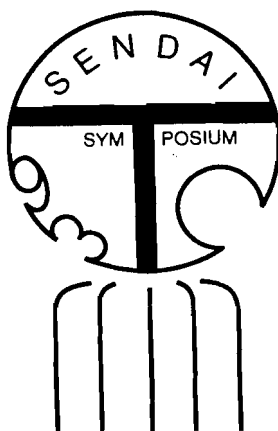


Topical Symposium on the Behavior and Utilization of Technetium '93

March 18 - 20, 1993

Sendai, Japan



Hosted by :

Faculty of Science, Tohoku University

Supported by :

Chemical Society of Japan

Atomic Energy Society of Japan

ACKNOWLEDGEMENT

This Tc '93 Symposium is financially supported by :

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Secretary

Dr. Tsutomu Sekine

Dr. Harumi Kaji

SOCIAL PROGRAM

Getting together :

March 17 (Wed) 18:00 - 20:00
Sendai International Center 3F
Conference Room Shirakashi II

Banquet :

March 19 (Fri) 17:30 - 19:30
Sendai Washington Hotel II 2F
Rainbow Hall

Excursion :

March 21 (Sun) 9:00 - 15:00
Matsushima Area (a famous sight-seeing
area with picturesque pine islands and old
temples)

Outline of Program (Symposium site : **Sendai Museum Hall** except otherwise indicated)

	March 17 (Wed)	March 18 (Thu)	March 19 (Fri)	March 20 (Sat)	March 21 (Sun)
9:00					
10:00		Registration	2-I-1 V.F.Peretrukhin	3-I-1 R.Alberto	
		Opening	2-I-2 K.G.Bukov	3-I-2 M.S.Grigoriev	
11:00		1-I-1 K.H.Lieser	Break	Break	
		1-I-2 P.K.Kuroda	2-I-3 M.Kubota	3-I-3 E.Deutsch	
12:00		1-I-3 E.Holm	2-O-4 M.Takeuchi	3-I-4 W.R.Heineman	
			2-O-5 K.Ito	3-O-5 X.Wang	
13:00		Lunch	Lunch	Lunch	
		1-I-4 N.Trautmann	2-I-7 K.Schwochau	3-I-6 W.A.Volkert	
14:00		1-I-5 J.A.Rard	2-O-8 B.Johannsen	3-O-7 B.Liu	
		1-I-6 L.Lakosi	2-O-9 J.Baldas	3-O-8 T.W.Jackson	
15:00		Break	2-O-10 T.I.A.Gerber	3-I-9 T.Isawa	
		1-O-7 T.Kobayashi	Break	Break	
16:00	Registration	1-O-8 H.Hidaka	2-I-11 S.V.Kryutckov	3-I-10 H.Matsuda	
		1-I-9 A.A.Zakharov	Award Ceremony	3-I-11 M.Hazue	
17:00	Sendai International Center	Break	2-I-12 U.Abram	Closing	
18:00		Poster Session	Banquet		
19:00	Getting together	Sendai International Center	Sendai Washington Hotel II		
20:00	Sendai International Center				

PROGRAM

(The indicated time interval for oral presentation contains 4 min discussion + 1 min chairperson's reservation.)

March 18 (Thu.), 1993

9:15~10:00 **Registration** (Sendai Museum Hall)

10:00~10:15 **Opening** (Sendai Museum Hall)

1-I-1 (Invited) Technetium in the Nuclear Fuel Cycle, in Medicine and in the Environment
(10:15~10:40) K.H.Lieser (Dept. Chem. Eduard-Zintl-Institut, Tech. Univ. Darmstadt, Germany)

1-I-2 (Invited) Technetium in Nature and Age of the Solar System
(10:40~11:20) P.K.Kuroda (Las Vegas, USA)

1-I-3 (Invited) Radioanalytical Studies of Tc in the Environment : Progress and Problems
(11:20~12:00) E.Holm (Dept. Radiat. Phys., Lund Univ., Sweden)

12:00~13:10 **Lunch**

1-I-4 (Invited) Ultratrace Analysis of Technetium
(13:10~13:50) N.Trautmann (Inst. Nucl. Chem., Mainz Univ., Germany)

1-I-5 (Invited) Current Status of Chemical Thermodynamic Measurements for Technetium
(13:50~14:20) and Its Inorganic Compounds and Aqueous Species
J.A.Rard (Phys. Dept., LLNL, Univ. of California, USA)

1-I-6 (Invited) Photonuclear Reactions on ^{99}Tc , Isomer Excitation and Deexcitation,
(14:20~14:50) Astrophysical Implications
L.Lakosi (Inst. Isot. Hung. Acad. Sci., Hungary)

14:50~15:05 **Break**

1-O-7 Half-Life of Technetium 97,98
(15:05~15:25) T.Kobayashi, K.Sueki, M.Ebihara, H.Nakahara,
M.Imamura, A.Masuda (School of Hygienic Sci., Kitasato Univ., Japan)

1-O-8 Geochemical Behaviour of ^{99}Tc in the Oklo Natural Reactor
(15:25~15:45) H.Hidaka, K.Shinotsuka, P.Holliger (Dept. Chem., Fac. Sci., Tokyo
Metropolitan Univ., Japan)

1-I-9 (Invited) Superconducting and Normal Properties of Tc and Tc-Mo Alloys
(15:45~16:15) A.A.Zakharov (Dept. Supercondct. Sol. State Phys., Inst. At. Energy,
Russia)

16:15~17:10 **Break**

17:10~19:30 **Poster Session** (Sendai International Center)

March 19 (Fri.) (Sendai Museum Hall)

2-I-1 (Invited) Technetium-99 : Investigations and Russian Experience of Application
(9:15~9:45) V.F.Peretrukhin (Inst. Phys. Chem., Russian Acad. Sci., Russia)

2-I-2 (Invited) Some Aspects of Physical Metallurgy of Technetium
(9:45~10:15) K.G.Bukov (Inst. Phys. Chem., Russian Acad. Sci., Russia)

10:15~10:30 **Break**

2-I-3 (Invited) Recovery of Technetium from High-Level Liquid Waste Generated in Nuclear
(10:30~11:00) Fuel Reprocessing
M.Kubota (Dept. Fuel Safety Res., JAERI, Japan)

2-O-4 Solvent Extraction of Tc(VII) and Re(VII) from Nitric Acid Solution with
(11:00~11:20) CMPO/TBP
M.Takeuchi, S.Tanaka, M.Yamawaki (Nucl. Eng. Res. Lab., Univ.
Tokyo, Japan)

