'99 Tc-99
2nd
Japanese–Russian
Seminar
Shizuoka

The Second Japanese–Russian Seminar on Technetium

ABSTRACTS

Shizuoka, Japan

Nov. 29 ～ Dec. 2, 1999

Scientific Topics

1. *Analytical and environmental chemistry of technetium*
2. *Coordination chemistry of technetium and rhenium*
3. *Radiopharmaceuticals of technetium and rhenium*
4. *Reprocessing of technetium*
5. *Other aspects of physics and chemistry of technetium*

Hosted by
Shizuoka University

Co-organized by
The Chemical Society of Japan
Atomic Energy Society of Japan
The Japan Society for Analytical Chemistry
The Pharmaceutical Society of Japan

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Japan Radioisotope Association
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----- PROGRAM -----

November 29 (Monday)

9:00–10:00 **Registration** (University Hall, Shizuoka University)
10:00–10:15 **Opening** (Chairperson: K. Okuno)

1. Coordination chemistry of technetium and rhenium

Chairperson: T. Sekine

2901 (10:15–10:45)
Behaviour of Technetium Acidoclusters in Acetonitrile Solutions
S. V. Kryutchkov and M. S. Grigoriev (Institute of Physical Chemistry, RAS)

2902 (10:45–11:05)
The Results of Quantum-Chemical Investigations of Technetium Cluster Compounds
Yu. V. Plekhanov and S. V. Kryutchkov (Institute of Physical Chemistry, RAS)

2903 (11:05–11:25)
Quantum Chemical Study of the Octanuclear Tetragonal Prismastic Cluster of Technetium with Bromide Ligands
Yu. V. Plekhanov and S. V. Kryutchkov (Institute of Physical Chemistry, RAS)

11:25–11:40 **Coffee break**

Chairperson: K. Hashimoto

2904 (11:40–12:00)
Investigation of Technetium Compounds by Methods of Conversion Electron Spectroscopy and X-Ray Electron Spectroscopy Combined
V. N. Gerasimov (Institute of General and Nuclear Physics, Russian Research Centre "Kurchatov Institute")

2905 (12:00–12:20)
NMR-^{99}Tc Study of Technetium Compounds and Alloys
V. P. Tarasov, K. E. Guerman, and V. F. Peretroukhin (Institute of Physical Chemistry and Institute of General and Inorganic Chemistry, RAS)

2906 (12:20–12:40)
The Quantum Chemical Models of Metallic Tc
Yu. V. Plekhanov (Institute of Physical Chemistry, RAS)

12:40–14:00 **Lunch**

Chairperson: V. N. Gerasimov

2907 (14:00-14:30)

Structural Characteristics of Polynuclear Rhenium Complexes and Their Relevance to Technetium Chemistry

Y. Sasaki (Graduate School of Science, Hokkaido University)

2908 (14:30-14:50)

Unusual Oxidation States of Rhenium and Their Properties

L. V. Borisova (Vernadsky Institute of Geochemistry and Analytical Chemistry, RAS)

2909 (14:50-15:10)

Synthesis and Structural Characterization of Technetium and Rhenium Complexes with Peptides Having KYC - sequence

T. Takayama, K. Suzuki, T. Sekine, and H. Kudo (Graduate School of Science, Tohoku University)

2910 (15:10-15:30)

Experimental and Theoretical Study on the Structure of Technetium(V) Amine Oxime Complexes with Nitrido Ligand

Y. Kani*, T. Takayama**, T. Sekine**, and H. Kudo** (*Power & Industrial Systems R&D Laboratory, Hitachi, Ltd., **Graduate School of Science, Tohoku University)

15:30-15:50 **Coffee break**

Chairperson: Y. Sasaki

2911 (15:50-16:10)

Coordination-Chemical Behavior of $Tc(CO)_3^+$ in Aqueous Solutions

N. I. Gorshkov, D. N. Suglobov, A. E. Miroslavov, and A. A. Lumpov (Khlopin Radium Institute)

2912 (16:10-16:30)

Kinetics of the Reaction of Pertechnetate with Sulphide

M. Simonoff, K. E. Guerman, and G. Simonoff (Institute of Physical Chemistry Russian Academy of Science and Laboratoir de chimie analytique et bioenvironmentale,URA 451,Universite Bordeaux 1, CNRS)

2913 (16:30-16:50)

Base Hydrolysis of Bis(acetylacetonato)nitridotechnetium(V)

T. Omori, S. Tanaka, K. Shinotsuka, and H. Suganuma (Faculty of Science, Shizuoka University)

17:30-19:00 **Getting together** (University Hall, Shizuoka University)

November 30 (Tuesday)

2. Radiopharmaceuticals of technetium and rhenium

Chairperson: V. M. Petriev

3001 (9:40-10:10)

Development of the ^{99m}Tc-Kit Production in Russia

G. Kodina and T. Tulskaya (DIAMED Ltd.)

3002 (10:10-10:30)

Labelling of Blood Cells with Technetium-99m

A. Malysheva, G. Kodina, and E. Medvedeva (State Scientific Center, Institute of Biophysics)

3003 (10:30-10:50)

Actual Aspects of Quality Control of ^{99m}Tc-Radiopharmaceuticals

G. Kodina, A. Inkin, and T. Doronchenkova (State Scientific Center, Institute of Biophysics)

10:50-11:10 **Coffee break**

Chairperson: G. Kodina

3004 (11:10-11:30)

Potentiometric Definition Sn^{2+} during a Labeling of Microspheres of Albumin by Radionuclides of Rhenium

D.N. Dyomin, V.M. Petriev, L.L. Bozadzhiev and V.G.Skvortsov

Medical Radiological Research Center RAMS, Obninsk

3005 (11:30-11:50)

Production of ^{186,188}Re and Recovery of Tungsten from Spent ^{188}W/^{188}Re Generator

K. Kobayashi, S. Motoishi, K. Terunuma, and Abdul A. Rauf* (Department of Research Reactor, Japan Atomic Energy Research Institute and *National Atomic Energy Agency (Indonesia))

3006 (11:50-12:10)

Synthesis and HPLC Analysis of Rhenium-188 Aminomethylenephosphonate Complexes

K. Hashimoto (Department of Research Reactor, Japan Atomic Energy Research Institute)

3007 (12:10-12:30)

Development of the Method of the Preparation of Albumin Microspheres Labeled 188-Re

V. M. Petriev, D. N. Dyomin, V. G. Skvortsov, and T. P. Rizhikova (Medical Radiological Research Center RAMS)

12:30-14:00 **Lunch**

Chairperson: N. Oku

3008 (14:00-14:30)

Strategies on Functional Biomimetic 99mTc-Radiopharmaceuticals (Tc-RPs) Development

K. Horiuchi S, A. Yokoyama, and H. Saji (Kyoto University, Graduate School of Pharmaceutical Sciences)

3009 (14:30-14:50)

Studies on Uptake and Distribution of Tc and Re Using the Mutitracer Technique

M. Yanaga , T. Ohyama, T. Yoshida, M. Iwama, M. Noguchi, T. Omori, K. Endo*, R. Hirunuma**, S. Enomoto**, S. Ambe**, and F. Ambe**(Faculty of Science, Shizuoka University, *Showa College of Phramaceutical Sciences, **The Institute of Physical and Chemical Research(RIKEN))

3010 (14:50-15:10)

Synthesis of Aqueous $Tc(CO)_3^+$ and Some Data on Its Pharmacokinetics

V. Yu. Sukhov, N. I. Gorshkov*, A. A. Lumpov*, A. E. Miroslavov*, D. N. Suglobov*, and G. E. Kodina** (Central Research Institute of Roentgenology and Radiology, *Khlopin Radium Institute, **Institute of Biophysics)

15:10-15:30 **Coffee break**

3. Environmental chemistry of technetium

Chairperson: N. Momoshima

3011 (15:30-15:50)

Behaviour of Technetium in Eutrophyc and Distrophic Fresh Water Lakes

K. E. Guerman, T. V. Khijnyak, V. F. Peretroukhin, E. S. German, E. V. Firsova, and N. N. Lyalikova (Institute of Physical Chemistry and Institute of Microbiology, RAS)

3012 (15:50-16:10)

Development of a Separation Method for ^{99}Tc in Environmental Samples Using a TEVA Resin and Its Concentration Levels in Japan

K. Tagami and S. Uchida (National Institute of Radiological Sciences)

16:10-16:30 **Coffee break**

Chairperson: K. Komura

3014 (16:30-16:50)

The Concentrations of Technetium-99 in *Sargassum thunbergii* around the Coasts of the Japanese Islands

S. Hirano (National Institute of Radiological Sciences)

3015 (16:50-17:10)

Measurement of Radionuclide Distribution Coefficients for Leached Mortar

N. Ashikawa*, N. Matsuoka*, T. Tajima**, H. Saito**, and A. Fujiwara*** (* Kyushu Environmental Evaluation Association, ** Obayashi Corporation, ***Radioactive Waste Management Center)

3016 (17:10-17:30)

Concentration of Technitume-99 in Litter/Humus Layer of the Japanese Forest

N. Momoshima, M. Sayad, and Y. Maeda (Faculty of Science, Kyushu University)

19:00-21:00 **Banquet (**Hotel Associa Shizuoka Terminal)

December 1 (Wednesday)

4. Reprocessing of technetium

Chairperson: S. Tachimori

0101 (9:30-9:50)

Extraction Behavior of Technetium in Nuclear Fuel Reprocessing

G. Uchiyama, T. Asakura, S. Hotoku, H. Mineo, K. Kamei, M. Watanabe, and S. Fujine (Department of Fuel Cycle Safety Research, Japan Atomic Energy Research Institute)

0102 (9:50-10:10)

Technetium Problem during Spent Nuclear Fuel Reprocessing and Possible Methods of Its Solution

V. I. Volk, A. Yu. Vakhrushin, and B. S. Zakharkin (SSC of RF Bochvar All-Russia Research Institute of Inorganic Materials)

0103 (10:10-10:30)

Technetium Extraction from High Radioactive Waste

V. I. Volk, A. Yu. Vakhrushin, and S. N. Veselov (SSC of RF Bochvar All-Russia Research Institute of Inorganic Materials)

0104 (10:30-10:50)

Diffusion Coefficients of Rhenium(VII) and Technetium(VII) in Nitric Acid and Tri-butyl Phosphate Diluted in Dodecane

M. Miratsu, R. Ludwig, N. T. K. Dung, G. Marx and M. Nabeshima* (Freie Universitaet Berlin, *Sumitomo Metal Mining Co. Ltd.)

0105 (10:50-11:10)

Evaporation Behavior of Diluted Nitric Acid Solutions of Nitrosyl Ruthenium and Perrhenate Ions with a Thin Film Evaporator

K. Ito (Institute for Advanced Materials Processing, Tohoku University)

11:10-11:25 **Coffee break**

Chairperson: V. I. Volk

0106 (11:25-11:45)

Methods of Technetium Recovery in Fuel Reprocessing

S. Tachimori and S. Suzuki (Japan Atomic Energy Research Institute)

0107 (11:45-12:05)

Solvent Extraction of Technetium(VII) from Alkaline Waste Using Crown Ethers: Fundamental Principles and Process Chemistry

B. A. Moyer, P. V. Bonnesen, J. C. Bryan, T. J. Haverlock, R. A. Leonard*, C. Conner*, and G. J. Lumetta** (Oak Ridge National Laboratory, *Argonne National Laboratory, **Pacific Northwest National Laboratory)

0108 (12:05-12:25)

Estimation of Necessary Separation Factor of ^{99}Tc and Ru after ^{99}Tc Transmutation for Use of Nuclear Ruthenium in Industry

A. A. Kozar, V. F. Peretroukhine, and B. F. Gulev (Institution of Physical Chemistry, RAS)

0109 (12:25-12:45)

Properties of Technetium and Technetium-Ruthenium Alloys for Transmutation of Technetium

K. Minato and Y. Shirasu (Japan Atomic Energy Research Institute, Department of Materials Science)

12:45-14:00 **Lunch**

5. Other aspects of physics and chemistry of technetium

Chairperson: H. Suganuma

0110 (14:00-14:20)

Technetium Ion Catalysis of Some HNO_3 Oxidation Reactions

V. S. Koltunov (A. A. Bochvar All-Russia Research Institute of Inorganic Materials (VNIINM))

0111 (14:20-14:40)

Laser Photoacoustic Spectroscopy Applied to a Study on Coagulation Processes of Tc(IV) Colloids

T. Sekine, S. Kino, Y. Kino, and H. Kudo (Graduate School of Science, Tohoku University)

0112 (14:40-15:00)

The Acceleration of U(VI) Reduction of Hydrazine in Alkaline Media in Presence of Technetium or Some Transition Elements Ions

V. I. Silin (Institute of Physical Chemistry, Russian Academy of Sciences)

0113 (15:00-15:20)

Physico-Chemical and Catalytic Properties of a Bimetallic System Me-Tc/Support

G. N. Pirogova, N. N. Popova, and Yu. V. Voronin (Institute of Physical Chemistry, RAS)

0114 (15:20-15:40)

The Effect of Support on Catalytic Properties of Tc in the Reactions of Different Types

G. N. Pirogova, N. M. Panich, Yu. V. Voronin (Institute of Physical Chemistry, RAS)

15:40–16:00 **Coffee break**

Chairperson: K. Okuno

0115 (16:00–16:20)

Effect of Chemical Matrix on ^{99m}Tc Decay Constant

V. V. Kol'tsov, D. N. Suglobov, L. G. Mashirov, A. E. Miroslavov, and N. I. Gorshkov (V. G. Khlopin Radium Institute)

0116 (16:20–16:40)

Half-lives of Technetium 97,98

T. Kobayashi, K. Sueki*, M. Ebihara*, and H. Nakahara* (College of Humanities & Sciences, Nihon University, *Tokyo Metropolitan University)

0117 (16:40–17:20)

Reevaluation of Ogawa's 'Nipponium' as the Element 75 (Rhenium) instead of 43 (Technetium)

K. Yoshihara (Japan Isotope Data Institute)

17:20–17:40 **Closing** (Chairperson: K. Okuno)

December 2 (Thursday)

Scientific tour to the Nuclear Training Center, the Hamaoka Nuclear Power Station of Chubu Electric Power Co., Inc.

November 29 (Monday)

Coordination chemistry of technetium and rhenium

2901

BEHAVIOUR OF TECHNETIUM ACIDOCLUSTERS IN ACETONITRILE SOLUTIONS

S.V.Kryutchkov, M.S.Grigoriev
Institute of Physical Chemistry, Russian Academy of Sciences
31 Leninsky prosp., Moscow, 117915, Russia

Cluster compounds are among the most interesting objects of the contemporary chemistry. The data available today for technetium cluster compounds prove that technetium is not only one of the most strong clusterforming agents, but also possesses a number of anomalous cluster-forming properties. Previous studies have shown than technetium forms several cluster structural types, unknown for other elements. One can mention, as an example, a novel type of polynuclear clusters with delocalized Tc-Tc bonds of high multiplicity [1, 2]. However, earlier studies in the field of the chemistry of technetium cluster compounds were carried out, for the most part, in aqueous solutions, and the ligands, coordinated around the cluster core, were anions of mineral acids (acidoligands) and the cluster fragments themselves - complex anions with metal-metal bonds of various formal multiplicity. Recently [3-5], a possibility of formation of binuclear cationic cluster with quadruple Tc-Tc bond has been shown using aprotonic solvents.

In the present work we have begun a study of the possibility of the conservation of Tc-Tc bonds in other structural types of technetium clusters (in particular, in hexanuclear clusters with delocalized Tc-Tc bonds of high multiplicity) for reaction in acetonitrile solutions. The reactions of the formation and destruction of the binuclear cationic technetium clusters in acetonitrile solutions were studied for the first time in [3]. A binuclear $[Tc_2(CH_3CN)_{10}]^{4+}$ complex with formally triple Tc-Tc bond has been separated and structurally characterized. It has been shown that this complex is stable against oxidation but not against reduction in acetonitrile solutions. The formation of this complex takes place in the process of the ligand substitution in other binuclear complexes as well as in the process of the reduction of mononuclear Tc(IV-III) complexes.

In the present work we have in general proved these conclusions and undertaken attempts to study the behaviour of technetium polynuclear clusters $[Tc_6X_{14}]^{n-}$ (X = Cl, Br) with Tc-Tc bonds of high multiplicity in acetonitrile solutions.

It has been shown that the stability of these clusters in acetonitrile solutions against destruction of Tc-Tc bonds and reduction is essentially lower then that of binuclear ones. Mononuclear complexes of the $[TcX_2(CH_3CN)_4]^+$ type were found to be one of the products of the destruction of polynuclear ones.

Earlier [1, 2] it had been shown that the stability of the $[Tc_6X_{14}]^{n-}$ (X = Cl, Br) clusters in aqueous solutions of hydrohalogenic acids is significantly higher, especially in reducing conditions. In oxidizing conditions the most stable product of the destruction of polynuclear clusters in aqueous solutions of hydrohalogenic acids is $[Tc_2X_8]^{3-}$ ion with formal multiplicity of Tc-Tc bond of 3.5. $[Tc_2X_6]^{2-}$ ion is the intermediate form of the existence of these clusters under the conditions described.

The X-ray structural study of $[TcBr_2(CH_3CN)_4][BF_4]$ single crystal (CAD4 autodiffractometer, λMoK_{α}, graphite monochromator) has shown that this compound is isostructural with analogous chloride complex, separated earlier [4]. This compound was synthesized according to the method described in [4] for $[TcCl_2(CH_3CN)_4][BF_4]$, but using $[(C_2H_5)_4N]_2[Tc_6(\mu\text{-}Br)_6Br_6]$ as initial material.

Crystal data: orthorhombic, space group *Ibam*, a = 6.272(2), b = 12.459(5), c = 20.864(8) Å, Z = 4; R = 0.033, R_w = 0.033 for 440 independent reflections with $I > 3\sigma(I)$ and 59 variables. Nonhydrogen atoms refined anisotropically, H atoms localized from difference Fourier synthesis and refined isotropically.

The structure is formed by pseudooctahedral $[TcBr_2(CH_3CN)_4]^+$ cations with *trans*-positions of bromide ligands and tetrahedral $[BF_4]^-$ anions. Atomic coordinates are presented in Table 1. The main bond lengths are: Tc-N 2.078(6) Å, Tc-Br 2.447(1) Å, N-C 1.11(1) Å, C-C 1.44(1) Å. The differences between the structures of bromide and chloride complexes are connected with the change in the size of halide ligands.

Table. Atom coordinates (x10^4) and equivalent isotropic temperature factors (Å^2, x10^3)

Atom	x	y	z	U
Tc	5000	5000	0	27(1)*
Br	2656(2)	6570(1)	0	47(1)*
B	0	0	2500	60(3)*
F	1195(12)	617(8)	2118(4)	124(2)*
N	3082(9)	4300(4)	-696(3)	31(1)*
C(1)	2056(11)	3901(5)	1057(4)	35(2)*
C(2)	725(15)	3404(7)	1536(5)	60(2)*
H(2a	123(5)	357(4)	-193(3)	80
H(2b)	-58(5)	369(4)	163(3)	80
H(2c)	68(5)	292(4)	-155(4)	80

* Equivalent isotropic U defined as one third of the trace of the orthogonalised U(i,j) tensor

References

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2. Kryutchkov S.V. Russian Chem. Rev. V.67 (1998), p. 883.
3. Burns C.J., Burell A.K., Cotton F.A. et al. Inorg. Chem. V.33 (1994), p. 2257.
4. Bryan J.C., Cotton F.A., Daniels L.M. et al. Inorg. Chem. V.34 (1995), p. 1875.
5. Cotton F.A., Haefner S.C., Sattelberg A.P. Inorg. Chem. V.35 (1996), p. 1831.

2902

THE RESULTS OF QUANTUM-CHEMICAL INVESTIGATIONS OF TECHNETIUM CLUSTER COMPOUNDS

Plekhanov Yu.V., Kryutchkov S.V.

Institute of Physical Chemistry RAS, 31, Leninskii prosp., Moscow, 117915 Russia

All calculations were carried out in approximation of the ab initio self-consistent field X_α-scattered waves method with the improved computing algorithm [1]. For low-symmetry complexes the ordinary algorithm for solving the system of nonlinear equations sometimes requires a number of reductions of the subintervals in solution area and accordingly, an increase in calculation time. So we used a linear approximation for matrix of the problem $S = A_i - EB_i$ in each rather wide energy interval $[E_i, E_{i+1}]$ and following solution by standard methods of linear algebra for equation $det\{S\}=0$. Width of these intervals is equal 0.5- 2eV in comparison with a usual one which could be less than 0.001eV. For the speedup of self-consistency the electronic density in each area of cluster is approximated on results of preceding iterations as a linear function from electronic densities in all cluster areas by the least squares method and is then corrected in the necessary direction.

In the diatomic models $[Tc_2]^{n+}$ [2] we determined the influence of bond length *r*(Tc-Tc) and cluster charge *n* on the position of electronic levels. With reduction of a charge is found rapprochement of group occupied molecular orbitals (MO-s) (*4d*-Tc) and free MO $2\sigma_{ga}$ (*5s*-Tc). This is connected with the diffuse nature of $2\sigma_{ga}$. Unlike occupied "*4d*" MO-s, its energy and composition weakly depend on the distance *r* and the charge *n*. It turned out that for the real Tc cluster compounds, when efficient charge $n < 2$, there always exists a distance r_0, under which the energies of empty free bonding level $2\sigma_{ga}$ and occupied anti-bonding level $1\delta_{u\beta}$ (*4d*-Tc) are equal. Profit in bond strength for configuration $2\sigma_{ga}(1)1\delta_{u\beta}(0)$ makes up 18% in contrast with $2\sigma_{ga}(0)1\delta_{u\beta}(1)$. For neighbors of technetium Mo and Ru such a change of electronic levels scheme is not found. Thereby, participation of the Tc 5s-orbital in M-M bond forming could possibly explain peculiarities of Tc cluster compounds discovered experimentally: forming a quintuple Tc-Tc bond in $[Tc_2Cl_6]^{2-}$, forming the infinite chains with the direct electronic exchange and so on.

The structure of binuclear cluster $[Tc_2Cl_8]^{n-}$ [3] (and their Mo-analogues) is the result of M-M bonds forming between two pyramid fragments $[TcCl_4]$. Eclipsed conformation D_{4h} (fig.1-1) is found experimentally, excluding the ion $[Tc_2Cl_8]^{4-}$. The latter formally enter into the polymeric compound in staggered geometry D_{4d} (fig.1-2) with torsion turning of pyramid bases on 45°. We determined the influences of symmetry, length of Tc-Tc bond and cluster charge *n* on features of electronic structure, in particular, for structure forming frontier MO-s. In D_{4h} clusters $[Tc_2Cl_8]^{2-}$ and $[Mo_2Cl_8]^{4-}$ the highest occupied (HO)MO is bonding δ-orbital $2b_{2g}$. When Tc oxidation state decreases the occupation of anti-bonding $\delta*$-MO $2b_{1u}$ takes place. In the staggered cluster $[Tc_2Cl_8]^{4-}$ MO-s $2b_{2g}$ and $2b_{1u}$ are degenerated into non-bonding $5e_2$ (δ), and an M-M bond was formed because of underlying bonding MO. Calculation of orbital forces, model potential curves [3] and orbital population indexes [5] for Tc-Tc bond has shown: 1)strength of Tc-Tc bond for all oxidation states is greater than for Mo-Mo bond 2)for the Tc complexes D_{4h} symmetry is preferred, and for $n=4$ only D_{4d} becomes advantageous 3)when changing a state of Tc oxidation weakening of bond strength does not exceed 20%,-whereas for the Mo complex it runs up to 50% (probably going over a threshold of stability), so the state with $n=5$ is not excluded for Tc-cluster 4)existing conception about M-M bond strength based both on cluster geometry and on formal multiple index have no single meaning (it causes the contradiction of Tc-Tc bond description earlier) 5)irregular shortening of Tc-Tc bond when reducing oxidation state of Tc could be explained semi-empirically using the criterion of invariability of net bond electron population as stability of complex (index value was based on $[Tc_2Cl_8]^{2-}$ cluster with the experimental length of Tc-Tc bond 0.215nm). Thereafter the criterion, when turning to $[Tc_2Cl_8]^{3-}$ with an occupying anti-bonding MO, system reaction must be shortening of Tc-Tc length less than 0.207nm (experiment 0.211nm), but with an additional electron, a transformation of system symmetry to D_{4d} and further shortening of bond to 0.205nm (experiment 0.204nm) must occur 6)features of lengths of Tc-Tc bonds to some extent depend on external crystal field of cluster surrounding and correlate with the size of unit cell (i.e. with lengths of metal-ligand and anion-cation bonds).

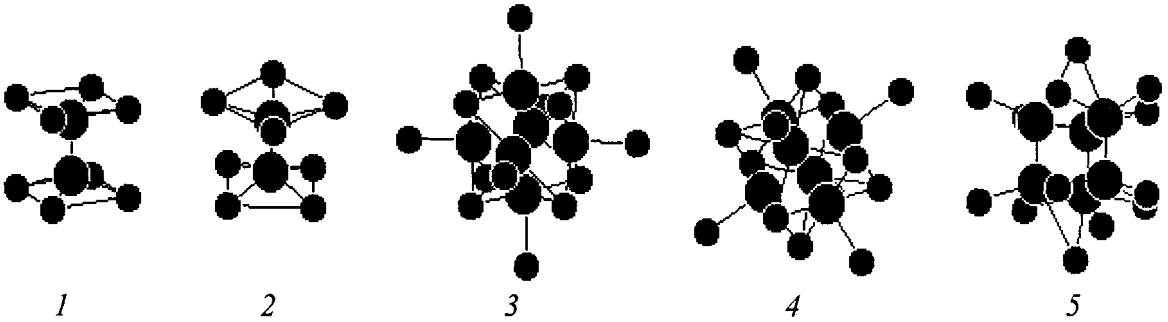
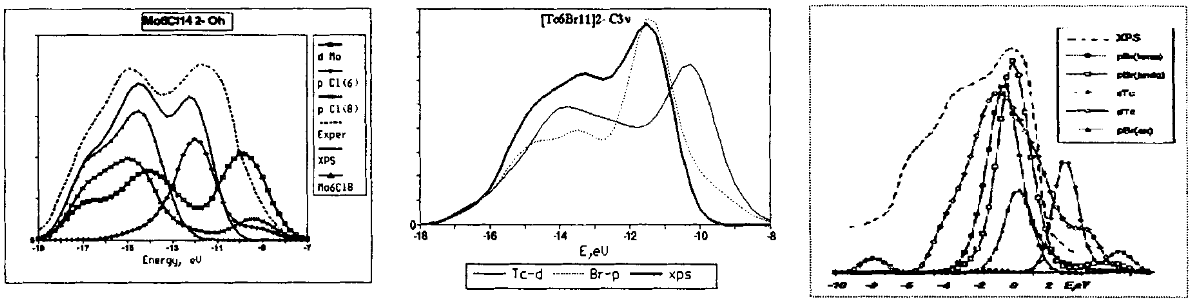


Fig.1

The structure of quasi-octahedral cluster $[Tc_6Br_6\mu Br_5]^{2-}$ [4] is similar to hexanuclear halogenid complex $[Mo_6\mu Cl_8Cl_6]^{2-}$ (fig.1-3), in which an octahedron from 6 metal atoms is surrounded by 8 bridge and 6 terminal Cl atoms. For Mo clusters we found (fig.2-1) a good correspondence of experimental and theoretical X-ray photoelectron spectra (XPS). An almost quantitative ratio of intensities of the high-energy peak (covalent Mo–μCl bond) and the shoulder in the spectrum (4d-electrons of Tc-Tc bond) was calculated. In the low-energy part of the spectrum it is reflected that the states of 3p-electrons of terminal Cl, which take part in covalent interaction with Mo, intensify the stability of Mo-framework, additionally split 4d-levels of Mo and partially donate the electrons to bonding M-M orbitals. Under general resemblance, electronic structure of hypothetical ideal O_h clusters $[Tc_6\mu Br_8Br_6]^{2-}$ and $[Tc_6\mu Br_8Br_6]^{4+}$ is distinguished by the appearance of M-M anti-bonding level $1b_{1g}$ in the spectrum of occupied states even for Tc^{3+}, that reduces stability of Tc-framework. Relative strength indexes of M-M bonds abreast Mo^{2+}-Tc^{3+}-Tc^{2+} are 1.18:1.02:0.76. A particular feature of the structure of the real Tc-cluster (fig.1-4) is the presence of three vacant μ-places of ligands statistically distributed inside the crystal. In the slightly idealized structure of C_{3v} symmetry, 4 μBr form a tetrahedron stretched along C_3 axis. There 6 Tc atoms (as distorted octahedron) situated on the ribs of the tetrahedron and linked with 6 terminal Br atoms (outer octahedron). Another occupied μ-position is located on the C_3 axis under the lower side of the tetrahedron. Calculated XPS (fig.2-2) reflecting the main features of cluster electron structure is inverted in contrast with O_h model. The peak beside the top of occupied valence area (*p*-electrons of terminal Br, *d*-electrons completely coordinated Tc centers) vastly exceeds a shoulder on its lower part (Tc - μBr interaction). An important feature is an absence of electrons on the Tc-Tc anti-bonding frontier MO. HOMO is filled by one unpaired electron (terminal Br) wholly accounting for the weak paramagnetic characteristics of the cluster. While geometry changes to C_{3v} strength index of Tc-Tc bond is enlarged up to 1.22.



