 to 60000 amu

pH	Concentration, mg/l					Selectivity, %		
	FA	U		Re		FA	U	Re
	after UF	before UF	after UF	before UF	after UF			
Concentration FA – 50 mg/l								
2,00	42	8,1	5,8	10,9	9,1	16,0	28,4	16,5
3,00	42	8,1	3,8	10,9	9,3	16,0	**53,0**	14,7

URANIUM SORPTION BY ACTIVE CARBON IN THE PRESENCE OF FULVIC ACIDS

Conditions: active carbon – SN-P (Russia), U – 8,6 mg/l, SO_4^{2-} – 10 g/l, Cl^- – 1 g/l,
phase ratio (active carbon : solution) – 1 : 1000

pH	Concentration of FA, mg/l	Concentration of uranium in solution after sorption, mg/l	Capacity of the sorbent for uranium, mg/g
2	**0**	**8,6**	**0**
	50	**8,6**	**0**
3,5	**0**	**8,6**	**0**
	50	**0,5**	**8,1**

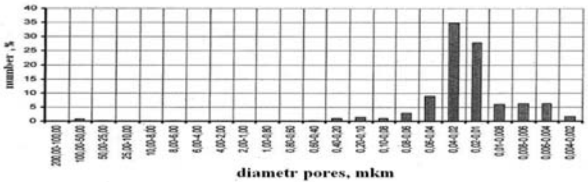
$$2FA\text{-}COOH + UO_2^{2+} \leftrightarrow (FA\text{-}COO)_2UO_2 + 2H^+$$

CHARACTERISTICS OF ION EXCHANGERS

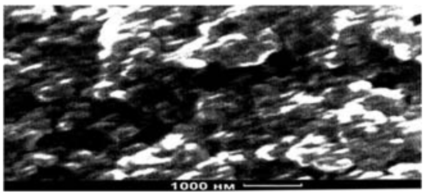
Ion exchanger	Purolite A-170	Lewatit MP-62	Purolite A-600	Lewatit K6367
	Weak base		Strong base	
Ionic form	The free base		Cl^-	
Functional group	Secondary amine	Tertiary amine	Quaternary ammonium base	
Matrix	Crosslinked polystyrene			
Structure	Microporous		Gel	
The limit on the exchange capacity for Cl^-, g-eqv/kg (l)	(1,3)	(1,7)	(1,4)	(1,4)

CHARACTERISTICS OF STRONG BASE ION EXCHANGERS ROSSION

Typical pore size distribution in nanostructured ion exchangers



Spherical microgranules (200-400 nm)



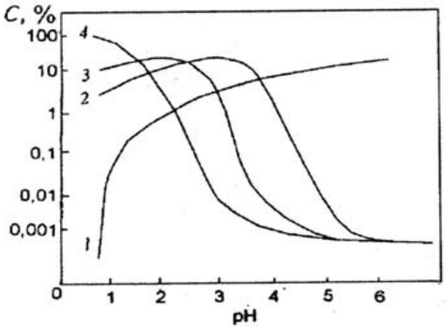
(Troshkina I.D., Balanovsky N.V., Shilyaev A.V. et al. *Chemical Technology*, 2011)

Parameter	25-35	25-65	*62*	510	511	610	611
Granulometric composition, mm	0,63 -2,0	0,63-2,0	*0,63-1,6*	0,63-1,6	0,63-1,6	0,63-1,6	0,63-1,6
Mechanical strength, %	97	99	*96*	97	96	97	95
Specific volume of swollen anion in water in the form of Cl^- , cm^3/g	2,42	2,43	*2,7*	2,4	2,7	2,6	2,85
The limit on the exchange capacity for Cl^- -ion, mg-eqv/g	5,63	4,88	*4,2*	3,3	3,5	3,8	3,7
Specific surface, m^2/g	9,0	9,0	*<1*	0,1	1	0,1	1
Total pore volume, cm^3/g	0,29	0,23	*0,12*	0,13	0,08	0,13	0,08

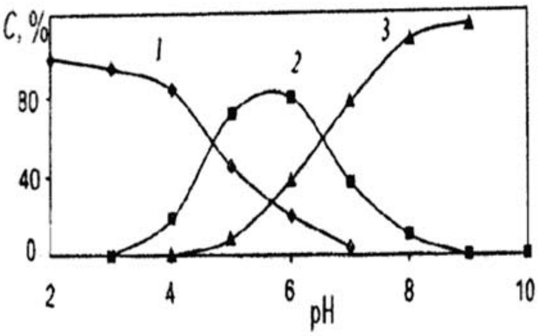
STATE OF URANIUM AND RHENIUM IN SOLUTIONS

URANIUM

The exit of uranyl sulfate complexes depending on pH of the solution: 1 – UO_2^{2+}, 2 – $[UO_2SO_4]$, 3 – $[UO_2(SO_4)_2]^{2-}$, 4 – $[UO_2(SO_4)_3]^{4-}$ (Lipilina, 1957)



The distribution of uranyl hydroxocomplexes depending on pH: 1 – UO_2^{2+}, 2–$[UO_2OH]^+$, 3 – $[UO_2(OH)_2]$



RHENIUM

Perrhenate-ion: ReO_4^-

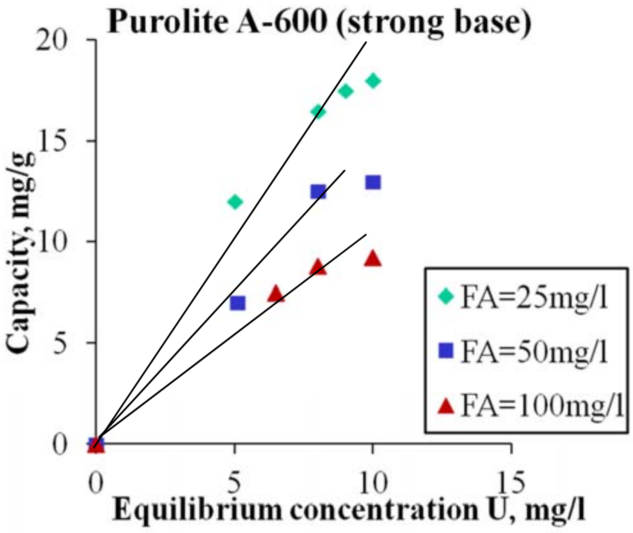
THE SORPTION CAPACITY OF THE ION EXCHANGER FOR URANIUM & RHENIUM BY THE URANIUM RECOVERY FROM SULFURIC ACID AND SULFURIC-FULVIC ACID SOLUTIONS

Terms: [Re]initial– 5 mg/dm^3, [U]initial – 5 mg/dm^3, [Fe^{+3}] – 100 mg/dm^3, [Cl$^-$] – 1 g/dm^3, [SO$_4^{2-}$] – 10 g/dm^3, [FA]initial – 50 mg/dm^3, pH 2

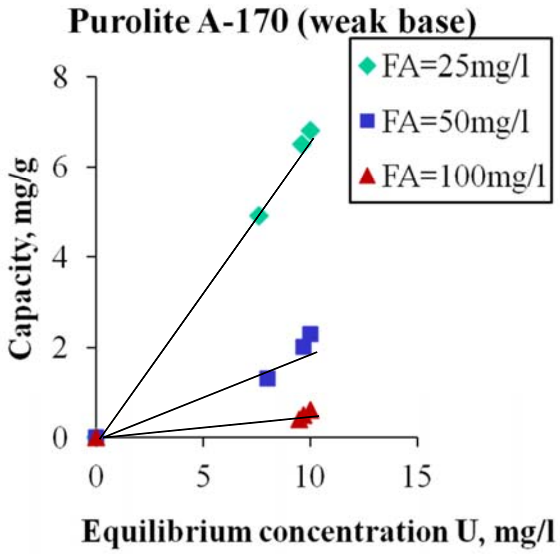
Resins	Capacity, mg/g (with no FA)		$S_{Re/U}$ (with no FA)
	U	Re	
strong base anion exchange resins			
Lewatit K6367	1,8 (4,3)	14,2 (17,1)	3,3 (10,7)
Purolite A-600	1,1 (3,2)	16,0 (19,1)	5,5 (20,8)
Rossion-62	8,8 (10,7)	15,5 (15,7)	18,0 (1,6)
weak base anion exchange resins			
Lewatit MP-62	4,3 (7,9)	15,3 (17,3)	3,7 (2,4)
Purolite A-170	0,5 (3,5)	18,4 (20,9)	47,4 (8,1)

I.D. Troshkina, A.V. Shilyaev, E.V. Butorina et al. Method of rhenium recovery from uranium solutions. Pat. RF 2523892/02. C22B 61/00. Bulletin of inventions, Number 21. Date published 27.07.2014. (rus.).

EFFECT OF FA CONCENTRATION ON URANIUM CAPACITY CHARACTERISTICS OF RESINS OF VARIOUS TYPES



Purolite A-600 (strong base)



Purolite A-170 (weak base)

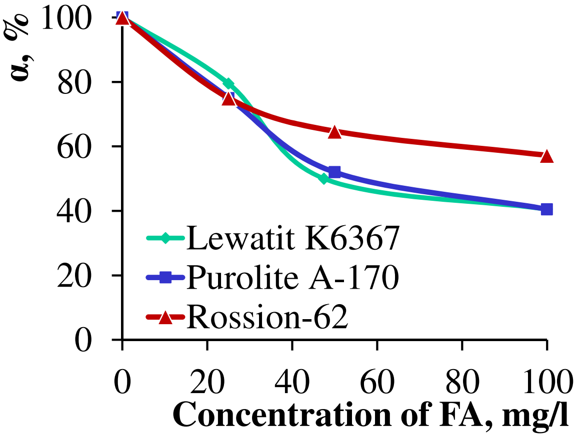
HENRY'S CONSTANT FOR ISOTHERMS OF ADSORPTION OF URANIUM AND RHENIUM FROM SULFURIC-FULVIC ACID SOLUTIONS

Resins	Capacity, mg/g (without FA)		$S_{Re/U}$ (without FA)	Henry's constant, l/g (correlation coefficient)	
	U	Re		U	Re
strong base anion exchange resins					
Rossion-62	8,8 (10,7)	15,5 (15,7)	18,0 (1,6)	1,77±0,66 (0,86) (2,25±0,74)(0,89)	3,68±1,04 (0,92) (3,71±1,04)(0,92)
weak base anion exchange resins					
Lewatit MP-62	4,3 (7,9)	15,3 (17,3)	3,7 (2,4)	0,83±0,18 (0,95) (1,53±0,68)(0,8)	3,63±1,02 (0,92) (4,28±0,86)(0,96)
Purolite A-170	0,5 (3,5)	18,4 (20,9)	47,4 (8,1)	0,08±0,04 (0,77) (0,69±0,12)(0,95)	4,67±0,80 (0,97) (5,66±0,80)(0,98)

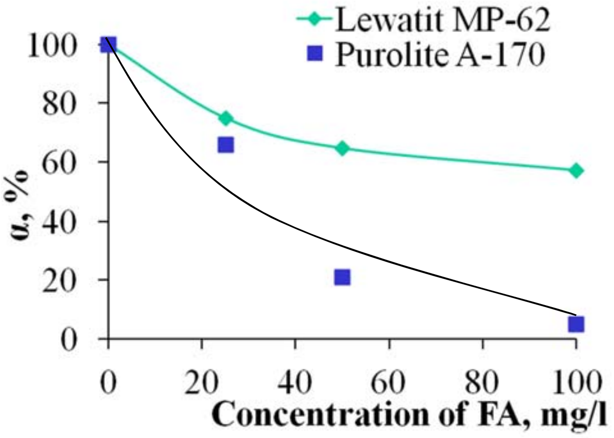
EFFICIENCY OF URANIUM SORPTION BY STRONG AND WEAK BASE RESINS IN THE PRESENCE OF FA

$$\alpha = 100 - (\Delta CE/CE \text{ without FA}) \cdot 100 \ \%$$

Strong base

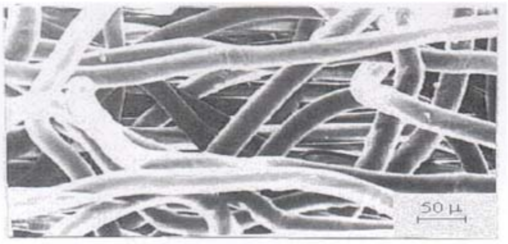


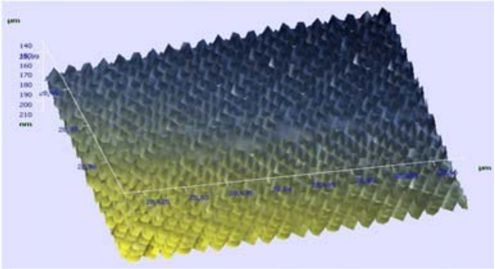
Weak base



Sorbents with improved kinetic properties:

fibrous ion exchange materials FIBAN

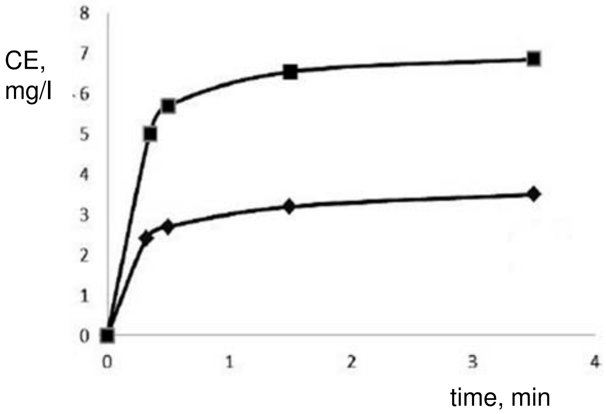




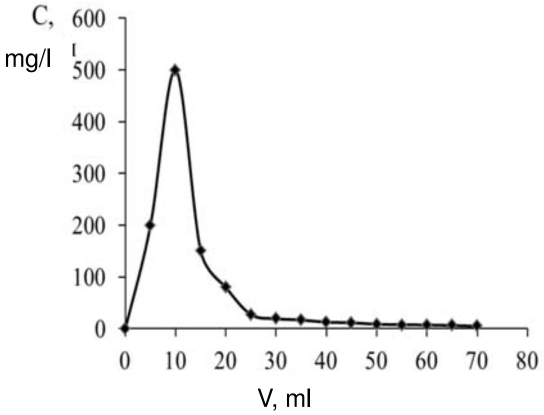
Physicochemical parameters of FIBAN ionites

Parameter	AK 22	A6
Functional group	≡N, ≡NH, –COOH	$(C_3H_5O)(CH_3)_2N^+Cl^-$, $-N(CH_3)_2$
Polymer base	Polyacrylonitrile cloth	Polyacrylonitrile cloth
Physical form	Staple cloth, nonwoven needle-punched fabric	Staple cloth, woven fabric
Optimal sorption capacity, mg-eq/g	>3.5 (by amino groups) 1.0 (by –COOH)	2.0 (by –N+≡) 0.8 (by $-NR_2$)
Working range of pH	0–8	0–13
Working temperature range	0–80°C	0–80°C
Optimal swelling, gH_2O/g ionite	0.7	1.2

Integral kinetic curves of rhenium sorption from sulfuric acid-chloride solutions with the FIBAN ionite



Kinetic curves of sorption of rhenium from the mineralized solution: FIBAN A-6 (♦), FIBAN AK-22

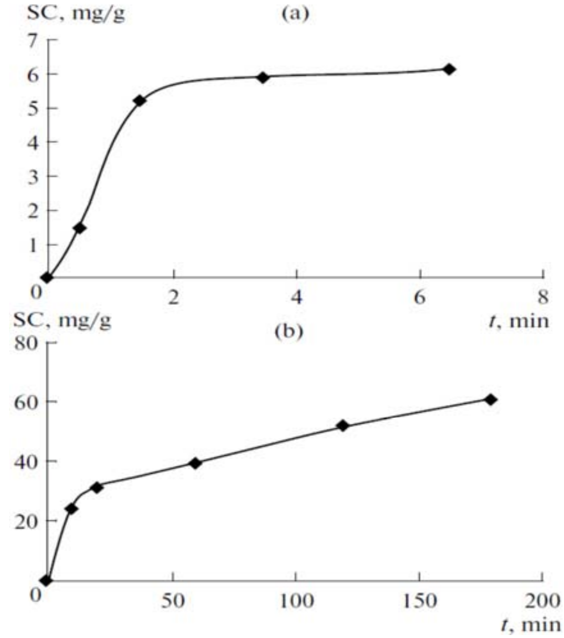


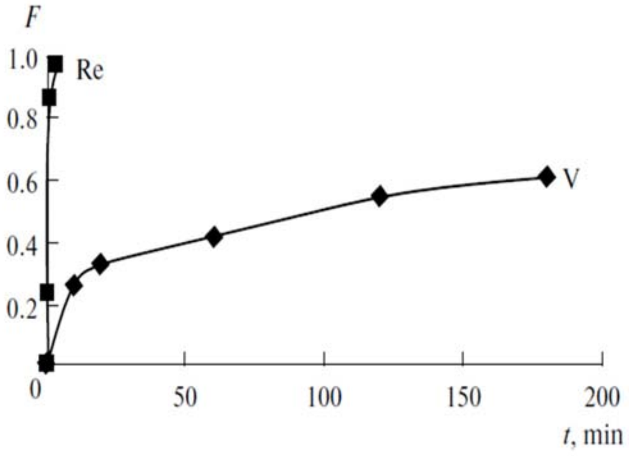
Breakthrough curve of desorption of rhenium by ammonia from ion exchanger Fiban AK-22

**Troshkina I.D., et al. Recovery of rhenium from aqueous solutions by fibrous materials // 7th Intern. Symp. on Technetium and Rhenium – Science and Utilization. Book of Proceedings. July 4-8, 2011, Moscow, Russia. P. 288–292.*

***Aye Minn, Shilyaev A.V., Troshkina I.D Sorption of rhenium from mineralised solutions by fibrous sorbents FIBAN // Sorption and chromatografic processes. 2013 (13), issue 2. P. 199–206 (rus.).*

Comparison of integral kinetic curves of sorption of (a) rhenium and (b) vanadium from sulfuric acid–chloride solutions with the FIBAN ionite of the AK-22 brand





Nway Shwan Oo, I.D. Troshkina, Aye Min, A.V. Shilyaev. *Russian Journal of Non-Ferrous Metals*. 2014, *55, № 3*, 242-246.

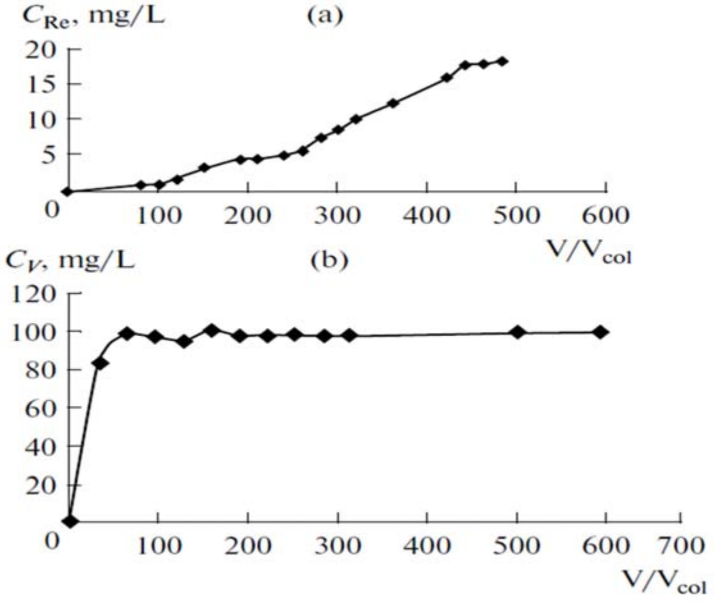
Kinetic characteristics of sorption of rhenium(VII) and vanadium(V) by the FIBAN AK-22 ionite

$$D = 0.06R^2/\tau_{0.5}$$

where D is the effective diffusion coefficients of metal in ionite, m^2/s; $\tau_{0.5}$ is the half-transformation time, s; and R is the fiber radius, m (its averaged magnitude is 30 μm)

Metal	$\tau_{0.5}$, s	D, m^2/s
Re	60	$9.0*10^{-13}$
V	7200	$7.5*10^{-15}$

Breakthrough sorption curves of (a) rhenium and (b) vanadium by the FIBAN ionite of the AK-22 brand from the sulfate–chloride solution

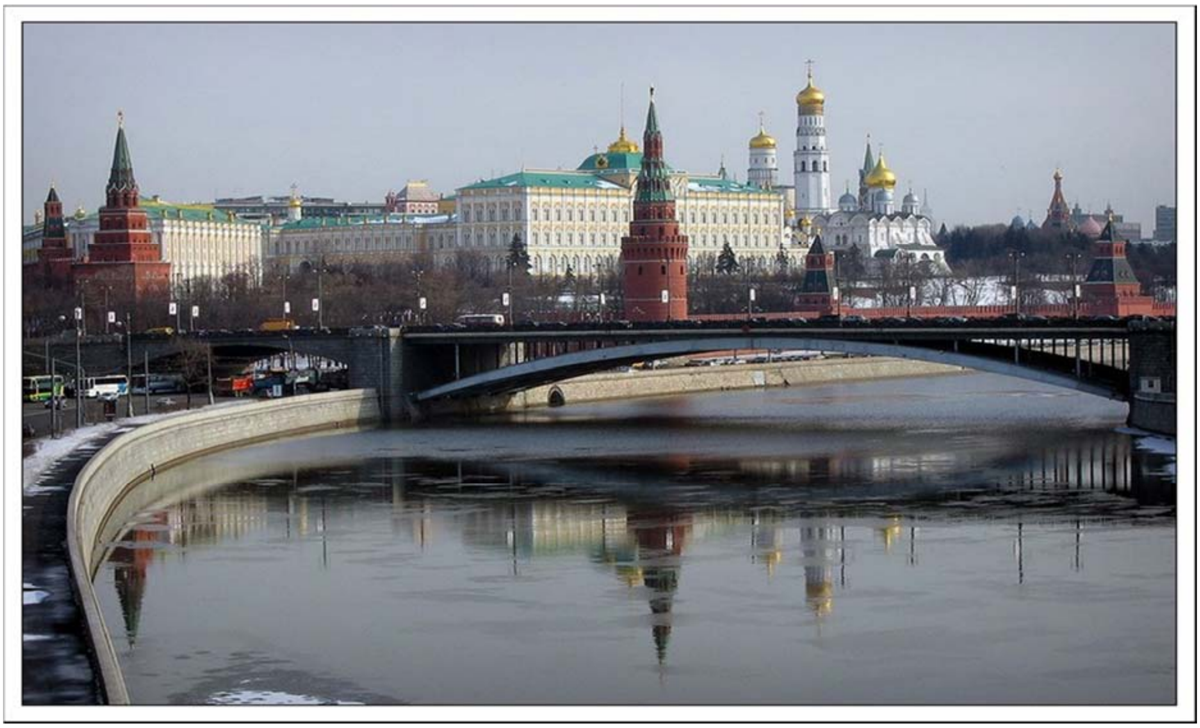


Column: volume 2.7 cm^3, diameter 0.7 cm, the height 7 cm

CONCLUSIONS

1. Capacitive characteristics for uranium of both strong base and weak base resins become worse in the presence of fulvic acids. At the same time the least negative effect is observed in case of uranium sorption by nanostructured ion exchanger Rossion-62.
2. The presence of fulvic acids has practically no effect on the sorption of rhenium from uranium mineralized solutions by ion exchangers of various types.
3. The separation factor of uranium and rhenium has a maximum (~ 50) by sorption from solutions containing 50 ÷ 100 mg FC/l.
4. It was established that effective diffusion coefficients of Re(VII) and V(V) in the sorption process by fibrous ion-exchange material FIBAN AK-22 differ by two orders of magnitude (Re – 9.0×10^{-13} m^2/s and V– 7.5×10^{-15} m^2/s), which makes it possible to separate them in dynamic conditions.

The 8th International Symposium on Technetium and Rhenium: Science and Utilization, September 29th - October 3rd 2014



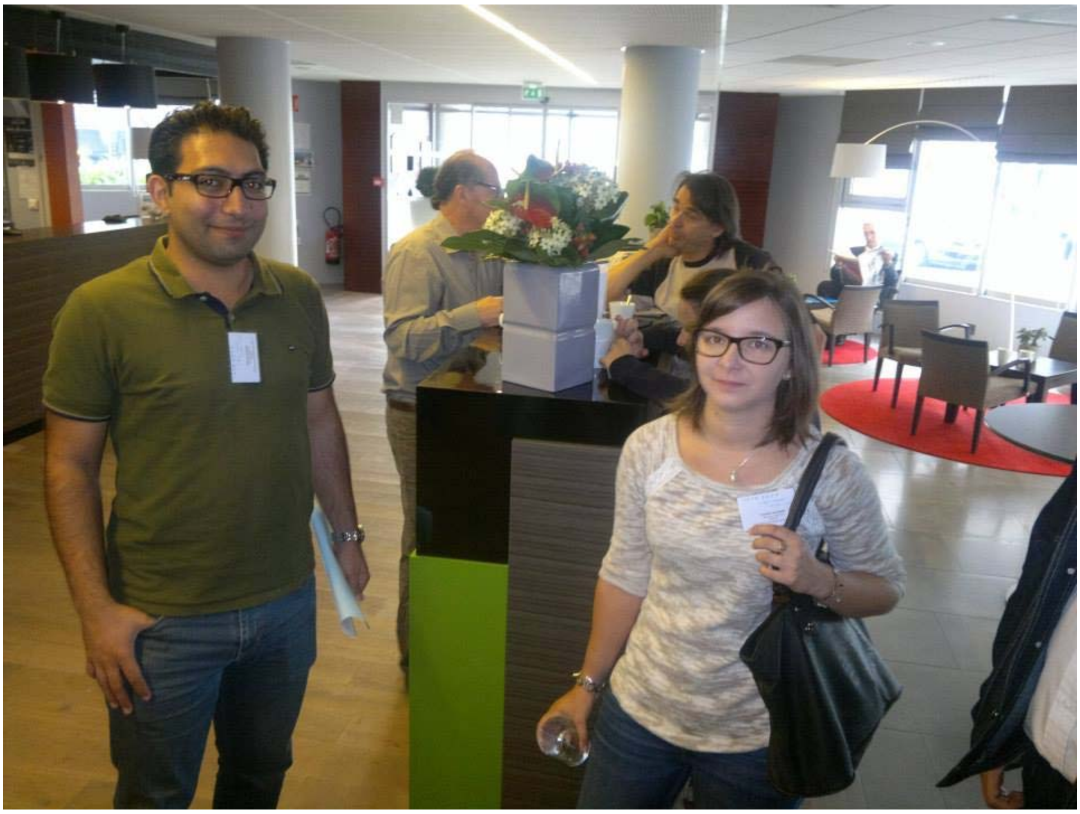
Thank you for your attention

Prof. Irina Troshkina presenting the sorption methods for Re separation

Presentation by A. Hagenbach from Frei University Berlin on Tc(V) and Re(V) oxido complexes with tetradentate thiocarbamoylbenzamidines for bioconjugation

Presentation by Peter Kelley on plasma thechnology for Re and Pt recovery

A. Safonov, Mm. Zakharyan, S. Zakharian, K. Cubova, W. Kerlin, U.Abram, B.Cabral



Ionosilicas for Ion Exchange Reactions

P. Hesemann[1], M. Gigue[2], P. Moisy[2], B. Prelot[1], U. D. Thach[1]

[1]Institut Charles Gerhardt, 34095 Montpellier Cedex 05, France
[2]CEA Marcoule DEN/DRCP, 30207 Bagnols-sur-Cèze, France

Ionosilicas are defined as silica based materials containing covalently tethered ionic groups.[1] These materials, situated at the interface of silica hybrid materials and ionic liquids, have large potential in catalysis, molecular recognition and separation. Ionosilicas are usually obtained *via* template directed hydrolysis-polycondensation reactions using ionic trialkoxysilylated precursors. Due to their ionic nature, these precursors often display very particular behavior in these bottom-up approaches, especially in the presence of ionic structure directing agents. Nanostructured phases can particularly be obtained *via* the formation of special precursor-surfactant assemblies, thus ensuring high accessibility of the immobilized ionic species.

This talk will focus on applications of ionosilicas as ion exchange materials. We will firstly show that imidazolium containing ionosilicas[2] are highly efficient anion exchange materials displaying high distribution coefficients for a large range of soft anionic species. Furthermore, we observed that these materials display Hofmeister selectivity. The distribution coefficients D differ according to the nature of the anion: for soft anions such as pertechnetate (TcO_4^-), considerably higher D-values were observed than for harder anions (chloride, bromide). This behavior enabled us to use the TcO_4^--anion as a probe revealing the hardness/softness of anionic species. In the second part of this talk, we will show that ionosilicas containing ammonium entities[3] are highly versatile anion exchange materials for a large variety of anionic species. Here, the sequestration of Cr(VI) was investigated by means of the effect of contact time, pH and initial concentration of Cr(VI). Kinetics of the exchange are fast, reflecting a good accessibility of the ionic sites. The adsorption was shown to be pH dependen.. The maximum adsorption capacity of ionosilica was found to be 2.5 mmol g^{-1}, which is at least two times higher than for commercial ion exchangers. Interestingly, this capacity corresponds to approx. 80% of the molar amount of incorporated ionic groups. Desorption studies indicated that the anion can be removed from the solid and therefore showed that the material can be re-used.

In conclusion, our results show that ionosilicas are highly efficient anion exchange materials. Besides the high potential of these materials for applications in water treatment, depollution of industrial wastewater or the nuclear fuel cycle, this study gives interesting information concerning the accessibility of functional groups in silica based materials.

References

1. P. Hesemann, S. El Hankari, T.P. Nguyen, *Materials* **7**, 2978 (2014).
2. B. Gadenne, P. Hesemann, J.J.E. Moreau, *Chem. Commun*. **2004**, 1768-1769
3. S. El Hankari, B. Motos-Pérez, P. Hesemann, A. Bouhaouss, J.J.E. Moreau, *J. Mater. Chem*., **21**, 6948 (2011)

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et des Matériaux de Montpellier

Ionosilicas
for Ion Exchange Reactions

P. Hesemann[1], P. Moisy[2], M. Gigue[2], U. D. Thach[1], B. Prelot[1]

[1] Institut Charles Gerhardt, 34095 Montpellier Cédex 05, France
[2] CEA Marcoule, DEN/DRCP, 30207 Bagnols-sur Cèze, France

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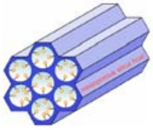
Outline

- **Ionosilicas**: *definitions and generalities*
- **Syntheses** of structured Ionosilicas
- **Ion Exchange Reactions** with Ionosilicas
  - TcO_4^- adsorption on surface functionalized ionosilicas
  - CrO_4^{2-} adsorption on hybrid ionosilicas
- **Conclusions**

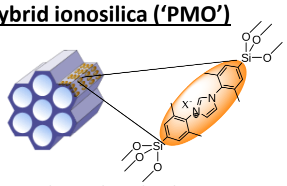
Ionosilicas

Elaboration of structured phases *via* ***'template directed syntheses'***

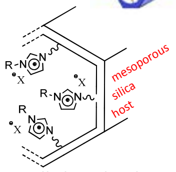
Surface functionalized ionosilica



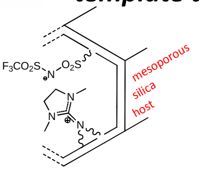
Hybrid ionosilica ('PMO')



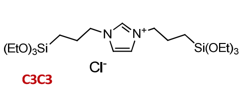
bis-aryl-imidazoliums
J. Mater. Chem. ***2009***



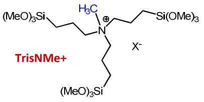
Di-alkyl-imidazoliums
Chem. Commun. ***2004***
EurJIC ***2006***



Guanidinium sulfonimides
J. Am. Chem. Soc. ***2009***

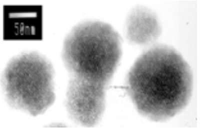


bis-alkyl-imidazoliums
Tetrahedron Lett. ***2007***
Microp. Mesop. Mater. ***2011***

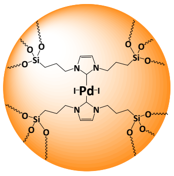


ammoniums
J. Mater. Chem. ***2010***
J. Mater. Chem. ***2011***
Microp. Mesop. Mater. ***2013***

Applications in catalysis…



Oxydation reactions : *Chem. Eur. J.* ***2006***
Hybrid *NHC catalysts*: *Tetrahedron Lett.* ***2007***
Organocatalysis: *J. Mater. Chem.* ***2011****, Chem. Commun.* ***2011,***
Appl. Organomet. Chem. ***2013,*** *27, 290*



…and separation!

Template directed synthesis of nanostructured silica

'***true liquid crystal templating***'

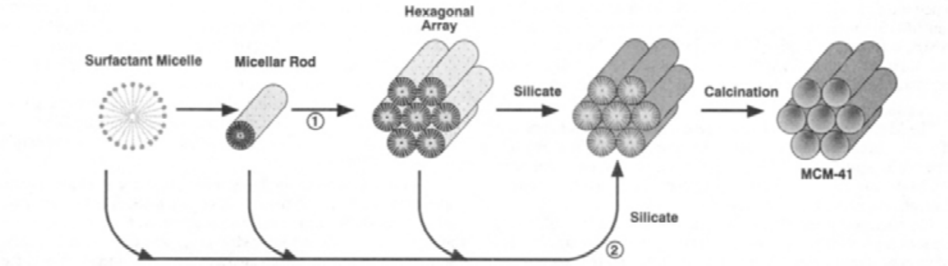
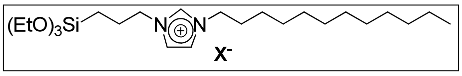


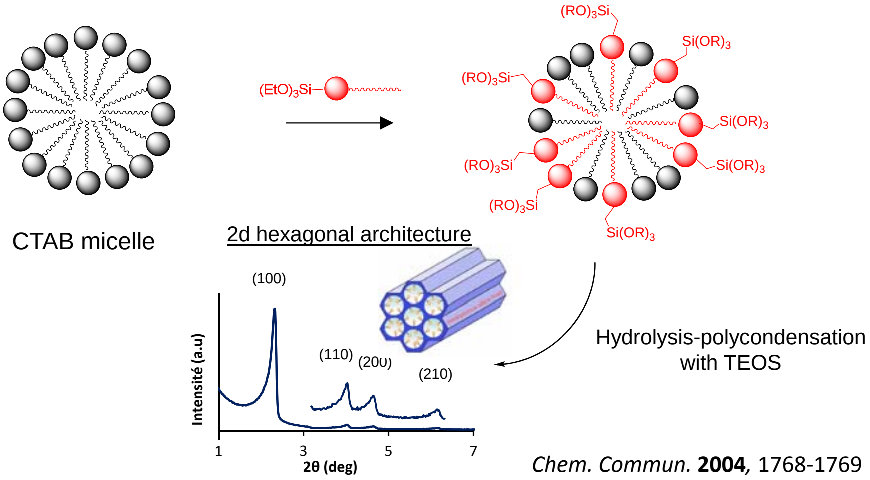
Figure 14. Possible mechanistic pathways for the formation of MCM-41: (1) liquid crystal phase initiated and (2) silicate anion initiated.