2-O-5 Extraction of Technetium(VII) in Hydrofluoric Acid System by Primary
(11:20~11:40) Amine - n-Heptane Solution
K.Ito (Inst. Adv. Mat. Processing, Tohoku Univ., Japan)

2-O-6 Volatilization of Tc(VII) from Simulated Reprocessing Solutions
(11:40~12:00) T.Hoshikawa, A.Sasahira, T.Nakamura, T.Fukasawa, F.Kawamura
(Energy Res. Lab., Hitachi Ltd., Japan)

12:00~13:10

Lunch

- 2-I-7 (Invited) Basic Coordination Chemistry of Technetium
(13:10~13:50) *K.Schwochau (Inst. Nucl. Chem., Res. Center Jülich, Germany)*
- 2-O-8 Technetium Complexes with Thioether Ligands
(13:50~14:10) *B.Johannsen, H.J.Pietzsch, H.Spies, P.Leibnitz,
G.Reck (Inst. Bioinorg. Radiopharm. Chem., Res. Center Rossendorf,
Germany)*
- 2-O-9 Monomer, μ -oxo Dimer, Di(μ -oxo) Dimer Interconversion of
(14:10~14:30) Nitridotechnetium(VI) Complexes in Acid Solution
*J.Baldas, J.F.Boas, S.F.Colmanet, Z.Ivanov, G.A.Williams
(Aust. Radiat. Lab., Australia)*
- 2-O-10 Novel Technetium and Rhenium Complexes with Multidentate Nitrogen
(14:30~14:50) Donor Ligands
*T.I.A.Gerber, H.J.Kemp, J G H du Preez, G.Bandoli (Dept. Chem., Univ.
Port Elizabeth, South Africa)*

14:50~15:05

Break

- 2-I-11 (Invited) Multiple Technetium-Technetium Bonds
(15:05~15:35) *S.V.Kryutchkov (Inst. Phys. Chem., Russian Acad. Sci., Russia)*

15:35~15:45

Award Ceremony

- 2-I-12 (Invited) EPR Spectroscopy of Technetium Compounds
(15:45~16:15) *U.Abram, R.Kirmse (Inst. Inorg. Chem., Univ. Tübingen, Germany)*

16:15~17:30

Break

17:30~19:30

Banquet (Sendai Washington Hotel II)

March 20 (Sat.) (Sendai Museum Hall)

- 3-I-1 (Invited) New Organometallic Complexes of Technetium in Its High and Low
(9:15~9:45) Oxidation States
R.Alberto (Paul Scherrer Inst., Switzerland)

3-I-2 (Invited) Structure and Physicochemical Properties of New Technetium Complexes
(9:45~10:15) M.S.Grigoriev, S.V.Kryutchkov (*Inst. Phys. Chem., Russian Acad. Sci., Russia*)

10:15~10:30 **Break**

3-I-3 (Invited) Aspects of the Chemistry of Technetium Phosphine Complexes
(10:30~11:10) E.Deutsch (*Mallinckrodt Med. Inc., St Louis, USA*)

3-I-4 (Invited) Chemical Sensors for Radiopharmaceutical Imaging Agents
(11:10~11:50) W.R.Heineman, B.H.Swaile, E.A.Blubaugh, D.A.Landis,
 C.J.Seliskar, E.Deutsch (*Dept. Chem., Univ. Cincinnati, USA*)

3-O-5 o-Tolueneboronic Acid Adducts of Technetium Tris(DMG): Synthesis,
(11:50~12:10) Structure Analysis and Characterization
 X.Wang, H.Li, Q.Yang, W.Zhou, Y.Wu, Y.Liu (*Dept. Tech. Phys., Peking Univ., China*)

12:10~13:10 **Lunch**

3-I-6 (Invited) The Design and Properties of ^{99m}Tc Chelates for Brain Perfusion Imaging
(13:10~13:50) W.A.Volkert (*Dept. Radiol., School of Med., Univ. Missouri-Columbia, USA*)

3-O-7 Stability of Isomers of ^{99m}Tc-HMPAO and Complex of ^{99m}Tc-CBPAO
(13:50~14:10) Based on CNDO/2 Method
 B.Liu, Z.Meng (*Dept. Chem., Beijing Normal Univ., China*)

3-O-8 The Chemistry and Physical Properties of Lipophilic
(14:10~14:30) Rhenium Di Amino Di Thiol Complexes
 T.W.Jackson, M.Kojima, R.M.Lambrecht (*Biomed. Health Prog., ANSTO, Australia*)

3-I-9 (Invited) Use of Technetium-99m in Pulmonary Nuclear Medicine
(14:30~15:00) T.Isawa (*Dept. Med., Res. Inst. Chest Diseases and Canc., Tohoku Univ., Japan*)

15:00~15:15 **Break**

3-I-10 (Invited) The Clinical Utility of Brain Perfusion SPECT Using Tc-99m HMPAO
(15:15~15:40) H.Matsuda, K.Hisada (*Div. Radiol. Nucl. Med. Nat'l. Center Hospital, NCNP, Japan*)

3-I-11 (Invited) Current Status and Trend in Demand of Tc-99m Radiopharmaceuticals in Japan
(15:40~16:05) Japan
 M.Hazue (*Nihon Medi-Physics Co.,Ltd., Japan*)

16:05~16:15 **Closing**

Poster Session (Sendai International Center) (17:10 ~ 19:30)

- 1-P-1 (n,n') Production of ^{99m}Tc by ^{252}Cf Fission Neutrons
J.Sáfár (*Inst. Isot. Hung. Acad. Sci., Hungary*)
- 1-P-2 Integral Cross Section of the $^{99}\text{Tc}(\gamma,\gamma')^{99m}\text{Tc}$ Reaction at 4 MeV
J.Sáfár, L.Lakosi, I.Pavlicsek, Á.Verés, T.Sekine, K.Yoshihara (*Inst. Isot. Hung. Acad. Sci., Hungary*)
- 1-P-3 ^{95}Tc and ^{96}Tc Production by (γ, xn) Reactions
T.Sekine, K.Yoshihara, J.Sáfár, L.Lakosi, Á.Verés (*Inst. Isot. Hung. Acad. Sci., Hungary*)
- 1-P-4 Nuclear Reactions of ^{99}Tc with Fission Neutrons
I.Yamagishi, M.Kubota, T.Sekine, K.Yoshihara (*Dept. Fuel Safety Res., JAERI, Japan*)
- 1-P-5 Determination of Technetium-99 in Environmental Samples by Inductively Coupled Plasma Mass Spectrometry
S.Morita, K.Tobita, M.Kurabayashi (*Envir. Prot. Sec., Health and Safety Div., Power React. Nucl. Fuel Devel. Corp., Japan*)
- 1-P-6 Analytical Procedure for Technetium-99 in Seawater by ICP-MS
N.Momoshima, M.Sayad, Y.Takashima (*Dept. Chem., Fac. Sci., Kyusyu Univ., Japan*)
- 1-P-7 Separation Procedure for Determination of Technetium-99 in Soil by ICP-MS
K.Tagami, S.Uchida (*Div. Radioecol., Nat'l. Inst. Radiol. Sci., Nakaminato, Japan*)
- 1-P-8 Concentration of Technetium-99 in Marine Algae and Seawater
S.Hirano, M.Matsuba (*Div. Mar. Radioecol., Nat'l. Inst. Radiol., Nakaminato, Japan*)