1 2 3

Fig.2

The metal framework of trigonal prismatic cluster $\{Tc_6Br_6[\mu Br_6]Br_2\}^{n-}$ [5] (fig.1-5) forms a prism with equilateral triangle bases. The vertical ribs of the prism are vastly shorter than the horizontal ones and are formally triple or quadruple, as in dimer Tc complexes. The metal framework is surrounded by terminal, bridge and axial ligands. Cluster symmetry is close to D_{3h}. This cluster is related to polynuclear clusters with delocalized multiple M-M bonds (intermediate type between the classical polynuclear clusters with delocalized equivalent single- and dual M-M bonds and binuclear complexes with multiple M-M bonds). The calculated scheme of electronic states satisfactorily describes all features of the experimental XPS of $[(CH_3)_4N)_3[Tc_6Br_{14}]$ (fig.2-3): high-energy shoulder (*4d*-Tc), intermediate shoulder (terminal Br) and the most intensive peak (*p*-levels μBr and axial ligands) in the low-energy area of the spectrum. For the cluster without axial ligands $[Tc_6Cl_{12}]^{2-}$, there is rather big gap between occupied and unoccupied levels that gives rise to sufficiently stable singlet configuration. Conversely, in $[Tc_6Br_{14}]^{2-,3-}$ in this gap there are located the levels of axial Br. In $[Tc_6Br_{14}]^{3-}$ an additional electron falls into the state with the a_1 symmetry (corresponds to data from EPR), bringing the paramagnetic properties of the structure. Relative values of strength indexes for short multiple bonds along C_3 axis (as in binuclear fragments) and for triangles planes (between binuclear fragments) are as 1.75:0.3 that plausibly reflects a correlation bond strength from X-ray structural data and obliquely confirms the offered earlier mechanism of these clusters forming in cycloassociating reactions of multiple bonds M-M in dimers. It has been confirmed, that all "metallic" MO in cluster are vastly delocalized on metal framework and simultaneously show bonding or anti-bonding nature depending on the directions of Tc-Tc bonds. The number of cluster electrons can have an influence upon the prevalence of bonding or anti-bonding in one of these directions up to bond destruction. Indeed, experiment shows that oxidation of a trigonal prismatic cluster brings it to destruction with formation of binuclear $[Tc_2Br_8]^{3-}$, whereas reduction results in it reforming in octahedral ones with equivalent Tc-Tc bonds.

Acknowledgments

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2903

QUANTUM CHEMICAL STUDY OF THE OCTANUCLEAR TETRAGONAL PRISMASTIC CLUSTER OF TECHNETIUM WITH BROMIDE LIGANDS

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The cluster $\{[Tc_8Br_4\mu\text{-}Br_8]Br_2\}^-$ (fig.1) is a fragment of the crystal $2H_2O\cdot[Tc_8Br_4\mu Br_8]Br$ and belongs by the molecular structure to the unique class of octanuclear cluster compounds of technetium [1]. The formal oxidation state of Tc is +1.625. A geometry of the cluster is formed by the metal framework, which is as a tetragonal prism with the rhombus in the base. The ribs of the prism are a complex system of non-equivalent metal-metal bonds. The short diagonal of the rhombus corresponds to single middle length bonds (0.2521nm). The sides of the rhombus are long bonds (0.2672-0.2705nm) with formal multiplicity 0.5. The short vertical ribs of the prism are formally quadruple Tc-Tc bonds (0.2145, 0.2147nm). An other feature of the cluster is a presence of three types of structurally different Br atoms: 4 terminal, 8 bridge and 2 ionic or axial (near vertical axis of the prism). Neighbor clusters in the crystal are combined through common axial ligand in the endless chain. The geometry of the real cluster by small angular and inter-atomic distance deformations is brought to idealized D_{2h} model.

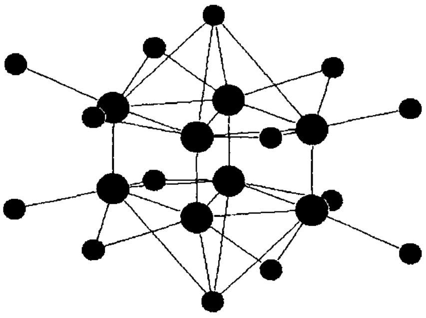

Fig.1

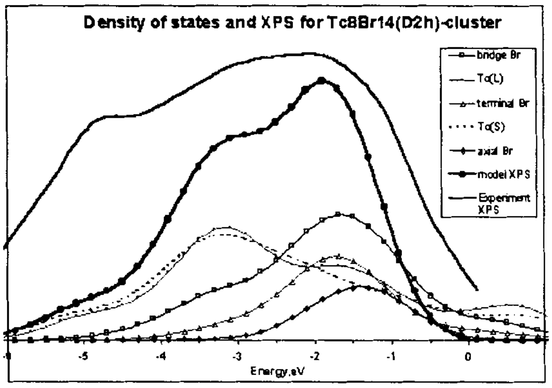

Fig.2

The total number of cluster electrons is 835. The 155 valency electrons occupied 78 molecular orbitals (MO-s), formed by the interaction of *4s*-, *4p*-Br orbitals and *5s*-, *5p*-, *4d*-Tc orbitals. Other 680 electrons were taken account by "frozen" core approximation in atomic configurations. Calculation of electronic structure has shown that the valency states of the cluster are presented by isolated group mainly Br 4s-MO-s with position 14.3eV relative to the high-occupied MO (HOMO) and by the set of three partly overlaying groups of MO-s:

1)The structure forming "metal" MO-s are mainly in the lower half of the spectrum with the maximum position from HOMO 2.3eV and band width 3.3eV. As well as in the case of the trigonal prismatic cluster [2] it was found that "metal" MO-s are vastly delocalised on the whole framework. Formally any MO of this type is M-M bonding or antibonding depending on the bond directions in the framework. For instance, MO a_{1u} is antibonding $\pi^*(d_{zx}\ d_{zy})\ \delta^*(d_{x2\text{-}y2})$ with respect to short vertical Tc-Tc bond and bonding $\sigma(d_{x2\text{-}y2})$ or antibonding $\delta^*(d_{zy},\ d_{zx})$ (depending on the ratio of *4d*-AO components in the MO) with respect to horizontal Tc-Tc bonds. The individual interactions forming the Tc-Tc bonds are possibly estimated by a split of the electron levels. For the short bonds these splits are $\Delta E_{\sigma-\sigma^*} = 5.7\text{–}6.1$eV, $\Delta E_{\pi-\pi^*} < 0.4$eV, $\Delta E_{\delta-\delta^*} < 0.2$eV. And for the comparison in respect to the middle length Tc-Tc bond (along a short diagonal of rhomb) a calculation brings to $\Delta E_{\sigma-\sigma*} < 0.5$eV, $\Delta E_{\pi-\pi*} < 0.2$eV, $\Delta E_{\delta-\delta*} < 0.1$eV.

2) The quantitatively main group of MO-s is the result of an interactions of Tc with μ-Br atoms, which are revealed almost in the all occupied electron states (width 3.1эВ).

3) The high-energy group MO with dominating contribution of ligand is basically bridge Br with the position of maximum from HOMO 0.6эВ and width 1.5эВ.

There is a 0.8eV energy gap between the occupied and free groups of MO-s with the noticeable contribution of (>50%), in which occupied and free predominantly Br-type MO-s are located. Thereby, the Tc-states practically do not participate in frontier MO-s (upper $12b_{1u}$ is occupied by 1 electron and free lowest $10b_{3g}$). The electronic density in these MO-s is approximately equally divided between axial and bridge ligands. It is possibly expected that main functions of the least bonded electrons near the upper edge of the valency band are the cluster ligand shell structure forming, the bonding of clusters in the polymeric chain and a charge transfer along the last. An so, the change of the number of cluster electrons in against to binuclear complex [3] just must not affects immediately on occupied "metal" MO-s. A modification of the metal framework geometry, in the opposite to hexanuclear trigonal prismatic Tc-cluster [2] must occur indirectly through the ligand shell and the redistribution of electronic density in the general MO structure, and will be small in accordance with experiment. Really [1], when the formal oxidation state of Tc decreases from +1.625 to +1.5 in $[Tc_8Br_4\mu Br_8]Br\,[H(H_2O)_2]$ and $[Tc_8Br_4\mu Br_8]Br_2\,[H(H_2O)_2]_2$, it occurs a small change occurs in clusters geometry, however, the interaction between clusters in the crystal maybe changes radically. For instance, the $[Tc_8Br_4\mu Br_8]Br_2^{2-}$ clusters in the crystal structure of $[Tc_8Br_4\mu Br_8]Br_2\,[H(H_2O)_2]_2$ are spatially isolated from each other [1].

The form of X-ray photoelectron spectrum (XPS) (fig.2) completely repeats the curve of occupied electronic states density. The visual features of XPS are shoulder in the lower part of the spectrum and main broad peak accordingly coincide with maxima of Tc states density and ligands ones (in sequence: bridge, terminal, axial). These maxima are divided by the interval 1.7eV. It possibly notices that the ratio of intensities of shoulder and peak in XPS does not correspond to the ratio of the numbers Tc and Br atoms in cluster (nearly 1:2) as this follows from our interpretation of the spectrum, (considering approximately equal atomic photoionization cross-sections *4d*-Tc and *4p*-Br [4]). This once again confirms a significant interaction between *4d*-Tc-states and *4p*-orbitals of μ-Br and the essential contribution of *p*-electrons of Br in the "metal" MO-s area. Note also, though it is good correspondence of model and experimental XPS forms, the widths of ones are vastly distinguished. It is possibly explained by an absence of the far interactions account in our cluster model. These interactions are sufficiently strong because of the neighbor clusters direct bonding through the common axial ligand.

Acknowledgments

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INVESTIGATION OF TECHNETIUM COMPOUNDS BY METHODS OF CONVERSION ELECTRON SPECTROSCOPY AND X-RAY ELECTRON SPECTROSCOPY COMBINED

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In synthesized chemical compounds technetium manifests a broad variety of valencies in limits from −1 to +7. Therefore , various modern analytical methods are required to study the chemistry of technetium. X-ray photoelectron spectroscopy (XPS) [1, 2] and conversion electron spectroscopy (CES) [3 - 5] are ones of the most effective physical-chemical methods.

Both XPS and CES provide valuable information about the electronic structure of the inner and outer electron orbitals. The difference is caused by the following.

1). The process of internal conversion of nuclei used in CES for excitation of the electron spectra, is strongly localized nearly to excited nucleus, while the photoeffect has not this property.

2). The contributions of the electron states with the different angular moments in an electron spectrum in CES is much sharper varied on intensity in comparison with XPS.

3). In CES the technique of tagged atoms is actually used, as nuclei of radioactive isotopes are implanted into researched samples in accordance with the choice of the investigator.

Thus XPS spectra contain practically complete information on the qualitative and quantitative chemical composition of samples (with the exception of hydrogen), and CES spectra contain information only about a chemical state of the tagged atom of technetium and its nearest atomic environment.

Results of our investigations of the technetium compounds (see [1 - 5] and references in them) show that the XPS and CES methods usually well supplement each other. In many cases the XPS data allow to specify the chemical composition of sample and the oxidation degree of technetium and other atoms, and the CES and XPS data combined allow to determine the nearest environment of technetium atoms. When the sensitivity of the XPS method is small for definition of a chemical state of technetium in samples (at small concentrations of technetium) the CES method can be used for it by higher sensitivity (approximately on two order) and identity of chemical shifts of the internal electron lines in the XPS and CES spectra. But it is necessary now to use available wider database on the chemical shifts of internal lines in XPS spectra [2], as it is not enough of the similar data on CES spectra. A peculiarities of the chemical bond of technetium in a compounds were studied by the XPS and CES methods (see [1-5] and references in them).

On the basis of the obtained experimental results the conclusions about features of the technetium behavior in the thin samples, used by us in researches are made. Though the chemical state of the prepared samples depended on the chemical method applied an influence of the substrate material is observed. This effect is increased with a reduction of the technetium content into sample. It is clear that the diffusion process happened. Technetium formed the dilute solid solutions with the substrate materials. A strong changes of the local electron structure of technetium was observed by CES in these cases.

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2905

NMR-^{99}Tc STUDY OF TECHNETIUM COMPOUNDS AND ALLOYS

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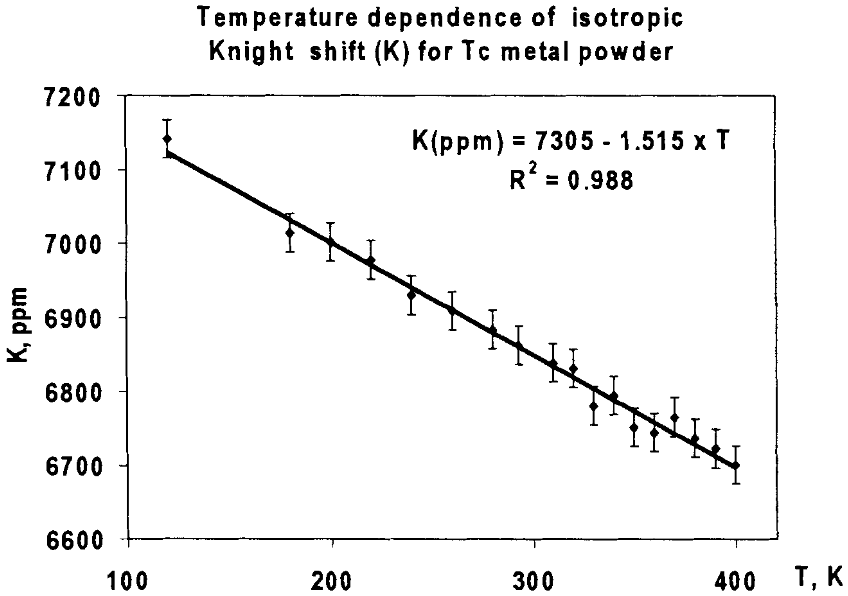
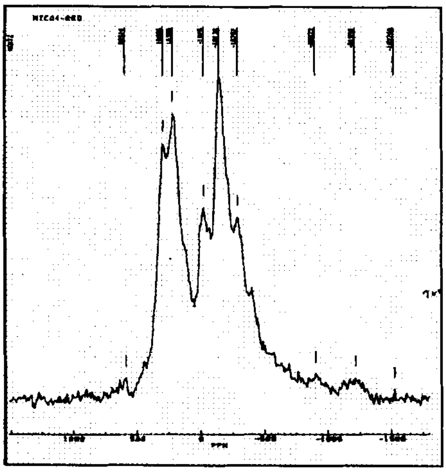
NMR-^{99}Tc spectra were recorded at Brucker AC-200 and Bruker MSL-300 radiospectrometers in 7.01T magnetic field at 67.5 MHz resonance friquency in impulse mode followed with FT. The shifts were mesured relative to standard 0.1M $KTcO_4$ solution. The spectra recorede for metal powder samples corresponded well to those reported by Van Ostenburg, Trapp and Lamm [i]. Fig. 1 presents the temperature dependence of isotropic Knight shift for technetium metal powder (particle size 150 – 80 □m) .





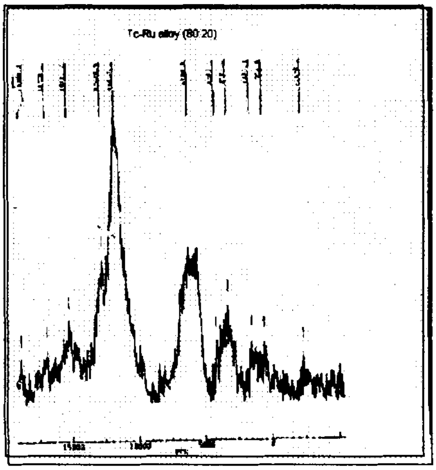


Fig 2. NMR-^{99}Tc spectrum of $HTcO_4$
The isotropic shift corresponds

Fig 3. NMR-^{99}Tc spectrum of metal disc made of Tc-Ru (80:20) alloy .

The splitting in the NMR-^{99}Tc spectrum of $HTcO_4$ (Fig 2) corresponds to presence of two species close to pertechnetate but carring smaller and higher effective chargses at Tc atoms.

The spectrum given in Fig.3 presents the states of technetium at the surface of metal disc made of Tc-Ru (80:20 weight percent) alloy .

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[i] Van Ostenburg, D.O., Trapp H., LammD.J. Phys.Rev. 1962, v.126, No 3 p.938-940.

2906

THE QUANTUM CHEMICAL MODELS OF METALLIC TECHNETIUM

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The existence of two forms of metallic technetium [1]: the massive crystal with hexagonal close packed (HCP) structure, and stable at the room temperature thin polycrystalline films (<15nm) with face-centered cubic (FCC) structure, leads to the cluster models with the symmetry of trigonal prism (D_{3h}) and octahedron (O_h) accordingly.

The calculations were realized in the approximation of the self-consistent field X_α-scattered waves (SCF X_α-SW) method [2].

For FCC structure 3 O_h cluster models were considered:

- the one-spherical model Tc_{13}, in which group of 12 equivalent atoms surrounds a central atom $\{Tc\text{-}Tc_{12}\}$ (fig.1-1);
- the two-spherical model Tc_{14}, in which an unoccupied cluster center is surrounded by groups of 6 and 8 equidistant from center atoms $\{0\text{-}Tc_6\text{-}Tc_8\}$ (fig.1-2);
- the two-spherical model Tc_{19}, in which the groups of 12 and 6 atoms surround a central atom $\{Tc\text{-}Tc_{12}\text{ -}Tc_6\}$ (fig.1-3).

The most simple one-spherical HCP model is $Tc_{13}\,D_{3h}$ cluster, in which central atom is located in a trigonal prism Tc_6 and else 6 atoms form a regular hexagon in the equatorial plane (fig.1-4). The extended cluster models for HCP lattice contain 17 atoms (3, 2 and 12 atoms around the non-occupied center, fig.1-5) and 25 atoms (the 3-layered fragment contains in 6 atoms in lower and upper layers and 13 atoms in central layer, fig.1-6).

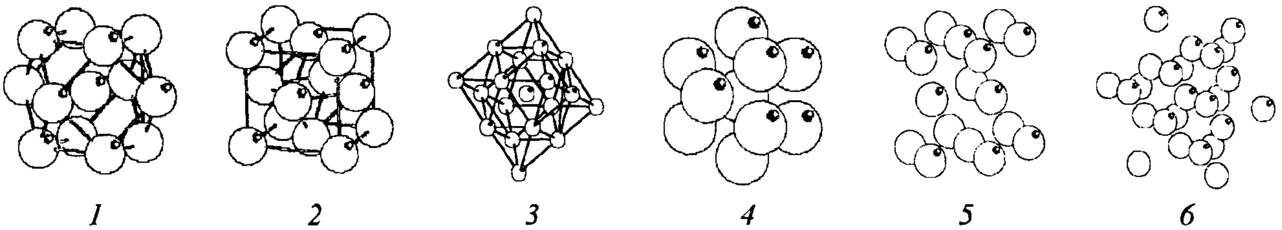
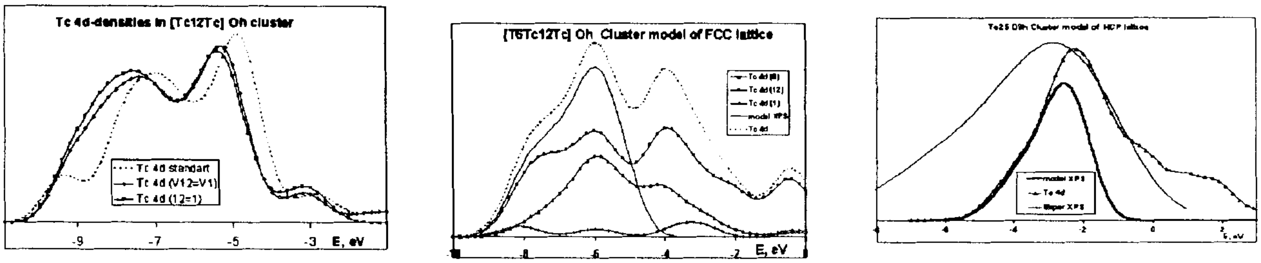


Fig.1

One of the imperfections of the metal cluster models is a nonequivalence of separate groups of cluster atoms as contrasted with their absolute equivalence in the crystal lattice [2]. In the calculations by the SCF X_α-SW method this usually occurs because of more deepen potentials of the internal cluster atoms with respect to peripheral ones. In the electronic spectrum this is revealed as the isolate peaks, which sometimes wrongly were interpreted as a result of specific atoms interactions. For partial indemnity of this model imperfection we used two ways. The first is adding of the constant potentials to separate groups of atoms to do equal even if their boundary electronic potential values for all atomic cluster spheres. In other, simplified variant a potential of peripheral cluster atoms is immediately used for all atomic cluster spheres. Herewith simultaneously the convergence of self-consistency iteration process repeatedly speeds up because of the reducing of a different atomic spheres types number, that in one's part facilitates a calculation of greater size cluster models.

From fig.2-1 it is possibly to see an observable difference of the electronic *4d*-states densities in O_h Tc_{13} cluster, which were calculated by the standard way and by the methods with corrected potentials. At the same time, the both ways of the potential correction bring to similar results. The defect of standard calculation method is graphically revealed from the examination of electronic populations in central P_1 and peripheral P_{12} cluster spheres. In the usual calculation it was obtained P_1=7.09e, P_{12}=5.65e, whereas after the potentials alignment it was calculated P_1=5.76e, P_{12}=5.79e.

On fig.2-2 it is given the density of electronic states and the model X-ray photoelectron spectrum (XPS) for the Tc_{19} O_h cluster, and on fig.2-3 it is showed ones for the Tc_{25} D_{3h} cluster together with the experimental XPS of valence region (V.Gerasimov, Kurchatov Institute, 1984). In spite of the different local symmetry the calculations of cluster with two coordinating spheres bring to similar distributions of the electronic states with the asymmetry of main spectrum maximum or the appearance of a shoulder in the low-energy spectrum part in accordance with the experiment, that reflects an additional interaction of coordinating spheres in extended cluster models. However, the smaller model spectrum width in contrast with the experimental one is evidence of importance of long-range interactions and it will be necessarily to include the next coordinating spheres in these cluster models for quantitative reproducing of the experimental data.



1 *2* *3*

Fig.2

The important result of band calculations is a number of electrons at the Fermi level $N(\varepsilon_F)$, that in a cluster case corresponds to the highest occupied molecular orbital (HOMO). The presence of one unpaired electron on HOMO of D_{3h} cluster is in a good agreement with the weak paramagnetic properties of metallic technetium (for the comparison in FCC O_h models HOMO is partially filled by 1, 2 or 3e). From the comparison of the temperatures of transition in superconducting state T_k for *4d*-metals [1] and $N(\varepsilon_F)$ from band calculations [2] it is obtained a near square-law dependence: $T_k \sim N^2(\varepsilon_F)$. It was found, that the square of the ratio of the near HOMO electron densities numbers (recalculated per 1 atom) for our HCP and FCC cluster models is 1.59 and it is well agreed with the observed ratio of T_k (°K) for these lattices [1]: 8.24:4.9=1.68.

Thereby, conducted calculations are evidence of adequacy of our quantum-chemical cluster approach for metallic technetium and can be useful for next investigations of the electronic structure of Tc alloys and hard solutions.

Acknowledgments

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2907

STRUCTURAL CHARACTERISTICS OF POLYNUCLEAR RHENIUM COMPLEXES AND THEIR RELEVANCE TO TECHNETIUM CHEMISTRY

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1. Introduction. Rhenium, heavier partner of technetium, is often useful in discussing chemistry of technetium, because the second and the third row transition metal ions in the same group often show very similar characteristics to each other. I would like to discuss here the coordination chemistry of rhenium. Characteristic features of the rhenium complexes will be introduced, and will be used to predict corresponding technetium chemistry. Rhenium is among the most versatile transition elements with respect to the wide variety of oxidation states and variety of structures of its complexes. The common oxidation states in coordination chemistry range from 0 to +7. The most remarkable feature of the rhenium chemistry is its strong tendency to form metal-metal direct bond in its lower oxidation states from +2 to +5. Depending on the number of d-electrons, possible number of 'hands' that are used for metal-metal bonds are limited. Thus, for example, Re(III) with 4 d-electrons can give dimers with Re-Re quadruple bond or hexamers with four Re-Re single bonds from each rhenium atom. Trimers with two Re-Re double bonds from each rhenium atom are also known (Figure 1). I would like to introduce two areas of our recent works on rhenium complexes with rhenium-rhenium direct bond.

2. Our Work on Re-Re Bonded Complexes. (1) Edge Shared Dinuclear Rhenium Complexes with Two Oxide Bridges. Rhenium ions in the oxidation states +3 - +5 often form edge shared bioctahedrons with two bridging ligands like oxides. The Re-Re direct bond is obvious from its rather short distance. We have prepared three new complexes, two in the oxidation state of Re(IV)$_2$, $[\mathrm{Re_2(\mu\text{-}O)_2(L)_2}]^{4+}$ (L = tris(2-pyridylmethyl)amine (tpa), ((6-methyl-2-pyridyl)bis(2-pyridylmethyl)amine (Metpa)) and one in the mixed valence oxidation states of Re(III)Re(IV), $[\mathrm{Re_2(\mu\text{-}O)_2(Metpa)_2}]^{3+}$.[1] Due to overlap of various d orbitals, one σ, one π and one δ bonding orbitals and their antibonding counterparts are possible in the bioctahedral configuration. The orbitals are in the order $\sigma < \pi < \delta < \delta^* < \pi^* < \sigma^*$, if only the metal ion orbitals are considered. However, due to the interaction with the bridging ligand orbitals, alternative order is also possible, namely $\sigma < \pi < \delta^* < \delta < \pi^* < \sigma^*$. Table 1 shows the expected Re-Re bond order for both configurations. Our X-ray structural analyses clearly indicated that the order should be $\sigma < \pi < \delta < \delta^* < \pi^* < \sigma^*$, since the Re-Re distances are longer for the Re(III)Re(IV) species (see Table 1).

