IST 2005
Oarai

International Symposium on Technetium
– Science and Utilization –

ABSTRACTS

Oarai, Japan
May 24 – 27, 2005

Organizer
IST-2005 Organizing Committee

Co-organizers
The Japan Society of Nuclear and Radiochemical Sciences
Atomic Energy Society of Japan
The Chemical Society of Japan
The Japan Radiation Research Society
Japan Nuclear Cycle Development Institute

International Symposium on Technetium
– Science and Utilization –

Oarai, Japan

May 24 – 27, 2005

Major Topics of the Symposium

- Physics and Chemistry of Group 7 Elements
- Coordination and Organometallic Chemistry of Tc and Re
- Tc and Re in Radiopharmaceuticals and Nuclear Medicine
- Environmental Behavior of Tc and Re
- Cosmo- and Geosciences of Tc and Re
- Nuclear Fuel Reprocessing
- Partitioning and Transmutation of Tc
- Other Topics

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	24-May-05	
9:00		*Chair*
15	**Registration**	
50	**Opening**	Kudo
10:00	Nagata	
15	2401-I R. Alberto	Kudo
11:00	2402 G.E. Kodina	Gerber
20	2403 T. Takayama	
40	2404 T. Yoshimura	
12:00	**Lunch**	
13:00		
30	2405-K Y. Sasaki	Yoshimura
14:00	2406 M. Abe	Ikeda
20	2407 T.I.A. Gerber	
40	2408 A. Abrahams	
15:00	**Break**	
20	2409 T. Ohashi	Sasaki
40	2410 Y. Miyashita	
16:00	2411 N. Koshino	
20	2412-K Y. Arano	Hashimoto
50	2413	Alberto
17:00	H. Matsuoka	
10	2414 K. Hashimoto	
30	2415 A.O. Malysheva	
50	2416-K	Omori
18:00	K.E. German	
20		

	25-May-05	
9:00		*Chair*
15	2501-I J.A. Rard	Fujii
10:00	2502 M. Fern	German
20	2503 R. Ludwig	
40	2504 I.D. Troshikina	
11:00	**Break**	
20	2505-K M. Garcia-Leon	Uchida
50	2506	
12:00	E. Leclerc	
10	**Lunch**	
13:00		
30	2507 K. Tagami	Suzuki
50	2508	
14:00	Y. Ohtsuka	
10	2509 M. Takeishi	
30	2510-K H. Hidaka	Sekine
15:00	**Break**	
20	2511 K. Furutaka	Fukasawa
40	2512 Y. Shirasu	
16:00	2513 J.M. Bonnerot	
20	2514 T. Aoyama	
40	**Poster** Short Presentation	
17:00		
10	Discussion 25P1 – 25P17	
40		
18:00		
10	**Banquet**	
20:10		

	26-May-05	
9:00		*Chair*
15	2601 M. Ozawa	Uchiyama
35	2602 T. Asakura	
55	2603	
10:00	T. Sekine	
15	**Break**	
35	2604 M. Fattahi	Ozawa
55	2605	
11:00	T. Yamamura	
15	2606-K Y. Nagame	Yoshida
45	**Closing**	Sekine
12:00	**Lunch**	
13:00		
30	**Technical Tour**	

27-May-05

One Day Excursion

International Symposium on Technetium – Science and Utilization – (IST-2005)

Program

Tuesday, May 24

9:15 - 9:50	**Registration**
9:50 – 10:00	**Opening** H. Kudo, Organizing Committee
10:00 – 10:15	**Welcome Address** T. Nagata, *Japan Nuclear Cycle Development Institute, Japan*

1. *Coordination Chemistry of Technetium and Rhenium*

Chairperson: H. Kudo

2401-I (10:15 – 11:00)

The Facettes of $[TcCl_3(CO)_3]^{2-}$ Chemistry and Its Application to Life Science

R. Alberto, *Zürich Univ., Switzerland*

Chairperson: T. I. A. Gerber

2402 (11:00 – 11:20)

Mechanism of Carbonylation Reactions of Technetium-99m

G.E. Kodina, A.O. Malysheva, O.E. Klement'eva, A.A. Inkin, N.I. Gorshkov, A.A. Lumpov, D.N. Suglobov, *SSC Institute of Biophysics, RPA Khlopin Radium Institute, Russia*

2403 (11:20 – 11:40)

Phenoxo-Bridged Dimeric Structure of Technetium(I) Tricarbonyl Complex with Schiff Base Ligand

T. Takayama, A. Harano, T. Sekine, H. Kudo, *Tohoku Univ., Japan*

2404 (11:40 – 12:00)

Synthesis, Structure and Properties of Technetium Complex with Polypyridyl Ligand

T. Yoshimura, Y. Tooyama, M. Kawai, T. Takayama, T. Sekine, H. Kudo, A. Shinohara, *Osaka Univ., Tohoku Univ., Japan*

12:00 – 13:30 **Lunch**

Chairperson: T. Yoshimura

2405-K (13:30 – 14:00)

Versatility of Technetium Chemistry as Viewed from the Recent Progress of Rhenium Cluster Complexes

Y. Sasaki, *Hokkaido Univ., Japan*

Chairperson: Y. Ikeda

2406 (14:00 – 14:20)

Redox-Assisted Structural Transformation of a Tpen-Coordinated Rhenium(V)-Oxo Complex and Synthesis of Heterometallic Clusters

M. Abe, T. Tabeya, A. Mitani, K. Tsuge, Y. Sasaki, *Hokkaido Univ., Japan*

2407 (14:20 – 14:40)

Versatility of Bidentate Aniline Derivatives as Ligands for Rhenium(V) and Technetium (V)

T.I.A. Gerber, *Nelson Mandela Metropolitan Univ., South Africa*

2408 (14:40 – 15:00)

Multidentate Dipyridyl Derivatives as Chelates for Rheium(V)

T.I.A. Gerber, A. Abrahams, P. Mayer, *Nelson Mandela Metropolitan Univ., South Africa, Ludwig-Maximilians Univ., Germany*

15:00 – 15:20 **Coffee Break**

Chairperson: Y. Sasaki

2409 (15:20 – 15:40)

Oxorhenium(V) Complexes with Quinolinylamido: Stereochemistry, Spectroscopy, Reactivity and OAT Catalytic Property

T. Ohashi, Y. Miyashita, N. Amir, K. Fujisawa, K. Okamoto, *Univ. Tsukuba, Japan*

2410 (15:40 – 16:00)

Rhenium-Containing Sulfur-Bridged Heterotrinuclear Complexes: Stereochemical, Spectrochemical, and Electrochemical Properties

Y. Miyashita, N. Amir, K. Fujisawa, K. Okamoto, *Univ. Tsukuba, Japan*

2411 (16:00 – 16:20)

A Kinetic Study on Ligand Substitution Reaction of N-Cyclohexyl-2-pyrrolidone for Triphenylphosphine in Trichlorooxorhenium(V) Complex

N. Koshino, S. Usui, T.R. Varga, S. Chowdhury, A.C. Bényei, Y. Ikeda, *Tokyo Institute of Technology, Japan*

2. *Radiopharmaceuticals of Technetium and Rhenium*

Chairperson : K. Hashimoto

2412-K (16:20 – 16:50)

Recent Advances in Technetium Radiopharmaceuticals

Y. Arano, *Chiba Univ., Japan*

Chairperson: R. Alberto

2413 (16:50 – 17:10)

Application of PZC to ^{188}W/^{188}Re Generators

H. Matsuoka, K. Hashimoto, Y. Hishinuma, K. Ishikawa, H. Terunuma, K. Tatenuma, S. Uchida, *Japan Atomic Energy Research Institute, KAKEN Co., Tokyo Nuclear Service, Co., Japan*

2414 (17:10 – 17:30)

Labeling of Bifunctional Chelating Agent, MAG3, with Carrier-Free ^{188}Re

K. Hashimoto, W.H.B.B. Wan Kamal, H. Matsuoka, *Japan Atomic Energy Research Institute, Japan, Malaysian Institute for Nuclear Technology Research, Malaysia*

2415 (17:30 – 17:50)

Synthesis and *in vitro* Evaluation of $Tc(CO)_3^+$ Complexes with Dithiocarbamate Ligands Containing Morpholine Moiety

G.E. Kodina, A.O. Malysheva, O.E. Klement'eva, N.I. Gorshkov, A.A. Lumpov, D.N. Suglobov, *SSC Institute of Biophysics, Khlopin Radium Institute, Russia*

3. *Inorganic Chemistry of Technetium and Rhenium*

Chairperson: T. Omori

2416-K (17:50 – 18:20)

Tc Carbide and New Orthorhombic Tc Metal Phase

K.E. German, V.F. Peretroukhin, K.N. Gedgovd, M.S. Grigoriev, A.V. Tarasov, Yu.V. Plekhanov, A.G. Maslennikov, G.S. Bulatov, V.P. Tarasov, M. Lecomte, *Institute of Physical Chemistry RAS, Russia, CEA-Marcoule, France*

Wednesday, May 25

Chairperson : Y. Fujii

2501-I (9:15 – 10:00)

Current Status of the Thermodynamic Data for Technetium and Its Compounds and Aqueous Species

J.A. Rard, *Lawrence Livermore National Laboratory, Univ. California, USA*

4. *Analytical Chemistry of Technetium and Rhenium*

Chairperson : K.E. German

2502 (10:00 – 10:20)

Recent Developments in the Analysis of Technetium-99

M. Fern, A. Thakkar, L. Jassin, *Eichrom Technologies, Inc., USA*

TF VA [illegible]

2503 (10:20 – 10:40)

Solvent Extraction of Tc(VII) by Calixarenes Bearing Pyridino Groups

R. Ludwig, N.T. Kim Dzung, *Freie University Berlin, Germany, Vietnam Atomic Energy Commission, Vietnam*

2504 (10:40 – 11:00)

Rhenium Ultrafiltration Recovery

I.D. Troshkina , A.M. Chekmarev, S.B. Maiboroda, N.S. Smirnov, *D. Mendeleyev University of Chemical Technology, Russia*

11:00 – 11:20 **Coffee Break**

5. *Environmental Science and Geoscience of Technetium and Rhenium*

Chairperson: S. Uchida

2505-K (11:20 – 11:50)

^{99}Tc in the Environment: Sources, Distribution and Methods

M. García-León, *Univ. Sevilla, Spain*

2506 (11:50 – 12:10)

Technetium Transfer Modelling into Biosphere in Order to Calculate Radiological Impact Assessment

E. Leclerc, *Andra, French National Agency for Radioactive Waste Management, France*

12:10 – 13:30 **Lunch**

Chairperson: T. Suzuki

2507 (13:30 – 13:50)

Soil-to-Plant Transfer Factors of Techneitum-99 for Various Plant Collected in Chernobyl Area

K. Tagami, S. Uchida, W. Rühm, M. Steiner, E. Wirth, *National Institute of Radiological Sciences, Japan, Ludwig Maximilians University Munich, BfS, Institute of Radiation Hygiene, Institute for Atmospheric Radioactivity, Germany*

2508 (13:50 – 14:10)

Simple Separation Methods for Trace-Level of Technetium-99 in Seaweed and Seawater Using an Extraction Chromatographic Resin

Y. Ohtsuka, Y. Takaku, J. Kimura, T. Sekine, S. Hisamatsu, *Institute for Environmental Sciences, Tohoku Nuclear Ltd., Co., Tohoku Univ., Japan*

2509 (14:10 – 14:30)

Investigation of Analytical Method for Technetium-99 in Liquid Effluent Discharged from Tokai Reprocessing Plant

M. Takeishi, Y. Hiyama, T. Mizutani, H. Watanabe, Y. Maruo, *Japan Nuclear Cycle Development Institute, Zuiho Co., Japan*

Chairperson : T. Sekine

2510-K (14:30 – 15:00)

Technetium in Cosmo- and Geochemical Fields

H. Hidaka, *Hiroshima Univ., Japan*

15:00 – 15:20 **Coffee Break**

6. *Transmutation and Reprocessing of Technetium*

Chairperson : T. Fukasawa

2511 (15:20 – 15:40)

Cross Section of Thermal-Neutron Capture Reaction by ^{99}Tc

Сов и TcC? Трансм.?

K. Furutaka, H. Harada, S. Nakamura, T. Katoh, T. Fujii, H.Yamana, S. Raman, *Japan Nuclear Cycle Development Institute, Kyoto Univ., Japan, Oak Ridge National Laboratory, USA*

2512 (15:40 – 16:00)

Fundamental Properties of Target for Transmutation of Technetium-99

Y. Shirasu, K. Minato, *Japan Atomic Energy Research Institute, Japan*

Совм. раб.?
с расч. механизм.

2513 (16:00 – 16:20)

Transmutation of Technetium: Irradiation Experiment ANTICORP 1 in PHÉNIX

B. Jean-Marc, P. Mayeul, F. Jean-Luc, V. Fréderic, A. Marie-France, *CEA Cadarache, CEA Valrhô Marcoule, France*

2514 (16:20 – 16:40)

Transmutation of Technetium in the Experimental Fast Reactor "JOYO"

T. Aoyama, S. Maeda, Y. Maeda, S. Suzuki, *Japan Nuclear Cycle Development Institute, Japan*

Poster Session (16:40 – 17:40)

Short presentation (16:40 – 17:10)
Discussion (17:10 – 17:40)

25P1 Technetium Recovery from Nitric Acid Solution by Electrolytic Extraction (EE) for Future Reprocessing
T. Asakura, S.-Y. Kim, Y. Morita, M. Ozawa, *Japan Atomic Energy Research Institute, Nuclear Cycle Development Institute, Japan*

25P2 Technetium Transmutation: Electronic Structure Changes Analysis by Quantum Chemical Models
Yu.V. Plekhanov, K.E. German, V.F. Peretrukhin, *Institute of Physical Chemistry of RAS, Russia*

25P3 Synthesis and Properties of Some Novel Pertechnetates: $LiTcO_4 \cdot 3H_2O$ and Onium Phospororganic Tripodandes
K.E. German, M.S. Grigoriev, A. Tarasov, V.P. Peretrukhin, V. Baulin, A.Yu. Tsivadze, *Institute of Physical Chemistry RAS, Russia*

25P4 Technetium Carbide: Quantum Chemical Model
Yu.V. Plekhanov, K.E. German, *Institute of Physical Chemistry of RAS, Russia*

25P5 Quartery Alkylammonium and Alkylphosphonium Pertechnetates: Properties and Application to TcO_4^- Selective Electrodes
K.E. German, A.V. Dorokhov, A.V. Kopytin, Yu. Politov, E.N. Pyatova, A.V. Tarasov, M. Simonoff, V.F. Peretroukhine, A. Yu. Tsivadze, *Institute of Physical Chemistry of RAS, Kurnakov Institute of General and Inorganic Chemistry of RAS, Russia, CNRS - Universite Bordeaux –1, France*

25P6 Model Experiments on Bioaccumulation of Technetium and Thorium by Bottom Sediments of Eutrophic Lakes of Moscow and Udomlya Regions
F.A. Barinova, N.G Bugaeva, K.E. German, V.F. Peretrukhin, M. Simonoff, *Institute of Physical Chemistry of RAS, Kalininskaya NPP, Russia*

25P7 Vertical Distribution of Rhenium in Seawater Samples Collected Three Locations of the Coast of Aomori, Japan
K. Tagami, S. Uchida, H. Tsukada, *National Institute of Radiological Sciences, Institute for Environmental Sciences, Japan*

25P8 Sorption of Rhenium on Carbon Fibrous Materials Modified with Chitosan
LA. Zemskova, A.V. Voit, Yu.M. Nikolenko , V.I. Sergienko, I.D. Troshkina, A.V. Plevaka, S.B. Maiboroda, A.M. Chekmarev, *Far Eastern Branch of Russian Academy of Sciences, D. Mendeleyev University of Chemical Technology, Russia*

25P9 Rhenium Recovery from Uranium Ores

A.M. Chekmarev, I.D. Troshkina, O.N. Ushanova, S.B. Maiboroda, *D. Mendeleyev University of Chemical Technology, Russia*

25P10 "2+1" Approach in $M(CO)_3$ (M = Tc, Re) Chemistry: Hint for Labeling Biomolecules

N.I. Gorshkov, R. Schibili, A.A. Lumpov1, A.E. Miroslavov, D.N. Suglobov, *Khlopin Radium Institute, Russia, Paul Scherrer Institute, Switzerland*

25P11 Rhenium Extraction from Biological Material and Forms of Its Presence in Fresh Plants

L.V. Borisova, V.V. Ermakov, O.D. Bozhov, *V. I. Vernadsky of RAS, Russia, Institute of General and Inorganic Chemistry of Bulgarian Academy of Sciences, Bulgaria*

25P12 Study of Sorption and Desorption of Technetium Species on Various Rocks Being in Contact with Simulated Groundwater Solutions

Y.M. Kulyako, M.N. Litvina, D.A. Malikov, N.N. Popova, B.F. Myasoedov, *V. I. Vernadskiy of RAS, Russia*

25P13 Studying of Regularity of ^{188}Re Binding with Albumin Microspheres

V.M. Petriev, V.G. Skvortsov, N.A. Demidova, T.P. Rizhikova, T.A. Tarasova, *State Institution Medical Radiological Research Center RAMS, Russia*

25P14 Geometric and Electronic Structures for Technetium Clusters by Density Functional Method

R. Sekine, T. Yamamoto, H. Onda, *Shizuoka Univ., Japan*

25P15 Sorption Photometrical Determination of Tc with Its Prior Concentrating on Fiber "Filled" Sorbents

N.N. Popova, Y.V. Voronin , I.G. Tananaev , G.V. Myasoedova, B.F. Myasoedov, *Vernadsky Institute, Institute of Physical chemistry of RAS, Russia*

25P16 Technetium(VII) Extraction by Tetraketones and Tetraethers of Calix[4]arenas from Acidic and Alkaline Media

I.S. Antipin, G.A. Pribilova, I.G. Tananaev, A.I. Konovalov, B.F. Myasoedov, *Vernadsky Institute, Arbuzov Institute of Organic and Physical Chemistry KazSC RAS, Russia*

25P17 Separation of Metal Ruthenium Out of Irradiated Technetium

K.V. Rotmanov, L.S. Lebedeva , V.M. Radchenko, V.A. Tarasov, E.G. Romanov, Yu.G Toporov, V.F. Peretroukhin, A.A. Kozar, *Federal State Unitary Enterprise State Scientific Centre, Institute for Physical Chemistry RAS, Russia*

18:10 – 20:10 **Banquet**

Thursday, May 26

Chairperson : G. Uchiyama

2601 (9:15 – 9:35)

Separation and Utilization of Tc and Other Rare Metal Fission Products by an Extended Aqueous Reprocessing

M. Ozawa, T. Suzuki, Y. Fujii, *Japan Nuclear Cycle Development Institute, Tokyo Institute of Technology, Japan*

2602 (9:35 – 9:55)

Technetium Separation for Future Reprocessing

T. Asakura, S. Hotoku, Y. Ban, M. Matsumura, Y. Morita, *Japan Atomic Energy Research Institute, Japan*

2603 (9:55 – 10:15)

Technetium(IV) Oxide Colloids and the Precursor Produced by Bremsstrahlung Irradiation of Aqueous Pertechnetate Solution

T. Sekine, M. Zakir, T. Takayama, H. Kudo, M. Lin, Y. Katsumura, *Tohoku Univ., Univ. Tokyo, Japan*

10:15 – 10:35 **Coffee Break**

Chairperson : M. Ozawa

2604 (10:35 – 10:55)

Speciation of Technetium(IV) Chloride in the Presence of Gamma Irradiation

M. Fattahi, L. Vichot, F. Poineau, B. Grambow, C. Houee-Levin, *Ecole des Nines de Nantes, CEA, Laboratoire de Chimie Physique, UMR8000, France*

2605 (10:55 – 11:15)

Behavior of Technetium in Supercritical Water

T. Yamamura, I. Satoh, N. Okuyama, Y. Shiokawa, T. Sekine, W. Sugiyama, K.-C. Park, H. Tomiyasu, *Tohoku Univ., Chubu Electric Power Co. Inc., Shinshu Univ., Japan*

7. *Superheavy Elements*

Chairperson : Z. Yoshida

2606-K (11:15 – 11:45)

Production and Chemistry of Transactinide Elements

Y. Nagame, *Japan Atomic Energy Research Institute, Japan*

11:45 – 12:00 **Closing** T.Sekine Organizing Committee

12:00 – 13:30 **Lunch**

13:30 – 15:00 **Technical Tour**

Friday, May 27

One-day Excursion

Tuesday, May 24, 2005

Coordination Chemistry of Technetium and Rhenium

Radiopharmaceuticals of Technetium and Rhenium

Inorganic Chemistry of Technetium and Rhenium

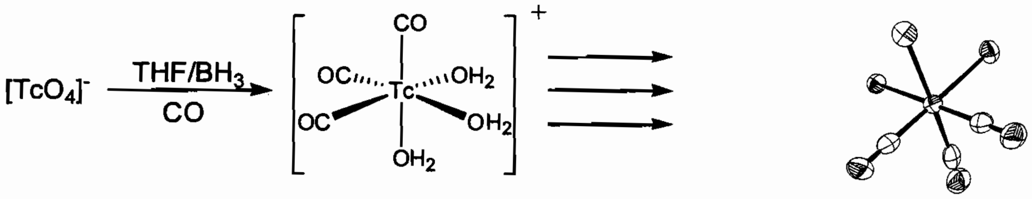
2401-I

THE FACETTES OF $[TcCl_3(CO)_3]^{2-}$ CHEMISTRY AND ITS APPLICATION TO LIFE SCIENCE

Roger Alberto
Institute of Inorganic Chemistry, University of Zürich, Winterthurerstr. 190, CH-8057 Zürich

Organometallic chemistry of low oxidation states is related to the availability of binary carbonyl complexes usually serving as versatile starting materials for organometallic reactions with other ligands. Technetium organometallic chemistry is, thus, less well developed than that of other elements. The complex $[Tc_2(CO)_{10}]$ can only be synthesized from autoclave reactions, a difficult process, mainly for reasons of radiation safety regulation. There is a persistent need for versatile low valent Tc synthons for fundamental research but also since organometallic complexes could impact radiopharmacy and bioorganometallic chemistry. We attempted to develop new approaches for reactive but stable Tc precursors comprising CO as ligands and found a method for the preparation of the title compound in good yields at 1 atm of CO.[1] It turned out that $[TcCl_3(CO)_3]^{2-}$ readily formed the stable "semi-aquo-ion" $[Tc(OH_2)_3(CO)_3]^+$ when dissolved in water.[2] This finding represented the start for the exploration of the "*fac*-$[^{99m}Tc(CO)_3]^+$" core for biological and pharmaceutical purposes.

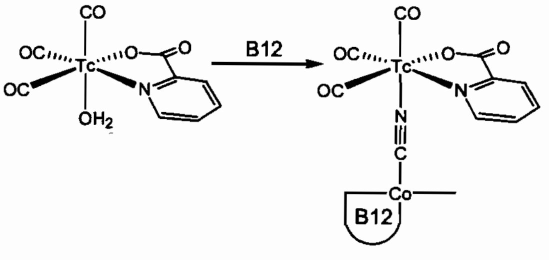
The presentation will review the realm of coordination chemistry with $[^{99(m)}Tc(OH_2)_3(CO)_3]^+$, show recent results in the context of chemistry and give perspectives for further developments in organometallic Tc chemistry and radiopharmacy. It is the aim of the presentation to show that this single core has more facettes than just its use in labeling chemistry but that the introduction of novel strategies in chemistry and radiopharmacy becomes feasible.

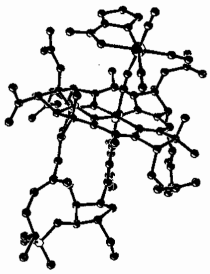


The complex $[Tc(OH_2)_3(CO)_3]^+$ displays an extremely rich coordination chemistry. The three water molecules can readily be substituted by almost any incoming donor.[3] The formed complexes are of high kinetic stability and the ligands are scarcely replaced by competitors. This characteristic represents the essential base for application in targeted radiopharmacy where the "*fac*-$[^{99m}Tc(CO)_3]^+$" moiety is bound via a bifunctional chelator to a biological vector. We developed a number of tripodal bifunctional chelators based on the natural amino acids cysteine and histidine. Their synthesis, coupling to biomolecules, labeling and biological properties will be presented.

The complex also binds to some uncommon ligand groups such as the nitrogen atom in coordinated cyanide. This concept can be used to directly label vitamin B12 which has a $[CN]^-$ bound to Co(III) in the corrin ring. The two remaining coordination sites on Tc (or rhenium) can be occupied with an additional bidentate chelator designed to fine tune the biological properties of B12. Alternatively, an additional biomolecule might be coupled to the chelator, leading to metal-mediated functionalization of vitamin B12 which is much more convenient than traditional functionalization at the periphery of the corrin ring framework.[4]

Combining chemotherapy and radiotherapy –diagnosis prompted us to investigate the reactivity of $[Tc(OH_2)_3(CO)_3]^+$ with the purin base guanine. Two bases coordinate in various relative orientations to Tc(I) thereby inducing structural changes in the tertiary structure of plasmide DNA, similar to those found when exposing pDNA to cisplatinum.[5] Within the same field, we will present attempts to use ^{99m}Tc as a therapeutic radionuclide. It is not very well known that the ^{99m}Tc decay produces a number of Auger and Coster-Kronig electrons of appropriate energy to induce double strand breaks in DNA if located sufficiently close to the double strand. Recent results clearly show that ^{99m}Tc induces cell death at low activity concentration if the radiopharmaceutical is transported into the nucleus.[6] Our biologically oriented experiments with Tc show, that there are still unexpected directions to explore just because new fragments become available. Such possibilities will ensure the role of ^{99m}Tc in nuclear medicine in particular and in life science in general.





Beside applications of $[Tc(OH_2)_3(CO)_3]^+$ in radiopharmacy, the complex serves also as an important synthon for further developments in organometallic chemistry. Of particular interest are starting materials comprising the $[C_5H_5]$, (Cp) ligand. Cytectren complexes of the composition $[CpTc(CO)_3]$ (and further Cp derivatives) are conveniently accessible through the reaction of the cluster compound $[Tc(\mu\text{-}OH)(CO)_3]_4$ with neat HCp. Since also of interest for radiopharmaceutical chemistry, we sought for a fully aqueous approach. Sufficiently acidic Cp derivatives of the form $H_3CCOC_5H_6$ (HACp) react in water to give $[(ACp)Tc(CO)_3]$ in good yield.[7] The convenient availability of cytectren Tc(I) compounds opens an avenue for the development of Cp-chemistry of Tc. Furthermore, under moderate CO pressure in aqueous solution, $[Tc(OH_2)_3(CO)_3]^+$ can be converted to the binary carbonyl cation $[Tc(CO)_6]^+$ which was previously only accessible by a rather tedious route.[8]

The radiopharmacy of $[^{99m}Tc(OH_2)_3(CO)_3]^+$ has recently been reviewed critically. [9] The presentation will mainly emphasize the many facettes and possibilities of this complex but also underline the need for new fragments or precursors and scope how some of these could look like based on the experience with the "*fac*-$[Tc(CO)_3]^+$" moiety. It will also be shown how the requirements from application can impact fundamental research not only but particularly in the field of Tc chemistry.

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2402

MECHANISM OF CARBONYLATION REACTIONS OF TECHNETIUM-99m.

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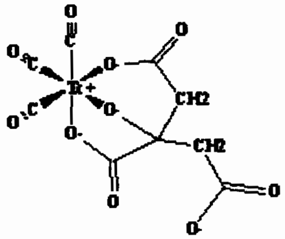
Over the last few years chemistry of novel technetium-99m organometallic precursor $Tc(CO)_3^+$ was intensively developed. Main advantages of $Tc(CO)_3^+$ fragment are relatively small size, low positive charge and only three coordination sites which can be occupied with electron donor ligands for attaching to various biomolecules. Original procedure for preparation of $^{99m}Tc(CO)_3^+$ was developed by R. Alberto (Switzerland) and based on reductive carbonylation of $^{99m}TcO_4$ by sodium borohydride at 1 atm CO pressure. Several years ago another convenient procedure for preparation of this precursor using sodium boranocarbonate was developed. Nowtime $^{99m}Tc(CO)_3^+$ is available as kit ("Isolink"). Alternative method for high-pressure carbonylation of sodium pertechnetate under elevated temperature in acidic media was developed in Khlopin Radium Institute (Russia). The main advantage of this procedure is absence of toxic organic and inorganic impurities in preparation, however it requires special microautoclave unit. The goal of this work was to study products produced in basic and acidic media upon atmospheric pressure and high-pressure carbonylation and to propose probable mechanism of reaction.