- 1-P-9 Transfer Factors of Technetium from Soil to Vegetables
K.Yanagisawa, Y.Muramatsu (Lab. Radioecol., Nat'l. Inst. Radiol.,
 Nakaminato, Japan)
- 1-P-10 Complexation of Technetium with Humic Acid
T.Sekine, A.Watanabe, K.Yoshihara, J.I.Kim (Dept. Chem., Fac. Sci.,
 Tohoku Univ., Japan)
- 1-P-11 Determination of Technetium by Laser Induced Photoacoustic Spectroscopy
 Coupled with a Wave-Length Shifter Method
T.Fujita, T.Sekine, H.Hiraga, A.Mutalib, K.Yoshihara, R.Alberto, J.I.Kim
 (Dept. Chem., Fac. Sci., Tohoku Univ., Japan)
- 1-P-12 The Method for Technetium-99(Tc-99) Analysis and Its Application to Human
 Tissues
Y.Takizawa, S.Gao, K.Komura (Dept. Pub. Health, Akita Univ., Japan)
- 1-P-13 Transport of Tc and Re through a Supported Liquid Membrane
S.Ambe, Y.Ohkubo, Y.Kobayashi, M.Iwamoto, M.Yanokura, H.Maeda,
F.Ambe (Inst. Phys. Chem. Res.(RIKEN), Japan)
- 1-P-14 Sensitivity Enhancement of PVC Membrane Based Perrhenate Ion-Selective
 Electrode by Attaching Anionic Polyelectrolyte Solution Layer
T.Imato, Y.Nakamura (Dept. Chem. Sci. Technol., Fac. Eng.,
 Kyusyu Univ., Japan)
- 1-P-15 Adsorption Mechanism of Pertechetate on Anion Exchange Resin
M.Kawasaki, T.Omori, K.Hasegawa (Radiochem. Res. Lab., Shizuoka
 Univ., Japan)
- 1-P-16 Adsorption Behavior of Oxyanions (MO_4^- , M = Tc, Re, Cl) on Non-Ionic
 Macro-Reticular Copolymer and Activated Carbon Fiber
S.Shibata, J.Uno, M.Abe, K.Watari (Nat'l. Inst. Radiol. Sci., Chiba,
 Japan)
- 1-P-17 Solubility, Speciation and Cycling of Tc in Natural Waters up to 300 °C
I.Puigdomenech, J.Bruno (MBT Tecnologia Ambiental, Spain)
- 1-P-18 Characterization of Interaction of Technetium(VII) with Uranium(IV)
 in Solutions of Mineral Acids
T.V.Gomonova, V.S.Koltunov (A.A.Bochvar AUSRI Inorg. Mat., Russia)

- 1-P-19 Specific Features of Kinetics and Mechanism of Reduction of Rhenium(VII) by Tin(II)
V.S.Koltunov, T.V.Gomonova (A.A.Bochvar AUSRI Inorg. Mat., Russia)
- 1-P-20 Behavior of Technetium-Cyclopentadienyl Complexes in Nuclear Recoil in γ -Irradiated Ruthenocene and Its β -Cyclodextrin Inclusion Compound
H.Matsue, T.Sekine, K.Yoshihara (Dept. Chem., Fac. Sci., Tohoku Univ., Japan)
- 1-P-21 Recoil Behaviours of Central Metal Aoms in Tris-bipyridineruthenium(III) Chloride
N.Ikeda, Y.Watanabe, H.Shoji (Dept. Chem., Univ. Tsukuba, Japan)
- 1-P-22 Re(V) and Re(VII) Complexes of Tetrakis(Pyrazol-1-YL)Borate
J.Marcalo, A.Paulo, L.Santos (Dept. Chem., LNETI, Portugal)
- 1-P-23 Investigation of Phase Transitions and Some Other Physico-Chemical Properties of Pertechnetates and Perrhenates
K.E.German, L.N.Grushevskaya, S.V.Kryutchkov, V.Pustovalov, V.Obruchikov (Inst. Phys. Chem. Acad. Sci., Russia)
- 1-P-24 Technetium and Rhenium Oxo and Halogenide Complexes with Ferricinium Cations
B.G.Antipov, V.N.Gerasimov, M.S.Grigoriev, P.E.Kazin, V.V.Kharitonov, S.V.Kryutchkov, V.G.Maksimov, V.S.Moisa, V.V.Sergeev, T.K.Yurik (Inst. Phys. Chem. Acad. Sci., Russia)
- 1-P-25 The Synthesis of $TcNCl_3$; New Approaches to $TcNCl_4^-$
U.Abram, R.Wollert (Inst. Inorg. Chem., Univ. Tübingen; Germany)
- 1-P-26 The Synthesis of New Tc(IV) Complexes from $TcCl_4$
U.Abram, R.Wollert, W.Hiller (Inst. Inorg. Chem., Univ. Tübingen, Germany)
- 1-P-27 Preparation and Evaluation of Cationic, Low Oxidation State Technetium o-Phenanthroline Complexes
K.H.Linse, C.Kremer, Z.F.Su, K.Schwochau (Inst. Nucl. Chem., Res. Center Jülich, Germany)
- 1-P-28 Reactions of Technetium(III)-Thiourea Derivative Complexes with Pyrimidine Derivatives
K.Hashimoto, H.Kudo, T.Omori, K.Yoshihara (JAERI, Japan)