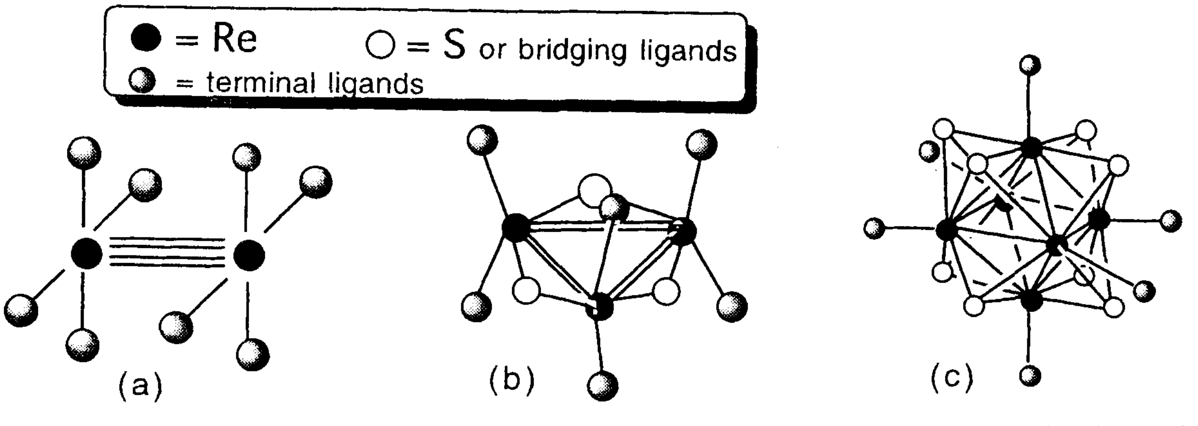

Figure 1. Rhenium(III) complexes with Re-Re bond. (a) Dimer with Re-Re quadruple bond, (b) Trimer with Re-Re double bond, and (c) Hexamer with Re-Re single bond.

Table 1. Re-Re bond order for the different orbital orders and observed Re-Re distances.

	Re(III)Re(III) (d^4d^4)	Re(III)Re(IV) (d^4d^3)	Re(IV)Re(IV) (d^3d^3)
$\sigma < \pi < \delta < \delta^* < \pi^* < \sigma^*$	2	2.5	3
$\sigma < \pi < \delta^* < \delta < \pi^* < \sigma^*$	2	1.5	1
Re-Re distance observed	----------------	2.426 Å	2.368 Å

(2) Chalcogenido-Capped Hexarhenium(III) Clusters. Hexarhenium clusters with $Re_6(\mu_3\text{-}E)_8$ (E = S, Se, Te) units (Figure 1c), are the subject of extensive studies, because of the establishment of synthetic methods of controlled introduction of terminal ligands (number and type of ligands are selectively introduced).We have found that these haxarhenium complexes show luminescence at room temperature in the solid state and in solution.[2,3] The luminescence characteristics (Table 2) are very similar to those of the isoelectronic hexatungsten(II) clusters with capping halide ligands.

We have further prepared new complexes having pyridine and its derivatives as terminal ligands.[4] We have also prepared one-electron oxidized species, $Re^{III}{}_5Re^{IV}$. Self-electron-exchange reaction between the $Re^{III}{}_6$ complex and the corresponding is very fast as expected from very small structural change as verified by the X-ray structural analysis. When two or more redox active ligands such as 4-cyanopyridine, 4,4'-bipyridine, and pyrazine are coordinated to the terminal position of the hexarhenium clusters, their redox wave in the cyclic voltammogram show small but distinctive splitting. This splitting indicate that the hexarhenium cluster unit acts as a 'mediator' of the redox communicate between the two ligands.

Table 2. Photophysical Data in CH_3CN at 298 K

Complex	λ_{max}/nm	ϕ_{em}	τ_{em} /μs
$[Re_6S_8Cl_6]^{4-}$ a	770	0.039	6.3
$[Re_6S_8Br_6]^{4-}$ a	780	0.018	5.4
$[Re_6S_8I_6]^{4-}$ a	800	0.015	4.4
$[Re_6S_8(CN)_6]^{4-}$	720	0.056	11.2
$[Re_6Se_8(CN)_6]^{4-}$	720	0.140	17.1
$[Re_6Te_8(CN)_6]^{4-}$	750	0.004	0.57

3. Implication to Technetium Chemistry. As the rhenium chemistry is now recognized as the richest one among the transition metals, it is certain that technetium has equally or even richer coordination chemistry. Although analogous technetium complexes to the above mentioned rhenium ones are not known, structural similarity of some other type of complexes indicates that it is worth trying to prepare them as they should provide valuable comparative information with those of the interesting properties that have been found in the rhenium chemistry. Major difference between the pair of complexes will be observed for their redox properties. Technetium complexes would be more difficult to oxidize by possibly ca. 0.5 V or so, and would be more appropriate to study the properties of reduced species. Moreover, mixed Tc-Re complexes with Tc-Re direct bond would provide further important information, as mixed Mo-W cluster complexes have shown. It is unfortunate that coordination chemists cannot handle technetium easily, and the collaboration with technetium chemists in general would be very much deserved.

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2908

UNUSUAL OXIDATION STATES OF RHENIUM AND THEIR PROPERTIES

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Rhenium(VI) compounds are the most exotic ones among all the compounds with high states of rhenium oxidation. They have not been used in practice because of the absence of simple methods for obtaining them in solution under usual conditions. The use of the compounds with «unusual» oxidation states of rhenium is mainly determined by the possibility of their stabilization in solutions. The quantitative formation of stable rhenium(VI) complexes in acid, neutral and organic solution, equilibrium diagrams of rhenium compounds, their properties (redox, complex formation, catalytic, etc.), mechanism of kinetic reactions were studied with the use of UV/VIS, IR , ESR, kinetic spectroscopy and other methods. More than 20 systems were studied in which Re(VI) compounds are formed. The quantitative formation of the stable Re(VI) oxohalide complexes ($ReOCl_5^-$ and $ReOBr_4$) has been established in the systems containing mixtures of conc. H_2SO_4, HCl and HBr. Under the same conditions (system: TcO_4^- - H_2SO_4 - HCl), technetium forms a chloride complex Tc(II-III). The mechanism of photochemical reduction of Re(VII) and reactions between Re(VI) oxochloride complex and aromatic amines were studied by means of flash photolysis. The conditions for the formation of stable $ReOCl_5^-$ in H_2SO_4 -HCl solution, equilibria between Re(VII), Re(VI), Re(V) were found. It was shown that $ReOCl_5^-$ is an oxidizer of organic substances and exhibits catalytic activity in reactions of organic substances oxidation. The catalytic reaction of aromatic amines (diphenilamine, its derivatives) oxidation by hydroxylamine catalyzed by rhenium was used to develop a highly sensitive kinetic method of Re determination (detection limit $5*10^{-10}$ g/ml) for the analysis of natural materials including some plants. Fast and quantitative formation and extraction by toluene of the stable $ReOBr_4$ complex has made it possible to develop highly selective methods of separation and determination of Re. Investigation of the interaction of oxohalide Re(VI) complexes with a series of N- and S-containing organic ligands (dithioles, thiophenols, thionaphthols, their derivatives) made possible the formation of stable complexes in organic solutions and development of a number of effective ESR methods of Re identification and determination. For example, for Re determination in organic solvents, some short-lived free radicals were investigated by a spin-trapping method in redox reaction of Re(VI) compounds with reducing agents (phenylhydrazine and others). The formation of the stable Re(VI) complex compound with hydroxylamido and (probably) nitrosyl ligands has been established in aqueous solutions in the wide rages of pH. It was found that Re(VII) oxo anion reacts with hydroxylamine in alkaline solution to give a yellow diamagnetic cation which was isolated as a chloride from the system ReO_4^- - NaOH - $NH_2OH.HCl$. It was shown that the redox process takes place in this case with intramolecular two-electron oxidation of a coordinated hydroxylamine ligand to a nitrosyl ligand with simultaneous reduction of Re(VII) to Re(V). The product of reaction is a Re(V) complex compound with a bidentate hydroxylamido ligand and a nitrosyl ligand. Treatment of the Re(V) complex with water or HCl quantitatively regenerates it to a paramagnetic Re(VI) complex. This reaction is reverse. The stabilization of the Re(VI) complex in aqueous solution may give a possibility to use it in medicine.

2909

SYNTHESIS AND STRUCTURAL CHARACTERIZATION OF TECHNETIUM AND RHENIUM COMPLEXES WITH PEPTIDES HAVING KYC- SEQUENCE

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Biological molecules (proteins, antibodies, and peptides) labeled with ^{99m}Tc, ^{186}Re and ^{188}Re have attracted much attention in diagnostic nuclear medicine for their affinity to tissues. The biological behavior of radiopharmaceutical is significantly influenced by chemical properties and structures of the coordination compounds. It is essential to know structures and structural changes of peptide complexes of Tc and Re for development of radiopharmaceutical.

In this work, we prepared ^{99}Tc- and Re-complexes with a peptide ligand having a KYC-sequence such as KYCAR (H_3L^5) and KYCAREPPTRTNAYWGQG-NH$_2$ (H_3L^{18}). These complexes were characterized by reversed phase HPLC, IR, UV-vis, MS and NMR.

The Tc(V) oxo complex of L^5 was prepared by a ligand exchange reaction of $[(n\text{-}C_4H_9)_4N][TcOCl_4]$ with H_3L^5 in methanol solution. The formation of only one species of the technetium complex was indicated by the reversed phase HPLC separation of the reaction mixture. The IR spectrum of $[TcO(L^5)]$ showed the absorption peak of the Tc=O bond at 979 cm^{-1}. The ^{13}C NMR signals of α-carbons of lysine, tyrosine and cysteine and that of β-carbon of cysteine in $[TcO(L^5)]$ showed a large downfield shift from that of the free peptide (Fig. 1). These downfield shifts would be originated from the coordination of heteroatoms adjacent to these carbons with electron donation to the technetium atom. The signals of α-protons in the ^{1}H NMR spectrum of this complex revealed the deprotonation of the coordinated amide groups of tyrosine as well as cysteine. The ^{1}H NMR resonances of two β-protons of cysteine indicated the coordination of the sulfur atom to the technetium atom in the thiolate form. These results suggest that the structure of this complex is a square pyramidal

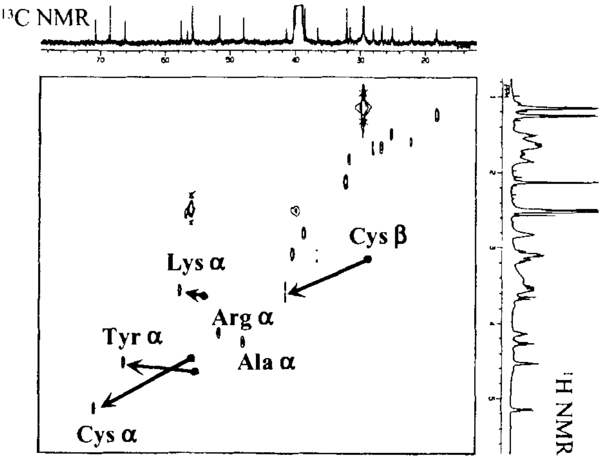
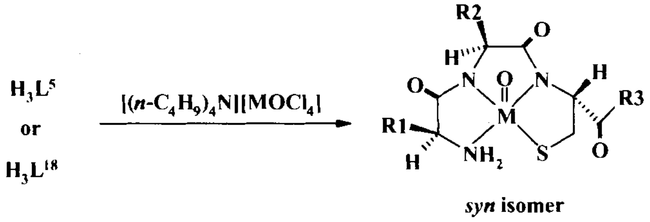


Fig. 1 ^{1}H-^{13}C COSY spectrum of *syn*-$[TcO(L^5)]$ (400MHz, DMSO-d_6). The arrows indicate shifts from free H_3L^5 peptide.

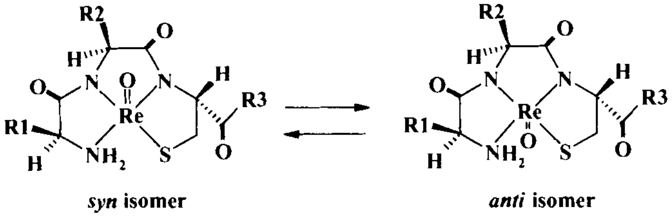
with the oxo ligand in the apical position and the peptide L^5 coordinates to the technetium-oxo core as the $N_2N'S$ type tetradentate ligand in the equatorial plane. Another striking result was that only the *syn* isomer was formed, although two geometrical isomers in the *syn* and *anti* configuration were expected (Scheme 1). The ^1H NMR resonance of lysine β-protons of the technetium complex shifted downfield from that of free H_3L^5. This downfield shift arises from a deshielding effect induced by the technetium-oxo core. The lysine $(CH_2)_4NH_2$ group of L^5 ligand has the *syn* comformation to the technetium-oxo bond in the complex. It is plausible that the steric hindrance between the side chains of peptide plays a role in the selective formation of the *syn* isomer.

The Re(V) oxo complex of L^5 was synthesised by the reaction of H_3L^5 with $[(n\text{-}C_4H_9)_4N][ReOCl_4]$ in the same manner as adopted in the synthesis of the technetium complex. The selective formation of the *syn* isomer was also found by the spectroscopic analysis. However, conversion of *syn*-$[ReO(L^5)]$ to the *anti* isomer was observed in aqueous solution at room temperature in contrast to the case of $[TcO(L^5)]$ (Scheme 2). The NMR signals of lysine and tylosine β-protons in the *anti* isomer appeared at an upfield region higher than that of the *syn* isomer. This result reflects a difference of the geometric structure around the rhenium-oxo core between the *syn* and *anti* isomers.

Only the *syn* isomer was produced by the reaction of $[(n\text{-}C_4H_9)_4N][TcOCl_4]$ with H_3L^{18} in DMF solution. The same was true for the reaction of $[(n\text{-}C_4H_9)_4N][ReOCl_4]$ with H_3L^{18}. The *syn*-to-*anti* conversion was not observed for both *syn*-$[TcO(L^{18})]$ and *syn*-$[ReO(L^{18})]$ in aqueous solution. The ^1H-^1H NOESY spectrum of *syn*-$[TcO(L^{18})]$ showed cross peaks between lysine and tryptophan. These two residues are spatially close to each other in the molecule. This result suggests the presence of the β-turn sturucture in the peptide ligand.



Scheme 1 Reaction of peptide ligand with $[(n\text{-}C_4H_9)_4N][MOCl_4]$. [M = ^{99}Tc or Re, R1 = $(CH_2)_4NH_2$, R2 = $CH_2(C_6H_4)OH$, R3 = AR (L^5), AREPPTRTNAYWGQG-NH_2 (L^{18})]



Scheme 2 Conversion between *syn* and *anti* conformations of $[ReO(L^5)]$.

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EXPERIMENTAL AND THEORETICAL STUDY ON THE STRUCTURE OF TECHNETIUM(V) AMINE OXIME COMPLEXES WITH NITRIDO LIGAND

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Among technetium complexes with amine oxime ligands, the complex with *d,l*-HMPAO (^{99m}Tc-*d,l*-HMPAO) is a well known radiopharmaceutical for measurement of cerebral blood flow.[1] Almost all known technetium amine oxime complexes have an oxo ligand (O^{2-}). There have been few studies on technetium amine oxime complexes with a nitrido ligand (N^{3-}).[2]

Recently, we have synthesized three nitridotechnetium(V) complexes with amine oxime ligands, $[TcN(pnao)(H_2O)][BPh_4]$ **1**, $[TcN(bnao)(H_2O)][BPh_4]$ **2**, and $[TcN(pentao)(H_2O)][BPh_4]$ **3**, and determined their X-ray crystal structures.[3] These complexes have an intramolecular hydrogen bond between the oxime oxygen atoms.[3] We discuss here structures of the nitridotechnetium(V) amine oxime complexes investigated by theoretical calculations as well as X-ray crystallography, focusing on the electron donating ability of the nitrido ligand and the intramolecular hydrogen bond.

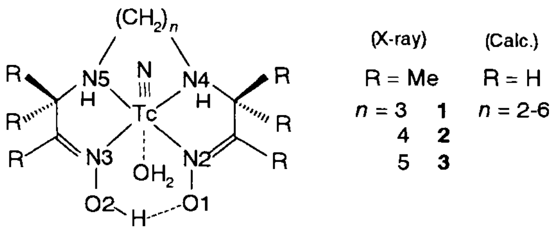

Figure 1. Synthesized complexes and model complexes used for theoretical calculations.

The complexes **1-3** (Figure 1) were synthesized by the reaction of $[^{99}TcNCl_2(PPh_3)_2]$ with each amine oxime ligand in a CH_2Cl_2/C_2H_5OH solution in the manner described previously.[3] The crystal structures of these complexes were determined by X-ray crystallography.[3]

Density functional theory (DFT) calculations and natural bond orbital (NBO) analysis with the Gaussian 94 program were performed for model complexes in which, for simplicity, methyl groups of the amine oxime ligand were replaced by hydrogen atoms (Figure 1). Geometries were optimized with the Becke's three parameter hybrid method using the LYP correlation functional (B3LYP). The basis sets reported by Stevens et al.[4] were used for Tc. The basis sets used for other atoms are 6-31+G(d) for N and O, 6-31G for C and H, and 6-31G(d,p) for the H involved in the hydrogen bond.

Figure 2 shows the ORTEP drawing of **3**. The selected bond distances and angles of **1-3** are listed in Table 1. The complexes **1-3** are six-coordinated monocationic compounds. The nitrido and H_2O ligands are at the apical position. The amine oxime ligands are coordinated in the equatorial plane. DFT calculation and NBO analysis show that the Tc≡N bond consists of one σ and two π bonds, and the polarity of the Tc≡N bond in technetium(V) amine oxime complexes with a nitrido ligand is smaller than that of the Tc=O bond in the complexes with an oxo ligand.

An intramolecular hydrogen bond is formed between the oxime oxygen atoms in **1-3**. The O1···O2 distance is 2.720(5) Å in **1**, 2.512(4) Å in **2**, and 2.531(3) Å in **3**. The O1···O2 distance in **1**, with the shortest carbon chain between amine nitrogens, is the longest of the three complexes. This fact

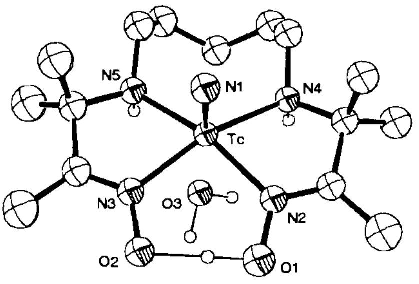

Figure 2. ORTEP drawing of $[TcN(pentao)(H_2O)]^+$ **3**.

Table 1. Selected bond distances and angles for complexes **1**-**3**

	1	**2**	**3**
Tc-N1 / Å	1.610(5)	1.604(4)	1.610(3)
Tc-O3 / Å	2.481(4)	2.472(3)	2.390(3)
N1-Tc-N_{amine} / deg	99.7	96.8	96.7
N1-Tc-N_{oxime} / deg	102.4	102.3	100.7
O1···O2 / Å	2.720(5)	2.512(4)	2.531(3)

suggests that a steric factor arising from the carbon chain length plays a role in determining the intramolecular hydrogen bond distance in these complexes.

To examine this suggestion, optimized geometries of the model complexes (Figure 1, R = H; n = 2-6) were calculated. Calculated N4–Tc–N5 angle increases and the N2–Tc–N3 angle decreases as the carbon chain length increases in the model complexes. Namely, these angles depend on the carbon chain length. Furthermore, the O1···O2 distance in the model complexes decreases with a decrease in the N2–Tc–N3 angle. Hence, the steric requirement arising from the carbon chain length plays an important role in determining the intramolecular hydrogen bond distance in nitridotechnetium(V) amine oxime complexes.

The intramolecular hydrogen bond in **1**-**3** is asymmetrical in the crystalline state. To understand the asymmetrical feature, the total energies of the model complexes with an asymmetrical hydrogen bond and with a symmetrical hydrogen bond were calculated. The model complex with an asymmetrical hydrogen bond is 2.9 kcal/mol lower in energy than that with a symmetrical hydrogen bond. In an asymmetrical hydrogen bond, the hydrogen atom is localized in either well of the double-well potential.[5] In complexes **1**-**3**, however, the hydrogen atom in the intramolecular hydrogen bond is located only at a place far from the oxygen atom involved in the intermolecular hydrogen bond in the crystalline state. The calculation results show that the formation of an intermolecular hydrogen bond between one of the oxime oxygens and the oxygen of another molecule makes the potential curve of the intramolecular hydrogen bond asymmetrical, and restricts the position of the hydrogen atom in the intramolecular hydrogen bond.

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2911

COORDINATION-CHEMICAL BEHAVIOR OF $Tc(CO)_3^+$ IN AQUEOUS SOLUTIONS

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Technetium(I) tricarbonyl ion is proposed to be a promising precursor for radiopharmaceuticals of a new generation and therefore its coordination-chemical behavior is of interest. Synthesis and some properties of $Tc(CO)_3^+$ ion and its analog $Re(CO)_3^+$ ion in aqueous solutions were reported for the first time in [1, 2]. The authors [1, 2] found that in the solution the Tc^+ and Re^+ ions are surrounded with three fac-arranged CO groups and three water molecules in the supposed coordination octahedron. The hydrolytic behavior of $Re(CO)_3^+$ was considered in details, and it was found that this ion actively binds OH^- groups with successive formation of OH/Re 1:1, 4:3, and 3:2 complexes.

We prepared aqueous solutions of technetium (I) tricarbonyl by reaction of $Tc(CO)_5Cl$ with hot water. The solutions obtained are free from any ligands concurrent with water and are convenient for studying complex formation of $Tc(CO)_3^+$ ion. The ^{99}Tc NMR spectroscopy was the main method of this study. The $Tc(CO)_3(H_2O)_3^+$ ion in aqueous solution is characterized by a sharp signal at -865 ppm relative to TcO_4^-. Complex formation of this ion usually shifts this signal to the lower field.

We found that in the region of hydrolysis technetium(I) tricarbonyl ion forms, in contrast to rhenium(I) tricarbonyl, only 1:1 mononuclear complex with OH^-, which polymerizes with time to form successively dimer and cubane-like tetramer described for the first time in [3]. The kinetics of this process depends on the technetium concentration and the OH^-/Tc ratio. At $OH^-/Tc > 1$, polymerization is sharply decelerated. The complex $Tc(CO)_3(OH)_2(H_2O)^-$ appears only in concentrated alkaline solutions (> 1.5 M NaOH).

Halide ions (Cl^-, Br^-, I^-) form with $Tc(CO)_3^+$ weak complexes. The ^{99}Tc NMR spectra demonstrate successive formation of $Tc(CO)_3Hal$, $Tc(CO)_3(Hal)_2^-$, and $Tc(CO)_3(Hal)_3^{2-}$. The absence of traces of the higher complex experimentally confirms that in aqueous solution technetium(I) coordination polyhedron contains three fac-CO ligands and three water molecules and that only the water molecules can be substituted with other ligands. Taking into account strong complex formation with OH^-, it is surprisingly that $Tc(CO)_3^+$ forms no complexes with fluoride ion, which is a species isoelectronic with OH^-.

Among the other examined anions, polydentate oxyanions (acetate, oxalate, citrate, etc.) and sulfur-containing anions (dithiocarbamate) form fairly strong complexes with $Tc(CO)_3^+$ in aqueous solutions.

Strong neutral ligands such as hexamethylphosphoric triamide, thiourea, etc. are weakly coordinated to $Tc(CO)_3^+$.

As a whole, in $Tc(CO)_3^+$ technetium(I) behaves as a typical soft acid and d-element.

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2912

KINETICS OF THE REACTION OF PERTECHNETATE WITH SULPHIDE

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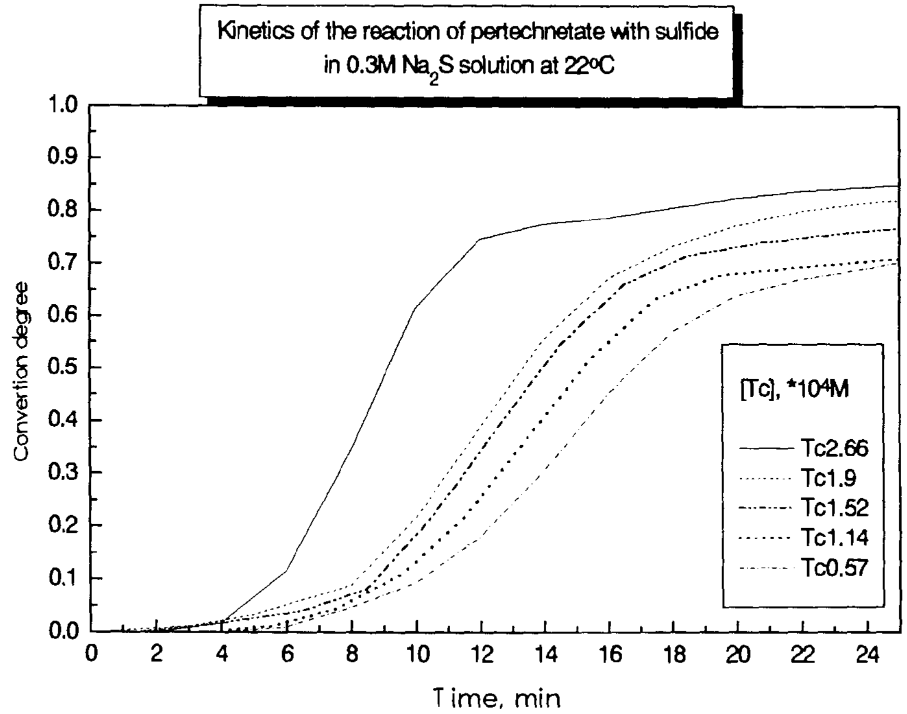
Technetium-99 is considered to be the one of the most environmentally mobile long-lived radionuclides. For this reason the factors reducing its migration rate in the natural surfacial and ground waters are of high importance. Formation of low soluble Tc_2S_7 could be one of the possible mode to reduce the technetium long-term hazard in radioactive waste depositories if the technetium sulphide colloid behaviour would be possible to predict and to effect. The analyses of the literature data shows that considerable impact of sulphide ions on technetium mobility could be possible in two main natural systems: 1) natural waters contacted to sulphide minerals (SM)[1] and 2) anaerobic natural waters containing some quantity of sulphate and contacted to sulphate reducing bacteria (SRB). Although several authors have reported the details of technetium sulphide synthesis [2, 3, 4,] analyses of literature data shows that there is exact data characterising neither kinetics of this reaction nor the equilibrium solubility value for Tc_2S_7. Only very limited data are available on the precipitation of technetium sulphide in sulphide and ferrous ions solutions [5]. In this work we were able to get the characteristics of technetium reaction with sulphide the experiments being based both on spectrophotometric kinetics control followed by radiometric and microcentrifugative speciation of Tc_2S_7 colloid formation and coagulation.

Technetium sulphide formation kinetics has been analysed in this work spectrophotometrically. It is characterised with induction period due to preliminary formation of several partly substituted technetium oxo-sulphides. Both the induction period and the technetium sulphide formation rates were depending on the concentration of technetium, acidity and temperature.



Collisions of Tc_2S_7 molecules result in slow coagulation, the later rate depending on temperature, ionic forth of the solution and especially on the presence of multiply charged ions. The colloids formed at low concentrations of technetium and sulphide were found to be rather stable toward coagulation and dispersed in the solution at least for 1 month while at higher concentration of technetium the particle size gradually increased in two to ten days depending on the ionic strength. The DLVO theory has been applied to analyse the growth rate of colloid particles. The knowledge of Tc_2S_7 kinetic and colloidal behaviour has permitted to determine the conditions necessary to equilibrate the technetium sulphide and its solutions and as a result to determine the solubility value and □H_f^o(Tc_2S_7).

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2913

BASE HYDROLYSIS OF BIS(ACETYLACETONATO)NITRIDOTECHNETIUM(V)

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Introduction

Complexes of technetium(III) and Tc(IV) exhibit generally substitution-inert character[1]. From the viewpoint of electronic structure, Tc(V) complexes containing Tc=O core is also classified to be substitution-inert[1]. Mechanism of the base hydrolysis has been investigated in a series of technetium β-diketone complexes such as tris(acetylacetonato)technetium(III) ($Tc(acac)_3$)[2], *cis*-dihalobis(acetylacetonato)technetium(IV) (*cis*-$[TcX_2(acac)_2]$, X=Cl, Br) and *cis*-chlorobis(β-diketonato)oxotechnetium(V) (*cis*-$[TcOClL_2]$, L= β-diketone; acetylacetone(Hacac), benzoylacetone (Hbzac) and dibenzoylmethane (Hdbm))[3].