'***cooperative processes***'

Beck et al., *J. Am. Chem. Soc.* **1992**, *114*, 10824

Surface functionalized ionosilicas

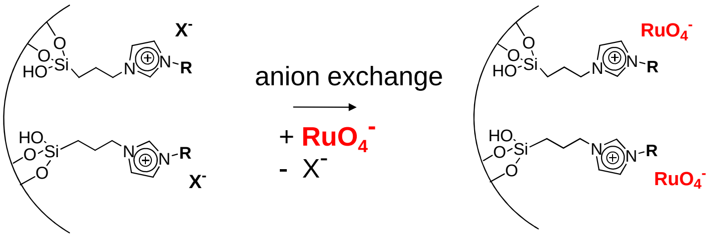




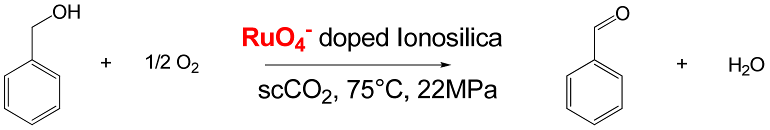
Chem. Commun. **2004**, 1768-1769

Catalytic Ionosilicas by Ion Exchange Reactions

(collaboration M. Pagliaro, Univ. Palermo, Italy)



Aerobic oxidation of alcohols using the RuO_4^--doped Ionosilica



Chem. Eur. J. **2006**, *12*, 5220

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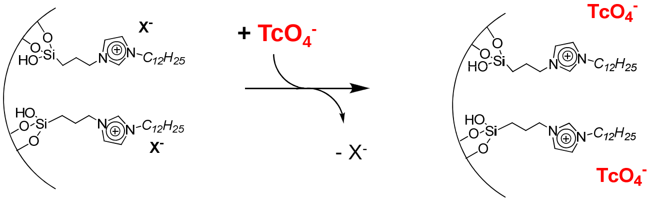
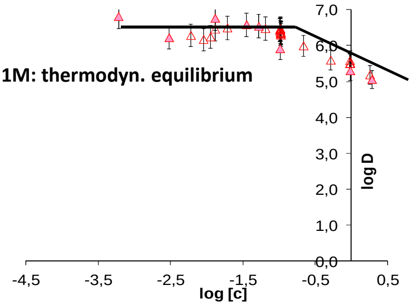
Applications of Ionosilicas: *Ion exchange reactions*

(collaboration P. Moisy, M. Gigue, CEA Marcoule, France)



Distribution coefficient of TcO_4^- at variable chloride concentration



c (Cl^-) < 0.1M: thermodyn. equilibrium

c (Cl^-) > 0.1M: Cl^- / TcO_4^- competititon

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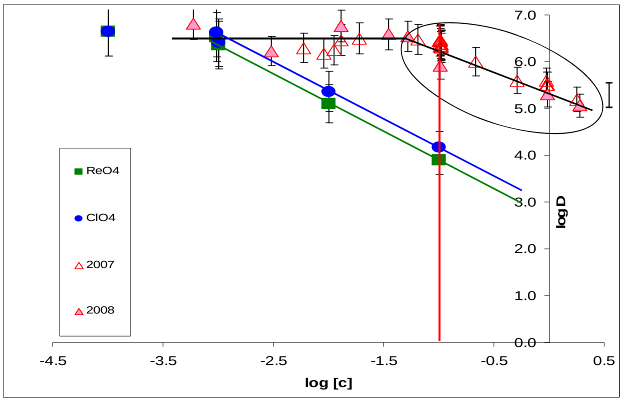
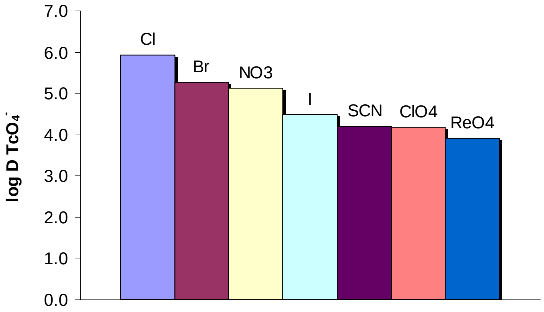
Distribution coefficient D[TcO_4^-] at variable [X^-]



counter-ion	log D (*0.1M*)
Cl^-	6.0
ClO_4^-	4.1
ReO_4^-	3.9
…	

log D values of TcO_4^- in the presence of various anions (c = 0.1 mol/L)



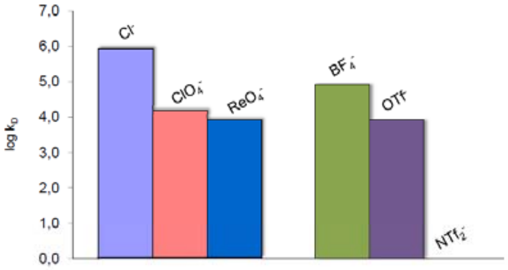
‘hard’ anion → ‘soft’ anion

TcO_4^- as a probe for the hardness/softness of anionic species

Qualitative and experimental reproduction of Hoffmeister’s series

A special case: fluorinated anions

Anion	**log D [TcO_4^-]**
BF_4^-	4.9
CF_3-SO_3^-	3.9
CF_3-CF_2-CF_2-CF_2-SO_3^-	**0**
NTf_2^-	**0**
For comparison:	
Cl^-	6.0
SCN^-	4.2
ReO_4^-	3.9

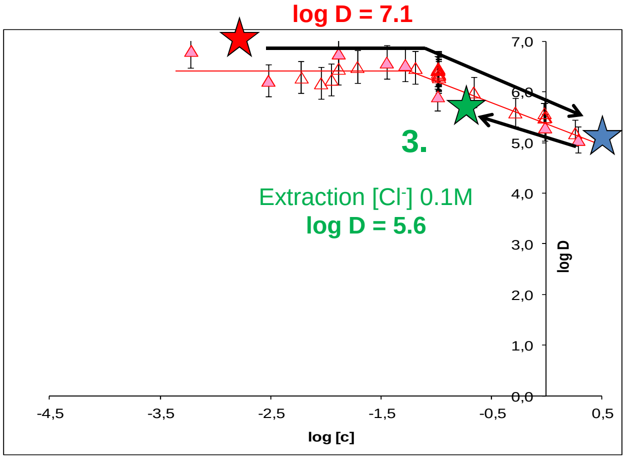


Particularly ‘*imidazophilic*’ behavior of fluorinated anions

(reason for the particular behavior of Ionic Liquids of the ***BMIM-NTf$_2$***-type?)

Reversibility of the process

1. extraction [Cl$^-$] 10^{-3}M:
log D = 7.1



3.

Extraction [Cl$^-$] 0.1M
log D = 5.6

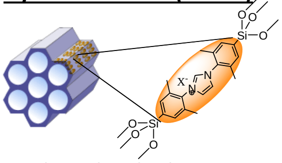
2.
Desextraction, [Cl$^-$] 2M
log D = 4.9

Ionosilicas

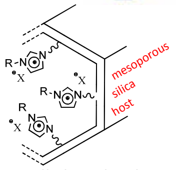
Elaboration of
structured phases *via*
'template directed syntheses'

Surface functionalized ionosilica

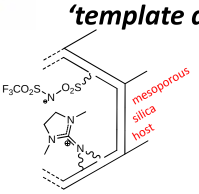
Hybrid Ionosilica ('PMO')



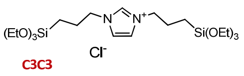
bis-aryl-imidazoliums
J. Mater. Chem. ***2009***



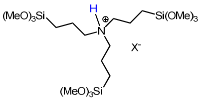
Di-alkyl-imidazoliums
Chem. Commun. ***2004***
EurJIC ***2006***



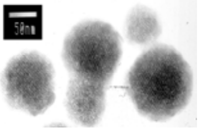
Guanidinium sulfonimides
J. Am. Chem. Soc. ***2009***



bis-alkyl-imidazoliums
Tetrahedron Lett. ***2007***
Microp. Mesop. Mater. ***2011***

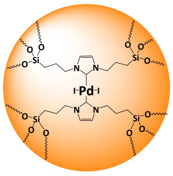


ammoniums
J. Mater. Chem. ***2010***
J. Mater. Chem. ***2011***
Microp. Mesop. Mater. ***2013***

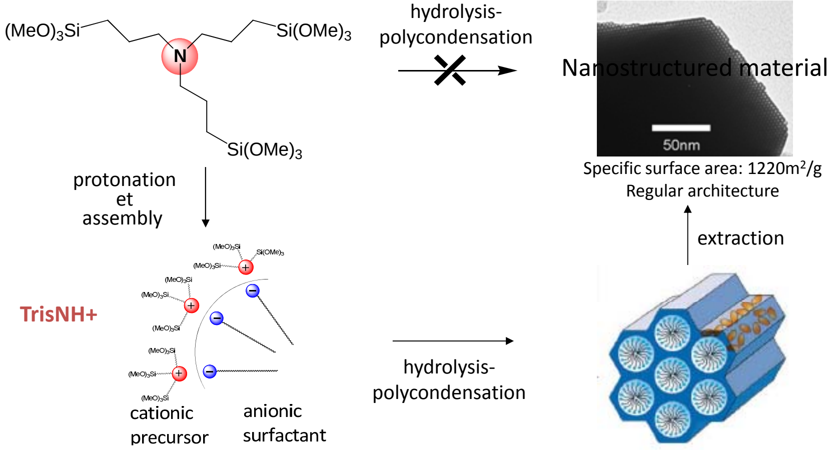


Applications in catalysis

Oxydation reactions : *Chem. Eur. J.* ***2006***
C-C coupling (Heck, Sonogashira…): *Tetrahedron* ***2007***
Hybrid *NHC catalysts*: *Tetrahedron Lett.* ***2007***
Organocatalysis: *J. Mater. Chem.* ***2011****, Chem. Commun.* ***2011****,*
Appl. Organomet. Chem. ***2013****, 27, 290*



Nanostructured silica hybrid materials bearing ammonuim groups

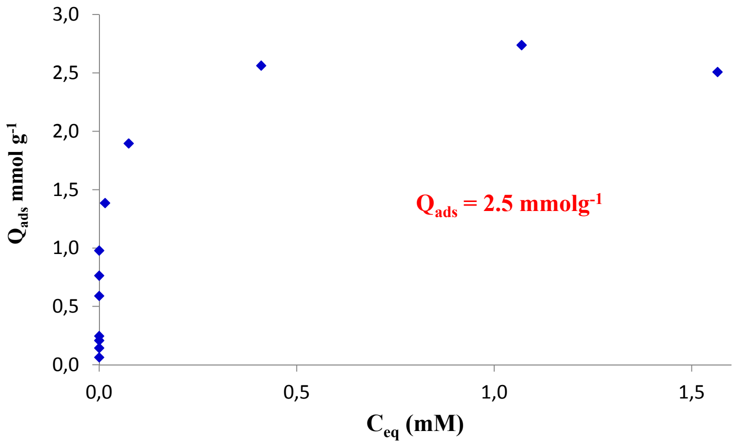


Assembly of cationic species, acting as masked organic amine functions

J. Mater. Chem. **2010**, *20*, 3910 - 3917

Ion-exchange reaction

Cr(VI) adsorption isotherm at 25 °C



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Conclusions

- Ionosilicas: structured silica based materials
  with covalently bound ionic groups

- Surface functionalized ionosilicas / Hybrid ionosilicas

- Ionosilicas are highly efficient Ion Exchange Materials
  a) High distribution coefficients
  b) Hofmeister selecivity
  c) Reversibility
  d) High capacities (hybrid ionosilicas)

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PhD students

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- Dr. Thy Phuong Nguyen
- Dr. Samir El Hankari
- Ut Dong Thach

Collaborators

- Dr. Philippe Moisy, Mireille Gigue
- Dr. Mario Pagliaro, Palermo, Italy
- Dr. Bénédicte Prelot, Montpellier, France

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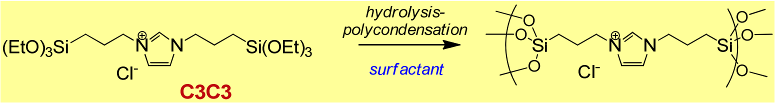
International Advisory Committee for ISTR-2017

Participants of ISTR-2014,
Pornichet - La Baule, France - Nov.2014

Ut Dong 2

Template directed hydroysis-polycondensation of ionic precursors

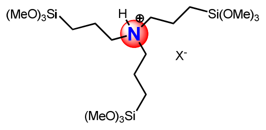
Example:



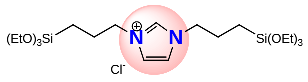
Synthesis of silica hybrid materials
bearing ***chemically anchored ionic species***

- ***Syntheses*** of nanostructured ionosilicas
- ***Applications***: catalysis, separation

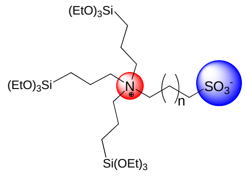
Hybrid ionosilicas / Periodic mesoporous ionosilicas



Ammonium



Imidazolium

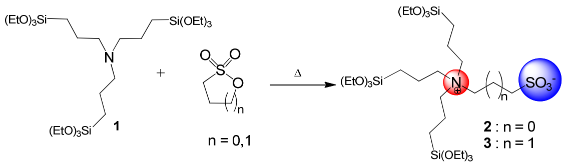


Zwitterionic

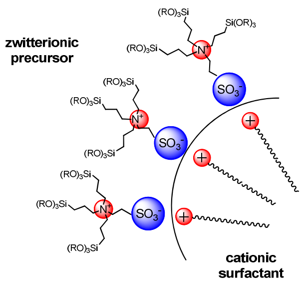
Structuration

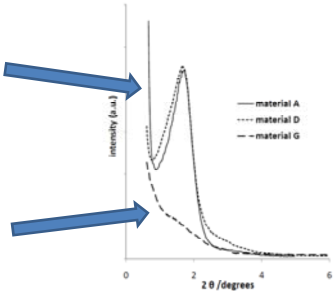
- Does the ionic nature of silylated precursors may **influence the architecture** of the formed *ionosilicas* ?
- Does it allow to obtain materials with **particular architectures**, inaccessible *via* other synthetic pathways ?

Zwitterionic silicas



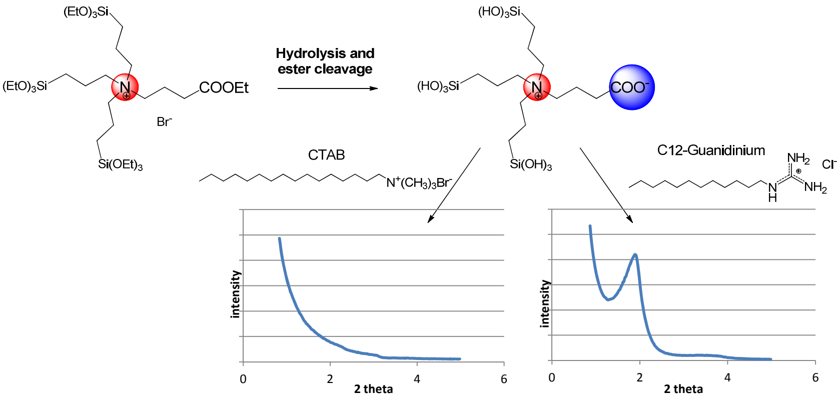
Supramolecular arrangement of the zwitterionic precursors with cationic surfactants (CTAB)





Chem. Commun. **2011**, *47*, 6704-6706

Influence of the *structure directing agent*



Structuration depends on the used surfactant

Precursor-induced structuration

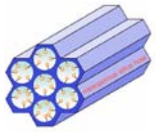
Structured phases are from appropriate **precursor-surfactant ion pairs**

Eur. J. Inorg. Chem. **2012,** 5288-5298

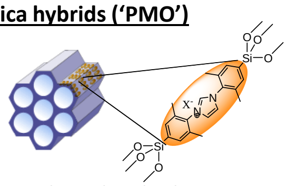
Ionosilicas

Elaboration of
structured phases *via*
'template directed syntheses'

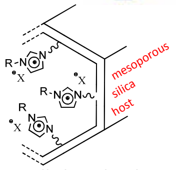
Functionalized silica



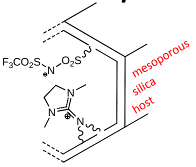
Silica hybrids ('PMO')



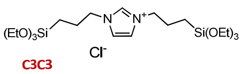
bis-aryl-imidazoliums
J. Mater. Chem. ***2009***



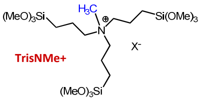
Di-alkyl-imidazoliums
Chem. Commun. ***2004***
EurJIC ***2006***



Guanidinium sulfonimides
J. Am. Chem. Soc. ***2009***

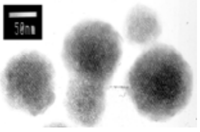


bis-alkyl-imidazoliums
Tetrahedron Lett. ***2007***
Microp. Mesop. Mater. ***2011***

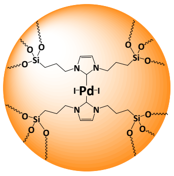


ammoniums
J. Mater. Chem. ***2010***
J. Mater. Chem. ***2011***
Microp. Mesop. Mater. ***2013***

Applications in catalysis



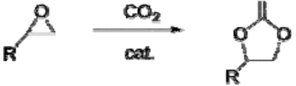
Oxydation reactions : *Chem. Eur. J.* ***2006***
C-C coupling (Heck, Sonogashira…): *Tetrahedron* ***2007***
Hybrid *NHC catalysts*: *Tetrahedron Lett.* ***2007***
Organocatalysis: *J. Mater. Chem.* ***2011,*** *Chem. Commun.* ***2011,***
Appl. Organomet. Chem. ***2013,*** *27, 290*



Applications of Ionosilicas: *Organocatalysis*

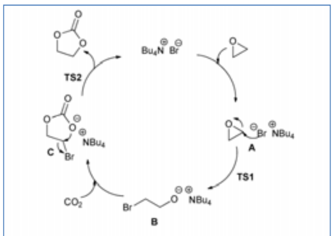
(collaboration A. Thomas, TU Berlin, Germany)

Cycloaddition of CO_2 to epoxides



Appl. Organomet. Chem., DOI: 10.1002/aoc.2974

Cooperative nucleophilic-electrophilic activation



Scheme 2 The proposed mechanism for fixation of CO_2 with EO.

Other examples: *Henry reaction, Baylis Hillman reaction, Michael additions...*

J. Mater. Chem. **2011**, *21*, *6948-6955*, *Chem. Commun.* **2011**, *47*, 6704-6706,

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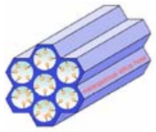
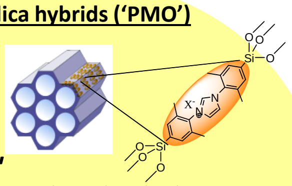
Ionosilicas

Functionalized silica



Elaboration of
structured phases
via ***'liquid crystal templating'***

Silica hybrids ('PMO')



bis-aryl-imidazoliums
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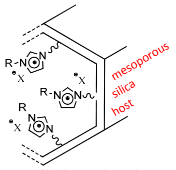

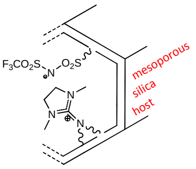

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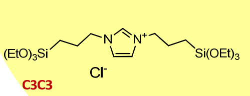
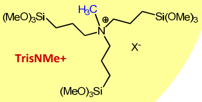
Chem. Commun. ***2004***
EurJIC ***2006***

Guanidinium sulfonimides
J. Am. Chem. Soc. ***2009***

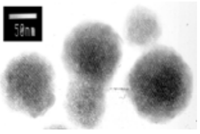




bis-alkyl-imidazoliums
Tetrahedron Lett. ***2007***
Microp. Mesop. Mater. ***2011***

ammoniums
J. Mater. Chem. ***2010***
J. Mater. Chem. ***2011***

Applications in catalysis



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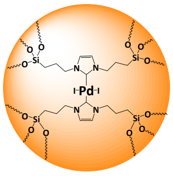
C-C coupling (Heck, Sonogashira…): *Tetrahedron* ***2007***
Hybrid *NHC catalysts*: *Tetrahedron Lett.* ***2007***
Organocatalysis: *J. Mater. Chem.* ***2011***, *Chem. Commun.* ***2011***



ICG Montpellier | Institut Charles Gerhardt

ILMAT 2013

Ionic Liquid Derived Materials

Montpellier, France
18-20 november 2013

Covered topics

- ILs as synthesis media
- ILs as material precursors
- Materials containing ionic species
- Building blocks inspired from ILs
- ILs as structuring or processing agents

http://ilmat2013.icgm.fr

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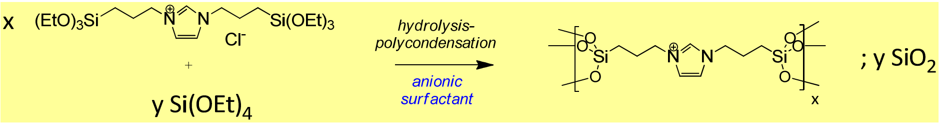
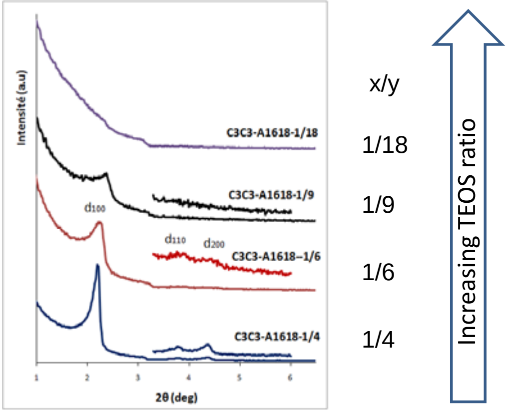
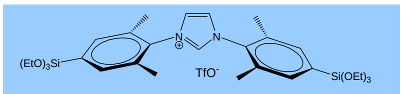


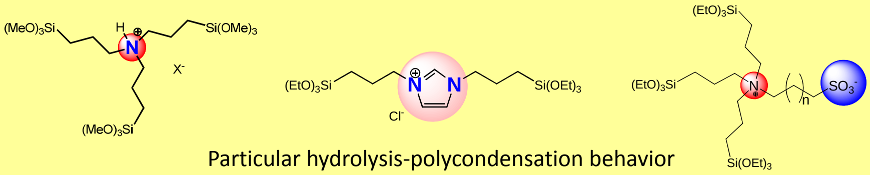


Formation of structured phases thanks to the presence of the ***ionic precursor***

Conclusion



Si-IMes-precursor
Classical behaviour
of silylated precursors

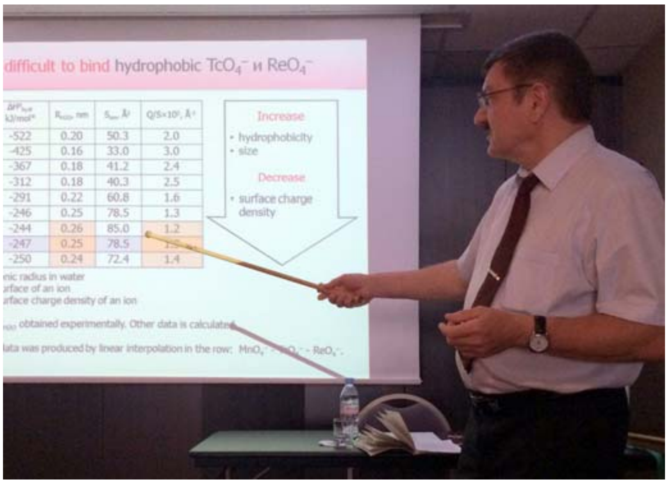


Particular hydrolysis-polycondensation behavior
due to specific ionic interactions with 'complementary' surfactants

Ionic precursors often play a determinant role in the formation of nanostructured silica hybrid materials and allow to access original ionosilicas displaying unique features.


U. Abram, Miss Johns, S. Balasekaran, B. Cabral


ISTR2014 delegates



"Triskem" sponsor with the delegates of ISTR-2014 : A. Safonov, Prof. M. Fattahi, S.Zakharian, W.Kerlin, A.Sattelberger

Tc-halogenists:
F. Poineau,
K.German,
A. Sattelberger,
W. Kerlin

ЖАУАПКЕРШІЛІГІ ШЕКТЕУЛІ СЕРІКТЕСТІГІ
КазГидроМедь
ТОВАРИЩЕСТВО С ОГРАНИЧЕННОЙ ОТВЕТСТВЕННОСТЬЮ

S. Zakharian from Kazakhstan gives the lecture on rhenium separation in industrial scale

TRISKEM
SHARING INNOVATION

ISTR Chairs :

Thomas Gerber
(South Africa,
Port Elizabeth – 2008)

Konstantin German
(Russian Federation,
Moscow - 2011)

Massoud Fattahi
(France,
Pornichet – 2014)


TRISKEM
SHARING INNOVATION

STUDY ONRHENIUM SORPTION ATHIGH RATE FROM WASHING ACID OF THE SULPHURIC ACID PLANT AT BALKHASH COPPER PLANT

S.V. Zakharian[**],A.B. Yun[**], E.I. Gedgagov[*], I.V.Terentieva[**]

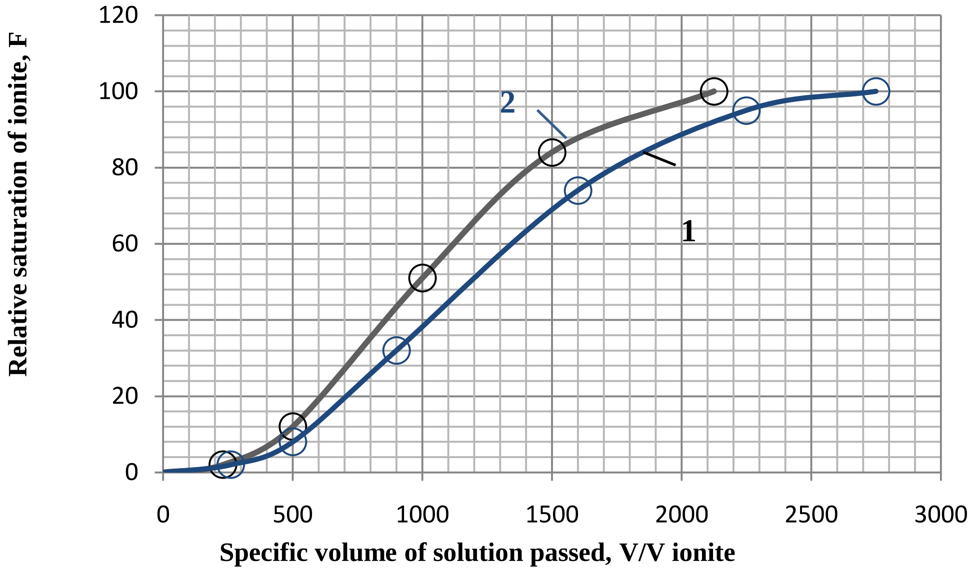
* - FSUE“GINTSVETMET Institute”, Moscow c., Russia
** - KazGidroMed LLP, Karaganda c., Kazakhstan

This studypurposeisindustrial rheniumsorption at high rate torecoverrhenium fromsulfuricprocesssolutionsintermsofrelativelylowconcentrationoftargetcomponentanddevelopmentofhigh ratedesorptionofrheniumforlow-basicanionite.

Asitseenbelow (Picture 1) sorptionofrheniumonisoporouslow-basicanionite (PuroliteA170)as the process solution (flushing acid from Sulphuric Acid plant at Balkhash Copper plant) passthrough the dense layers of sorbent at different rate.

AsitisseenonPicture 1, sorbentisfullysaturatedasabout 3000 ofspecificvolumeofsolutionarepassedthrough, and anioniteA170 capacity for rhenium is 13-18 g/l of ionite, where solution content for saturation is almost equal to solution used for sorption of rhenium on strongly basic tars. AsitisseenonPicture 1, rheniumsorptioncurvesgiven arealittledifferent.Itmeansthatsorptionofrheniummaybeperformed with solution passingathighrate, and therate should be adjusted due to rhenium concentration in sorption solution.

Asarule, decrease of C_{Re}in base solution should be accompanied by increase of sorption rate.



Pic. 1Abovegivenrheniumsorptioncurve(dependenceofrheniumfractionalabsorptionF, % tospecificvolumepassedthroughalayerofPuroliteA 170 forprocesssolution– washing acid from the Sulhuric Acid Plant at Balkhash Copper Plant at different throughput rate.

1 – sorptionrate 10 vol/vol ofionite per hour:
2 – sorption rate 15 vol/vol ofioniteperhour.

$$F = \frac{C_i}{C_{max}} \cdot 100\,\%, where$$

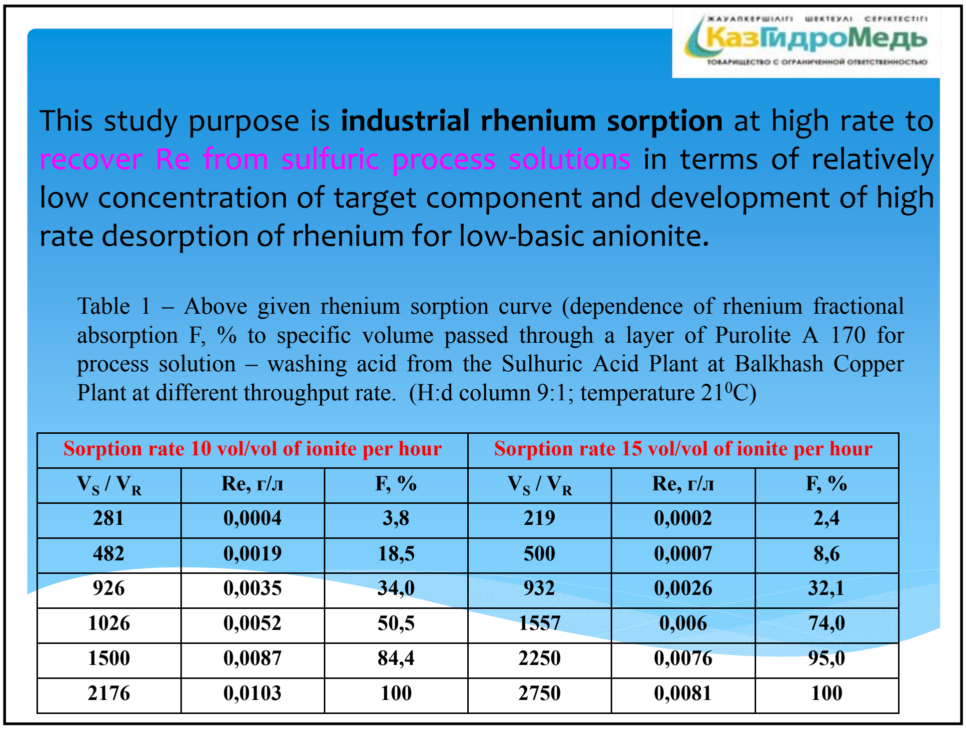
$C_i - concentration\ of\ rhenium\ in\ solution\ after\ a\ sorption\ column\ at\ the\ point\ of\ curve;$
$C_{max}\ - concentration\ of\ rhenium\ in\ solution\ after\ ionite\ is\ fully\ saturated\ with\ rhenium.$

Content of base solution to sorption,g/l:
0.007-0.009 Re; 0.011-0.030 Se; 1.5 As; 40 H_2SO_4.

STUDY ON RHENIUM SORPTION AT HIGH RATE FROM FLUSHING ACID OF THE SULPHURIC ACID PLANT AT BALKHASH COPPER SMELTER

S.V. Zakharian[**], **A.B. Yun**[**], **E.I. Gedgagov**[*],
I.V. Terentieva[**]

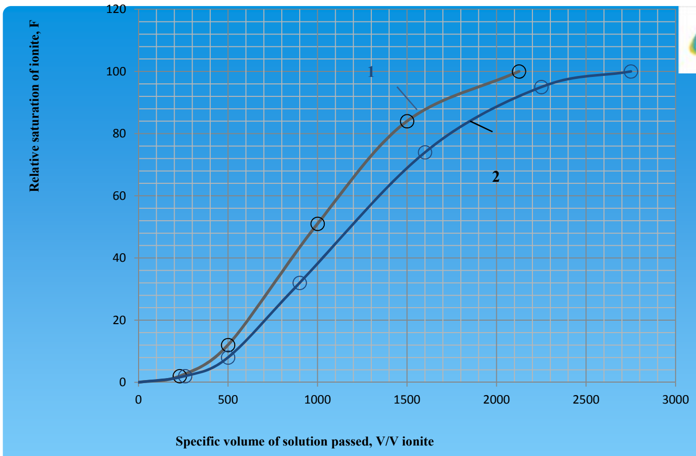
* - FSUE “GINTSVETMET Institute”, Moscow c., Russia
** - KazGidroMed LLP, Karaganda c., Kazakhstan



This study purpose is **industrial rhenium sorption** at high rate to recover Re from sulfuric process solutions in terms of relatively low concentration of target component and development of high rate desorption of rhenium for low-basic anionite.

Table 1 – Above given rhenium sorption curve (dependence of rhenium fractional absorption F, % to specific volume passed through a layer of Purolite A 170 for process solution – washing acid from the Sulhuric Acid Plant at Balkhash Copper Plant at different throughput rate. (H:d column 9:1; temperature 21^{0}C)

Sorption rate 10 vol/vol of ionite per hour			Sorption rate 15 vol/vol of ionite per hour		
V_S / V_R	Re, г/л	F, %	V_S / V_R	Re, г/л	F, %
281	0,0004	3,8	219	0,0002	2,4
482	0,0019	18,5	500	0,0007	8,6
926	0,0035	34,0	932	0,0026	32,1
1026	0,0052	50,5	1557	0,006	74,0
1500	0,0087	84,4	2250	0,0076	95,0
2176	0,0103	100	2750	0,0081	100



Pic. 1 Above given rhenium sorption curve (dependence of rhenium fractional absorption F, % to specific volume passed through a layer of Purolite A 170 for process solution – washing acid from the Sulhuric Acid Plant at Balkhash Copper Plant at different throughput rate.