According to literature data TC-^{99m}Tc (technetium tricarbonyle), produced in basic media, have $R_f = 0.4$ (SiO_2, elution system – MeOH/HCl 99:1), whereas TcO_4^- have R_f close to 1. However, on TLC at pH 11 we observed two peaks with R_f 0.0-0.1 and 0.4, respectively. Based on ^{99}Tc NMR data at pH 11 we evaluated constant of hydrolysis of $Tc(CO)_3^+$ which was c.a. 10^7. Thus, it could be expected that on n. c. a. level of TC-^{99m}Tc is partially hydrolyzed. Starting zone on TLC can be assigned to complex with proposed composition $Tc(CO)_3(OH)X_2$ ($X = H_2O$, halide).

Quantive yield of target TC-^{99m}Tc is possible only in presence of tartrate ion. Presumably it stabilizes intermediate five-valent state of technetium, which is reduced to univalence state under elevated temperature and excess of carbonylation agent (CO, boranocarbonate). The same effect was observed in the case of preparation of isocyanide technetium complexes. Since citrate and cysteine are known as stabilizers of intermediate reduced state of technetium it is possible to change composition for preparation of TC-^{99m}Tc. Cysteine is also known as powerfull tridentate ligand for linking of $Tc(CO)_3^+$ species and corresponding complex was isolated and characterized earlier.

When sodium citrate was added to both neutralized and unneutralized preparations on TLC we observed single peak with R_f 0.8-1.0. We isolated and characterized (IR, ^{1}H NMR, ^{99}Tc NMR, elem. anal.) complex with overall structure $Tc(CO)_3(Cit)^{-3}$ with tridentate coordination of ligand which have the same R_f. Thus we can conclude that starting $^{99m}Tc(CO)_3^+$ precursor completely converted to $^{99m}Tc(CO)_3(Cit)^{-3}$ at concentration of citrate $5*10^{-3}$M. Proposed structure is shown below.

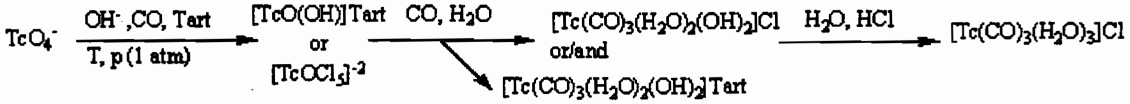


When citrate or cysteine was introduced in reaction mixture instead of tartrate we observed significantly changed TLC's. In the case of citrate R_f was 0.8 and in the case of cysteine 0.3, respectively. It should be noted, that impurities hydrolysed forms of technetium were absent in preparations. Thus, we can conclude, that cysteine and citrate are more powerfull ligands than that of tartrate and substitutes weakly bounded water molecules in metal coordination sphere and decoposed TC-Tc hydrolysed forms.

Upon autoclave carbonylation of $^{99m}TcO_4^-$ on TLC we observed two components (R_f 0.8-1 and 0.4). One of them was assigned to unreacted pertechnetate, and another one to target TC-^{99m}Tc. We prepared artificial mixture of "ground" TcO_4^-, $Tc(CO)_3^-$ and $Tc(CO)_5Cl$ and analyzed it by HPLC with UV detection. In elution system acetonitrile-0.1% phosphoric acid three peaks with RT's 3.7 min (TC-Tc), 4.0 (probably, $Tc(CO)_4(H_2O)_2]^+$), 4.1 (TcO_4^-), 4.9 min $Tc(CO)_5Cl$ were detected. Comparision of UV HPLC tracers with HPLC radioactive tracers of corresponding "hot" preparation allowed us to conclude, that on the first stage of autoclave synthesis $Tc(CO)_5Cl$ is produced. Upon standing or heating it is quantatively decarbonylated to TC-^{99m}Tc. In HPLC radioactive tracer of TC-^{99m}Tc prepared under atmospheric pressure single peak was detected and assigned to $^{99m}Tc(CO)_3^+$.

Thus, following mechanisms for reductive carbonylation of technetium pertechnetate are proposed:

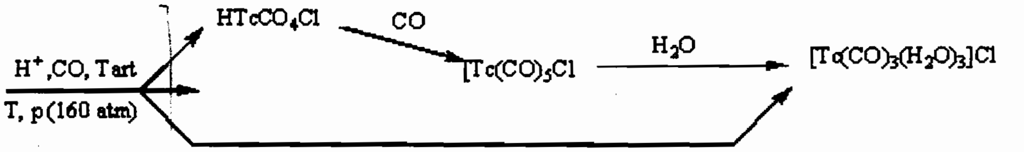
1. For atmospheric pressure carbonylation in presence of tartrate (basic media).



2. For atmospheric pressure carbonylation in presence of cysteine and tartrate (basic media).

$$TcO_4^- \xrightarrow[t^\circ,\ p\ (1\ \text{атм})]{OH^-,\ CO,\ Cit} [TcOCit] \xrightarrow{CO,\ H_2O} [Tc(CO)_3Cit]$$

3. For high-pressure carbonylation (acidic media).



This work was financially supported by ISTC (Grant 1723).

2403

PHENOXO-BRIDGED DIMERIC STRUCTURE OF TECHNETIUM(I) TRICARBONYL COMPLEX WITH SCHIFF BASE LIGAND

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The coordination chemistry of technetium(I) carbonyl complexes attracts considerable interest in recent years. In this study, novel technetium(I) carbonyl complexes with Schiff base ligand 2-(1-butylnitrilomethylidyne)phenol (Hsalbut) were synthesized and their structures in crystal and solution were characterized.

Schiff base Hsalbut and $(Et_4N)_2[^{99}Tc(CO)_3Cl_3]$ were stirred in acetonitrile at room temperature. Addition of a base such as triethylamine is necessary for this ligand exchange reaction. Reaction mixture was evaporated and the residue was dissolved in benzene. Slow evaporation of the solution gave crystals of $[Tc(CO)_3(salbut)]_2$ suitable for X-ray crystallography.

The molecular structure of $[Tc(CO)_3(salbut)]_2$ in crystal is shown in Fig. 1. This dinuclear complex is composed of two $Tc(CO)_3(salbut)$ subunits bridged by two oxygen atoms of the phenoxo group. The two $Tc(CO)_3(salbut)$ subunits are in inversion symmetry each other. The inversion center is located at the center of the Tc_2O_2 ring. Each technetium atom is six-coordinate in octahedral geometry. Schiff base Hsalbut loses a phenol proton through the ligand exchange reaction and coordinates to the technetium atom as a bidentate ligand with nitrogen and oxygen atoms. Unshared electron pairs on an anionic oxygen atom of the phenoxo group enable to form a Tc-O-Tc bridge. Three carbonyl ligands

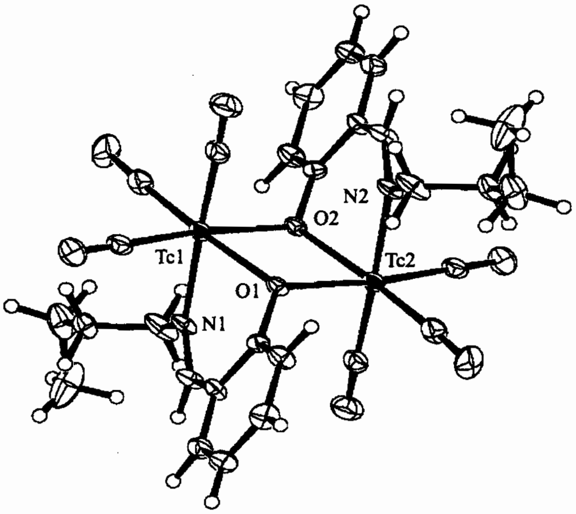

Fig. 1. ORTEP drawing of $[Tc(CO)_3(salbut)]_2$. Thermal ellipsoids drawn at the 50 % probability level.

coordinate to the technetium atom in a *facial* configuration.

The distance of the Tc1-O1 bond (2.142(4) Å) is shorter than that of the Tc2-O1 bond (2.172(4) Å), suggesting that the Tc1-O1 bond in the six-membered chelate ring has an ionic character and the Tc2-O1 bond has a covalent character. The two technetium atoms and the two bridging oxygen atoms are fairly in the same plane. These four atoms form a Tc_2O_2 parallelogram with the Tc1-O1-Tc2 angle of 75.8(2) degree and the O1-Tc1-O2 angle of 104.2(2) degree. The distance between two technetium atoms is very long (3.40 Å), and the metal-metal bond does not exist in this complex.

Structures of $[Tc(CO)_3(salbut)]_2$ in several solvents were examined by NMR and UV-vis spectroscopy. When $[Tc(CO)_3(salbut)]_2$ was dissolved in dichloromethane or benzene, no structural change was observed. In acetonitrile or pyridine, mononuclear complex with neutral charge was formed as a result of the dissociative solvolysis of $[Tc(CO)_3(salbut)]_2$ (Fig. 2). The molecular formula of these mononuclear complexes can be written as $Tc(CO)_3(salbut)L$ (L = acetonitrile or pyridine). A strong Lewis base such as acetonitrile and pyridine substitutes the bridging oxygen atom of $[Tc(CO)_3(salbut)]_2$.

When $Tc(CO)_3(salbut)(CH_3CN)$ was dissolved in a weak Lewis-base solvent like dichloromethane and benzene, it gradually changed to $[Tc(CO)_3(salbut)]_2$, and both of the monomeric and dimeric complexes existed in the solution. The result suggests that $Tc(CO)_3(salbut)(CH_3CN)$ is an intermediate leading to the formation of $[Tc(CO)_3(salbut)]_2$.

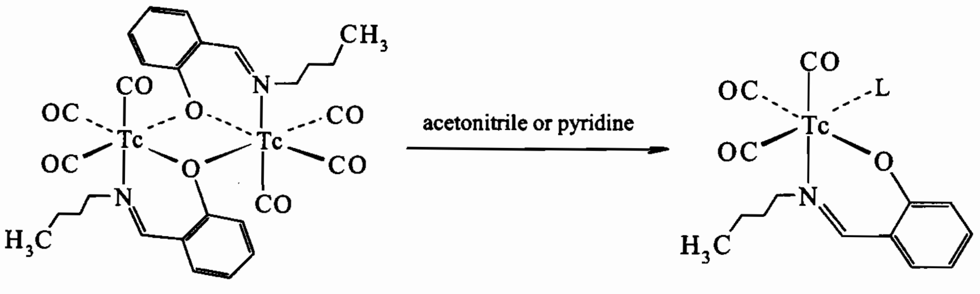

Fig. 2. Reaction of $[Tc(CO)_3(salbut)]_2$ in acetonitrile or pyridine.

2404

Synthesis, Structure, and Properties of Technetium Complex with Polypyridyl Ligand

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The chemistry of the group seven complexes has been attractive because the complexes take a wide range of the oxidation state and they show rich structural and physical properties. Various pyridine type ligands have been utilized for the chemistry of the Mn and Re complexes, for example the rhenium tricarbonyl polypyridine complexes which have been receiving a great deal attention with photoluminescence. We report about synthesis and characterization of the two types of the new technetium polypyridine complexes. The former complex can be expected to have photoluminescence, and the latter, which is the seven coordinate complex, is the rare example for technetium. It is found that the structural and physical properties of the new technetium complexes in this research are very similar to those of the rhenium analogs.

1. Mononuclear Technetium(I) Having 2,2'-Bipyridine

The new complex, *fac*-[TcCl(CO)$_3$(bpy)] (bpy = 2,2'-bipyridine) (**1**) was synthesized by the reaction of (Et$_4$N)$_2$[*fac*-TcCl$_3$(CO)$_3$] with excess amount of bpy in acetonitrile at room temperature. Figure 1 shows the ORTEP drawing of **1**. The technetium atom exhibits a distorted octahedral geometry, coordinated by one chloride anion, three CO, and one bpy ligand. The three CO ligands are mutually oriented in *fac* position. The Tc-C bond lengths (av. 1.906 Å) of **1** are very similar to the known technetium(I) tricarbonyl complexes. The Tc-N (av. 2.187 Å) and Tc-Cl (2.496 Å) distances and the bond angles of **1** resemble those of the rhenium analogs. The IR spectrum of **1** showed three absorptions of carbonyls and absorptions of bpy. The carbonyl absorption bands were observed at 1900, 1930, and 2015 cm^{-1}. The bands of carbonyls are almost the same as the manganese and rhenium analogues. The UV-vis absorption spectrum of **1** in acetonitrile showed the absorption maximum at 350 nm (ε ≒2700). It is known that the

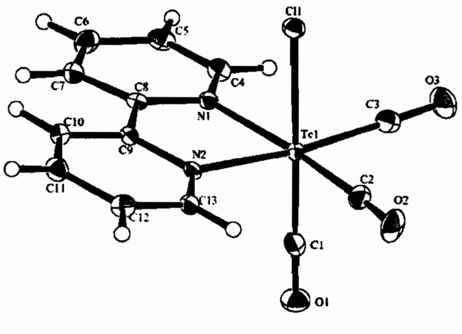


Figure 1. ORTEP drawing of **1**.

complexes of the manganese and rhenium analogs show the absorption maximum of the MLCT band at 360～375 nm (ε ≒ 2000). Therefore, the absorption of 350 nm for **1** is assignable to the MLCT band.

2. Mononuclear Oxotechnetium Complex Having N,N,N',N'-Tetrakis(2-pyridylmethyl)-ethylenediamine

Treatment of (n-Bu_4N)[$Tc(O)Cl_4$] with N,N,N',N'-tetrakis(2-pyridylmethyl)ethylenediamine (tpen) in a 1:1 ratio in ethanol at room temperature gave a brown solution, from which dark brown crystals (**2**) were isolated by the addition of large amount of NH_4PF_6 in ethanol. The IR spectrum of **2** showed absorption bands for tpen and PF_6^-, besides the Tc=O band at 1022 cm^{-1}. Figure 2 shows UV-vis absorption spectrum in acetonitrile. The absorption spectral feature is very similar to that of the seven coordinate oxorhenium complex, $[Re^{IV}(O)(tpen)]^{2+}$.[1] The absorption band at 833 nm (836 nm for $[Re^{IV}(O)(tpen)]^{2+}$) is assignable to d-d transition. The positions of the intense bands at 366 and 332 nm for **2** are blue-shifted from those of the $[Re^{IV}(O)(tpen)]^{2+}$ (428, 381, 361 nm). Thus, the bands at 366 and 332 nm for **2** are ascribed as the metal-to-ligand charge transfer band. From these data, we characterized the complex **2** as the seven coordinate technetium(IV) complex, $[Tc^{IV}(O)(tpen)](PF_6)_2$. The preliminary X-ray crystal structure of **2** also supports the formation of the seven coordinate complex. The coordination environment of the cation of **2** resembles that of $[Re^{IV}(O)(tpen)]^{2+}$.

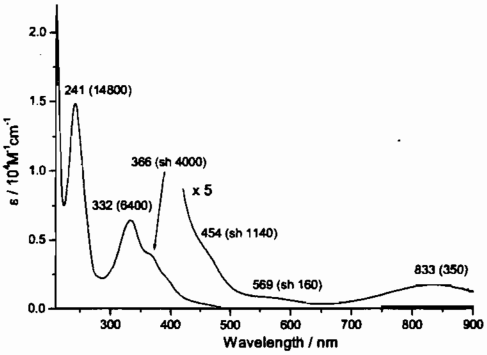
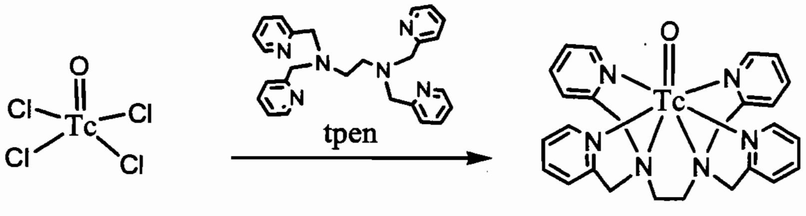


Figure 2. UV-vis Spectrum for **2** in acetonitrile.

Scheme 1



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2405-K

VERSATILITY OF TECHNETIUM CHEMISTRY AS VIEWED FROM THE RECENT PROGRESS OF RHENIUM CLUSTER COMPLEXES

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Rhenium located just below technetium in the periodic table has the most versatile chemistry among transition elements. Rhenium as a member of group 7 transition metals shows characteristics of both early and late transition metal complexes. Thus, while rhenium tends to form direct metal-metal bond to give various cluster complexes, numerous monomeric complexes are also known. Such structural diversity would be inherently found in Tc chemistry, although the research is limited so far. Here I will summarize the current status of rhenium cluster chemistry, and try to discuss possible versatility of corresponding technetium chemistry.

1. Similarity and Differences between Rhenium and Technetium Complexes.

In general, second transition metals and their congener of third transition series, give structurally similar complexes. The most significant difference in the structurally analogous rhenium and technetium complexes would be found in their redox potentials. From the general trends found in the pairs of complexes in other groups such as Mo-W, Ru-Os, and Rh-Ir, it is expected that a technetium complex would show more positive redox potentials by ca. 0.5 V than its rhenium analogue. Thus lower oxidation state is more stabilized in technetium. Ligand substitution lability would be expected to be somewhat higher in Tc than corresponding Re compounds.

2. Cluster Complexes of Rhenium.

Rhenium in its lower oxidation states gives stable Re-Re bonded cluster complexes. Figure 1 shows the core structures of some typical cluster complexes with d electron numbers. The Re-Re bonded core structures depend on the number of d-electrons, although the correlation in Figure 1 is not strictly applied. Thus Re(III) with d^4 electronic configuration forms the highest number of Re-Re bond per each Re atom giving well known Re-Re quadruple bonded dimers as well as Re-Re single bonded octahedral hexanuclear complexes. With lower number (or higher number) of d electrons, Re gives di-, tri- and tetranuclear complexes. Although not all of these structures are found in technetium so far, they will be very likely found in Tc.

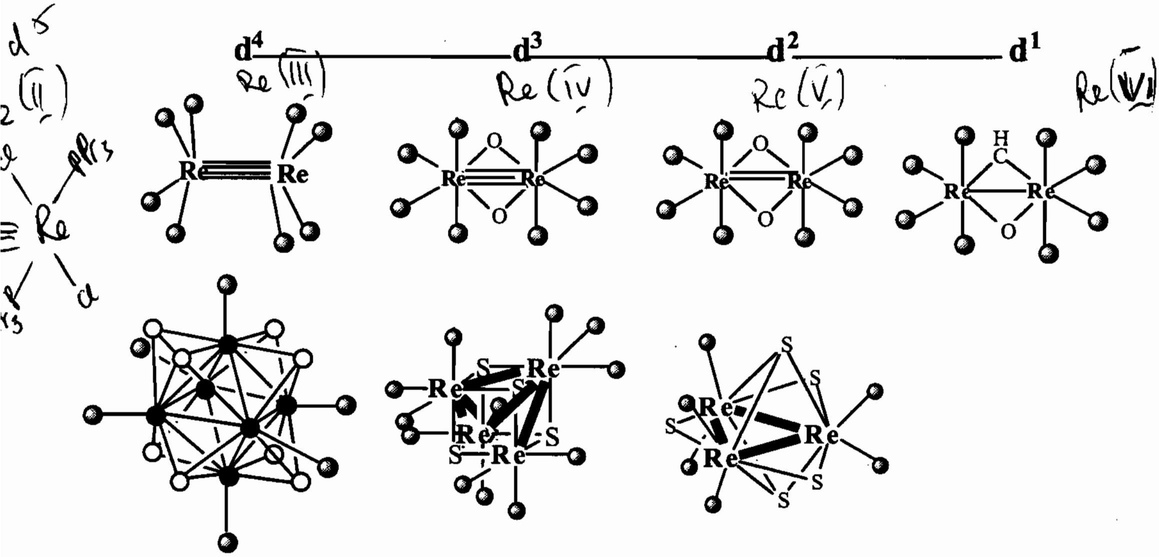

Figure 1. Various structures of Re-Re bonded cluster complexes.

3. Octahedral Hexarhenium Complexes.1)

Among various Re cluster complexes, hexarhenium(III) complexes have been studied most extensively in these years. The most significant aspect of the hexarhenium(III) complexes is their strong luminescence with relatively long lifetime (in the order of μs).2,3) Emissions are observed also for other d^4 octahedral complexes such as Mo(II) and W(II). This fact indicates that corresponding hexanulcear Tc(III) clusters would also be strongly luminescent if prepared. The hexarhenium core is extremely stable, and its terminal sites (gray circles in the Figure) can be substituted in a stepwise manner by various ligands such as halide ion, CN^-, NCS^-, pyridyl ligands, phosphine ligands, CH_3CH. DMSO, and so on. This has been used to intoduce functional moieties to the hexanulcear core and also to construct supramolecular assemblies based on the core.

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3 14

REDOX-ASSISTED STRUCTURAL TRANSFORMATION OF A TPEN-COORDINATED RHENIUM(V)-OXO COMPLEX AND SYNTHESIS OF HETEROMETALLIC CLUSTERS

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N,N,N',N'-tetrakis(2-pyridylmethyl)ethylenediamine (abbreviated as tpen, Figure 1) affords a versatile array of coordination compounds. It usually acts as a hexadentate ligand (*i.e.*, all the six nitrogen atoms are used for coordination), while some other coordination modes, in which the number of coordinating atoms is limited to five or less, has been described.[1] We have recently reported synthesis and characterizations of $[Re^{V}O(tpen)]^{3+}$ (**1**) and one electron reduced derivative $[Re^{IV}O(tpen)]^{2+}$ (**2**), both of which showing full coordination of tpen to the $Re^{V/IV}O$ group.[2] Here we report our finding that the fully coordinated tpen in **1** displays a redox-assisted disproportionation reaction in solution, in which one of two bis(2-pyridylmethyl)amine moieties of tpen within **1** partly dissociates from the $\{Re^{V}O\}$ group to form a novel Re^{VII} complex $[ReO_3(\kappa^3\text{-tpenH})]^{2+}$ (**3**) (Figure 2). Complex **3** contains a protonated dangling arm of the bis(2-methylpyridyl)amine and can be employed as a rhenium-containing tridentate ligand to form a range of heterometallic complexes.

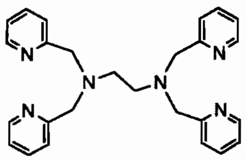

Figure 1. Chemical structure of tpen.

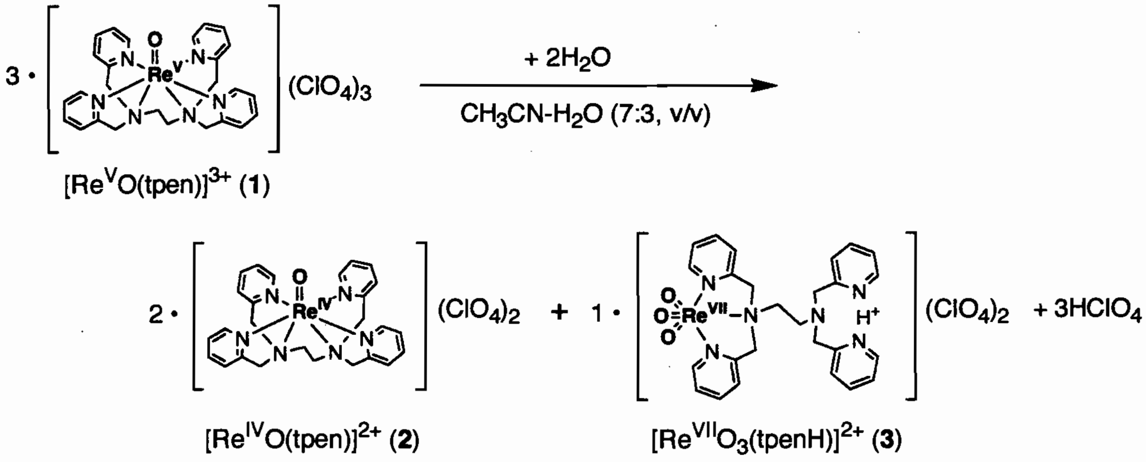

Figure 2. Redox-assisted disproportionation of $[Re^{V}O(tpen)]^{3+}$ (**1**).

Complexes **1** and **2** were structurally characterized previously.[2] Analytically pure **3** was initially obtained unexpectedly during the synthetic work-up intended for the isolation of **1** employing $\mathrm{ReOCl_3(PPh_3)_2}$ and tpen as synthetic sources.[3] Colorless single crystals of **3** suitable for X-ray diffraction analysis were grown from an aqueous solution by slow evaporation (10 days) at room temperature. The molecular structure of **3** (Figure 3) shows the *fac*-$\mathrm{ReO_3}$ center which is supported by one of two bis(2-pyridylmethyl)amine moieties of tpen while the other tridentate moiety is left uncoordinated. This coordination mode of tpen is unprecedented.

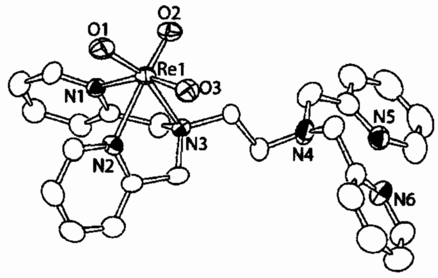

Figure 3. X-ray structure of **3**.

Complex **1** is stable in organic solutions, but, in the presence of water, it gives rise to ^{1}H NMR and UV-vis spectral change. ^{1}H NMR spectrum of **1** dissolved in $\mathrm{CD_3CN}$-$\mathrm{D_2O}$ (7:3, *v/v*) exhibits pyridyl protons due to **1** which gradually decreased in intensity with time while new pyridyl peaks due to **3** emerged. The decay of **1** was well described by the first-order kinetics from which the rate constant $1.9 \times 10^{-3}\ \mathrm{s^{-1}}$ (25 °C) was obtained. The concomitant generation of paramagnetic **2** was confirmed by observing the sequential change in UV-vis spectra in which the intensity of absorption bands due to **2** (λ_{max} = 358, 423, 500 (sh), and 850 nm) was increased with time. These measurements also provided the basis for stoichiometry of the disproportionation reaction (Figure 2).

The synthetic ability of **3** to form heterometallic complexes was studied. Thus, reaction of **3** with 1 equiv. of $\mathrm{Fe(ClO_4)_3}$ in water in the presence of $\mathrm{CH_3COONa}$ afforded a tetranuclear complex $[\mathrm{Fe_2}(\mu\text{-O})(\mu\text{-CH_3COO})_2\{(\mu\text{-}\kappa^3\text{:}\kappa^3\text{-tpen})\text{-ReO_3}\}_2]^{4+}$ (**4**) in a 40% yield. The molecule consists of a (μ-oxo)bis(μ-acetato)diiron(III) core which is supported by two bis(2-pyridylmethyl)amine ligands of **3** (Figure 4). Studies on synthetic derivatization of **3** with Re(I), Cu(I), $\mathrm{Rh_2(CH_3COO)_4}$, and some other metal ions and clusters will be also discussed.

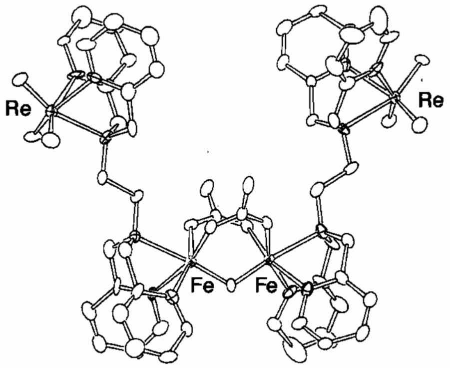

Figure 4. X-ray structure of **4**.

References: 1) For example: M. Sokolov, K. Umakoshi, and Y. Sasaki, *Inorg. Chem.*, **41**, 6237 (2002); 2) H.-Y. Jin, S. Ikari, K. Kobayashi, K. Umakoshi, H. Sugimoto, A. Mitani, M. Abe, Y. Sasaki, and T. Ito, *Bull. Chem. Soc. Jpn.*, **77**, 1139 (2004); 3) A. Mitani, M. Abe, K. Tsuge, and Y. Sasaki, *Chem. Lett.*, **32**, 502 (2003).