Various square-pyramidal $[TcN(\beta\text{-diketonate})_2]$ complexes have recently been prepared by ligand exchange of $[TcNCl_2(PPh_3)_2]$ with acetylacetone, benzoylacetone, dibenzoylmethane and dipivaloylmethane in the presence of $KHCO_3$[4]. In analogy with $[Tc(acac)_3]$, $[TcN(acac)_2]$ has no labile halide ion in the coordination sphere. The present paper will report the base hydrolysis of bis(acetylacetonato)nitridotechnetium(V) ($[TcN(acac)_2]$) from the viewpoint of the *trans* influence of the nitrido ligand.

Experimental

Ammonium pertechnetate [^{99}Tc] was obtained from the Radiochemical Centre, Amersham. All the other reagents used were of guaranteed reagent grade. Bis(acetylacetonato)nitridotechnetium(V) was synthesized from $[TcNCl_2(PPh_3)_2]$ by modifying the method described in the literature[4]. Finally $[TcN(acac)_2]$ was purified by the extraction with benzene from the reaction mixture. Prior to kinetic runs an acetonitrile solution of $[TcN(acac)_2]$ was prepared from the benzene solution

Results and Discussion

Bis(acetylacetonato)nitridotechnetium(V) is stable in acetonitrile over 10 days. However, when an aqueous solution of sodium hydroxide was added to acetonitrile solution of $TcN(acac)_2$, the absorbance at 385 nm decreased with time. On the other hand, the absorbance at 295 nm increased. An example of the spectral change with time is shown in Fig. 1, exhibiting the isosbestic point at 310 nm. Decomposition of $TcN(acac)_2$ can be seen in the decrease of the absorbance at 385 nm. An increase in the absorbance at 295 nm is considered to be the formation of free acetylacetonate ion liberated from the decomposition of $TcN(acac)_2$. On the basis of linear plots of $\ln(A_{385,t} / A_{385,0})$ against time, it was found that two successive reactions proceed in the present system. The first step reaction is independent of the concentration of hydroxide ion, while the second step depends on the concentration of hydroxide ion. These facts suggest that [TcN(acac)$_2$] (**A**) produces an intermediate (**B**) by solvolysis and then **B** decomposes further by an attack of hydroxide ion. This sequence can be expressed as follows:

$$\frac{d[A]}{dt} = -k_1[A] \quad \text{and} \quad \frac{d[B]}{dt} = k_1[A] - k'_2[B] \qquad (1)$$

By integration of Eq. (1) and replacement of the concentration by the absorbance, the following equation can be derived.

$$\frac{A_{385,t}}{A_{385,0}} = e^{-k_1 t} + \frac{\varepsilon_B}{\varepsilon_A}\frac{k_1}{k_1 - k'_2}(e^{-k'_2 t} - e^{-k_1 t}). \qquad (2)$$

where ε is the molar absorption coefficient at 385 nm. Unknown parameters in Eq. (2) could be determined by a curve-fitting method. Furthermore, a linear relation between k'_2 and the concentration of hydroxide ion was observed. Thus, the rate constants k_1 and k_2 could be determined to be

$k_1 = (6.3 \pm 0.3) \times 10^{-4}\ s^{-1}$ and

$k_2 = (8.3 \pm 0.4) \times 10^{-4}\ M^{-1}s^{-1}$

(25℃).

Mechanism of the base hydrolysis reactions of TcN(acac)$_2$ will be discussed.

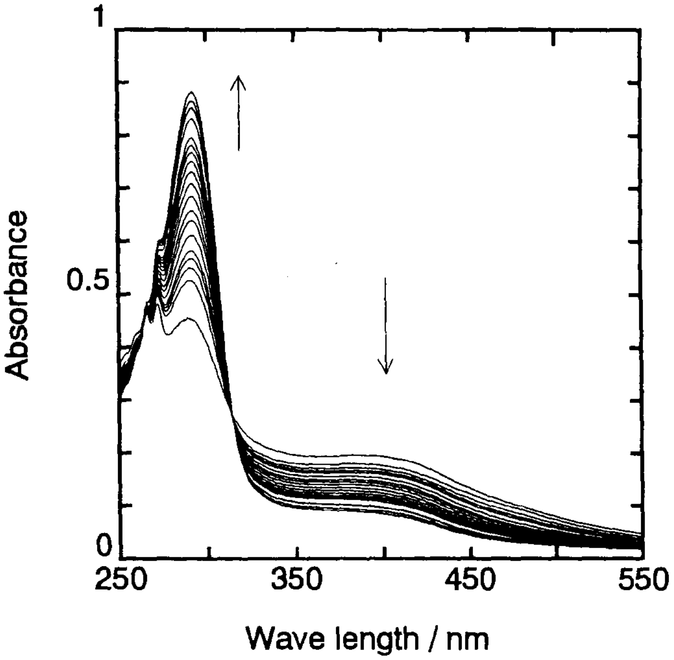

Fig. 1. Spectral change of TcN(acac)$_2$ in 0.017 M NaOH aqueous acetonitrile solution

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November 30 (Tuesday)

Radiopharmaceuticals of technetium and rhenium

and

Environmental chemistry of technetium

3001

DEVELOPMENT OF THE ^{99m}Tc-KIT PRODUCTION IN RUSSIA

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Nowadays we have 20-years experience in the development and production of the ^{99m}Tc-kits for the needs of the domestic clinics. Practically all the Russian clinic use the kits produced only by the domestic manufactures. These kits are also delivered to the different radiopharmaceutical departments, which are situated in the former Republics of the USSR. During the latest 10 years one can follow the growth of the ^{99m}Tc-radiopharmaceutical usage in the routine clinical practice. This tendency is in turn favorable to the development of the kit production.

In 1996 - 1998 the annual volume of production was 20 000 kits of 12 different names. (Each kit contains 5 vials). About 60 % from the total volume are accounted for the kits used for the preparation of the osteotropic (30 %) and hepatotropic (30 %) radiopharmaceuticals.

Only specially synthesized or purified compounds are used in the kit technologies. This allows obtaining the radioparmaceuticals of high quality.

The production includes the following divisions:

- Synthesis of the initial compounds;
- Kit-production;
- Sterilization of the products;
- Quality control of the initial compounds and final products;
- Control of the microbiological situation'
- If it is necessary the control of the biological behavior in the animals (pharmacokinetics) is carried out.

The reliable guarantee of the high quality of the produced kits lies in the fact that the investigators of these kits take part in their production.

3002

LABELLING OF BLOOD CELLS WITH TECHNETIUM- 99m

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Labeled blood cells have been used in nuclear medicine for about 50 years. However, they are widely used only during the last 20 years when the methods of labeling with the radionuclides with optimal nuclear physical characteristics were developed. Technetium-99m is one of these radionuclides, which is used for this purpose. Nowadays many companies manufacture the kits for leucocytes labelling and red blood cells labelling in vitro and in vivo with ^{99m}Tc.

In this report we touch upon the following questions:

1. Labelling of the red blood cells (RBC) in vitro with ^{99m}Tc.
   All of the commercially produced kits for RBC labeling in vitro contain different amount of Sn (II) for technetium reduction. And, as a rule, the RBC labelling with these kits is carried out in many stages. We found the principal possibility of one-step RBC labeling with technetium-99m using tin (II)-oxabiphore (oxa-bis(ethylenenitrilo)tetramethylenephosphonic acid) complex. In this report we discuss the RBC labelling in vitro with technetium-99m using domestic commercial kit "ERYTROTECH". The labelling efficiency of RBC labelling using this kit is over 95 %. The labelling is completed in 15 min. The retention time of the label by RBC is several hours (till the full decay of the tracer). During the clinical trials of "ERYTROTECH" the results of estimation of circulated blood volume were compared with those obtained using ^{131}I-albumin.

2. Labelling of the red blood cells in vivo with ^{99m}Tc : for this purpose we use the domestic commercial kit "PYRPHOTECH"

3. Labelling of the white blood cells with ^{99m}Tc: for this purpose we use the domestic commercial kit "TEOXIM". The labelling efficiency is about 45 %.

3003

ACTUAL ASPECTS OF QUALITY CONTROL OF ^{99m}Tc-RADIOPHARMACEUTICALS

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One of the main moments defining the efficiency and correctness of the diagnosis in clinic is the quality of the used radiopharmaceutical.

The nuclear physical and chemical properties of the technetium-99m, define from one hand, the possibility of synthesis of great amount of different radiopharmaceuticals. However, from another hand a great amount of impurities can form during production and using of a radiopharmaceutical. The incorrect results of the examination can be obtained when use the ^{99m}Tc-radiopharmaceuticals containing the impurities.

That is why, from our point of view, the quality control on the each stage of the production of the cold kit and radiopharmaceutical is an actual task.

We suppose that the main characteristics that define the quality of a radiopharmaceutical are the quantitative determination of the Sn (II) content in the kit and radiochemical purity (RCP) or radiochemical content (RCC) of the radiopharmaceutical. In these conditions the correlation between these two indexes and also between RCP (RCC) and biological behavior should be found.

The main problem in the analysis of the Sn (II) content in the cold kit is the necessity of its determination in the small quantities in the presence of the other compounds in high concentrations (complex compounds, antioxidants, buffer agents). Besides this, during the development of the method for the quantitative determination of Sn (II) we cannot get the standard sample which can store for a long time. In practice every time we should prepare the standard solutions.

The main problem in the determination of the RCP (RCC) of the final radiopharmaceuticals is the correct identification of the radioactive components. For the write identification of these components we should know the valiancy of the technetium-99m in all these components and the content of each of the obtained complex. However it is very difficult to do in the case when the radionuclide-microcomponent presents in the solution with macro-quantaties of other compounds. In this case rather difficult to prepare any standards or artificial mixtures. To solve this problem as a rule it is necessary to compare the results of the RCP determination in several chromatographic systems and also to determine the dependence between RCP (RCC) on the carrier concentration in the model solutions of the radiopharmaceuticals.

The mentioned above problems and the ways of their solutions on the concrete examples of radiopharmaceutical analysis would be discussed in this report.

POTENTIOMETRIC DEFINITION Sn2 + DURING A LABELING OF MICROSPHERES OF ALBUMIN BY RADIONUCLIDES OF RHENIUM

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To achieve a high degree of selective accumulation of radionuclides in the pathological organs carriers play the important role for their delivery. Among a wide spectrum complex agents albumin microspheres (MSA) have overwhelming advantage - they can be prepare with any sizes and small dispersibility. At presence of the effective carrier the main problem is the degree of binding it with radionuclides possessing the optimal nuclear - physical characteristics. One of them is the generating rhenium - 188.

Directly rhenium(VII) does not react with protein. Therefore for obtaining stable binding the rhenium(VII) is necessary to reduce up to lower valent states at the presence of approaching complexing ligands. The optimal reducer for rhenium is chloride of divalent tin. The role of tin thus consists, at first reducing protein with derivation reactionary -S- of groups capable to creation of very strong binding to rhenium - 188. Secondly, - protection these high reactionary -S- of groups from their involvement in reverse reaction. Thirdly, - reducing ions of rhenium.

Thus, at development of a radiopharmaceuticals on the basis of albumin microspheres one of the main tasks is to define an optimal amount of divalent tin, and also develop analytical techniques of definition of two and quadrivalent tins in modified microspheres.

Therefore determination of divalent tin was carried out by potentiometric titration with application of a platinum electrode. For accomplishing of a method the standard solution of tin prepared from chloride of tin of the corporation ALDRICH was used. A degree of cleanness of the standard was 99,999 %. The standard solution $SnCl_2$ was prepared at the condition of a contents of tin in a set MSA(Sn), i.e. 40 μg $Sn2^+$ per 5 μg MSA. As a dissolvent the normal saline solution applied for carrying out was used planned in further radiobiological trials.

Among oxidizing agents the solution permanganate of potassium was proposed. The concentration titrant was picked up those, that the equivalent relation of reagents of oxidation-reduction response has compounded 5:2.

In sort that a sample and titrant react with oxygen of air, changing the rates of oxidation, the titration was carried out in an argon medium. Operating range of an ionometer was from 0 up to -1000 mV. Flow rate of titrant was equal to 0,702 milliliter per minutes. The point of equivalence of titration was installed on the first derivative of a curve of titration.

For more precise calculation of contents of divalent tin in a standard solution the calibration curve of titration was constructed. Thus it was revealed, that permanganate of a potassium is a suitable oxidizing agent only in a narrow range of concentrations of tin, namely from 0.75 μg Sn^{2+} per milliliter till 1.25 μg Sn^{2+} per milliliter

Chloramin B therefore would be proposed, which one is most practical titrant for albumin radiopharmaceuticals. The application of chloramin B would allow to carry out determination of tin in wider range of concentrations with a linear relation from concentrations.

Thus, it is possible to draw a conclusion:

- what expediently to use chloramin B as titrant in a wide range of concentrations of tin
- if necessary it is possible to do permanganese of a potassium in a range from 0.75 μg Sn^{2+} per milliliter till 1.25 μg Sn^{2+} per milliliter, in which one concentration of tin in a set MSA(Sn) ranges.

3005

PRODUCTION OF ^{186,188}Re AND RECOVERY OF TUNGSTEN FROM SPENT ^{188}W/^{188}Re GENERATOR.

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Introduction Radioactive rhenium of ^{186}Re (90.64 h) and ^{188}Re (16.98 h) are of current interest for therapeutic applications in the field of nuclear medicine. Typical methods of ^{186}Re production are the ^{186}W(p,n)^{186}Re reaction with a cyclotron, which can produce no-carrier-added ^{186}Re [1], and the ^{185}Re(n, γ)^{186}Re reaction in a reactor. Rhenium-188 is obtained carrier-free from decay of the long-lived ^{188}W (69.4 d) parent produced by the double neutron capture reaction of ^{186}W in a reactor. The purpose of this study is to develop production techniques of ^{186}Re and ^{188}Re using a reactor, and recovery methods of the enriched ^{186}W from spent alumina-based ^{188}W/^{188}Re generators.

Production of ^{186}Re The target material was 97.4% enriched ^{185}Re metallic powder (2.6% ^{187}Re). The target (about 5 mg) in a quartz ampoule was irradiated for 3-4 days at JRR-3M in JAERI. Schematic diagram of the apparatus is shown in Fig. 1. The irradiated target was dissolved in 6 M HNO_3. The HNO_3 solution was diluted with water and was evaporated to dryness to eliminate HNO_3 thoroughly. This procedure was repeated five times. The ^{186}Re was taken-up in water. The chemical form of the ^{186}Re product was found to be perrhenate ion ($^{186}ReO_4^-$) by thin-layer chromatography and ion-chromatography. The radioactivity of ^{186}Re was measured with an ionization chamber which was calibrated by the calorimetric method [2]. When the concentration of ^{186}Re in the final product was prepared to be 0.4-0.5 GBq/ml, the concentration of rhenium was about 0.3 mg/ml, pH was 3 - 5. The concentration of NO_3^- in the ^{186}Re product was found to be less than 10 ppm by ion-chromatography. Specifications of the ^{186}Re products per a batch

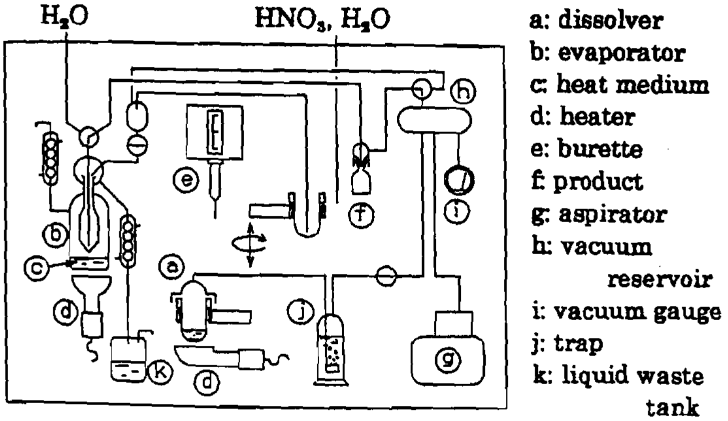

Fig. 1. Schematic diagram of the apparatus used for the production of ^{186}Re.

are as follows : Production yields, 60-90%; specific radioactivity, 17-20 TBq/g Re; total radioactivity, 50-100 GBq; radionuclidic purity, >99%.

Production of $^{188}W/^{188}Re$ generator The target material was 99.79% enriched $^{186}WO_3$ (ISOTEC Inc, USA or Euriso-top, France). The target (about 25 mg) in a quartz ampoule was irradiated for 1 to 2 cycles (1 cycle = 26 days) at JMTR in JAERI. The irradiated target was allowed to stand for more than 4 weeks for decay of ^{187}W (23.72 h), and then was dissolved in 2 M NaOH with heating. The pH of the ^{188}W solution was adjusted to about 2, using HCl solution. The ^{188}W solution was loaded onto the alumina column (10 mm ϕ ×60 mm; BIO-RAD, AG-4, 100-200 mesh) which was conditioned with 0.01 M HCl solution. The coloumn was then washed with 0.9% NaCl after the equilibrium between ^{188}W and ^{188}Re had almost been reached. The elution yield of ^{188}Re was about 80%, and the radionuclidic purity of ^{188}Re was more than 99.9%.

Recovery of tungsten from spent $^{188}W/^{188}Re$ generator

The mock W/Re generators were prepared using tungsten (natural isotopic abundance) solution containing $^{187}WO_4^{2-}$ and $^{186}ReO_4^-$ as tracers to elucidate the desorption of tungsten from alumina-based W/Re generators. The desorption yield of tungsten from the alumina column with NaOH or NH_4OH is shown in Fig. 2. The recovery yields were more than 99% and 70% using 4 M NaOH and 3 M NH_4OH solution, respectively. By calcining the precipitate from the eluent, the tungsten trioxide of considerably high purity was obtained from spent $^{188}W/^{188}Re$ generators, and may also be reused as target material.

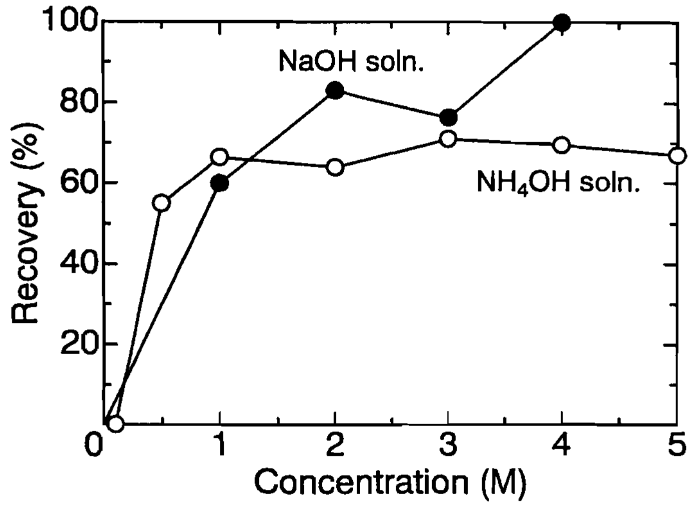

Fig. 2. Recovery of tungsten with NaOH and NH_4OH.

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3006

SYNTHESIS AND HPLC ANALYSIS OF RHENIUM-188 AMINOMETHYLENEPHOSPHONATE COMPLEXES

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Introduction

The radioactive rhenium isotopes, ^{186}Re (half-life: 90.64 h) and ^{188}Re (16.98 h), have been suggested as radiopharmaceuticals for cancer therapy because of their energetic beta particles and gamma rays suitable for imaging. The ^{186}Re-HEDP (Diphosphonate) and ^{153}Sm-EDTMP (Aminomethylenephosphonate) have been used as agents for effective palliative treatment of widespread skeletal metastases. However, the labelling studies with carrier-free ^{188}Re have so far been limited. In this paper, the labelling of aminomethylenephosphonate derivatives (EDTMP - Ethylenediamine-N,N,N',N'-tetrakis(methylenephosphonic acid), EDBMP – Ethylenediamine-N,N'-bis(methylenephosphonic acid) and NTMP – Nitrilotris(methylenephosphonic acid)) with carrier-free ^{188}Re from the ^{188}W/^{188}Re generator was reported. Furthermore, the ^{188}Re-EDTMP was analyzed by HPLC (ion-exchange and reversed-phase ion-pair chromatography) and the effects of carrier existence and the reducing agent ($SnCl_2$ or $NaBH_4$) on the chromatogram were investigated.

Experimental

The ^{188}W/^{188}Re generator was prepared by the alumina column system 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}). Rhenium-188 solution (2×10^5 – 1×10^6 Bq ml^{-1}) was obtained from the generator in a 0.9% NaCl solution and was used for labelling purposes without further purification.

The labelling studies were carried out by mixing all the solutions (ligand, l-ascorbic acid, a solution for pH adjustment, ^{188}Re and reducing agent) in a vial. Stannous chloride or sodium borohydride was used as the reducing agent for the reduction of rhenium.

The ^{188}Re-EDTMP was analyzed by ion-exchange (TSKGel SAX and TSKGel DEAE-2SW) and reversed-phase ion-pair chromatography (Hypersil BDS-5C18). The eluents were 0.37 – 0.85 M sodium acetate / HCl (pH 5.5 – 6.0) for the ion-exchange chromatography and 0.008 M tetrabutyl ammonium hydroxide (TBA) / 10% methanol (pH 6.0) – 0.008 M TBA / 60% methanol (pH 6.0) for the reversed-phase ion-pair chromatography.

Results and Discussion

The dependence of the labelling yield upon the reaction conditions such as the concentrations of the reducing agent and the ligand (aminomethylenephosphonate), pH, temperature and the addition of a carrier was examined. The dependence of the labelling yield on pH using stannous chloride as a reducing agent was shown in Fig. 1. The maximum labelling yields of all the tin-reduced ^{188}Re complexes (^{188}Re(Sn) complexes) were obtained in the acidic pH region less than pH 3 and the yields decreased sharply above pH 3. Under the optimum conditions, the labelling yields of ^{188}Re(Sn)-EDTMP and ^{188}Re(Sn)-EDBMP were more than 95%, the yield of ^{188}Re(Sn)-NTMP was more than 90% using carrier-free ^{188}Re and the labelling yields of all the carrier-added (20 μg Re/ml) ^{188}Re(Sn) complexes were more than 95%. On the other hand, the maximum labelling yield of borohydride-reduced ^{188}Re-EDTMP (^{188}Re($NaBH_4$)-

EDTMP) was about 80% using carrier-added ^{188}Re and about 50% using carrier-free ^{188}Re.

The stability of the ^{188}Re(Sn) complex was studied against pH change and dilution with 0.9% NaCl. It was found that the formation condition of the ^{188}Re(Sn) complex, that is the temperature, pH and the addition of a carrier, influenced the stability of ^{188}Re(Sn) complex. The carrier-added ^{188}Re(Sn) complex was more stable than the carrier-free ^{188}Re(Sn) complex. Furthermore, the stability decreased in the order ^{188}Re(Sn)-EDTMP > ^{188}Re(Sn)-EDBMP > ^{188}Re(Sn)-NTMP for both carrier-free and carrier-added ^{188}Re(Sn) complex.

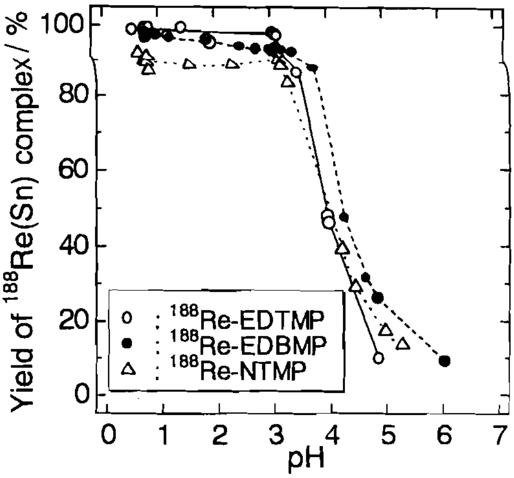

Fig. 1. Influence of pH on the yields of ^{188}Re(Sn) complexes using carrier-free ^{188}Re at room temperature.

The most stable ^{188}Re-EDTMP was analyzed by anion exchange and reversed-phased ion-pair chromatography. The effects of carrier existence and the reducing agent on the chromatogram were investigated. Anion exchange HPLC analysis (TSKGel SAX) showed that both carrier-free and carrier-added ^{188}Re(Sn)-EDTMP were complex mixtures of components and the distribution of these complexes in each chromatogram was almost the same, as shown in Fig. 2. However, more than 70% of ^{188}Re remained into the TSKGel SAX column after an analysis. On the other hand, the analyses by TSKGel DEAE-2SW anion-exchange chromatography and reversed-phase ion-pair chromatography showed that the distribution of the carrier-added ^{188}Re(Sn)-EDTMP mixtures was clearly different from that of the carrier-free ^{188}Re(Sn) complex.

Anion exchange HPLC (TSKGel SAX) chromatogram of carrier-added ^{188}Re(NaBH$_4$)-EDTMP is shown in Fig. 3. The ^{188}Re(NaBH$_4$)-EDTMP was also complex mixtures of components, but the number of components was less than that of ^{188}Re(Sn)-EDTMP. One component of ^{188}Re(Sn)-EDTMP has the same retention time as a component of ^{188}Re(NaBH$_4$)-EDTMP (t_R = ~20 min in Figs 2 and 3). These results suggest that at least one component of ^{188}Re(Sn)-EDTMP is a complex which does not contain Sn.

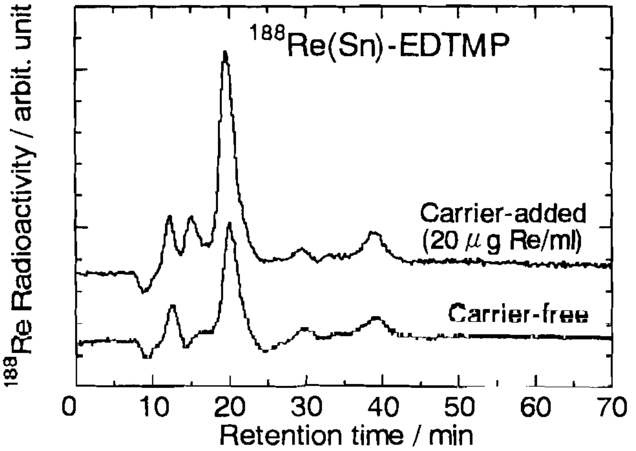

Fig. 2. Anion-exchange HPLC of ^{188}Re(Sn)-EDTMP (TSKGel SAX, 0.85 M sodium acetate / HCl (pH 5.5), Flow rate: 0.3 ml/min).

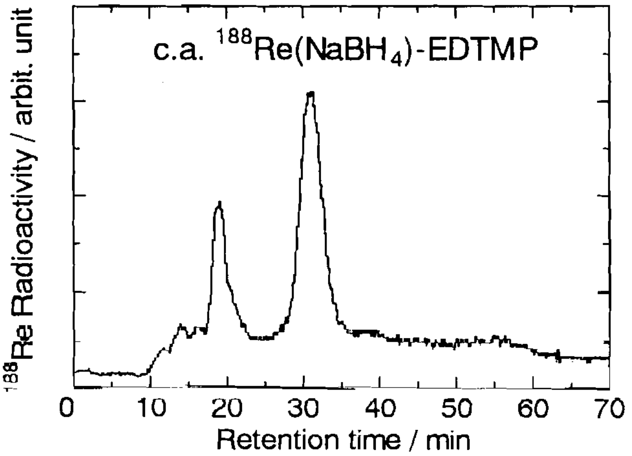

Fig. 3. Anion-exchange HPLC of carrier-added ^{188}Re(NaBH$_4$)-EDTMP. Conditions are the same as in Fig. 2.

3007

DEVELOPMENT OF THE METHOD OF THE PREPERATION OF ALBUMINE MICROSPHERES LABELED 188-RHENIUM

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A basis of effective and wide usage radioisotope of methods in diagnostic and therapy of tumbrel and not tumbrel diseases is development of new radiopharmaceuticals, described by high functional value and safety.