1 – sorption rate 10 vol/vol of ionite per hour:

2 – sorption rate 15 vol/vol of ionite per hour.

Content of base solution to sorption, g/l:

0.007-0.009 Re; 0.011-0.030 Se; 1.5 As; 40 H_2SO_4.

As it is seen on Table 1 and Picture 1, sorbent is fully saturated as about 3000 specific volume of solution are passed through, and anionite A170 capacity for rhenium is 13-18 g/l of ionite,

where solution content for saturation was almost equal to solution used for rhenium sorption on strongly basic tars.

As it is seen on Picture 1, rhenium sorption curves given are a little different.

It means that **sorption of rhenium may be performed with solution passing at high rate, and the rate should be adjusted due to rhenium concentration in sorption solution.**

As a rule, decrease of C_{Re} in base solution should be accompanied by increase of sorption rate.

STUDY ON RHENIUM DESORPTION AT HIGH RATE FROM MACROPOROUS LOW BASE IONITES

S.V. Zakharian[**], A.B. Yun[**], E.I. Gedgagov[*], V.A. Chen[**]

* - FSUE “GINTSVETMET Institute”, Moscow, Russia

** - KazGidroMed LLP, Karaganda, Kazakhstan

Table 2 – Comparison results of ammoniac desorption of rhenium with Purolite A170 saturated from washing acid from the sulfuric acid plant at Zhezkazgan smelter, KAZAKHMYS Corporation LLP , at various rate of desorbent solution passing through ionite layer.

(Composition of ZhMZ solution for saturation, g/l: 0,22 Re; 0,001 Se; 0,52 As; 84,5 H2SO4)
Desorption temperature – 22^{0}C. Desorbiruyushchy solution – 8% of NH3.

V_s / $V_{i.}$	Σ V_s / $V_{i.}$	Rate of desorbent throughput 2 vol./vol. ionites per hour			Rate of desorbent throughput 9 vol./vol. ionites per hour		
		t, min.	Re, g/l	% des. Re	t, min.	Re, g/l	% des. Re
1,5	1,5	45	16,95	45,6	10	26,23	61,4
1,5	3,0	45	15,93	86,3	10	15,75	98,28
1,5	4,5	45	3,59	95,8	10	0,69	99,9
1,5	6,0	45	1,14	99,0	10	0,021	99,93
1,5	7,5	45	0,27	99,7			
		The average maintenance of Re in commodity desorbate 9,37 g/l			The average maintenance of Re in commodity desorbate 21,0 g/l		

As you see on table 2, an eluate sellable (or commodity) fraction at high rate desorption (9,0 vol/vol of ionite per hour) is achieved as ionite 3rd vol. /vol. are passed with an average rhenium content 21,0 g/l, and for a standard option (speed 2 vol/vol of ionite per hour) the average rhenium content in commodity fraction is 2,25 times less than at high rate desorption. It was observed that first – a degree of rhenium desorption equaled to 98,5-99,0% at high rate desorption achieved for (after) 3 specific volumes, and during standard – for 6 vol/vol of ionite per hour. The second – desorption cycle duration to recover rhenium from ionite to eluate, equaled to 98,5-99,0%, is reached at high rate process in 25-30 minutes and at standard rate – in 180 minutes. In other words, the high rate desorption of rhenium saturated with ionite Purolite A170 reduces the desorption cycle duration more than 6 times. Sorption capacity of ionite Purolite A170 calculated by desorption results, was 64,5 g/l of sorbent or 153,5 mg/g of ionite in conversion to air-dry condition. So, during ammoniac desorption of rhenium at high rate the rhenium concentration in commodity eluate is clearly seen, thus the commodity fraction output at high rate is almost cut by half.

Table 3 – Comparison results of ammonia desorption of rhenium with Purolite A170 saturated from washing acid from Balkash Copper Smelter of KAZAKHMYS Corporation LLP, at various rate of desorbent solution passing through an ionite layer.
(Composition of BMZ solution for saturation, g/l: 0,0094 Re; 0,015 Se; 50 H_2SO_4)
Desorption temperature – 23 °C.
Desorption solution – 8% of NH3.

$V_s / V_{i.}$	$\Sigma V_s / V_{i.}$	**Rate of desorbent throughput 2 vol./vol. ionites per hour**			**Rate of desorbent throughput 9 vol./vol. ionites per hour**		
		t, min.	**Re, g/l**	**% des. Re**	**t, min.**	**Re, g/l**	**% des. Re**
0,5	0,5	30	0,216	0,98	3,3	17,4	80,0
0,5	1,0	60	7,48	35,08	6,7	3,7	97,0
0,5	1,5	90	13,42	96,18	10,0	0,65	98,8
0,5	2,0	120	0,574	98,78	13,3	0,013	99,9
1,0	3,0	180	0,076	99,47		-	-
1,0	4,0	240	0,022	99,67		-	-
		The average maintenance of Re in commodity desorbate 5,41 g/l			The average maintenance of Re in commodity desorbate 7,25 g/l		

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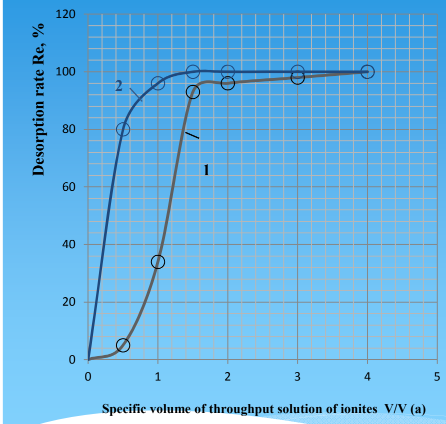
As you see in table 3 the same conclusions obtained as in table 2, namely:
-eluate commodity fraction during high rate desorption is 7,25 g/l on rhenium, during standard rate – 5,41, that is 25% more;

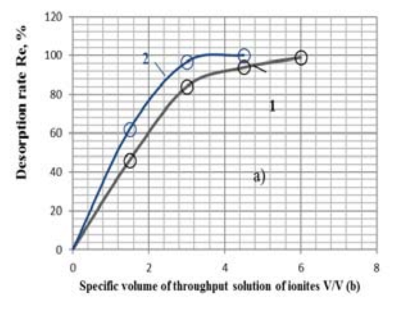
-during high rate option the process completes as not less than 1,5 specific volumes of desorbent are passed, during standard – after 2 vol/vol of ionite per hour;

- desorption duration was respectively 120 and 10 minutes, that is full desorption duration at high rate is 12 times less than the standard one'.
The sorption capacity on rhenium ionite Purolite A170, as per desorption process, was 10,88 g/l of a sorbent or 25 mg/g of ionite in conversion to air-dry conditing.

ЖАУАПКЕРШІЛІГІ ШЕКТЕУЛІ СЕРІКТЕСТІГІ
КазГидроМедь
ТОВАРИЩЕСТВО С ОГРАНИЧЕННОЙ ОТВЕТСТВЕННОСТЬЮ



On Picture 2 – desorbing solution versus desorption of rhenium ammonia with isoporous PuroliteA170 saturated from washing acid from the Sulphuric Acid Plant at Balkhash and Zhezkazgan Copper Plant, Kazakhmys Corporation LLP, volumes of desorbent solutions passed for low ammonia desorbent passing at different rates ionites layers in columns.
As it is seen below rhenium desorption at high rate has an advantage over a standard method.



Therefore, during ammonia desorption of rhenium at high rate the increase of rhenium concentration in commercial eluate is clearly seen, whereas commercial (or commodity) fraction output at high rate is nearly decreased twice.

Pic. 2 – Desorbing solution volume versus desorption of rhenium with isoporous PuroliteA 170, saturated from washing acid of the Sulphuric Acid Plant at Balkhash (a) and Zhezkazgan (b) Copper Plant, Kazakhmys Corporation LLP, of volumes passed through desorbing solutions at different rate of desorption.

In both cases content of desorbent – 6 % NH_3.

Rate of desorbent throughput:

1 – 2 vol./vol. ionites per hour;

2 – 9 vol./vol. ionites per hour.

Thank you for your attention!

STUDY ON RHENIUM DESORPTION AT HIGH RATE FROM MACROPOROUS LOW BASE IONITES

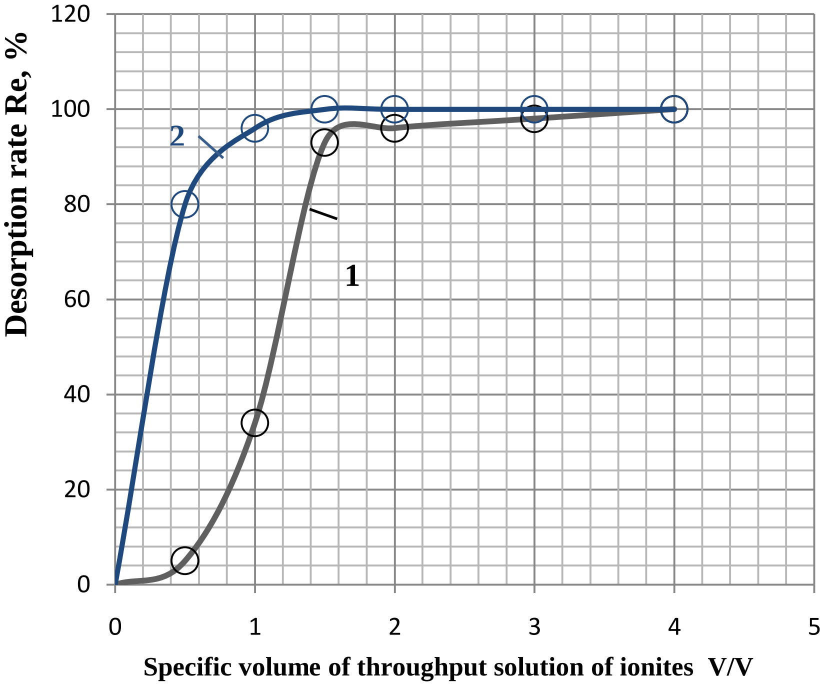
S.V. Zakharian[**]**,A.B. Yun**[**]**, E.I. Gedgagov**[*]**, V.A. Chen**[**]

* - FSUE“GINTSVETMET Institute”, Moscow c., Russia
** - KazGidroMed LLP, Karaganda c., Kazakhstan

This study purpose is development of rhenium desorption at high rate for low-baseionites,in particular, with macroporousPurolite F170 which is advised for rhenium sorption in terms of washing acid from the Sulphuric Acid Plant at Balkhash Copper Plant, Kazakhmys Corporation LLP.

OnPicture1 – desorbing solution versus desorptionofrheniumammoniawith isoporousPuroliteA170 saturated from washing acid from the Sulphuric Acid Plant at Balkhash Copper Plant, Kazakhmys Corporation LLP, from of weak ammonia desorbent through ionites layers in columnsat different rate.

Asitisseenbelowrheniumdesorptionathighratehas an advantage over a standard method.



Pic. 1– DesorbingsolutionvolumeversusdesorptionofrheniumwithisoporousPuroliteA 170,saturatedfromwashingacidof the Sulphuric Acid Plant at Balkhash Copper Plant, Kazakhmys Corporation LLP, of volumes passed through desorbing solutions at different rate of desorption.

In both cases content of desorbent – 6 % NH_3.

Rate of desorbent throughput:

1 – 2 vol./vol. ionites per hour;

2 – 9 vol./vol. ionites per hour.

Therefore, during ammonia desorption of rhenium at high rate the increase of rhenium concentration in commercial eluate is clearly seen, whereas commercial fraction output at high rate is nearly decreased twice.

MOLYBDENUM-99 PRODUCTION FROM A THORIUM TARGET IRRADIATED BY LIGHT CHARGED PARTICLES UP TO 70 MeV

Charlotte DUCHEMIN[a]*,Arnaud GUERTIN[a], FeridHADDAD[a,b], Vincent MÉTIVIER[a], Nathalie MICHEL[b]

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Introduction

The irradiation of a thorium target by light charged particles leads to the production of several isotopes of medical interest. Direct nuclear reaction allows the production of ^{230}Pa which decays to ^{230}U the mother nuclei of ^{226}Th, a promising isotope for the alpha radionuclide therapy. The fission of ^{232}Th produces fragments of interest like ^{99}Mo, ^{131}I and ^{115g}Cd. ^{99}Mo is of particular interest since it is the mother nucleus of ^{99m}Tc which is used in nuclear medicine for imaging. The production cross section measurements and production yields of ^{99}Mo have been determined in this study.

Description of the Work or Project

The cross section measurements were made using the stacked-foil technique and the experiments were carried out at the ARRONAX cyclotron (France) with deuteron and proton beams up to 34 and 70 MeV, respectively.

Since high Z target can encounter fission, 22 fission fragments cross sections are reported for the first time as a deuteron energy distribution on the range 8-33 MeV. Fission data induced by protons have been already published up to 22 MeV. As our proton beam reached 70 MeV,our values comesupplement the existing ones.

These data allow us to determine production yield with a high accuracy and in particular for the ^{99}Mo production which have been estimated in the past by extrapolating low proton energy data [Abbas et al., 2012].

Conclusions

This work complementsnuclear data onproduction cross section induced by protons and deuterons. It also gives new results on the fission of ^{232}Th induced by light charged particles.

Larger quantities of ^{99}Mocan be obtained using the fission of ^{232}Th than the ^{96}Zr(α,n) direct production, and the specific activity is higher than the ^{100}Mo(p,2n)^{99}Mo reaction channel.

Keywords: Cross section measurements, thorium target, fission, medical isotopes, ^{99}Mo/^{99m}Tc generator.

^{188}Rhenium: application for glioblastoma internal radiotherapy.

Annabelle Cikankowitz, Micro et nanomédecines biomimétiques, Labex IRON,
AMaROC, ONIRIS, PRIMEX

The aim of the proposed work is to provide evidences that stereotactic internal radiotherapy through lipid nanocapsules loaded with Rhenium-188 (LNC^{188}Re-SSS) is an alternative radiotherapeutic strategy for glioblastoma (GB) that can be translated to human medicine.

That strategy implies Convection-Enhanced Delivery (CED), a new local infusion method for brain application that can be defined by two parameters: the volume of infusion (Vi) and the volume of distribution (Vd). The distribution of therapeutical agent by CED can be improved with the use of a vector which brings a retention effect. However, many parameters such as the kind of tissue, tumor size, pressure… influence the CED efficacy. Herein, we would like to determine the best injection modalities of our LNC^{188}Re-SSS by CED depending on the role of the flow rate, the injected volume and its tissue localization.

Materials and methods:

The orthotopic human GB Lab1 xenograftmodel in nudemice was infusedlocallybyconvection-enhanceddelivery (CED) with an increasingvolume (3µL, 5µL, 10µL or 15µL) of LNC loadedwith a lipophilicfluorescentredstain (DID) orLNC^{188}Re-SSS (3MBq), 12 or 18 days after theinjectionof Lab1 cellsintothestriatum . The influenceoftwoflowrates (0,25 or 0,5 µL/min) on the LNC distributionwithinthetumormass was tested. Tumor progression was monitored by µMRI through theselection of RegionsOf Interest(ROI) in order to determine the tumorvolume the day previous the LNC injection.Vd of LNCs was evaluated by immunofluorescence (brain frozen 1h after infusion of DID-LNC) and by autoradiography (brain harvested 1h and 24h after the injectionofLNC^{188}Re-SSS).

The efficacy of LNC^{188}Re-SSS in the orthotopic human GB Lab1 xenograftmodel with a selected infusion mode (volume and flow rate set) was tested through a fractionated treatment at day 12 and day 19 after the tumor cell injection. The influence of this treatment on the immunological brain environment, the angiogenesis and the tumor proliferation was analysed by immunofluorescence at day 18 (CD31, ki67, CD45R and F4/80).

Results:

Preliminary findingswith Lab1-Nude models at day 12 suggested a suitable LNC-DID distribution after a personalized tumor targeting with injection modalities of 3µL; 0,5µL/min (mean tumor volume of 2,3µL). This Vi is acceptable because of high Vd for the injection of 10 and 15µL. No more than 5µL could be injected in mice striatum because of leakage in the left brain hemisphere with higher Vi. Thus, the tumor volume should be determined by µMRI the day before in order to define Vi at best. Vd is also influenced by flow rate: a weak flow rate of 0,25µL gives a higher Vd (12,6µL vs 15,8µL).

Results indicated thatLNC^{188}Re-DID show the same tendency as fluorescence. Indeed, at day 12 and 1h after the injection of 3µL , we obtain a Vd of 10,2µL ± 1,9µL by fluorescence analysis and a same range in 1mm brain slices with the blue DID color: 12,6µL ± 3,8µL. There is a 2-fold increase for the Vd between 1h and 24h. Autoradiography data are under analysis.

Immunofluorescence results indicated a decrease of Ki67+ cells number, a disorganization of vessels and an infiltration of macrophages around big tumour cells (1918 F4-80+/mm² vs 258 F4-80+/mm²) and B lymphocytes (270 CD45R+/mm² vs 3 CD45R+/mm²) 7 days after the first injection at D12.

Beta radiation could explain this recruitment and efficacy in in vivo model since after a fractionated D12-D19 treatment is associated with a significative increase of the median survival time to 56 days versus 20 days for control mice. We have 50% of long-term survivors (> 100 days). After the rechallenge, we observe a slowing down of Lab1 development. In n=3 mice per group MST reaches 27 days versus 19,5 days for control.

Conclusion:

To conclude, the fractionated day 12 – day 19 treatment is effective in a human glioblastoma model. The better description and understanding of LNC^{188}Re-SSS effects on tumor environment will lead to the validation of this innovative glioblastoma therapeutical strategy and the establishment of the first phaseI clinical trial: (1) Single CED in recurrence situation, (2) Dosimetric evaluation (SPECT acquisition) and (3) Biological parameters analyses.

Starch based microparticles radiolabelling with ^{99m}Tc and ^{188}Re for diagnostic and therapy of Hepatocellular carcinoma

E.Verger[1,4,8], A. Cikankowitz[1,8], A. Bouvier[2], N. Lepareur[5,8], J. Benoit[1,8], J. Deloye[6], C. Aubé[2], O. Couturier[1,3,8], F. Lacoeuille[1,3,7,8], R. Hustinx[4], F. Hindré[1,7,8].

[1]INSERM U1066 MINT (Micro et Nanomédecines Biomimétiques), University of Angers, FRANCE ; [2]Radiology department, CHU d'Angers, University of Angers, FRANCE ; [3]Nuclear medicine department, CHU d'Angers, University of Angers, FRANCE ; [4]Nuclear medicine department, CHU de Liège, University of Liège, BELGIUM ; [5]Centre Régional de Lutte Contre le Cancer (CRLCC) Eugène Marquis, Rennes, FRANCE ; [6]Cyclopharma Laboratoires, Saint-Beauzire, FRANCE ; [7]PRIMEX (Plateforme de Radiobiologie et d'IMagerie EXpérimentale), University of Angers, FRANCE ; [8]Labex IRON, Nantes-Angers, FRANCE.

The HepatoCellular Carcinoma (HCC) is the 6th most common cancer worldwide. There are few curative treatments, (ablation, resection and transplantation) and most of the patients cannot benefit from it because of underlying liver diseases. Among recent developments in palliative treatment, Selective Internal Radiation Therapy (SIRT) which efficacy has been assessed but is still in experimental stage, is currently proposed for patients in intermediate stage HCC who are not eligible for the standard therapy[1]: Transarterial chemoembolization (TACE). SIRT consists of the intra-arterial injection of ^{90}Y-microspheres which requires a pre-therapeutic angiography done with ^{99m}Tc-macroaggregated albumin (MMA) to evaluate the hepatopulmonary shunt. However MMA and ^{90}Y-microspheres are not similar in shape and size, and these differences can lead to dosimetry approximation.

In this context Starch-Based Microparticles (SBMP), first developed in our laboratory (UMR-S1066) for lung scintigraphy by the optimization of ready-to-use ^{99m}Tc-radiolabelling kit[2,3], are potential good vectors for SIRT of HCC by their characteristics (size, radioisotope complexation). As technetium-99m (^{99m}Tc) a pure gamma-emitter and rhenium-188 (^{188}Re) a beta and gamma emitter have similar physical chemical properties, both of them can label the SBMP, with the advantage of a unique system for diagnosis purpose and therapy of HCC. The aim of this work is to develop and optimize a ready-to-use kit allowing the fast and stable labeling of SMBP with ^{188}Re.

SBMP are obtained by sodium metaperiodate ($NaIO_4$) oxidization of native starch particles to open the glucose cycles, allowing the linkage of a polyamine ligand (cadaverine). This link needs to be stabilized by a reducing step using sodium borohydride ($NaBH_4$). Different parameters like amout of microparticles, of reducing agent: stannous chloride dihydrate ($SnCl_2$, $2H_2O$), of perrhenate (ReO_4^-) activity or reaction's volume were changed to optimize the radiolabelling reaction. The efficiency of the radiolabelling is assessed with measure of the radiochemical purity (RCP) by filtration of 1mL of the labeled microparticles on a 5-µm filter. Also stability studies were performed following the RCP up to 24h.

In comparison with ^{99m}Tc, the ^{188}Re needs strengthened reducing conditions for a complete complexation onto the SBMP. Reducing agent and amount of microparticles are major influencing factors. At this stage of optimization we obtained a RCP around 90% (±5%) and a 24h stability.

SBMPs show promising characteristic as a single agent for the diagnosis and SIRT therapy of HCC. Biodistribution and efficacy studies are planned on a rabbit VX2 model.

Keywords: SIRT; Hepatocellular carcinoma; Starch-Based Microparticles; rhenium-188; technetium-99m;

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Rhenium-tricarbonyl with a new tripodal N_2O ligand: from structural investigations to a therapeutic radiopharmaceutical

Romain Echeynne[1], Sihem Guizani[2], Mariusz Wolff[3], Eric Benoist[1], Nicolas Lepareur[4]

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2-National Center of Sciences and Nuclear Technology, Radiopharmaceutical Unit, Sidi thabet 2020, Tunisia
3- University of Silesia, Department of Crystallography, Institute of Chemistry, 40-006 Katowice, Poland
4- Centre Eugene Marquis, Nuclear Medicine Department, INSERM UMR-S 991, 35042, Rennes, France

Introduction:

Selective localisation or destruction of tumour cells by means of a radiopharmaceutical is a simple and attractive concept, based on the recognition properties of biomolecules – in particular small peptides – towards tumour cells. The challenge is to design effective and stable radiotracers based on a suitable radioisotope, a bifunctional chelate and a biomolecule, appropriate to target the organ of choice. Among radioisotopes for targeted therapeutic applications, rhenium-188 is very promising, thanks to its suitable properties (β^- emitter, $E_{max} = 2.12$ MeV, $t_{1/2} = 17$ h), and to the fact that it is a homologous element to technetium-99m, the radioelement of choice in nuclear medicine. Complexes based on the Re(I) tricarbonyl core and a “click-to-chelate” approach, recently developed by Schibli *et al.,* have brought new opportunities for the preparation of radiopharmaceuticals. The aim of this study was to design a new tripodal N_2O ligand, based on a triazolyl moiety, and to evaluate its ability to chelate rhenium-188 as well as the possibility to conjugate a peptide.

Materials and methods:

Tripodal N_2O bifunctional chelating ligands (BCLs) have been synthesised through a copper-catalysed cycloaddition between an alcyne and an azide. Rhenium complexes have been prepared with “cold” $^{185/187}$Re, using these BCLs. They were subsequently fully characterised (NMR, IR, elemental analysis, MS, X-Rays and cyclic voltammetry). The analogous ^{99m}Tc and ^{188}Re have been prepared, using Isolink kits for ^{99m}Tc and a modified procedure for ^{188}Re, and their HPLC and TLC profiles were compared with the fully characterised “cold” complexes.

Results:

BCLs with different functionnalisations (ester, amine and nitro) have been prepared and their synthesis optimised. Rhenium complexes have been prepared and characterised. The feasibility of the labelling with rhenium-188 has been demonstrated. Reaction conditions are however still to be optimised.

Conclusions:

We are currently trying to link a peptide to our BCL, to target hepatocellular carcinoma metastases. Once the radiolabelling of the biomolecule will be done and its stability assessed, its biological evaluation is planned.

Interdisciplinary consortium collaboration for the development of radiopharmaceutical approach for effective diagnostics and therapy of prostate cancer in Russia

K. German[1,2], O. Vlasova[3], V. Petriev[4], V. Skvortsov[4], G. Kodina[5], A. Maruk[5], N. Airapetova[6], N. Epshtein[6], N. Nerozin[3], A. Safonov[1,2], V. Lebedev[1], Ya. Obruchnikova[1,2], Yu. Shevko[3]

1 - A.N. Frumkin Institute of Physical Chemistry and Electrochemistry RAS, Moscow
2 - Medical Institute Reaviz, Moscow branch, Russia
3 - A. I. Leipunsky Institute for Physics and Power Engineering, Obninsk, Russia
4 - Medical Radiological Research Center of Ministry of Health of Russia, Obninsk, Russia
5 - Burnazyan Federal Medical Biological Center of FMBA, Moscow, Russia
6 - National Research Nuclear University MEPhI, Obninsk, Russia

Effective diagnostics and therapy of prostate cancer is an important issue for Russia due to constantly increasing number of decease cases herein. Rational development of new radiopharmaceuticals for the management of advanced and metastatic prostate cancer requires an improved cooperation of the organization thus involved. For this reason an interdisciplinary consortium collaboration for the development of radiopharmaceutical approach is established with principle aim to improve the situation within the 3 coming years. The PSMA markers are focus selection of the project due to their ability not only for cancer but also for methastatic object detection. Draw investigation indicated that the prostate-specific membrane antigen (PSMA) based markers could be the key substrate matter for the solution of the problem. PSMA is highly expressed in prostate cancer, and small-molecule radiopharmaceuticals targeting PSMA helps to rapidly detect the location and extent of disease. Comparative study provided with a selected row of substrates including several MIP derivatives and some others. Synthetic procedures were optimized for better yields, purities and prices.

Production of Tc-99m (for radiodiagnostics) and Re-188 (for radiotherapy) isotopes were improved with optimized generator design aimed to high specific activity production.

Special educational interdisciplinary program for specialist training for technetium application to prostate radiodiagnostics is elaborated.

The development of new radiopharmaceuticals and generators for the management of advanced prostate cancer will help to improve the treatment of this disease in Russia.

ISTR 2014
8th International Symposium on Technetium and Rhenium
Pornichet LA BAULE, France
29th September - 3rd October 2014

Interdisciplinary consortium collaboration for the development of radiopharmaceutical approach for effective diagnostics and therapy of prostate cancer in Russia

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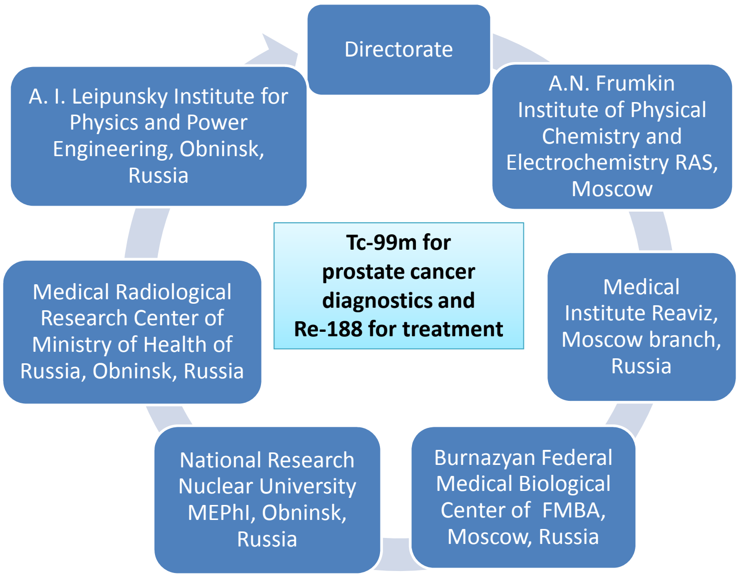
Consortium organigram



Directorate

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Medical Radiological Research Center of Ministry of Health of Russia, Obninsk, Russia

A. I. Leipunsky Institute for Physics and Power Engineering, Obninsk, Russia

Tc-99m for prostate cancer diagnostics and Re-188 for treatment

A.N. Frumkin Institute of Physical Chemistry and Electrochemistry RAS, Moscow

Technetium chemistry laboratory

- K. German, Project CEO, Head of Tc laboratory, PhD , Doc., Prof.
- A. Safonov, Deputy head of Tc laboratory, PhD
- Ya. Obruchnikova, PhD
- V. Tregubova, PhD student
- M. Glazkova

Innovation department

- V. Lebedev, General manager for innovations

Laboratory of new physical-chemical problems

- A. Tsivadze, Director of IPCE RAS, Academician
- A. Filyanin, liquid extraction group, PhD
- V. Tarasov, NMR analysis, Professor

Laboratory of substance radiation chemistry

- B. Ershov, Head of laboratory, corr. member RAS, Professor
- E. Abkhalimov, PhD
- R. Solovov, PhD student

Laboratory of interphase boundaries and electocatalysis

- V. Andreev, Head of laboratory, Professor

Laboratory of radioactive material analysis

- M. Grigoriev, Head of laboratory, Professor

- The main purpose of the Institute is to carry out fundamental and applied scientific research in various fields of physical chemistry, electrochemistry, chemical resistance of materials, radiochemistry and radiation chemistry.

A. I. Leipunsky Institute for Physics and Power Engineering, Obninsk, Russia

ГНЦ РФ - ФЭИ

- O. Vlasova, N. Nerozin, Yu. Shevko, I. Zhuk
- multidisciplinary scientific organization, conducting complex investigations of physical and technical problems of nuclear science and technology.

РОСАТОМ

Medical Radiological Research Center of Ministry of Health of Russia, Obninsk, Russia

- V. Skvortsov, V. Petriev
- Mission: Development of concepts, regulatory documents related to radiation safety of a human and the environment, health security and reduction of socioeconomic prejudice caused by radiation.
- The Institute was founded in 1962 to develop and improve methods of radiation diagnostics and radiation therapy, prevention and treatment of radiation injury, the study of the biological and medical effects of ionizing radiation.

National Research Nuclear University MEPhI, Obninsk, Russia

- N. Airapetova, N. Epshtein
- Development of analytical procedures for quality control of radiopharmaceuticals and staff training
- Mission: to generate, disseminate the use and to preserve scientific knowledge aiming to address global challenges of the XXI century, as well as to provide innovative transformations in Russia accompanying development of the country competitiveness in the global energy and non-energy high-tech markets.

Burnazyan Federal Medical Biological Center of FMBA, Moscow, Russia

- G. Kodina, PhD, Department head
- A. Maruk, PhD, Laboratory Head
- Production of Tc-99m (for radiodiagnostics) and Re-188 (for radiotherapy) isotopes and preclinical medicine tests

- Fundamental and applied research in the field of radiation medicine, radiobiology and radiation protection;
- Research in the field of biomedical technologies, radiopharmacy;
- Development of new radiation technologies (including photon and neutron capture therapy);
- Research in the field of chemical and radiation safety in the use of technology for special applications.

Medical Institute Reaviz, Moscow branch, Russia

- K. German, Chair of Natural science, Professor
- A. Safonov, docent, PhD
- Ya. Obruchnikova, assistant prof., PhD
- V. Tregubova, PhD student

- Training of medical staff for modern medicine

“The main aim of Reaviz is the training of health care staff, of young people who should become highly professional physicians in the nearest future. The most important quality for these professionals should be the integration of the greatest responsibility and the inner freedom of this profession, of scientific research and practical achievements.” Rector of Samara Medical Institute “REAVIZ”, Doctor of Medical Science, professor Nikolay A. Lyssov

What we intend to obtain

In the course of this project should be developed

- production technologies of ^{99m}Tc generators and high-value ^{188}Re generators with reduced transport index,
- technologies of ^{188}Re concentration, development of analytical methods for detection of radioactive and chemical impurities in the ^{188}Re preparation,
- quality assurance of ^{99m}Tc and ^{188}Re generator eluates in accordance with the requirements of potential radiopharmaceuticals based on them, specifically binds to the receptor tissue of prostate cancer.

What we already have for radionuclide imaging

- 2-^{18}F-fluoro-2-deoxy-D-glucose (FDG);
- ^{111}In-7E11 antibody (ProstaScint);
- ^{18}F-fluorodihydrotestosterone (^{18}F-FDHT);
- radioacetate analogs;
- radiocholine analogs;
- anti-1-amino-3-18F-fluorocyclobutane-1-carboxylic acid (anti-[^{18}F]FACBC)

Production of Tc-99m (for radiodiagnostics) and Re-188 (for radiotherapy) isotopes were improved with optimized generator design aimed to high specific activity production.

- Potential consumer of radiopharmaceuticals (RPh): medical institutions at various levels, cancer medical centers, cancer clinics, licensed to work with sources of ionizing radiation and equipped with diagnostic equipment, SPECT or PET.
- Objects of RPh application: patients with the disease of prostate cancer (about 30 thousand pers. / year).
- Over the past few years in Russia approximately 40,000 new cases of prostate cancer per year were recorded, and only for 30% of them brachytherapy is performed with an efficiency of 75%

Effective diagnostics and therapy of prostate cancer is an important issue for Russia due to constantly increasing number of decease cases herein.

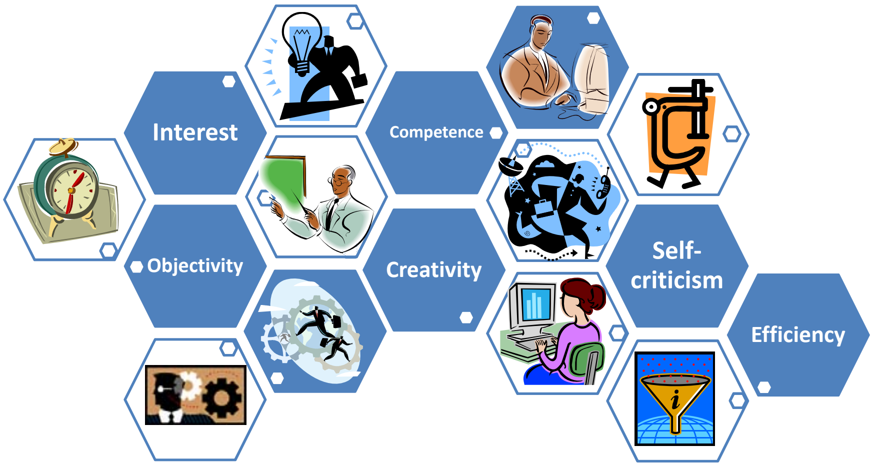
Rational development of new radiopharmaceuticals for the management of advanced and metastatic prostate cancer requires an improved cooperation of the organization thus involved. For this reason an interdisciplinary consortium collaboration for the development of radiopharmaceutical approach is established with principle aim to improve the situation within the 3 coming years.