2407

VERSATILITY OF BIDENTATE ANILINE DERIVATIVES AS LIGANDS FOR RHENIUM(V) AND TECHNETIUM(V)

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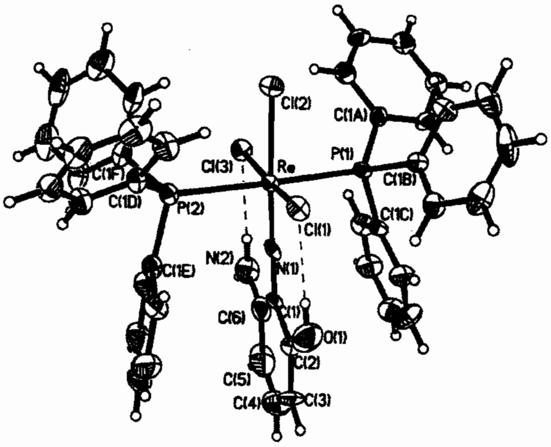
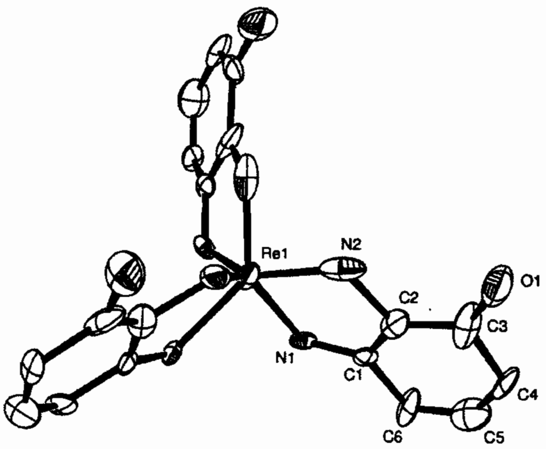
The exploration of aniline derivatives as ligands for Re(V) and Tc(V) has led to the isolation of unusual complexes. The reaction of *trans*-[$ReOCl_3(PPh_3)_2$] and *trans*-[$ReO_2(py)_4$]I under aerobic conditions in ethanol with the ambidentate 3-hydroxy-1,2-diaminobenzene (H_2dab-OH) has led to the formation of [Re^V(dab-OH)$Cl_3(PPh_3)_2$] (**1**) and [Re^{IV}(dab-OH)$_3$]I (**2**) respectively. In **1** dab-OH is coordinated monodentately as an imide, and in **2** it is present as a diamide. Also, with *trans*-[$ReOCl_3(PPh_3)_2$] and 3-nitro-1,2-diaminobenzene (H_2dab-NO_2) the oxo-free complex [ReCl(PPh_3)(dab-NO_2)$_2$] (**3**) was produced, with bidentate diamide coordination of each dab-NO_2. The neutral *cis*-dioxo complex [ReO_2(Hdab)(py)$_2$] (**4**), with Hdab coordinated as a monoamide, was obtained from *trans*-[$ReO_2(py)_4$]Cl and 1,2-diaminobenzene (H_2dab).



1



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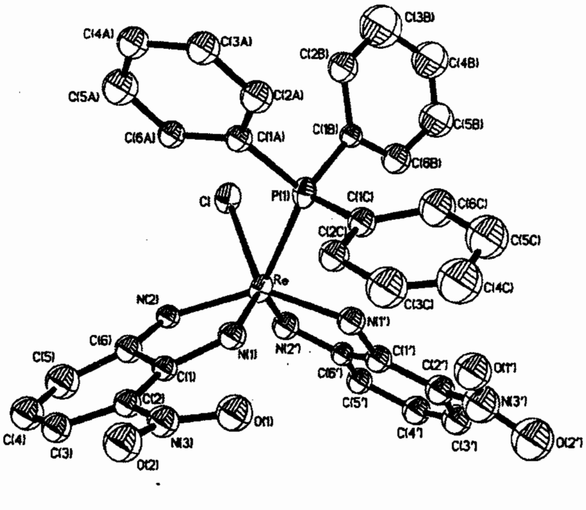

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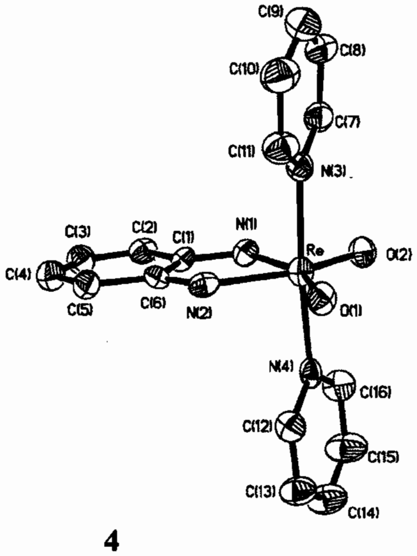

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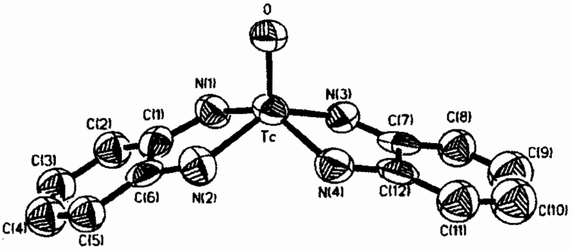
The simple reaction of (n-Bu_4N)[$MOCl_4$] (M=Tc, Re) with H_2dab and 2,3-diaminopyridine (H_2dap) gave the anionic complex (Bu_4N)[MO(dab)$_2$] (**5**) and the cationic [ReO(dapH)$_2$]Cl (**6**) respectively. DapH is coordinated in the diamidopyridinium mode.



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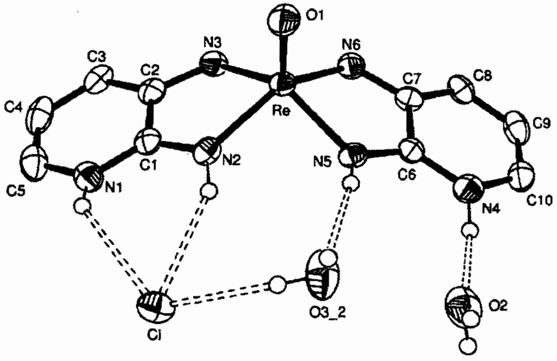
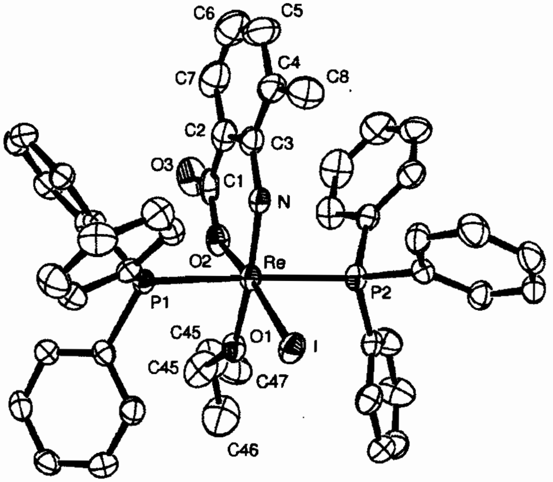


6

Three different coordination modes were observed for the potentially bidentate ligand 2-amino-3-methylbenzoic acid (H_3amb). In [Re(amb)(OEt)I(PPh_3)$_2$] (**7**) amb acts as a trianionic bidentate chelate *via* a double deprotonated amino nitrogen and a carboxy oxygen. In [ReO(Hamb)(H_2amb)(PPh_3)] (**8**) Hamb is coordinated in the amidobenzoate (Hamb) and symmetrically chelating carboxylate form (H_2amb).



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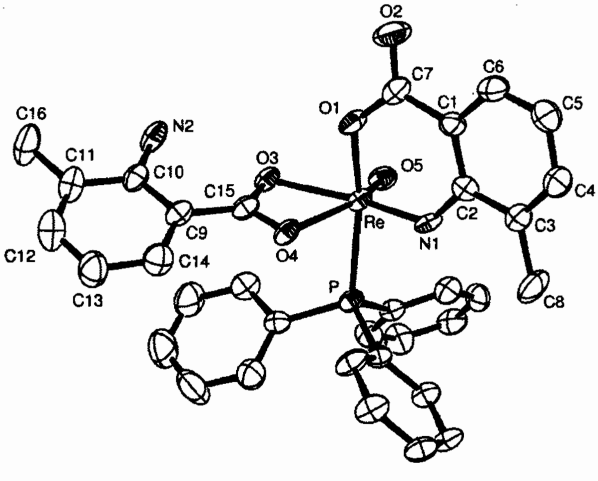

8

The synthesis and structural features of complexes **1**-**8**, as well as related compounds, will be presented and discussed.

2408

MULTIDENTATE DIPYRIDYL DERIVATIVES AS CHELATES FOR RHENIUM(V)

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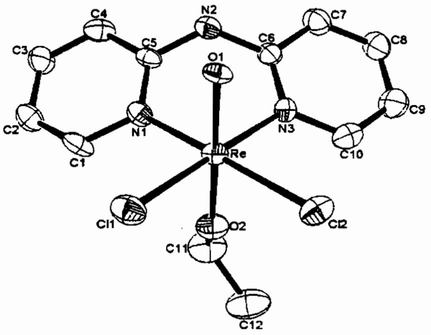
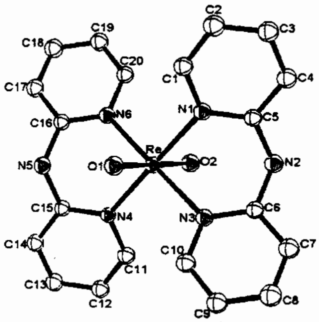
Coordination compounds of rhenium in oxidation state +V are of great interest due to the application of the metal as a therapeutic agent in nuclear medicine [1]. In our ongoing efforts to synthesise new rhenium complexes, we report here the preparation and characterisation of oxorhenium(V) complexes with multidentate dipyridyl ligands. Reaction of a two-fold molar excess of the potentially *N,N*-donor ligand 2,2'-dipyridylamine (dpa) with *trans*-$[ReO(OEt)Cl_2(PPh_3)_2]$ in ethanol led to the isolation of the monomer $[ReOCl_2(OEt)(dpa)]$ **(1)**.

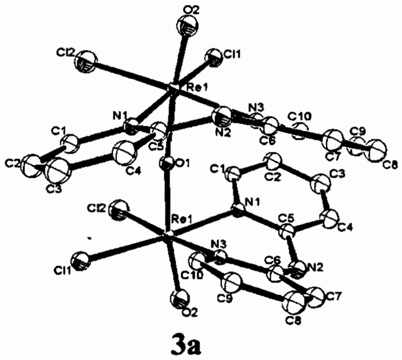


1

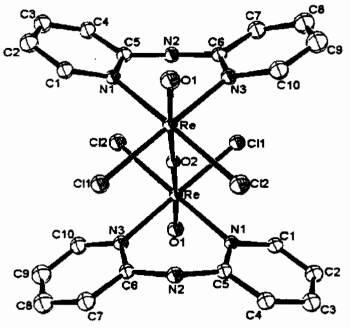


2

Treatment of *trans*-$[ReOCl_3(PPh_3)_2]$ with a tenfold molar excess of dpa in ethanol at reflux yielded the *trans*-dioxo complex $[ReO_2(dpa)_2]Cl$ **(2)**, but with a two-fold molar excess the dimer (μ-O)[{$ReOCl_2(dpa)_2$}] **(3a)** was isolated. The latter reaction with (*n*-Bu_4N)[$ReOCl_4$] as starting material in ethanol at room temperature led to a dark green product, also with the formulation (μ-O)[{$ReOCl_2(dpa)_2$}] **(3b)**.

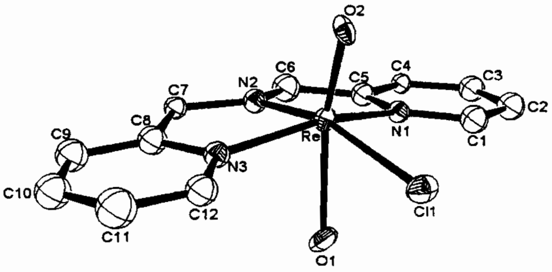


3a



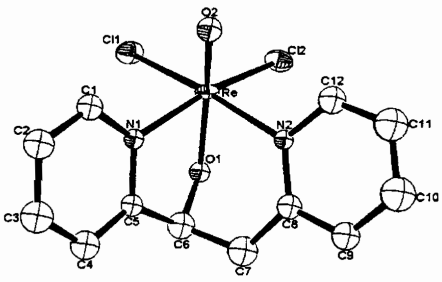
3b

Reacting equimolar quantities of (n-Bu_4N)[$ReOCl_4$] and di-(2-picolyl)amine (Hdipa) in acetone at room temperature led to the formation of an apple green solid with formulation [$ReOCl(dipa)(OH_2)$]Cl (**4**) in which Hdipa acts as a monoanionic tridentate chelate.

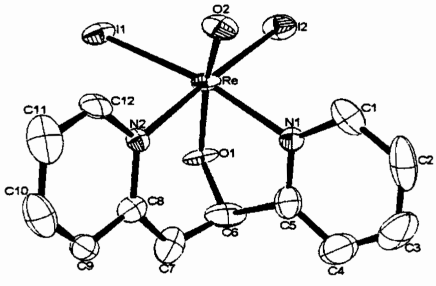


4

The reaction of either *trans*-[$ReOCl_3(PPh_3)_2$] or *cis*-[$ReO_2(PPh_3)_2I$] with 1,2-*bis*(2-pyridyl)ethylene (bpe), in which bpe undergoes a metal-promoted nucleophilic attack by a water molecule, produces two complexes with general formula [$ReO_2(bpe)L_2$], where L = Cl^- (**5a**) and L = I^- (**5b**).



5a



5b

The preparation of the complexes, and the crystal structures of **1**, **2**·$3H_2O$, **3a**, **3b**·2DMSO, **4**, **5a** and **5b** will be presented and discussed.

Reference

[1] M. Nicolini and U. Mazzi, Technetium, Rhenium and other Metals in Chemistry and Nuclear Medicine 5 (Servizi Grafici Editoriali, Padova, 1999).

2409

OXORHENIUM(V) COMPLEXES WITH QUINOLINYLAMIDO: STEREOCHEMISTRY, SPECTROSCOPY, REACTIVITY, AN OAT CATALYTIC PROPERTY

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[Introduction] Rhenium compounds have received much attention for a variety of causes. Particular interest in rhenium compounds arises from the potential in radiotherapy because of similarity with chemical property of technetium applied to nuclear medicine. Therefore, it is important to explore stereoselective synthesis and reactivity of rhenium complexes. We have been interested in stereochemistry and reactivities of oxorhenium(V) complexes with didentate-*N,N* ligands having two types of coordination sites. The oxorhenium(V) complex [$ReOCl_2$(Hamq)(PPh_3)] containing 8-amino-2-methylquinoline (H_2amq), recently reported, shows unique replacement reactions of monodentate ligands PPh_3 for $OPPh_3$ or py derivatives with changing coordination geometry around the oxorhenium(V) core.[1] Spectroscopic analyses indicated that their structures do not retain in solution, and they have probably the same five coordination structure [$ReOCl_2$(Hamq)] which releases the monodentate ligands. Furthermore, [$ReOCl_2$(Hamq)(PPh_3)] showed oxygen atom transfer (OAT) catalytic property from pyO to PPh_3. It is expected that OAT reaction proceeds on the vacant site, since py acts as an inhibiter to combine to the vacant site and form a py complex [$ReOCl_2$(Hamq)(py)]. Therefore, in order to investigate the change of reactivity, we introduced negatively charged didentate ligands, tetrachlorocatechol (H_2Cl_4cat), instead of two chlorides, and synthesized new '2+2+1' complexes [ReO(Cl_4cat)(Hamq)(PPh_3)]. In our presentation, stereochemistry, spectrochemistry, reactivity, and OAT catalytic property of the obtained '2+2+1' oxorhenium(V) complexes will be discussed.

[Results and Discussion] To a suspension containing H_2Cl_4cat in acetone/water was added [$ReOCl_2$(Hamq)(PPh_3)] and stirred for 1 h. After concentrating this solution until the precipitate appeared, the precipitated, catecolato complex [ReO(Cl_4cat)-(Hamq)(PPh_3)], was collected and washed with water.

The X-ray crystal analysis of [ReO(Cl_4cat)(Hamq)(PPh_3)] (Figure 1) showed different coordination geometry from precursor [$ReOCl_2$(Hamq)(PPh_3)]. In the case of the precursor complex, the *trans* position of oxo ligand is occupied with amido N atom of quinolinylamido ligand. On the other hand, in the catecolato complex, O atom of catecolato ligand lies in the *trans* position of oxo ligand.

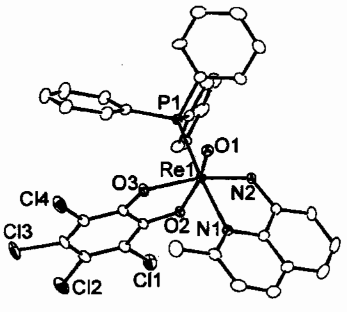


Figure 1. X-ray crystal structure of [ReO(Cl_4cat)(Hamq)(PPh_3)]

UV-vis absorption spectra of the catecolato complex in CH_2Cl_2 solution showed concentration dependence (Figure 2). In dilute solution, the complex does not retain the structure observed in the X-ray analysis. Moreover, it indicates that they have five-coordination geometry which releases the PPh_3 like precursor complex. IR and far-IR spectra of the catecolato complex showed characteristic bands due to Re=O (936 cm^{-1}) and absence of Re-Cl bonds in the region of 300 cm^{-1}.

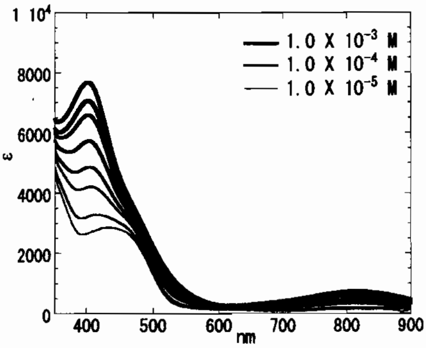


Figure 2. UV-vis absorption spectra of $[ReO(Cl_4cat)(Hamq)(PPh_3)]$

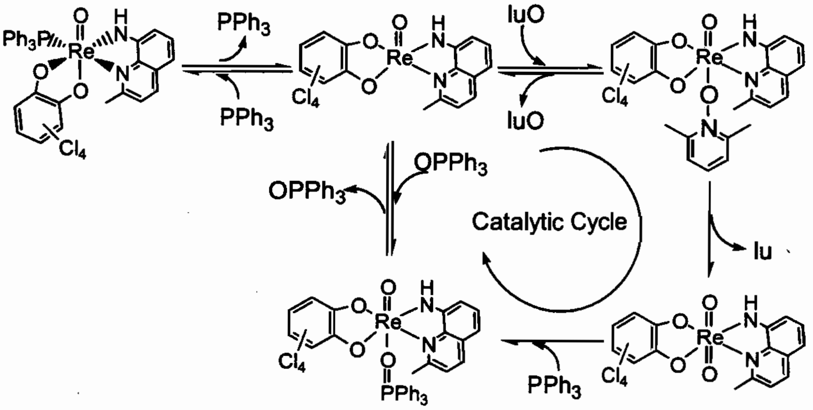
By using the easy PPh_3 replacement property of the catecolato complex, we attempted to introduce different neutral ligand L, such as $OPPh_3$ and pyridine derivatives, same as observed in the precursor complex $[ReOCl_2(Hamq)(PPh_3)]$.[1] When L are $OPPh_3$, 4-Mepy, or 4-*t*-Bupy, the replaced complexes [ReO(Cl_4cat)(Hamq)L] were obtained. These complexes also show concentration dependence in solution state.

OAT catalytic reactions of the catecolato complex (eq. 1) were monitored by UV-vis absorption spectra. The control experiment of the reaction of luO (2,6-lutidine oxide; oxygen

$$PPh_3 + luO \xrightarrow{[ReO(Cl_4cat)(Hamq)(PPh_3)]} OPPh_3 + lu \qquad (1)$$

donor) and PPh_3 (oxygen acceptor) without the catecolato complex show no reaction. Under the condition of 1.0×10^{-5} M of catalyst $[ReO(Cl_4cat)(Hamq)(PPh_3)]$ and 1.0×10^{-2} M of luO and PPh_3 in CH_2Cl_2 at r.t., the initial rate v_0 was 1.8×10^{-5} M s^{-1}. From the results of measurement of a variety of concentration conditions, it was revealed that the reaction order with respect to the catalyst $[ReO(Cl_4cat)(Hamq)(PPh_3)]$ and luO concentration was 1. On the other hand, the reaction order with respect to PPh_3 concentration was -1 (eq. 2). The expected reaction scheme is shown in Scheme 1.

$$v_0 = k\,\frac{[ReO(Cl_4cat)(Hamq)(PPh_3)]\,[luO]}{[PPh_3]} \qquad (2)$$



Scheme 1

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[1] T. Ohashi, Y. Miyashita, Y. Yamada, K. Fujisawa, and K. Okamoto, *Bull. Chem. Soc. Jpn.*, **76**, 1199 (2003).

2410

RHENIUM-CONTAINING SULFUR-BRIDGED HETEROTRINUCLEA COMPLEXES: STEREOCHEMICAL, SPECTROCHEMICAL, AND ELECTROCHEMICAL PROPERTIES

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Rhenium complexes are well known as technetium surrogate to design many types of coordination compounds because of the chemical similarities with these group 7 elements. Rhenium as well as technetium can take a variety of oxidation numbers and coordination structures such as metal-metal multiple bonds and linear-type oxometal clusters. Although many rhenium complexes with phosphorus or nitrogen donor ligands have been widely investigated so far, rhenium complexes containing coordinated sulfur atoms are still rare except for sulfide cluster compounds. Therefore, we were interested in electrochemistry and stereochemistry of rhenium ions incorporated into S-bridged heteropolynuclear structures. We have synthesized a number of S-bridged heteropolynuclear complexes using thiolato-type mononuclear complexes *fac*(*S*)-[M(aet)$_3$] (M = Co^{III}, Rh^{III}, Ir^{III}; aet = 2-aminoethanethiolate) as building blocks. In this presentation, we report stereochemical, spectrochemical, and electrochemical properties of heterotrinuclear complexes involving the rhenium ion in comparison with other related complexes [1,2].

The trinuclear complexes [Re{M(aet)$_3$}$_2$]$^{3+}$ (M = Rh^{III}, Ir^{III}) were obtained by chemical reduction of an acidic mixture of *fac*(*S*)-[M(aet)$_3$] and NH$_4$ReO$_4$. These complexes were separated into *meso* (ΔΛ) and *rac* (ΔΔ/ΛΛ) isomers by column chromatography or selective crystallization. The single crystal X-ray analyses indicated that all isomers have a linear-type trinuclear structure (Figure 1). The central rhenium atom is coordinated by six sulfur atoms of the terminal *fac*(*S*)-[M(aet)$_3$] units, and situated in an octahedral environment. The Re···M distances are short and the Re-S-M angles are acute in comparison with the corresponding complexes [M'{M(aet)$_3$}$_2$]$^{3+}$ (M' = Co^{III}, Rh^{III}) (Table 1).

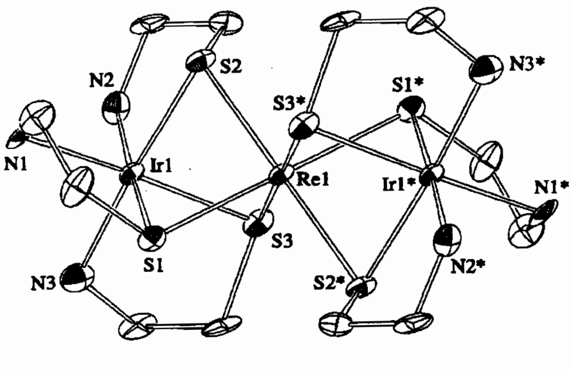

Figure 1 Structure of the representative complex ΔΛ-[Re{Ir(aet)$_3$}$_2$]$^{3+}$.

The IR spectra of *meso* and *rac* isomers of [Re{M(aet)$_3$}$_2$]$^{3+}$ showed a similar pattern, which is typical for the S-bridged linear-type trinuclear structure. Their NMR spectra in D$_2$O displayed six sets of ^{1}H signals and two ^{13}C signals due to the aet ligands, indicating that

Table 1 Selected Bond Distances (Å) and Angles (°) for [M'{M(aet)$_3$}$_2$]$^{n+}$

[M'{M(aet)$_3$}$_2$]$^{n+}$	M'-M	M'-S	M-S	S-M'-S	S-M-S	M'-S-M
$\Delta\Lambda$-[Re{Rh(aet)$_3$}$_2$]$^{3+}$	2.8248(9)	2.383(6)	2.330(6)	86.5(2)	89.0(2)	73.7(2)
$\Delta\Delta/\Lambda\Lambda$-[Re{Rh(aet)$_3$}$_2$]$^{3+}$	2.840(2)	2.386(9)	2.315(10)	85.6(3)	88.9(4)	74.3(3)
$\Delta\Lambda$-[Re{Ir(aet)$_3$}$_2$]$^{3+}$	2.7961(4)	2.397(3)	2.330(3)	86.97(10)	90.14(10)	72.52(8)
$\Delta\Delta/\Lambda\Lambda$-[Re{Ir(aet)$_3$}$_2$]$^{3+}$	2.810(2)	2.41(1)	2.33(1)	86.4(4)	90.3(5)	72.8(4)
$\Delta\Lambda$-[Re{Ir(aet)$_3$}$_2$]$^{4+}$	2.7523(3)	2.411(3)	2.334(3)	87.87(9)	91.56(9)	70.88(7)
$\Delta\Lambda$-[Rh{Ir(aet)$_3$}$_2$]$^{3+}$	3.0194(3)	2.380(2)	2.325(2)	82.03(8)	84.45(9)	79.84(7)
$\Delta\Lambda$-[Co{Ir(aet)$_3$}$_2$]$^{3+}$	2.906(1)	2.297(2)	2.307(2)	84.7(1)	84.2(1)	78.3(1)

the S_6 or D_3 symmetrical S-bridged trinuclear structures observed in the crystals are retained in their aqueous solutions. The UV-Vis absorption spectra in H_2O showed characteristic d-d and CT bands due to the ReS_6 chromophore in the visible region. The *rac* isomers were optically resolved into $\Delta\Delta$ and $\Lambda\Lambda$ isomers using Na$_2$[Sb$_2$(*R*,*R*-tartrato)$_2$]. The $\Delta\Delta$ and $\Lambda\Lambda$ isomers showed enantiomeric CD bands to each other.

The cyclic voltammograms of *rac*-[Re{M(aet)$_3$}$_2$]$^{3+}$ in H_2O showed a reversible redox wave in a positive region ($E°'$ = +0.60 V for M = Rh^{III}, +0.37 V for M = Ir^{III}, vs Ag/AgCl). From spectroelectrochemical experiments, some oxidized species is observed in the case of M = Ir^{III} (Figure 2). Indeed, chemical or electrochemical oxidation of [Re{Ir(aet)$_3$}$_2$]$^{3+}$ yielded an oxidized complex [Re{Ir(aet)$_3$}$_2$]$^{4+}$. This complex is *meso* isomer of linear-type S-bridged trinuclear complex from X-ray analysis. The Re···Ir distances and Re-S-Ir angles in this oxidized complex [Re{Ir(aet)$_3$}$_2$]$^{4+}$ are significantly shorter and acuter than those in the reduced complex [Re{Ir(aet)$_3$}$_2$]$^{3+}$ (Table 1). The oxidized complex [Re{Ir(aet)$_3$}$_2$]$^{4+}$ was slowly decomposed by additional oxidation to form a dinuclear Ir complex without rhenium ions.

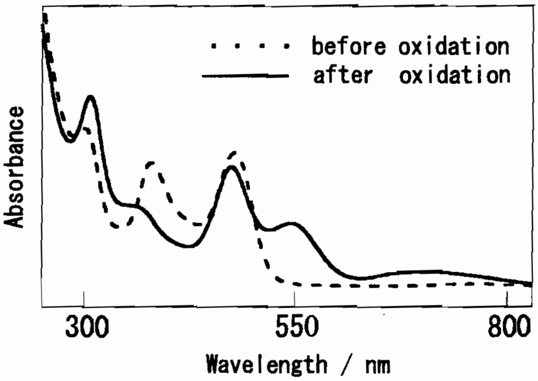

Figure 2 UV-Vis absorption spectra of [Re{Ir(aet)$_3$}$_2$]$^{3+}$ and [Re{Ir(aet)$_3$}$_2$]$^{4+}$.

References

[1] Y. Miyashita, N. Mahboob, S. Tsuboi, Y. Yamada, K. Fujisawa, and K. Okamoto, *Bull. Chem. Soc. Jpn.*, **74**, 1295 (2001).