- 1-P-29 Formation of Tc(III) Complexes with Polyaminopolycarboxylic Acid
M.Hashimoto, H.Wada, T.Omori, K.Yoshihara (JAERI, Japan)
- 1-P-30 Synthesis and Characterization of Technetium(V) Nitrido Core β -Diketone Complexes
A.Mutalib, T.Sekine, T.Omori, K.Yoshihara (Dept. Chem., Fac. Sci., Tohoku Univ., Japan)
- 1-P-31 Preparation of ^{99m}Tc Nitrido β -Diketone Radiopharmaceuticals
A.Mutalib, T.Sekine, T.Omori, K.Yoshihara (Dept. Chem., Fac. Sci., Tohoku Univ., Japan)
- 1-P-32 Occurrence and Nature of Different Tc(V) and Re(V) Complexes with Mercapto/Amide Ligands
B.Johannsen, B.Noll, P.Leibnitz, G.Reck, St.Noll, H.Spies (Inst. Bioinorg. Radiopharm. Chem., Res. Center Rossendorf, Germany)
- 1-P-33 Unusual Isomerization of Tc and Re-DMSA Complexes
S.Seifert, H.Spies, B.Johannsen, H.J.Pietzsch (Inst. Bioinorg. Radiopharm. Chem., Res. Center Rossendorf, Germany)
- 1-P-34 Technetium(III) Complexes with Tetradentate Thioether Ligands : Preparation and Preliminary Biological Evaluation
H.J.Pietzsch, S.Seifert, R.Syhre, H.Spies, B.Johannsen (Inst. Bioinorg. Radiopharm. Chem., Res. Center Rossendorf, Germany)
- 1-P-35 High Performance Ion Exchange Chromatography of ^{99m}Tc Labeled Human Serum Albumin Using a Macromolecular Sn(II) Complex
K.Harada, M.Nakayama, S.Uda, A.Sugii (Fac. Pharm. Sci., Kumamoto Univ., Japan)
- 1-P-36 Development of ^{99m}Tc -Galactosyl Human Serum Albumin Diethylene Triamine Pentaacetate (^{99m}Tc -GSA) as a Hepatic Functional Imaging Agent
Y.Yamamichi, K.Washino, Y.Shirakami, M.Kurami (Cent. Res. Lab., Nihon Medi-Physics, Japan)
- 1-P-37 Evaluation of Hydroxamamide-Based Ligand as a Chelating Moiety for ^{99m}Tc Radiopharmaceuticals
M.Nakayama, H.Saigo, K.Ozeki, K.Harada, A.Sugii (Fac. Pharm. Sci., Kumamoto Univ., Japan)

- 1-P-38 Technetium-99m Phytate and Gallium-67 Citrate Scintigram in Liver Cancer-Bearing Rats
A.Ohta, T.Matsubayashi, K.Ishii, K.Yoda (Dept. Radiol., Kitasato Univ., Japan)
- 1-P-39 Technetium-99m Labeling on Monoclonal Antibodies via N,N'-Ethylene-bis-L-Cysteine
T.Qu, Y.Wu, X.Wang, Y.Liu, Y.Ye (Dept. Tech. Phys., Peking Univ., China)
- 1-P-40 Synthesis and Characterization of a New ^{99g}Technetium(V) Complex with 2-Thiohydantoin
R.M.Mahfouz, A.A.Hassan (Dept. Chem., Fac. Sci., Assiut Univ., Egypt)
- 1-P-41 Technetium-Aspirin Like Molecule Complexes
A.S.El-Shahawy, R.M.Mahfouz, A.A.M.Aly, M.El-Zohry (Dept. Chem., Fac. Sci., Assiut Univ., Egypt)
- 1-P-42 Radiochemical Properties and Electronic Structure of ^{99m}TcO-HMPAO
G.E.Kodina, V.I.Khleskov, A.B.Smirnov, S.M.Nikitin, A.O.Malysheva, E.I.Medvedeva, E.G.Bychkova, T.I.Petrova (Dept. Radiopharm., Inst. Biophys., Ministry of Health, Russia)
- 1-P-43 The Influence of L-Cysteine on the Radiochemical Purity and Properties of the Complex Tc-99m-MIBI
G.E.Kodina, A.O.Malysheva, T.A. Babushkina, V.V. Sergeev (Dept. Radiopharm., Inst. Biophys., Ministry of Health, Russia)
- 1-P-44 Production of Tc-99m-Generators in Russia
G.E.Kodina, V.N.Korsunsky, V.V.Kuzin, O.V.Starkov (Dept. Radiopharm., Inst. Biophys., Ministry of Health, Russia)
- 1-P-45 Critical Temperature Oscillations for Thin Films of Technetium at Various Thickness of Carbon Covering
V.M.Golyanov, M.N.Mikheeva, M.B.Tsetlin (RSC Kurchatov Inst., Russia)
- 1-P-46 Superconducting Properties and Structure of the Thin-Film Samples of Technetium and Technetium-Carbon System
V.M.Golyanov, L.A.Elesin, M.N.Mikheeva, A.A.Teplov, M.B.Tsetlin (RSC Kurchatov Inst., Russia)

- 1-P-47 Application of the Technetium-99 Foil for the Defectoscopy of Light Materials
V.P.Ljutov, K.G.Bukov (Inst. Phys. Chem., Russian Acad. Sci., Russia)
- 1-P-48 Effect of Tritium on Hydrogen-Isotope Exchange Reaction in
a Heterogeneous System
H.Imaizumi (Dept. Mat. Chem. Eng., Fac. Eng., Niigata Univ., Japan)

Technetium in the Nuclear Fuel Cycle, in Medicine and in the Environment

K.H.Lieser

Department of Chemistry (Eduard-Zintl-Institut)

Technical University, D-6100 Darmstadt, FRG

In nuclear reactors ^{99}Tc is produced in amounts of about 1 kg per ton of uranium, and about 10 % of the mass of the fission products are made up of ^{99}Tc . The chemistry and the fate of Tc in the nuclear fuel cycle are discussed. The major part goes with the highly active waste, minor parts, depending on the conditions, with low active waste streams.

The short-lived isomer $^{99\text{m}}\text{Tc}$ is one of the most widely used radionuclides in nuclear medicine. The two ways of production of the mother nuclide ^{99}Mo and their advantages, disadvantages and problems are discussed. The need for fast and reliable methods of radionuclide purity control is emphasized.

Although the radiotoxicity of ^{99}Tc is not high, there is a strong interest in the behaviour of this radionuclide in the environment because of its long half-life of $2.13 \cdot 10^5$ y. The redox potential of the system is of great importance. Whereas TcO_4^- is very mobile and shows little interaction with inorganic components of the geosphere, Tc(IV) is strongly sorbed. Better understanding of the reactions of Tc with organic components of the geosphere and in particular of the behaviour of Tc in the biosphere is needed.