The development of new radiopharmaceuticals and generators for the management of advanced prostate cancer will help to improve the treatment of this disease in Russia.

- Special educational interdisciplinary program for specialist training for technetium application to prostate radiodiagnostics is elaborated.
- The development of new radiopharmaceuticals and generators for the management of advanced prostate cancer will help to improve the treatment of this disease in Russia.
- Innovative character of this project requires special attention on staff training.
- New technologies worked out by **Igor Zhuk and Yury Shevko** (A.I. Leipunsky Institute for Physics and Power Engineering, Obninsk, Russian Federation) are to be used in this project

A new approach to form a competent team of specialists

What makes a good specialist?

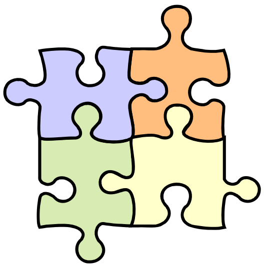


Many issues written by leading scientists state that the **expert is endowed mainly the following qualities,** namely:

1) has a degree in the subject area;
2) has a positive experience with previous expertise in the subject area;
3) must work at least 10 years;
4) objective;
5) must constantly improve their knowledge and so on.

Is it true?

In our opinion, these qualities are of a **formal nature** and **do not meet the full competencies** that have been proposed by the European community as one of the core competences for professionals of the twenty-first century.



Five basic EU competencies were chosen as the most necessary for the Expert of the XXI century :

1. Communication in the mother tongue.
2. Communication in foreign languages.
3. Mathematics skills and core competencies (skills) in science and technology.
4. Information technology competence.
5. The ability to find new information and produce new knowledge for expert's professional area.

Ask yourself: “Are you sure that You have all this basic competencies?”

Or Do You think that the expert and specialist of technetium application to prostate radiodiagnostics do not need this competencies?

Unfortunately, it is not a simple question.

Please, think about quantity of the wrong diagnosis in different countries

- The PSMA markers are focus selection of the project due to their ability not only for cancer but also for methastatic object detection. Draw investigation indicated that the prostate-specific membrane antigen (PSMA) based markers could be the key substrate matter for the solution of the problem. PSMA is highly expressed in prostate cancer, and small-molecule radiopharma-ceuticals targeting PSMA helps to rapidly detect the location and extent of disease. Comparative study provided with a selected row of substrates including several MIP derivatives and some others. Synthetic procedures were optimized for better yields, purities and prices.

Expert assessments in Russia

- Expert assessments are applied with success in various fields of human activity and find their reflection in the works of such Russian scientists as Azgaldov G.G., Beshelev S.D., Evlanov L.G., Gurvich F.G., Larichev O.I., Litvak B.G., Novikov, D. A., Orlov, A.I., Raichman I.P., Sidelnikov Y.V., and many other authors involved in problem of expert assessments.

Evlanov L.G. thought that the expert has the following requirements:

1) Competence;
2) Creativity;
3) Respect to the examination;
4) Conformism;
5) Constructive thinking;
6) Teamwork;
7) Self-criticism.

In the work of Raichman A.P. and Azgldov G.G. the quality of the expert has the following requirements:

1) Competence;
2) Interest;
3) Efficiency;
4) Objectivity.

The competence of the expert should be applied to the object quality assessment (professional competence) and methodology (qualitative competence).

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Influence of oxygen isotopes on the NMR parameters of the pertechnetate anion TcO_4^- . Use of technetium-99g in PET nuclear chemistry technology: application of ^{99g}Tc-NMR for analysis of O-18 content in water

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2 – Frumkin Institute of Physical Chemistry and Electrochemistry RAS
3 – Medical Institute Reaviz

The new method for ^{17}O and ^{18}O analysis is proposed being based on addition of isotopically saturated water samples to solid $M^{99}TcO_4$ (M = NH_4 or Na) followed by quantification of ^{99}Tc-NMR spectrum fine structure in the coordination sphere of pertechnetate. The isotopic shifts $^{16/17}\Delta$, $^{16/18}\Delta$ NMR ^{99}Tc and the constants of spin-spin interaction of isotopomers: $Tc^{16}O_2{}^{17}O_2^-$, $Tc^{16}O_3{}^{18}O^-$,$Tc^{16}O_3{}^{17}O^-$, $Tc^{16}O_2{}^{17}O^{18}O^-$,$Tc^{16}O_2{}^{18}O_2^-$ are determined. In the solution of ammonium pertechnetate for the anions $Tc^{16}O_3{}^{18}O$ and $Tc^{16}O_3{}^{17}O^-$ at the temperature interval 278-333K the isotopic shift is given by liner dependencies $^{16/18}\Delta = -0.616 + 6.45\times10^{-4}T$ (ppm) and $^{16/17}\Delta = -0.302 + 2.67\times 10^{-4}$ T (ppm), correspondingly
In the solution of sodium pertechnetate for the isotopomer $Tc^{16}O_3{}^{17}O^-$ the absolute value of the isotopic shift $^1\Delta(^{16/17}O)$ is nonlinearly depending on the temperature due to the equilibrium of contact and hydrate-separated ionic pairs.

$[^{18}\mathbf{O}]H_2O$ 2-$[^{18}\mathbf{F}]$fluoro-2-deoxi-D-glucose (^{18}FDG)

Most popular Radiopharmaceutical for PET

Very important consummation of $[^{18}O]H_2O$ in medical centers

It should be recycled

- ^{18}F – decay ~110 min $^{18}O(p,n)^{18}F$,
- Mass-spectroscopic test for $^{12}C^{18}O^{16}O$ and $^{12}C^{16}O_2$

Alternative analytical procedure is being developed in my lab Use of Mn-NMR and Tc-99g-NMR

Field 7.04Tl at Bruker AVANCE-300.

Oxygen isotopic exchange in MnO_4^- or TcO_4^- vchange the spectral splitting shape

Isotope shifts from ^{16}O to ^{18}O is

0,59 ppm for ^{55}Mn and

0,43 ppm for ^{99}Tc [1].

(>98% $[^{18}O]H_2O$)

Crystaline NH_4TcO_4, $NaTcO_4$, $KMnO_4$ added to form 0.25-0.3 M.

^{18}O in initial water was >95% $H_2{}^{18}O$, and after irradiation for ^{18}F preparation it was 72% $H_2{}^{18}O$ (Fig).

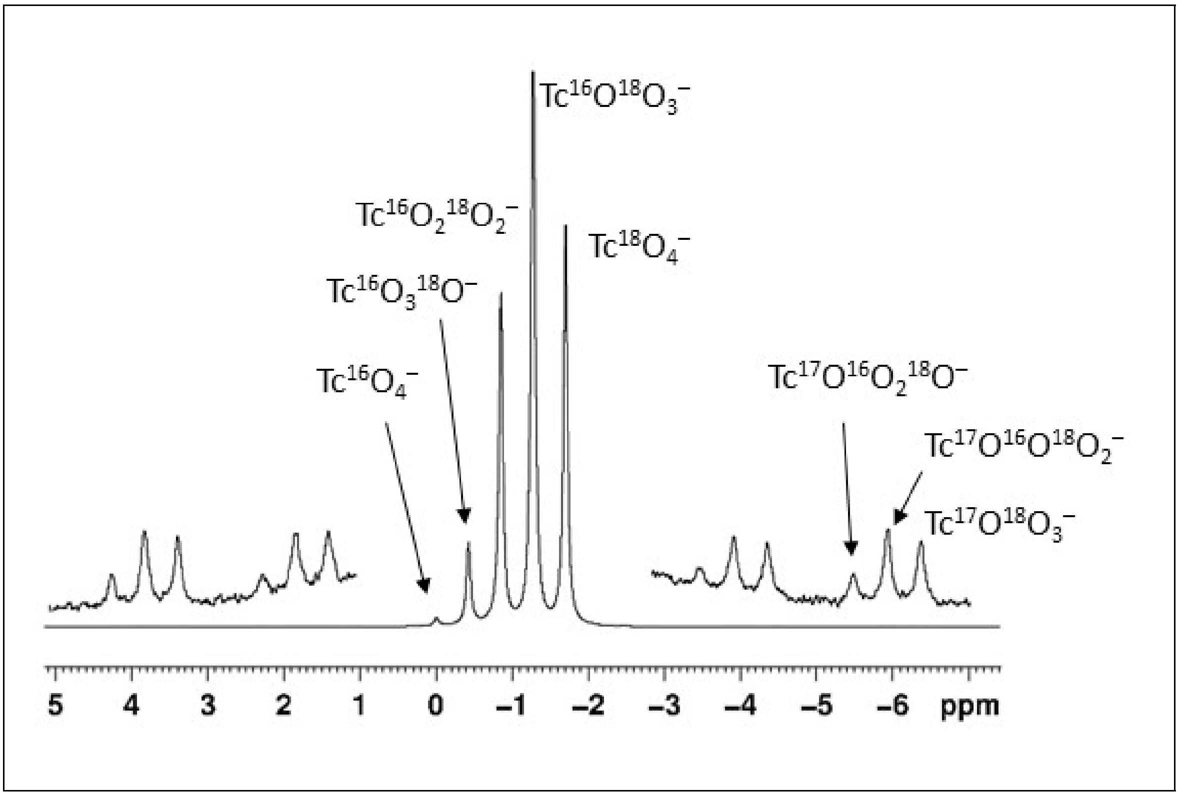
ISOTOPEOMERES NUMBER Z IS

$Z = (n+s-1)!/n!(s-1)!$ = 15, где n=4-

$\mathbf{Ç = n!(r_{16})^{a} (r_{17})^{b} (r_{18})^{c}/(a!b!c!)}$ **WHERE** $\mathbf{r_{16}}$, $\mathbf{r_{17}}$ AND $\mathbf{r_{18}}$ –, $(\mathbf{r_{16}}+\mathbf{r_{17}} + \mathbf{r_{18}}) =1$;

$a+b+c =4$.

$MO_4^- + H_2{}^{18}O = M^{16}O_a{}^{17}O_b{}^{18}O_c^-$,



^{99}Tc NMR (67.55MHz) spectrum of an equilibrated 0.2 M $NaTcO_4$ solution in recycled water containing ~72% $H_2{}^{18}O$ at 298K.

КССВ $^{99}Tc–^{17}O$ составляет 130 Hz,

КССВ $^{55}Mn–^{17}O$ =16.5 Hz.

Tc usage provides with more precise data

1. В.П.Тарасов, Г.А.Киракосян, К.Э.Герман // Химическая физика. (2014). Т.33 (в печати)

TECHNETIUM AND RHENIUM SULFIDES – FORMATION KINETICS, STRUCTURE AND PROPERTIES

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Keywords: technetium-99, rhenium, sulphide, environmental chemistry,

Abstract

Sulfur is an element of high environmental importance, especially for understanding of many different metals behavior. Tc – S system is not an exclusion in this respect. The sulfur, its different compounds and their derivatives are often present in the natural waters, minerals and rocks and being leached by dissolution mechanism or microbiological transformation affect drastically the Tc environmental dissipation or concentrating routs. For better understanding the Tc behavior in the different natural environments we need quantitative data for the composition and properties of Tc sulfide species that could be formed. This work is aimed to analyze the progress in the field of Tc-S system with the principle focus to its formation kinetics and size speciation.

Historical data and its reconsideration.

So-called technetium heptasulfide was among the first synthesized Tc compounds [1-2] because it was considered as a convenient route for Tc separation from aqueous solutions. Already in the first works its composition was established as Tc_2S_7, thus supposing that Tc is present in its higher oxidation state. This experimental data were sufficiently precise although rather surprising in view of Tc(VII) redox potentials being in contradiction with those of S^{2-}. Spitsyn and Kuzina in IPCAS, Moscow, as well confirmed this composition [3]. Meanwhile the crystallographic characterization of technetium heptasulfide was not possible as the precipitate was completely X-ray amorphous. All the attempts of recrystallization in solution failed and no explanation of the composition and the structure was available for more than 45 years [4].

Lee and Bondietti in 1979-83 studied the effects of Fe(II) and of S^{2-} on Tc solubility having found out that, in the absence of S^{2-}, the pertechnetate was reduced by Fe(II) and Tc(IV) hydroxide precipitated from the solution [5-6]. Meanwhile, in the presence of S^{2-}, Tc_2S_7 precipitated, and the authors concluded that Tc(VII) was not reduced with this ion [6]. When both Fe(II) and S^{2-} were present, Tc was reduced and coprecipitated with a FeS phase as a carrier.

Amorphous Tc(IV) sulfide was also described by Boyd having been prepared while heating Tc_2S_7 in the absence of O_2 [7]. Crystalline TcS_2 in turn was prepared by chemical transport reaction along a temperature gradient (1423-1353 K) in a sealed tube. According to [8] the presence halogen as a carrier gas, improved transport efficiency [8]. This TcS_2 formed triclinic crystals.

Sodium thiosulphate or thioacetamide were shown being able to produce Tc_2S_7 in treatment of acidic Tc(VII) solutions [9, 10].

Important Tc accumulation by some sulfide minerals was observed [11-13], the most effective sorbents being the sulfides with higher solubility or possessing reducing metal ions. The mechanism for Tc sorption differed for different minerals [13].

The Tc_2S_7 solubility was investigated based on the measurements of Tc concentration in the aqueous solutions equilibrated with the previously precipitated and washed technetium sulfide [13]. No reasonable value was possible to establish because of its complicated hydrolyses behavior under the applied conditions as described in [3, 13] and references therein.

Formation kinetics was studied spectrophotometrically [14] providing with the data on the Tc(VII) reaction with sulfide reaction while the further colloidal particle size speciation studies supported with ultramicrocentrifuge technics [15-16] provided with the reliable information on Tc concentration dependences.

The TcO_4^- and S_2^- solutions have important absorbances in the UV region, being completely transparent in the region of visible light. In course of the reaction of the pertechnetate with S_2^-, the brown color of the solution develops, the corresponding spectrum being attributed to the technetium sulfide formation [14]. For the kinetic studies in [14] the λ= 450 nm was chosen (Fig.1 – 2). Some kinetic curves registered for solutions with different with initial $[TcO_4^-]_0$, $[Na_2S]$ and pH are illustrated at Fig. 2-4.

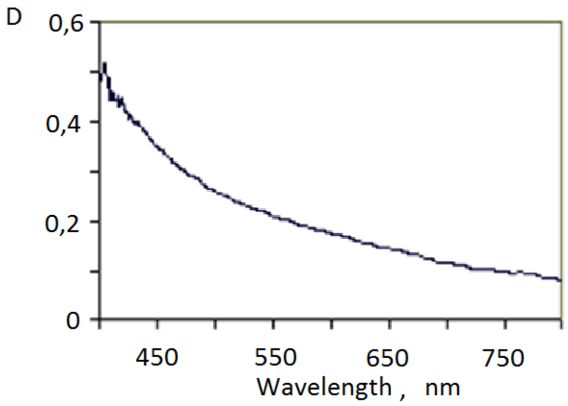


Fig.1. Typical spectrum for technetium sulfide formed after exposition for t = 4560 s, in the solution with initial $[TcO_4^-]_0 = 1*10^{-4}$ M, $[Na_2S]$ = 0,27 M and pH = 11,8.

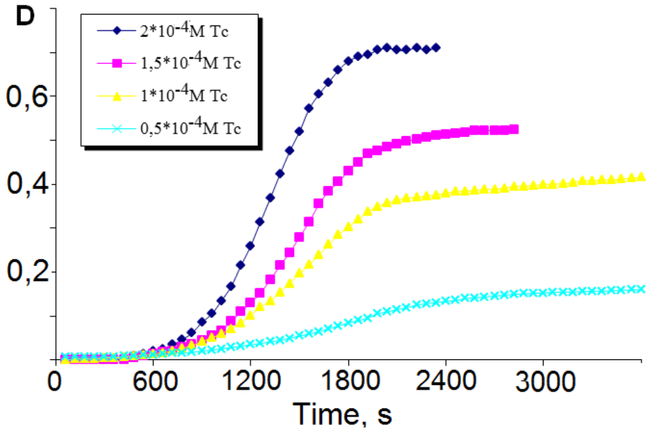


Fig. 2. Kinetic curves registered at 450 nm for the reaction of pertechnetate with sodium sulfide: $[TcO_4^-]_0$ = (0,5 – 2)$*10^{-4}$ M, $[Na_2S]$ = 0,27 M, pH = 11,8.

As the pH of the solution could be affected by hydrolyses and sulfide oxidation, some tests were conducted in buffer solutions [14]. In all cases the pH was kept within pH = 8 – 12 region as lover pH are favorable for hydrolyses of sulfide and hydrosulfide ions and conversion of elementary sulfur formed in the reaction into disulfide ion. The typical kinetics for phosphate buffers is demonstrated in the Fig. 3.

Three stages are characteristic for this reaction, the first one being induction period (from 13500 and up to 35000 s (= 9.7 h) dependent on the pH) its duration being dependent on the initial accumulation of disulfide ion, the second – intermediate reduction of pertechnetate to mixed Tc oxosulfide(V,IV) (14000 – 50000 s dependent on the pH) and the third – final formation of trinuclear Tc disulfide [14-15]. The colloidal solutions of the technetium sulfide thus formed were rather stable. Similar solutions were described by T. Sekine and co-authers in [16]. The composition of the precipitate separated from this solution by 10 kD ultramirocentrifuge membranes was determined by chemical analyses and by Rutherford back scattering (CENBG Bordeaux-Gradingan in collaboration with Lab. Pierre Sue, Saclay) and was equal to Tc:S = 2 : 6,73(25) [15]. This precipitate was analyzed by EXAFS studies at ESRF, Grenoble the results (see Fig. 4.) had confirmed its identity with the technetium sulfide studied by different authors [17-18].

The rate constant K_1 for the initial step of Tc(VII) reduction with sulfide (producing Tc(IV) and polysulfide ions) was determined as $7.0\cdot10^{-6}$ $сек^{-1}$ while K_2 constant for the final formation of technetium sulfide (in fact trinuclear technetium(IV) polysulfide) as shown in [17]) was $2.0*10^{-4}$ $сек^{-1}$, being by 2 orders of magnitude higher than K_1.

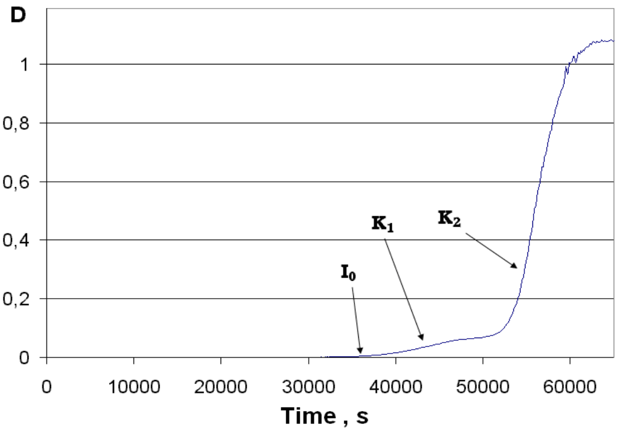


Fig. 3. Technetium sulfide formation kinetics (registered at 450 nm) in the reaction of pertechnetate with sodium sulfide at constant pH provided with buffer solution: $[TcO_4^-]_0 = 1.57*10^{-4}$ M, $[Na_2S] = 0.09$ M, buffer solution $[HPO_4^{2-}]/[H_2PO_4^-] = 3/1$, $^-[PO_4]_\Sigma = 0,19$ M, pH = 8.2

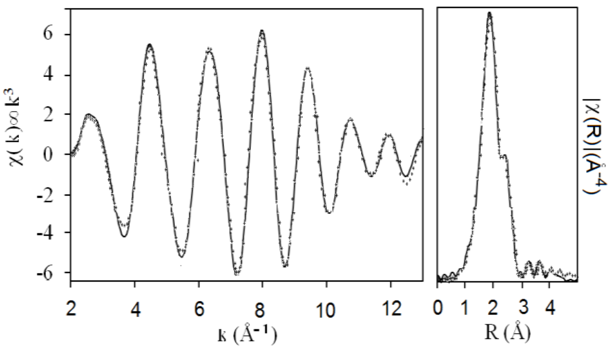
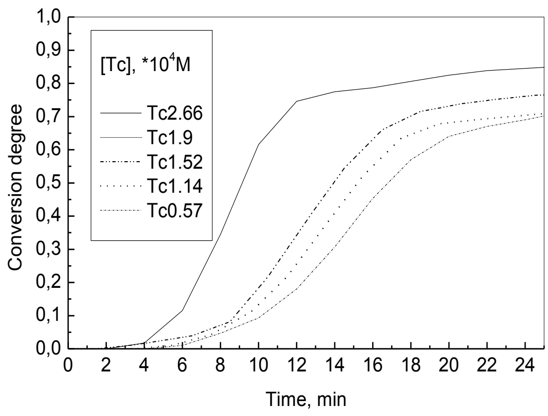


Fig.4. Tc K-edge EXAFS spectra (left) and their Fourier transforms (right) of the Tc sulfide colloidal solution corresponding to the reaction of pertechnetate with sodium sulfide for $[TcO_4^-]_0 = 2,0*10^{-4}$ M, $[Na_2S] = 0,27$ M, pH = 11,8.

The influence of initial technetium(VII) concentration (within the range of $(0,57-2,66)*10^{-4}$ M $KTcO_4$ and constant $[Na_2S] = 0.3$M) on the reaction rate of Tc and sulfide was determined from the data shown in Fig. 2 . The rate constant was practically lineary dependent on the technetium concentration within the range $(0,57 - 2,66)*10^{-4}$M.

The kinetics data recalculated from concentration to conversion degree axes are presented at the Fig5. Under the listed conditions the reaction of Tc(VII) with sulfide was also characterized with induction period and the kinetics dependent on the $[Na_2S]$ in the solution and the pH of the solution. Reaction of $NaTcO_4$ with 0,3M Na_2S was completed within 2000 s, the further development of the precipitate was due to aging effects. The S/Tc ratio in the sediment was obtained by chemical analyses as 3.36(7) on a macroammount of the precipitate and confirmed by RBS (Fig.6) [15].



. Fig.5. Reaction kinetics of $NaTcO_4$ with 0,3M Na_2S , pH=11.8, t=20°C [15]

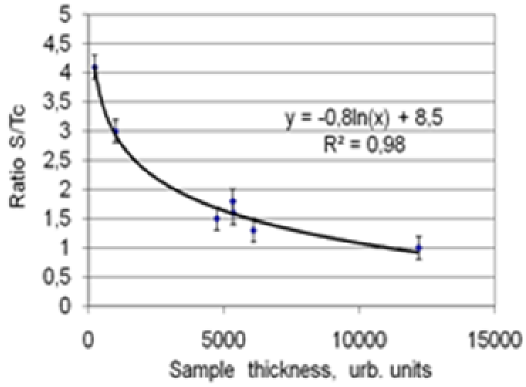


Fig. 6. RBS determination of S/Tc ratio in technetium sulfide [10]

Particle growing processes were investigated for technetium(VII) sulfide (Tc_2S_7) colloids produced in a mixture of Na_2S and TcO_4^- solutions by laser-induced photoacoustic spectroscopy (LPAS). Analysis of the LPAS signal intensities indicated that the particle size increased in the solution with an increase of standing time, while the number of particles remained constant. It was revealed that the size of colloid particles increased by deposition of Tc_2S_7 on the particle surfaces, not by coagulation of colloid particles. The formation mechanism and growing process of the colloids are discussed based on the LaMer model, which deals with nucleation processes.

In the aging process of Tc-S colloid system, the size of colloid particles was shown to increase by deposition of Tc sulfide on the particle surface, not by coagulation of the particles [11].

The final ideas for explanation of Tc – S system became possible only based on EXAFS studies [12]. It was demonstrated that -S-S- disulfide ligands are present in the structure thus explaining the reduction mechanism for Tc(VII) to Tc(IV) with no notable change in Tc:S stoichiometric ratio that remained close to the value within the interval of 3,3 – 3,5.

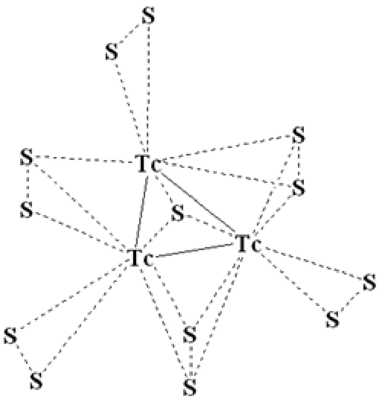


Fig.7. Structure unit fragment Tc_3S_{13} for technetium sulfide acc. to EXAFS studies[17]

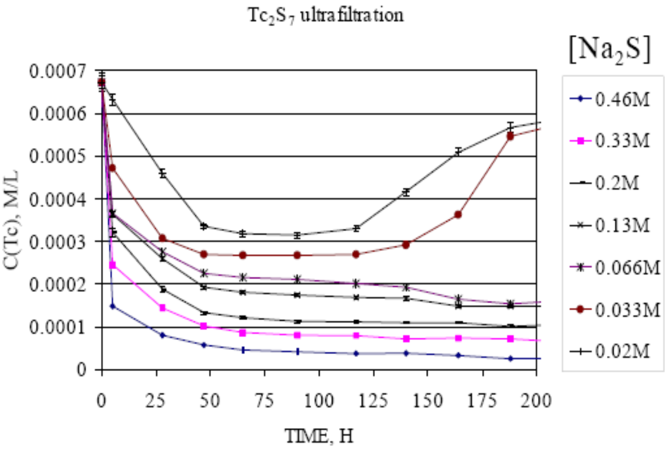


Fig.8. Concentration of free Tc species as fractionized with separation of ionic or nanocolloidal particles with 5 kD "Sartorius" ultramicrocentrifuge tubes [15]

At the same time the presence of S_2^{2-} ligand in the compound explains some other properties that was not well understood before. The determination of the concentration of free Tc species as fractionized with separation of ionic or nanocolloidal particles with 5 kD "Sartorius" ultramicrocentrifuge tubes [15] gave evidence on the Tc_3S_{10} nanosulfide formation (Fig.3) similar to that observed in [17].

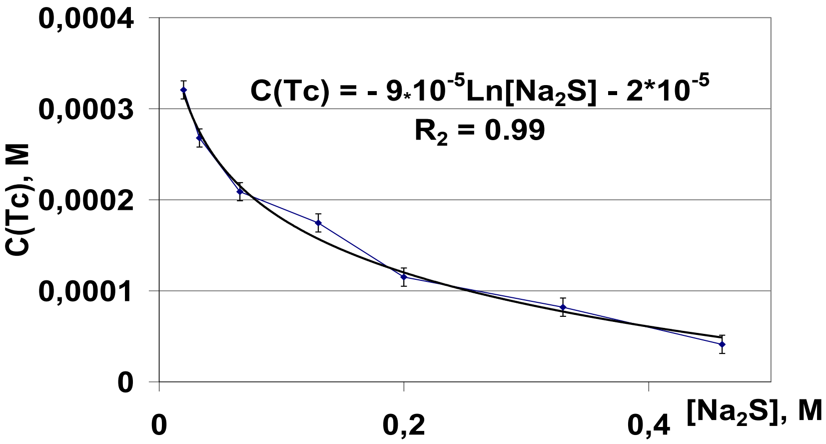


Fig. 9. Solubility of Tc sulfide at τ = 75 - 110 h as evaluated for different [Na2S] by separation of nano-colloidal particles with 5 kD "Sartorius" ultramicrocentrifuge tubes [15]

The stability of Tc_3S_{10} in the resulting solution was dependent of the S^{2-} concentration in it. When higher than 0.06M Na_2S, further grouth of Ts sulfide particles occurred for $\tau \geq 150$ h similar to observations made in [11]. For $[Na_2S] \leq 0.04$ M, the Tc_3S_{10} was reoxidized by present air to Tc(VII) within 175-200 hours thus being resolubilized.

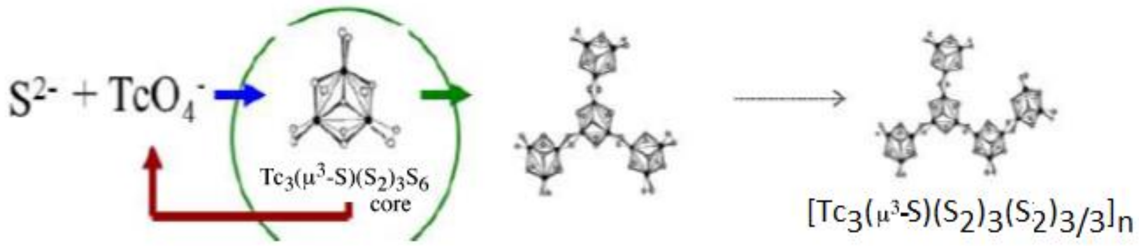
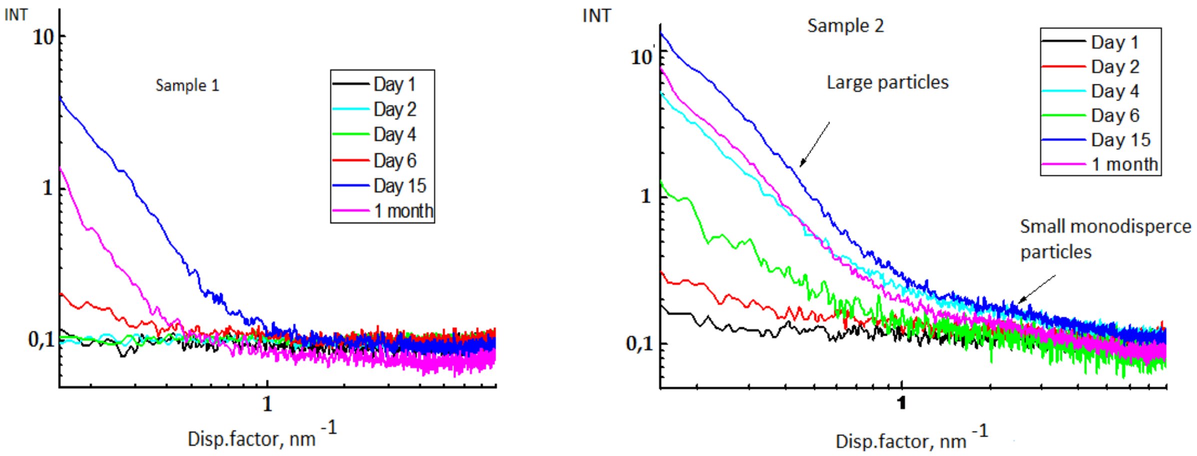


Fig. 10. The scheme of Tc reaction with sulfide describing precipitation and ultracentrifugal speciation tests the follows the ideas drawn based on the results of Lukens et all. , Sekine et all and German et all [15 - 17].

The determination of the free Tc species concentration with separation of ionic or nanocolloidal particles with 5 kD "Sartorius" ultramicrocentrifuge tubes [10] (Fig. 4) gave evidence on the Tc_3S_{10+x} nanosulfide formation similar to that observed in [12]. The equation for the Tc sulfide solubility based on these figures was evaluated (Fig.9). We carried out additional microcentrifuge size speciation in course of the reaction of Tc(VII) and Re(VII) with sulfide and followed it with size speciation of generated particles in the solution by SAXS at specialized small angle diffractometer SAXSess (Anton Paar (Austia), CuKα (1.54 A), transmission analises after collimation correction mode, sealed glass capillaries, registration with ImagingPlate) (Fig.11).



A B

Fig.11. SAXS spectra of two Re sulfide samples differing in the order of reagent mixing (a – Na sulfide to Na perrhenate and b – Na perrhenate to Na sulfide), $[NaReO_4] = 10^{-4}$M, $[Na_2S] = 0.3$ M.

Based on $Log(I) = f(s^2)$ plots, $s = 4\pi\sin(\Theta)/\lambda)$ for the aged samples two types of species were observed in Re sulfide colloidal solution by SAXS. Small particles were monodisperse and quite isotropic with Rg = 0.31 – 0.45 nm. Large particles were disc shaped with 40 nm in diameter and 5 nm height.

Both methods supported induction period and kinetic dependent on the $[Na_2S]$ in the solution and the order of mixing the reagents. Based on the similarity of chemical behavior we suggest similarity in composition of technetium and rhenium species obtaind in the identical conditions.

The stability of M_3S_{10} (M = Tc, Re) in the resulting solution was dependent of the S^{2-} concentration in it. When higher than 0.06M Na_2S, further grouth of Tc and Re sulfide particles occurred for $\tau \geq 150$ h similar to observations made in [16]. For $[Na_2S] \leq 0.04$ M, the M_3S_{10} was reoxidized by present air to Tc(VII) within 175-200 hours thus being resolubilized.

The determination of the free Tc and Re species concentration with separation of ionic or nanocolloidal particles with 5 kD "Sartorius" ultramicrocentrifuge tubes gave evidence on the M_3S_{10} nanosulfide formation similar to that observed in [17]. The equation for the Tc sulfide solubility based on these figures was evaluated.The stoichiometry of technetium sulfide precipitated from aqueous solutions by sulfide action was recently confirmed by Liu, Tery and Jurisson in [18]. Some important data on the FeS effect onto Tc environmental behavior was reported by the same authors in [19]. Although the proposed technetium dioxide formula applied in [19] for the processing of the EXAFS data differs in the number of water molecule bounded to the TcO_2 from the recommended value (that is 1.6 H_2O according to [4], and very similar to 1.5 H_2O observed earlier for Re(IV) hydroxide), the results of [18,19] support in principle the evidence for the formulation of common technetium sulfide established by Lukens and co-workers [17]. Also the results of [20] are not in contradiction with [17]. Therefore we consider that the latter works provide a correct and important description of technetium sulfide as a complex compound formed from water solutions by reaction of pertechnetate with sulfide source while the intermediate Tc oxosulfides described in [21] are completely converted to sulfides in excess of S^{2-} ions.