The efficiency and safety radiopharmaceuticals are defined by the nuclear - physical characteristics of radionuclides, and also physicochemical and biological properties of carriers of radionuclides. Therefore important direction in radiopharmaceuticals is the search, the development and estimation of particular properties radiopharmaceuticals for a radiotherapy of tumbrel and not tumbrel diseases, where main is choice of optimal carriers and radionuclides.

Optimal the carrier of radionuclides are microspheres of human serum albumin. The exact spherical form of particles extends the stability of an albumine matrix. It allows to prepare them in a narrow range of sizes by a mechanical or ultrasonic fractionating. The albumine microspheres are rather fast metabolised and are eliminated from an organism. The rate of elimination can be regulated by change of a degree of a sewing together of an albumine matrix of particles.

From radionuclides 165Dy, 166Ho, 186Re, 188Re, 153Sm, 211At, 212Bi, used in the last years at development radiopharmaceuticals for a radiotherapy, 188Re is most optimal. 188Re are a generating radionuclide with a half-life 16,9 h. The presence of the gamma-component with a radiation energy 0,155 MeV allows to observe of behaviour of a labelled preparation in an organism by gamma-camera. Besides, 188Re can be used for a label of preparations directly before injection to patients by analogy with 99mTc.

The quality radiopharmaceuticals are determined by efficiency of binding of a radionuclide with the carrier and its stability.

In the present abstract are cited data of efficiency of binding 188Re with albumine microspheres.

Albumine microspheres prepare by heating an emulsion of a solution of protein in vegetable oil. The microspheres separated with filtering and washed by ether. A fraction of particles with a size 15 - 30 microns prepared by ultrasonic sieving. Into microspheres introduced Sn(2+) in an amount 0,004 mg/g. For a labelling of microspheres have used 1 ml of eluate 188Re with specific activity 2,0 mCi/ml. Study of efficiency binding carried out in an range 0,02 - 0,2 mCi/mg. Percent of labelling of microspheres for initial activity 0.200, 0.100, 0.068, 0.05, 0.04, 0.033, 0.029, 0.025, 0.022, 0.020 mCi/mg were 19.6, 28.9, 38.5, 48.0, 52.4, 58.5, 68.1, 69.2, 71.8, 70.3%, respectively.

Thus the labelling efficiency is increase with decrease of the initial amount of microspheres.

3008

STRATEGIES ON FUNCTIONAL BIOMIMETIC 99mTc-RADIOPHARMACEUTICALS (Tc-RPs) DEVELOPMENT

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The function of metals in biological systems (catalyst, electron carriers, redox reactions, oxygen carriers, gene expression etc) has been well recognized. Technetium (Tc), a transition metal with its labile d-electron system, should have great potential for novel Tc-RP development based on the exploitation of its metal characteristics. As a mean to stimulate new development of Tc-RPs, properties of the metal Tc, explored in the author laboratory for biomimetic drug modeling are:

I. ***Metal Hydrolytic Polynucleation*** : A common property to transition metals in aqueous solution was explored for the development of tumoral Tc-radiopharmaceutical to biomimic ^{67}Ga(III)-citrate, an agent with extensive clinical use in tumor diagnosis. The polynuclear-mononuclear equilibrium of gallium complexes as related to the biological utilization of metals, served as the bases for building up this approach. Various polycarboxylic (glucoheptonic, citric) and thiol (thiomalic, dithiotreitol, penicillamine, dimercaptosuccinic acid) ligands were screened under differential radiolabeling condition to promote hydrolytic polynucleation of the metal technetium favored in the alkaline pH region. Biological functionality of each polynuclear Tc-complexes screened by in-vivo and in vitro studies; metal-complex equilibrium principle played an important role in the tumoral cell uptake as well as in the tumor bearing mice biodistribution. From the kinetical aspect of those polynuclear technetium complexes, the polynuclear pentavalent technetium chelate of dimercaptosuccinic acid (DMS) known as Tc(V)-DMS agent, was selected; the biological functionality of the thus radiolabeled agents to biomimic the parent molecule, ^{67}Ga-citrate were well supported not only by animal studies but by the great abundance of clinical publications. If we are to appreciate the skill displayed by the living systems in the uptake and utilization of Tc-species in normal and pathological tissues, then this is an important aspect in tumor targeting. The role of pH in tumor tissue lower than in normal tissue, is explored. Good bases as a factor influencing its metal technetium utilization was found. If Tc(V)-DMS complex is to reach lower tumoral pH region, changes on effective binding constant or Tc-complex dissociation might occur, reflected in higher target tissue retention. The principle was also applicable in the formulation of the rhenium complex, the ^{186}Re(V)-DMS complex; major differential aspect from the Tc-based agent was not only the differential redox potential, but the great effect of the carrier amount present in Re-186. Differential aspect of both metals in the hydrolytic polynucleation of DMS complexes will be discussed.

II.***Metal Redox Reaction*** : an inherent property of metals, is exploited for the modeling of an hypoxia Tc-imaging agent. Among biochemical functions of metals, transition metals have been associated with biological redox reactions. Biofunctionality of Mn, Fe, Co, Ni, Cu, Mo containing complexes could be mimicked if proper radiolabeling conditions could be attained with the multivalent technetium.

In recent years, copper containing dithiosemicarbazone (DTS) complexes, based on the bioreductive character of the metal has been reported for the bioimaging of disturbed mitochondrial electron flow caused by hypoxia, ischemia. The versatility of DTS skeleton to hold variable number of alkyl substituents, makes it very suitable for the tuning and selection of Tc-RPs with bioreductive properties. The main challenge lies on dealing with the chemistry rich, multivalent Tc metal. For pursuing a Cu-DTS mimetic Tc-agent, a thorough review of the literature indicated that among multiple possibilities, low Tc-valence state, favored in acid pH might provide the needed redox accessible properties. Thus, under those premises, various DTS ligands were tested; the Tc-radiolabeling and its redox accessibility depended not only on the radiolabeling condition but also on the number of alkyl substitutions. Validity of the approach is tested in various in-vitro and in-vivo experiments and animal models, and the procurement of Cu-DTS mimetic Tc-DTS agent is demonstrated by bio-imaging techniques; undergoing studies on the bioreductive mechanism involved in the mitochondrial electron transport mechanism of ischemia tissue will be discussed. .

The two exploited principles, the metal hydrolytic polynucleation (polynuclear Tc(V)-DMS) and the metal redox reaction (the redox sensitive Tc-DTS drugs) offered functionally active Tc-agents with biomimetic characteristics; they constituted a strategy toward properties and functions rather than toward structure but these approaches might help an understanding of the biological utilization of those technetium metal properties for kinetically active drugs or bioreductive drugs opening a new road for the development of Tc-agents.

3009

STUDY ON UPTAKE AND DISTRIBUTION OF Tc AND Re USING THE MULTITRACER TECHNIQUE

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The multitracer technique can deal simultaneously with a number of radioactive isotopes, which are chemically separated from target metals irradiated with a high-energy heavy-ion beam, under strictly identical experimental conditions. In the present work, this technique was applied to the investigation of the uptake and excretion behaviour of many trace elements including Tc and Re in rats and mice. Two types of experiments were carried out. The first experiment was performed with a multitracer solution prepared from gold target in order to investigate the uptake and excretion behaviour of orally administered trace elements including Tc and Re in rats. (Exp. 1) The second one was performed using the trace elements including Tc separated from silver target to examine the behaviour of elements intraperitoneally injected in mice, especially Zn-deficient mice. (Exp. 2)

(Exp. 1)

Gold foil was irradiated with a 135 MeV/nucleon ^{14}N-ion beam accelerated by the RIKEN Ring Cyclotron. The irradiated target was dissolved in aqua regia and the solution was evaporated to dryness. After the residue was dissolved in 3 M HCl, gold ions were removed by extraction with ethyl acetate. The aqueous phase was again evaporated to dryness and was converted to a solution of pH 3 with diluted HCl for oral administration to rats. The obtained multitracer solution was orally administered to 7-week old male Wistar rats. After dosing, faeces and urine were collected at adequate intervals. The γ-rays of radioactive nuclides in excreta were measured with pure-Ge detectors.

The uptake and excretion rates of 24 elements, Be, Mn, Co, Zn, As, Rb, Sr, Y, Zr, Tc, Ce, Pm, Eu, Gd, Tb, Er, Tm, Yb, Lu, Hf, W, Re, Ir and Pt, were determined. Only a small amount of the administered dose of Re was found in the faeces (< 1%), which indicates that Re was completely absorbed into rats' bodies. The urinary excretion of Re was composed of at least two phases. More than 85% of the Re administered was excreted in the urine with a half-life of about 3 h, but 3 -

5% was eliminated with a half-life on the order of days. Most of the Re remaining in the rats' bodies (< 7%) was found in hair and a trace amount (< .0.01%) was found in bone. Rapid elimination behaviour was also observed for Tc although its excretion behaviour could not be determined precisely because of its weak radioactivity. However, it was found that 45 - 54% of the Tc administered was excreted in the faeces, indicating less absorption into the rats' bodies than that of Re.

(Exp. 2)

Silver target irradiated with ^{12}C-ion beam was first dissolved in (1:1) HNO_3. Then, Ag was precipitated as AgCl with conc. HCl. After the precipitate was filtered out, remained multitracer solution was evaporated under reduced pressure. The residue was dissolved in physiological saline for intraperitoneally injection.

Thirty-four male mice of the ICR strain, 8-week old, were devided into two groups. One group was fed with Zn-deficient diet pellets and distilled water (Zn-def. mice), and the other with control diet pellets and distilled water (control mice). After three weeks of feeding, an appropriate amount of the multitracer solution was injected intraperitoneally into each mouse. Six, 24 and 72 hours after injection, 8 - 9 organs and tissues were removed under diethyl ether anesthesia. They were weighed and bottled. The radioactivities of the samples were measured with HP Ge detectors.

Disitribution of 16 trace elements, such as Be, Sc, V, Mn, Fe, Co, Zn, As, Se, Rb, Sr, Y, Zr, Tc, Ru and Rh, in the oragans and tissues were determined. Uptake rates of Zn in the bones of Zn-def. mice, 24 and 72 hours after injection of multitracer solution, were significantly lower than those of control mice although there were no differences in uptake rates of Zn in the bones between two type of mice 6 hours after injection, whereas uptake rates in the liver, kidney and spleen of Zn-def. mice were higher than those of control mice. We also determined trace elements in organs and tissues of Zn-def. mice and control mice by means of instrumental neutron activation analysis. Zinc concentration in the bone of Zn-def. mice was significantly lower than that of control mice whereas concentrations in many organs and tissues of Zn-def. mice were not lower than those of control mice. These results may sugest that Zn accumulated in bone was transferred to liver, kidney and spleen etc., and supports various functions in these organs in Zn-def. mice.

On the other hand, there were no differences in uptakes of Tc, whose valence state at the time of injection was estimated to be TcO_4^- under the present experimental conditions, although it is known that Zn interacts with many other trace elements.

3010

SYNTHESIS OF AQUEOUS $Tc(CO)_3^+$ AND SOME DATA ON ITS PHARMACOKINETICS

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Although $Tc(CO)_3^+$ ion is proposed, first of all, as a promising precursor for development of new radiopharmaceuticals, its own pharmacokinetical properties are also of interest. We patented an original method for synthesizing aqueous solutions of carrier-free $^{99m}Tc(CO)_3Cl$ by an one-stage carbonylation of an $K^{99m}TcO_4$ aqueous solution at elevated temperature and pressure [the yield of technetium(I) > 96%]. The product contains no alien substances. This allows direct use of $Tc(CO)_3^+$aq and its simple complexes in nuclear medicine and biology studies.

We carried out a preliminary study of the distribution of aqueous technetium tricarbonyl and its some complexes in the organisms of laboratory animals (rabbits and rats) post intravenous injection.

The planar images of organs were obtained with a large-field-of-view gamma camera using a high resolution collimator in 1-3 view projections, 5 min per view at photopeak of 140 keV with a 20% symmetric window at 128x128 matrix with zoom of 1.5 word mode.

The uptake of $Tc(CO)_3^+$aq is likely to be similar to that of the technetium isonitrile complex and is due to the nonspecific transfer of the lipophilic cation across the plasma membrane in response to a charge gradient. Our study showed that high quality images of the heart can be obtained as early as 15 min p.i. because of the rapid myocardial uptake. When compared to known data on ^{99m}Tc-sestamibi, technetium tricarbonyl is characterized by the similar blood and lung clearance kinetics. However, the heart uptake appears to be significantly higher (10% vs 2.5%), retention longer, and clearance from the liver much slower.

The complex formation of technetium tricarbonyl with some oxianions modifies parameters of images and radionuclide clearance.

The behaviour of some technetium tricarbonyl complexes is unexpected. For instance, under definite conditions the phosphate system gave good visualization of lung. Inoculated tumors in rats was also visualizated.

In a whole, the study performed shows that aqueous technetium tricarbonyl and its simple complexes can be the promising preparations for new diagnostic radiopharmaceuticals.

3011

BEHAVIOUR OF TECHNETIUM IN EUTROPHYC AND DISTROPHIC FRESH WATER LAKES

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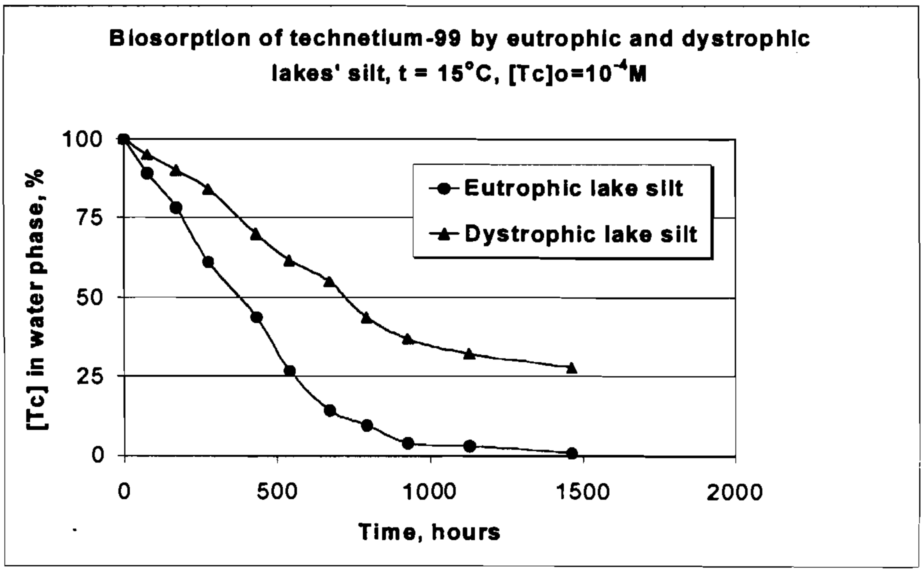
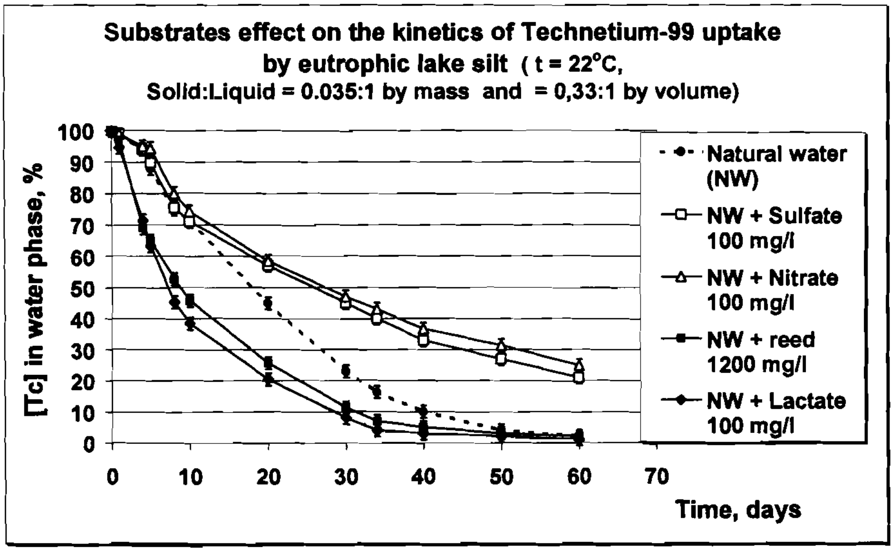
Technetium accumulation by natural associations of microorganisms contained in the sediments is is the key for comprehension of their behaviour in freshwater ecosystems. Its investigation could also provide us with the biomethod for contaminated water treatment. The absorption of the long-lived ^{99}Tc (VII) by the samples of the fresh-water silt, taken from the eutrophic lake Beloye, Kosino (Moscow region) and a typical dystrophic lake (Shatura region). Eutrophic lake water contained 4 ppm of dissolved organic carbon (DOC, including fatty and amino acids, lipides and proteines) in summer - autumn seasons and 0.5 ppm DOC in winter – spring seasons, while the dystrophic lake water contained 60 - 80 ppm of DOC (95 % of which was humic acids). The kinetics' analysis has shown that the half-time values of the initial Tc content removal from the eutrophic lake water phase were about 350 - 450h. Hydrosulphide, produced by sulphate reducing bacteria, that are the component of the silt, is thought to be responsible for the Tc precipitation.



The higher technetium uptake rate was observed not for the humic rich lake sediments but in eutrophic lake sediments rich in freshly fermentated organics.

Some difference in Tc bioaccumulation rate by the silts, taken in winter (from under the ice cover) and in summer periods from the eutrophic lake Beloye, especially in the case of sterilized samples, was found out. However the temperature dependence of Tc uptake rate was not very high, the uptake halftimes increasing from 16 to only 18 days with the temperature decrease from 15°C to 6 °C. This was partly associated with the hydrosulphide concentration decrease in winter period due to the artificial aeration and the depression of metabolism at low temperatures. At the same time it was shown that the hydrosulphide concentration is not the only parameter being important for the intensity of Tc uptake. The influence of concentration and diffusion factors as well as the presence of humic acids in the samples taken from dystrophic lake were also studied.



The grey silt samples from Lake Beloye were shown to be effective sorbents for technetium for the periods of more than 2 years for the solutions containing up to 20 mg/l of Tc. Feeding with cut reed could prolong and increase the decontamination activity. Application of natural association containing sulphate-reducing bacteria for contaminated ponds treatment is discussed.

3012

DEVELOPMENT OF A SEPARATION METHOD FOR ^{99}Tc IN ENVIRONMENTAL SAMPLES USING A TEVA RESIN AND ITS CONCENTRATION LEVELS IN JAPAN

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Introduction

In order to determine global fallout ^{99}Tc in soil samples collected in Japan, a simple and rapid separation method by ICP-MS was developed. ICP-MS is attractive for ^{99}Tc determination because the detection limit is lower than that of any radiation counting method. Although ICP-MS gives several advantages for ^{99}Tc analysis, the radioisotope should be concentrated in a solution, and Ru, which has an abundance of 12.7% at mass of 99, is to be removed. Besides, total elements' concentration in the solution should be less than 300 ppm due to instrumental limitation. Previously, a combustion apparatus was used to separate ^{99}Tc from soil matrices by volatilization and the Tc was collected in a water trap.[1] The total element concentrations can be effectively decreased by the step. Then, Tc was separated and concentrated by liquid-liquid extractions into 5 mL aqueous solution for ICP-MS measurement without Ru contamination. However, a small amount of organic matter remained in the 5 mL solution.

In this study, we developed a new separation method for ^{99}Tc in environmental samples using TEVA resin (Eichrom Industries Inc.) which was used instead of liquid-liquid extractions to avoid inclusion of organic solvents in the final solution. Technetium-99 contents in several soil samples collected in agricultural fields in Japan were determined by the developed method.

Experimental

Separation of Ru from Tc with TEVA resin. Figure 1 is a flow chart for Tc separation from deionized water and seawater containing Ru, by TEVA resin. The total element concentration in trap solutions is thought to be between those of deionized water and seawater samples. After the solutions were introduced into TEVA resin columns, a series of nitric acid solutions, that is, 2M HNO_3 for wash and 8M HNO_3 for strip solutions or 1M HNO_3 for wash and 12M HNO_3 for strip solutions were used to leach the remaining Ru from the column, and then, to concentrate Tc into a small amount solution from both samples. The latter, which was the recommended combination by the resin column's manufacturer, was carried out for comparison.

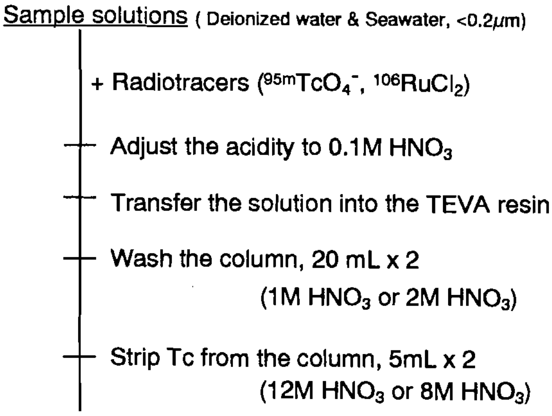

Fig. 1. Separation procedure for Tc by TEVA resin

Determination of ^{99}Tc in Japanese agricultural soils. Ten surface soil samples (0 - 20 cm) were collected in agricultural fields. Each sample was air-dried and passed through a 2 mm mesh sieve. Before separating Tc from the soil sample, it was incinerated for 8 h at 450°C to decompose organic matter. For the determination, 300 to 500 g of the incinerated soil samples were used. Technetium-99 determination was carried out by the developed method, that is, Tc separation from soil by the combustion apparatus, removing Ru and concentrating Tc from the trap solution with the TEVA resin and ^{99}Tc measurement by ICP-MS.

Throughout the experiments, ^{95m}Tc produced by the ^{93}Nb (a, 2n) ^{95m}Tc reaction was used as a yield monitor. The tracer solution does not contain ^{99}Tc, Ru, or Mo.[2]

Results and Discussion

Separation of Ru from Tc with TEVA resin. The results are shown in the Table 1. Technetium could be extracted on the resin even from seawater sample. Tc was collected in a 12M HNO_3 strip solution with almost 100% recovery, while 1% of Ru might enter the strip solution. Most of the Ru passed through the column with the sample solutions and ca. 4% of Ru was sorbed on the resin. The Ru retained by the resin was easily removed with 40 mL of 1M HNO_3 wash solution and some of it appeared in the eluate of 12M HNO_3. Then, 2M HNO_3 and 8M HNO_3 were applied. When the column was washed with 40 mL (20 mL x 2) of 2M HNO_3, Tc was well retained and Ru was removed. Tc recoveries with the first 5 mL of 8M HNO_3 strip solution from the deionized water and seawater samples were about 100%; that is, the same as the 12M HNO_3 strip solution. The Ru concentration in the first strip solution was decreased, being less than 0.2%. Thus we used 2M HNO_3 for wash and 8M HNO_3 for strip solutions.[3] From these results it was clear that TEVA resin can concentrate Tc and remove Ru.[4]

Table 1. Recoveries of Tc and Ru for deionized water and seawater through the TEVA resin column.

		Deionized water		Sea water	
	Volume	Recovery (%)		Recovery (%)	
	(mL)	Tc	Ru	Tc	Ru
Eluate (0.1M HNO_3)	200	0.0	96.0	0.0	95.9
Wash solution	20	0.0	3.0	0.1	3.9
(1M HNO_3)	20	0.0	0.0	0.0	0.2
Strip solution	5	100.1	0.5	101.3	0.9
(12M HNO_3)	5	0.2	0.3	0.2	0.1
Eluate (0.1M HNO_3)	200	0.0	96.8	0.0	95.6
Wash solution	20	0.0	3.1	0.1	4.2
(2M HNO_3)	20	0.1	0.1	0.1	0.1
Strip solution	5	99.7	0.0	99.8	0
(8M HNO_3)	5	0.1	0.0	0.1	0.1

Concentration of ^{99}Tc in Japanese agricultural soils. Fallout ^{137}Cs was used as an indicator for ^{99}Tc behavior because there are many fallout ^{137}Cs data and the fission yields of both radionuclide from ^{235}U and ^{239}Pu are close. The ranges of ^{99}Tc and ^{137}Cs concentrations were 0.004 - 0.11 Bq/kg dry and 1.1 - 28.2 Bq/kg dry, respectively. The observed activity ratios of ^{99}Tc/^{137}Cs are (0.9 - 5.9) x 10^{-3}. The activity ratio of ^{99}Tc/^{137}Cs could be calculated theoretically from fission as 1.4 x 10^{-4} at the time of nuclear weapons' detonations, and the ratio would now be estimated to be about 3.0 x 10^{-4} with correction of decay out. The measured ratios were one order of magnitude higher than the theoretical one from fission. However, this ratio in soil presumably depends not only on migration characteristics of both radionuclides in the soil, but also their distributions on the earth's surface. Our results, at least, lead to a tentative conclusion that more Tc might be fixed on the soil than we had expected before.

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The Concentrations of Technetium-99 in *Sargassum thunbergii* around The Coast of The Japanese Islands

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Summary: Concentrations of technetium-99 in *Sargassum thunbergii* were determined in the samples collected around the coasts of the Japanese Islands and were in the range of 4.5~36 mBq/kg wet except for Hitachinaka City where much high concentrations were observed. Most of the values obtained for the algae were attributed to global fallout but those for Hitachinaka City might come from waste disposal from the nuclear facilities sited in Tokai Village which is adjasent to Hitachinaka City,Ibaraki Prefecture.

Technetium-99 is already present in the terrestrial and the marine environment as a result of nuclear weapon tests carried out in the past. It is very important to study the distribution of the nuclide in the marine environment in regards to increasing number of power plants all over the world because of its high yield in nuclear fission, of its long half-life, of its high solubility and stability in water media and of its high concentration factor(CF) by brown algae.

We have been determining the concentration of the nuclide in algae collected along the coasts of the Japanese Islands to assess an internal exposure to Japanese through marine foods. The concentration of the nuclide was also determined in seawater collected at the coast of Hitachinaka City.

It was found that the present level of the nuclide was very low in algae collected in most of the areas of Japan and this level is attributed to the global fallout. However, it was found that relatively high concentration of the nuclide was detected in the samples collected at the Coast of Hitachi-naka City which is neighboring Tokai Vil. where there are many nuclear facilities in operation. The concentration of the nuclide in the algae was in the range of 50 to 1,500 mBq/kg wet. It was found that the level of the nuclide in the algae in Kitaibaraki City was the same as that in other areas except Hitachinaka City despite that Kitaibaraki City is near to Tokai Vil. There is a down current on the coasts of those areas so that northern coasts are free from the influence of the emission of waste from Tokai Vil. The level of the nuclide in the alga collected in Chiba Pref.was found that the level of the nuclide was low and the waste from Tokai vil. did not reach this far and the concentration of the nuclide in the algae was below 10 mBq/kg wet.

The concentration of the nuclide in seawater was not detected in most of the samples along the Coasts of the Japanese Islands. However, in Hitachinaka City it was found that the concentrations of the nuclide were detected several times through the year and the values were varied from below the detection limit, 10mBq, to 230mBq/m^3.

3014

MEASUREMENT OF RADIONUCLIDE DISTRIBUTION COEFFICIENTS FOR LEACHED MORTAR

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Low-level radioactive waste (LLRW) generated at nuclear power plants and nuclear reprocessing plant will be disposed by shallow burial (Fig. 1). Technetium-99 is one of the radionuclides in LLRW. Reinforced concrete is used for the radioactive waste repository. The buried concrete structure is in contact with water and will gradually degrade over an extended period of time through leaching and chemical attack. In this study, accelerated leaching test for mortar, based on the electrical potential gradient, was carried out to prepare degraded mortar (leached mortar) due to dissolution of cement hydrate. The mortar which leached Ca and other ions are similar to the degraded concrete in contact with underground water for a long time. After that, we measured the distribution coefficients (Kd) between radionuclides and the mortars.

EXPERIMENTAL Ordinary Portland cement (OP), Low Heat Portland cement (LH) and Toyoura sand (standard sand in Japan) were used for the preparation of the mortar samples. Leached mortar was prepared by electrical potential gradient method. The degradation degree of leached mortar is evaluated by CaO/SiO_2 mole ratio (Ca/Si ratio) in calcium silicate hydrate (C-S-H) of mortar.