Technetium in Nature and Age of the Solar System

P.K. Kuroda

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The investigation on the occurrence of element 43 in nature during the 20th century began with the experiments performed by Masataka Ogawa in 1905, in his all-out attempt to find a new element 'nipponium(Np)' in a sample of thorianite from Ceylon. In 1925, Noddack, Tacke and Berg have also attempted to isolate a new element 'masurium(Ma)' from various minerals, including a columbite, but all of these attempts made during the first half of the 20th century have yielded inconclusive results. Then, Perrier and Segrè discovered the first artificial element 'technetium(Tc)' in 1937 and their discovery became formally accepted by the scientific community in 1947. The age of discovering new elements by artificial means thus began in 1937 and some of these artificial elements found important practical applications. Following the discovery of ^{99}Tc in pitchblende in 1961, however, it became increasingly obvious that the most stable of all the artificial elements, namely ^{244}Pu with a half-life of 8.2×10^7 years, was present in nature during the early solar system. This means that the extinct radionuclide ^{244}Pu plays a key role as a tracer in the study of the formation of the solar system from the debris of a supernova explosion.

RADIOANALYTICAL STUDIES OF Tc IN THE ENVIRONMENT : PROGRESS AND PROBLEMS

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Twenty-one isotopes of technetium with mass numbers 90-110, along with seven isomers, are known. None of these are stable. There are three long-lived isotopes : ^{97}Tc ($T_{1/2} = 2.6 \times 10^6 \text{ a}$), ^{98}Tc ($T_{1/2} = 4.2 \times 10^6 \text{ a}$) and ^{99}Tc ($T_{1/2} = 2.13 \times 10^5 \text{ a}$). Of these radionuclides only ^{99}Tc is a fission product and is present in the environment in significant amounts. The interest for studying Tc in the environment is mainly related to its radiological importance in long-term storage of nuclear waste and its ability to act as a tracer especially for oceanographic processes.

The total world deposition from nuclear tests is estimated to be 140 TBq or 220 kg and over 300 TBq has, for example, been released from the Sellafield nuclear fuel reprocessing plant into the Irish Sea. Other sources are the different steps in the nuclear fuel cycle : reactor operation, UF_6 conversion, uranium enrichment and U fuel fabrication and the use of $^{99}\text{Tc}^m$ in nuclear medicine but these sources are less significant. The Chernobyl accident contributed relatively small amounts of ^{99}Tc .

Since ^{99}Tc is a pure β emitter with long physical half life requiring radiochemical separation, radiometric methods are troublesome at low levels. Other methods such as neutron activation have been tried and recent developments in mass spectrometry (ICPMS) are promising. There is a need for analytical quality control exercises and low-level reference material samples.

The fallout of Tc has been studied by using carpets of lichen and soil showing an integrated deposition of about 540 mBq m^2 on the Northern hemisphere. The distribution of ^{99}Tc from European reprocessing plants has been mapped in temperate and arctic waters of the North Atlantic, over a distance further than 6000 km, particularly by using macroalgae as bioindicator. In areas of the North Atlantic and the Mediterranean contaminated only from global fallout, surface water concentrations are in the order of 40 mBq m^{-3} .

Still several areas/fields remain to be investigated such as Tc in fresh water systems, anoxic basins and Tc compounds in the human body.

ULTRATRACE ANALYSIS OF TECHNETIUM

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Ultratrace analysis of technetium is important for the investigation of environmental samples and for the measurement of the fluence of high-energy solar neutrinos. The radioecology of ^{99}Tc is of special interest because of the long half-life of this isotope (2.1×10^5 y), its high fission yield ($\approx 6\%$), its decay mode (β^-), and the concurrent problems associated with its storage and disposal. Other candidates for low-level detection are ^{98}Tc (4.2×10^6 y) and ^{97}Tc (2.6×10^6 y). These nuclides should be produced in nature by neutrino interactions with molybdenum and their concentrations, e.g. in molybdenite, should yield the average ^8B solar neutrino flux over the past several million years.

In general, radiometric techniques are used for the determination of trace amounts of technetium. However, the detection limit of radioactivity measurements is fixed by the half-life of the isotope to be measured and careful chemical separations are required to prevent interferences from other β -ray emitters. Very recently inductively coupled plasma mass spectrometry (ICP-MS) combined with chemical separations has been applied as an alternative to the radiochemical detection of technetium. By negative thermal ionization mass spectrometry technetium isotopic compositions down to 10^6 atoms can be determined. Pertechnetate ions are formed with $> 2\%$ using rhenium filaments containing lanthanum oxide in conjunction with calcium nitrate. Another approach is resonance ionization mass spectrometry which combines high sensitivity with extreme selectivity. Here excitation and ionization of the technetium atoms are performed by resonant absorption of photons followed by a time-of-flight detection of the produced ions. This method has a detection limit of $\approx 10^7$ atoms and guarantees an unambiguous element and isotope assignment. The detection efficiency of resonance ionization mass spectrometry can further be improved by means of a laser ion source, consisting of a hot cavity with a small hole to inject the laser beams and to extract the photoions. For technetium an ionization efficiency of 14% was obtained with such a laser ion source.

The advantages and disadvantages of the various methods for ultratrace analysis of technetium are outlined and possible improvements, leading to lower detection limits, are briefly discussed.

CURRENT STATUS OF CHEMICAL THERMODYNAMIC MEASUREMENTS FOR TECHNETIUM AND ITS INORGANIC COMPOUNDS AND AQUEOUS SPECIES

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The Nuclear Energy Agency of the Organisation for Economic Co-operation and Development has organized specialist teams to perform detailed critical analyses of the chemical and thermodynamic data of various elements of importance to radioactive waste isolation. One such team (organized in 1984) has been systematically compiling and reanalyzing such information for technetium, all of its known inorganic compounds, certain organo-metallic compounds, and its aqueous species and aqueous complexes. These thermodynamic data are currently being reanalyzed according to NEA guidelines; the results are being made compatible with CODATA; and critically assessed values of standard Gibbs energies of formation, enthalpies of formation, entropies, and heat capacities are being derived for those systems with adequate thermodynamic data. An over-view is given of this project, and the extent of the available data is described. Large gaps exist in our knowledge of the chemical and thermodynamic behavior of technetium, and attention is brought to the most critical needs for making the data base complete enough for modeling of the speciation of technetium under environmental conditions.

PHOTONUCLEAR REACTIONS ON ^{99}Tc , ISOMER EXCITATION AND DEEXCITATION, ASTROPHYSICAL IMPLICATIONS

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Photonuclear reactions on target ^{99}Tc were studied experimentally and theoretically at the Radiochemical Laboratory of the Department of Chemistry, Tohoku University, and Institute of Isotopes, Budapest. Using bremsstrahlung beams up to 50 MeV, (γ, xn) and $(\gamma, \gamma')^{\text{m}}$ reaction cross sections were determined for the first time, by means of gamma-spectrometry. Calculations were also carried out in the framework of neutron evaporation and statistical gamma-ray cascade models, respectively. As a result, the photoexcitation function was shown to exhibit a maximum at neutron emission threshold, but then drops abruptly and no comparable second peak appears even at giant resonance. This seems to be a general feature of (γ, γ') reactions proved also for other nuclides (^{115}In , ^{103}Rh), in sharp contrast with the long-standing belief in a two-humped excitation function based on earlier reports.