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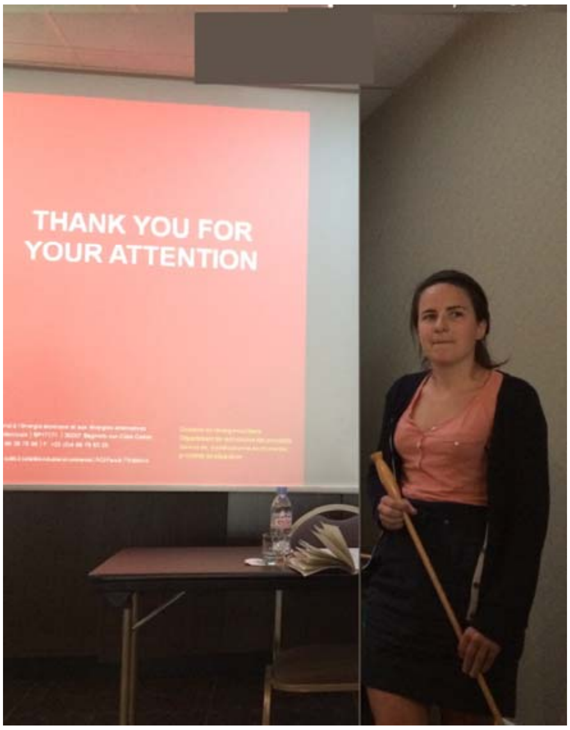

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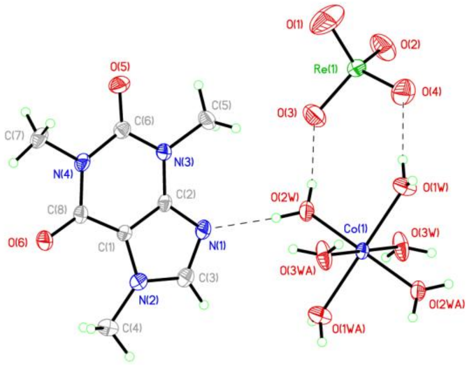
at La Baule - Le Croisic Bike Excursion Tour

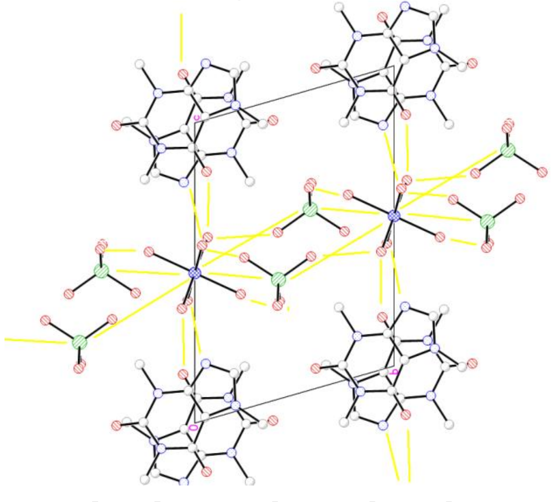
Supramolecular interactions of caffeine molecules with each other, water molecules and oxygen atoms of tetraoxidoanions in the three new different compounds **$Me(H_2O)_6[ReO_4]_2 \cdot$ caffeine** (Me = Co, Cd, Mg)

K.E. German[1,2], M.N. Glazkova[2], M.S. Grigoriev[1], Ya.A. Obruchnikova[1,2],
G.V. Kolesnikov[3], Yu.A. Ustynyuk[3], F. Poineau[4], O.S. Kryzhovets[2]

1 - A.N. Frumkin Institute of Physical Chemistry and Electrochemistry RAS, 31, Leninsky prospekt, Moscow, 119071, Russia. * - *guerman_k@mail.ru*
2 – Medical Institute REAVIZ, Moscow branch, Krasnobogatyrskaya str. 2 , Russia
3 – Lomonossov Moscow State University, Leninskie gory , 1, Moscow - Russia
4 – UNLV, Las Vegas, Nevada, USA

The antitumor and radiosensitizing drugs being caffeine derivatives that penetrate easily through blood brain barrier have been developed [1]. They are effective with radiation and chemotherapy treatment for cases of brain tumors. The caffeine derivatives were perspective for preparation of therapeutic agents to be used in a combined therapy for primary and metastatic brain tumors [1]. The mechanism of caffeine interaction was not clear anyhow. The precise structural data for caffeine are necessary for proper understanding of its action but are very limited. To increase the accuracy of the structural date and to simulate the interaction of caffeine with tetraoxidoanion and hydration water molecules the synthesis of new set of compounds of caffeine with three metal hexahydrate perrhenates was carried out from saturated water solutions and the single crystal thus obtained were subjected to X-ray structural study at Bruker KAPPA APEX II diffractometer. All three compounds have similar stocheometry but different coordination types. One type of coordination is represented at the figures for Cd salt.





Supramolecular interactions of caffeine molecules with each other, water molecules and oxygen atoms of tetraoxidoanions as in three different new compounds of **$Me(H_2O)_6[ReO_4]_2 \cdot$ caffeine (Me = Co, Cd, Mg)** are analyzed in these study through comparison of their different structures with quantum chemical analyses. The difference in structures is explained by the balance of cations hydration and coordination to perrhenate.

1. Vartanyan L.P., Kolesova M.B., Gornaeva G.F., Pustovalov Yu.I. Caffeine derivatives — perspective method of the search for anticancer and radiomodifying drugs in combined therapy for malignant brain tumors // Psychopharmacol. Biol. Narcol. — 2005. — Vol. 5, N 4. — P. 1093–1095.

Supramolecular interactions of caffeine molecules with each other, H_2O molecules and O-atoms of tetraoxidoanions in the three new different compounds

$Me(H_2O)_6[ReO_4]_2 \cdot$ caffeine (Me = Co, Cd, Mg)

K.E. German[1,2], M.N. Glazkova[2], M.S. Grigoriev[1], Ya.A. Obruchnikova[1,2],
G.V. Kolesnikov[3], Yu.A. Ustynyuk[3], F. Poineau[4], O.S. Kryzhovets[2]

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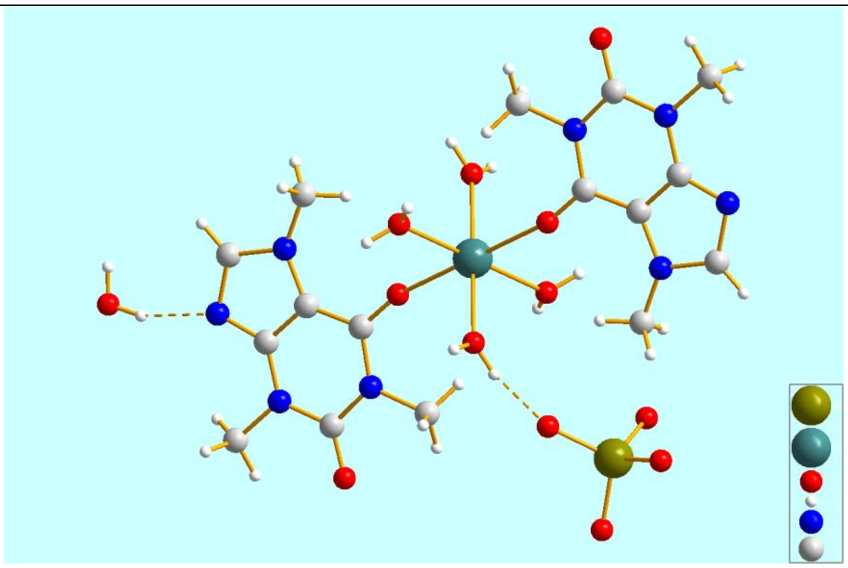
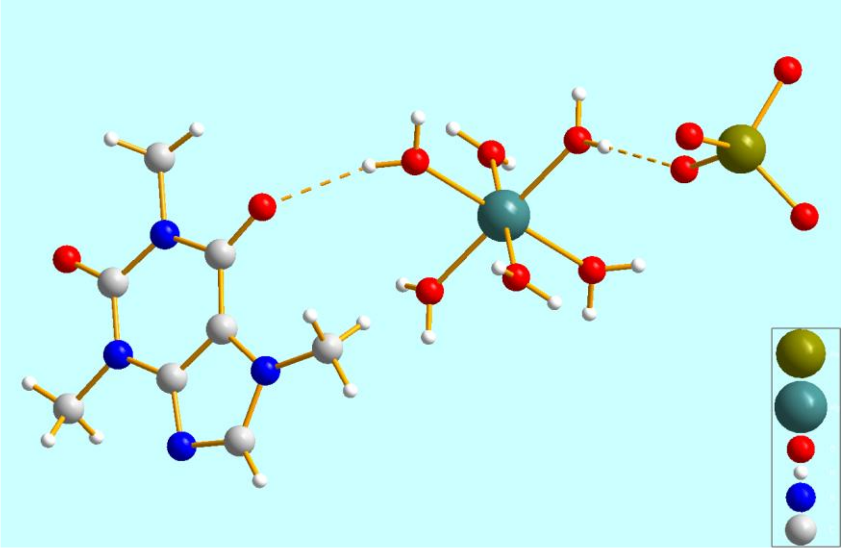
2 – Medical Institute REAVIZ, Moscow branch, Krasnobogatyrskaya str. 2 , Russia
3 – Lomonossov Moscow State University, Leninskie gory , 1, Moscow - Russia
4 – UNLV, Las Vegas, Nevada, USA

Goal

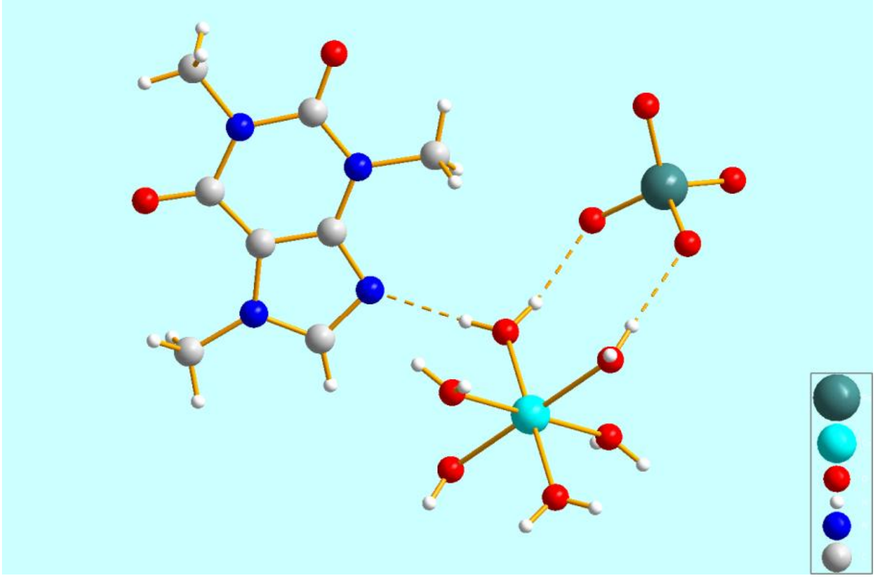
- We considered the modern database for caffeine derivatives and found out that the best R_f was disgraceful as 8 – 10 – 15 %
- Metal atoms were considered as a helpful tool for improving R_f for caffeine derivatives making possible its further modeling
- Secondary goal was the analyses of the possibility of weak and very weak H-bond interactions with hydrophobic ReO_4^- tetraoxidoanions



Cd

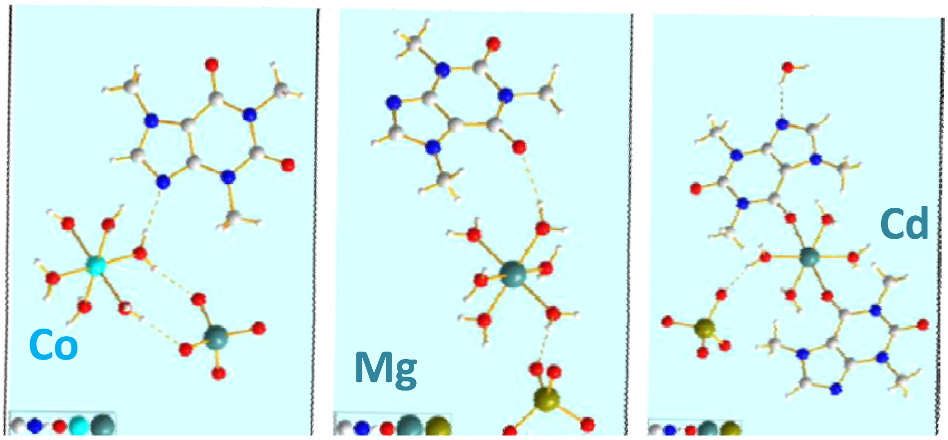


Mg

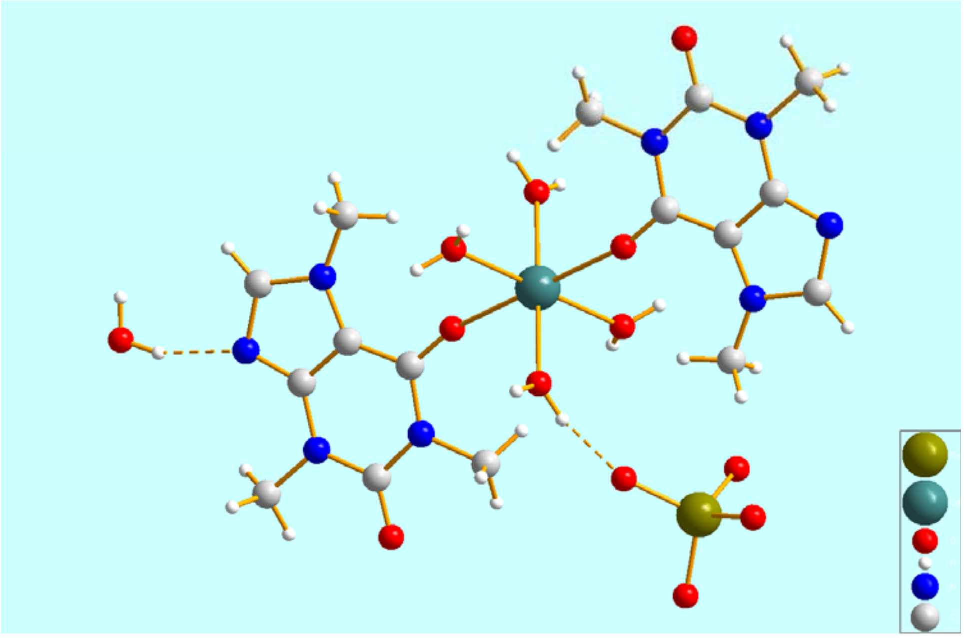


Co

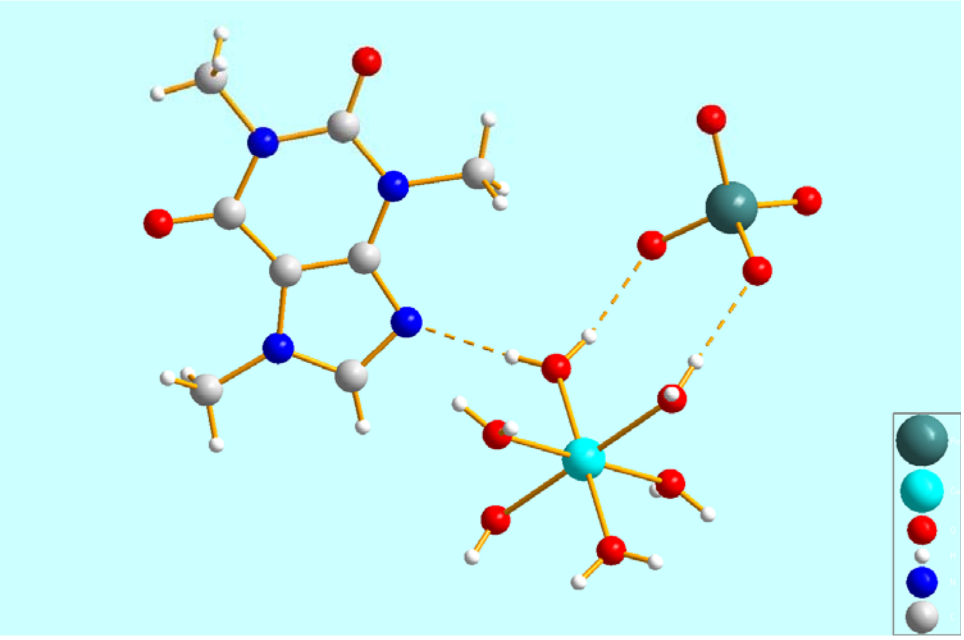
3 new different compounds
with identical general formula
Me $[ReO_4]_2 \cdot$ caffeine $\cdot$ $6H_2O$ (Me = Co, Mg, Cd)



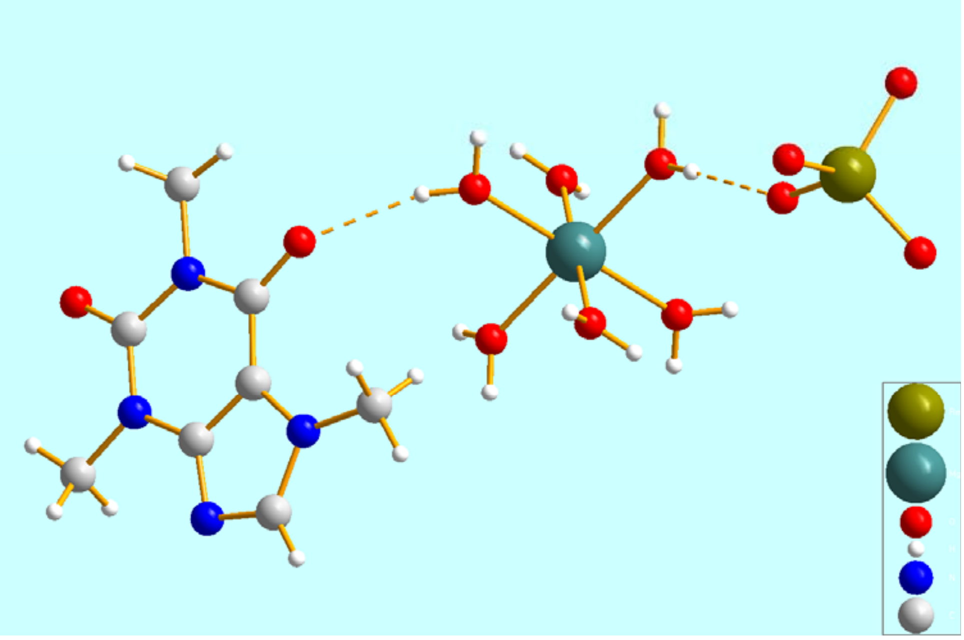
$Co(H_2O)_4[ReO_4]_2 \cdot Caffeine * 2H_2O$



$Co(H_2O)_6[ReO_4]_2 \cdot$ caffeine



$Mg(H_2O)_6[ReO_4]_2 \cdot$ caffeine



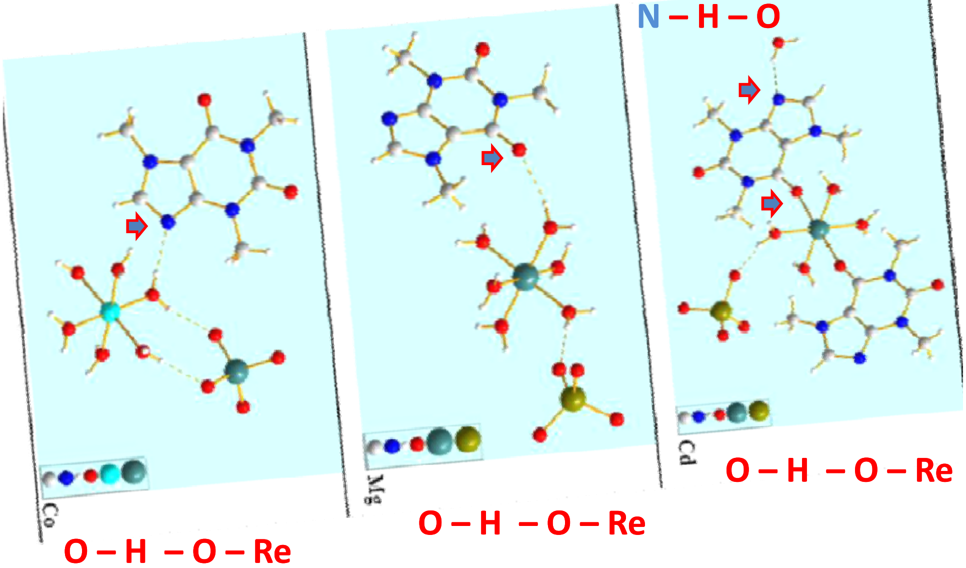
Comparing the structures

N – H – O – Co

O – H – O – Mg

O – H – O – Cd

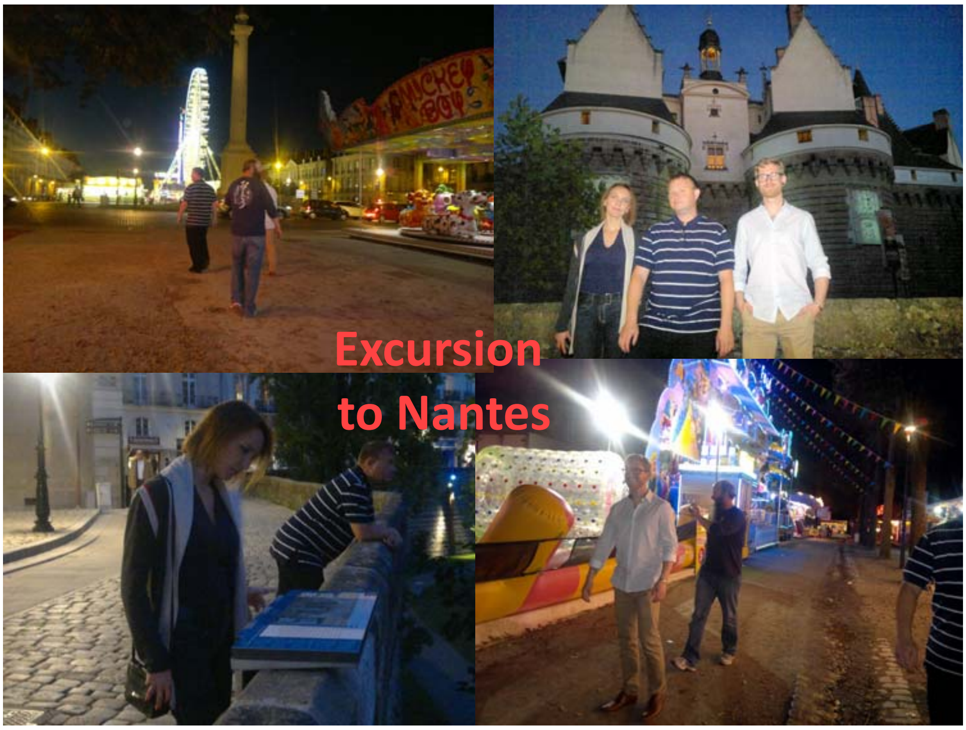
N – H – O



O – H – O – Re

O – H – O – Re

O – H – O – Re



Excursion to Nantes

500 m along Radioactivity

Biological reduction of pertechnetate ion in the implementation of technology biobarrer into aquifers contaminated with radioactive waste

A. Safonov[1,2], T. Khijniak[3], V. Ilin[1], K. German[1,2]

[1]Frumkin Institute of Physical Chemistry and Electrochemistry, RAS, Moscow, Russia
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The contamination of many sites with pertechnetate is a long-term problem due to its long half-life and extreme mobility in the environment. Microbial reduction of Tc (VII) is possible under neutral, acidic and alkaline environments. Cells of sulfate-reducing bacteria (*D. desulfuricans, D. vulgaris, D. fructosovorans*), metal-reducing bacteria (*S. putrefaciens, S. oneidensis* MR-1, *G. sulfurreducens*) and *Escherichia coli* anaerobically reduced soluble pertechnetate in neutral environments (Lloyd et al., 1997, 1999; Wildung et al., 2000) to form an insoluble oxide $TcO_2 * nH_2O$. It is assumed that reduction occurs with hydrogenase (De Luca et al., 2001; Lloyd et al., 1997).

The purpose of this investigation is to explore the possibility of microbial reduction of pertechnetate anions in groundwater horizons to insoluble tetravalent state reducing the risk to humans and the environment. Radioactive wastes with low activity are often accompanied by a large amount of nitrates, therefore there will be a competition between nitrate and pertechnetate in course of their reduction.

Preliminary experiments in batch cultures with sulfate-reducing bacteria show that in case of simultaneous presence of pertechnetate and nitrate, pertechnetate reduction was significantly reduced or completely blocked depending on nitrate concentration. Only after the complete exhaustion of nitrate, the pertechnetate reduction starts and could be effective. Experiments of bioaccumulation of pertechnetate by sediments of different organic content shows that amount of soluble organic matter and microbial activity plays a major role in the reduction and immobilization of extremely mobile pertechnetate ion.

To optimize the choices of potential bacteria, which will be used for biobarrer we have isolated the bacteria from different extreme habitats with neutral and alkaline pH - nitrate-reducers, sulfare-reducing and haloalkaliphilic bacteria. In this investigation, we study the features and dynamics of the reduction process of pertechnetate anion by communities of microorganisms and pure cultures isolated from groundwater of different environments depending on the concentration of oxygen and nitrate anions in batch cultures and columns.

On the basis of the obtained data the rates and characteristics of the processes will be calculated for the biotechnological process of reduction of nitrate ions in the contaminated environment in situ.

Lloyd J. R., Cole J. A., Macaskie L. E. Reduction and removal of heptavalent technetium from solution by *Escherichia coli*. // Journal of Bacteriology.- 1997.-179.- 2014–2021.
Lloyd J.R., Ridley J., Khizniak T., Lyalikova N.N., Macaskie L.E. Reduction of technetium by *Desulfovibrio desulfuricans*: biocatalyst characterization and use in a flowthrough bioreactor. // Applied and Environmental Microbiology.- 1999.- 65.- P. 2691–2696.
Wildung R. E., Gorby Y.A., Krupka K.M., Hess N.J., Li S.W., Plymale A.E., McKinley J.P., and Fredrickson J.K. Effect of electron donor and solution chemistry on products of dissimilatory reduction of technetium by *Shewanella putrefaciens*. // Applied and Environmental Microbiology.- 2000.- 66.- P. 2451–2460.
De Luca G., de Philip P., Dermoun Z., Rousset M., Verméglio A. Reduction of technitium(VII) by *Desulfovibrio fructosovorans* is mediated by a nickel iron hydrogenase. // Applied and Environmental Microbiology.- 2001.- 67(10).- P. 4583- 4587.

This work is supported by Russian Foundation for Basic Research project № 14-03-00067, 12-04-00646

Development of Bio filtration system for cleaning solutions from uranyl and pertechnetate anions

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[1]Frumkin Institute of Physical Chemistry and Electrochemistry, Russian Academy of Sciences, Moscow, Russia

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Liquid radioactive wastes (LRW) are the one of important problems in radioactive waste management. Nowadays because of the large volumes of LRW one of the treatments ways is purification. Most of purification techniques are based on physical-chemistry processes (ion exchange, liquid extracting and so on). Microbial – metal interaction has been studied intensively and mechanisms of metal and radionuclide reduction were described. To date, considerable information on biotechnological methods for purification of solutions containing uranium, strontium, cesium and iodine (Macaskie, 1991) are accumulated and considered as cost and environmentally effective.

Ability to enzymatic reduction of hexavalent uranium has been found in a number of sulfate and iron-reducers. Some mesophilic bacteria could not only reduce, but also to obtain energy for growth (*Geobacter*, *Shewanella, Desulfotomaculum*) (Lovley, 1993; Pietzsch, Babel, 2003), while others were only able to reduce uranium *(Desulfovibrio*). Also, technetium reduction was detected .

The aim of this study is to develop technique, based on biological processes for cleaning LRW solutions from uranyl and pertechnetate anions.

Previously, for purification (detoxification) of low-radioactive LRW the model laboratory system based on immobilized cells of sulfate-reducing bacteria was developed and tested. The system operated in flow providing complete removal of sodium pertechnetate (50 μM) at flow rate of 16 ml/h under neutral pH conditions. The use of immobilized cells of bacteria for biotechnological solutions has several advantages compared with the slurry. The cells attached to the carrier aren’t washed out with passing through solution. It has a longer lifetime of the system and higher resistance to environmental stress (Lloyd J.R. et al, 1999).

In the presented investigation we will use the haloalkaliphilic and sulphate-reducing bacteria for reduction of technetium and uranium under alkaline and neutral conditions. The bacteria of genus *Halomonas* were tested and were able to reduce oxyanions under different conditions (Shapovalova A.A. et al, 2008).

Our experiments show that in case of mixture of anions (nitrate, senate and vanadate), consecutive reduction occurs, nitrate being reduced firstly, than selenate was the following and, at last, vanadate is reduced in accordance with their oxidation potentials.

Designed laboratory system will be tested for simultaneous reduction of uranium and technetium at the “Radon”.

Lovley D.R., Roden E.E., Phillips E.J., Woodward J.C. Enzymatic iron and uranium reduction by sulfate-reducing bacteria. // Marine Geology.- 1993.- 113.- P. 41-53

Lloyd J.R., Ridley J., Khizhniak T.V., Lyalikova N.N., Macaskie L.E. Reduction of technetium by *Desulfovibrio desulfuricans*: biocatalyst characterization and use in flow-through bioreactor. *J. Appl. Environ. Microbiol.*, 1999, v. 65, N 6, p. 2691-2696

Shapovalova A.A., Khijniak T.V., Tourova T.P., Muyzer G., Sorokin D.Y. Heterotrophic denitrification at extremely high salt and pH by haloalkaliphilic Gammaproteobacteria from hypersaline soda lakes. *Extremophiles*, 2008, N 12, p. 619-625

Platinum And Rhenium Recovery From Pt-Re Reforming Catalysts via Plasma Arc Technology

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[b]Tetronics International

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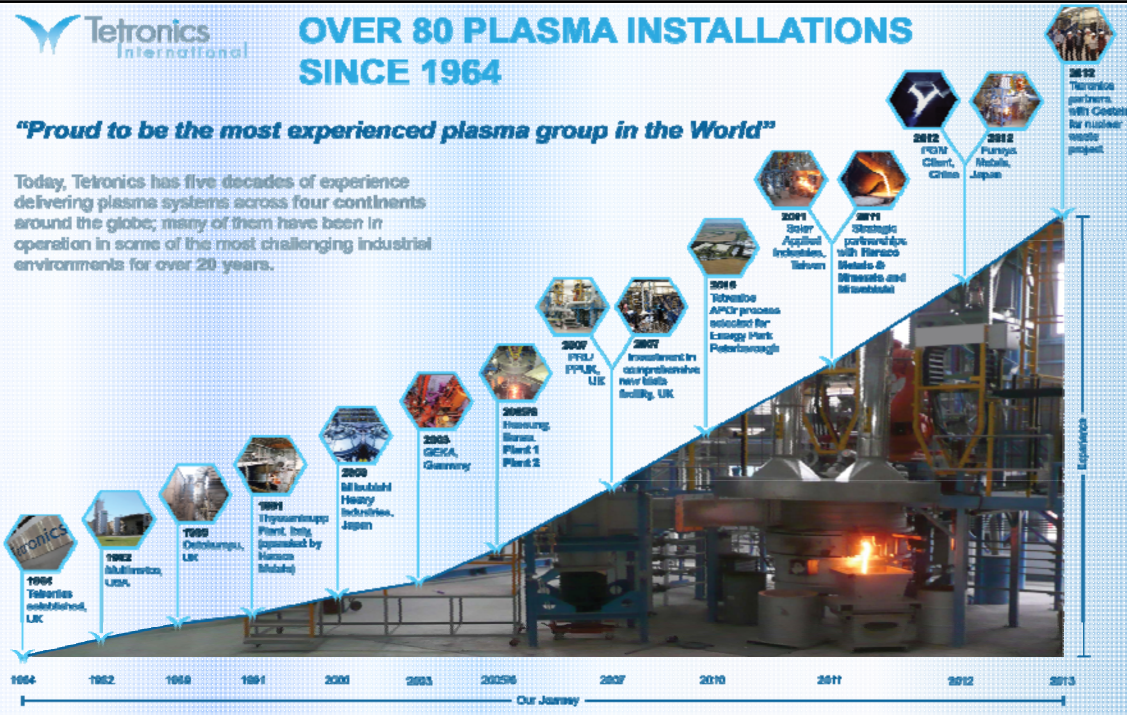
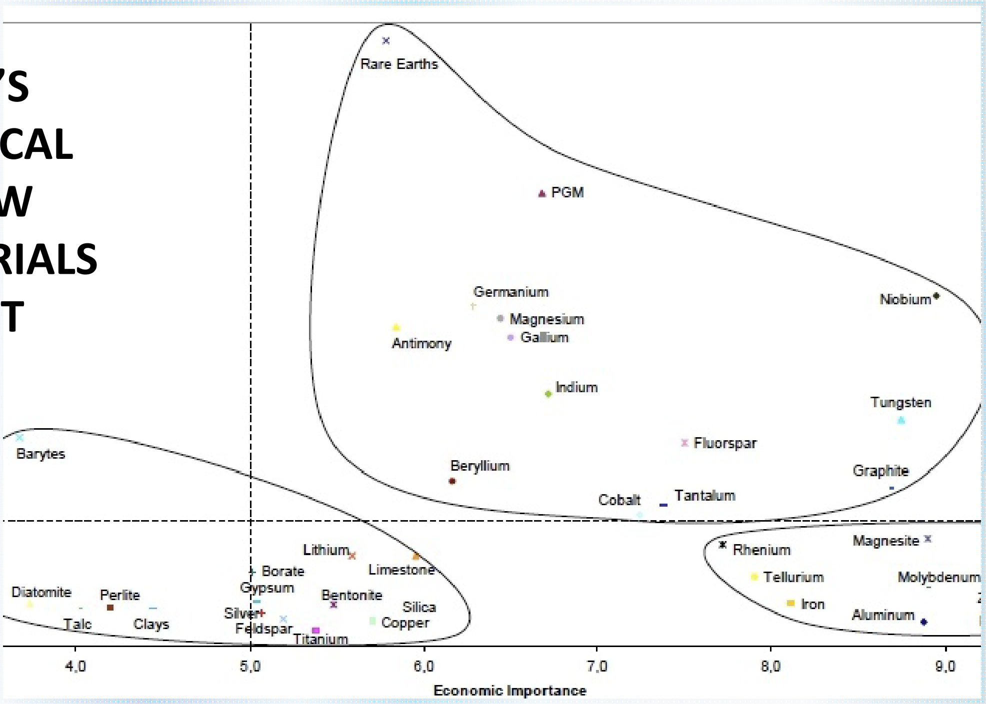
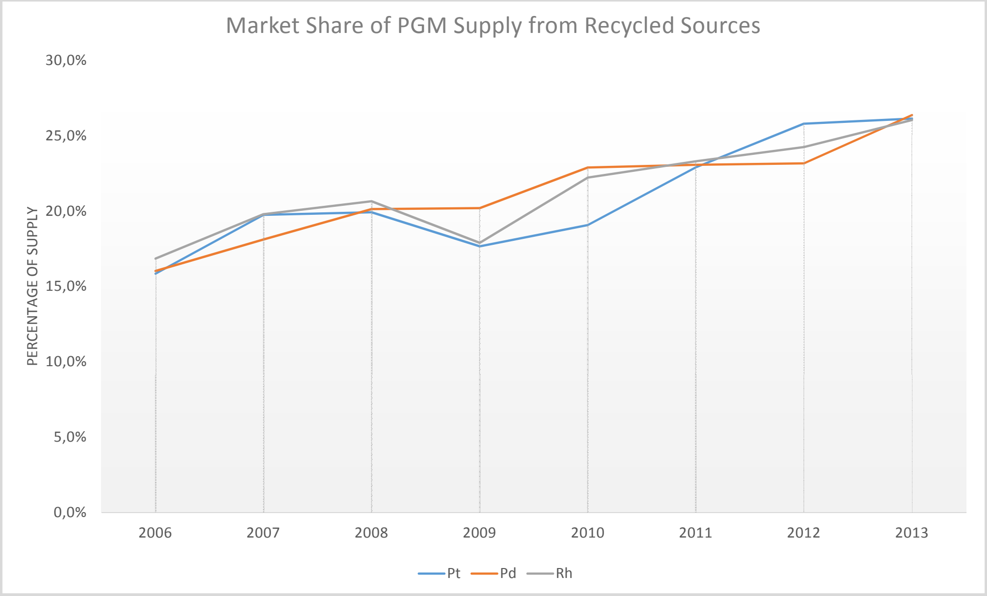


EU'S CRITICAL RAW MATERIALS LIST



Increasing Importance of Secondary Sources of PGMs



Thermal Plasma Technology

An electric current heats gas molecules to >5000K which causes electrons to be stripped from atoms forming a stream of ionised species

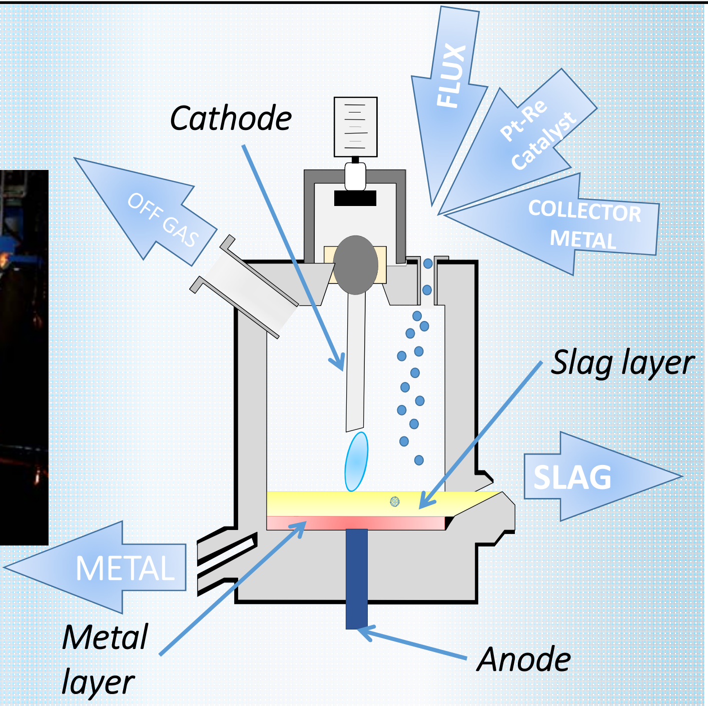
A high degree of ionisation causes a local thermodynamic equilibrium to be established between the electrons and the heavier species.