Distribution coefficient of radionuclides between mortar-equilibrated water and leached mortar was determined by the following procedures. A hardened mortar was crushed and sieved to obtain the granules in the size range 2 - 5 mm. The granule (3 g) was placed in a 50ml polyethylene vessel and then 30 ml of deionized water was added. The vessel was sealed and left to equilibrate for 20 days at 15℃. After that, concentrated radionuclide standard solution was added into the solution in the vessel. Radionuclides for Kd experiment were divided into four groups (A, B, C and D) owing to the difference of determination method of radioactivity.

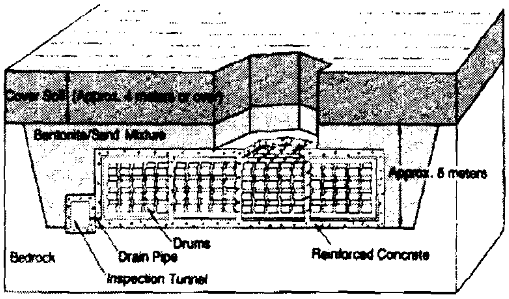

Fig. 1 Schematic of shallow burial of LLRW in Japan[1].

A (^{95m}Tc, ^{85}Sr, ^{110m}Ag and ^{137}Cs) : Ge (Li) semiconductor detector
B (^{125}I and ^{241}Am) : NaI(Tl) scintillation detector
C (^{238}Pu) and D (^{14}C) : liquid scintillation detector

The sample solution containing radionuclides was left for 7 days at 15℃. After that, the sample solution was filtered through 0.45-micrometer membrane filter. Kd was calculated from the radioactivity in the filtrated sample solution.

RESULTS and DISCUSSION It is important to measure ion concentration in mortar-equilibrated water to get some useful information on pore water in mortar. Since Ca^{2+} is the main component in mortar-equilibrated water, it is useful to consider the relationship between dissolved Ca^{2+} and degradation of the mortar. Therefore, the relationship between the Ca/Si ratio in C-S-H and the Ca^{2+} concentration in mortar-equilibrated water is as shown in Fig. 2. When the Ca/Si ratio is in the range of 0 to 1.3, the Ca^{2+} concentration was steady at about 1 mmol/L. When the Ca/Si ratio was 1.8, the Ca^{2+} concentration remarkably increased to 20 mmol/L. The data measured by Greenberg and Chang[2] agrees closely with the results of this study. Greenberg and Chang's data showed a rapid increase in the Ca^{2+} concentration when the Ca/Si ratio was 1.5, suggesting that the chemical composition of mortar changed near the Ca/Si ratio (1.5).

Figure 3 shows the dependency of Kd for the eight kinds of radionuclides on Cs/Si ratio in C-S-H of leached mortar. The relation between Kd and Ca/Si ratio is roughly divided into the following three types.

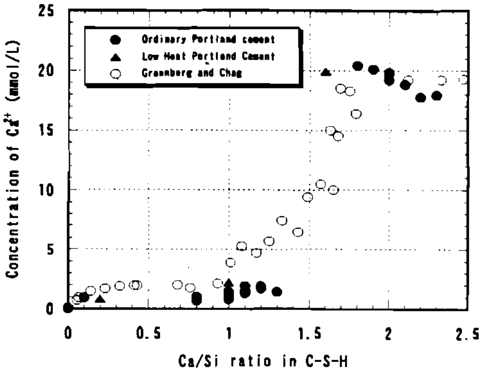

Fig.2 Relationship between Ca/Si ratio in C-S-H and Ca^{2+} concentration in mortar- equilibrated water.

(1) ^{137}Cs and ^{85}Sr -- Kd value decreases with an increase in Ca/Si ratio.
(2) ^{95m}Tc and ^{238}Pu -- No correlation between Kd and Ca/Si ratio.
(3) ^{110m}Ag, ^{14}C, ^{241}Am and ^{125}I -- Kd value increases with an increase in Ca/Si ratio.

One of the main sorption factors of radionuclides is the chemical form of the radionuclide in liquid phase. It is clear that Cs (alkaline group) and I (halogen group) are present as Cs$^+$ and I$^-$ in mortar-equilibrated alkaline solutions, respectively. Therefore, on the assumption that the sorption of Cs$^+$ and I$^-$ on the mortar surface is mainly carried out by ion-exchange. Mortar-equilibrated water (liquid phase) prepared by un-leached mortar (solid phase) contains many Ca^{2+} ions and other cations. Since the surface of the mortar is negatively charged (-SiO$^-$), Ca^{2+} ions are adsorbed on the surface. This means that the surface of the solid phase is positively charged (-SiO$^-$Ca^{2+}).

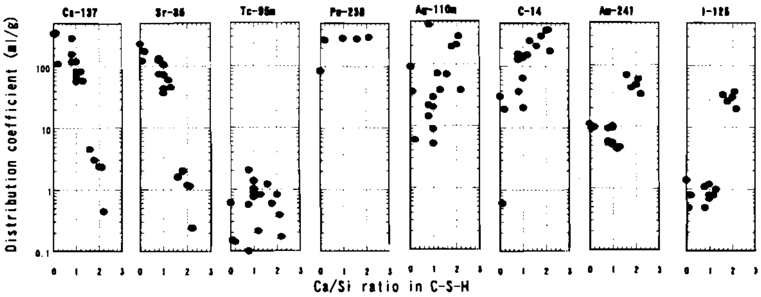

Fig.3 Dependency of distribution coefficient for radionuclides on Ca/Si ratio in C-S-H.

When Cs$^+$ ions in liquid phase are adsorbed on the surface of un-leached mortar, Cs$^+$ ions compete with Ca^{2+} ions. Accordingly, Cs$^+$ ions are difficult to adsorb on the surface of un-leached mortar. On the other hand, I$^-$ ions in liquid phase are easily adsorbed on the surface of un-leached mortar because the surface is positively charged. Mortar-equilibrated water (liquid phase) prepared by leached mortar (solid phase) contains fewer Ca^{2+} ions than that prepared by un-leached mortar. Because the Ca^{2+} concentration in liquid phase is dilute, Cs$^+$ ions are easily adsorbed on the surface of leached mortar. However, I$^-$ in liquid phase is difficult to adsorb on the surface of leached mortar because the surface is negatively charged.

This adsorption mechanism can be explained by the dependence of Kd (^{137}Cs, ^{85}Sr and ^{125}I) for Ca/Si ratio in C-S-H of leached mortar. The sorption mechanisms of ^{95m}Tc, ^{238}Pu, ^{110m}Ag, ^{14}C and ^{241}Am are complicated and depend not only on ion-exchange but also on complexation, precipitation and pore structure of mortar.

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3015

CONCENTRATION OF TECHNITUME-99 IN LITTER/HUMUS LAYER OF THE JAPANESE FOREST

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Major sources of ^{99}Tc in the environment are fallout from nuclear tests and reprocessing plants. In the general environment of Japan, the fallout would be the only source of ^{99}Tc. We examined ^{99}Tc concentrations in litter/humus sample to elucidate environmental behavior of fallout ^{99}Tc.

Litter/humus samples rich in organic materials were collected at a pine forest and a Japanese cedar forest of an experimental forest of Kyushu University in Fukuoka, Japan. The wet samples were dried in an air oven at 110 °C overnight. Soil component in a sample was removed by passing through a 32 mesh screen and the small rocks in the cedar sample were removed by picking up with hand. The dried samples were put in porcelain dishes and incinerated in a furnace. The ash samples were subjected to gamma spectrometry and ^{99}Tc analysis.

All amounts of the ash was taken in a beaker, 6% NaOCl solution was pored slowly and digested under stirring by a magnetic stirrer for 2 h at temperature 80 - 90°C. After two times digestion, the sample solution reduced with evaporation. Yield tracer of ^{99m}Tc and NaOH were added to the solution and MEK extraction was carried out. The MEK phase with Tc was gently evaporated to dryness on a hot plate. A part of the residue was dissolved in electrolyte and Tc was electrodeposited on a copper disk. The activity of ^{99}Tc electrodeposited on the copper disk was measured by the gas-flow Geiger-Müller counting system for 3,000 min. A blank sample for background determination was also prepared. The remaining residue was dissolved in ultra pure HNO_3 and the ^{99}Tc concentration was measured by ICP-MS (Momoshima et al., 1993, 1995).

Background counting rates in the measurement of ^{99}Tc by beta-ray counting were determined by using a reference sample. However, a bias of the counting rate originated from ^{99m}Tc yield tracer was not statistically significant because of high background counting rates associated with the beta-ray counting. The measurement of ^{99}Tc activity was carried out after waiting a complete decay of ^{99m}Tc to ^{99}Tc. The concentrations of ^{99}Tc measured by radiometric assay and by ICP-MS are shown in Table 1. Concentrations of other radionuclides determined by gamma spectrometry are listed in Table 2.

Table 1. Concentrations of ^{99}Tc in the litter/humus samples (μBq g^{-1} dry weight)

Sample	beta-ray counting	ICP-MS
Pine sample	40.2 ± 1.5[a]	42.9 ± 0.1[a]
Cedar sample	13.0 ± 1.2	19.1 ± 0.1

[a] Counting error.

Table 2. Concentrations (mBq g^{-1} dry weight) of ^{7}Be, ^{40}K and ^{137}Cs in the litter/humus samples.

Sample	^{7}Be	^{40}K	^{137}Cs
Pine sample	108.2 ± 1.4[a]	302.7 ± 12.4	34.4 ± 0.4
Cedar sample	189.2 ± 4.1	62.8 ± 9.9	13.9 ± 0.3

[a] Counting error.

The observed ^{99}Tc concentrations in the litter/humus samples are one order magnitude lower than that of the paddy soils; 460 and 110 μBq g^{-1} dry soil for two in Akita Prefecture, and 210 μBq g^{-1} for an unplowed soil in Ibaragi Prefecture (Tagami and Uchida, 1993). The activity ratio of ^{99}Tc /^{137}Cs is $(1.2\text{-}1.3)\times10^{-3}$ for the litter/humus samples, which is lower than that of the paddy soils, 3.9×10^{-3} - 3.8×10^{-2}. The difference of the activity ratio would be attributed to the difference of sample type; the paddy soils are rich in soil minerals, while our samples are rich in organic matters. Morita *et al.* (1993) have reported a depth profile of ^{99}Tc in soil; the concentration decreases with depth from 180 μBq g^{-1} dry soil at the surface soil to 1.4 μBq g^{-1} at 20 cm depth. They also observed the mobility of ^{137}Cs larger than that of ^{99}Tc into the deep layer. Leaf fall would cause an accumulation of ^{99}Tc in organic matters, but such an accumulation system is not found for Cs. The fixation of ^{99}Tc in living trees would elevate an activity ratio ^{99}Tc /^{137}Cs in the litter/humus layer.

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December 1 (Wednesday)

Reprocessing of technetium

and

Other aspects of physics and chemistry of technetium

0101

EXTRACTION BEHAVIOR OF TECHNETIUM IN NUCLEAR FUEL REPROCESSING

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Development of an advanced PUREX process, PARC process (Partitioning Conundrum key process), has been carried out which can reduce the radioactive waste volume containing TRU elements (Np, Pu, Am and Cm) and the environmental hazard risk due to long-lived nuclides such as ^{99}Tc, ^{14}C and ^{129}I. In the separation of neptunium and technetium from plutonium and uranium solutions before the U/Pu partitioning step in the PARC process, the selective reduction of Np(VI) to Np(V) by normal-butyraldehyde and the high acid scrubbing of technetium are considered. The solvent extraction behaviors of nuclides such as technetium and neptunium in the PARC process were studied in a chemical flow sheet experiment using miniature mixer-settlers in an alpha-gamma cell in NUCEF.

The dissolver solution of spent fuel of 8,000 MWD/tU as a feed contained 257 g/l uranium, 900 mg/l plutonium, 15 mg/l neptunium and 54 mg/l technetium, 263 mg/l zirconium, 118 mg/l ruthenium, 149 mg/l cesium and 3.1 M nitric acid. Two mixer-settlers were used to measure the extraction behaviors of uranium, plutonium, neptunium, technetium and tracers (zirconium, ruthenium, cesium and iodine) in the solvent extraction steps. The flow sheet consists of three steps: co-decontamination, Np separation, Tc separation steps.

The concentration profiles of nuclides in the mixer-settlers showed that more than 99.9 % of both uranium and plutonium, about 50 % of neptunium and 99 % of technetium in the dissolver solution were extracted by the TBP solvent in the co-decontamination step.

In the Np separation step, the concentrations of U and Pu were almost constant in both the organic and the aqueous phases in the Np and the Tc separations steps. As for Np and Tc, concentrations in both the organic and the aqueous phases decreased with approximately the same gradient as in both the Np and the Tc separation steps. About 95 % of the Np that flowed to the Np separation step was back-extracted from the solvent stream loaded with uranium and plutonium and flowed to the Np product. This implies that Np(VI) was reduced to Np(V) by n-butyraldehyde. As for technetium, about 60 % of the technetium that flowed to the Np separation step was back-extracted from the solvent stream and flowed to the Np product. In a kinetic study, it was found that the reduction rate of Tc(VII) by n-butyraldehyde was very slow in 3 M nitric acid solution. The decrease of U and Pu concentrations in the aqueous and organic solutions by addition of organic solvent with n-butyraldehyde affected the Tc back-extraction in the Np separation step.

In the Tc separation tep, the rest of the technetium was back-extracted with 6 M nitric acid. It is considered that the mixed complexes of $UO_2(NO_3)(TcO_4) \cdot 2TBP$, $Pu(NO_3)_3(TcO_4) \cdot 2TBP$ or $Zr(NO_3)_3(TcO_4) \cdot 2TBP$ in the organic phase were decomposed to extractable complexes of $UO_2(NO_3)_2 \cdot 2TBP$, $Pu(NO_3)_4 \cdot 2TBP$ and $Zr(NO_3)_4 \cdot 2TBP$ and inextractable $HTcO_4$ in high nitric acid in the Tc separation step.

In this study, it was found that n-butyraldehyde was a selective reductant of neptunium(VI) in the presence of uranium, plutonium and technetium. It was confirmed that high acid scrubbing was effective for technetium separation.

0102

TECHNETIUM PROBLEM DURING SPENT NUCLEAR FUEL REPROCESSING AND POSSIBLE METHODS OF ITS SOLUTION.

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The versions of the technetium-99 distribution driving on the head-end operations of the spent nuclear fuel reprocessing were considered. The preferable way is technetium localization in the organic uranium-plutonium flow. The means for such localization is recycled organic flow that circulated between suitable areas of the uranium stripping and head-end extraction processes. For technetium negative rule out on the redox reactions of plutonium technetium removal (extraction) is carried out before the operation of uranium and plutonium separation.

For technetium extraction the special process was developed that based on the polyphase transport (organic flow - auxiliary aqueous flow - high selectivity anion exchange resin) of the pertechnetium ion from the organic phase to the resin phase. As the anion exchange resin the contained quaternary ammonium or phosphonium compounds are used. Auxiliary aqueous flow is contained a complexing agent and inputted like emulsion together with organic flow to the ion exchange treatment that allow to use this flow (after ion exchange treatment and organic flow separation) for plutonium removal from the fuel reprocessing process.

High selectivity to the TcO_4^- anion an exchange resin provides quantity extraction of technetium from organic flow but requires the special conditions for technetium desorption. This conditions are the force of the reductant for technetium (VII) and complexing agent for the reduced form at the same time. The best results by the using two valency iron in phosphate or sulphate medium were obtained.

Technetium can be outputted from the sorbat together with iron hydroxide as hydrated dioxide during the sorbat neutralization.

In case of the purified technetium compound fabrication the separation of the iron and technetium with technetium oxidation to technetium (VII) in an alkali medium by hydrogen peroxide and subsequent technetium affinage can be used.

0103

TECHNETIUM EXTRACTION FROM HIGH RADIOACTIVE WASTE

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For technetium that is transferred in part in the high radioactive raffinate of the Purex-process the method of its extraction was considered. The method takes account of a complicated salt composition and low content of technetium in the raffinate. For this conditions the flow sheet of the continuos counter-current accumulation-free concentrating of technetium in the process with the based on a trialkylamine circulated extractant was used.

This method is based on the consecutive transport of the extracted component into the volume lowering product stream and separation of the extracting task (external extraction cycle) and concentrating (internal extraction cycle) one. There are the deep extraction of technetium, extract washing and complete stripping of component in the external cycle. After acid adding stripping solution is loaded in internal cycle for the secondary technetium extraction, extract washing and component stripping. In this case the internal cycle raffinate serves the washing solution in the external one while extract of this cycle is sent to the control stripping in the external cycle. In this streams structure the completeness of technetium transport in the internal cycle is not necessary that allows to achieve in this process any required concentration ratio. From the other side the secondary cleaning operation (extraction, washing and stripping) into the internal cycle is quarantined the high purify of the final product.

The process has not any limitations in the extraction equipment application (extraction columns, mixer-settlers, centrifugal extractors).

For the final stage (ammonia pertechnetate crystallization) the solubility in the system NH_4NO_3-NH_4TcO_4 was studied and phase fields of system NH_4NO_3 and NH_4TcO_4 crystallization were determinated.

DIFFUSION COEFFICIENTS OF RHENIUM(VII) AND TECHNETIUM(VII) IN NITRIC ACID AND TRI-BUTYL PHOSPHATE DILUTED IN DODECANE

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1. Experimental

Exact amount of reagent-grade $KReO_4$ was dissolved in nitric acid. Technetium-containing solutions were prepared from a $NH_4{}^{99}TcO_4$ solution by evaporating to dryness with nitric acid and 3% H_2O_2 below 330 K. The dried, white residue was dissolved in a HNO_3 solution with or without 0.1 M uranyl nitrate. Concentrations of Tc were determined by β-counting with a liquid scintillation counter. A Tc(VII)-containing solution was contacted with an organic solution of 30% TBP in dodecane. Uranyl - TBP complex was prepared by dissolving the metal salts in pure TBP until saturation of the organic phase, followed by drying with molecular sieve. Organic solutions containing both Tc(VII) and uranyl-TBP complex were prepared by dissolving pure $UO_2(NO_3)_2$ 2TBP into the Tc-containing organic solutions.

A cell consisting of two compartments interconnected with capillary tubes was installed in a rotor of an analytical ultracentrifuge. The rotor was accelerated to 8000 rpm to push the solution in one compartment through the capillary into the other at 298 or 323 K. A Schlieren optical system was used to monitor the diffusion of Re(VII) and Tc(VII) in the cell, where only one solute was subjected to a concentration gradient.

2. Results and Discussion

Rhenium(VII)

In the 3 M nitric acid, the diffusion coefficient of ReO_4^- was increased by the presence of 0.1 M $UO_2(NO_3)_2$, which may be caused by coupled-transport of uranyl and perrhenate ions resulting from ionic association. (Fig.1) The limiting diffusion coefficient of 1.46×10^{-5} cm^2 s^{-1} for ReO_4^- at infinite dilution at 298 K agreed well with the data obtained in the present study.

Technetium(VII)

The limiting diffusion coefficient of 1.43×10^{-5} and 1.95×10^{-5} cm^2 s^{-1} for TcO_4^- at infinite dilution at 298 K are in agreement with the present result in the absence of uranium. In the 3 M nitric acid, the Tc(VII) diffusion coefficient was significantly increased by the presence of 0.1 M $UO_2(NO_3)_2$, which may also be caused by coupled-transport. (Fig.2)

In the 30%TBP solutions, the diffusion coefficient is almost independent on the concentration of Tc(VII).(Fig.3) In the presence of 0.1 M $UO_2(NO_3)_2$ • 2TBP, the diffusion coefficients of Tc(VII) are increased to 6.34×10^{-6} and 6.47×10^{-6}

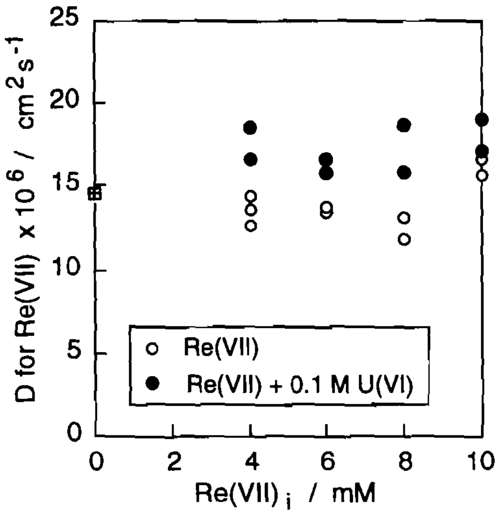

Fig. 1 Diffusion coefficient of Re(VII) in 3 M nitric acid at 298 K.

$cm^2\ s^{-1}$ at 298 and 323 K, respectively. Thus, a similar influence of coupled-transport can also take place in the organic system to enhance the diffusion of Tc(VII). From the analysis of extraction equilibria, Tc(VII) is reported to be coextracted with U(VI) by TBP, where majority of Tc(VII) are considered to exist as $UO_2(NO_3)(TcO_4)$ 2TBP complex. This fact supports the coupled-transport. Besides, negative Schlieren peaks were observed by the diffusion of Tc(VII).

3. Conclusion

In the 3 M nitric acid solutions, coupled-transport of either Re(VII) and Tc(VII) anions with uranyl ions may occur, since their apparent diffusion was increased. In the organic solutions of 30%TBP in dodecane, the diffusion of Tc(VII) was also enhanced by the presence of 0.1 M U(VI). This is in consistent with the chemical form of the complex $UO_2(NO_3)(TcO_4) \cdot 2TBP$.

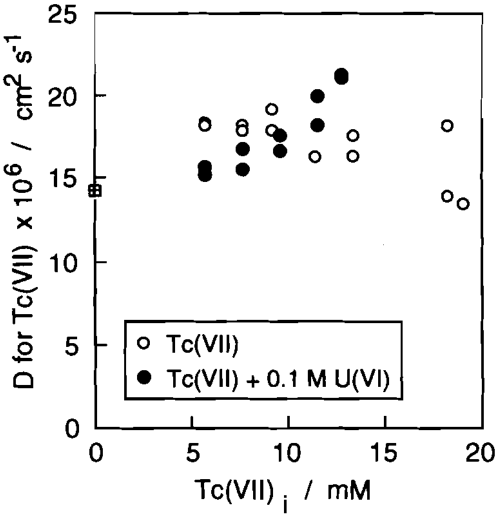

Fig. 2 (a) Diffusion coefficient of Tc(VII) in 3 M nitric acid at 298 K.

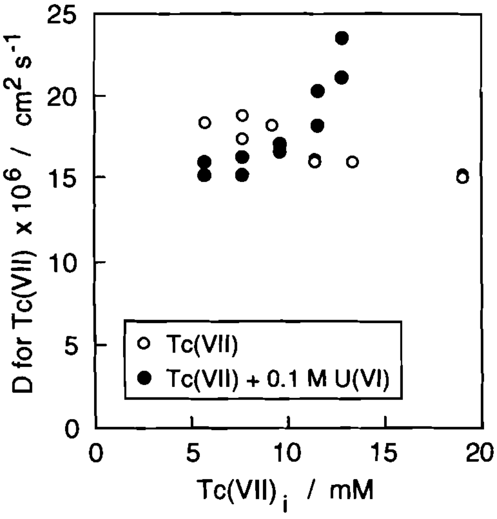

Fig. 2 (b) Diffusion coefficient of Tc(VII) in 3 M nitric acid at 323 K.

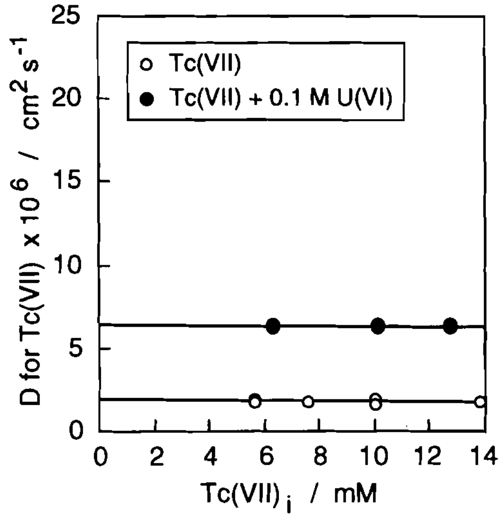

Fig. 3 (a) Diffusion coefficient of Tc(VII) in 30% TBP in dodecane at 298 K.

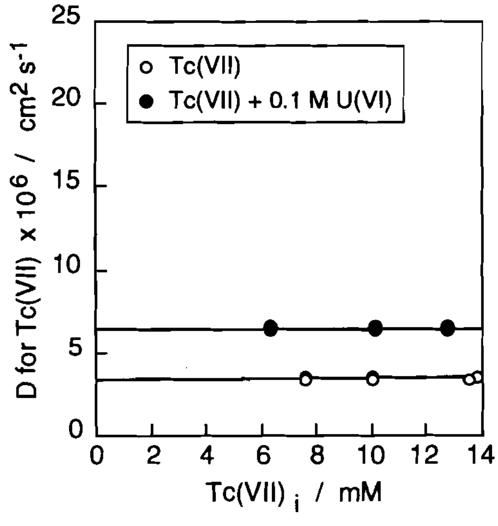

Fig. 3 (b) Diffusion coefficient of Tc(VII) in 30% TBP in dodecane at 323 K.

EVAPORATION BEHAVIORS OF DILUTED NITRIC ACID SOLUTIONS OF NITROSYL RUTHENIUM AND PERREHENATE IONS WITH A THIN FILM EVAPORATOR

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To decrease radioacitivities in natural environments, low level radioactive liquid wastes containing miner actinoid, technetium, and ruthenium need to be reduced to solid forms for their disposal. Reduction procedures for the aqueous solution containing nitrosyl ruthenium and perrhenate ions have been studied here by using a thin film evaporator. A study is on the way for pertechnetate ions solution reduction.

A thin film evaporator consists basically of an upright tube that is heated from outside. The vessel's inner surface rotational wiper system evenly spreads to the continuously fed product to be evaporated. Generally this evaporator is used by perfume and medicament industries to reduce volumes of liquid solutions containing thermally unstable material.

Evaporation experiments were performed using 1 dm^3 (L) of an aqueous nitric acid solution containing nitrosyl ruthenium nitrate or perrhenate ions. Evaporation behaviors were investigated with changing feed rates and rotational wiper's speed of wiper for making thin film under the condition of 50℃ and 10 mmHg. The amounts of ruthenium and rhenium in the distillate were determined by using an Inductively Coupled Plasma (ICP) Mass Spectrometry (MS); the amounts in the residue were determined by using an ICP Atomic Emission Spectrometry (AES). The nitrate ion concentrations in both the distillate and residue were analyzed from optical densities of 200 nm using an ultra violet spectra photometer.

Decontamination factors for ruthenium in the distillate were between 1.1×10^4 and 5.8×10^4, which are nearly equal to the findings obtained by the Japan Nuclear Cycle Development Institute. The factors for nitrate ions were between 72 and 211. The concentration ratio of ruthenium and nitrate ions in the residue was below 10.

The decontamination factors for Re was a factor of the order of 10^5. The various materials in the aqueous solution increase evaporative ability in approximately the following descending order: nitrate, nitrosyl ruthenium, perrhenate. In order to reduce the evaporation rate of the ions, some denitration reagents were adjusted in the experiments.

A thin semicircle of Teflon--splash guard, positioned on the shaft of the wiper, acts as a splash guard to prevent entering liquid from splashing into the interior and to decrease the amounts of analyte in the distillate. A higher feed rate of simulated waste solution produced much more residue.

METHOD OF TECHNETIUM RECOVERY IN FUEL REPROCESSING

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The necessity of controling the flow of technetium (Tc) in the LWR reprocessing process has been well recognized after the work by Garraway and Wilson[1),2)], and Vialard and Germain[3)]. At the 1st cycle of the Purex, Tc takes a hepta-valent state, TcO_4^-, which is prone to be extracted by TBP along with U, Pu and Zr, particularly when a high burn-up spent fuel is treated. These extraction behaviors were fully examined so far[4)-11)]. Owing to these works, a Tc scrub flowsheet, which splits Tc from the U-Pu bearing organic solvent to the aqueous flow by scrubbing with a concentrated nitric acid, has been adopted in the recent large commercial reprocessing plants to suppress the Tc-leaks to the partitioning stage. Thus almost all dissolved Tc (^{99}Tc) is put into the high-level liquid waste (HLW). There are keen discussions about the fate of Tc fixed into the HLW-glass, because the TcO_4^- is relatively soluble and reaches to the biosphere quicker than other nuclides after dissolved in a ground water.