[2] N. Mahboob, Y. Miyashita, Y. Yamada, K. Fujisawa, and K. Okamoto, *Polyhedron*, **21**, 1809 (2002).

2411

A KINETIC STUDY ON LIGAND SUBSTITUTION REACTION OF *N*-CYCLOHEXYL-2-PYRROLIDONE FOR TRIPHENYLPHOSPHINE IN TRICHLOROOXORHENIUM(V) COMPLEX

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Attila C. Bényei,‡ Yasuhisa Ikeda
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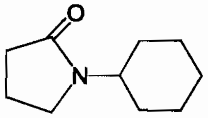
Abstract The wide use of ^{99m}Tc as diagnostic agents and the recent development of ^{186}Re and ^{188}Re radiopharmaceuticals have promoted studies for Tc and Re coordination chemistry. It is known that ^{186}Re and ^{188}Re decay by β-ray emission as well as γ-ray emission. Therefore, ^{186}Re and ^{188}Re compounds should be used as diagnostic and therapeutic medicines.[1] From the point of view, a number of Re complexes have been synthesized.[2] In the syntheses, $ReOCl_3(PPh_3)_2$ is often used as a starting material.[3] However, the ligand substitution behavior of this complex is little known. In this study, we have investigated the ligand substitution reaction (1) of *N*-cyclohexyl-2-pyrrolidone (NCP) for PPh_3 in $ReOCl_3(PPh_3)_2$ complex.

$$ReOCl_3(PPh_3)_2 + NCP \underset{reverse}{\overset{forward}{\rightleftharpoons}} ReOCl_3(PPh_3)(NCP) + PPh_3 \quad (1)$$



NCP

A green crystal was obtained by mixing of $ReOCl_3(PPh_3)_2$ with NCP, and the molecular structure was determined by means of X-ray diffraction. The obtained molecular structure is shown in Figure 1 and crystallographic data and selected bond lengths are listed in Table 1. It was revealed that NCP coordinates to Re center on the *trans*-position of Re1–O1 bond, and Re(V) center has a distorted octahedral geometry. The geometry around Re(V) center is almost identical to that of $ReOCl_3(PPh_3)(OPPh_3)$.[5]

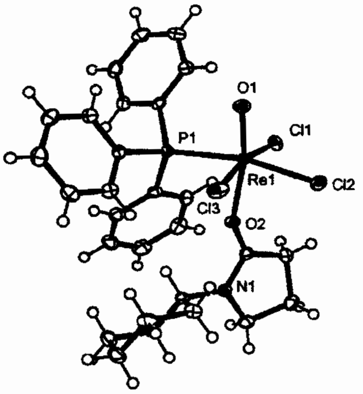


Figure 1. Molecular structure of $ReOCl_3(PPh_3)(NCP)$ complex.

Table 1. Crystallographic data and selected bond lengths of $ReOCl_3(PPh_3)(NCP)$ complex

Crystal system	Monoclinic
Space group	$P2_1/c$
Bond length	
Re1–O1	1.671(2) Å
Re1–O2	2.100(2) Å
Re1–Cl1	2.383(1) Å
Re1–Cl2	2.362(1) Å
Re1–Cl3	2.392(1) Å
Re1–P1	2.487(1) Å

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The equilibrium reaction (1) was examined in CH_2Cl_2 at 25 °C. Figure 2 shows each spectrum measured by addition of NCP to a solution of $ReOCl_3(PPh_3)_2$. From the absorbance change, the equilibrium constant of the reaction (1) was determined to be 0.33 ± 0.1 in CH_2Cl_2 at 25 °C. This indicates that NCP has relatively high donicity to the oxorhenium(V) moiety, which corresponds with our previous work for UO_2^{2+} ion.[4]

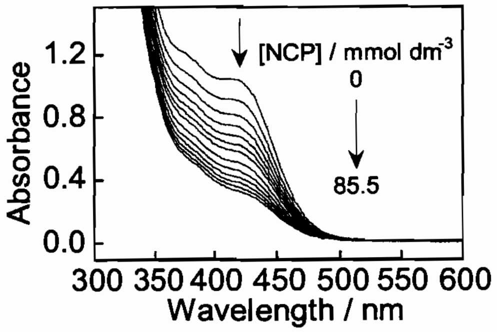

Figure 2. Spectral change in the reaction of $ReOCl_3(PPh_3)_2$ with NCP.

The kinetic study of the reaction (1) was carried out in CH_2Cl_2 by UV/Vis spectrophotometer. The rate constants of the *forward* reaction were measured by mixing a solution of $ReOCl_3(PPh_3)_2$ with NCP. It was found that the rate constants are independent of the concentrations of NCP as shown in Figure 3. The *reverse* reaction of (1) was also examined by mixing a solution of $ReOCl_3(PPh_3)(NCP)$ with PPh_3. Figure 4 shows that the rate constants are not affected by the concentration of PPh_3. These findings indicate that the rate determining steps of both directions of the reaction (1) are dissociation of leaving ligand (PPh_3 from $ReOCl_3(PPh_3)_2$ in the forward reaction, and NCP from $ReOCl_3(PPh_3)(NCP)$ in the reverse reaction). The overall reaction mechanism of the reaction (1) will be discussed.

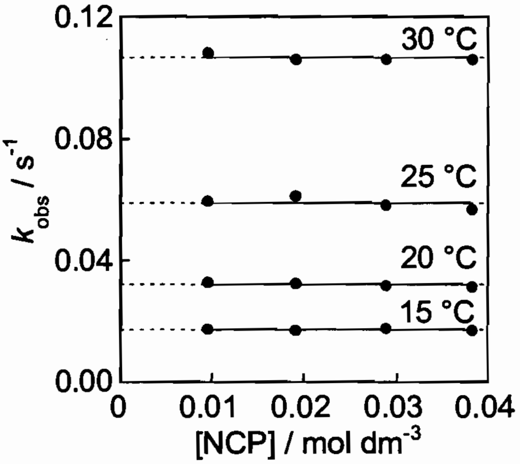

Figure 3. Rate constants of the *forward* reaction (1) : $ReOCl_3(PPh_3)_2$ + NCP.

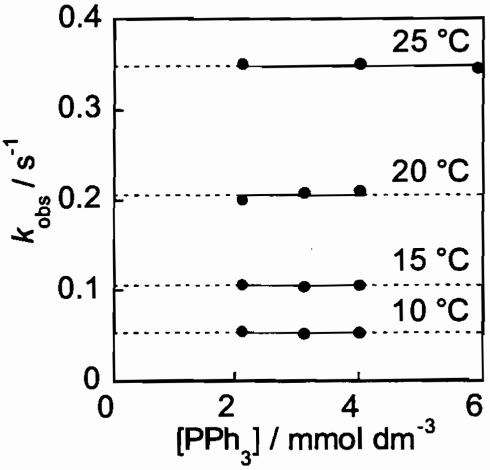

Figure 4. Rate constants of the *reverse* reaction (1) : $ReOCl_3(PPh_3)(NCP)$ + PPh_3.

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2412-K

RECENT ADVANCES IN TECHNETIUM RADIOPHARMACEUTICALS

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Technetium-99m (^{99m}Tc) is one of the most desirable radionuclides for external imaging in diagnostic nuclear medicine, due to the emission of a gamma ray of optimal energy (140 keV), a suitable half-life (6 h), and its availability from ^{99}Mo-^{99m}Tc generator systems. In addition, development of ^{99m}Tc radiopharmaceuticals for tumor imaging paves the way for therapeutic radiopharmaceuticals with high-energy beta emitters ^{186}Re or ^{188}Re because of the similar chemical properties of technetium and rhenium. At the initial stage of ^{99m}Tc radiopharmaceuticals, however, major efforts were focused on bone imaging and on excretory functions of liver or kidney since it was thought that Tc is a foreign substance and should be recognized and handled as such in the body.

In 1982, Yokoyama et al. reported that a ^{99m}Tc complex of bis(thiosemicarbazone) with a glucose backbone penetrated the intact blood-brain barrier of laboratory animals. They also reported that ^{99m}Tc complexes of bis(thiosemicarbazone) appended with a tertiary or a quaternary amine group showed myocardial uptake. Meanwhile, Davison and Jones demonstrated that pentavalent oxotechnetium (5+) forms a mononuclear complex of high stability with a N_2S_2 ligand. These studies stimulated the development of ^{99m}Tc complexes that cross the blood-brain-barrier, and a variety of ligands were developed that form mononuclear, neutral, lipophilic and stable ^{99m}Tc complexes. These include diaminodithiolate and propylene amine oxime.

The development of ^{99m}Tc radiopharmaceuticals for measuring myocardial blood flow constituted another challenge. Efforts were focused to develop monocationic ^{99m}Tc complexes with appropriate lipophilicity. The first cationic ^{99m}Tc complex that exhibited significant myocardial uptake in animals was Tc complexes of *tr*-$[^{99m}\mathrm{Tc(III)(DIARS)_2X_2}]^+$, where DIARS represents the *o*-phenylenebis(dimethylarsine) ligand and X represents chloride or bromide. Follow up studies showed that 1,2-bis(dimethylphosphino)ethane (DMPE) provided cationic ^{99m}Tc complexes of *tr*-$[^{99m}\mathrm{Tc(III)(DMPE)_2Cl_2}]^+$ and $[^{99m}\mathrm{Tc(I)(DMPE)_3}]^+$, which stimulated the development of organometallic ^{99m}Tc(I) hexakis(isonitrile) complexes, prototype compounds of currently being used ^{99m}Tc myocardial perfusion agent. .

Current efforts are directed toward the development of ^{99m}Tc radiopharmaceuticals that provide diagnostic information compatible to that of ^{11}C-, ^{18}F- and ^{123}I-lableled compounds.

Two chemical approaches are conceptually divided to develop ^{99m}Tc radiopharmaceuticals. One constitutes conjugating inert ^{99m}Tc complexes to carrier molecules that possess high and specific binding abilities to target molecules. The carrier molecules vary form high molecular weight polypeptides such as monoclonal antibodies to small molecular weight compounds such as receptor antagonists. Based on the molecular design, ^{99m}Tc complexes for central nervous dopamine transporter imaging agents became available by conjugating neutral and lipophilic ^{99m}Tc complexes to parental tropane moieties. Another strategy involves ^{99m}Tc complexes that acquire biological abilities to localize the target tissues after complexation with appropriate ligands that do not localize to their targets in the absence of the Tc. Based on this concept, a ^{99m}Tc complex of R-3-quinuclidinl-benzilate (QNB) derivative was designed as a ligand for muscarinic acetylcholine receptor in the hope that a neutral and lipophilic ^{99m}Tc complex could act as the dephenyl methanol moiety of QNB. The former approach is called bifunctional radiopharmaceutical or conjugated (or tethered) design, and the latter integrated design.

^{99m}Tc polynuclear complexes constitute another class of radiopharmaceuticals that are widely being applied in diagnostic nuclear medicine. ^{99m}Tc complexes of bisphosphonate (diphosphonate) involve representative compounds of this class, where bisphosphonates serve as both a coordinating ligand and a bone binding functional group. High accumulation of ^{99m}Tc bisphosphonate to cancerous bone promoted palliative treatment of bone metastases with ^{186}Re complexes of bisphosphonate. On the other hand, a ^{99m}Tc-labeled tumor-seeking agent was developed using dissociation characteristic of ^{99m}Tc polynuclear complex per se. After screening of various ligands, dimercaptosuccinic acid (DMS) was found to be suitable as a ligand to form a pentavalent technetium polynuclear complex. Studies on tumor accumulation of ^{99m}Tc-DMS indicated that the increase in the tumor uptake of ^{99m}Tc DMS was observed by dilution-induced complex equilibrium displacement.

For the past 20 years, great progress in technetium chemistry has contributed to the development of a variety of ^{99m}Tc radiopharmaceuticals that are now being used in clinical studies. At the same time, significant knowledge has become available in the design of radiopharmaceuticals based on their characteristics of high sensitivity and extremely low substance amount. Future combination of the radiopharmaceutical design and technetium chemistry may pave the way to molecular imaging of a variety of disorders with ^{99m}Tc radiopharmaceuticals. The development of a new ^{99m}Tc radiopharmaceutical is a multidisciplinary effort and should need the collaboration of scientists in a variety of chemical and nuclear medicine fields. Without their joint efforts, nuclear medicine would not be where it is today, nor will it progress.

2413

APPLICATION OF PZC TO ^{188}W/^{188}Re GENERATORS

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Rhenium-188 is an attractive radionuclide for radiotherapy and can be obtained at carrier-free levels from a ^{188}W/^{188}Re generator. The concentration of ^{188}Re is relatively low from traditional alumina-based ^{188}W/^{188}Re generators, because the parent ^{188}W is produced in a relatively low specific activity by the double neutron capture reaction of enriched ^{186}W. Newly developed poly zirconium compound (PZC) [1] as the adsorbent of ^{99}Mo has more than 100 times higher adsorption capacity of molybdenum than alumina. In this study, applicability of PZC to an adsorbent for a ^{188}W/^{188}Re generator system was investigated.

Tungsten-188 was produced by the double neutron capture reaction of ^{186}W. The target material was 99.79% enriched $^{186}WO_3$ (ISOTEC Inc., USA or Euriso-top, France). The target (25–50 mg) in a quartz ampoule was irradiated for 26-52 days in JMTR (thermal neutron flux, 2.7×10^{14} $cm^{-2}\cdot s^{-1}$). The irradiated target was allowed to stand for more than 4 weeks for decay of ^{187}W (23.72 h). The irradiated target was dissolved in 2 M NaOH with heating. Preparation of ^{188}W/^{188}Re generators based on PZC was shown in Fig.1. $Na_2WO_4 \cdot 2H_2O$ which corresponds to the maximum adsorption capacity of W to 1 g of PZC, PZC and the ^{188}W

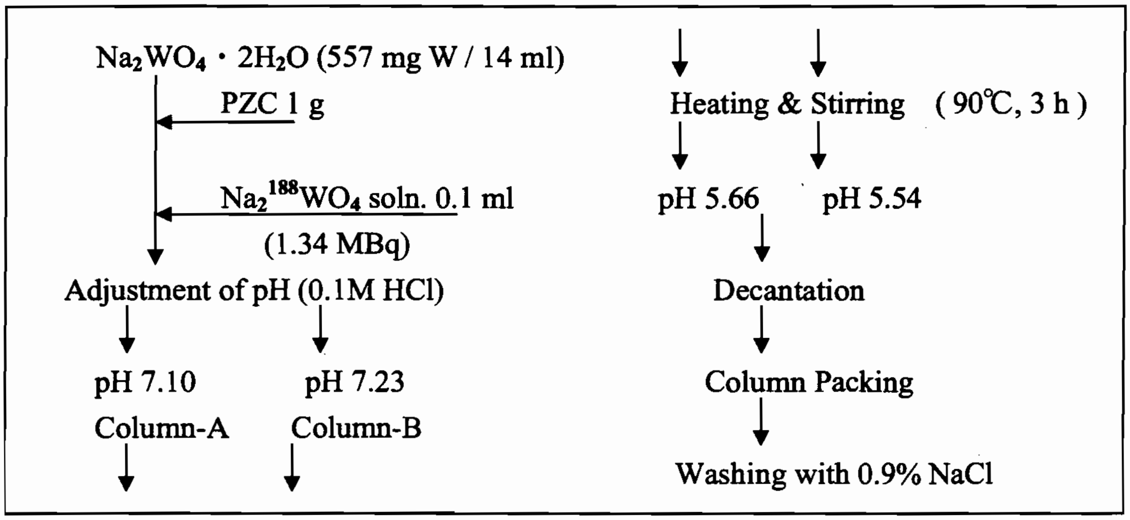

Fig. 1. Preparation of ^{188}W/^{188}Re generators based on PZC.

solution were added and pH was adjusted to about 7 with 0.1 M HCl. The solution was heated to 90℃ for 3 hours with occasional stirring. After eliminating the fine powdered PZC by decantation, the PZC adsorbed ^{188}W was packed to a glass column. The column was then washed with normal saline. Rhenium–188 was eluted with normal saline after the equilibrium between ^{188}W and ^{188}Re had almost reached.

The adsorption yield of ^{188}W to PZC was 90-95%. The elution profiles of ^{188}Re from the ^{188}W/^{188}Re generator by using a normal saline were shown in Fig. 2. More than 90% of ^{188}Re was eluted in the first 4 ml. The ^{188}Re elution yields were 60-75% during 154 days corresponding to twice of the half-life of ^{188}W (69.4 day). The parent ^{188}W breakthrough was observed to be 0.03% by measuring γ-rays of the daughter ^{188}Re.

The labeling yields of hydroxyethyliden diphosphonic acid (HEDP) and mercaptoacetyltriglycine (MAG3) with ^{188}Re eluted from the PZC column were high enough and equal to the results using ^{188}Re eluted from the alumina system.

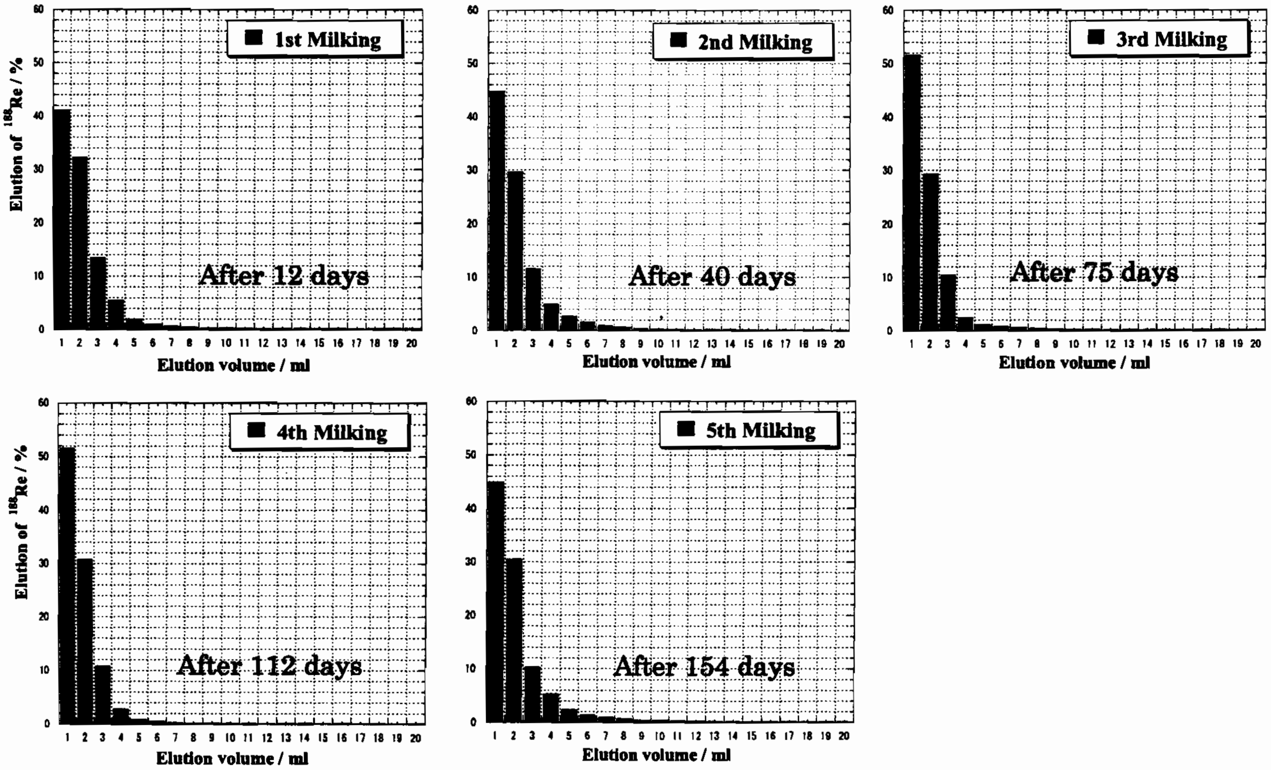

Fig. 2. Elution behavior of ^{188}Re from the generator.

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2414

LABELING OF BIFUNCTIONAL CHELATING AGENT, MAG3, WITH CARRIER-FREE ^{188}Re

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The radioisotopes of rhenium (^{186}Re and ^{188}Re) are attractive radionuclides for radiotherapy because of their energetic beta particles and gamma rays suitable for imaging. Oxorhenium(V) and oxotechnetium(V) complexes with quadridentate ligands such as N_3S and N_2S_2 ligands are often used as radiopharmaceuticals. Mercaptoacetyltriglycine, MAG3 (N_3S ligand, Fig. 1), is a useful bifunctional ligand in labeling monoclonal antibodies with metallic radionuclides. In this study, the labeling of MAG3 with carrier-free ^{188}Re from a ^{188}W/^{188}Re generator was investigated in detail. The ^{188}Re-MAG3 complex was synthesized by the direct labeling method (solid-phase synthesis) [1] and by the indirect labeling method using a transfer ligand (citric acid [2] or gluconic acid). The dependence of the labeling yield upon the reaction conditions such as the concentrations of tin(II) chloride dihydrate as a reducing agent, S-benzoyl MAG3 and the transfer ligand, pH, temperature, reaction time and the addition of a carrier (final concentration: 20 μg Re/ml) was examined.

The ^{188}W/^{188}Re generator was prepared by the alumina column system [3] with $^{188}WO_3$ produced by the irradiation in JAERI JMTR (a thermal neutron flux of 2.7×10^{14} n cm^{-2} s^{-1}) or JAERI JRR-3 (1.0×10^{14} n cm^{-2} s^{-1}) for 26-52 days. Rhenium-188 solution (2×10^5 - 3×10^6 Bq ml^{-1}) was obtained from the generator in a 0.9% NaCl solution and was used for labeling

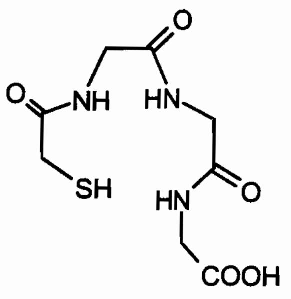

Fig. 1. Chemical structures of MAG3.

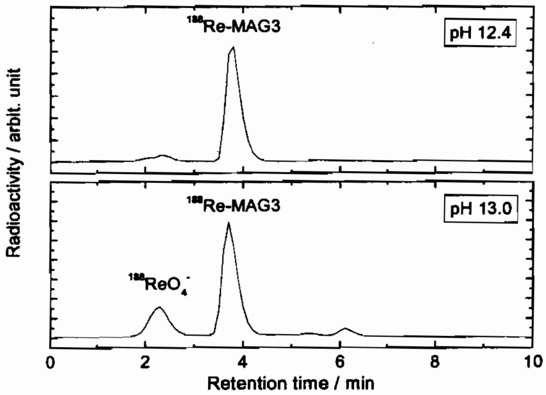

Fig. 2. Typical chromatograms of ^{188}Re-MAG3 synthesized at different pH by the direct method.

purposes without further purification. Radiochemical yield of ^{188}Re-MAG3 was determined by reversed phase HPLC (Hypersil C_{18} BDS-5, 4.6 mmΦ×150 mm) using 4% EtOH - 0.01 M phosphate buffer (pH = 7). The flow rate was 1.0 ml/min. Typical chromatograms are shown in Fig. 2. Retention times of $^{188}ReO_4^-$ and ^{188}Re-MAG3 were 2.4 min and 3.7-3.9 min, respectively.

The influences of the labeling yield on pH are shown in Fig. 3. Optimal pH region were 12.1 – 12.6 for the direct method, 2 – 5 for use of citric acid and 2.6 – 3 for use of gluconic acid. However the differences of the optimum conditions such as pH and reaction time at room temperature were observed by using a different transfer ligand, the labeling yield of ^{188}Re-MAG3 synthesized by the all method was over 90% under the optimum conditions.

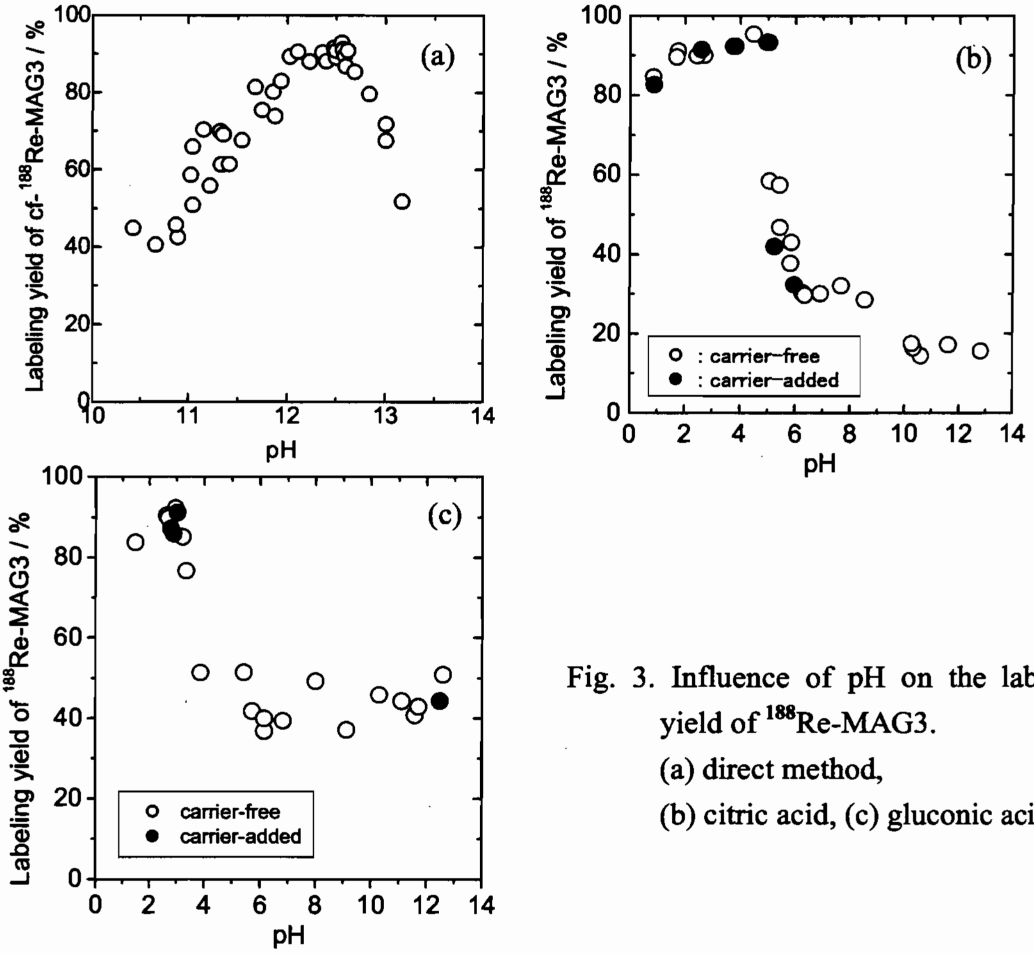

Fig. 3. Influence of pH on the labeling yield of ^{188}Re-MAG3.
(a) direct method,
(b) citric acid, (c) gluconic acid

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2415

SYNTHESIS AND IN VITRO EVALUATION OF $Tc(CO)_3^+$ COMPLEXES WITH DITHIOCARBAMATE LIGANDS CONTAINING MORPHOLINE MOIETY.

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Over the last few years combination of monodentate and bidentate ligands were studied for linking of $M(CO)_3^+$ (M = Tc, Re) to biomolecules. In the case of such “2+1” chelation system targeted molecule can be attached to organometallic fragment via bidentate or via monodentate ligand.

It was found earlier [1,2] that dithiocarbamates reacts with $M(CO)_3(H_2O)_3^+$ to form extremely stable complexes. Isocyanide ligand was found to be most promising for blocking of third coordination position on $M(CO)_3$ core.

The aim of this work was to synthesize and study complexes of $M(CO)_3^+$ with combination of dithiocarbamate and isocyanide ligands with morpholine moiety attached to dithiocarbamate chelation unit. We chose morpholine pharmacophore due to its high affinity to melanoma [3].

The technetium complexes (A,B,C,D) were synthesized by simultaneous mixing of $^{99m}Tc(CO)_3(H_2O)_3^+$ prepared from "Isolink" kit and corresponding dithiocarbamate and isocyanide ligands ($C_L = 10^{-3}$ M) in the aqueous solution. The mixture was heated at 100 C for 20 min. The reaction mixture was analyzed using TLC on silica gel in MeOH/HCl 99:1 and in acetone.

Dithiocarbamate ligands containing morhpoline moiety L_1 and L_2 were synthesized by reaction of corresponding amine with carbon disulfide in basic medium (KOH) in methanol. Precipitated potassium salt was filtered and washed with ether. Isocyanoacetic acid L_3 was synthesized via hydrolysis of ethylisocyanoacetate by potassium hydroxide according to method described in [4].