The extremely low-energy (2 keV), long-lived (6 h) isomeric transition of ^{99}Tc may represent a special possibility for induced deexcitation without population inversion, including a method for incineration of $^{99\text{m}}\text{Tc}$, e.g. with the aid of intense synchrotron radiation (SR). Considerations, however, show that existing SR intensities are still many order of magnitude too low.

Allowed β -transitions from photoexcited states of ^{99}Tc to ^{99}Ru levels may reduce dramatically the terrestrial half-life of ^{99}Tc in stellar environments. Significance of Tc abundance measurements in stars and shell-model calculations in determining the parameters of the astrophysical s-process will be discussed.

HALF-LIFE OF TECHNETIUM 97, 98

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No technetium isotope of primary origin exists on earth, except for the ^{99}Tc produced by spontaneous fission of ^{238}U . The primordial occurrence of any long-lived isotope in the earth crust requires its half life comparable or more than the earth's age of about 4.6×10^9 years. However, a recent report on the possible existence of technetium in nature prompted us to re-examine the currently accepted half lives of ^{97}Tc and ^{98}Tc . The half life of ^{97}Tc , 2.6×10^6 y, was determined by Katcoff in 1958 by measuring Tc and Mo K-Xrays with a proportional counter and critical X-ray absorbers, and by estimating the number of ^{97}Tc atoms from the parental relationship between ^{97}Ru and ^{97}Tc in the β^- decay chain. The half life of ^{98}Tc , 4.2×10^6 y was quoted in Nuclear Data 11(1974) as a private communication from O'Kelly et al. in 1973. From the known mass of the A=98 isobars and from the reported level scheme of ^{98}Mo , it can easily predicted that ^{98}Tc should decay not only by β^- mode as reported, but also by EC mode.

The aim of the present work is to re-determine the half lives of ^{97}Tc and ^{98}Tc , and to give a definite answer to the long standing dispute on the existence of technetium of primary origin on earth.

^{97}Tc and ^{98}Tc isotopes have been produced by using SF-Cyclotron at the Institute for Nuclear Study, University of Tokyo. The irradiation of a ^{95}Mo metal pellet(94.9%) was performed with 22MeV α -particles for 12hours in order to prepare ^{97}Ru from which pure long lived ^{97}Tc could be milked.

^{98}Tc was produced from a 100 mg/cm^2 thick ^{97}Mo self-supporting target(92.9%) by the bombardment of the 14MeV deuteron beam for 12hours.

We measured the γ -ray spectra of ^{97}Ru (214 keV) and $^{97\text{m}}\text{Tc}$ (96.5 keV) and obtained the branching ratio of ^{97}Ru decaying to $^{97\text{m}}\text{Tc}$ to be 0.017%. Half-lives of ^{97}Ru and $^{97\text{m}}\text{Tc}$ were determined to be 2.78 ± 0.03 day and 92.2 ± 1.8 day, respectively. K-X rays of Tc and Mo emitted after the IT decay of $^{97\text{m}}\text{Tc}$ and the EC decay of $^{97\text{g}}\text{Tc}$ measured were with a Si(Li) detector.

The preliminary result of the half live of $^{97\text{g}}\text{Tc}$ estimated form the intensity ratio of Tc/Mo K-Xrays and from the known ratio of number of atoms of $^{97\text{m}}\text{Tc}/^{97\text{g}}\text{Tc}$ is 3.8×10^6 y.

As for the ^{98}Tc source, the EC decay of ^{98}Tc is expected to lead to emission of two γ -rays in cascade mode with the energies of 0.722MeV and 0.78MeV. But no clear photopeakes from sample were observed and this gives the upper limit for $\text{EC}/\beta^- < 0.04$.

GEOCHEMICAL BEHAVIOUR OF ^{99}Tc IN THE OKLO NATURAL REACTOR

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Oklo uranium ore, in the Republic of Gabon, has been known as a fossil of natural nuclear reactors. Investigation of fission products in the Oklo reactor leads to the storage of radioactive waste in geological media. It is of particular interest to estimate the behaviours of long-lived radioactive nuclides such as ^{99}Tc , ^{107}Pd , ^{126}Sn , ^{135}Cs and so on. Radioactive ^{99}Tc has 2.1×10^5 y half-life, and decays to ^{99}Ru . In this study, the behaviour of technetium in a reactor zone at Oklo was inferred from precise isotopic measurements of ruthenium.

Four samples (1469, 1480, 1485 and 1492) were systematically collected from one of drill-cores, SF84, at the reactor 10, and one sample (SD.37-S2/CD) was from reactor 13. These two reactor zones are newly discovered, and being actively researched by CEA-CEC. Each sample was dissolved by 7M-HNO_3 without heat, and the residue was decomposed by HF and HClO_4 . Ruthenium was effectively separated from sample solution by distillation with $\text{K}_2\text{Cr}_2\text{O}_7$ and H_3PO_4 . The ruthenium fraction obtained by above method was redissolved in ca. 0.1M HNO_3 , and the isotopic composition of ruthenium was determined by ICP-MS (VG PlasmaQuad). Furthermore, we found Ru enriched metallic inclusions at the uranium grain boundaries in SD.37-S2/CD, and also carried out *in-situ* isotopic analysis by SIMS (Cameca IMS 3f).

Considering that theoretical fission product yields of ruthenium isotopes are high and that natural ruthenium abundance in common crustal rocks is extremely low (less than a few ppb), it is reasonable that only four fissiogenic ruthenium isotopes, ^{99}Ru , ^{100}Ru , ^{101}Ru , ^{102}Ru and ^{104}Ru , were detected (see Table). ^{100}Ru is not directly produced by fission, but is probably produced by the neutron captures of ^{99}Tc and/or ^{99}Ru . In the Oklo natural reactors, ^{235}U , ^{238}U and ^{239}Pu had fissioned. After the determination of fission proportion of the fissiles by use of isotopic abundances of ^{101}Ru , ^{102}Ru and ^{104}Ru , the isotopic deviation of ^{99}Ru from calculated values was evaluated. The deviation, $\Delta^{99}\text{Ru}$, indicates the degree of chemical fractionation between Tc and Ru. A metallic inclusion of SD.37-S2/CD contains large excess ^{99}Ru derived from migration of ^{99}Tc , while there is no large chemical fractionation between Tc and Ru in whole rock samples.