Japanese OMEGA Project has taken initiatives to proceed the strategy of Partitioning and Transmutation (P & T), in which long-lived minor actinides and fission products, i.e., ^{99}Tc and ^{129}I, should be separated and transmuted to short-lived or stable nuclides by fission or neutron capture reactions in order to alleviate the burden of the future generations. The yield of Tc in the spent LWR fuel is approx. 1 kg/ton of HM and the recovery yield of Tc from the HLW to attain the goal is, for example ~98%, by the Schmidt's criterion [12)].

The Project also includes the R & D to stimulate the utilization of the fission product noble metals as resources. The metals like platinoids seem to be very valuable but actually radioactive.

The present investigation has been carried out by regarding ^{99}Tc not only as a hazardous nuclide to be eliminated due to its long-lived radioactivity but also as resources due to its novelty of element 43 (man-made) and to its potential value. The separation of Tc would be accomplished either at the Purex process or from the HLW which contains a great variety/amount of elements.

The goal of the present study was to develop a flowsheet for Tc recovery at the 1st cycle of the Purex process, because the feed solution contains a less amount of fission products compared with that of HLW.

First we have measured distribution ratios of Tc(VII); D_{Tc7}, in a 30%TBP-n-dodecane-HNO_3 system with U(VI), Pu(IV) and/or Zr(IV), then D_{Tc7} was modeled by a numerical equation expressed by functions of concentration of the components. The equation includes several parameters whose value were determined by a least-square fitting using the distribution database, DISTEX which assembled not only the above results but also other reported data. The D_{Tc7} model was used in the Purex simulation code, EXTRA-M, whose main futures were explained elsewhere[13),14)]. A simulation study of Tc(VII) behavior over an extraction-scrub stage in the 1st cycle of the Purex by using the EXTRA-M showed that the concentration profile of Tc(VII) of the 1st cycle is very sensitive to; i) concentration of an extractable Zr(IV) in the feed solution, ii) flow rate of a nitric acid solution for stripping Tc(VII)[15]. And finally a simple Tc-strip flowsheet was envisaged[15]. According to the Tc-simulation for the flowsheet, almost all Tc(VII) is ushered into the aqueous stream comeing-out from the Tc-stripping stage. This aqueous stream (named Tc-ST1 hereafter) also contains approx.10 g Ul^{-1} and 0.2g Pu l^{-1}.

To recover Tc completely from the Tc-ST1, we have developed several cyclic amides, butyrolactam, valerolactam, caprolactam and their derivatives having an octyl chain to increase the lipophilicity. Among them a mixture of 3-octyl-N-2-ethylhexyl-valerolactam and 4-octyl-N-2-ethylhexyl-valerolactam (abbr. to as 3,4,OEHVLA) exhibited the highest extractability for Tc(VII)[16]. Based on the good extractability of 3,4,OEHVLA, the Tc-recovery process in the 1st extraction cycle of the Purex process was proposed (***Figure***).

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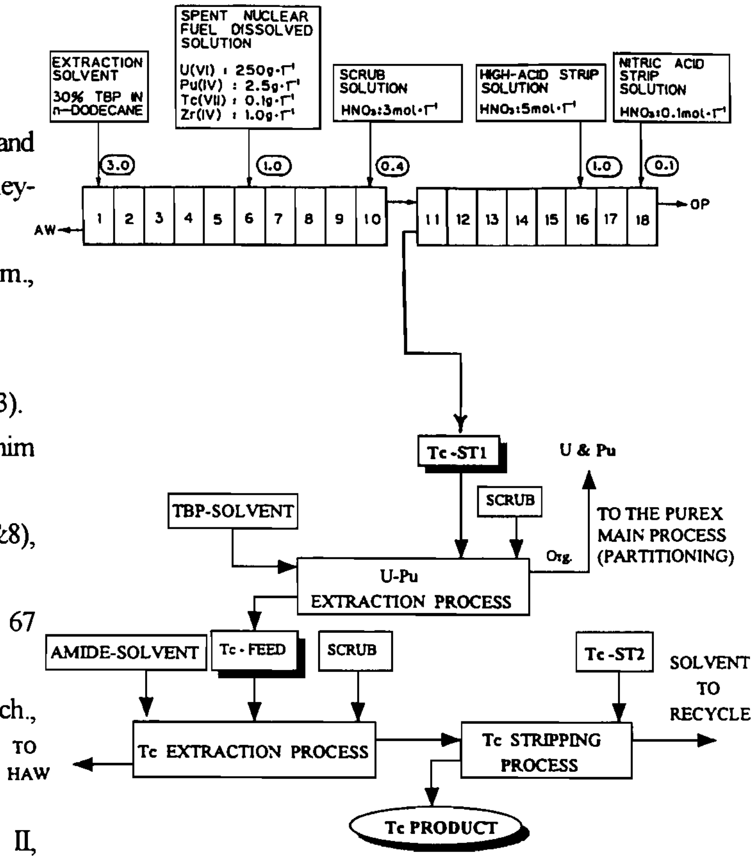

Technetium Recovery Process attached to the 1st Cycle of the PUREX Reprocessing

SOLVENT EXTRACTION OF TECHNETIUM(VII) FROM ALKALINE WASTE USING CROWN ETHERS: FUNDAMENTAL PRINCIPLES AND PROCESS CHEMISTRY

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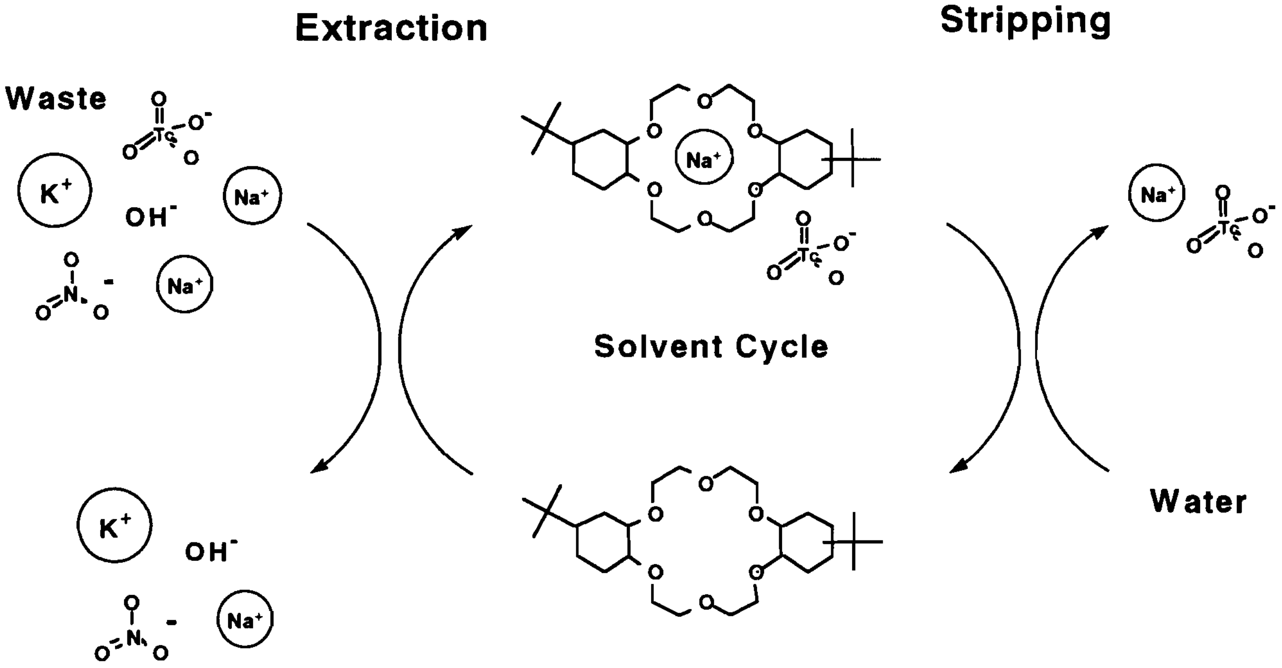
A combination of fundamental principles and process development has led to an effective method for extracting heptavalent technetium (Tc) from alkaline nitrate waste solutions by the use of crown ethers. Technetium is found in reprocessing wastes stored at several DOE sites. Almost two metric tons of ^{99}Tc are stored in underground tanks at the Hanford site, where it is planned to separate the Tc from the 55 million gallons of other waste components in the tanks. Because of its environmental mobility and long half-life, technetium must be placed in a geologic repository along with the other radiotoxic metals in the waste. Research in the Chemical Separations Group of the Chemical and Analytical Sciences Division at ORNL has recently suggested an extractive method that could be used to remove the technetium from the highly salted wastes stored in the tanks. Although it had been well known that crown ethers possess the ability to efficiently extract sodium salts by



SRTALK process for removing technetium from nuclear waste binding the sodium ion, a key question of interest at ORNL concerns what factors determine which salt would be extracted selectively from a mixture of sodium salts. An electrostatic model of ion-pair extraction together with some key literature reports supported the prediction that sodium pertechnetate could be selectively separated from the Hanford waste. In subsequent process development, this prediction was validated through invention of the SRTALK process. No pre-treatment of the waste solution is necessary, and the technetium can be recovered using a safe and inexpensive stripping process, regenerating the crown ether for many more cycles with minimal generation of secondary waste. Engineering tests with a waste simulant in a cascade of centrifugal contactors gave 89% removal of Tc from the waste, meeting the decontamination requirements. Remarkably, the tests gave a product stream concentrated 10-fold in practically pure sodium pertechnetate. Considering that the source of the recovered Tc would be the highly toxic and complex waste at Hanford, the remarkable expected purity of the Tc product would make for an ideal feed for production of waste forms for final disposal, with expected major cost savings. On the other hand, the ability to recover a pure product would support other options such as transmutation, research, or industrial application.

A chemical depiction of SRTALK is shown above. The waste is a mixture of salts concentrated in sodium, potassium, hydroxide, nitrate, nitrite, aluminate, and carbonate, but with a trace of radioactive contaminants such as ^{99}Tc. Most of the Tc is in the form of the negatively charged pertechnetate ion, which has the formula TcO_4^-. The crown ether complexes with sodium ions (Na^+) as shown but can also complex with potassium ions (K^+). The transfer of either of these metal ions into the solvent by the crown ether must also be accompanied by a negatively charged ion. Among the most easily transferred negative ions is pertechnetate with a selectivity over nitrate on the order of a thousand to one. When the solvent is contacted with water or preferably dilute nitric acid, the sodium pertechnetate may be back-extracted, regenerating the crown ether for further extraction cycles. The process is described by a 1995 patent and in numerous publications.

The foundation leading to this development was provided by the USDOE Office of Basic Energy Sciences, Chemical Sciences Division, and the process development was supported under the USDOE Office of Science and Technology, Efficient Separations and Processing Crosscutting Program, under contract number 1) DE-AC05-96OR22464 with Oak Ridge National Laboratory, managed by Lockheed Martin Energy Research Corp.; 2) W-31-109-Eng-38 with Argonne National Laboratory; and 3) DE-AC06-76RLO1830 with Pacific Northwest National Laboratory operated by Batelle Memorial Institute.

0108

ESTIMATION OF NECESSARY SEPARATION FACTOR OF ^{99}Tc AND Ru AFTER ^{99}Tc TRANSMUTATION FOR USE OF NUCLEAR RUTHENIUM IN INDUSTRY

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The product of ^{99}Tc transmutation is valuable platinum metal ruthenium (~$ 30 per gramme), which can have application in an industry after the purification. Global Ru sales volume coincides with rate of ^{99}Tc accumulation in the fulfilled fuel of atomic power stations and is equal about 8 tons per years, therefore ^{99}Tc transmutation could give ~$ 200 millions per years. Hence, the problem of radiochemical separation of ^{99}Tc and Ru has the important practical meaning.

Ruthenium can be applied without restrictions if residual ^{99}Tc contents in it will be less than $5.88 \cdot 10^{-6}$ g/kg of Ru. The permissible level of ^{99}Tc concentration equal $2.94 \cdot 10^{-5}$ g/kg of Ru for application of Ru only in a nuclear industry. Probably limited Ru use in nuclear industry is possible if its surface β-activity will be lower than the permissible level for a surface of the equipment in nuclear branch. It was shown that surface activity of Ru-Tc alloys, containing 20, 50 and 80 % of ^{99}Tc, depends on ^{99}Tc concentration practically linearly. Hence, Ru use is possible when ^{99}Tc concentration in it is below than 10^{-2} g/kg of Ru for the specified case.

^{99}Tc concentration in Ru will be equal $\mathbf{C_{Tc}=(q^{-1}-1)/K}$, where $\mathbf{q}$ is target burnup, $\mathbf{K=\prod_{i}(k_i)^{j_i}}$ is total separation factor of Ru and ^{99}Tc after unloading, $\mathbf{k_i}$ is separation factor during purification method number $\mathbf{i}$, which is applied $\mathbf{j_i}$ times.The optimum burnup can be estimated on the basis of relation $\delta(\mathbf{q},\gamma)$ of parasitic reactions of neutrons capture by $^{100-102}$Ru nuclei to useful reaction of neutrons capture by ^{99}Tc nucleus, where γ is neutron spectrum hardness. The function $\delta(\mathbf{q},\gamma)$ depends on γ poorly into burnup area up to 90%. Increase of $\delta(\mathbf{q},\gamma)$ becomes faster than exponential one after achievement of burnup of about 50 %, when the useful neutrons consumption by a target decreases two times. This fact can be the basis of irradiation stop for target regeneration. The burnup area of more than 90 % deserves attention in case of compound target (possible variant is a liquid target) irradiation with continuous ^{99}Tc loading-unloading. The curvature of $\delta(\mathbf{q},\gamma=\mathbf{const})$ function diagrams is $(d^2\delta/dq^2)/[1+(d\delta/dq)^2]^{3/2}$. It has points of maxima, maximal increase acceleration and maximal increase rate into burnup interval of $\mathbf{q}$=93–98% for spectrum hardness of γ=0.05–0.5. Therefore unloading of compound target part can be carried out after burnup of $\mathbf{q}\approx 95\%$.

Total separation factor $\mathbf{K}$ should be equal $1.7*10^8$ for $\mathbf{q}$=50% and $9*10^6$ for $\mathbf{q}$=95% in case of Ru use without restrictions. This factor can be five times less for Ru application only in nuclear branch. The expected values of separation factors $\mathbf{k_i}$ equal 10^2–10^4 therefore two-four purification cycles are necessary for preparation of commodity Ru. Ru surface β-activity will be lower than the permissible level after one-two purification cycles with $\mathbf{K}\approx 10^5$ for $\mathbf{q}$=50% and $\mathbf{K}\approx 5*10^3$ for $\mathbf{q}$=95%.

The factor $\mathbf{K}$ changes discretely and can equal only certain values. Smooth adjustment of $\mathbf{C_{Tc}}$ can be carried out by change of burnup.

Rhodium and palladium accumulation will be significant after high target burnup. Their relative contents will be equal $\sim 10^{-5}$ and $\sim 2*10^{-3}$ for $\mathbf{q}$=50% and $\mathbf{q}$=95% accordingly at $\gamma=0.05$ and these sizes will be five times less at $\gamma=0.5$. Rhodium and palladium can bond ^{99}Tc by form of triple alloys of Tc-Ru-Rh and Tc-Ru-Pd. The Ru purification factor from these alloys should be into interval of 10^2–10^5 in case of complete inclusion of Rh and Pd in their structure.

The ^{99}Tc transmutation purpose is decrease of its environmental danger 10^2 and more times. Therefore its total relative losses should not be above of 1% in nuclear fuel cycle:

$$\mathbf{W_\Sigma = 1 - q(1-w_0)/[1-(1-q)(1-w)] < 1\%},$$

where $\mathbf{w_0}$ are ^{99}Tc losses at extraction from the fulfilled fuel, $\mathbf{w}$ are losses for one cycle of target regeneration. The aspiration to decrease of $\mathbf{w}$ has sense until $\mathbf{w_0}$ and $\mathbf{W_\Sigma - w_0}$ will be approximately equal in order of size. One target regeneration cycle consists of several Ru purification cycles:

$$\mathbf{w = w_1 + w_2/k_1 + w_3/(k_1*k_2) + \ldots + w_i/\{\prod_{m=1}^{i-1}(k_m)\} + \ldots},$$

where $\mathbf{w_i}$ are relative losses for one Ru purification cycle of number $\mathbf{i}$ ($\mathbf{i}$ is not number of purification methods, therefore situation is possible when $\mathbf{k_{i+1}=k_i}$). As $\mathbf{k_i}>10^2, \mathbf{w_i}<10^{-2}$ the most ^{99}Tc losses occur during application of first purification method amongst used ones: $\mathbf{w\approx w_1}$ with error $<10^{-2}$ %. Hence first purification method should not be based on various volatility of ^{99}Tc and Ru chemical combinations. It is obvious, that $\mathbf{k=w_0/w>1}$ and $\mathbf{w<1\%}$, therefore $\mathbf{W_\Sigma = w(q^{-1}+k-1)}$. The real situation is following: $\mathbf{w}$=0.3–0.5%, $\mathbf{k}$=2–5. Consequently it is necessary that $\mathbf{q}$>50% for $\mathbf{W_\Sigma}$<1%.

The transmutation of about 200 tons of ^{99}Tc, already produced today, to ruthenium would give ~$5–7 milliard (billion). The expenses for realization of transmutation should be included in cost of the nuclear electric power as they are necessary for maintenance of ecological safety of nuclear branch. Then the price of a nuclear ruthenium is the price of its purification and such way of Ru production can compete with ore mining.

PROPERTIES OF TECHNETIUM AND THECHNETIUM-RUTHENIUM ALLOYS FOR TRANSMUTATION OF TECHNETIUM

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Technetium-99 is a long-lived fission product with a half-life of 2.1x10^5 years, which decays by beta-emission with a maximum energy of 293.5 keV. The cumulative yields for ^{99}Tc from thermal neutron fission of ^{235}U and ^{239}Pu are 6.11 and 6.16 %, respectively. In storage of high-level waste (HLW) from nuclear reactors, ^{99}Tc contributes dominantly to the beta radiotoxicity for a very long time. The transmutation of ^{99}Tc to stable ^{100}Ru by a single neutron capture is an attractive option to reduce the long-term risk of the storage of HLW.

We, JAERI, started an experimental study concerning transmutation of Tc. A metal form of Tc was placed in the reliable chemical form of the target to be transmuted, since the irradiation experiment of EFTTRA-T2 in Europe revealed no technical limitations to the use of Tc metal as a target for transmutation. When the target of Tc metal is transmuted, the target will change to Tc-Ru alloy, whose Ru concentration increases with irradiation dose. Although the basic properties of Tc metal and some of its alloys were studied mainly in 1960's and 1970's, the data of Tc metal and Tc-Ru alloys needed for a design of the target and for evaluation of the irradiation behavior of the target are very limited.

To begin with, Tc metal powder purchased for the research on Tc metal and Tc-Ru alloys was analyzed by the inductively coupled plasma-atomic emission spectrometry (ICP-AES) and inductively coupled plasma-mass spectrometry (ICP-MS). The main impurities were found to be iron and aluminum, and the total amount of impurities was about 15 ppm. No impurity nuclide with gamma-emission was found by the gamma-ray spectrometry. The measured X-ray diffraction pattern of the powder was identical with the data of technetium metal reported by Muller et al. The lattice parameters obtained were almost the same as the reported values. The theoretical X-ray density was found to be 11.479 Mg/m^3 when an atomic weight of 98.913 was assumed.

For the characterization of Tc-Ru alloys, five disk-shaped samples of Tc metal, Tc-25%Ru, Tc-50%Ru, Tc-75%Ru and Ru metal were prepared by arc-melting technique. To prepare the samples, the mixed powders of technetium metal and ruthenium metal with the desired compositions were pressed into tablets of 10 mm in diameter and about 3 mm in thickness at room temperature and a pressure of 980 MPa. Each tablet was then arc-melted to form a button on a water-cooled copper hearth in an atmosphere of purified argon. The button was remelted several times to assure homogenization, followed by arc-drop-cast to form a rod of 5 mm in diameter and about 10 mm in length. The rods were cut by a diamond cutter to obtain disks of 5 mm in diameter and 1 mm in thickness. The disks were then annealed at 1573 K for 1 h in vacuum.

The disk samples were analyzed by X-ray diffraction method, using Ni-filtered Cu Kα radiation. Tc and Ru metals are isostructural, having a hexagonal close packed structure (space group $P6_3/mmc$), and form a complete solid solution. The formation of a solid solution with a single phase was confirmed in each sample and the lattice parameters of the a- and c-axes of the samples were obtained. Both the lattice parameters of the a- and c-axes decrease with increasing the Ru concentration, which almost follow Vegard's law. The immersion density of each disk sample measured with methylene iodide was found to be almost the same as the theoretical X-ray density.

The thermal diffusivity was measured on the disk samples from room temperature to about 1200 K by the laser flash method. The thermal diffusivity was determined by the logarithmic method. The thermal conductivity of each Tc-Ru alloy was determined by the measured thermal diffusivity and density, and the reported specific heat capacities of Tc and Ru:

$$\lambda = \alpha C_p \rho, \tag{1}$$

where λ is the thermal conductivity, α the thermal diffusivity, C_p the specific heat capacity and ρ the density of the sample. No specific heat capacity was measured in the present study.

Figure 1 shows the thermal conductivity of the Tc-Ru alloys as a function of temperature. It is noted that the thermal conductivity of Tc metal is smaller than that of Ru metal in the present temperature range. The thermal conductivity of Tc metal in the present experiment shows a minimum around 400 K, above which the thermal conductivity increases with temperature. The thermal conductivity of Ru metal, on the other hand, decreases with increasing temperature. For Tc-25%Ru, Tc-50%Ru and Tc-75%Ru alloys, the thermal conductivity increases with temperature as well as Ru concentration.

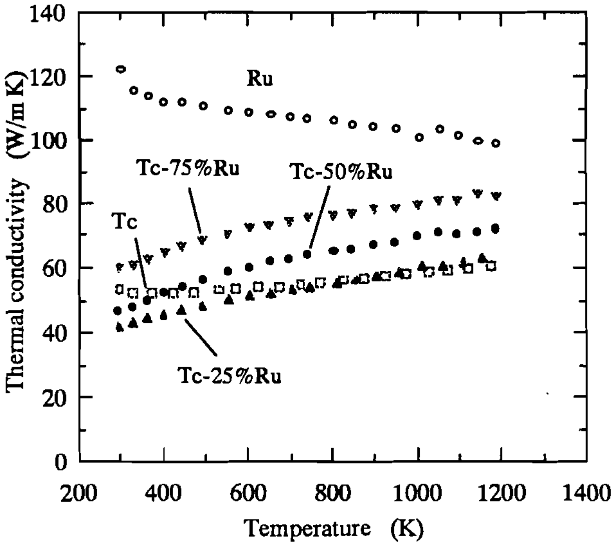

Fig. 1. Thermal conductivity of Tc-Ru alloys.

0110

TECHNETIUM ION CATALYSIS OF SOME HNO_3 OXIDATION REACTIONS

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Of specific theoretical and practical interest is the stability of reductants such as Pu(III) and U(IV) in nitric acid solutions as well as the kinetics and mechanism of the respective reactions of oxidation with HNO_3 in presence of technetium ions as a catalyst.

As a rule, the oxidation of various reductants with HNO_3 in autocatalytically accelerated with HNO_2 formed. For this reason, to stabilize Pu(III) and U(IV) antinitrites are introduced into nitric acid solutions that are promptly react with HNO_2. Hydrazine and its derivatives, hydroxylamine and other nitrogen containing compounds are usually used as antinitrites. However, their stability is substantially reduced if technetium ions are available.

This paper reviews the basic regularities inherent in the technetium ion catalysis of the HNO_3 oxidation of Pu(III), U(IV), hydroxylamine, hydrazine and oxyethylhydrazine.

Table

Kinetic Equations, Rate Constants (k) and Activation Energies (E) of HNO_3 Oxidation Reactions Catalyzed with Tc Ion (at 25°C, μ is ionic strength) [1-6]

Kinetic Equation	μ	k (M,min)	E kJ/M
$-d[Pu(III)]/dt = k [Pu(III)][Tc(VII)][H^+]^{2.3}$	4	$1.61 \cdot 10^{-2}$	27.6
$-d[U(IV)]/dt = k_1[Tc(IV)][H^+]^2[NO_3^-] + k_2[Tc(IV)]$	5	$k_1=4.55 \cdot 10^{-3}$ $k_2=0.074$	115
$-d[NH_2OH]/dt = k[NH_2OH][Tc(VII)]$	4	$2.34 \cdot 10^{-4}$	92.3
$-d[N_2H_4]/dt = k[N_2H_4]^{0.85}[Tc(VII)][H^+]^{1.4}$	2.1	$2.91 \cdot 10^{-2}$	21.8
$-d[HOC_2H_4N_2H_3]/dt = k[HOC_2H_4N_2H_3]^{0.9}[Tc(VII)][H^+]^{1.4}$	3.1	$8.75 \cdot 10^{-3}$	-

As is evidenced by the kinetics studies [1-6] and the data listed in the table all the reactions except for the U(IV) oxidation are of the first order in relation to Tc(VII) and the reductant and of the zero order in relation to HNO_3. These regularities indicate that the reactions are limited by the slow stages of the Tc(VII) – Tc(V) reduction while the re-oxidation of Tc(VI) with HNO_3 proceeds promptly. Hence, the overall schematics of the catalysis can be presented as:

$$Tc(VII) + Red \rightarrow Tc(V) + Ox \quad (1)$$

$$Tc(V) + HNO_3 \rightarrow Tc(VII) + HNO_2 \quad (2)$$

stage (1) being slow and stage (2) being prompt.

As distinct from the above schematics, the oxidation of U(IV) via the main reaction route is described by the first order in relation to Tc and NO_3^- ions, by the second one in relation to H^+ ions and by the zero one in relation to U(IV). This reaction is apparently limited by the stage of the Tc(IV) oxidation with HNO_3.

When discussing the detailed mechanism of the limiting stage (1) one is to focus the attention on the orders of the reactions of Pu(III), hydrazine and oxyethylhydrazine relative to H^+

ions that equal 2.3, 1.4 and 1.4, respectively; hence, Tc(VII) may be assumed to interact with those reductants in the form of TcO_4^- ions and also TcO_3^+ cation that forms according to the reaction of TcO_4^- ion protonation:

$$TcO_4^- + 2H^+ \leftrightarrow TcO_3^+ + H_2O \qquad (3)$$

Hence, the slow stages of these reactions are to be written down as

$$TcO_4^- + Red \rightarrow TcO_4^{2-} + Ox \qquad (4)$$

$$TcO_3^+ + Red + H_2O \rightarrow TcO_4^{2-} + Ox \qquad (5)$$

While the subsequent slow stages of Tc(VI) disproportionation and Tc(V) oxidation with HNO_3 proceed as

$$2TcO_4^{2-} + 2H^+ \rightarrow TcO_3^- + TcO_4^- + H_2O \qquad (6)$$

$$TcO_3^- + HNO_3 \rightarrow TcO_4^- + HNO_2 \qquad (7)$$

The high rates of reactions (6) and (7) are corroborated in the work [7-8].

Since the rate of the Tc(VII) – hydroxylamine interaction is independent of the concentration of H^+-ions this reaction is apparently limited by stage (4) only.