Complexes of rhenium (A and B) were prepared by simultaneous mixing of bidentate (dithiocarbamate) and monodentate (isonitrile) ligands with $[Re(CO)_3Br_3][NEt_4]_2$. The reactions were carried out in methanol. Solvent was removed in vacuum. The target complexes A and B were extracted from residue by tetrahydrofuran (for $[NEt_4]Br$ removal) and purified from by-products by chromatography on silica gel.

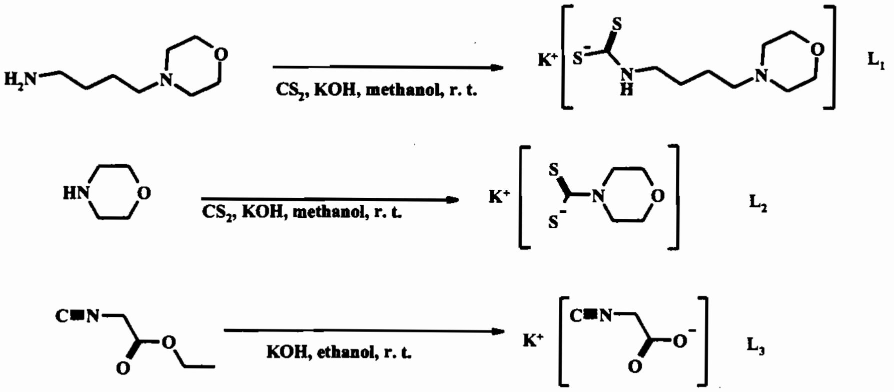
Analytical data:

L1	^1H NMR (DMSO-d6), 8.54 s (NH), 3.57 m CH_2 + CH_2 (morph), 3.48 m(CH_2 morph) 2.43 t (CH_2), 1.78 q(CH_2)
L2	^1H NMR (DMSO-d6) 4.29 m, 3.47 m
L3	^1H NMR ($CDCl_3$) 3.92 s
Complex A	^1H NMR($CDCl_3$), 7.56 s (NH), 3.57 m CH_2 + CH_2 (morph), 3.48 m(CH_2 morph) 2.43 t (CH_2), 1.78 q(CH_2) 1.58 s (CH_3 ISO)
Complex B	^1H NMR ($CDCl_3$), 4.34 m (morph), 3. 86s (CH_2 ISO) 3.51 m (morph)

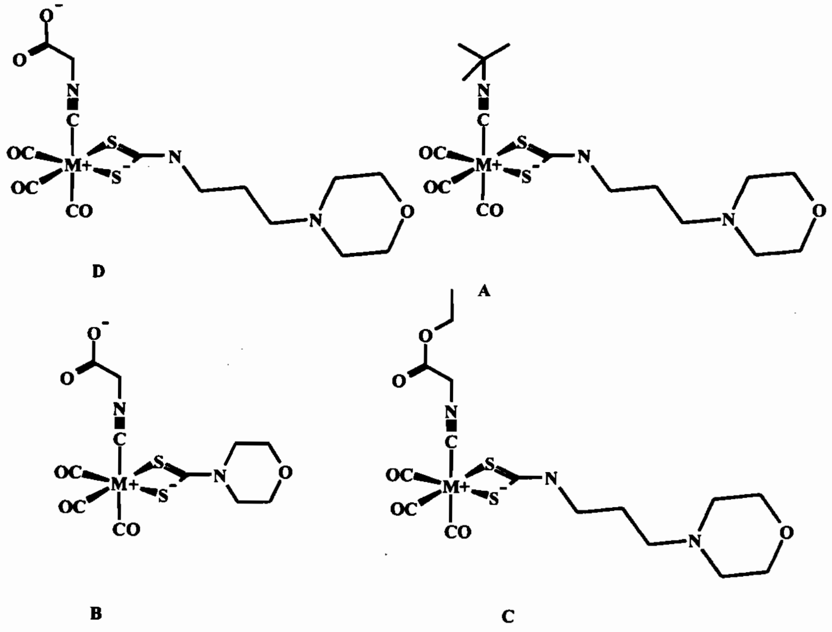
For the comparative evaluation of these technetium-99m complexes for diagnostics of melanoma the study of affinity of these complexes to the cells of melanoma B 16 in vitro was carried out. $^{99m}Tc(CO)_3$Cit, which was earlier described in [5], was used as a comparative radiopharmaceutical.

According to the experiments in vitro it was found that technetium-99m in the form of pertechnetate does not bind with cells. The maximal accumulation in the cells was observed after 90 – 120 min from the beginning of incubation. Complex A has the highest affinity toward the cells (about 25 % from the experimental activity). The affinity of the other complexes were in 3 – 4 times lower and decreases in the following sequence A > > C > D > Cit >B.

Ligands



Complexes



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2416

Tc CARBIDE AND NEW ORTHORHOMBIC Tc METAL PHASE

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The preparation and properties of technetium carbide are poorly described in the technical literature. The published data are not sufficient for the prediction of technetium behavior in the carbide fuel during and after irradiation in nuclear reactors.

The initial metal technetium was prepared by reduction of synthetic $(CH_3)_4NTcO_4$ in Ar-6%H_2 gas in a gas-flow tubular furnace at 500°C followed with annealing just only at 800°C to avoid microparticle adhesion). The resulting Tc metal was finely grinded and the fine fraction of 20 or 50 micrometer in diameter was sieved out for the experiment. The metal was vigorousely grounded and mixed with some % of ultrapure carbon and the 5 mm-thick pellets were pressed at 100 kPa. The pellets with variable Tc:C atomic ratio (7.34, 10.35, 14.16, 23.21 and 49.75 at.%C) were prepared and annealed in high temperature vacuum furnace at the temperatures 800°C, 1000°C and 1150°C for 8 hours.

X-ray powder diffraction analyses and spectroscopic (^{13}C- and ^{99}Tc-NMR) ones as well as microhardness measurements have been applied to this study of the formed phases. The obtained results led to the conclusion on the formation of the biphasic composition that includes the technetium carbide Tc_xC where ($x > 1$, in most cases $2 < x < 6$) and the excess carbon starting from 17 at.%. In the range of low carbon concentrations (Tc - C mixtures of 1-2 wt %C, 10 to 15 at. %C) at 800 °C the formation of intermediate orthorhombic Tc metal was observed. The unit cell parameters were a = 2.805(4), b = 4.958(8), c = 4.474(5)Å (V/z = 15.55 Å^3) for Tc-C with 1.38 wt.% C and a = 2.815(4), b = 4.963(8), c = 4.482(5) Å (V/z = 15.65 A^3) for Tc-C with 1.96 wt.% C. The parameters of Tc could be explained by distortion of the well known *hcp* Tc metal structure. Further heating led to its transformation back to stable hexagonal phase.

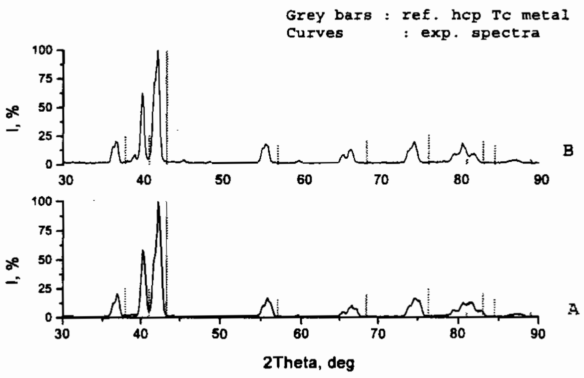

Fig. 1 X-ray Diffraction spectra of pellets Tc - C annealed for 8 hours at 800°C: **A** – 1.38 wt.% C ; **B** – 1.96 wt.% C

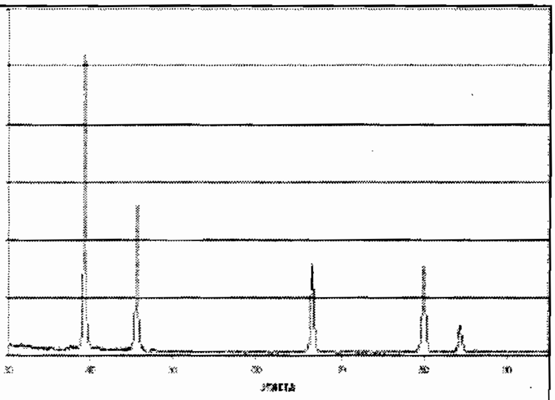

Fig. 2. Experimental X-ray diffraction pattern of Tc metal annealed with 50 at.% C at 1150°C for 8 hours

These researches show that technetium carbide is being formed somewhat easier if compared to previously known data, indicating that its formation in the spent carbide nuclear fuel is quite possible. The *fcc* Tc carbide phase is defective in respect of carbon. Some estimates of the boundary frames of Tc carbide composition were obtained although the exact composition of Tc carbide should be précised. Micro-hardness of Tc carbide depends on the C content and the temperature of preparation, and it is by the factor of 2 - 2.5 higher compared to the micro-hardness of pure technetium metal.

Tc metal specific cell volume (per 1 Tc atom) increases by ~10% with the increase in C content from 1 to 20 % and then presents a steady value (Fig. 3).

Our findings are in good agreement with the predicted phase Tc-C diagram in [1], based on [2--5] and taking into account the results of calculating the liquidus of graphite in the Tc-C systems. The Tc alloy with 17.5% (at) C in the cast and annealed (at 1400°C [4] and at 1150°C [6]) conditions had always a single-phase for structure of the metallic sub-lattice with the lattice periods close to 3.98(2) A and $V/z=15.76$ A^3 (Fig.2). This phase can be regarded as a virtual modification of cubic technetium metal stabilized with carbon or a technetium carbide with the cubic lattice of the NaCl type (δ-phase) defective in respect of carbon.

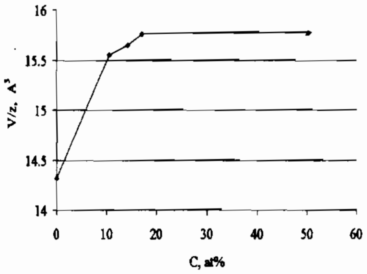

Fig. 3. Tc metal specific cell volume (V/z, per 1 Tc atom) as a function of C content.

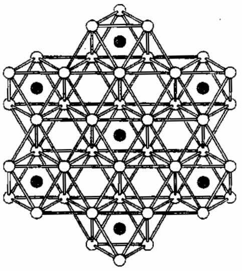

Fig. 4. Typical model for *fcc (a=3.98 A)* virtual Tc metal 42-atomic cluster filled with 7 carbon atoms

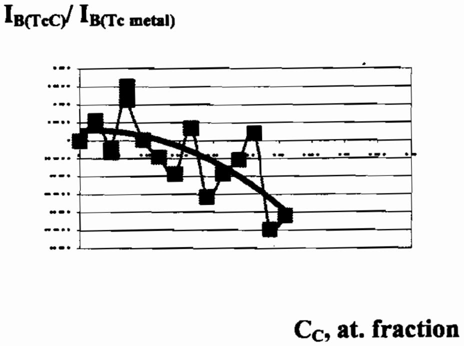

Fig. 5. The $I_{B(TcC)}/ I_{B(Tc\ metal)}$ increase in mean bond strength relative to Tc metal, attributed to 1 cluster atom in Tc carbide with variable C as a function of C content

To analyze the stability of phases in Tc-C system the calculation was carried out by the non-empiric quantum chemistry method $X_\alpha DV$ using the program DVSCAT. Two cluster models with 18 and 42 metal atoms were studied (Fig.4 - 5) gave evidence that : 1) small amounts of carbon atoms addition (1-10 at.%) results in the important increase of the cluster stability; 2) the tendency of decrease in Tc carbide stability with increase of carbon content starts at least at 12% of C; 3) the latter tendency is not monotonic but is characterized with *sine*-type dependency, the last stable maximum being close to 17% C that corresponds to $Tc_{42}C_7$ in the frame of our model or to Tc_6C in general infinite mode. The composite with 26% Ñ has much less probability and could doubtfully be formed as also reported at [6].

In conclusion these researches showed that technetium carbide is being formed much easier compared to previous data most probably due to the formation of newly observed intermediate orthorhombic Tc metal phase. Its formation in the spent carbide nuclear fuel became quite possible and would result in important increase in specific cell volume and hence - in the specific fuel volume.

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Wednesday, May 25, 2005

Inorganic Chemistry of Technetium and Rhenium

Analytical Chemistry of Technetium and Rhenium

Environmental Science and Geoscience of Technetium and Rhenium

Transmutation and Reprocessing of Technetium

Poster Session

2501-I

CURRENT STATUS OF THE THERMODYNAMIC DATA FOR TECHNETIUM AND ITS COMPOUNDS AND AQUEOUS SPECIES

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Technetium is a major product of nuclear fission of uranium and plutonium isotopes, and several tonnes of ^{99}Tc are produced each year in nuclear reactors. Technetium is also used extensively in nuclear medicine in the form of compounds and complexes of ^{99m}Tc, which is produced by the irradiation of ^{99}Mo with neutrons. ^{99m}Tc decays with a 6.0 hour half-life by emitting a 140 keV gamma ray to yield ^{99}Tc, and ^{99}Tc in turn decays to ^{99}Ru with a 2.15×10^5 year half-life by emitting a low energy beta ray. Outside of its use in scientific research, ^{99}Tc has few applications, and much of it will ultimately need to be disposed of as radioactive waste.

Performance assessment in the field of nuclear waste management requires the prediction for extended time periods (currently 1×10^4 years in the USA) of the concentrations of various radionuclides that may escape from degraded waste packages in a nuclear waste repository and migrate into the accessible environment. The predictions of chemical speciation and concentrations are usually made using thermodynamic modeling computer codes. These model predictions require knowledge of the geology and subsurface hydrology at the repository site; a knowledge of the chemical forms (speciation) and concentrations of the radionuclides that occur in the groundwater as functions of pH, redox potential, and concentration of other ions present in the groundwater; and knowledge of the interactions (both sorption and chemical reactions) of the dissolved radionuclides with the surrounding rocks and tunnel backfill (if used) within the repository. The presence of radioactive technetium in nuclear waste is of major concern in repository safety assessments because many of its compounds readily dissolve to form soluble TcO_4^- salts under oxic conditions, and TcO_4^- can easily be released to and transported by the moving groundwater. The anticipated high concentrations (relative to most of the other radionuclides) of ^{99}Tc in the groundwater, together with its long half-life of 2.15×10^5 years, gives it the potential for becoming a major source of radioactive contamination.

Meaningful thermodynamic modeling calculations can be performed only if reliable and critically assessed thermodynamic property databases are available. In 1984 teams organized by the Nuclear Energy Agency (NEA) began evaluating the thermodynamic properties (standard state Gibbs energies of formation, enthalpies of formation, entropies, and heat capacities) of the pure compounds and aqueous species of selected radioactive elements pertinent to radioactive waste management. Five books, including an update volume, containing critical evaluations of these thermodynamic properties for the inorganic compounds and aqueous species of Tc, U, Np, Pu, and Am have since been published. Expert teams are currently evaluating thermodynamic data for selected organic compounds and complexes of these elements, along with several other fission product elements and waste package materials (Se, Ni, Zr, Th, Fe, Sn, and Mo).

This lecture is concerned with the thermodynamic database for one of the major fission product elements, technetium. A critically-assessed thermodynamic database was published under the sponsorship the Nuclear Energy Agency in 1999 [Joseph A. Rard, Malcolm H. Rand, Giorgio Anderegg, and Hans Wanner, *Chemical Thermodynamics of Technetium*, edited by M. C. Amaia Sandino and Erik Östhols, Chemical Thermodynamics Volume 3, North-Holland/Elsevier, Amsterdam, 1999]. Four years later an update of the NEA database was published [Robert Guillaumont, Thomas Fanghänel, Jean Fuger, Ingmar Grenthe, Volker Neck, Donald A. Palmer, and Malcolm H. Rand, *Update on the Chemical Thermodynamics of Uranium, Neptunium, Plutonium, Americium, and Technetium*, edited by Federico J. Mompean, Myriam Illemassene, Christina Domenech-Orti, and Katy Ben Said, Chemical Thermodynamics Volume 5, Elsevier, Amsterdam, 3003]. However, no changes to the technetium database were recommended in this update volume.

The available thermodynamic database for technetium is described, along with an assessment of the reliability and limitations of the various evaluated quantities. The present thermodynamic database for aqueous technetium species is essentially limited to the temperature 298.15 K (25.00 °C); very few inorganic complexes and no organic complexes are included. Additional thermodynamic measurements are needed in order to fill gaps in the present database, to extend the database to include other relevant compounds and aqueous complexes, and to extend the database to other temperatures. These additional thermodynamic data are needed not only to properly understand and quantify the migration of technetium in groundwater from a breached waste canister or leaking waste storage tank, but also for modeling vapor phase transport of technetium compounds during reprocessing of spent nuclear fuel.

This work was performed under the auspices of the U. S. Department of Energy by University of California, Lawrence Livermore National Laboratory under contract No. W-7405-ENG-48.

2502

RECENT DEVELOPMENTS IN THE ANALYSIS OF TECHETIUM-99

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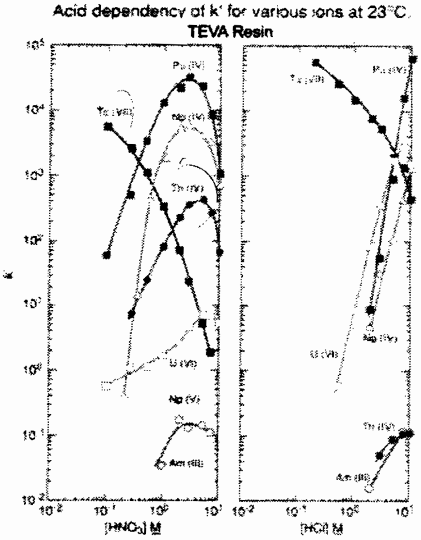
In recent years the use of extraction chromatography has grown significantly in methodologies for technetium-99 measurement. An aliphatic quaternary amine, impregnated on a polymeric support, trade named TEVA® Resin has become the industry standard in separating and pre-concentrating pertechnetate prior to Tc-99 measurement by liquid scintillation or ICP-MS.

TEVA Resin has a very high affinity for pertechnetate anion from low acid and even basic solutions. The figure below shows the uptake of TcO_4^- as a function of nitric acid and HCl concentration. It can be seen that the TcO_4^- uptake increases with decreasing acid concentration, while all the actinide elements show declining retention. This behavior indicates that the TEVA Resin can be used to separate pertechnetate anion from a wide variety of potentially interfering radionuclides. The k' values in the range of 10^4 – 10^5 show that the resin can be used to pre-concentrate pertechnetate from very large volume samples (e.g., up to 4 liters of water.)



The technique has been applied to a variety of matrices including water, soil, urine and waste samples. It has also been applied to process control samples in nuclear fuel reprocessing and waste treatment applications. TEVA Resin has been used in several formats: slurry-packed columns for gravity flow use, dry packed cartridges for us in vacuum manifold systems, and glass fiber filter discs to process very large liquid samples with fast flow rate (~100 ml/min.)

As this methodology has been applied to broader and broader sample types, several challenging matrix interferences have been encountered that have made accurate measurements difficult. Two examples of matrix challenges are high levels of Th-234 present in natural uranium samples and the Bi-210 daughter of Pb-210 found in certain air filter samples from dusty environments. In both of these cases, the beta emissions from the interfering isotope are measured in the Tc-99 window of the LSC. This can lead to a bias in the measurement of Tc-99. Solutions to these problems have been developed.

This paper will review the breadth of the application of TEVA Resin to the analysis of Tc-99 and discuss how the stated matrix challenges have been overcome.

2503

SOLVENT EXTRACTION OF TC(VII) BY CALIXARENES BEARING PYRIDINO GROUPS

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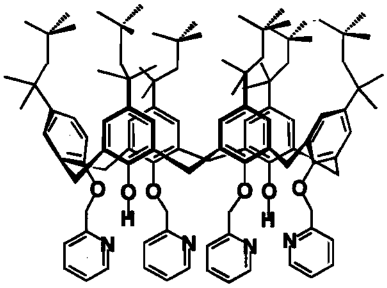
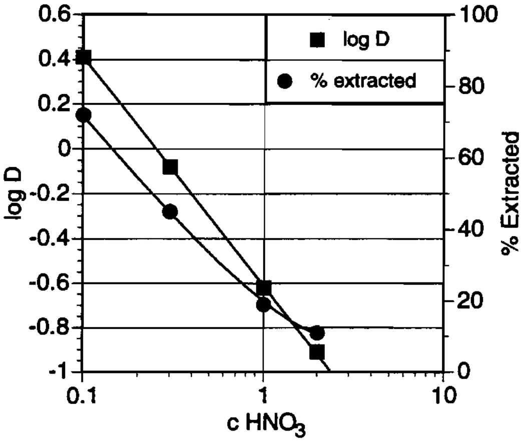
In the course of studies on coupled transport of Tc(VII) and U(VI) by conventional extractants such as TBP [1], we realized the importance of protonation equilibria for the separation of Tc(VII). For example, the protonation of TcO_4^- may cause the decrease in its extraction by amines at increasing acidity [2]. We were interested whether macrocyclic ligands are able to extract Tc(VII) better compared with non-cyclic or monodentate ligands. It would prove a macrocyclic effect and cooperative binding to the anion in addition to electrostatic interactions, as it was recently observed for HPO_4^{2-} as example [3]. So far, few reports on the extraction of Tc(VII) by nitrogen-containing [4,5] and by ketone-derviatized [6] calixarenes were published. We therefore synthesized a series of calixarenes bearing pyridino or amido groups and investigated their ligating behaviour as ion-pair extractants. The results are discussed in terms of the relationship between ligand structure and extraction power.





Example 1: Structure of a pyridino-derivatized calix[6]arene and its extraction behaviour towards Tc(VII) at low ligand/metal ratio.
Aqueous phase: 1 mM ^{99}Tc in HNO_3,
Organic phase: 3 mM ligand in $CHCl_3$.
log D_{Tc} = -1*(log c_{HNO_3}) - a.

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2504

RHENIUM ULTRAFILTRATION RECOVERY

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Membrane techniques have been proven for selective recovery and concentration of rhenium from complex multi-component systems, in particular, the method of complex formation and ultrafiltration (CF-UF) based on addition of polyelectrolyte (PE) to the solution to form a complex with the valuable constituent and subsequent ultrafiltration. As a complexing agents soluble synthetic polyelectrolytes have been used: cationic polyelectrolytes having the functional groups of quaternary ammonium base (QAB), VA-2, VA-112, VA-212, VPK-402, Praestol 658, Praestol 859; flocculant having primary and secondary aminogroups, Epaflok-2, and experimental samples syntezed at the D.Mendeleyev University of Chemical Technology (Russia) [AS-362-11 and AS-362-91 - copolymers based on dimetylaminoisopropylmetacrylate and ethylthioetylmetacrylate (1:1) and (9:1); AS-362-111 - copolymer based on dimetylaminoethylmetacrylate, ethylthioethylmetacrylate and N-vinylmetapyridine (1:1:1)]. Preliminary studies were carried out to investigate aggregate stability of PE in aqueous systems with introduction of anions. The coagulation threshhold depends significantly from the nature of anion and remains constant for given anion at the concentration of PE (VA-212) >0.1 g/l growing up in the following order:

$NO_3^- > Cl^- > SO_4^{2-} > NO_2^-$ [1].

The CF-UF characteristics of rhenium recovery have been studied at the laboratory installation involved standard ultrafilter with semipermeable polymer (polysulfone fiber) and ceramic membranes. The effects of external factors (pH value, ratio of PE to perrhenate ion, behaviour of impurities) on the separation characteristics of the CF-UF process were studied. PE regeneration conditions were determined. The effect of the number of extraction-regeneration cycles on the rhenium recovery was investigated. The maximal selectivity has been observed by using of PE VA- and Praestol-types having the functional groups of QAB. Basic process flow – sheets were developed and successfully tested to recover rhenium from effluents and recycled solutions at ore treatment plants containing 0.05-0.10 mg/l of rhenium.

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2505-K

^{99}TC IN THE ENVIRONMENT: SOURCES, DISTRIBUTION AND METHODS

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Introduction

The element Technetium (Z=43) was discovered by Perrier and Segré in 1937 (Perrier and Segré, 1937). Ten years later, Paneth (Paneth, 1947) suggested the name of technetium, from the greek word τεχνικοζ (artificial), due to the fact that it was the first element artificially produced. Nowadays 33 isotopes of the element are known. All of them are radioactive with half-lives ranging from some few milliseconds to some few million years.
From an environmental viewpoint only ^{99}Tc seems to be relevant. It is a β emitter with a E_{max}=292 keV and a $T_{1/2}=2.11\times10^5$ y and is produced during the fission of ^{235}U and ^{239}Pu at a rate similar to that of ^{137}Cs. For that it is considered as an important contributor to the future collective dose to the population due to the use of nuclear energy, playing an important role in the problem of nuclear waste management. An excellent view on the topic of environmental ^{99}Tc can be found in (Yoshihara K. 1996).

Sources

Although very small amounts of ^{99}Tc have been found in Nature due to the spontaneous fission of ^{238}U (Kenna and Kuroda, 1961) in pechblende, the most important way of ^{99}Tc production and, consequently, the main source to the environment is fission in nuclear reactors and weapons. ^{99}Tc produced in reactors enters the nuclear fuel cycle from where it is released in different amounts to the environment from the different steps. The production of ^{99}Tc from the use of Nuclear Medicine ^{99}Mo-^{99m}Tc generators should be also taken into account although its contribution is clearly less important than the other sources.
Although some more detail will be given in the full paper it can be said that about 140 TBq of ^{99}Tc can be estimated to have been produced by nuclear weapon detonations (Aarkrog et al. 1986). Also, it is estimated that, up to 1983, 15000 TBq of ^{99}Tc has been produced in nuclear power stations worldwide. From this date to 1993 the produced radioactivity is estimated to be 49000 TBq. And it can be said that only 1000 TBq of ^{99}Tc have been released into the environment mainly from the nuclear fuel reprocessing (Luykx 1986). According to E. Holm (Holm 1993), Nuclear Medicine contributes with some few GBq of ^{99}Tc to this inventory.

Distribution

Due to its chemical characteristics, ^{99}Tc is known to behave as a conservative radionuclide in marine and fresh waters. Its concentration in open sea sediments is very low due to this fact. In the case of soils, ^{99}Tc needs the existence of reduction conditions to be absorbed in it. Should this happens its transference to vegetal species decreases very much, which is certainly relevant for agricultural soils (Tagami 1997). ^{99}Tc has also been found in the atmosphere, although very few data exist on that (Attrep et al. 1971). Atmospheric nuclear detonations provoked its introduction in the stratosphere. From it, ^{99}Tc enters into the

troposphere according to an exponential time pattern. Gaseous emissions from nuclear fuel reprocessing plants has to be also taken into account when studying the concentration of ^{99}Tc in the atmosphere, specially in the last years.
A complete account of these facts will be given in the full paper.

Methods

In general terms the concentrations of ^{99}Tc in the environment are very low. Therefore very sensitive methods are needed for its determination. In all the cases chemical separation of Tc from the sample is required and the addition of tracers to measure the yield necessary. Furthermore, chemical methods are generally complicated and time consuming.
It has been reported in the literature the use of low-background gas and scintillation, liquid or plastic, counters for the measurement of the β radiation emitted by 99Tc (García-León M. 1990; Koide and Goldberg 1985). The conventional radiometric techniques have, however, limitations due to the long ^{99}Tc half-life. Non-radiometric methods can help to overcome the difficulties. Historically they have already played its role. In fact, very early works used neutron activation for ^{99}Tc measurements (Foti et al. 1972). More recent and refined approaches have used other reactions as (γ,γ'), instead of the traditional (n,γ) activation reaction (Sekine et al. 1989). Nevertheless, only mass spectrometric techniques can nowadays compete with radiation counters. Thus the number of groups using ICP-MS, RIMS or even Accelerator Mass Spectrometry (AMS) is growing. See, for instance, (Tagami and Uchida, 1996) and (Fifield et al. 2000).
It is expected to make a detailed comparative report of these methods in the paper

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2506

TECHNETIUM TRANSFER MODELLING INTO BIOSPHERE IN ORDER TO CALCULATE RADIOLOGICAL IMPACT ASSESSMENT

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In order to perform radiological impact assessments of radioactive waste disposals, a compartimental model taking into account generic data for biosphere transfer parameters values is usually used. A few years ago, in order to improve its performance assessments calculations, Andra (French national radioactive waste management agency) decided to launch, in collaboration with different laboratories, specific experimental studies to understand technetium environmental behaviour and to adapt its technetium transfer into biosphere model to its sites conditions. Indeed, biosphere transfer factors values are issued from experimental studies adapted to Andra context : soil characteristics, climate, agricultural habits and species.