This causes the temperature of the heavier species and the temperature of the electrons to converge.

Thermal plasma streams reach temperatures between 10000 and 30000K at atmospheric pressure.

70 mm cathode torch argon plasma ~650 mm long; 1000 A, 450 kW

The Process Essentials

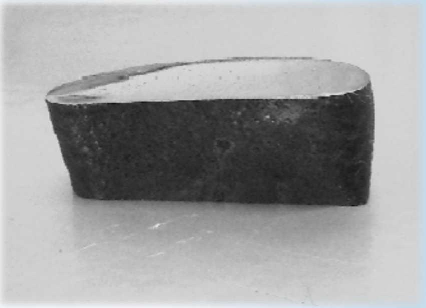


Platinum and Rhenium Recovery From Pt-Re Reforming Catalyst

1000 kg of catalyst fed (PGM value £180,000) into the plasma furnace over 5 trials.

Pt-Re/Al_2O_3 Catalyst with metal loadings of ***0.34 wt% Pt*** *and* ***0.24 wt% Re.***

Pt and Re were extracted from the catalyst into an iron collector metal with a concentration of **2 wt% Pt and 1.5 wt% Re.**



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Technetium and Rhenium Complexes with Heavy Arylchalcogenolates

Bruno N. Cabral[1*], Ernesto S. Lang[1], Adelheid Hagenbach[2], Lars Kirsten[2], Ulrich Abram[2]

[1]*Universidade Federal de Santa Maria, Brazil*; [2]*Freie Universität Berlin, Germany*

*e-mail: cabral@zedat.fu-berlin.com

Aryltellurolate and arylselenolate anions, which can be prepared from reactions of diaryldiselenides or diarylditellurides with $LiBH_4$, have been used for the synthesis of novel complexes with M–Se and M–Te bonds. Square-pyramidal oxidometallates of the general formula $[M^{V}O(EAr)_4]^-$ or trigonal-bipyramidal $[M^{III}(PPh_3)(L)(EAr)_3]$ complexes (M = Tc, Re; E = Se, Te) have been isolated from respective reactions with $[MOCl_4]^-$ or $[MCl_3(PPh_3)(CH_3CN)]$ (Fig.1).

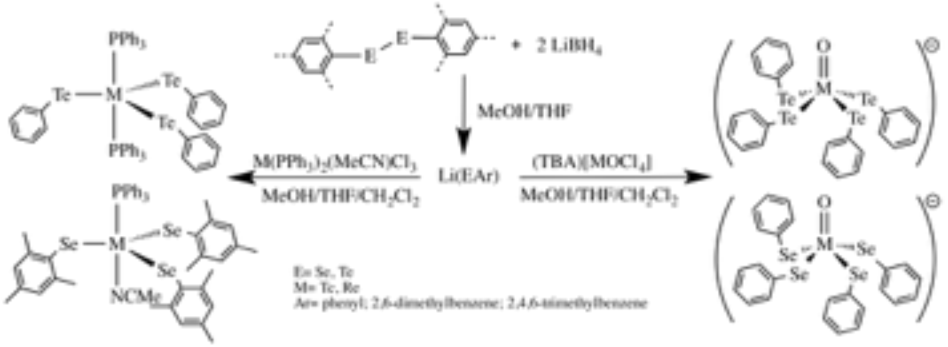


Fig. 1: Syntheses performed.

The structures of some selected compounds are shown in the Fig. 2. The complexes show similar coordination features as observed for the arylthiolato compounds.[1-4] A remarkable difference is the formation of $[M^{III}(PPh_3)_2(TePh)_3]$ complexes (Fig. 2c) with two axial PPh_3 ligands. Presumably, the long M–Te bonds (2.57 Å) allow the formation of coordination pockets being sufficient large for the accommodation of PPh_3, which is not the case for the selenium analogs or complexes with more bulky aryltellurolates, where the second axial position is occupied by acetonitrile.

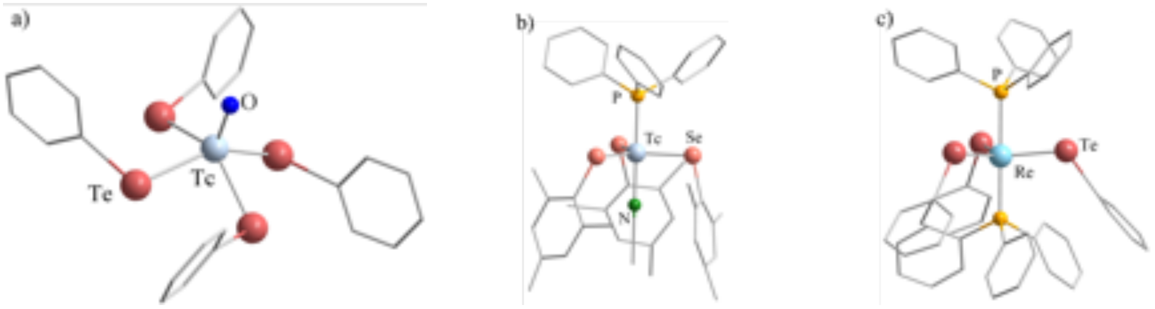


Fig. 2: Molecular structures of a) $[TcO(TePh)_4]^-$, b) $[Tc(PPh_3)(MeCN)(SeMes)_3]$ and c) $[Re(PPh_3)_2(TePh)_3]$

1. McDonell, A. C.; Hambley, T. W.; Snow, M.R .; Wedd, A. G. *Austr. J. Chem.,* **1983**, *36,* 253

2. Dilworth, J. R.; Neaves, B. D. *Inorg. Chim. Acta ,* **1982**, *65,* L223

3. Hamorl, T. A.; Hussain, W.; Jones, C.J .; McCleverty, J. A.; Rothin, A. S. *Inorg. Chim. Acta.,* **1988**, *146,* 181

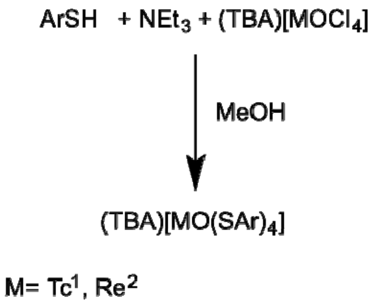
4. Davison, A.; de Vries, N.; Dewan, J.C .; Jones, A. G. *Inorg. Chem.* **1988**, *27,* 1574

Technetium and Rhenium Complexes with Heavy Arylchalcogenolates

Bruno N. Cabral[1*], Ernesto S. Lang[1], Adelheid Hagenbach[2], Lars Kirsten[2], Ulrich Abram[2]
[1]Universidade Federal de Santa Maria, Brazil; [2]Freie Universität Berlin, Germany

2nd October 2014

Arylthiolates of Tc(V)/Re(V)

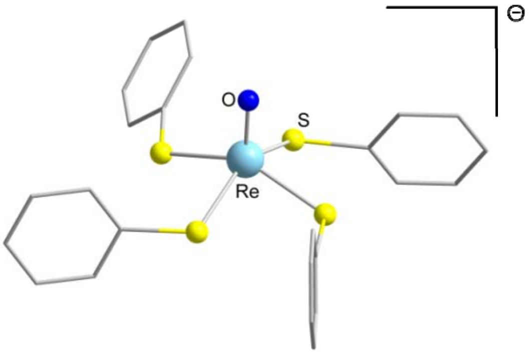


$ArSH + NEt_3 + (TBA)[MOCl_4]$

MeOH

$(TBA)[MO(SAr)_4]$

M= Tc[1], Re[2]



1. Hamorl, T. A.; Hussain, W.; Jones, C.J .; McCleverty, J. A.; Rothin, A. S. *Inorg. Chim. Acta.,* **1988**, *146,* 181
2. McDonell, A. C.; Hambley, T. W.; Snow, M.R .; Wedd, A. G. *Austr. J. Chem.,* **1983**, *36,* 253

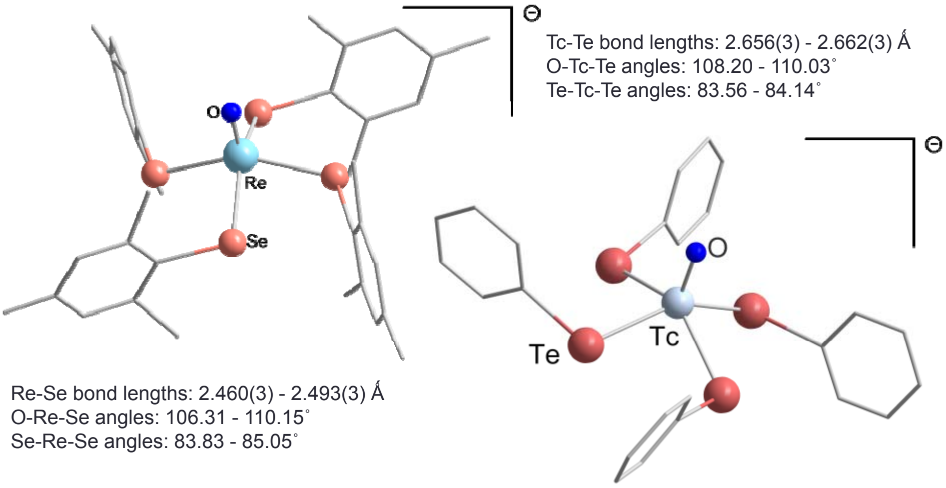
Heavy Arylchalcogenolates of Tc(V)/Re(V)

$$(ArE)_2 + 2\ LiBH_4 \xrightarrow[Ar]{MeOH/THF} 2\ Li(EAr)$$

$$2\ Li(EAr) + 0.5\ (TBA)[MOCl_4] \xrightarrow[Ar]{MeOH/THF/CH_2Cl_2} 0.5\ (TBA)[MO(EAr)_4]$$

M= Tc, Re
E= Se, Te
Ar= $-C_6H_5$, $-2,6\text{-}Me_2C_6H_3$, $-2,4,6\text{-}Me_3C_6H_2$

Heavy Arylchalcogenolates of Tc(V)/Re(V)



Tc-Te bond lengths: 2.656(3) - 2.662(3) Å
O-Tc-Te angles: 108.20 - 110.03˚
Te-Tc-Te angles: 83.56 - 84.14˚

Re-Se bond lengths: 2.460(3) - 2.493(3) Å
O-Re-Se angles: 106.31 - 110.15˚
Se-Re-Se angles: 83.83 - 85.05˚

Arylthiolates of Tc(III)/Re(III)

Htmbt + NaOMe + $(NH_4)_2[TcCl_6]$ + Zn^0

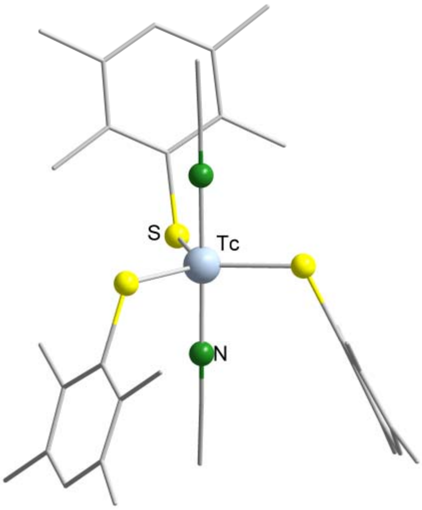
$\downarrow$ MeCN/MeOH

$[Tc(tmbt)_3(MeCN)_2]^3$

$[Re(SPh)_3(MeCN)(PPh_3)]^4$

$\uparrow$ MeOH

PhSH + NEt_3 + $ReCl_3(MeCN)(PPh_3)_2$



3. Davison, A.; de Vries, N.; Dewan, J.C .; Jones, A. G. *Inorg. Chem.* **1988**, *27,* 1574
4. Dilworth, J. R.; Neaves, B. D. *Inorg. Chim. Acta ,* **1982**, *65,* L223

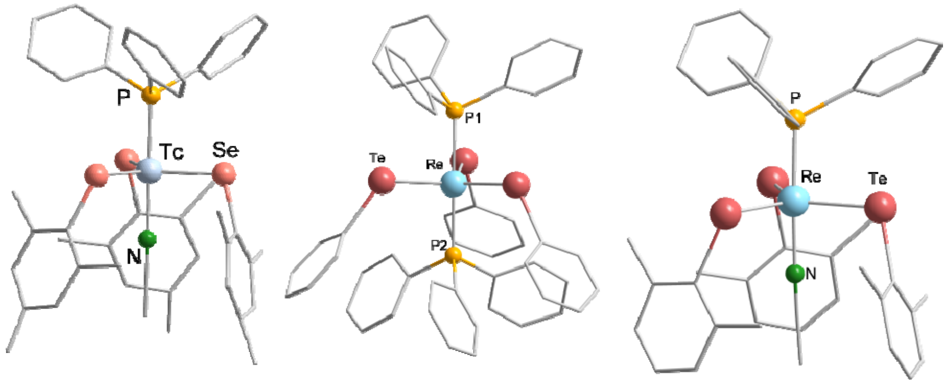
Heavy Arylchalcogenolates of Tc(III)/Re(III)

$$1.5\ (ArE)_2 + 3\ LiBH_4 \xrightarrow[Ar]{MeOH/THF} 3\ Li(EAr)$$

$$3\ Li(EAr) + M(PPh_3)_2(MeCN)Cl_3 \xrightarrow[Ar]{MeOH/THF/CH_2Cl_2} \begin{array}{c}[M(PPh_3)_2(TePh)_3] \\ [M(PPh_3)(MeCN)(TeAr)_3] \\ [M(PPh_3)(MeCN)(SeAr)_3]\end{array}$$

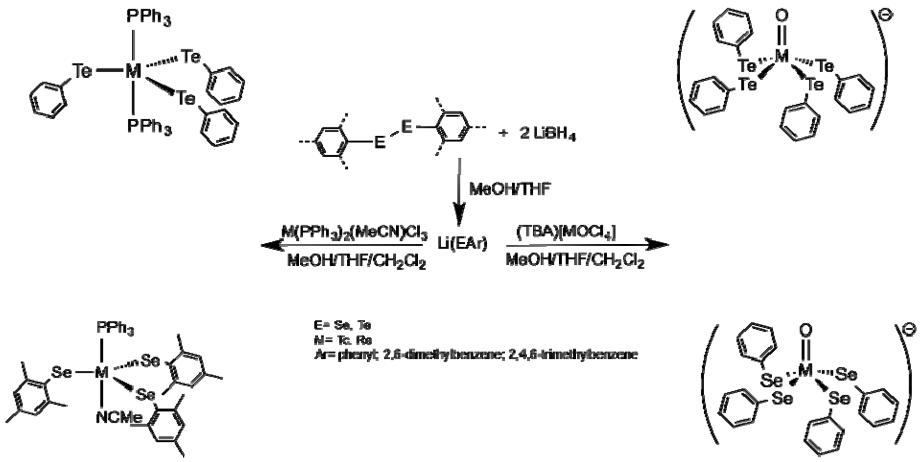
M= Tc, Re
E= Se, Te
Ar= $-C_6H_5$, $-2,6\text{-}Me_2\text{-}C_6H_3$, $-2,4,6\text{-}Me_3C_6H_2$

Heavy Arylchalcogenolates of Tc(III)/Re(III)



Complex	M-E (Å)	M-P (Å)	M-N (Å)
$[Tc(MeCN)(SAr)_3]^3$	2.24 - 2.25	-	2.04
$[Re(TeDmph)_3(PPh_3)(MeCN)]$	2.54 - 2.56	2.35	2.08

Summary



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3 OCTOBER 2014

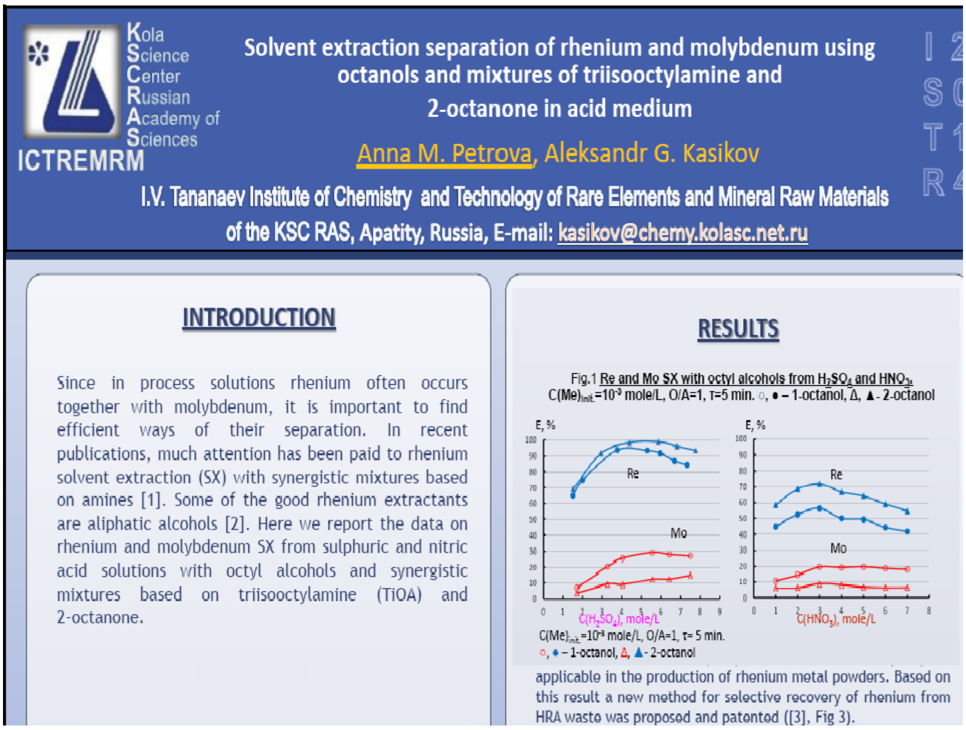
OFFICIAL CERTIFICATE

The International Advisory Committee of ISTR-2014 and International Jury of ISTR-2014 has resolved that the 1st prize and Mendeleev medal for the best poster presentation at ISTR-2014 is awarded to **Bruno Noschang Cabral** for the presentation **“Technetium and Rhenium Complexes with Heavy Arylchalcogenolates”** .

Professor Massoud Fattahi-Vannani
For the Local Committee

Professor Konstantin German
For the International Jury

Prof. Massoud Fattahi (Chairman Organising Committee);
Telephone +33251858407 ; e-mail: fattahi@subatech.in2p3.fr



Solvent extraction separation of rhenium and molybdenum using octanols and mixtures of triisooctylamine and 2-octanone in acid medium

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INTRODUCTION

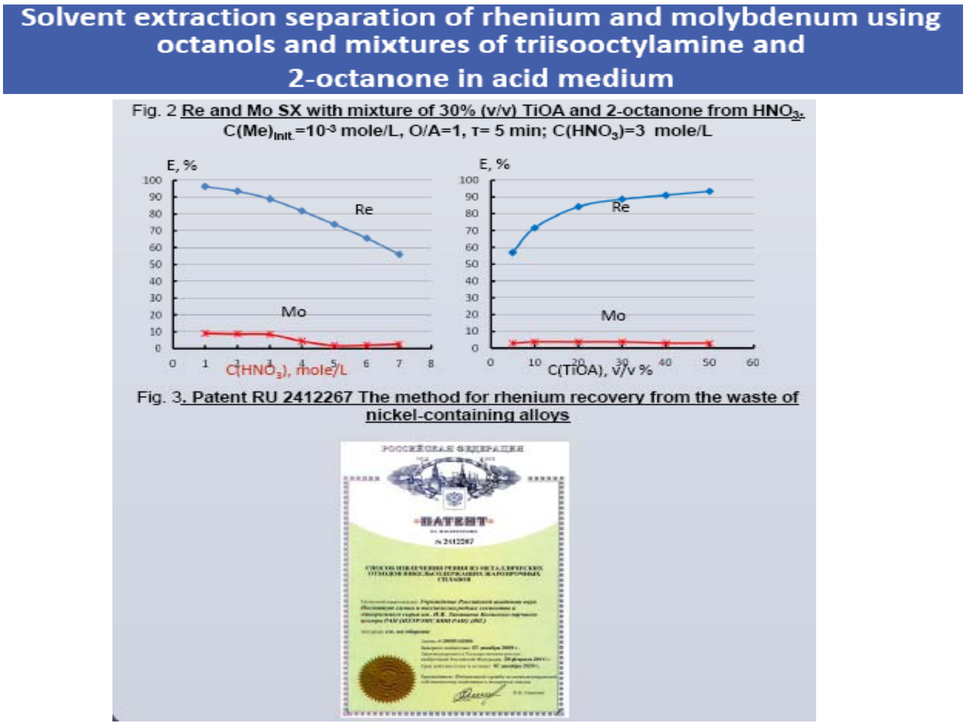
Since in process solutions rhenium often occurs together with molybdenum, it is important to find efficient ways of their separation. In recent publications, much attention has been paid to rhenium solvent extraction (SX) with synergistic mixtures based on amines [1]. Some of the good rhenium extractants are aliphatic alcohols [2]. Here we report the data on rhenium and molybdenum SX from sulphuric and nitric acid solutions with octyl alcohols and synergistic mixtures based on triisooctylamine (TiOA) and 2-octanone.

RESULTS

Fig.1 Re and Mo SX with octyl alcohols from H_2SO_4 and HNO_3. $C(Me)_{init.}=10^{-3}$ mole/L, O/A=1, τ=5 min. ○, ● – 1-octanol, Δ, ▲ - 2-octanol

$C(Me)_{init.}=10^{-3}$ mole/L, O/A=1, τ= 5 min.
○, ● – 1-octanol, Δ, ▲ - 2-octanol

applicable in the production of rhenium metal powders. Based on this result a new method for selective recovery of rhenium from HRA waste was proposed and patented ([3], Fig 3).



Solvent extraction separation of rhenium and molybdenum using octanols and mixtures of triisooctylamine and 2-octanone in acid medium

Fig. 2 Re and Mo SX with mixture of 30% (v/v) TiOA and 2-octanone from HNO_3. $C(Me)_{init}=10^{-3}$ mole/L, O/A=1, τ= 5 min; $C(HNO_3)=3$ mole/L

Fig. 3. Patent RU 2412267 The method for rhenium recovery from the waste of nickel-containing alloys

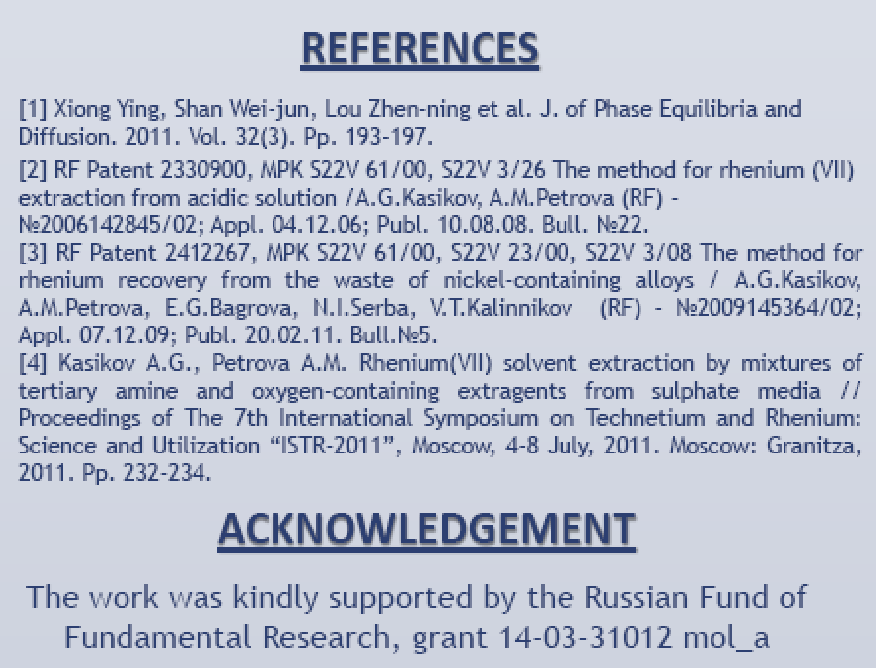
CONCLUSIONS

1. It has been established that rhenium SX with aliphatic alcohol performs better in sulphuric acid medium than in nitric one. When separating rhenium and molybdenum, alcohol should be secondary since it makes a good extractor for rhenium(VII) and poor - for molybdenum (Fig. 1). For example, extracting from 6 mole/L H_2SO_4 provides a maximal rhenium distribution ratio of ~ 55 for 2-octanol. At the same time, the Mo distribution ratios do not exceed 0.4. So, the metal separation factor is $B_{Re/Mo}>100$, which makes 2-octanol a selective extractant for Re solvent extraction from sulphuric acid solutions in the presence of Mo.

2. Secondary octyl alcohol was tested for rhenium selective SX from sulphuric acid leaching solution of a ZhS-32 superalloy waste, and it gave satisfactory results for rhenium recycling from nickel-based heat-resistant alloy (HRA) waste, yielding the NH_4ReO_4 salt applicable in the production of rhenium metal powders. Based on this result a new method for selective recovery of rhenium from HRA waste was proposed and patented ([3], Fig 3).

3. Experiments have shown that for selective extraction of rhenium from nitric acid solutions it is appropriate to use a synergistic mixture of triisooctylamine with octyl ketone [4]. Since in solutions with pH<1, Mo(VI) is predominantly present as oxycations not prone to form complex anions in the HNO_3 medium, it is almost unextractable by a tertiary amine following the anion-exchange mechanism. Even at a TiOA concentration increased in 2-octanone from 5 to 50%, when extracting from 3 mole/L HNO_3, the D_{Mo}, did not exceed 0.09, whereas D_{Re} increased more than 10 fold (from 1.3 to 14). Increasing of the nitric acid concentration from 1 to 7 mole/L resulted in decreasing of the distribution coefficient from 26 to 1.3 for 30% TiOA in 2-octanone. Noticeable Mo(VI) SX terminates in solutions with more than 5 mole/L HNO_3.

4. A synergistic mixture of TiOA with 2-octanone can be considered as a promising extractant for separating rhenium and molybdenum in acid solutions, which has been proved in trial experiments on rhenium separation from nitric acid leaching solutions of ZhS-32 alloy.



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[2] RF Patent 2330900, MPK S22V 61/00, S22V 3/26 The method for rhenium (VII) extraction from acidic solution /A.G.Kasikov, A.M.Petrova (RF) - №2006142845/02; Appl. 04.12.06; Publ. 10.08.08. Bull. №22.

[3] RF Patent 2412267, MPK S22V 61/00, S22V 23/00, S22V 3/08 The method for rhenium recovery from the waste of nickel-containing alloys / A.G.Kasikov, A.M.Petrova, E.G.Bagrova, N.I.Serba, V.T.Kalinnikov (RF) - №2009145364/02; Appl. 07.12.09; Publ. 20.02.11. Bull.№5.

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ACKNOWLEDGEMENT

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Anna Petrova and Yana Obruchnikova at the Thursday session

Evaluation of Rhenium Production Rates in Tungsten Irradiated in Fast Reactors by Using Continuous Energy Monte Carlo Code MVP

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Après ORIENT research program, newly initiated in 2011, includes transmutation of stable elements to create rare metals / rare earth (RE) elements by (n,γ) reaction with subsequent β^- decays in the reactors. In this paper, we discuss Rhenium (Re) production by irradiating Tungsten (W) metal in fast reactors. Re is one of the rarest metals, and W-Re is well-known forefront, heat-resistant super-alloy for jet- engine, for instance.

Fig. 1 shows the transmutation scheme of W to Re including neighbor element chains.

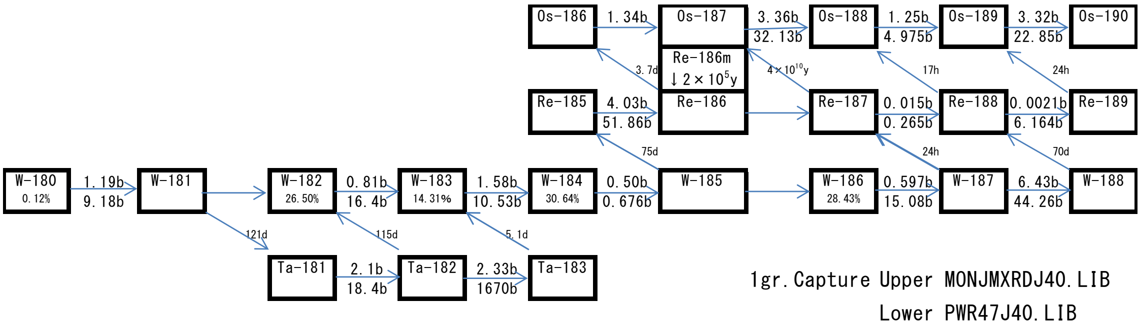

Fig.1 Transmutation scheme of Re production from irradiated W in reactors

In the figure, upper data of each horizontal line indicates the neutron energy averaged capture cross section in fast reactors while the lower does that in light water reactors (LWRs). The differences are one order or more, which means that the exact evaluation of neutron energy spectra of the reactors or zones of the reactor where W is irradiated is crucial to determine the production rate of Re. Thus we employed the continuous energy Monte Carlo Code MVP[*1], where the neutron energy spectra of each zone of reactors are exactly simulated as well as detailed configurations for evaluating the effective neutron cross sections and neutron flux, while the conventional ORIGEN-2 with one group cross section system[*2] is used for calculating the transmutation of each nuclides.

The total flux of fast reactor is generally one order higher than that of LWRs, thus a middle scale fast reactor is employed to irradiate the target assembly that contains W pellets in the pins.

Fig.2 illustrates the core layout and target assemblies for Re production from W irradiated in the fast reactor with 710 MWt. A total of 54 target assemblies containing inner 19 pins of tungsten (W) pellets surrounded by 42 pins of zirconium hydride(ZrH_2) pellets are located at the peripheral of the core, the equivalent diameter and height of which is about 1.8 m and 0.9 m, respectively. Hydride is employed to increase the transmutation rate by slowing down the fast neutrons, where the capture cross section of W is larger at lower neutron energy regions.

Case 1 of Table 1 lists the weight of the transmutation from natural W to total Re after one year irradiation and Fig.3 shows the change of the isotopes during two years including one year cooling time after the irradiation.