The independence of the U(IV) oxidation rate on its concentration and the observed orders of this reaction relative to Tc, H^+ and NO_3^- ions allow an assumption to be made that at the slow stage Tc(IV) is oxidized with nitronium ions NO_2^+:

$$TcO^{2+} + NO_2^+ \rightarrow TcO^{3+} + NO_2 \qquad (8)$$

that are known to form by the protonation of NO_3^- ions:

$$NO_3^- + 2H^+ \leftrightarrow NO_2^+ + H_2O \qquad (9)$$

The resultant Tc(V) is readily oxidizable to Tc(VII) according to reaction (7) while NO_2 disproportionates

$$2NO_2 + H_2O \leftrightarrow HNO_2 + HNO_3 \qquad (10)$$

As is demonstrated in our other work [6] the oxidation of U(IV) with TcO_4^- ions proceeds at a high rate.

It is easily shown that the given schematics of the Tc ion catalysis of the HNO_3 oxidation reactions comply with the tabulated experimentally found results on the kinetics.

In conclusion it is to be noted that the side route of the Tc(VII) oxidation governed by the rate constant k_1 is likely to be realized via the slow stage of the reproportionation of Tc(V) [2]:

$$TcO_4^- + 2TcO^{2+} + 3H_2O \rightarrow 3TcO_3^- + 6H^+ \qquad (11)$$

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0111

LASER PHOTOACOUSTIC SPECTROSCOPY APPLIED TO A STUDY ON COAGULATION PROCESSES OF Tc(IV) COLLOIDS

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Migration of long-lived fission products and actinides in the environment is of interest from a viewpoint of nuclear waste disposal in deep underground. For technetium, pertechnetate is reduced to Tc(IV) in the chemical form of $TcO(OH)_2$ in neutral solutions under reductive conditions. It is believed that aqueous Tc(IV) species does not migrate in ground water owing to strong absorption properties on clays or minerals. However, little attention has been paid to the formation as well as the coagulation processes of the colloidal technetium species in aqueous solutions and the knowledge is limited.

In this paper, Laser-Induced Photoacoustic Spectroscopy (LPAS), which is known as a sensitive detection method of chemical species in solutions, was applied to the determination of the concentration and size of colloid particles. We applied this technique further observing coagulation of Tc(IV) colloids in aqueous solutions, and a coagulation model was newly developed.

The LPAS system includes a nitrogen gas laser and a dye laser generating monochromatic pulses (500nm, pulse width 10 ns). Photoacoustic signals from colloid particles were detected with piezo-electric transducers (PZT). The signals were amplified and stored in a digital oscilloscope. Mono-dispersed polystyrene latex particles, gold sols and silver sols were used as reference materials to analyze photoacoustic signal intensity of colloid particles differing in materials, size and concentration.

The signal amplitude normalized to the laser power is expressed as

$$I(W,d) = \Gamma \cdot N(d) \cdot Q_{abs}(W,d) \cdot l, \qquad (1)$$

where $I(W,d)$ is the photoacoustic signal intensity from particles with the size d in diameter, $N(d)$ the number of particles in a unit volume of solution, $Q_{abs}(W,d)$ the absorption cross section of light per one particle at a given wave length (W) of the light, l the path length, and Γ a constant given for the present system.

Figure 1 shows an example of intensity change of photoacoustic signals from the gold sols solution prepared by the reduction of auric acid with sodium citrate. As the intensity increased with the reaction time, the average size of the gold sols was enlarged

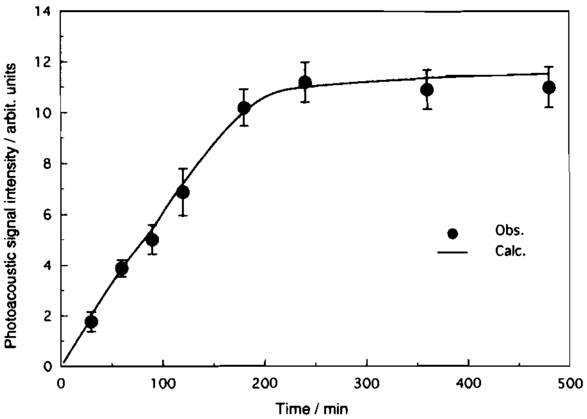

Fig. 1 The photoacoustic signal intensity change of the gold sols depending on the reaction time. The solid line exhibits the calculated intensity using Eq.(1).

from 5 nm at 30 min to 20 nm at 4 h. In the same period, the quantity of gold sols also increased. With $Q_{abs}(W,d)$ calculated from the light scattering theory derived by Mie, Eq.(1) successfully reproduces the experimental values, as shown in Fig.1 (solid line). Equation (1) was also applicable for the cases of silver sols and polystyrene particles.

Technetium(IV) colloids were prepared by reduction of pertechnetate (6 x 10^{-5} mol·dm^{-3}) with Sn(II) at pH 4.4 in acetate buffer solutions. The average size of Tc(IV) colloids was determined by measuring the sedimentation velocity based on the Stokes' law. When the ionic strength of the solution was 10^{-4}, the size of Tc(IV) colloids gradually increased from 200 nm at 7 h to 700 nm at 120 h after addition of Sn(II) to the solution. Ultrafiltration results showed that the amount of Tc(IV) colloids was constant irrespective of the standing time, suggesting that the particles have grown by the coagulation process of small particles. In this period, the intensity of photoacoustic signals monotonously decreased with the standing time as shown in Fig.2, indicating the size change of the colloids. The best fit of Eq.(1) for the Tc(IV) colloids was obtained when the optical constants of the complex index of refraction were assumed to be n = 1.3 and m = 0.6. Thus, the LPAS was a useful tool for analysis of coagulation of colloid particles ranging from a few nm to μm.

The coagulation model was developed to analyze growing processes of Tc(IV) colloids. In this model, the coagulation takes place only in a system composed of the particles with kinetic energy larger than a potential barrier given by the DLVO (Derjaguin-Landau-Verwey-Overbeek) theory . The observed particle size change (Fig.3) was successfully reproduced by the model (solid line), the Maxwell-Boltzmann distribution of the kinetic energy of the particles being taken into account.

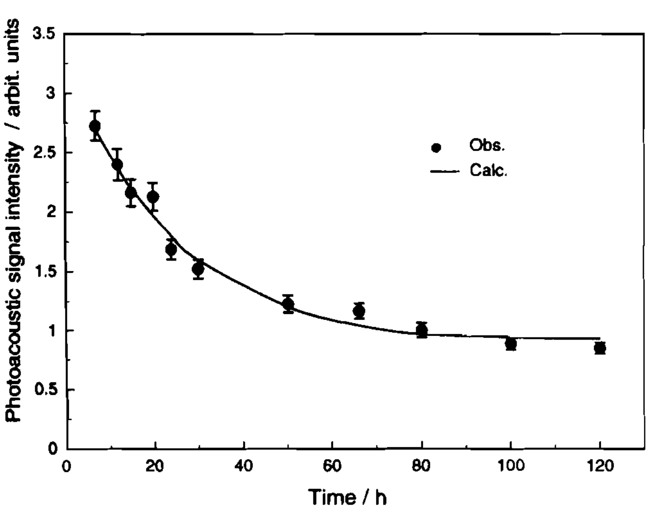

Fig.2 The photoacoustic signal intensity change of the Tc(IV) colloids depending on standing time. The calculated intensity assuming the complex index of refraction of Tc(IV) colloids as n = 1.3 and m = 0.6 is shown as the solid line.

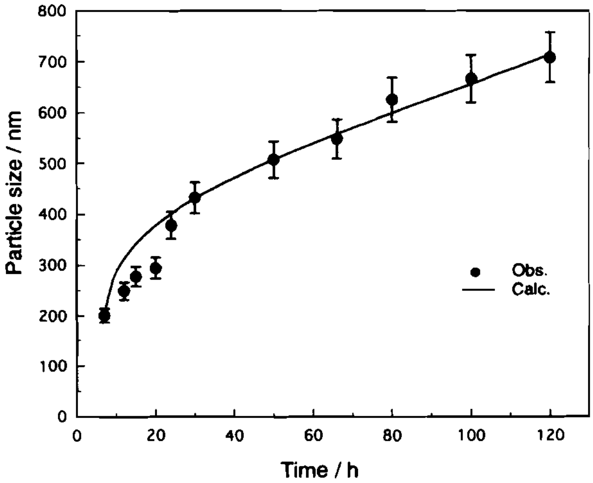

Fig.3 The size change of Tc(IV) colloid particles in aqueous solution (pH 4.4, ionic strength 10^{-4}) against standing time. The solid line is the result calculated based on the coagulation model.

THE ACCELERATION OF U(VI) REDUCTION BY HYDRAZINE IN ALKALINE MEDIA IN PRESENCE OF TECHNETIUM OR SOME TRANSITION ELEMENTS IONS

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The accelerating effect of Tc(VII) ions and some transition metal ions in acide media is well known from literature [1-3]. It was shown also [4] the reduction of Np(V) is accelerated in the presence of Pd(II) in alkaline media. In the previous work (V.F.Peretroukhine, V.I.Silin at al., [5]) it was shown that the reduction of uranium-VI as diuranate up to uranium-IV as hydroxide is significantly accelerated in the presence of $5.0*10^{-5}$ mol/l Tc(VII) and 0.4 mol/l hydrazine in alkaline solutions.

The investigation of accelerating effect of technetium ions Tc(VII) and some transition metal ions Re(VII), Mn(II), Co(II), Pd(II) and Pt(IV) on the reduction of U(VI) by hydrazine in alkaline media (0.25-2.0 mol/l NaOH) has been carried out in this work. The solutions of uranyl chloride UO_2Cl_2 or its peroxo complex $Li_4[UO_2(O_2)_3]$ $(0.25\ -2.5)*10^{-2}$ mol/l were used as stock-solutions in these experiments. The reduction of U(VI) by hydrazine was carried out in the presence of accelerating specie (or in its absence) at 70°C during 1-3 hours. It is proposed, that in a deaerated alkaline solution the Tc(VII) accelerates the reduction of U(VI) to U(IV) in presence of hydrazine through Tc(IV) according to following mechanism:

$$\mathrm{Tc(VII)} + N_2H_4 \rightarrow \mathrm{Tc(IV)} + N_2 + H_2O$$

$$\mathrm{U(VI)} + \mathrm{Tc(IV)} \rightarrow \mathrm{U(V)} + \mathrm{Tc(V)}$$

$$\mathrm{Tc(V)} + N_2H_4 \rightarrow \mathrm{Tc(IV)} + N_2 + H_2O$$

$$2\mathrm{U(V)} \rightarrow \mathrm{U(IV)} + \mathrm{U(IV)}.$$

The transition metals of platinum group carry out cataltic function here.

The precipitate of uranium-IV, -VI hydroxides mixture, after cooling up to room temperature and separation its from liquid phase, was solved in 2.5 ml of HCl acid 1.0 mol/l. The percentages of U(IV) and U(VI) concentrations in such solutions were determined by spectrophotometric and polarographic analysis.

It was found about 50% of U(VI) has been reduced up to U(IV) in presence Pt(IV) in NaOH solution 0.5-1 mol/l and of hydrazine 0.33-0.44 mol/l at these conditions. More than 30% of U(IV) was found when Tc(VII) or Pd(II) is used as cataltic specie. Only about 5% was found when Re(VII) is used. In the same time, Mn(II) and Cd(II) have no effect of acceleration in these conditions of experiment. The reduction of U(VI) is poor in the absence of mentioned above species, besides of hydrazine, in alkaline solution. The percent of reduced U(IV) depends on: a) NaOH concentration, b) the type of uranium stock-solution, c)uranium(VI) concentration in start solution, d) the quantity of introduced hydrazine and e) previous deaeration of a alkaline and a uranium solutions. The best conditions for reduction of U(VI) were found to be as follows: 0.5 mol/l of NaOH concentration in the final solution, deaerated solution of uranyl chloride as stock-solution, 0.025 mol/l of U(VI) in final solution and ≥ 0.44 mol/l of hydrazine solution in the experimental mixture. The catalytic function is decreased in row: Pt >Pd >Tc >Re.

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PHYSICO-CHEMICAL AND CATALYTIC PROPERTIES OF A BIMETALLIC SYSTEM Me-Tc/SUPPORT.

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The state of the surface of supported mono- and bimetallic catalysts Me-Tc/support type (Me=Pt, Pd,Rh, Ru, Ni; support - Al_2O_3, SiO_2, MgO, Y_2O_3, TiO_2) has been investigated by means of the following physico-chemical methods: chemisorption of H_2 and CO, termoprogrammed reduction, optical spectra, IR-spectra of adsorbed CO, electron microscopy, microdiffraction of electrons.

The decreasing of chemisorption ability for CO for the samples there two metals states on the surface in the same time with comparison for monometallic catalysts has been established.

By means of termoprogrammed reduction we can see that temperatures of decomposition of supported on the carrier compounds in bimetallic catalysts are distinguished for that for monometallic samples. This fact indicates the appearing of the new surface compounds.

The data of diffuse reflectance spectra helped us to observe the ionic forms of the supported metals and cluster compounds Me_xTc_y type on the surface of bimetallic catalysts.

The studies of IR-spectra of adsorbed carbon monoxide confirmed the supposition about the interaction between the metals on the surface of a carrier. Thus the new band in spectrum of bimetallic samples may be attribute to carbon monooxide adsorbed on the complex Me_xTc_y.

Phase analysis of mono- and bimetallic catalysts carried out according to the microdiffraction of electrons on electron microscope also indicated the presence of compounds of Me-Te type on the surface. Most probably that the interactions between two metals take place that on ions of Tc stabilisated on octahedral and tetrahedral vacancies on the support.

The catalytic activity of Me-Tc- and Tc-catalysts in process of hydrogenation of acetone has been investigated. The phenomenon of nonadditive increasing of the catalytic activity of bimetallic catalysts in comparison with monometallic systems has been observed. The comparison of physico-chemical and catalytic properties followed for our samples allowed to make the conclusion that the synergistic effect observed connected with the formation of the new high active bimetallic clusters Me_xTc_y.

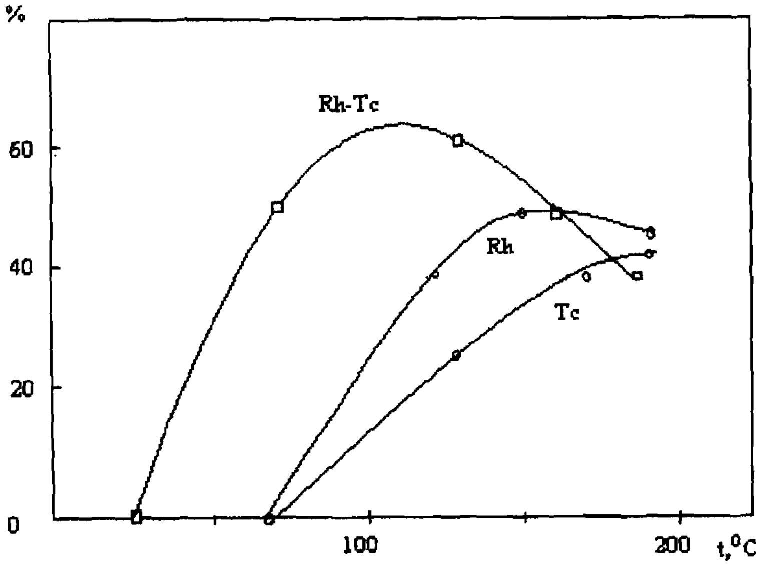

Fig. 1. Effect of synergism on Rh-Tc/Al_2O_3.

Inter influence of metals on electron station of each other lead to changes of effective charge on cluster. As a result of the donorno-aception interrecsion between two metals the vacant-non saturated lobil complexes with less enarge bond reagent-metal is formed, that is a reason of synergistic effect.

0114

THE EFFECT OF SUPPORT ON CATALYTIC PROPERTIES OF TC IN THE REACTIONS OF DIFFERENT TYPES

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It is known that Tc deposited on support is an active catalyst in the reactions of different types. The role of the support is specific for each reaction.

The results of physico-chemical studies of Tc catalysts by methods of IR spectroscopy of adsorbed CO and thermoprogrammed desorption (TPD) are presented in this paper. The activity of Tc contacts are compared for reactions of dehydrogenation of cyclic hydrocarbons and hydrogenation of monocarbon molecules (carbon monoxide, carbon dioxide).

IR spectra of adsorbed CO depends on electronic states of adsorption centres. The adsorption bands (a.b.) 1955 and 2055, 1948 and 2053 sm^{-1} appear for Tc/Al_2O_3 and Tc/Y_2O_3 accordenly. Spectra of CO adsorpted on Tc/MgO contains five bands: 2080, 2043, 1950, 1905, 1855 sm^{-1}. A.b. 2000 - 2100 sm^{-1} are assigned to linear carbonyl forms, 1950 - to bridging forms, 1905 and 1855 - to multicentre adsorption. The increasing number bands indicates on appearing of additional adsorption centres. The catalytic activity of Tc contacts in the dehydrogenation of hydrocarbons increases with increasing of number of adsoption centres. Tc/MgO is the most active catalyst (Fig.1). The corelation between the number of adsoption centres and active centres of catalytic reactions exists.

The rule in the hydrogenation of CO is changed (Fig.2). TPD measurements (at 1 MPa) showes that the number of peaks cnanges with adsorption temperature: at $t_{ads} \sim t_{room}$ only one type of CO was observed, whereas at $t_{ads} > 100^{\circ}C$ a high-temperature form of CO adsorption appeard. Thus the adsorption has an activated character. The products reaction yields (CH_4 and CO_2) increase in the temperature region in which the content of strongly bound CO is higher. Part of adsorption centres is not active in hydrogenation of CO. The contacts containing the additional adsorption centres - Tc/MgO, Tc/Y_2O_3 are the least active.

Thus Tc/support is complex system with nonhomogeneous surface containing different adsoption centres. The extent of participation these centres in catalytic reaction differs.

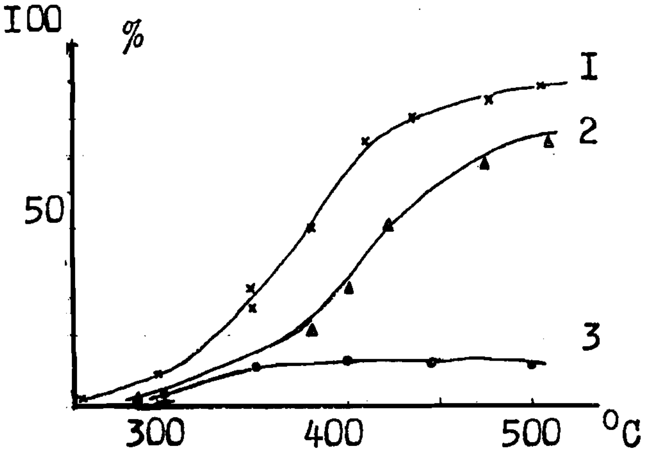

Fig.1 Conversion of cyclohexane on Tc/support(1-MgO, 2- Y_2O_3, 3- Al_2O_3)

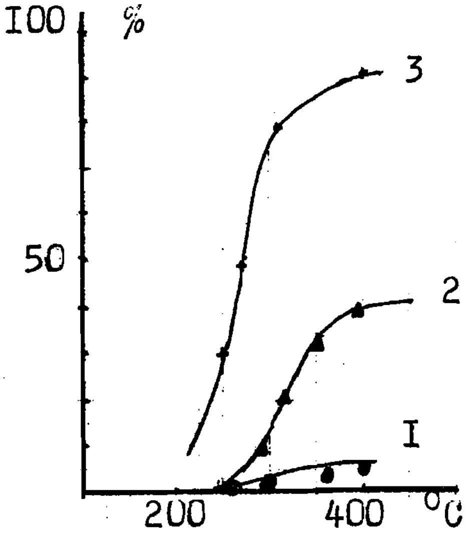

Fig.2 Conversion of CO on Tc/support(1-MgO, 2- Y_2O_3, 3- Al_2O_3)

0115

EFFECT OF CHEMICAL MATRIX ON ^{99m}Tc DECAY CONSTANT

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The decay constant λ of the atomic nuclei with low-energy transitions slightly depends on the chemical state of atoms due to the change in the atomic electron wave functions. For instance, λ of ^{99m}Tc with isomeric transition energy 2.1 keV in the matrix of metallic technetium is lower than in pertechnetate ion by some tenths of percent [1, 2]. The most substantial change in the atomic electron wave function is usually related to the change in the oxidation state of the atom. In this work, we intended to study the correlation between λ and an oxidation state of ^{99m}Tc. It is follows from calculations [3] that that internal conversion coefficients (ICC) of technetium electronic subshells increase with increasing ionization state of Tc atom in the series 0, 3+, 5+, and 7+. Based on these results, we can expect an increase in λ with increasing the ^{99m}Tc oxidation state from Tc^0 to Tc^{VII}. The experimental data reported are insufficient to test this assumption [1, 2]. To study the correlation between λ and the oxidation state of ^{99m}Tc, we measured λ for $Tc^{VII}O_4^-$, Tc^{IV} chloride, and $Tc^I(CO)_3Cl$ in aqueous solutions and for solid solutions of Tc^0 in metallic copper, silver, and gold. In these measurements , special attention was paid to various corrections for counting rate, particularly, dead time of counter. The results are presented in table.

Tc matrix	$T_{1/2}$, h	$\delta\lambda_{exp}$, %
TcO_4^- aq. sln.	6.001±0.003	
$TcCl_4$ aq. sln	6.014±0.003	0.22±0.06
$Tc(CO)_3Cl$ aq. sln.	6.020±0.003	0.32±0.06
Tc in Cu metal	6.032±0.004	0.30±0.09
Tc in Ag metal	6.028±0.004	0.25±0.06
Tc in Au metal	6.032±0.004	0.32±0.06

As seen, the trend in increasing of $T_{1/2}$ (decreasing of λ) in the series from Tc^{VII} to Tc^{0i} is observed.

It is interesting to compare the range of λ_{exp} variation as a function Tc oxidation state obtained in our experiments with the range of variation of λ calculated for Tc ionization series. We estimated λ_{calc} by summation of the absolute ICC values for their partial electon subshells listed in [3] and calculated $\delta\lambda$ referred to λ^0_{calc} of Tc(0). The value of λ for $Tc(CO)_3Cl$ was taken as λ^0_{exp} taking into account the problems of determination of Tc valence state in the metals. The results of the comparison that λ_{calc} for technetium ions are substantially (by a half order magnitude) greater than $\delta\lambda_{exp}$ for the correspondent technetium oxidation states. These results can indicate that the real charges which are localized on Tc atom in its chemical compounds are substentially lower than formal charges and correspond to a high degree of the covalent character of the chemical bond in the above technetium compounds

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HALF-LIVES OF TECHNETIUM 97, 98

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According to Table of Isotopes (8th ed.), the half-lives of ^{97}Tc and ^{98}Tc are $(2.6 \pm 0.4) \times 10^6$y and $(4.2 \pm 0.3) \times 10^6$y, respectively. Katcoff measured the half-live of ^{97}Tc in 1958. The half-live of ^{98}Tc was measured by Geoking for his MS thesis work and reported to the Nuclear Data compiler by O'Kelly, in 1973.

As some people still claim from time to time that primordial Tc is present on this planet, we have decided to re-determine the half-lives of ^{97}Tc and ^{98}Tc by use of currently available advanced radiation detectors and an ICP mass spectrometer.

Technetium97: ^{97}Tc sources were prepared by the reaction of ^{95}Mo(α, 2n)^{97}Ru using an enriched ^{95}Mo metal as a target. The EC decay branching of ^{97}Ru to ^{97}Tc was newly determined. The radioactivity of ^{97}Tc was measured by observing Mo and Tc KX-rays by a high resolution Si(Li) detector. The determination was made both by the comparative way used by Katctoff and by the direct way using low-energy gamma-ray standards. The number of atoms of ^{97}Tc in the source sample was determined by two different methods. One is from the parental relationship between ^{97}Ru and ^{97}Tc as used by Katcoff and the other is a direct measurement of the number of atoms by the isotope dilution method using ^{99}Tc as a spike and an ICP-MS as a mass spectrometer. The proposed half-live is $(4.21 \pm 0.16) \times 10^6$y. The half live of ^{97m}Tc and the EC decay branching ratio of ^{97m}Tc to ^{97}Mo were determined to be (91.4 ± 0.8)d and (3.94 ± 0.18)%, respectively. The EC decay branching ratio of ^{97}Ru to ^{97m}Tc was also re-determined to be $(1.71 \pm 0.02) \times 10^{-4}$.

Technetium98: ^{98}Tc sources were prepared by the ^{97}Mo(d, n) reaction using enriched ^{97}Mo targets. The decay characteristic of ^{98}Tc was studied and found that the EC/β ratio was less than 0.037 and the photon abundance of the 652 keV and 745 keV gamma-rays could be approximated as 100% per decay of ^{98}Tc. The number of atoms of ^{98}Tc was determined by isotope dilution method using ^{99}Tc as a spike and an ICP-MS as a mass spectrometer. Our preliminary half-live for ^{98}Tc is $(6.6 \pm 1.0) \times 10^6$y. Our new determinations of half lives of Tc-97 and 98 reconfirms that there can not be any primordial Tc present, on the earth and that the Tc present in terrestrial ores must have been produced by spontaneous fission of ^{238}U as reported by Kenna and Kuroda in 1961.

0117

RE-EVALUATION OF OGAWA'S 'NIPPONIUM' AS THE ELEMENT 75 (RHENIUM) INSTEAD OF 43 (TECHNETIUM)

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In the history of discovery of elements, technetium (Z=43) looks a specific case because of its difficulty to attain to the true goal. The name of this element was temporally called ilmenium (1846, Hermann), davyium (1877, Kern), lucium (1896, Barriere), nipponium (1908, Ogawa) and masurium (1925, Noddack et al.). All of the cited works had not been justified. At last, Perrier and Segré found the element among radioactive ones in 1937. They named it technetium later when the element was produced in a large scale in a nuclear reactor, and any doubt with its presence was swept out.

In this presentation, I would like to discuss that in the name of nipponium, Ogawa found rhenium (Z=75) instead of the element 43 and purified it in the metallic form. There was spectroscopically unquestionable evidence in his work.

Ogawa's work on nipponium

A Japanese chemist Masataka Ogawa went to England to study at University College, London under the supervision of William Ramsay in 1904. Ramsay received the 4th Nobel prize for chemistry for his great contribution of discovery of rare gases in 1904. Ramsay gave him thorianite, that was a curious mineral found at Ceylon Island, for the search of new elements. Ogawa worked very hard and finally he found an unknown component which emitted a new spectral line of 4882 Å in thorianite. Then, he separated the element with classical chemical procedures and determined its atomic weight as 100 which was just between those of molybdenum and ruthenium. The element (corresponding to Z = 43) was named nipponium after strong recommendation of Ramsay. The result was published in 1908, and nipponium was accepted in the Lohring's periodic table in 1909.

However, the nipponium was subjected to various criticism by other chemists and forgotten for many years without correct evaluation with its true entity.

Recent re-evaluation of nipponium

Ogawa put his new element at the position under manganese in the periodic table according to the atomic weight of 100. However, his atomic weight calculation was based on the false assumption that nipponium was a metallic element with valency 2. His observation of spectral line of 4882 ± 10 Å indicates that nipponium is spectroscopically rhenium which emits a line of 4889 Å. None of other metallic elements emits such a spectral line. When nipponium is replaced by rhenium, what happens ? Valency 2 is quite unstable in the ordinary conditions. Ogawa's chlorination procedure leads to the formation oxychloride of the element with valency 6. Therefore his atomic weight calculation should be revised.

Ogawa's neglected work showed that he found a new element the same as rhenium. In 1996 when I was invited at the International Symposium "Discovery of Elements", I re-evaluated Ogawa's work in what extent he was correct. Except for atomic weight calculation, he did nice experiments in which no essential faults were found.

My re-evaluation on Ogawa's nipponium work is summarized in the table. The table shows that nipponium is rhenium itself. Ogawa's work was done 17 years before Noddack and his coworker recognized rhenium in 1925.

Table Comparison of nipponium with rhenium

	nipponium	rhenium
Spectral line	4882 ± 10 Å	4889 Å
Atomic weight	185.2 *	186.2
Occurrence	rich in molybdenite	concentrated in molybdenite
Chemical properties	hydroxide, oxide and sulphide are similar in both cases	

* recalculated

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