Andra experimental results deals with retention of Tc depending of soils (Echevarria, Morel et al. 2003), uptake of Tc from pot experiments (Echevarria, Vong et al. 1998), leaching of Tc in undisturbed soil cores (Denys, Echevarria et al. 2003) and role of bacteria on reduction of Tc(VII) (Abdelouas, Fattahi et al. 2004).
These specific data are useful to reduce uncertainty and range of variation of impact calculations and ensure a consistent model. It helps also to achieve scientific community approval by showing mastery of radionuclides environmental processes and public understanding by focusing demonstration on real local conditions. The soil-plant system is a major compartment for biosphere modelling. For technetium (^{99}Tc), the mobility in soils mainly depends on the redox potential. In oxidising conditions, Tc is on the pertechnetate form species (TcO_4^-) very mobile, but in reducing conditions, its species (TcO_2) is not mobile at all (Sheppard, Sheppard et al. 1990; Echevarria, Vong et al. 1997). Usually, the soil presents oxidising conditions but, if the hygromorphy is important (i.e ; in case of flooding); conditions become reducing. Most of the time, meadows at the bottom of a valley are inundate a part of the year (in winter). So, at these places, the mobility of Tc will vary during the year. In a long term context (a few thousands hundreds of years), under cold climate, the soil is frozen all the year (permafrost). Only the top of the soil can be melted in summer (mollisol), involving reducing conditions. So this phenomena will become really important for technetium mobility. In biologically-active and organic matter-rich surface soils, TcO_4^- is reduced and precipitated. Another important factor affecting the mobility of Tc is the concentration of NO_3^- (Echevarria, Vong et al. 1996), but its effect is less important than the redox potential. In nitrate-rich soils denitrifying bacteria inhibited the reduction of TcO_4^-. Organic matter combined with microorganisms and to lesser extent to iron oxyhydroxides plays major roles in Tc-immobilization. Iron sulphide doesn't contribute significantly into Tc-retention but maintains low redox potential that insures the stability of Tc (IV) (Abdelouas, Fattahi et al. 2004).

In this paper, Andra presents its specific methodology to model ^{99}Tc transfer into the food-chains taking into account recent experimental results in order to calculate radiological impact to human.

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2507

SOIL-TO-PLANT TRANSFER FACTORS OF TECHNETIUM-99 FOR VARIOUS PLANT COLLECTED IN CHERNOBYL AREA

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Introduction

Technetium-99 is one of the most important radionuclides for dose assessment because of its high mobility in soil and availability to plants. Although Tc is highly soluble and rarely adsorbed onto soil particle surfaces as TcO_4^-, the chemical form apt to change with environmental conditions. For a realistic assessment, obtaining transfer parameters, such as soil-to-plant transfer factors (TFs), under natural conditions is needed. However, the data have been limited due to trace levels of ^{99}Tc. Therefore, we focused on the Chernobyl site where ^{99}Tc concentration levels have already been shown to be higher than those from global fallout Tc [1].

Experimental

Soil and plant samples were collected at the Chernobyl site in 1994 and 1995. Forests D1 and D3 are 28.5 km and 26 km to the south of the Chernobyl Reactor, while forest K2 is 6 km to the southeast. The surface organic soil layers (L, Of and Oh) collected at each site were mixed and submitted for the measurements of their ^{99}Tc activities. The plant samples were leaves of strawberry and raspberry plants, oak, birch and black alder trees, and ferns.

A simple separation method for ^{99}Tc in soil samples was used [2]. For plant samples, a wet digestion method in combination with the resin was adopted. Then TEVA extraction steps were carried out to separate and concentrate Tc. The volume of the ^{99}Tc fraction from a TEVA column solution was reduced to near dryness and then dissolved in 5mL of 2% HNO_3 solution [3]. Then the solution was introduced into an ICP-MS (Yokogawa, PMS-2000) to measure ^{99}Tc for 10 min.

Results and Discussion

In general, TF is defined as the ratio of activity concentration of a radionuclide in plant (in Bq g^{-1} dry weight (DW)) to activity concentration of the radionuclide in soil (in Bq g^{-1} DW). Table 1 shows the TFs of Tc and Cs for the leaves of strawberry, raspberry and ferns obtained in K2 forest. The TF-Tc ranged from 0.006 to 0.47 based on the ^{99}Tc contents of the organic layers. The TFs of Tc were much lower than the expected values of 12 - 2600 for vegetables reported by IAEA [4]. The TF-Cs for fern is high as expected since it is known as a Cs accumulator. The TFs of Cs for strawberries, 0.03 - 0.17, were within the range of TF-Cs for grass and mixed green vegetables by IAEA [4].

The corresponding TFs for Tc were between two to five times larger than those for Cs for the sites K2 and D1 (data not shown). To the contrary, at D3 the TF for Tc was lower by a factor of about 5 compared to that for Cs. This might be due to the fact that D3 was a so-called wet forest, and accordingly Tc might be in insoluble forms i.e., TcO_2, which is less available to plants than Tc in TcO_4^-.

Table 1. The transfer factors of Tc and Cs for the plants obtained in K2 forest.

	TF-Tc	TF-Cs
Sample	(organic)	(organic)
Strawberry-1A	0.13 ± 0.01	0.10 ± 0.003
Strawberry-1B	0.16 ± 0.02	0.13 ± 0.004
Strawberry-2	0.62 ± 0.03	0.17 ± 0.005
Raspberry-1	0.41 ± 0.03	0.15 ± 0.004
Raspberry-2	0.37 ± 0.02	0.027 ± 0.0008
Fern-1A	0.25 ± 0.01	2.8 ± 0.08
Fern-1B	0.24 ± 0.02	2.8 ± 0.08
Fern-1C	0.24 ± 0.03	3.2 ± 0.09
Fern-2	0.062 ± 0.003	0.082 ± 0.002
Fern-3	0.39 ± 0.02	1.4 ± 0.04

Note: ± shows statistical error (1 s.d.).

Acknowledgement

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2508

SIMPLE SEPARATION METHODS FOR TRACE-LEVEL OF TECHNETIUM-99 IN SEAWEED AND SEAWATER USING AN EXTRACTION CHROMATOGRAPHIC RESIN

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Simple separation methods for low-level ^{99}Tc were developed for seaweed and seawater samples, respectively, and examined to background level samples. The ^{99}Tc is a β-emitting radionuclide with a half-life of $2.11 \cdot 10^5$ y, and is produced by thermal fission of ^{235}U and ^{239}Pu with relatively high yield of approximately 6%. This nuclide has been mainly released into the environment by atmospheric weapon testing and nuclear fuel reprocessing. The ^{99}Tc derived by the former was globally dispersed, and the latter distributed locally around the facilities, particularly Sellafield in UK and La Hague in France. The released amounts were estimated to be 221 kg (140 TBq)[1] and 1787 kg (1130 TBq)[1-2] by the testing and the reprocessing plants, respectively. Concentrations of ^{99}Tc in seawater, sediments and seaweeds such as in Irish Sea[4] and Baltic Sea[5] are high in comparison with the global background level.

In Japan, a commercial nuclear fuel reprocessing plant is now being constructed in Rokkasho Village, where is located in the Pacific Ocean side of Aomori Prefecture, and will be fully operated in 2006. Since the plant will release small amount of ^{99}Tc to the ocean, the concentration of ^{99}Tc in seawater nearby the plant will possibly increase in the future. It is important to get background levels of ^{99}Tc in seawater and/or biological samples around the plant site. Hirano measured the ^{99}Tc concentrations in seaweed samples collected on the coast of Japan, and reported higher concentration for samples near a nuclear reprocessing plant in Tokai Village[3]. Since some seaweeds have high concentration factors $(10^2\text{-}10^5)$[3, 6] and many kinds of seaweed are eaten in Japan, the ^{99}Tc concentration level in edible seaweeds is important for monitoring purpose. The ^{99}Tc concentration in seawater is also required for better understanding the behavior of Tc in the marine environment.

Therefore, we developed simplified analysis methods for ^{99}Tc in seaweed and seawater sample using TEVA resin (Eichrom Industries, US) and an inductively coupled plasma mass spectrometry (ICP-MS). Since pre-concentration of Tc in the samples are generally troublesome and time consuming procedure, we tried to simplify this step. Batch extraction method using TEVA-Spec. resin and adsorption to TEVA disk (Eichrom Industries, US) were adopted for the pre-concentration of Tc in dissolved seaweed samples and seawater samples, respectively.

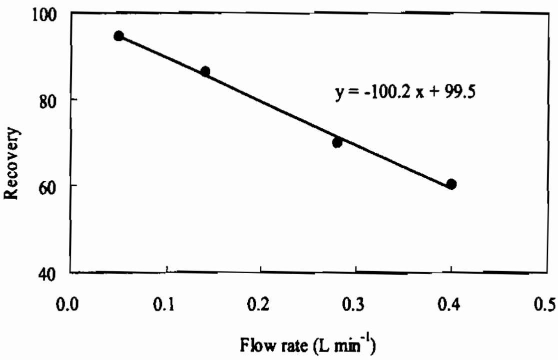

Fig. 1 Correlation between recovery of ^{99}Tc by TEVA disk and flow rate of sample solution.

A seaweed sample was dried at 110°C for 48 hours, then ashed at 450°C for 8 h. A known amount of ^{95m}Tc tracer for recovery monitor was spiked to 50 g of the ashed sample, then the sample was completely decomposed using HNO_3+H_2O_2. After this decomposed sample was dissolved with pure water, pH of the solution was adjusted to 2 with HNO_3. Then, 5 g of TEVA-Spec. resin was put into the solution. After stirring for 10 min, the resin was filtered and passed with 5 mL of 7M HNO_3 to elute Tc. Recovery of Tc in this procedure was in a range of 90 to 95%.

For seawater sample, pre-concentration with TEVA disks was applied. After 50 L of seawater sample was passed through 0.45 μm pore size membrane filter, a known amount of ^{95m}Tc was spiked to the filtrate, and pH was adjusted to 2 with HNO_3. The solution was passed through a TEVA disk at 0.05 – 0.4 L min^{-1} of flow rate. Then, the Tc adsorbed on the disk was completely eluted by using 5 mL of 7M HNO_3. The recovery varied from 60% to 95% depending on the flow rate of the seawater sample solution (Fig. 1). The flow rate was adopted as 0.3 L min^{-1} for further experiment on balance between recovery and consuming time.

Pre-concentrated Tc by these methods was further purified by a glass column (6 mm i.d. x 10 cm) filled with TEVA Spec resin. Details of this separation condition were followed to Tagami *et al.*[8] ^{99}Tc was determined by using a high-sensitive quadrupole type ICP-MS (VG Elemental, PQ-Excell-s, UK).

In applications, ^{99}Tc in a seaweed (*Laminaria japonica*) sample and a seawater sample, which were collected at Rokkasho, were analyzed by this method. To examine reproducibility of the analysis, quadruplicate samples were analyzed. Mean recoveries of Tc were 62±5% and 72±7% for the seaweed and the seaweed samples, respectively.

Acknowledgement
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2509

Investigation of Analytical Method for Technetium-99 in Liquid Effluent Discharged from Tokai Reprocessing Plant

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The low level radioactive liquid effluent from the Tokai Reprocessing Plant (TRP) is discharged in batch mode through the 3.7 km long pipeline from the shoreline.

The radioactivity concentrations in liquid effluent are certified to be less than discharge limits set. The gross-alpha, gross-beta and gamma–ray radionuclide concentrations are measured prior to discharge in every batch of discharge. The Pu isotopes (^{238}Pu, $^{239+240}$Pu), ^{90}Sr and ^{129}I in liquid effluent are measured by radiochemical analysis in a composite sample for a month. Technetium-99 can be measured as part of the gross-beta radioactivity with approximately ten percent counting efficiency. The concentrations of ^{99}Tc in the effluents were implied to be very low from the results of these monitoring as compared with the ^{129}I and Pu isotopes. Consequently, the analytical method was developed using large amount of liquid samples (8-litter) [1] and was applied for special monitoring of ^{99}Tc in liquid effluent from TRP. The ^{99}Tc releases in the liquid effluent from TRP during 1990-2000 were measured and the normalized release of ^{99}Tc, which were normalized by annual energy generated (GWa) derived from the treated spent fuels, were compared with that of other radionuclides.

1. Analytical method for ^{99}Tc

A known ^{95m}Tc was added to 8-litter of liquid effluent sample as chemical yield tracer. After $FeSO_4$ with HCL(2+1) and $FeCL_3$ were added to the sample, the ^{99}Tc in the sample was co-precipitated with $Fe(OH)_2$ by adjusting over pH 9 by ammonia. The precipitate is dissolved by H_2SO_4(1+5) and $K_2S_2O_8$ was added to it. The ^{99}Tc is extracted by 15mL of TBP with 2mL of HF using a separation funnel and the organic phase was washed by using H_2SO_4(1+5) with 0.5mL of HF in twice. After discarded aquatic phase, the 45 mL of Xylene and 15 mL of NaOH(8w/v%) were added to it and shaken. The ^{99}Tc in organic phase was re-extracted to aquatic phase. The solution was neutralized by H_2SO_4 and H_2SO_4(1+5) was more added. The process from the TBP extraction to by the re-extracted procedure was repeated. Finally, the ^{99}Tc was electoroplated onto stainless steel disk for 2-hour at 0.3 A current. This disk was measured by the low background gas-flow counter. The chemical yield was evaluated with measurement of gamma-ray from ^{95m}Tc by Ge-detector.

2.Results and discussion

The results of the average concentrations of ^{99}Tc in liquid effluents during 1990-2000 were ranged from N.D. ($< 5\times10^{-7}$ Bq/ cm^3) to 6.7×10^{-5} Bq/ cm^3. These concentrations were approximately one ten thousandth of the discharge limit of ^{99}Tc for liquid effluent as 1 Bq/cm^3

(Fig. 1), which is authorized by Japanese law as corresponding to the effective dose limit for the public as 1mSv, if a person could drink it everyday for one year. On the other hand, annual releases of ^{99}Tc were ranged from $1.3\text{x}10^{-5}$ GBq/y to $1.5\ \text{x}10^{-3}$ GBq/y. The normalized releases of ^{99}Tc were smaller than that of other detected radionuclides (Table 1). Furthermore, according to the safety assessment of TRP based on the experiments of the dispersion, the radioactivity concentrations in the sea water near the discharge point can be diluted approximately one thousandth of the original concentration of liquid effluent by discharging from 24 m beneath the sea surface through the 3.7 km long pipeline. Consequently, the effective dose due to release of ^{99}Tc for the public was estimated as negligibly smaller than the dose limit. This method was confirmed to be useful for determination of low level radioactivity of ^{99}Tc in liquid effluent.

Table 1 Normalized releases of nuclides (GBq/GWa)

	Range			Average
Tc-99	**$1.3\text{x}10^{-6}$**	**—**	**$2.1\text{x}10^{-3}$**	**($7.4\text{x}10^{-4}$)**
H-3	**$7.2\text{x}10^{4}$**	**—**	**$3.3\text{x}10^{5}$**	**($2.1\text{x}10^{5}$)**
I-129	**$2.0\text{x}10^{-2}$**	**—**	**$8.3\text{x}10^{-2}$**	**($4.1\text{x}10^{-2}$)**
Pu(α)	**$2.7\text{x}10^{-3}$**	**—**	**$1.1\text{x}10^{-2}$**	**($5.1\text{x}10^{-3}$)**

1990-2000

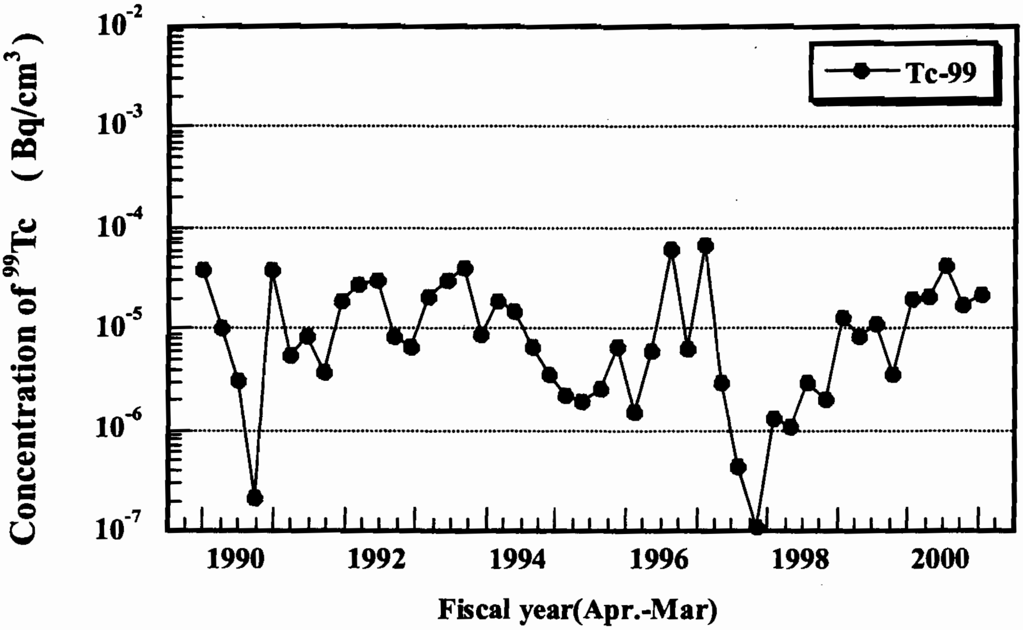

Fig.1 Average Concentrations of ^{99}Tc in Liquid effluent from TRP

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2510-K

TECHNETIUM IN COSMO- AND GEOCHEMICAL FIELDS

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Physicochemical behavior of extinct nuclide Tc in natural environments at planetary surface is one of major concerns for geochemists. Since ^{98}Tc and ^{99}Tc decay to ^{98}Ru and ^{99}Ru, respectively, via the β^- transition, the property of Tc in cosmo- and geochemical fields can be deduced from precise isotopic studies of Ru. Through the approaches on isotopic analyses of Ru in cosmo- and geochemical samples, mass spectrometric techniques with thermal ionization mass spectrometry (TIMS), inductively coupled plasma mass spectrometry (ICP-MS) and secondary ion mass spectrometry (SIMS) have been effectively used. I report herewith current three topics related with the behavior of Tc in cosmo- and geochemical fields.

In order to estimate the primordial abundance of Tc in the solar system, precise isotopic analyses of Ru in several meteorite samples have been performed [1-3]. Quantitative treatment of ^{98}Tc-^{98}Ru and ^{99}Tc-^{99}Ru decay systems may provide chronological information on the chemical evolution processes of planetary materials in the early solar system. However, Ru isotopic compositions of primitive materials in the solar system have been also affected by extra addition of r- and s-process nucleosynthetic components, and therefore Ru isotopic deviations due to Tc decay have not been clearly found in any meteorite samples yet. The lack of Ru isotopic deviations due to Tc decay in meteorites (iron meteorites and chondritic meteorites) suggests low abundance of Tc (^{98}Tc/^{96}Ru<$2\mathrm{x}10^{-5}$ as upper limit) in the solar system [3]. I am now searching for isotopic evidence of primordial Tc by precise Ru isotopic analyses of metallic grains in carbonaceous chondrite meteorites as the most primitive materials in the solar system.

One rare example that Tc behavior can be studied in terrestrial field is natural reactors at the Oklo and Bangombé uranium deposits at Republic of Gabon. Large-scale fission chain reactions spontaneously occurred in the natural reactors around 2.0 billion years ago. Four of seven Ru stable isotopes, ^{99}Ru, ^{101}Ru, ^{102}Ru and ^{104}Ru, are produced by fission. In the natural reactor samples, only four fissiogenic Ru isotopes plus ^{100}Ru produced by neutron-captured ^{99}Ru can be detected because of high fission product yields of Ru and extremely low abundance of non-fissiogenic Ru in terrestrial crustal samples. The Ru isotopic compositions of natural reactor samples are expected from the fission product yields of ^{99}Ru, ^{101}Ru, ^{102}Ru and ^{104}Ru. However, significant variations of ^{99}Ru isotopic abundances have been often observed in the natural reactor samples [4,5]. In particular, micro-metallic grains consisting mainly of Pb, S, Ru, Rh and As found in the reactor samples show large excess of ^{99}Ru. This result suggests the chemical fractionation between Tc and Ru during and after fission reactions. Since ^{99}Ru experienced long-lived ^{99}Tc as a radioactive precursor, differentiation between Tc and Ru can be seen at the present as enrichment or depletion of ^{99}Ru isotopic abundance.

Double beta decay is known as the rarest nuclear phenomenon having extremely long half-life over 10^{18} years. Geochemical analysis of isotopic excesses in geological materials caused by the accumulation of the decay daughter isotope is useful method as detection of the double beta decay products. The half-life of ^{100}Mo-^{100}Ru double beta decay has been recently determined from ^{100}Ru isotopic excess in geologically old molybdenum minerals [6]. However, the half life of ^{100}Mo estimated from our geochemical analysis, 2.1×10^{18} years, is a factor of 4 lower than that from direct counting measurements. There are some possible sub-reactions to provide Ru isotopic anomalies in Mo matrices through Tc production by muon-induced reaction and proton capture reaction of Mo [7] and spontaneous fission of ^{238}U. However, it is implausible to produce isotopic excess of only ^{100}Ru by thus sub-reactions. Therefore, the production rates of Tc in Mo matrices under natural circumstances are too small to detect by isotopic studies.

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2511

Cross section of thermal-neutron capture reaction by ^{99}Tc

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The nuclide ^{99}Tc, with a half-life of 2.1×10^5 years, is one of the long-lived fission products (LLFP) which are produced in commercial nuclear power plants with relatively large yields. The nuclide ^{100}Tc, which is produced in neutron capture reaction by ^{99}Tc, β-decays to its stable daughter nuclide ^{100}Ru, with a short half-life of 15.3 s. Also, cross section of the reaction is reported to be relatively large. These facts make the nuclide ^{99}Tc among the possible candidates for transmutation using neutrons. Therefore, accurate ^{99}Tc(n,γ) cross section is needed in order to design transmutation systems.

Among neutron cross sections of ^{99}Tc, the one at thermal energy (2200 m/s) is important, because not only is it used by itself but also it is often used to normalize cross section data in the resonance region.

In order to experimentally determine cross section of thermal-neutron capture reaction by ^{99}Tc, the following studies have been performed:

- Measurement of the cross section using an activation method in which gamma rays in ^{100}Ru were observed,
- Measurement of emission probabilities of gamma rays in ^{100}Ru, and
- Measurement of the cross section from yields of the prompt gamma rays emitted in the reaction.

In this presentation, details of these studies will be reviewed, and the obtained results will be compared to others. Possible improvements of the experimental methods will also be discussed.

A part of the present work has been done as the collaboration between Japan Nuclear Cycle development institute (JNC) and Oak Ridge National Laboratory (ORNL) operated by UT-Battelle, LLC, under the contract No. FERD-01-2094. A part of the experimental work in the present study was sponsored by the U.S. Department of Energy, under Contract No. DE-AC05-00OR22725 with UT-Battelle, LLC.

2512

FUNDAMENTAL PROPERTIES OF TARGET FOR TRANSMUTATION OF TECHNETIUM-99

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Technetium-99 is a long-lived fission product with beta-decay of a half-life of 2.111×10^{5} years. ^{99}Tc can be transmuted to stable isotopes by neutron irradiation. The transmutation of ^{99}Tc is based on that ^{99}Tc is transmuted to radioactive ^{100}Tc by a neuron capture, and then ^{100}Tc decays to stable ^{100}Ru with beta-emission of a very short half-life of 15.8 s. Even if the stable ^{100}Ru captures neutrons further, it would be transmuted to stable ^{101}Ru, stable ^{102}Ru, and stable ^{103}Rh produced from radioactive ^{103}Ru by beta-decay of a half-life of 39.26 d successively. The capture cross sections for thermal neutron of ^{99}Tc, ^{100}Ru, ^{101}Ru, and ^{102}Ru are about 20 b, 5 b, 3.4 b, and 1.2 b respectively. A metal form of Tc is the most promising chemical form of the target for transmutation of ^{99}Tc from the result of the irradiation experiment of EFTTRA-T2 in Europe [1]. By neutron irradiation Tc metal target will be changed to Tc-Ru alloy, in which Ru concentration increases with irradiation dose.

JAERI has measured fundamental properties of lattice parameters [2, 3], densities [3], thermal expansions [4], heat capacities [5], thermal conductivities [3, 6] for Tc metal, Tc-Ru alloys and Ru metal to estimate the change of properties for the ^{99}Tc metal target during neutron irradiation. Both disk and rod samples of Tc, $Tc_{0.76}Ru_{0.24}$, $Tc_{0.51}Ru_{0.49}$, $Tc_{0.26}Ru_{0.74}$ and Ru were prepared by arc-melting technique.

Figure 1 shows the lattice parameters of the alloys as a function of the Ru concentration [3], together with the values reported by Darby et al. [7]. Both the lattice parameters of the a- and c-axes decrease with increasing the Ru concentration, which almost follow Vegard's law. The lattice parameters agreed well with the reported values as shown in Figure 1.

Immersion densities measured and theoretical X-ray densities of the alloys calculated from both the lattice parameters and the atomic weights of 101.07 for Ru and 98.913 for ^{99}Tc [8] are shown in Figure 2. The immersion density was found to be almost the same as the theoretical X-ray density. The result indicates that there are few cavities, if any, in the

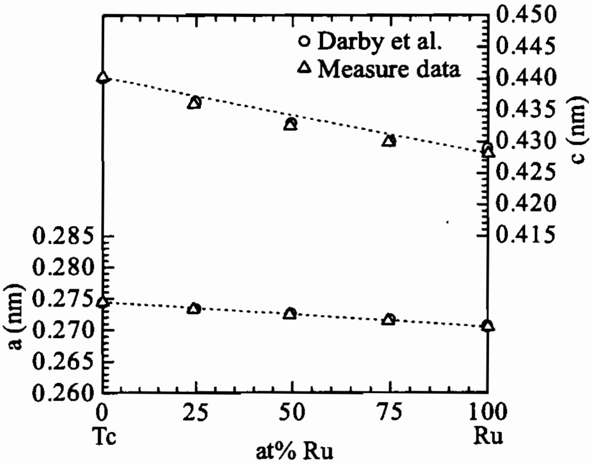

Figure 1. Lattice parameters of Tc metal, Tc-Ru alloys and Ru metal, together with the reported ones [7].

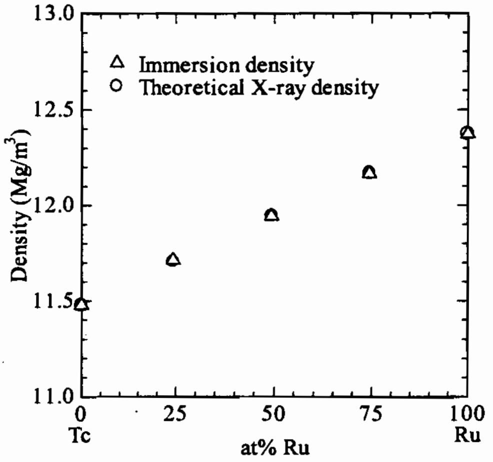

Figure 2. Immersion densities and theoretical X-ray densities of Tc metal, Tc-Ru alloys and Ru metal.

samples. Densities of Tc-Ru alloys increase with Ru concentration.

The thermal expansions of Tc metal, Tc-Ru alloys and Ru metal are shown in Figure 3 [4]. Thermal expansions of Tc-Ru alloys decrease with increasing Ru concentration. For comparison between the thermal expansion of Tc metal and those of candidate cladding materials of stainless steel (SS316) and 2 1/4Cr-1Mo, the thermal expansions of the materials are also shown in Figure 3. Since the thermal expansions of these materials are about twice as large as that of Tc metal, the gap between outer surface of Tc target and inner surface of cladding would increase with temperature.

Figure 4 shows the thermal conductivities of Tc metal, Tc-Ru alloys and Ru metal determined from the thermal diffusivities, the specific heat capacities and the densities [6]. Thermal conductivities of Tc-Ru alloys increase with Ru concentration.

During the transmutation of ^{99}Tc, neutrons will be captured by not only ^{99}Tc but also Ru isotopes produced. In order to realize an efficient transmutation, it is important to separate Ru from the target after the irradiation of a suitable duration. The separation process has to be developed, where the separated ruthenium should not contain technetium.