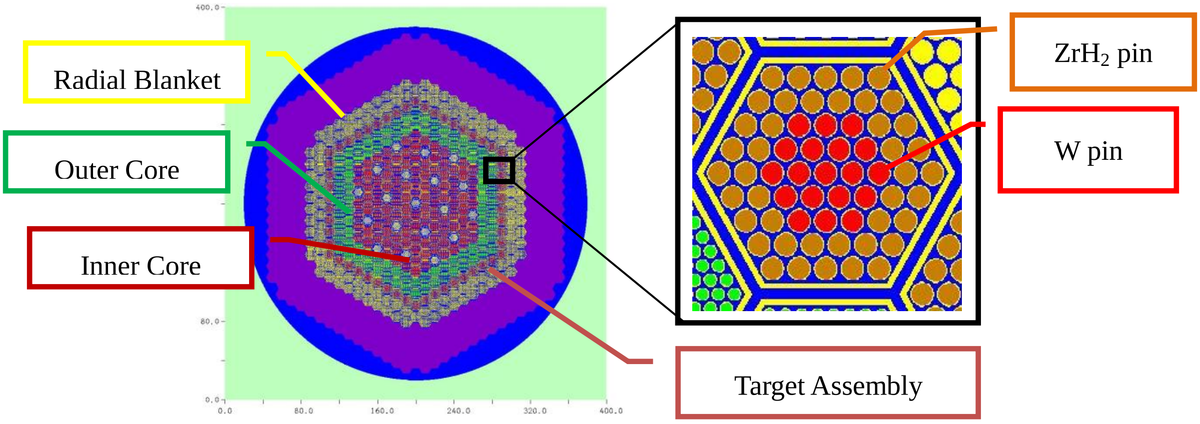

Fig.2 Core layout and target assemblies with tungsten and hydride pins

Fig. 3 indicates the main radioactivity istope of Re, Re-188, will be decayed rapidly if Re is separeted from W just after the irradiation because the parent of Re-188 is W-188. In 4 months cooling, the secondly intensive radioactivity, Re-186, is decreased less than the exemption level, 1000 Bq/g. Case 2 of Table 1 is the Re production when neutron moderator is not used and the whole 61 pins of the target assembly are W metal. The loaded weight of W in Case 2 is 4 times more than that of Case 1, though the production of Re is less by one order than that of Case 1. This is mainly due to the neutron spectrum softening effect of zirconium hydride.

The effective capture cross section of W-186, the main parent of Re, is 1.731 barn for Case 1 evaluated by MVP code, while that of Case 2 is 0.012 barn. This cross sections of Case 2 seems much smaller than 0.597 barn shown in Fig. 1, because the former is the effective one considering the heterogeneous effect on neutron self shielding and the latter is that for infinitely diluted nuclide. Precise seaparation of Re from rad. W, Ta and Os will be issue.

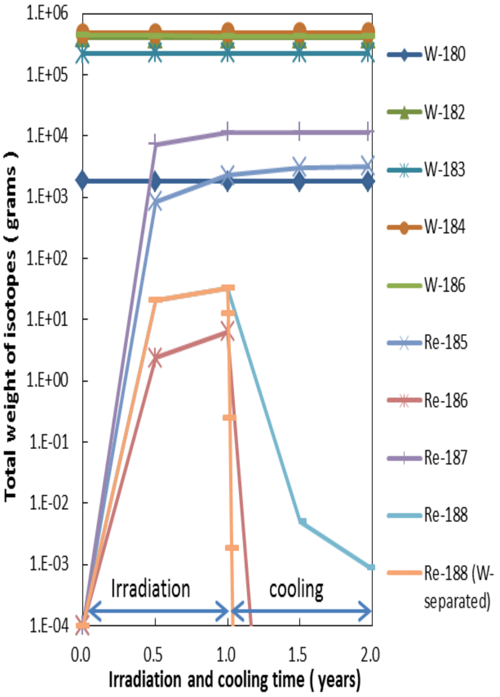

Fig.3 Change of isotopes during irradiation and cooling

Table1 Total mass of W and Re along with irradiation and cooling

Case	Number of W pins	Number of ZrH_2 pins	Loaded weight of W(g)	Produced weight of Re after one year irradiation(g)
1 (Reference)	19	42	1.6×10^6	1.4×10^4
2(No moderator)	61	0	5.0×10^6	1.5×10^3

*1) Nagaya,Okumura,Mori and Nakagawa、” MVP/GMVP Version 2 : General Purpose Monte Carlo Codes for Neutron and Photon Transport Calculations based on Continuous Energy and multigroup Methods”(MVP/GMVP Version 2 JAERI 1348,June 2005 Japan Atomic Energy Research Institute.
*2) Okumura, Sugino, Kojima, Jin, Okamoto, Katakura, JAEA-Data/Code 2012-032
A Set of ORIGEN2 Cross Section Libraries Based on JENDL-4.0: ORLIBJ40, Dec. 2012, Japan Atomic Energy Research Institute.

Evaluation of Rhenium Production Rates in Tungsten Irradiated in Fast Reactors by Using Continuous Energy Monte Carlo Code MVP

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The Significance of Producing Rhenium

- In recent years, the demand for rhenium is growing as an additive to super alloys for jet engines.
- However, rhenium is one of the rarest elements in earth.
- Because there is no ore containing rhenium alone, and it is mainly included in copper or molybdenum ore, production amount of them significantly affect the supply of rhenium.
- Therefore, active technology for creation of rhenium that we advocate has a great value.
- Après ORIENT research program, newly initiated in 2011, includes transmutation of stable elements to create rare metals / rare earth (RE) elements by (n , gamma) reaction with subsequent beta decays in the reactors.

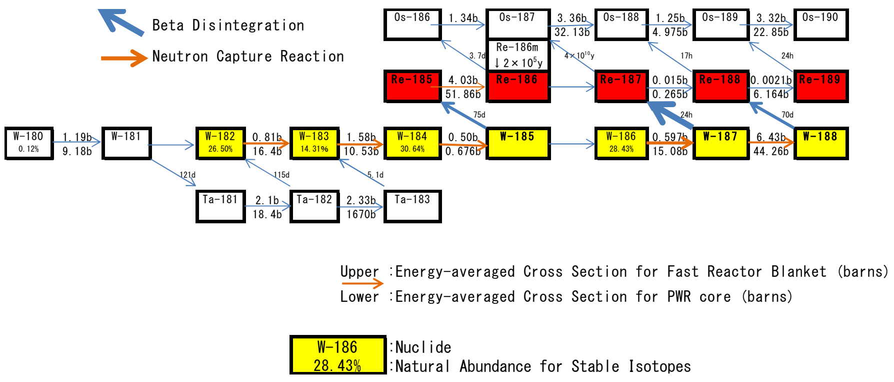
Objectives

To clarify the feasibility of Rhenium (Re) production by irradiating Tungsten (W) metal in fast reactors by using the Monte Carlo Calculations.

Irradiation Core Model and Evaluation Method

Fig. 1 shows the transmutation scheme of W to Re including neighbor element chains. In the figure, upper data of each horizontal line indicates the neutron energy averaged capture cross section in fast reactors while the lower does that in light water reactors. The differences are one order or more, which means that the exact evaluation of neutron energy spectra of the reactors. Thus we employed a continuous energy Monte Carlo Code MVP[*1], where the neutron energy spectra of each zone of reactors can be exactly simulated as well as detailed configurations for evaluating the effective neutron cross sections and neutron flux, while the conventional ORIGEN-2 with one group cross section system[*2] is used for calculating the transmutation rates of each nuclides by applying the effective cross section and flux evaluated by the MVP code.

We employed a medium size fast reactor illustrated in Fig. 2, as the energy integrated neutron flux is higher than that of typical LWRs. The target assemblies are located at the peripheral of the core for minimizing the impact to the core performances.

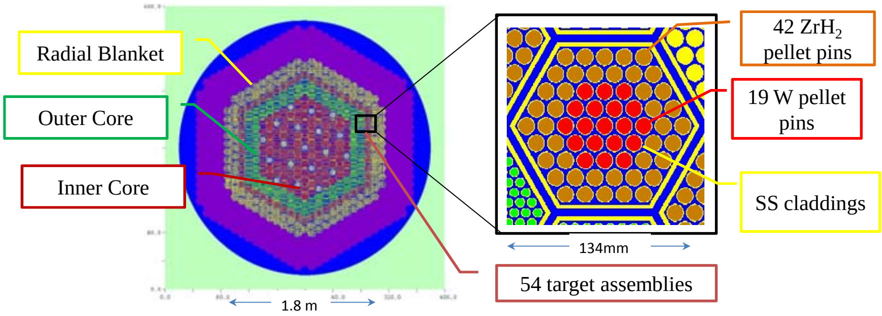


Major scheme of Re production:

W-186 → W-187 → Re-187

Neutron capture Beta disintegration

Fig.1 Nuclear Transformation Scheme of Tungsten(W) to Rhenium(Re)



Horizontal Cross Section of Fast Reactor

Target Assembly and W pins (Reference Case)

Core : 710 MWt sodium cooled fast reactor, 1.8m in diameter and 0.9 m in height.
Target Assembly : 54 target assemblies at the peripheral of the core.
Pin layout of assembly: 19 pins of W pellets surrounded by 42 pins of zirconium hydride pellets.
(Reference Case)
: 61 pins of W pellets.
(No moderator Case)

Fig.2 Core layout and Target Assembly for Re Production

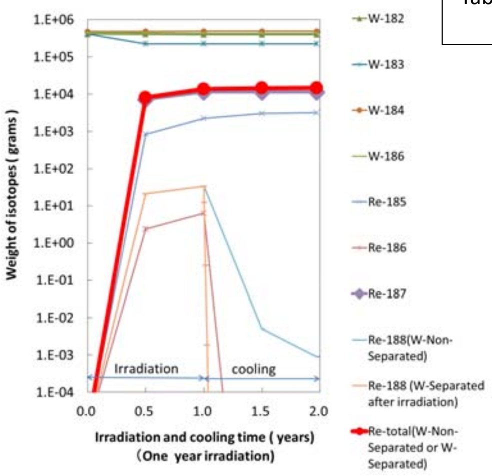


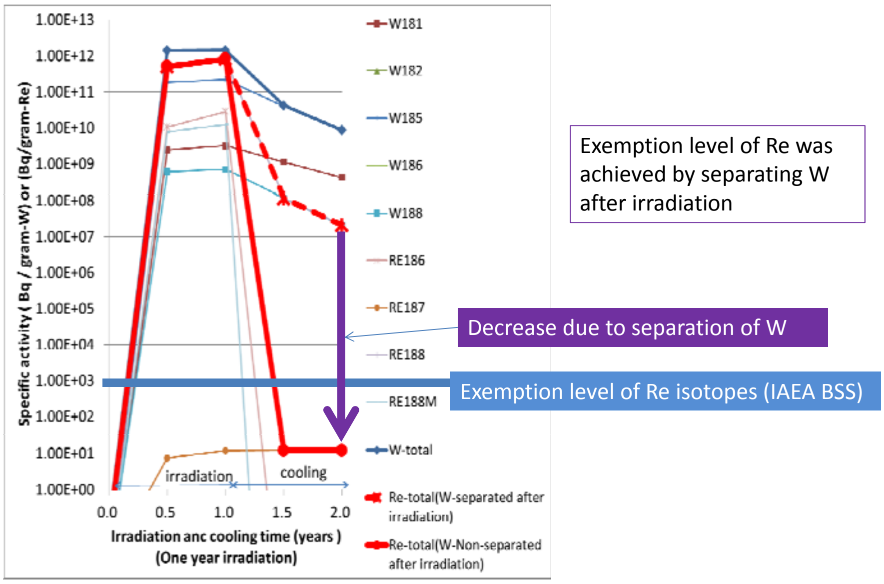
Fig.3 Change of Weight of Major Isotopes for Reference Case

Table 1 Amount of Produced Re for Reference Case and No moderator case Case

Case	No. of W pins	No. of ZrH_2 pins	Loaded weight of W (g)	Produced weight of Re after one year irradiation (g)
Reference	19	42	1.6×10^{6}	1.4×10^{4}
No moderator	61	0	5.0×10^{6}	1.5×10^{3}

Use of moderator increases Re production by 10 times.

Amount of Re production hardly depends whether W is separated or not.



Exemption level of Re was achieved by separating W after irradiation

Decrease due to separation of W

Exemption level of Re isotopes (IAEA BSS)

Fig. 4 Change of specific activities and the effect of W separation for reference case

Results and Discussion

Table 1 lists the weight of the transmutation from natural W to total Re after one year irradiation

No moderator case of Table 1 is the Re production when neutron moderator is not used and the whole 61 pins of the target assembly are W metal. The loaded weight of W in No moderator Case is 4 times more than that of the reference case, though the production of Re is less by one order than that of the reference case. This is mainly due to the neutron spectrum softening effect of zirconium hydride.

Fig.3 and Fig.4 show the weight and the specific activities of the isotopes during two years including one year cooling time after the irradiation for the reference case.

Fig. 4 indicates the main radioactivity isotope of Re, Re-188, will be decayed rapidly if Re is separated from W just after the irradiation because the parent of Re-188 is W-188. In 4 months cooling, the secondly intensive radioactivity, Re-186, is decreased less than the exemption level, 1000 Bq/g.

The effective cross section of W-186 is 1.731 barn for reference case evaluated by MVP code, while that of no moderator case is 0.012 barn because these effective cross sections are considering the neutron spectrum as well as the heterogeneous effect on neutron self shielding.

Precise separation of Re from radioactive W, Ta and Os will be issue.

Conclusions

- ·The feasibility of Rhenium (Re) production by irradiating Tungsten (W) metal in a medium size fast reactor was evaluated by using the Monte Carlo Calculation MVP.
- · The production rate of total Re is 14 kilograms per year, where the main contributor is Re-187, when the target assemblies are located at the core peripherals with neutron moderators.
- ·The specific activity of Re can be reduced below the exemption level if W is separated after the irradiation because the main contributor of activity is Re-188, which is the daughter of W-188.
- ·The ways of separation and allowable concentration of W, Ta and Os will be issue in future.

References

*1) Nagaya,Okumura,Mori and Nakagawa、"MVP/GMVP Version 2 : General Purpose Monte Carlo Codes for Neutron and Photon Transport Calculations based on Continuous Energy and multigroup Methods"(MVP/GMVP Version 2 JAERI 1348,June 2005 Japan Atomic Energy Research Institute.

*2) Okumura, Sugino, Kojima, Jin, Okamoto, Katakura, JAEA-Data/Code 2012-032
A Set of ORIGEN2 Cross Section Libraries Based on JENDL-4.0: ORLIBJ40, Dec. 2012, Japan Atomic Energy Research Institute.

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The authors would like to thank Dr. Konstantin German of Institute of Physical Chemistry and Electrochemistry of Russian Academy of Sciences for his support towards this work and presentation.

Application of Solvent Extraction Preconcentration methods for Spectrophotometric Determination of Traces of Molybdenum in Radiopharmaceutical Praparation using 1,5- Diphenylcarbazide.

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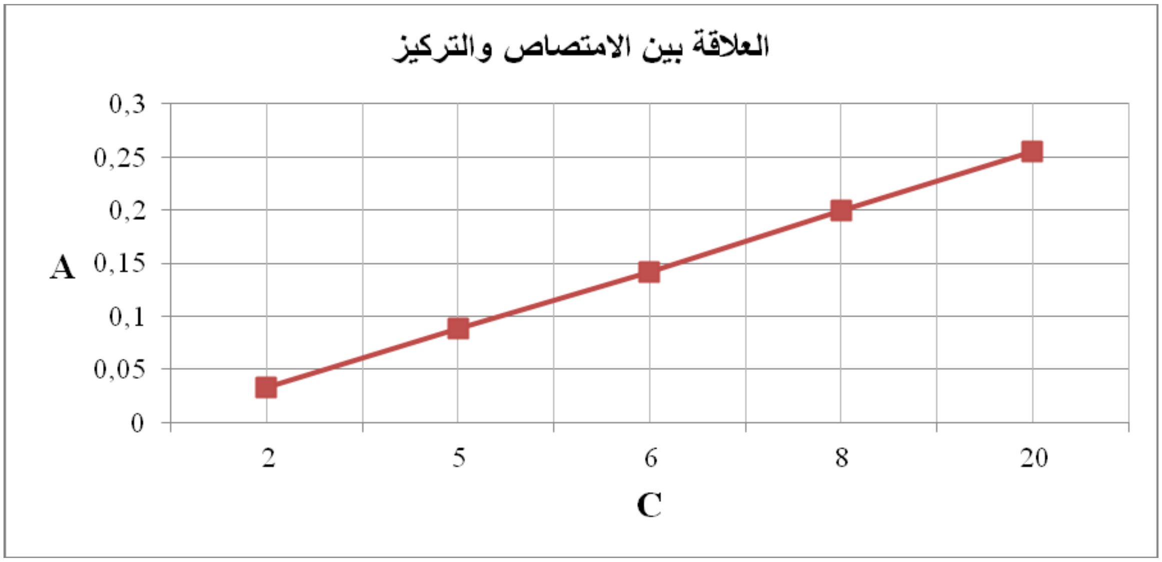
One of the most important tasks of Tagoura Nuclear Research Center is the production of Radioisotopes for Radiopharmaceutical preparations. Tc^{99m} and I^{131} are the main isotopes usually prepared for medical use in local hospitals. Radiochemical purity [RCP] for the prepared isotopes is very important, Where Mo traces in the final product has to be less than 10 ppm.

The main porpoise for the present work were to develop an accurate and simple method for the determination of Mo in a trace level, which satisfy the know how requirements. A solvent extraction pre concentration method for spectrophotometric determination were obtained, the method were based on the reaction of Mo with 1,5-diphenylcarbazide to form a soluble complex in carbon tetrachloride. The complex show a maximum absorbance at λ= 550 nm. , and obeys Beer's law with a molar absorption coefficient [ε] of $4x10^3$ l/mol.cm.

Mole ratio and continuous variation methods were applied to determine the metal to ligand ratio and a ratio of 1:***2*** respectively were found, also the optimum pH has been found between [3.5-5] and the effect of adverse ions like [Al, Sn, Se, Te] were studied. Finally, the proposed method has been applied for the analysis of Mo eluted from old generators imported from Polish company (POLATOM) and found to be sensitive, simple, accurate, less time consuming, and can be applied inside the Hot-cells.



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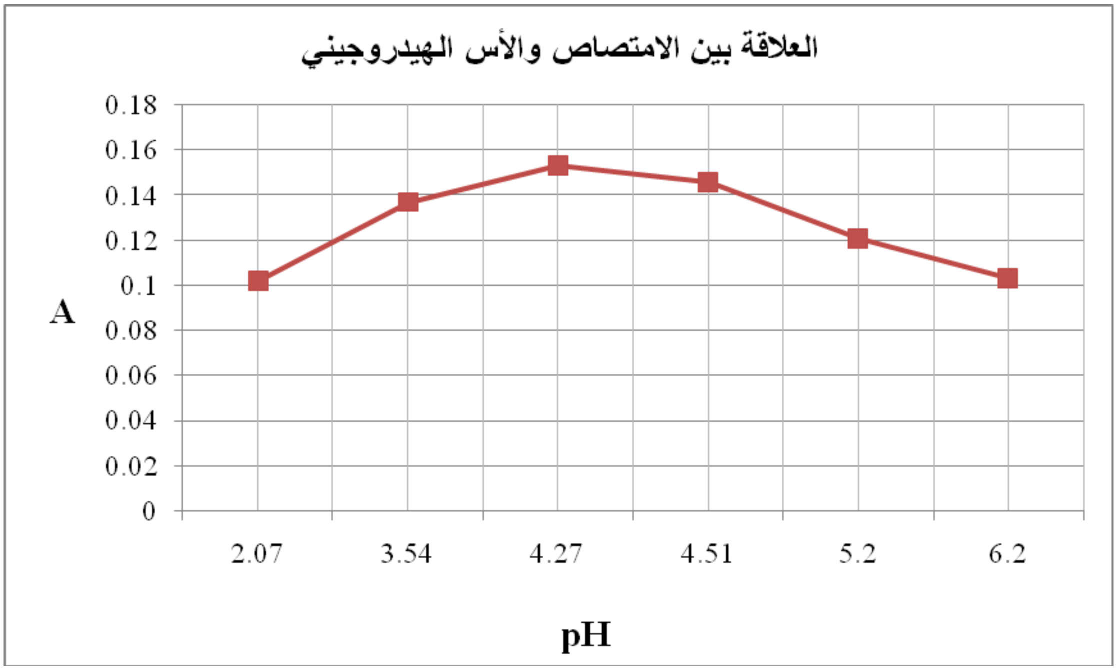

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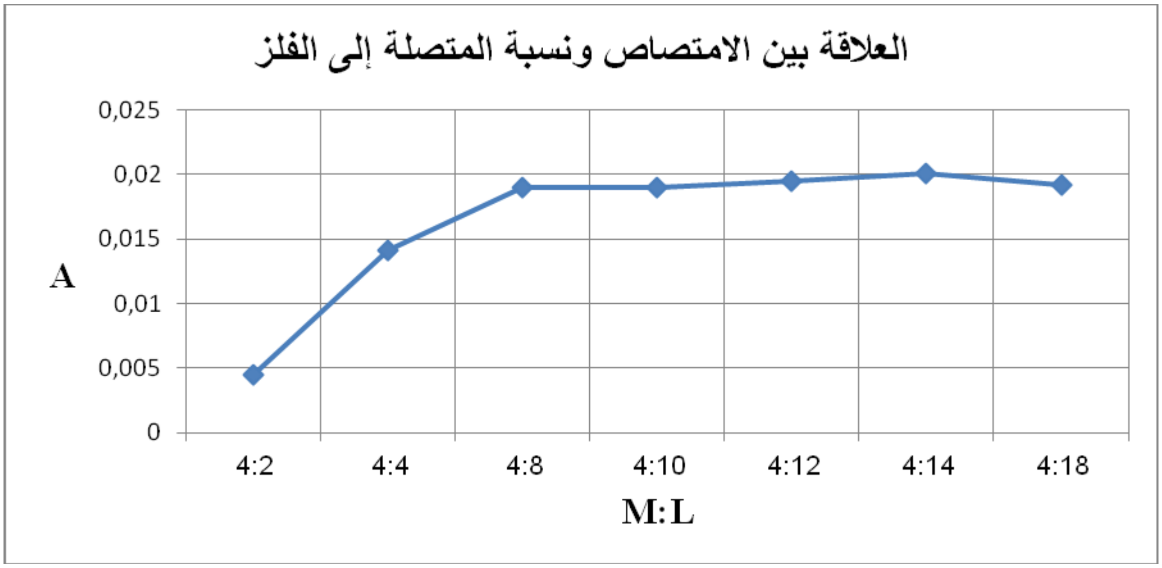
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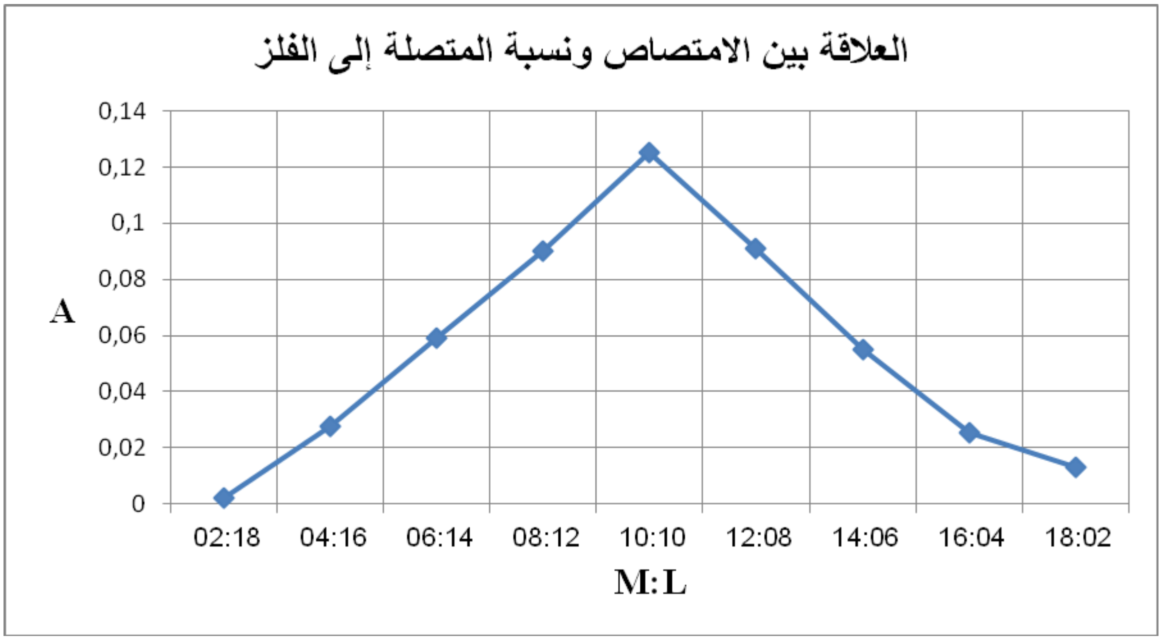
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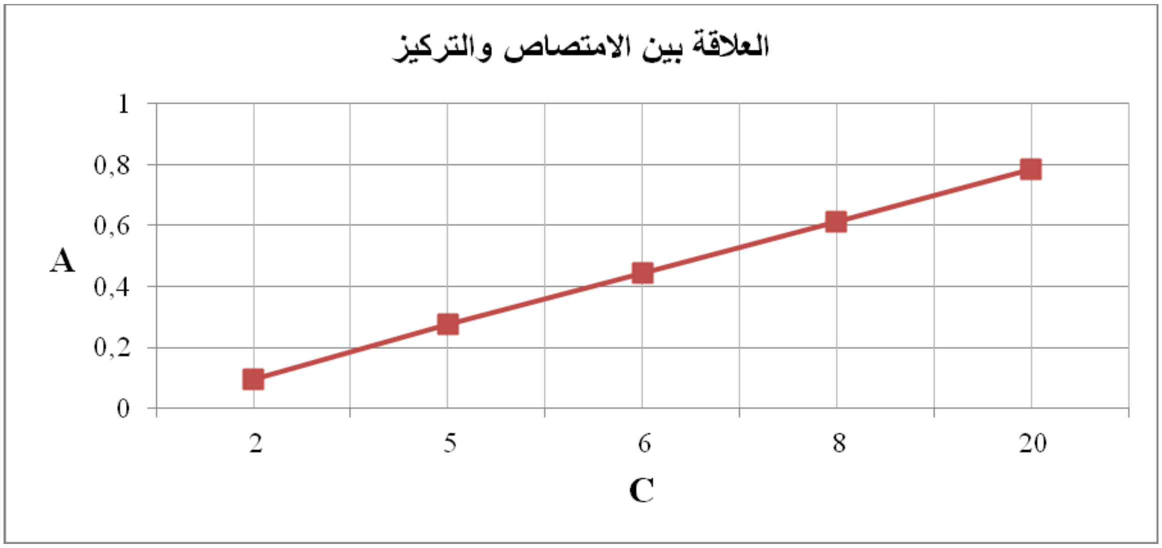
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BIO-SORPTION PROCESSES FOR RADIOACTIVE WASTE PURIFICATION FROM Tc, U, Sr AND Cs

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The main sources of environments contamination with radionuclides are nuclear explosions for military or civilian purposes, technological and accidental releases at facilities of the nuclear fuel cycle (NFC), nuclear facilities of naval and civilian fleets, radiation accidents, mining and processing of uranium ores, production and processing of the waste issued from nuclear reactors, materials nuclear power plants (NPPs), disposal processing of solid and liquid radioactive waste. A wide range of man-made radionuclides, including long-lived (U, Pu, Tc), and the most concentrated in LRW (Sr, Cs) into the environment remains an environmental hazard for hundreds and thousands of years.

Microbial cells can affect the chemical parameters of radionuclides with biosorption, bioaccumulation and dissimilatory reducing of metals and metalloids such as U(VI), Tc(VII) and others. Microorganisms are able to immobilize radionuclides by the concentration in the biofilm, formation of dominant types of radionuclides and mineral phases, including new mineral formations, production of complexing agents, the change of pH and Eh in waste solutions.

In this paper, we study the processes of radionuclide biosorption on laboratory waste models by biomass of microorganisms isolated from the deep repository of liquid radioactive waste. For the experiment, were obtained pure culture of Pseudomonas Putida (put), Native culture, containing a wide range of microorganisms (nat) and a mixture of the above two cultures.

Activity of radionuclides (except for ^{137}Cs), remaining in the liquid phase was measured by liquid-scintillation spectrometer SCS-07P-B11 (Russia) using a scintillator «Opti Phase HiSafe-3." Most solutions containing ^{137}Cs, were measured using a semiconductor gamma spectrometer with a coaxial detector of purity germanium (Ge-2520, Canberra). We made two types of experiments: a chemical sorption type, when bacteria was treated by metals during two hours in physiological liquid, and a living type, when the microorganisms were cultivated in a mineral Adkins medium following composition: NH_4Cl – 1 g / l, NaCl - 0,8 g / l, CH_3COOH - 2 g / L, $NaNO_3$ - 1 g / l, KCl, $MgSO_4$, Na_2SO_4 - 0,1 g / l, in anaerobic conditions, at neutral pH, 20 ° C for 10 days with the addition of the metals. For both experiments we used following concentrations of radionuclides: Cs (195Bk/ml) -, Sr (38 Bq / ml) -, U (as $UO_2(NO_3)_2$ -1 mg / ml) -, Th (1 mg / ml),-Tc (253,9 Bq / ml). The final biomass concentration was 1.5 -2 g / l.

The experiment found that 1 g of biomass is able to sorb 0.177 g UO2,; 0.217 g of Th; 10.16 Bq Sr; 10.42 Bq Cs; 31.47 Bq-Tc. According to the study, the sorption of Th was almost 100%, U - 85%, the sorption of Cs, on average - 10%, Sr - 50%, and Tc - 25%. The results of the percentage of sorption are shown in Fig. 1.

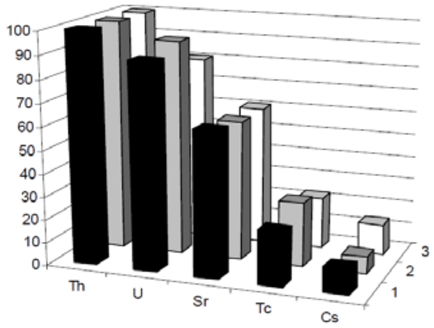


Fig 1. Percentage of sorption of radionuclides by microorganisms □ - Put, ▯- Nat, ■ - Mix

Thus, studied microorganisms were found to be able to immobilize artificial radionuclides in the model RW solutions, sorbing them on surface, and inside the cell. Bacteria can be used for develop the new cheap and nontoxic technology for RW treatment.

This work was supported by the financial assistance of the Russian Foundation for Basic Research 13-04-92105

Presentation of the selected posters by Dr. A. Safonov

MEASUREMENT OF ^{99}Tc VIA CHERENKOV COUNTING

Mojmír Němec, Kateřina Čubová

CTU in Prague, Czech Republic

WHAT

testing the possibility to measure ^{99}Tc via Cherenkov counting after its selective extraction.

WHY

finding a system allowing a one-step extraction and measurement in a scintillation vial.