Table Ruthenium isotopic ratios of Oklo samples

sample	96/101	98/101	99/101	100/101	102/101	104/101	$\Delta^{99}\text{Ru}(\%)^*$
1469	-	-	1.187 ± 9	0.02139 ± 45	0.8553 ± 13	0.4287 ± 23	+4.41
1480	-	-	1.175 ± 10	0.01879 ± 30	0.8509 ± 88	0.4215 ± 8	+2.82
1485	-	-	1.089 ± 5	0.01560 ± 30	0.8468 ± 57	0.4111 ± 22	-5.15
1492	-	-	1.134 ± 8	0.01624 ± 55	0.8469 ± 31	0.4089 ± 34	-1.21
SD.37	-	-	1.226 ± 16	0.03507 ± 21	0.8871 ± 25	0.5066 ± 14	+11.6
Inc-1**	-	-	1.934	0.1486	0.8986	0.5230	+85.9
Inc-2**	-	-	1.561	0.1189	0.8970	0.5242	+49.9
Inc-3**	-	-	2.284	0.1578	0.9020	0.5551	+118
STD***	0.3249 ± 11	0.1096 ± 11	0.7286 ± 90	0.7272 ± 21	1.869 ± 9	1.092 ± 6	

* $\Delta^{99}\text{Ru} = [(^{99}\text{Ru}/^{101}\text{Ru})_{\text{sample}} / (^{99}\text{Ru}/^{101}\text{Ru})_{\text{calcd.}} - 1] \times 100 (\%)$

***In-situ* analysis of metallic inclusions in SD.37-S2/CD by SIMS.

***STD means terrestrial standard values measured by ICP-MS. Errors are 2 σ means.

SUPERCONDUCTING AND NORMAL PROPERTIES OF Tc AND Tc-Mo ALLOYS

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Experimental observations (inelastic neutron scattering, tunnel and point-contact spectroscopy, Raman spectra) of Tc are reviewed from the view point of its unusual superconducting properties. This element differs greatly from his neighbors Ru and Re in the 7th group of the periodical table. The reason for this seems to be a strong selective electron-phonon interaction (EPI) and so all our experimental methods one way or another touch upon precisely this aspect of physics of Tc. We have shown that the anomalous temperature dependence of the phonon spectrum and the selective EPI are seen in Tc not only on the differential level but also on the integral one, as a shift of the phonon density of states (PDS) $F(\omega)$ down the energy scale with decreasing temperature and as a difference between the positions of the maxima of $F(\omega)$ and the point-contact (PC) function of the EPI $G_{pc}(\omega)$. The PC investigations were carried out for the normal state of Tc as well as for the superconducting one. It is shown that the IV characteristics of Tc-Ag PC in superconducting state contain the information about the position of the maximum of EPI function. By this technique we have studied Tc_{1-x}Mo_x alloys. The softening of the EPI spectra with increasing x correlates with the growth of the critical temperatures in these alloys (up to $T_c=14K$ at $x=0.2$). This can result from both the softening of the phonon spectrum of the alloy and the growing contribution of low frequency phonons to the EPI function.

Tunneling experiments carried out on the Tc-Ta-I-Pb thin film sandwiches reveal the large enough value of $2\Delta_0/kT_c=4.1$ for Tc (Δ_0 is the energy gap at $T=0K$) taking into account the low value of ratio $T_c/\theta_D=0.02$ (θ_D is the Debye temperature) in this metal. At the same time the experimental temperature dependence of the energy gap for Tc has the systematic deviation from the calculated BCS curve which describes the majority of the low- T_c superconductors rather well.

The anomalous temperature dependence of attenuation of the E_{2g} optical phonon in the Raman spectra of films and bulk Tc was discovered. That is evidence of the presence of considerable influence of the EPI on the optical phonon features of the Raman spectra.

So we believe that the whole complex of experimental data presented may be explained taking into consideration the selective anisotropic EPI in Tc and its alloys.

SOME ASPECTS OF PHYSICAL METALLURGY OF TECHNETIUM

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Tc-99 nowadays is known to be the most available for investigation and practical applications. Tc-99 powder is found to be produced using as chemical reduction as electrodeposition processes. KTcO_4 in both cases is used as starting material. Tc powder may be pressed to pellets and remelted to form ingots. Compact Tc metal appears to be heavy, possessing silver grey color, very much alike Mo, Pt or Re. Remelted metal is soft and plastic enough, these properties strongly dependent on its purity.

Tc-99 radionuclide emits beta-decay with $E_{\text{max}} = 294$ keV. Maximum surface radiation dose of Tc metal was found to be $\text{Do} = 25.3 \text{ cGy} \cdot \text{min}^{-1} \cdot \text{cm}^{-2}$ when metal thickness reaches 40-50 μm . Tc foil with thickness up to 30 μm (length - 200 mm; width - 55 mm) may be produced using facilities, developed while carrying out the present study. Tc metal is found to possess high chemical stability: 15 year storage of Tc sample in the usual laboratory atmosphere did not result in the loss of surface brightness. Tc does not interact with HCl but is found to be easily oxidized by *aqua regia*, HNO_3 , H_2SO_4 and H_2O_2 . Tc metal is stable to alkali, fresh and sea water. Carrying out the present study Tc stability was checked in continuous marine experiments (Barentz and Japan Sea) and in the lab 5000 h storage in 3% NaCl solutions did not result in weight and appearance changes of Tc samples. The heating of Tc metal samples in the air to 300°C results in the metal oxidation to volatile Tc_2O_7 . Under further heating (>350°C) the simultaneous formation of $\text{Tc}_2\text{O}_7 + \text{TcO}_2$ the last compound covering metal surface with the black film. Tc oxidation in the air at 300°C-1000°C and normal pressure may be characterized by weight loss, lineary depending on time. Activation energy of Tc oxidation was found to be $90 \text{ kJ} \cdot \text{mol}^{-1}$. No other oxide phases (for example TcO_3 , oxygen solid solution in Tc) were not noticed, studying the Tc oxidation in air. Tc metal does not react with hydrogen at normal conditions. The hydrogen solid solution formation was noticed at the $T > 300^\circ\text{C}$ and pressures ($P > 1.9 \text{ MPa}$). X-ray analysis has shown that the Tc hydrides form the solid hydrogen solution in hexagonal closed- package structure of Tc metal cell.