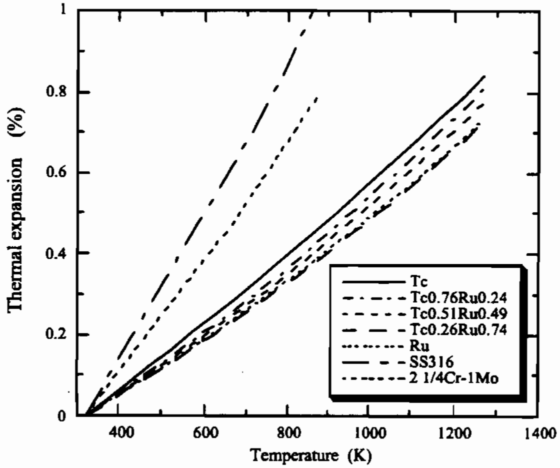

Figure 3. Thermal expansions of Tc metal, Tc-Ru alloys and Ru metal.

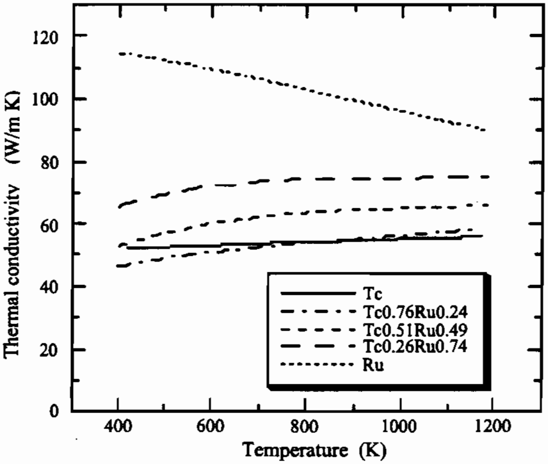

Figure 4. Thermal conductivities of Tc metal, Tc-Ru alloys and Ru metal.

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2513

TRANSMUTATION OF TECHNETIUM: IRRADIATION EXPERIMENT ANTICORP 1 IN PHÉNIX

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The irradiation experiment ANTICORP 1 is performed in the frame of the first line of the French law of December 1991, aiming at the evaluation of the partitioning and transmutation strategy to reduce the quantity and the radio toxicity of the high level waste from nuclear reactors.

A large research and development program is undergoing in France[1], to demonstrate the feasibility of transmutation of minor actinides (americium, curium and neptunium), which represent the majority of the long term radio toxicity elements in the waste, and also the main long live fission products (technetium, iodine and caesium).

ANTICORP 1 takes part of the extensive program of irradiation carried out in fast reactor Phénix since 1991 [2], to test different concepts of targets or fuels in appropriate reactor configuration (fast reactor cooled by sodium). This experiment is specifically related to technetium transmutation and consist in the irradiation of 3 targets, each containing 2 ingots of ^{99}Tc in metallic form (6 g/ ingot), encapsulated inside a stainless steel pin.

During irradiation under a neutron flux, the ^{99}Tc, with a half life of 2.11 10^5 years and a specific activity of 6.25 10^8 Bq.g^{-1}, is transmuted by neutron capture into stable ^{100}Ru :

$$^{99}\mathrm{Tc} + \mathrm{n} \longrightarrow {}^{100}\mathrm{Ru} + \beta^-$$

Two previous experiments in the High Flux Reactor (HFR) at Petten [3,4] have shown no technical obstacle to the use technetium in metallic form as target for the transmutation of ^{99}Tc.

The irradiation conditions reported for these two experiments are:

	EFTTRA-T1	EFTTRA-T2
Transmutation rate (at %)	6	15 to 18
Total fluence (n.m^{-2})	2.0 10^{26}	5.4 10^{26}
Fast fluence (n.m^{-2})	8.3 10^{25}	2.5 10^{26}
Temperature (K)	1100	1100

No significant changes in the characteristics of the targets (dimension and microstructure) were observed after irradiation in the two cases. However, the Ru radial profile determined on a section of the rod after irradiation shows a strong effect of resonance shielding of the epithermal neutrons, which leads to a sharp decrease of the concentration of Ru created in the outer 150 µm of the rod, that leveled off in the inner region.

The technetium rods of ANTICORP 1 were fabricated at the Institute for Transuranium elements (ITU) at Karlsruhe, starting with powder obtained by reducing ammonium pertechnetate (NH_4TcO_4) in a furnace at 873 K. The fabrication method of the ingots is described in the ref. [5].

The main characteristics of the technetium rods are: Diameter: 5.2 mm, length : 25 mm and density 11.5 $g.cm^{-3}$.

The cladding used for the pins is a standard Phénix cladding, made of 15x15Ti stainless steel, with an inner diameter of 5.65 mm.

The 3 pins are placed inside a capsule and maintained at the level of the maximum flux of the Phénix core by mean of a specific internal holder.

The capsule is then introduced inside the central hole of a special irradiation rig that allows a local moderation of the fast neutron flux. Actually, the neutron spectrum is shifted toward the epithermal neutron zones by using a moderator material, CaH_x, placed inside the special rig, which allows rising the epithermal resonance neutron capture of ^{99}Tc.

The irradiation rig and the capsule are internally cooled by sodium.

The neutronic calculations performed for ANTICORP 1 permits to determine the irradiation conditions able to lead to the maximum rate of ^{99}Tc transmutation until the final shutdown of Phénix. The main values calculated are reported in the table below:

Irradiation time (EFPD)	720
Total fluence ($n.m^{-2}$)	$1.3\ 10^{27}$
Fast fluence E > 100 keV ($n.m^{-2}$)	$4.3\ 10^{26}$
^{99}Tc transmutation rate (%)	24.85
Linear power at beginning of life ($W.cm^{-1}$)	17.5
Integrated dose (dpa)	18.2

The temperature of the technetium rod during irradiation is evaluated by using a finite element modeling. The maximum temperature reaches about 760 K during irradiation in normal operating conditions.

The main options chosen for the design and the safety study of the experiment are described in the paper.

ANTICORP 1 was authorized to be loaded in the Phénix reactor by the safety authority on March 2003. The capsule will remain in Phénix until May 2008 and will be examined after irradiation, in the hot cells laboratories of Marcoule and Cadarache CEA centers.

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TRANSMUTATION OF TECHNETIUM IN THE EXPERIMENTAL FAST REACTOR "JOYO"

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One of the most important roles of Partitioning & Transmutation (P&T) is to reduce the practical risk ascribed to the disposed nuclear waste. Based on the current safety evaluation for a deep geologic repository, the transmutation of Long-Lived Fission Product (LLFP) could be more effective at reducing risk than minor actinide transmutation due to the higher mobility of LLFP in groundwater.

The present study examines the potential for the demonstration of fission product transmutation in the experimental fast reactor JOYO at JNC's Oarai Engineering Center. JOYO has operated since 2003 as a high flux irradiation test bed (MK-III core[1]) with the primary mission of developing fuels and materials considered in the feasibility study on commercialized fast reactor systems. The possibility of creating a highly-efficient transmutation irradiation field by loading neutron moderating subassemblies in the reflector region of JOYO was examined in a series of scoping calculations.

Figure 1 shows a layout of the JOYO core used for this study, where a cluster of reflector subassemblies was replaced with new moderator and target subassemblies. Six of the row 7, 8 and 9 reflectors were replaced with beryllium or zirconium hydride ($ZrH_{1.65}$) moderated subassemblies. These moderated subassemblies surrounded one central test subassembly that would contain ^{99}Tc or ^{129}I target material.

The ORIGEN2 code was used to provide preliminary transmutation rates. The one group cross sections used in ORIGEN2 were collapsed using the 70 group JFS-3-J3.2R set based on JENDL-3.2[2] without considering the neutron self shielding effect. The neutron flux distribution in the core was calculated with the three-dimensional diffusion code routinely used for JOYO core management. The absolute value of the neutron flux was determined from the heat balance at the 140 MWt full power condition. Five operational cycles per year were assumed, where each cycle runs 60 effective full power days.

Figure 2 shows the 18 group neutron spectrum and flux values in the target subassembly compared with those in driver fuel and stainless steel reflector regions. In these cases, the volume fraction of moderator was 65% and the rest was stainless steel and coolant sodium. Table 1 compares the corresponding transmutation rates at the core mid-plane in JOYO. The ^{99}Tc transmutation rate was 23.8% using $ZrH_{1.65}$ and 22.2% using beryllium as moderator. These results suggest that the transmutation ratio might be further improved by adjusting the $ZrH_{1.65}$ moderator composition to optimize the neutron spectrum.

On the other hand, the transmutation ratio of ^{129}I varies between beryllium and $ZrH_{1.65}$ moderators depending on the neutron flux level below 0.1 keV which dominates the capture reaction of ^{129}I.

As a result of this study, basic characteristics of LLFP transmutation in JOYO using relevant moderator materials were investigated and the future feasibility was shown.

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Table 1. Fractional Transmutation Ratio (unit: %/yr)

Item	Fuel Region	Reflector Region		
			Moderator	
		SUS	Be	$ZrH_{1.65}$
^{99}Tc	5.9	3.4	22.2	23.8
^{129}I	3.8	2.3	6.8	14.1

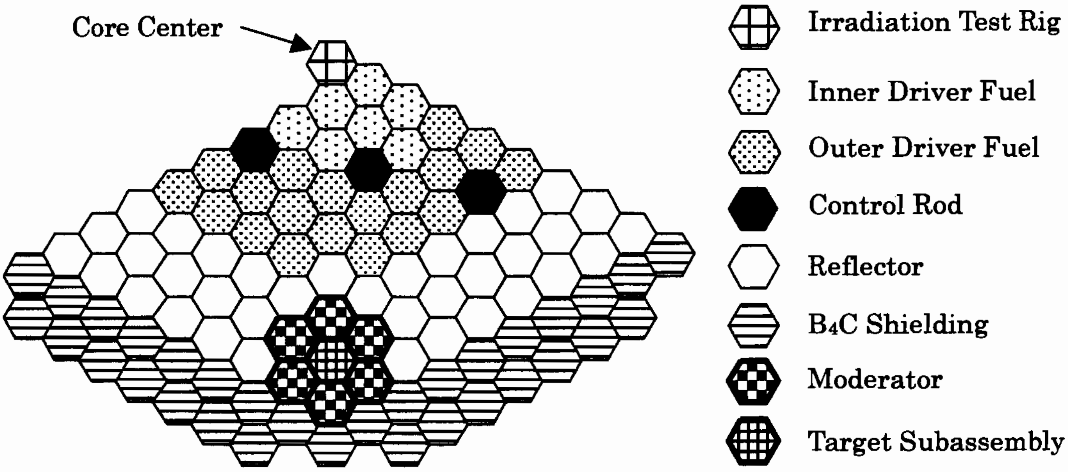
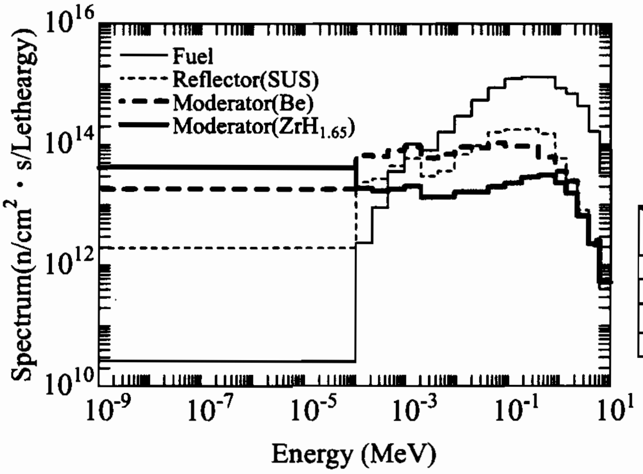


Fig. 1. Target Locations in JOYO Core (1/3rd core model)



	Neutron Flux(n/cm²·s)			
	≧1.0MeV	≧0.1MeV	≦0.1keV	Total
SUS	3.63E+13	4.04E+14	2.64E+13	8.67E+14
Be	2.80E+13	2.10E+14	2.52E+14	1.01E+15
$ZrH_{1.65}$	1.95E+13	8.32E+13	5.76E+14	7.78E+14
Fuel	9.18E+14	3.82E+15	3.61E+11	5.57E+15

Fig. 2. Neutron Spectrum in Target Subassembly

25P1

TECHNETIUM RECOVERY FROM NITRIC ACID SOLUTION BY ELECTROLYTIC EXTRACTION (EE) FOR FUTURE REPROCESSING

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In spent fuel reprocessing, many potentially useful and rare metallic elements, such as Pd, Ru, Rh, Tc, Te, Se, are vitrified as high-level waste. If it is possible to recover and utilize these elements in future, spent fuel reprocessing will be much more attractive. Thus, we studied the electrolytic extraction (EE) of Tc (NH_4TcO_4) dissolved in nitric acid solution by reductive deposition onto electrodes.

Figure 1 shows the experimental results of constant potential electrolysis by a carbon working electrode (three plates, 1 cm square, total area 6 cm^2). As shown in Figure 1a, Tc concentration decreased from the initial value after 30 min of electrolysis at the potential of –0.3 V vs. SSE (Standard Silver Electrode, Ag/AgCl in 3 M KCl). After 60 min, however, the concentration value increased to nearly equal value to the initial one, and it hardly changed for further electrolysis until 120 min. Therefore, it is expected that Tc deposited until 30 min by electrolysis. Deposited Tc, however, might re-dissolve after 30 min. At more noble potential, –1.0 V vs. SSE, the concentration hardly changed.

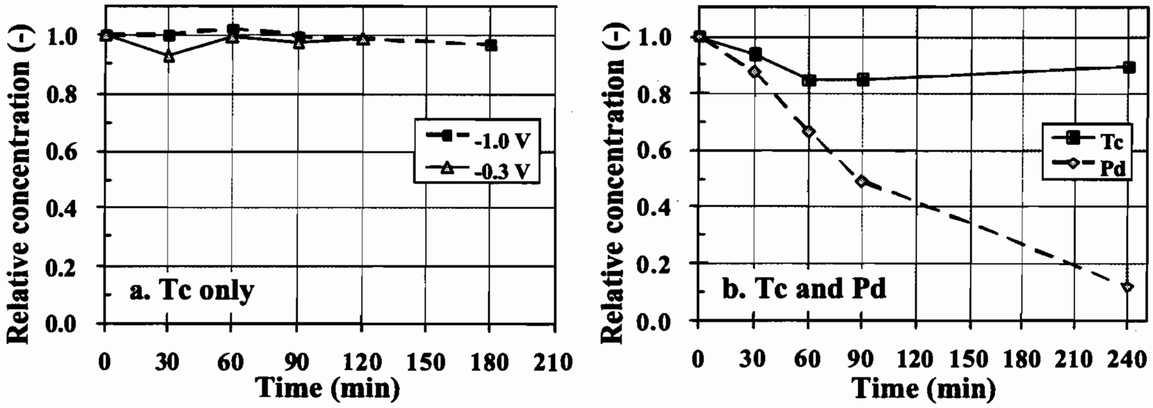

Figure 1. Time dependence of elemental concentration (Tc, Pd) in electrolyte solution with constant potential electrolysis determined by ICP-AES.
a) Tc only. Electrolyte: 3 M of HNO_3, 5 mM of initial Tc. Electrolysis conditions: potential of –0.3 V vs. SSE and current density about 2 mA/cm^2, or –1.0 V vs. SSE and about 6 mA/cm^2.
b) Tc and Pd. Electrolyte: 1 M of HNO_3, 1.8 mM of initial Tc and 6.1 mM of initial Pd. Electrolysis conditions: potential of ±0.0 V vs. SSE, current density about 0.3 mA/cm^2.

From the previous results about Re [1], co-existence of Pd, which easily deposits, is expected to improve Tc deposition (promoter effect). As shown in Figure 1b, Tc concentration in the Tc-Pd solution (1 M HNO_3) decreased until 60 min by electrolysis at ±0.0 V vs. SSE. In this case, Tc is expected to deposit onto the electrode together with Pd-black as Re. The concentration, however, increased again for further electrolysis, and Tc might re-dissolve, again.

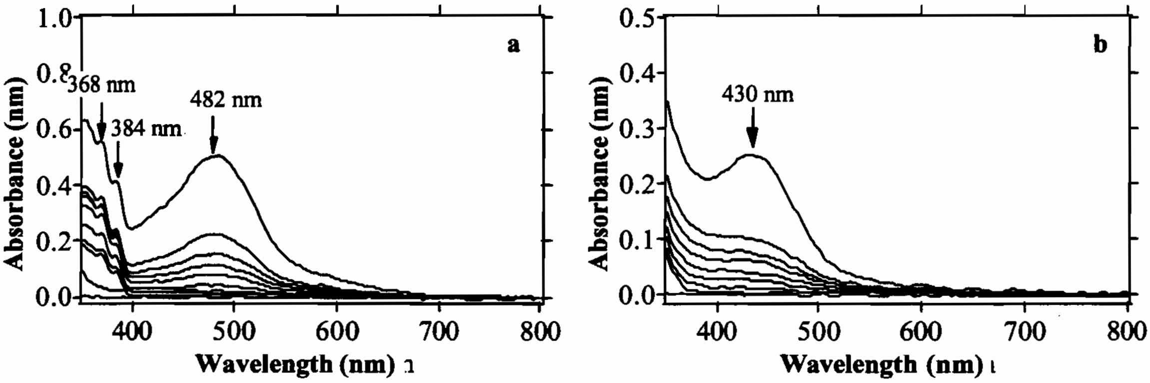

Figure 2. Absorption spectrum change of Tc solution by electrolysis.
a) Electrolyte: 3 M of HNO_3, 1.5 mM of Tc. Electrolysis conditions: Potential of −0.3 V vs. SSE, current density of roughly 2 mA/cm^2, until 210 min.
b) Electrolyte: 3 M of HNO_3, 1.5 mM of Tc, 0.1 M of hydrazine. Electrolysis conditions: Potential of −0.3 V vs. SSE, current density about 14 mA/cm^2, until 120 min.

Maslenikov et al. [2] proposed that co-produced HNO_2 may accelerate Tc re-dissolution. In Figure 2a, absorption spectrum change of Tc solution by electrolysis at the potential of −0.3 V vs. SSE is shown. As is clear from the figure, HNO_2 did evolve during the electrolysis (peaks at 368 and 384 nm). The concentration of HNO_2 in the solution was also checked by colorimetric measurements. It was confirmed by the measurements that the concentration increased up to 6 mM for 60 min of electrolysis. The peak at 482 nm in Figure 2a, which is not attributed to HNO_2, can be attributed to Tc in a reduced form. As shown in Figure 2b, an absorption peak was observed at 430 nm if the solution contained hydrazine. In this case, little HNO_2 is expected to exist. Boukis et al. [3] reported about chemical reduction of Tc by hydrazine and complex formation. They observed an absorption peak at 450 nm for reduced Tc, and the peak moved to longer wavelength, 472 nm, by complex formation with DBP^-. The wavelength of 482 nm, observed here, is still longer. Therefore, it is reasonable to assign the absorption peak to some complex of reduced Tc, possibly with NO_2^-. This complex formation can be the explanation of Tc re-dissolution, which is supposed from Figure 1a and b.

This work was done under the collaboration research, “research on selective separation and recovery of long-lived fission products from spent fuel,” between JAERI and JNC.

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25P2

TECHNETIUM TRANSMUTATION: ELECTRONIC STRUCTURE CHANGES ANALYSIS BY QUANTUM CHEMICAL MODELS

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Previous [1] quantum chemical DV-X_α [2] calculations based on the density functional theory proved adequacy and reliability of cluster models for the metallic technetium electronic structure analysis. We extended these models for mixed Tc_xRu_y phase appearing due to transmutation of radioactive Tc^{99} into stable Ru^{100} [3]. As a bulk phase our simple model clusters (Fig.1) used the same electronic density for volume and surface sites. Interatomic distances for mixed models were linear interpolated by content between pure Tc and Ru metal ones as it's shown in [4]. We took into account all low concentration models of Tc or Ru, but in the middle concentration area we used only statistically averaged data for rather small (~10) random sets of atom positions.

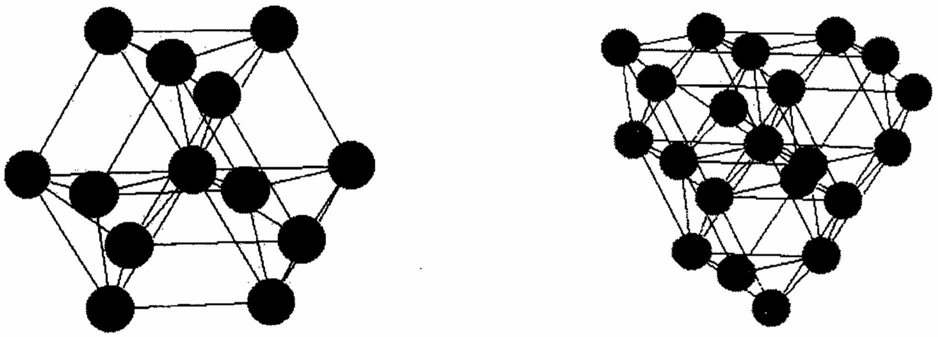

Fig.1. Tc (or Ru) 13-atomic and 21-atomic fragments of hexagonal lattice

Because it is similar character of results for both fragments, only the most informative electronic structure characteristics of 21-atomic model graphic data will be given further.

The electronic configurations of pure metallic models Tc $4d^{5.66}5s^{0.73}5p^{0.60}$ and Ru $4d^{6.67}5s^{0.71}5p^{0.60}$ for mixed models vary slightly. It is about 10% for 5s5p-states and up to 3% for 4d-states. The most modification of 4d-Tc population is 0.15å for 13-atomic model. 4d-Tc population is monotone weakly logarithmically decreasing while Ru part enlarges. At the same time for effective charges we found approximately linear dependence from Ru content (Fig.2). For all atomic positions and some Ru concentration it was occured electronic density displacement toward Ru and very similar tendencies.

Fermi level position in our models approximately corresponds to the high occupied cluster orbital. Relative location of this level also linearly drops (Fig.3). Density of states (DOS) at Fermi level dependence has a rather intricate shape (Fig.4). At the low concentration of some metal DOS is relatively less then the same one for the pure metals or for the central part of the graphic. DOS absolute maximum position corresponds to ~70% output of transmutation products. Commonly this parameter has arising tendency during the transmutation process (dashed line).

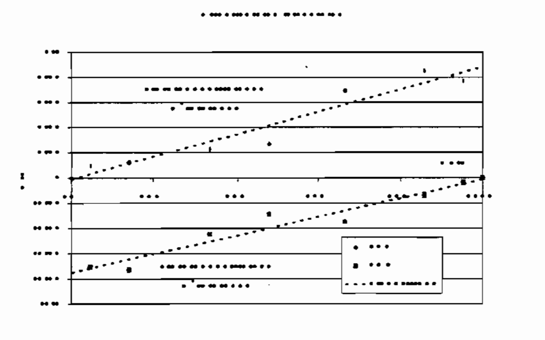

Fig. 2

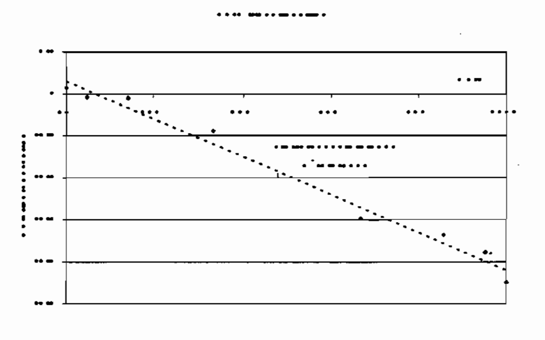

Fig. 3

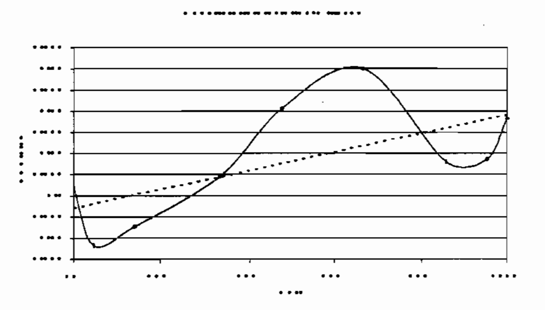

Fig. 4

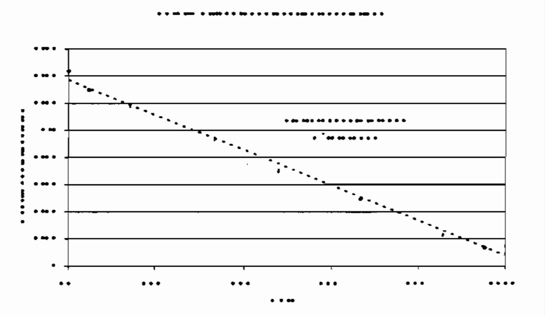

Fig. 5

Finally, we estimated models stability by sum of Mulliken bond overlap population indexes over all bonds per one atom of model (Fig.5). It is excellent linear tendency for the bond weakening during transmutation.

All this facts also well corresponds with general qualitative theory [5]: new more electronegative atom sublattice results to more strength bonding, correlates with the shift of occupied states in the lower energy area; descends Fermi level from the middle to the end of transition metal row and decreases density of states at Fermi level.

Therefore the same behaviour of electronic structure characteristics for both models arises the probability of these conclusions for the real samples. We can sum up that transmutation causes serious changes in electronic structure of initial metallic Tc, which influences on its chemical activity, physical-chemical and mechanical properties.

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25P3

SYNTHESIS AND PROPERTIES OF SOME NOVEL PERTECHNETATES: $LiTcO_4 \cdot 3H_2O$ AND ONIUM PHOSPORORGANIC TRIPODANDES

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The solubility of technetium compounds is an important item for its separation from the spent fuel reprocessing solutions and for the use in Tc sensors [1-2]. Two different methods – precipitation and electrodeposition - are considered to be the most useful for Tc separation and conversion, while the sensor construction is based normally on the application of easily extractable compounds. The precipitation method requires pertechnetates that are low soluble in aqueous solutions. For the electrodeposition the highly soluble compounds are desirable. The two groups of Tc compounds studied in this work comprise 1) some novel low soluble pertechnetates with organic cations, and 2) lithium pertechnetate known for its high solubility in aqueous solution.

In this work we have prepared some novel low soluble pertechnetates with organic cations of phospororganic tripodandes that could be useful as Tc-sensor components. Tris[[o-(diphenylphosphinyl)phenoxyethyl]amine (**I**) and tris[[o-(diphenylphosphinylmethyl)phenoxyethyl]-amine (**II**) were prepared as described in [2]. The corresponding pertechnetate salts were prepared by reacting the solutions of (**I** or **II**) in CH_2Cl_2 with excess of aqueous 0.2M $HTcO_4$ followed with evaporation to dryness. Tc extraction from 0.1M HNO_3 by **I** or **II** was quite efficient with the distribution coefficients were 5.7 and 6.1 correspondingly. The P-analogue of **I** - (tris[o-di(phenyl)phosphinyl]phenoxy]phosphine oxide) was not able to extract Tc under the similar conditions.

It is well known that lithium pertechnetate (**III**) is highly soluble in aqueous solutions. The first data on preparation of **III** was given by Keller and Kanellakopulos [3] who stated that the compound is isostructural to corresponding perrhenate. Zaitseva with co-workers reported on the preparation of **III** dihydrate that was also isostructural to corresponding perrhenate while the unhydrous **III** and perrhenate were not isostructural [4]. The Li-ReO_4-H_2O system, according to Smith and Long [5], provides with the formation of two hydrates – mono and dihydrate - at 20-87.5 °C and a unhydrous compound for the higher temperatures. In view of common isostructural properties of pertechnetates and perrhenate we examined the data of Khrustalev [6] who found that lithium perrhenate has the formula $LiReO_4 \cdot 1.5H_2O$ and the structure formed of almost ideally tetrahedral Re(VII)O_4 and the Li^+ that occupy octahedral coordination positions with three water molecules and three oxygen atoms of different ReO_4 tetrahedra. These tetrahedra and octahedra share vertices while the tetrahera themselves do not contact each other. Khrustalev has found doubtful the data given for the **III** and perrhenate in [4]. No more data were found in literature concerning the composition and structure of lithium pertechnetates. Here we report on the newly synthesized lithium pertechnetate trihydrate.