HOW

- **Dependence of the efficiency of Cher. counting on the refractive index (n)**
- **Possible solution: to find a system for the extraction of ^{99}Tc into organic phase with high n**
- **Organic phase: CS_2 - n = 1,74 (20°C) and CCl_4 n = 1,4596 (20°C)**
- **Extraction of ^{99}Tc using tetraphenylarsonium chloride from alkaline solution (pH > 10)**
- **The emitted Cherenkov radiation was measured using the LSC**

CONCLUSIONS

- **measurement of ^{99}Tc via Cherenkov counting should be possible.**
- **unfortunetaly the system is unstable - in a short time ^{99}Tc is re-extracted back to the aqueous phase**

FUTURE

- **To identify stable extraction system conditions**
- **Determination of the detection efficiency of the Cherenkov counting**

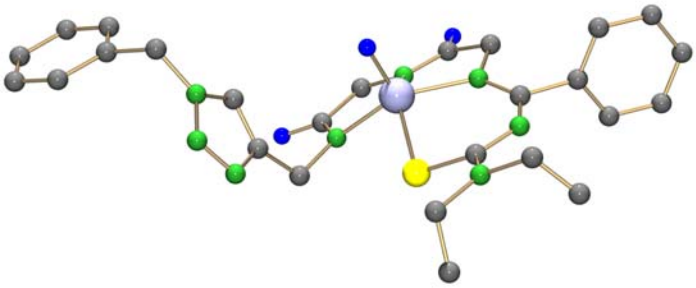
ACKNOWLEDGEMENT

This work was supported by grant project of the Ministry of Industry and Trade of the Czech Republic MPO TIP FR-TI3/245

Freie Universität Berlin

Tc(V) and Re(V) oxido complexes with tetradentate thiocarbamoylbenzamidines for bioconjugation

Adelheid Hagenbach, U. Abram and co-workers



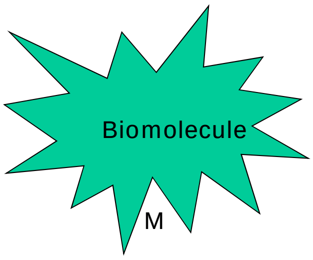
Principal Labeling Procedures

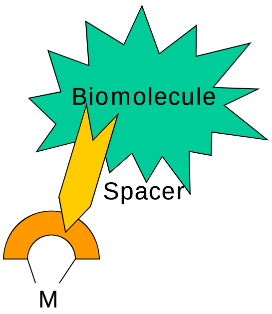
Direct Labeling

- Direct Labeling of a biomolecule via functional groups of the molecule

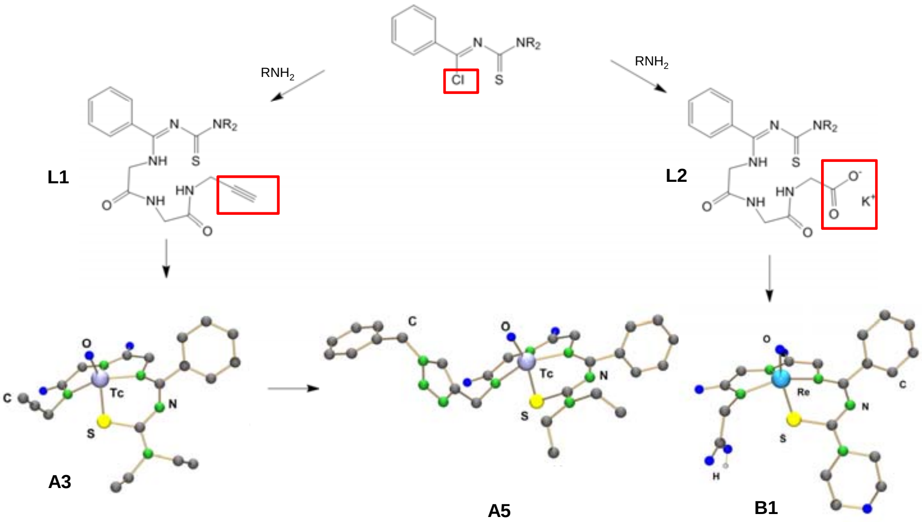
Bioconjugate Approach

- Encapsulating of a radionuclide with the help of a chelator and coupling on a biomolecule

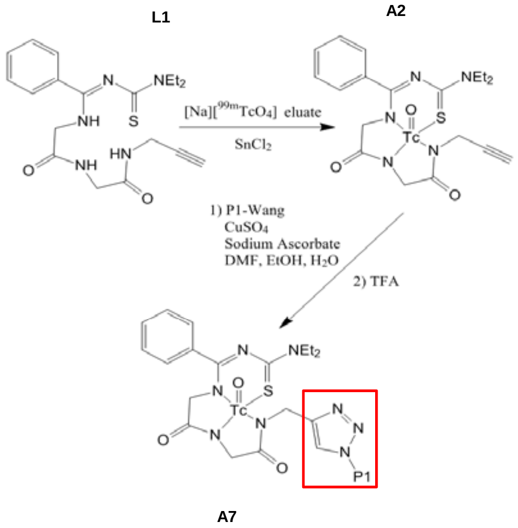


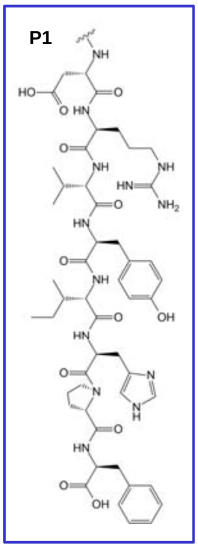


The ligands and their Re and ^{99}Tc complexes

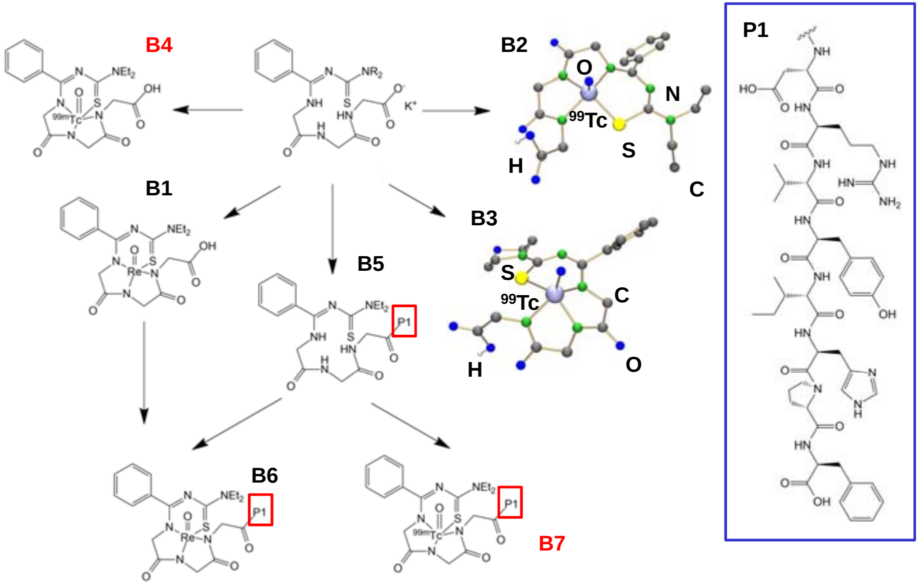


^{99m}Tc-Labeling for ‚click‘-Chemistry

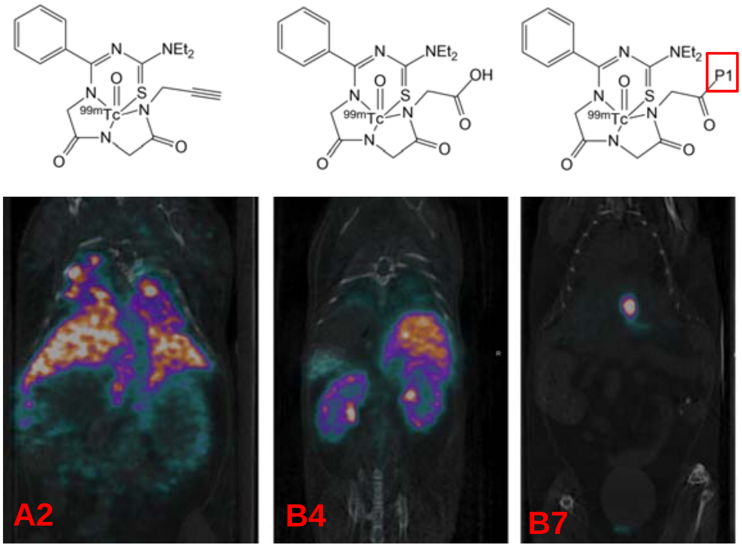




Bioconjugation with H_3L^2



SPECT



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Review on Chemical Separation of Tc with Extraction Chromatographic Resins

A. Bombard, S. Happel

- Monitoring of Tc-99 in environment for dose assessment
- 2 extraction chromatographic resins based on anionic exchanger can be used for Tc(VII) isolation/purification
  - **TEVA**
  - **WBEC**
- TcO_4^- carried by Re as ReO_4^- for chemical yield determination
- Separation scheme made of 2 steps: pretreatment and purification prior to measurement
- Resins tested for environmental samples

Microorganisms from extreme habitats for use in biological technologies to LRW treatment

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[1]Frumkin Institute of Physical Chemistry and Electrochemistry, Russian Academy of Sciences, Moscow, Russia
[2]Winogradsky Institute of Microbiology, Russian Academy of Sciences, Moscow, Russia
[3]Mendeleev University of Chemical Technology Moscow, Russia

Why bacteria?

Small agents for Me reducing in environments in big quantities (10^2-10^3 cell per ml in water 10^3 - 10^7 per 1 cm^3 in soils

High speed of division rate of bacteria 1 time per 30 min in geometrical progression

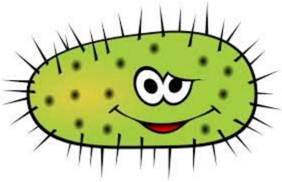
Bacteria can survive and be efficient in extreme conditions: ***thermophilic*** 50-90 °C, **alkaliphile** pH 10-11, **acidophile** (pH 1-2), ionizing radiation dose up to 1-10 kGr

Good economic parameters in comparison with some chemical methods

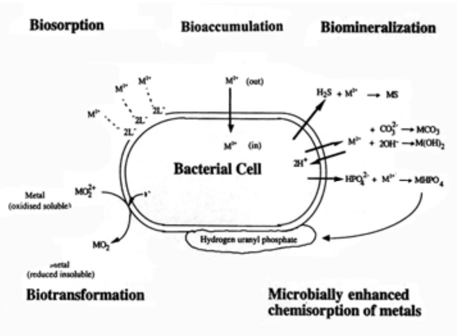
Ability to live in anaerobic conditions, synthesizing C_{org} for cell growth from CO_2 and H_2O

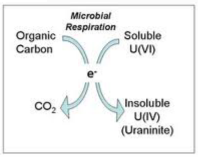
"Green chemistry techniques": no toxic reagents, acids, alkalines in high concentrations

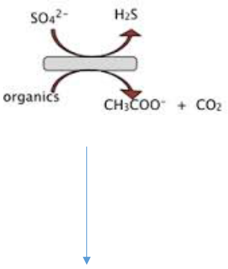
Different abilities of cells biochemistry: oxidizing organic matter, reducing nitrate, sulphate, metals, sorption metals on cell wall, membrane and other organoids.



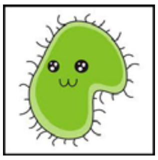
Some mechanism of Me interaction







Tc (VII, IV) precipitation
in insoluble sulfide



Strategy of work

Searching microorganisms in samples from extreme conditions

Bacteria isolating on different cultural media

Studying of bacteria metabolic activity for Me insolubilization

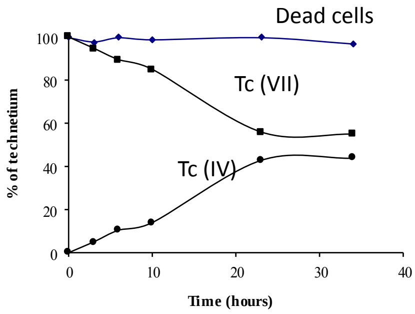
Development of methods for bacteria using in situ and in apparatus

WANTED

Bacteria from
High salinity, high & low pH conditions, high temperature
for good job!

Bacteria from high salinity and alcaliphilic condition

Kulunda Steppe soda lake, in south-eastern Siberia (Altai, Russia), salinity up to 150 g/l, pH 10,5-11



Are able to:

1. reduce Tc (VII) to Tc (IV) in alkaline conditions (pH 10.5)
2. reduce Re (VII) to Re (IV)
3. reduce U (VI) to U (IV)
4. Reduce NO_3^- to N_2

Bacteria from high temperature condition

Thermal springs of **Kuril** Islands t>90°C
salinity up to 70 g/l

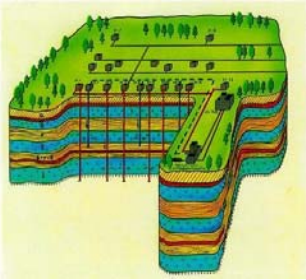
uramphite; **$(NH_4)(UO_2)(PO_4)\cdot 3H_2O$**

↓

ningyoite; **$(CaU(PO_4)_2\cdot H_2O)$**

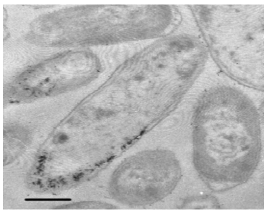
Are able to:

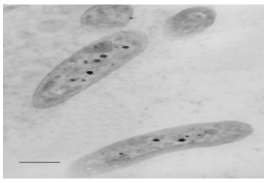
1. reduce Tc (VII) to Tc (IV) in neutral and acid conditions (pH 4.5-8)
2. reduce U (VI) to U (IV)



Bacteria from repository of liquid medium RW

Deep (380-410 m) liquid repository of radioactive wastes Severniy, Russia Krasnoyarsk region. C NO_3^- 1-300 g\l,



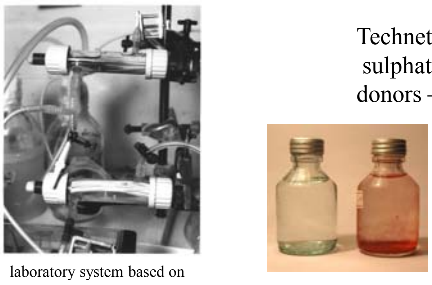


Are able to:

1. reduce Tc (VII) to Tc (IV) in neutral conditions (pH 7-8)
2. reduce U (VI) to U (IV)
3. Reduce NO_3^- to N_2
4. Reduce SO_4^{2-} to H_2S
5. Sorb U on cell wall and in cytoplasm

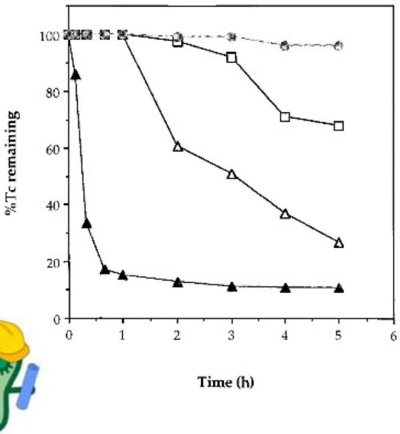
Perspective ways of using

1. Development and design of flow-through bioreactor for the decontamination of LLRW from uranyl cations, pertechnetate anions



laboratory system based on immobilized cells of sulfate-reducing bacteria. Pertechnetate reduction with and without donor, respectively.

Technetium reduction by sulphate-reducing bacteria with different donors – H2 (▲), formate (Δ), lactate (☐).

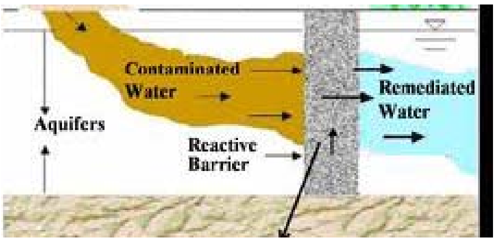


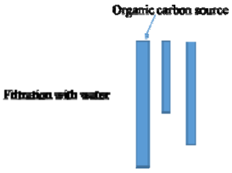
Designed laboratory system will be tested for simultaneous reduction of uranium and technetium at the “Radon”.

Re precipitation from liquids

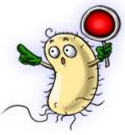
Perspective ways of using

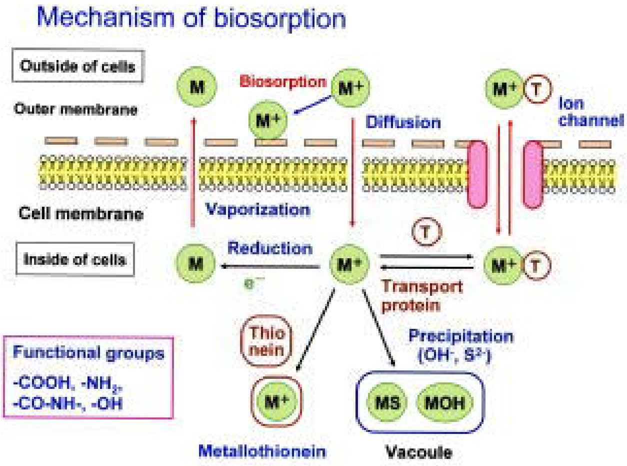
Biological reduction of pertechnetate ion in the implementation of biobarrer technology





1. reducing Tc (VII) to Tc (IV)
2. reducing U (VI) to U (IV)
3. Reducing NO_3^- to N_2
4. Reducing SO_4^{2-} to H_2S and precipitation Tc in sulfides form
5. Sorption U on cell wall and in cytoplasm
6. Consumption O_2 and Decreasing Eh to “-” zone





OCTAHEDRAL CHALCOGENIDE RHENIUM CLUSTER COMPLEXES WITH PHOSPHINE AND PYRIDINE DERIVATIVES: SYNTHESIS, STRUCTURE AND PROPERTIES

Ivanov A.A.[1,2,3], Khlestkin V.K.[1], Shestopalov M.A.[1,2,3], Brylev K.A.[1,2,3], Mironov Y.V.[1,2,3]
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Chemistry of octahedral chalcogenide rhenium cluster complexes $[\{Re_6Q_8\}L_6]$ (Q = S, Se, L = any ligands) is nowadays efficiently developing. A number of rhenium cluster complexes with inorganic and organic terminal ligands has been synthesized. One of the most significant aims is to obtain complexes with ligands bearing functional groups such as carboxy-, amino- and hydroxy group. Such compounds may potentially combine a number of physicochemical properties like luminescence or radiocontrast with biocompatibility or biological activity.

In this work we present an investigation of the interaction of octahedral chalcogenide rhenium cluster complexes $Cs_4[\{Re_6S_8\}X_6]$ and $Cs_3[\{Re_6Se_8\}X_6]$ (X = Cl, Br, I) with different organic ligands: 4-aminopyridine (4-NH_2-py), pyrazine (pyz), triphenylphosphine (PPh_3), 3-(diphenylphosphine)propionic acid ($PPh_2(CH_2)_2COOH$). All reactions were carried out in a sealed tube in the melt of ligand. Thus, cluster complexes: $[\{Re_6Q_8\}(4\text{-}NH_2\text{-}py)_6]Br_2$, *trans*-$[\{Re_6Q_8\}(pyz)_4I_2]$, *trans*-$[\{Re_6Q_8\}(PPh_3)_4X_2]$, $[\{Re_6Q_8\}(PPh_2(CH_2)_2COOH)_6]Br_2$ (Fig. 1) (Q = S, Se, X = Cl, I) were obtained. All synthesized compounds were characterized by X-ray diffraction on the single crystal and powder, IR-spectroscopy and elemental analysis. For the complexes with triphenylphosphine and 4-aminopyridine ligands luminescence properties were studied.

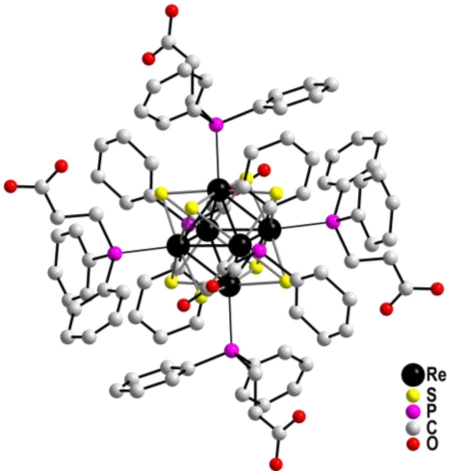

Fig. 1
$[\{Re_6S_8\}(PPh_2(CH_2)_2COOH)_6]^{2+}$

The work was financially supported by the Russian Foundation for Basic Research (project№ 13-03-90402, № 14-04-01816).

PROSPECTS OF OCTAHEDRAL RHENIUM CLUSTER COMPLEXES IN BIOLOGY AND MEDICINE

Michael A. Shestopalov[1,2,3], Anna A. Krasilnikova[3], Kristina E. Zubareva[1],
Konstantin A. Brylev[2,3], Yuri V. Mironov[2,3]
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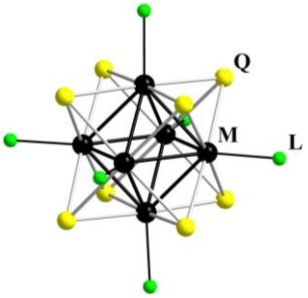
Complexes with the general formula $[\{Re_6(\mu_3\text{-}Q)_8\}L_6]^n$ contain a robust cluster core $\{Re_6(\mu_3\text{-}Q)_8\}^{2+}$ with a nearly regular Re_6 octahedron residing inside a Q_8 cube (Q = S^{2-} or Se^{2-}) (**Figure**). In addition, each rhenium atom is coordinated by an outer L ligand. The cluster core is responsible for phosphorescence in the red and near-infrared regions with a microsecond excited-state lifetime upon UV-visible excitation and radiopacity due to high local concentration of heavy elements.



Representation of the $[\{Re_6Q_8\}L_6]$ cluster units

We have succeeded in preparing the first water-soluble hexarhenium cluster complexes with a heterocyclic outer ligand environment $[\{Re_6(\mu_3\text{-}Q)_8\}(BTA)_6]^{4-}$ (Q = S or Se). The complexes exhibit red phosphorescence with lifetime and quantum yield values among the highest ones reported so far for chalcogenide cluster complexes making them promising bioimaging and PDT agents. To prove the potential, the cellular uptake and toxicity were evaluated for the complexes. It was found that the both clusters were taken up by the cells and, at the same time, did not exhibit acute cytotoxic effects at the concentration level of practical biological applications. The complexes $[\{Re_6(\mu_3\text{-}S)_8\}(BTA)_6]^{4-}$ and $[\{Re_6(\mu_3\text{-}Se)_8\}(BTA)_6]^{4-}$ were localized in the cell cytoplasm. The preparation of such complexes may be the first step toward the creation of a new class of NIR phosphorescent dyes based on hexanuclear metal clusters.

Also we have demonstrated the radiopacity of different cluster compounds based on $\{Re_6Q_8\}$-cluster core (Q = S, Se or Te) by the X-ray computed tomography *in vitro*. Despite of the highest radiopacity of the complex with $\{Re_6Te_8\}$-cluster core revealed, the most perspective radiocontrast agents are the $\{Re_6Se_8\}$-based compounds since their outer ligands can be purposefully modified allowing us to create various compounds with necessary properties. The cellular uptake and the toxicity were evaluated for the cluster complex $Na_2H_8[\{Re_6Se_8\}(P(CH_2CH_2CONH_2)(CH_2CH_2COO)_2)_6]$. It was shown that the complex was not taken up by the cells and, at the same time, did not exhibit acute toxic effects on Hep2 cell culture and BALB/C mice. That motivated us to carry out the X-ray computed tomography *in vivo*. The intravenous administration of cluster complex solution into Wistar rat leads to contrasting kidneys and urinary bladder and excretes through the kidneys rapidly. These experiments may constitute the first step toward the creation of a new class of effective X-ray contrast agents based on of hexanuclear metal clusters.

This work was supported by the Russian Foundation for Basic Research (Grant 14-04-01816).

Kola
Science
Center
Russian
Academy of
Sciences
ICTREMRM

Rhenium recovery from secondary raw materials

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of the KSC RAS, Apatity, Russia, E-mail: Petrova_AM@chemy.kolasc.net.ru

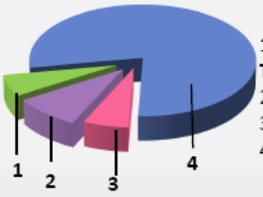
I 2
S 0
T 1
R 4

Introduction

Rhenium market

Rhenium is irreplaceable as component in some catalysts and heat-resistant alloys. Although much required, rhenium production from natural minerals is limited due to its scarcity and dissipation in different mineral deposits. The only way therefore is in improving the rhenium recovery from process and machining wastes [1].

World rhenium demand (2013) - 65 mt [1, 2]



1 – **Industrial Gas Turbine:** 4 mt
2 – **Catalysts:** 6 mt
3 – **Other:** 4 mt
4 – **Aerospace:** 51 mt

World rhenium production (2013) - 53 mt [3]

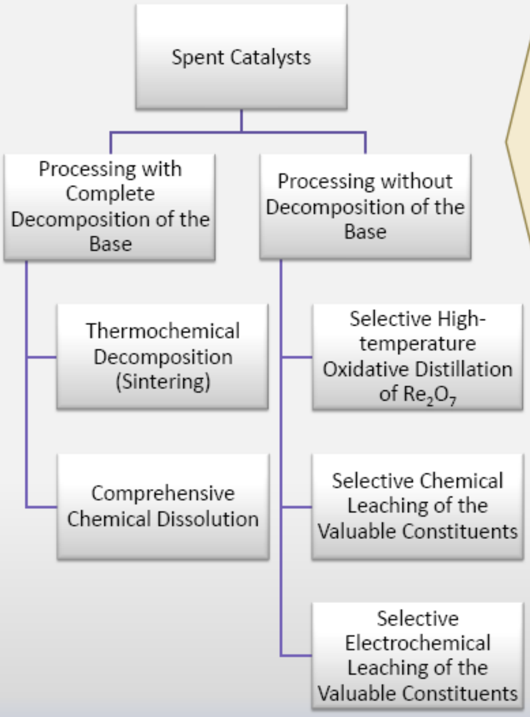
In 2013, the price of catalytic-grade APR remained at **$3,800** per kilogram until April, when the price slowly began to decrease to **$3,150** per kilogram in July and remained at that level until the year end. Rhenium metal pellet price started out the year at **$3,420** per kilogram until the beginning of May, when it began to slowly decrease until July where it remained at **$2,980** per kilogram until yearend.

Consumption of catalyst-grade APR by the petroleum industry was expected to remain at high levels. Demand for rhenium in the aerospace industry, although more unpredictable, was expected to continue to increase.

However, the major aerospace companies were expected to continue testing superalloys that contain one-half the rhenium used in currently designed engine blades, as well as testing rhenium-free alloys for other engine components. New technologies continued to be developed to allow recycling of superalloy scrap. Secondary rhenium recycling rates continued to increase worldwide [3].

Catalysts recycling

Rhenium catalysts


Spent Catalysts

Processing with Complete Decomposition of the Base
- Thermochemical Decomposition (Sintering)
- Comprehensive Chemical Dissolution

Processing without Decomposition of the Base
- Selective High-temperature Oxidative Distillation of Re_2O_7
- Selective Chemical Leaching of the Valuable Constituents
- Selective Electrochemical Leaching of the Valuable Constituents

The technologies available for recycling of the ***spent platinum-rhenium catalysts*** can be roughly divided into two groups, one incorporating *decomposition of catalyst aluminum oxide base*, the other – *selective extraction of rhenium without the base decomposition*. In the former, the catalyst is decomposed by chemical (acid or base leaching) and thermochemical methods (sintering with base), yielding much rhenium but undesirable due to high reagent consumption and sizeable aluminate waste.

The other group incorporates *selective high-temperature distillation* Re_2O_7, *selective chemical leaching* (with weak acid under oxidative conditions) and *electrochemical leaching* (with acid solutions under direct or alternating current).

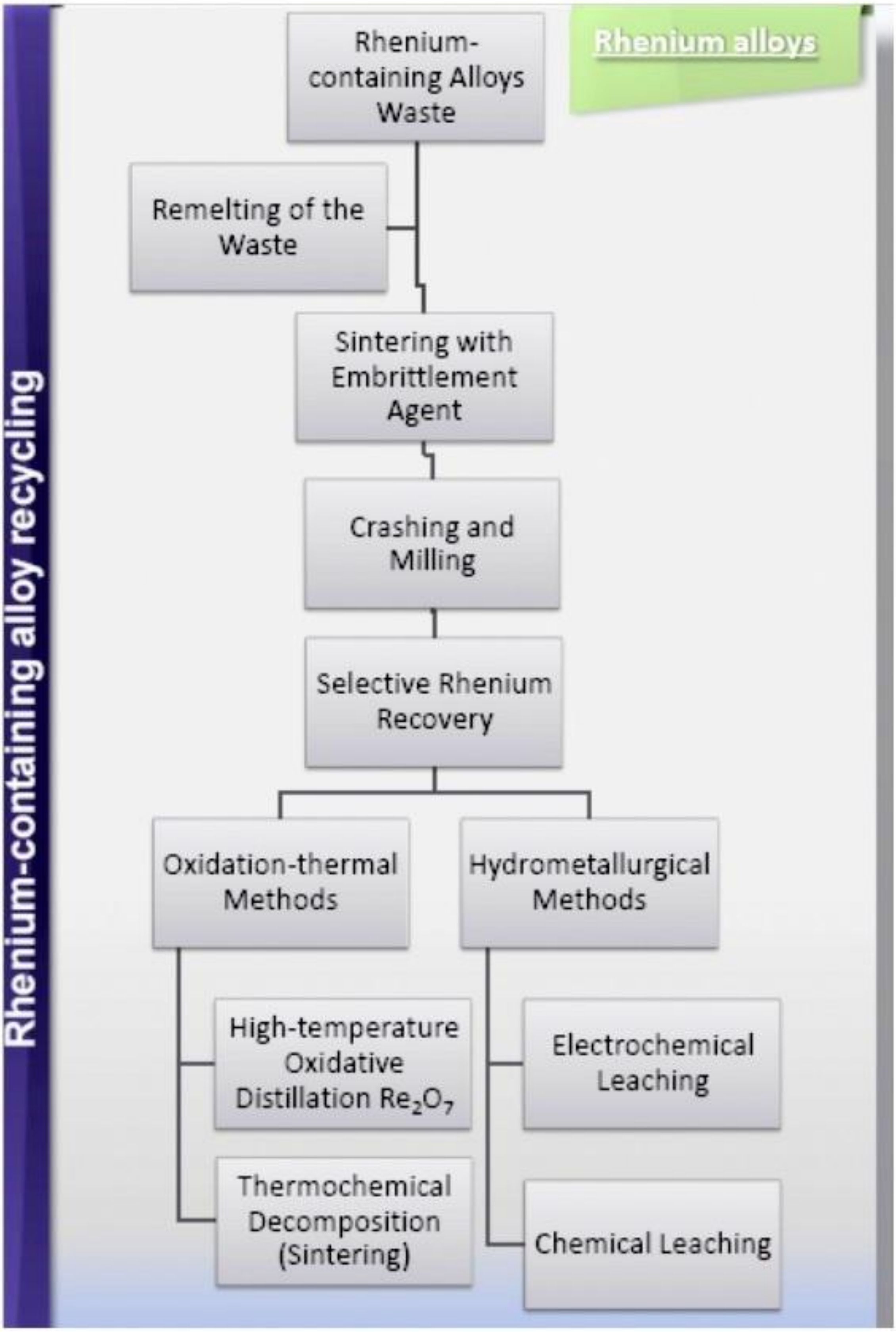
The most economical processing of **rhenium-containing** heat-resistant **alloys waste** is vacuum *remelting* developed at FSUE VIAM (Russia, Moscow). *Selective rhenium recovery* from the waste can proceed by two routes: *oxidation-thermal* or *hydrometallurgical methods* (after preliminary *disintegration* of the metal wastes if necessary).

The group of oxidation-thermal methods also includes high-temperature oxidative distillation of Re_2O_7 and thermochemical decomposition (sintering); Hydrometallurgical methods are chemical and electrochemical leaching (usually in acid media).

More about these processes can be found in the monograph [1]:

ACKNOWLEDGEMENTS:

The work was kindly supported by the Russian Fund of Fundamental Research, grant 14-03-31012 mol_a



Rhenium-containing alloy recycling

Rhenium alloys

Rhenium-containing Alloys Waste

Remelting of the Waste

Sintering with Embrittlement Agent

Crashing and Milling

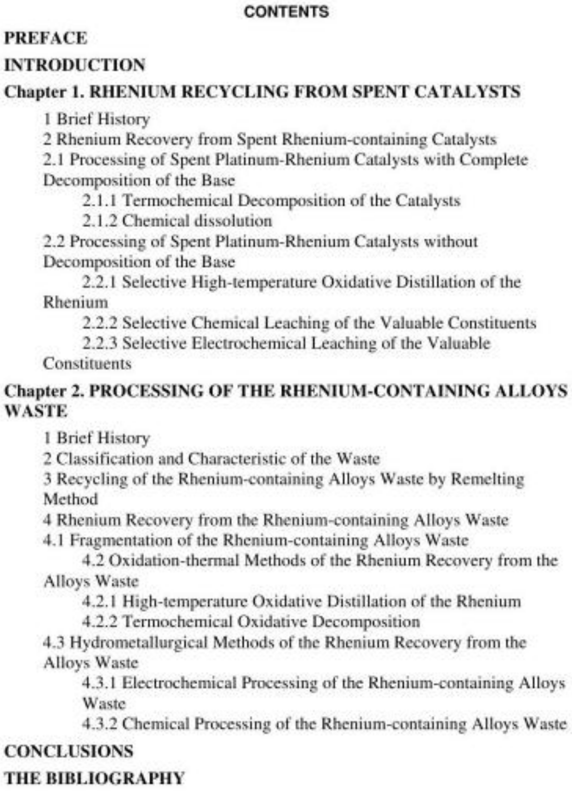
Selective Rhenium Recovery

Oxidation-thermal Methods

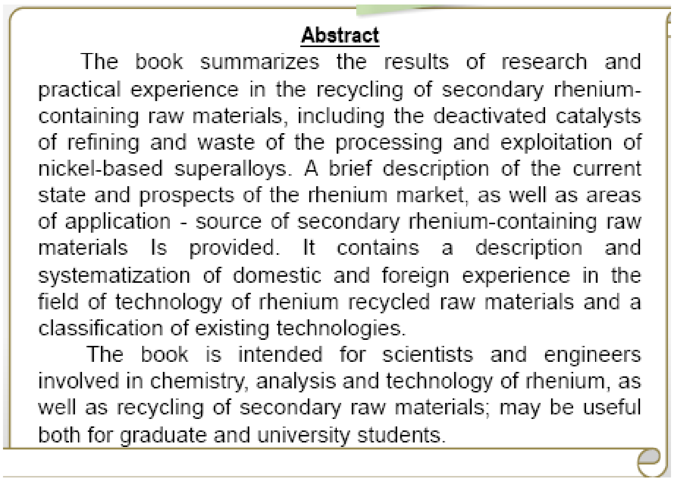
- High-temperature Oxidative Distillation Re_2O_7
- Thermochemical Decomposition (Sintering)

Hydrometallurgical Methods

- Electrochemical Leaching
- Chemical Leaching



CONTENTS



Abstract

The book summarizes the results of research and practical experience in the recycling of secondary rhenium-containing raw materials, including the deactivated catalysts of refining and waste of the processing and exploitation of nickel-based superalloys. A brief description of the current state and prospects of the rhenium market, as well as areas of application - source of secondary rhenium-containing raw materials Is provided. It contains a description and systematization of domestic and foreign experience in the field of technology of rhenium recycled raw materials and a classification of existing technologies.

The book is intended for scientists and engineers involved in chemistry, analysis and technology of rhenium, as well as recycling of secondary raw materials; may be useful both for graduate and university students.

[1] Kasikov A.G., Petrova A.M. **Rhenium recycling.** M.: RIOR INFRA-M. Moscow, 2014. 94 P.
[2] http://www.lipmann.co.uk/articles/metal-matters/rhenium-updated (2014)
[3] http://minerals.usgs.gov/minerals/pubs/commodity/rhenium (2014)

Full-text of the monograph is available on-line (in Russian) at web site http://znanium.com/go.php?id=453154

8th INTERNATIONAL SYMPOSIUM ON TECHNETIUM AND RHENIUM
29 SEPTEMBER - 3 OCTOBER 2014
Pornichet, FRANCE

Subatech,EMN/Universite de NANTES/ CNRS, Nantes, France

3 OCTOBER 2014

RESOLUTION

The International Advisory Committee of ISTR-2014 has resolved that the next ***International Symposium on Technetium and Rhenium*** will be held in Sydney (Australia) in the year 2017.

The International Advisory Committee for ISTR-2017 consists of the following scientists:

- U. Abram (Germany)
- R. Alberto (Switzerland)
- M. Chotkowski (Poland)
- K. Czerwinski (USA)
- M. Fattahi (France)
- T.I.A. Gerber (South Africa)
- K.E. German (Russia)
- F. Moisy (France)
- Ya. Obruchnikova (Russia)
- F. Poineau (USA)
- A. Sattelberger (USA)
- I. D. Troshkina (Russia)
- G. Thorogood (Australia) – Chairman
- A.Yu. Tsivadze (Russia)
- T. Yoshimura (Japan)

We hope to meet you in Sydney.

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Massoud FATTAHI	Gordon THOROGOOD
Chairman Organizing Committee ISTR-2014	Chairman Organizing Committee ISTR-2017

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