The pure chemicals were purchased from "Merck" and used for the synthesis. Tc_2O_7 was dissolved in water giving the 0.5 M pertechnic acid. The later was neutralized with LiOH to pH 7±0.02. The equivalent point was fixed with pH-ion analizer OP-2000 (Radelkis, Hungary). The solution of **III** was evaporated at 98 % H_2SO_4 to dryness, then 30% of water was added and the solution was kept in a batch closed with a watch glass over P_4O_{10} for some about 6 months at 25 °C. The crystals formed were colorless needles. The crystals were easily recrystallized when taken from the low humidity box and putting it back or under the nujol. The crystals were analised for Li, Tc and water content by AAS, β-scintillation counting and thermogravimetry, correspondingly. The analyses gave evidence for the formula $LiTcO_4 \cdot 3H_2O$: Found, %: Li^+— 3,12; TcO_4^- — 72,80; H_2O — 24,12. For the $LiTcO_4 \cdot 3H_2O$ calc., %: Li^+— 3,10; TcO_4^- —72,77; H_2O — 24,08.

X-ray powder diffraction pattern of $LiTcO_4 \cdot 3H_2O$ was registered in Guinier camera (CuKa1 radiation, Si powder as internal standard) and analyzed by CRYSFIRE program suit. It was indexed in hexagonal lattice, at 25 °C: $a = 7.9240(4)$, $c = 5.4860(4)$ Å, $\gamma = 120^\circ$. V = 295.13 Å^3. $LiTcO_4 \cdot 3H_2O$ was found to be isostructural to $LiBrO_4 \cdot 3H_2O$ and $LiClO_4 \cdot 3H_2O$ (sp.gr. $P6_3/mc$, Z = 2) and had no analogues among the perrhenates and permanganates [7].

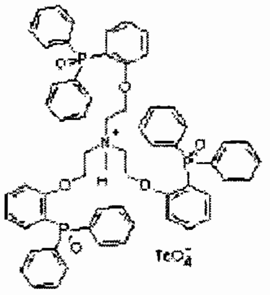

Fig.1. Molecular structure of tris[[o-(diphenylphosphinyl)phenoxyethyl]ammonium pertechnetate(I)

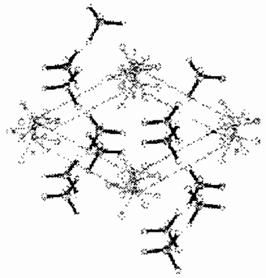

Fig. 2. Crystal structure of the lithium pertechnetate trihydrate

Table 1. X-ray powder diffraction pattern of $LiTcO_4 \cdot 3H_2O$

No	h	k	l	2Th(obs)	2Th(Calc)	I,%	No	h	k	l	2Th(obs)	2Th(Calc)	I,%
1	0	1	0	12.898	12.890	40	16	1	2	2	48.242	48.250	40
2	0	1	1	20.704	20.712	100	17	1	3	1	50.723	50.730	60
3	1	1	0	22.417	22.422	70	18	0	1	3	51.699	51.690	20
4	0	2	0	25.934	25.947	40	19	0	3	2	52.006	52.013	20
5	0	2	1	30.719	30.709	60	20	0	4	0	53.359	53.359	40
6	0	0	2	32.615	32.619	30	21	0	2	3	57.021	57.022	40
7	1	2	0	34.517	34.553	50	22	2	2	2	57.316	57.325	5
8	0	1	2	35.201	35.207	30	23	2	3	0	58.589	58.587	10
9	1	2	1	38.347	38.356	60	24	1	3	2	59.029	59.024	40
10	0	3	0	39.346	39.358	10	25	2	3	1	61.193	61.199	20
11	1	1	2	39.935	39.944	50	26	1	4	0	61.918	61.914	20
12	0	2	2	42.129	42.143	20	27	1	2	3	62.024	62.049	10
13	0	3	1	42.779	42.797	5	28	0	4	2	63.976	63.955	5
14	2	2	0	45.787	45.765	40	29	0	3	3	65.299	65.271	10
15	1	3	0	47.747	47.747	10	30	0	0	4	68.340	68.340	5

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25P4

TECHNETIUM CARBIDE: QUANTUM CHEMICAL MODEL

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Technetium carbide is alternative material of the metallic technetium manufacture. Because of identification difficulty of structure, recently this compound was considered as possible non-equilibrium metallic phase in contrast to well-known hexagonal structure.

The problem clarification of this compound formula $\mathbf{Tc_6C}$ [1] parallel with experiment necessitates of quantum chemical calculations of the hypothetical structure models with the different carbon concentration. The calculations were made by non-empirical electron density functional in DV-X_α approximation [2]. All details are the same as in [3].

As the starting model of metallic face-centred cubic (a = 3.98Å) lattice [2] we used the fragment $\mathbf{Tc_{42}}$, containing of two metal layers. In this fragment the number of octahedral holes with diameter 3.98Å is 13 or 25% to **Tc**. Moreover 24 unoccupied tetrahedral sites have visibly smaller diameter. Regular carbon allocation in accordance with the stoichiometry realised as $\mathbf{Tc_{42}C_7}$ (Fig.1). Model size completely satisfied to the problem conditions, as the relative limiting number of placing carbon atoms exceeds the expecting value **1:6**.

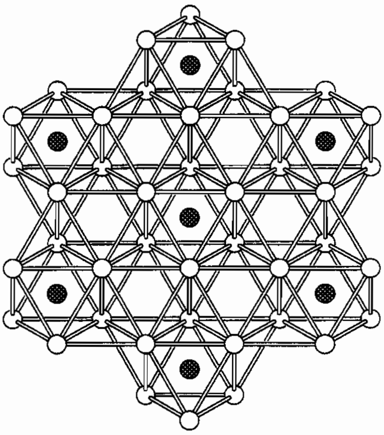

Fig. 1

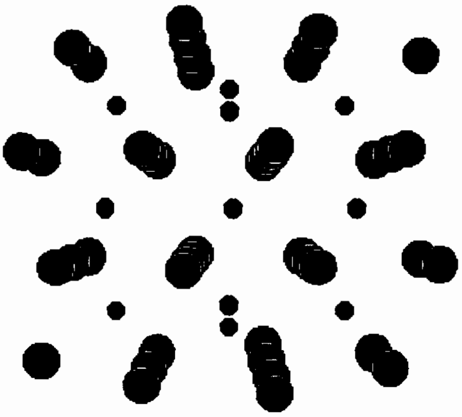

Fig. 2

Unfortunately now the straight energy calculations of the such size Tc compounds are not reliable through significant errors. However, for diatomic molecules the stability may be estimated by the Mulliken bond overlap population index *P* [4]. For more complex compounds it may be used the sum of these indexes by overall bonds. For comparable results should be better to use this value related to one atom. For carbide models the stability may be found as the difference *ΔP* between carbide and pure metal indexes.

The verification of *ΔP* –criterion we carried out for nearest Tc neighbour. The most stable carbide α-$\mathbf{Mo_2C}$ (Fig.2) crystallises in orthorhombic lattice [5]. Octahedral hole sites in this lattice half occupied by carbon regularly. In the several tens of atoms models without surface **C**-atoms the stoichiometry must be greater then **2:1**. $\mathbf{Mo_{44}C_x}$ fragments contained 4 metal layers. There are 17 octahedral holes in this model. The real carbide composition corresponds to x = 11 (25%). *ΔP* series (Fig.3) makes not quite regular row because small size of model and slight volume of trial carbon positions. So minimum area at C/Mo = 16% (or 33% for crystal) should be defined more exactly using expanded models. Nevertheless these data show *ΔP* tendency fairly good. The stable composition corresponds to $\Delta P > 0$. The maximum **C:Mo** value is slightly greater then 25%. On the contrary, metal body-centred lattice holes filling is accompanied by *ΔP* decreasing and in fact this carbide doesn't exist.

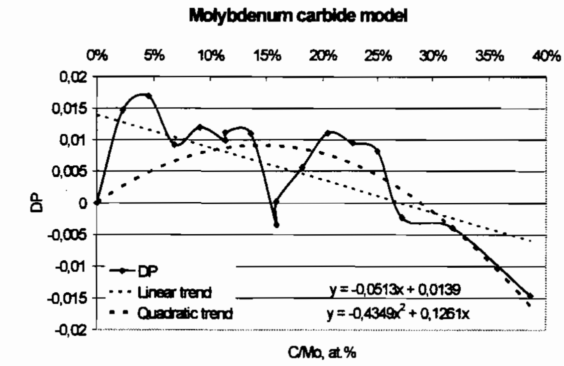

Fig. 3

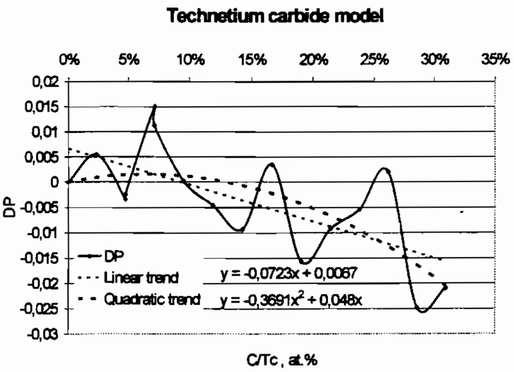

Fig. 4

The good estimator for accepted criterion of **Mo_2C** composition allows to apply it for **Tc**-carbide **$Tc_{42}C_X$**.models. Analysis of different coordination holes filling by this criterion shows that octahedral carbon position is much prefer. That's why we can use only octahedral carbon coordination models (Fig.1). Indeed, the tendency of *ΔP* changing (Fig.4) gives the stable area closed to experiment. So **C/Tc** doesn't exceed 15% and within the theory error limits (~as for **Mo_2C**) in good agree with **Tc_6C** composition.

Otherwise, *ΔP* curve in the stable area contains sine-like parts. This regions correspond to local carbon concentration for more (maximum) and less (minimum) compound stability. It can be suppose that alternate carbide phase formation is unregularly and unordered. It can included statistically averaged set of dissimilar fragments based on more stable local concentrations.

To sum up, we can conclude, that *ΔP* criterion model is adequate for the same problems. The experimental Tc-carbide composition can be described by two possible models (regular and unregular) using *ΔP* dependence.

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25P5

Quartery alkylammonium and alkylphosphonium pertechnetates: properties and application to TcO_4-selective electrodes

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New pertechnetate-selective electrode based on liquid ionites in polyvinylchloride matrix is developed with much better operational characteristics compared to liquid membrane ISE described earlier[1]. The new electrodes do not contain high radioactive solutions, possess high selectivity to main inorganic components of spent nuclear fuel reprocessing and radioactive waste solutions and environmental waters (nitrate, phosphate, sulfate, chloride etc.). The pertechnetates of quaternary ammonium and phosphonium cations were used as electrode-active component. o-Nitrophenyl-octylether was used as plastificator. The electrode response function of new ISEs was linear (10^{-6} – 10^{-2} M TcO_4^-, with 59±2 mV/pTc at 25°). Optimal membrane composition was determined.

Tetradecyltrimethylammonium pertechnetate $[CH_3(CH_2)_{13}N(CH_3)_3]TcO_4$ **(I)**, tetradecyltrimethylphosphonium pertechnetate $[CH_3(CH_2)_{13}P(CH_3)_3]TcO_4$ **(II)**, ethyldiphenyltetradecylphosphonium pertechnetate $[CH_3(CH_2)_{13}P(C_2H_5)(C_6H_6)_2]TcO_4$ **(III)**, terakisheptyl ammonium pertechnetate $[(C_7H_{15})_4N]TcO_4$ **(IV)** and terakisdecylammonium pertechnetate $[(C_{10}H_{21})_4N]TcO_4$ **(V)** were synthesized by liquid-liquid extraction of Tc-99 from 0.1M aqueous solution of $NaTcO_4$ into organic solution of quaternary ammonium/phosphonium bromide in CH_2Cl_2. Distribution / separation factors for Tc separation from aqueous solution and outer-sphere complex formation constants were determined. Properties of these compounds were studied by DTA, IR, Raman spectroscopy and X-ray diffraction.

The salts **(I-V)**, were tested and used as electrode-active components of the membrane ion-selective electrode (ISE) for Tc determination. ISE characteristics were tested for variable membrane and inner solution compositions. The electrode response function of the **(I-III)** pertechnetate based ISEs was linear in the range 10^{-6} – 10^{-2} M (TcO_4^-), with the slope equal to 59±2 mV/pTc at 25° (see Fig.1). High potentiometric selectivity factors of the new ISEs to main anions was found (see Fig.2). The electrodes are workable in the wide range of pH – from 0.5 to 13 (see Fig.3). The new Tc-ISE has much better characteristics compared to the one with liquid membrane that was earlier proposed[1]. Studies of some new Tc-ISE are in progress.

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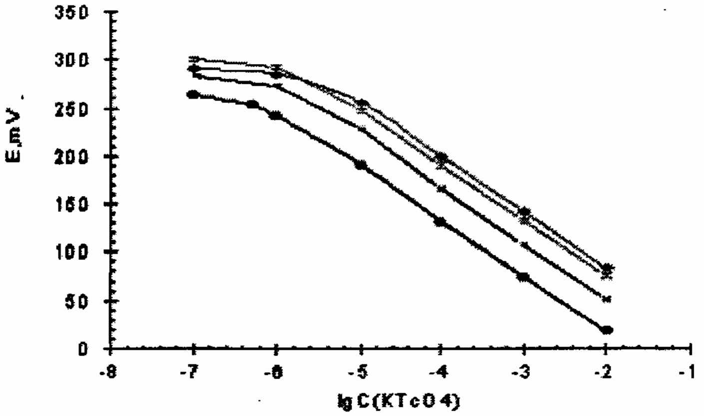

Fig. 1. Electrode response function for ISEs with different inner solution concentrations:
● – 10^{-6}M $KTcO_4$, 10^{-5}M KCL; **X** – 10^{-4}M $KTcO_4$, 10^{-3}M KCl;
∗ – 10^{-3}M $KTcO_4$, 10^{-2}M KCl; ◆ – 10^{-2}M $KTcO_4$, 10^{-1}M KCl.

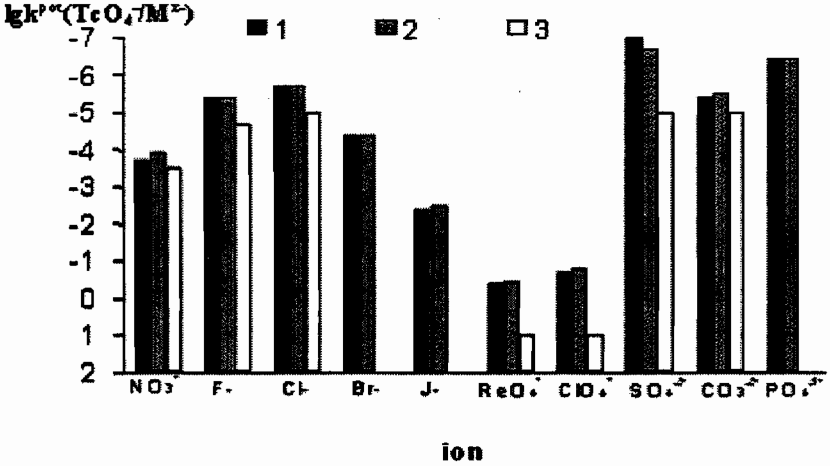

Fig. 2. Potentiometric selectivity factors (inner solution composition: 1 – 10^{-3} M KCl, 10^{-4} M $KTcO_4$; 2 – 10^{-5} M KCl, 10^{-6} M $KTcO_4$). 3 – electrode based on tetradecylphosphonium pertechnetate (see footnote 1 at the previous page).

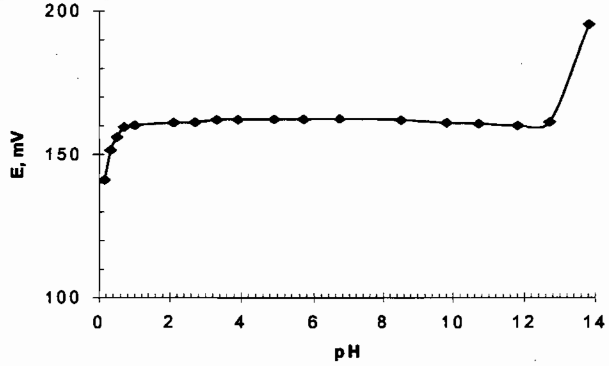

Fig. 3. Influence of pH on the electrode response function (10^{-4}M $KTcO_4$ in HCl solutions, background electrolyte - 1M KCl).

25P6

MODEL EXPERIMENTS ON BIOACCUMULATION OF TECHNETIUM AND THORIUM BY BOTTOM SEDIMENTS OF EUTROPHIC LAKES OF MOSCOW AND UDOMLYA REGIONS

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Radionuclides' accumulation by natural associations of microorganisms is important item for comprehension of their behavior in natural and technogenic water ecosystems. Different microorganisms are shown to exhibit different concentration factors from very low to very high, and the situation is complicated when we analyze the behavior of natural sediments composing of the association of some about 100 microbial species with some mineral. Tc transfer factors from water to sediments were analysed in some works [1, 2, 3 and ref. therein].The influence of natural water composition onto radionuclides sorption by lake sediments is not thoroughly studied. We present the results of model laboratory study of the bioaccumulation of the long-lived radionuclides. The isotopes were introduced as pertechnetate solution (^{99}Tc (VII)) or nitrate solution (^{234}Th (IV) - as a tracer for typical behavior of four-valent actinides) into batch samples containing lake water and sediments taken from the 3 eutrophic lakes 1) Beloye Kosino (Moscow reg.), 2) l. Kezadra and 3) l. Navolok, both - Udomlya reg., near from Kalininskaya NPP). The initial concentrations of Tc have been adjusted to 10^{-6}-10^{-7} M and that of ^{234}Th (IV) to 3000 cpm per initial aliquote. Eutrophic lake Beloye Kosino sediment was mainly formless organic detritus, gray colored, H_2S odoriferous. Udomlya reg. lakes sediment were 30% organic detritus and humics, 60% sand and 10% (Fe_2O_3 and other inorganic minerals).

Table.1. Main eutrophic lake Navolok sediment and water phase content

Microorganism	Cells' number N/ml	Comments
		Ratio in batch: $V_{sediment} : V_{liquid}$ = 1:3
Microalgae	10^6	
Bacteria:		Total = $2{\cdot}10^9$ bacteria/g,
Sulphate reducing	10^4	pH = 7.0 (stable);
Methanogenic	$10^4 - 10^5$	Eh = -0.20V NHE (inner sediment part);
Nitrifying	10^3 - 10^4	water phase: [HCO_3^-] = 1 – 4 mg-C/l;
Denitrifying	10^5	[HSO_4^-] = 0 – 50 mg/l, [Cl^-] = 35 mg/l.

Two equilibration modes were modeled (overhead agitation and hipolimnionic Tc transfer to sediment). Centrifuge MPW-210 (48G, 15 min), and microfilterfuge tubes – (5 kD "Sartorius") were used for phase separation.

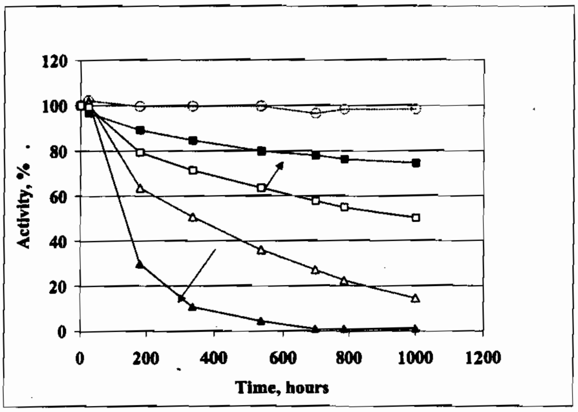

Fig.1. Tc uptake by Lake Sediments: O – steril sample; ϵ-Torfyanoe, ∇-Beloe; white points - sedimentation; black points – agitated in overhead

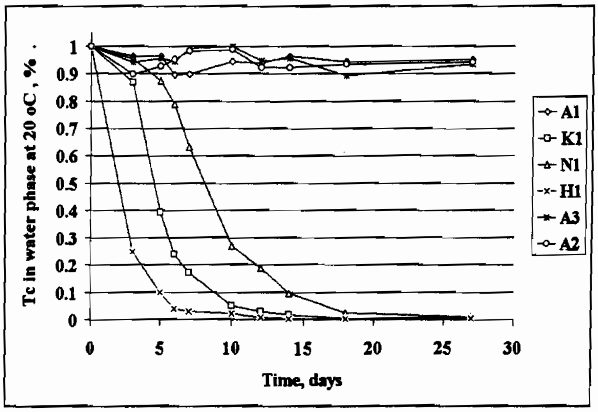

Fig.2.Tc uptake by Lake Sediments A1 – steril sample; K1 – Kezadra, N1- Navolok; H1-Homutovka

No more than 5 % of water phase was sampled during the experiments in total. More than 95% of Tc-99 were truly dissolved species of TcO_4^- in water phase all time through the experiment. The kinetics' analysis of data from Fig.1 has shown that the half-time values of the initial content removal from the water-phase form 400h for Tc. Two different uptake rates were characteristic for Tc sorption for some samples from Udomlya reg. : fast uptake during the first 2 when 40% of initial input was sorbed by sediment of eutrophic sediment of river source of X-lake, and a slow bioaccumulation period when Tc uptake was completed in 11 days.

The Tc uptake rate differed for different lakes sediments, the time of half-uptake being ½ month for eutrophic lake Beloye Kosino (Moscow reg.) and much less (4-7 days) for the two lakes of Udomlya reg. Concentration factors at 1600 hours of equilibration of Tc with sediments and natural water were 1710 ml/g for eutrophic lake Beloye Kosino and 1850 ml/g for the two lakes of Udomlya reg. The complete Tc accumulation by sediment took place after 1.0 months and 0.8 month respectively. Speciation by centrifuging at 10000 rpm, ultrafilterfuging or filtration through 0.05 - 0.22 μm membranes, has shown that the Tc fraction remaining in water phase was present as truly ionic species up to 90%. The microflora of lake played important role in the accumulation and reduction of radionuclides. Some microorganisms (being able of anaerobic respiration) had competition relationships between SO_4^{2-} or NO_3^- and TcO_4^- so that the additions of SO_4^{2-} or NO_3^- decreases the rate of Tc accumulation by the sediment.

Reduction of Tc(VII) to Tc(IV) and sorption of hydrolyzed species are the main mechanisms for Tc accumulation in this biosystem. We suppose that Tc(VII) reduction and further uptake by the lake sediment is due to microbial activity of the sediment components, most probably to sulfate-reducing bacteria, that are known to reduce Tc(VII) [4]. The difference in the uptake rate is associated with the higher chemical stability of TcO_4^-. This mechanism is supported by Tc uptake rate slowing down when concurrent anions like sulfate or nitrate are injected into the water phase (firstly observed in [5]).

The sediments from freshwater lakes have a considerable sorption capacity. The consecutive sorption runs have demonstrated only small decrease of Tc uptake rate. The desorption of technetium was carried out with H_2O, 1M HCl, 1M $NaClO_4$ or 15% H_2O_2 and gave the desorption factors of 0.05, 0.05, 0.08 and more 0.99 thus indicating the reduction of technetium to be the main mechanism of its uptake.

Thorium (IV) uptake by the sediments of both types was complete in 3 to 5 hours due to much more important sorption affinity of four-valent elements. Some about 20 % was sorbed by microparticulated organic matter and were removed only by microfilterfuge tubes ultrafiltration (5 kD "Sartorius").

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25P7

VERTICAL DISTRIBUTION OF RHENIUM IN SEAWATER SAMPLES COLLECTED THREE LOCATIONS OFF THE COAST OF AOMORI, JAPAN

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Introduction

Rhenium may be studied as a chemical analogue for Tc, which is just above Re in the periodic table. The element is one of the less abundant metals in the earth's crust, however, Re concentration in seawater is remarkably higher than those of neighboring elements such as Ru, Rh, Ir, and Os (1). For instance, Ru concentration is 0.7 pg mL^{-1} in seawater, while most average Re values reported are about 7-9 ng kg^{-1} (2-4). The behavior of Re in seawater is interesting because the concentration is low yet fairly constant among sampling points. It is, however, still difficult to explain the fate of Re. Although Anbar et al. (2) concluded that there was Re input to the ocean surface and Re scavenging near the surface, we could not find any difference from the surface to the bottom for the samples collected in Tokyo Bay (4). To clarify Re behavior in surface seawater, Re vertical concentrations collected three locations off the coast of Aomori were measured in this study.

Experimental

Seawater sampling was carried out by the Institute for Environmental Sciences at three locations off the coast of Aomori; Pacific Ocean side, Mutsu Bay and Japan Sea side in 1993, 1994 and 1995, respectively. Samples were taken at depths of 0, 2, 5, 20 and 30 m using a Go-flo sampler, and the sample, 250-mL each, was immediately acidified with 1 mL concentrated HNO_3. The beaker was covered with a watch glass and the solution boiled on a hot plate for 1 h to convert Re chemical forms into ReO_4^-. After the sample had cooled to room temperature, it was filtered with a 0.45-μm filter. Each sample solution was passed through TEVA resin column, and the column was washed with 40 mL of 0.8 M HNO_3. The Re fraction was then eluted with 5 mL of 8 M HNO_3. Finally, the solution was evaporated near dryness (~0.1 mL) at 80° C. The solution was diluted to 5 mL with deionized water for ICP-MS measurements (Yokogawa, Agilent 7500a).

Results and Discussion

For Re measurement in low salinity water samples, direct sample injection to ICP-MS is possible, however, if the Re concentration is low in a solution with a high matrix content (i.e., more than 300 mg L^{-1}), separation and preconcentration was needed. Since the applied separation method, the Re recovery is high and steady (near 100%, for example), application of an isotope dilution method with ^{185}Re is not important (4).

The average Re concentrations in seawater samples are shown in Fig. 1. The measured concentrations, 6.15 - 7.39 ng kg^{-1}, were within the reported values. Comparison of the data with the average value in Tokyo Bay, 7.45 ng kg^{-1} (4), the measured concentrations were slightly small. This difference might depend on sampling points, sampling conditions, *etc.*

The data for the samples collected at Japan Sea sides were smaller than those of Pacific Ocean sides. Although vertical distribution of Re in the surface seawater samples at each location was almost constant (a part of results are shown in Fig.1), the concentration in surface 0 and 2 m of Japan Sea side showed a slight decrease. It is necessary to consider about inputs to this area, such as river waters from Japan and/or the continent, rain, *etc.* Possibly, the low Re seawater mass moves to north with the current and is mixed well with other water mass so that the low Re concentration trend could not be seen in other sampling locations.

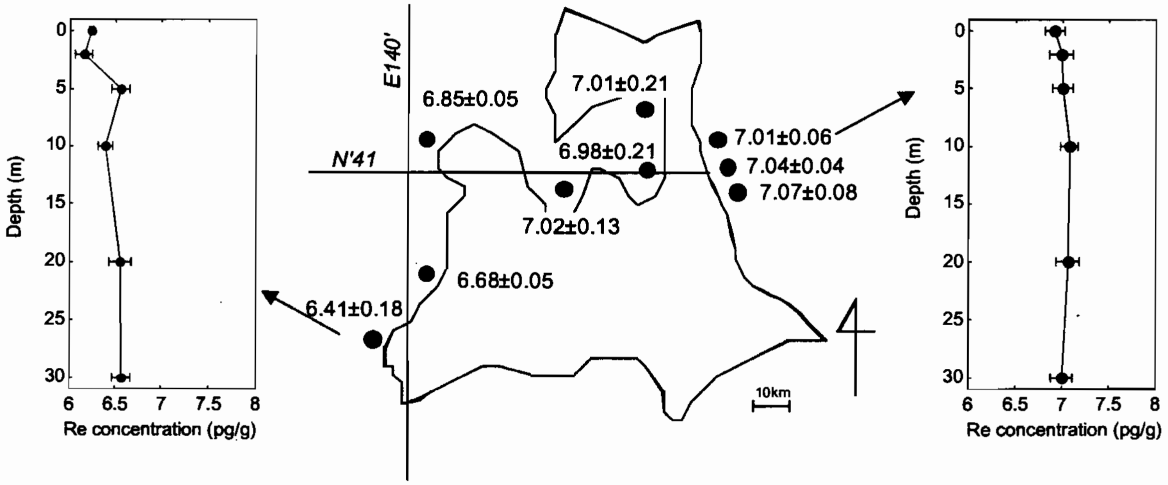

Fig. 1. Re concentrations (ng kg^{-1}) in seawater samples collected off the coast of Aomori, Japan in 1993-1995, and vertical distributions in two sampling locations at depth of 0-30m.

Acknowledgements

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