To create the copper based alloy for Tc foil soldering the interaction between Tc metal (99,8% purity) and Cu (99,7 %) was studied. No interaction was found either in solid or in liquid state. Tc solubility in copper was found not to exceed $4,3 \cdot 10^{-3} \text{ at.}\%$ and Tc in copper - $3,4 \cdot 10^{-4}$. So, Tc-Cu phase diagram seems to be characteristic for two immixible fluids. In spite of the lack of chemical interaction copper was found to adhere effectively on Tc metal surface. Copper soldering results in formation of the qualitative junction between Tc foils and target materials. For the search in the field of Tc metal the interaction in the systems Tc-Fe, Tc-Ni, Tc-Ti in solid state was studied in temperature interval 900°C - 1300°C. The studies were carried out using samples with the purity not less than 99%. Different techniques: (cathode effusion, electrodeposition, diffusion welding) were used for the attachment of Tc films to the metal surfaces. Tc-Ti interaction was found to result in formation of χ -phase, CsCl-type phase and Tc solid solution in β -titanium. Tc appeared to be effective stabilizer for Ti high temperature phase up to room temperatures. When the iron surface is saturated with Tc σ -phase and solid solutions are formed. In case of Ni-Tc interaction solid solution was found to be the only product of the reaction. In all cases the phase growth were found to obey the parabolic law.

At the present time the ionising radiation Tc sources have found their application in the metrology, industry, medicine.

RECOVERY OF TECHNETIUM FROM HIGH-LEVEL LIQUID WASTE GENERATED IN NUCLEAR FUEL REPROCESSING

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Partitioning of elements in the high-level radioactive liquid waste (HLLW) generated in nuclear fuel reprocessing and transmutation of long-lived nuclides are expected to increase the efficiency of high-level waste disposal and will seek the utilization of existing resources in a spent fuel.

In 1988, Japan's Atomic Energy Commission (AEC) submitted a report entitled "Long Term Program for Research and Development on Nuclide Partitioning and Transmutation Technology", which plots a course for technological development up to the year 2000. The program is called "OMEGA" which is the acronym derived from Options Making Extra Gains of Actinides and fission products.

In this program, a partitioning technology should be developed for separating elements in HLLW into four groups; transuranic elements (TRU), Sr-Cs, Tc-platinum group elements (PGE) and others. Necessity of the Tc separation was recommended not only for reducing the long-term hazard of high-level waste but also for promoting its beneficial use as artificial resource which is available only from a spent fuel.

At the Japan Atomic Energy Research Institute (JAERI), the development of a partitioning method was initiated about 20 years ago and the present study is mainly focussed on the four group separation. Main items to be established are how to separate TRU and Tc from HLLW. The preferential separation of TRU should be considered to avoid its spread into many fractions generated in a partitioning process. The Tc separation was therefore considered to the raffinate (0.5M nitric acid solution) generated from the TRU extraction with diisodecylphosphoric acid (DIDPA). Two kinds of chemical methods; precipitation and adsorption, have been developed for the Tc separation and experimented by using mainly a simulated HLLW containing Tc-99 or Tc-95m.

As to the precipitation method, more than 95% of Tc was found to be coprecipitated along with PGE when the simulated HLLW was denitrated with formic acid to reduce its acidity to above pH 2. The Tc precipitated was found to be selectively dissolved with hydrogen peroxide. However, this precipitation method₃ was not applicable when a Rh and Pd concentration was lower than 5×10^{-3} M.

The adsorption of Tc was tested with several inorganic adsorbents and active carbon was found to have a distribution coefficient of more than 100 ml/g and an adsorption capacity of 0.60 meq/g at 0.5M nitric acid solution. The elution of Tc adsorbed on an active carbon column was also studied, and potassium thiocyanate was found to be very effective for its complete elution.

The partitioning process including Tc separation will be demonstrated by using an actual HLLW at the Nuclear Fuel Cycle Safety Engineering Research Facility (NUCEF), which is under construction and comes into hot operation in 1994.

SOLVENT EXTRACTION OF Tc(VII) AND Re(VII)
FROM NITRIC ACID SOLUTION WITH CMPO/TBP

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Technetium-99 makes up a dominant portion of the radioactive nuclides remaining in radioactive wastes after decay periods of hundreds of years. The solvent extraction is a useful way to separate it.

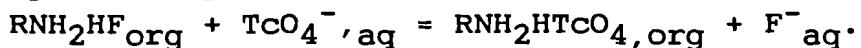
The distribution mechanism of Tc(VII) or Re(VII) from nitric acid solution with octyl(phenyl)-N,N-diisobutylcarbamoylmethylphosphine oxide(CMPO) / tributyl phosphate(TBP) was studied. The distribution coefficient for Tc(VII) increased with increasing aqueous acidity until a maximum was reached at around 0.5M nitric acid concentration. Above 1M nitric acid concentration, the distribution coefficient fell off rapidly by competition from the significant amounts of nitric acid present in the organic phase, which reduced the amount of free CMPO/TBP available to extract Tc(VII). Acid concentration dependence of Re(VII) extraction was very similar to the results of Tc(VII), however the magnitude of extraction efficiency for Re(VII) was lower than that of Tc(VII). The distribution curve for TBP against aqueous acidity was also similar to that of CMPO/TBP or CMPO but the extraction efficiency for the mixture of CMPO and TBP was slightly larger than linear relationship. This suggested a certain chemical interaction between CMPO and TBP, which increased metal-extractant affinity. In order to evaluate the structure of Tc(VII)- or Re(VII)-CMPO complex, the solvation number of CMPO, the infrared spectra and the results of kinetic research were discussed.

EXTRACTION OF TECHNETIUM (V11) IN HYDROFLUORIC ACID SYSTEM
BY PRIMARY AMINE - n-HEPTANE SOLUTION

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The fundamental extraction behavior of technetium (V11) from an aqueous 4 M hydrofluoric acid solution was studied through experiments in the extraction of Tc(V11) using as extractant primary amine (Primene JMT) dissolved in n-heptane solution. The above extraction reaction is expressed by



Repetitive cycles performed of this reaction using Primene JMT proved to ensure quantitative extraction of the Tc(V11), but higher extraction percentage was obtained on the first—as compared with the second—cycles. Phase separation was poor when the Tc(V11) was extracted from 1 M HF solution, but good when extracted from a mixed solution of 1 M HF and 3 M NH_4F . In the latter case, the distribution ratio D was found to maintain steady values with changing Primene JMT concentration in extraction process, whereas in stripping process, the ratio increased appreciably with rising extractant concentration. The most satisfactory Tc(V11) extraction performance was obtained with 0.6 M Primene JMT in n-heptane from 2 M HF solution. Stripping of Tc(V11) into 3 M ammonium carbonate aqueous solution was enhanced to quantitative level by repetition of the stripping procedure. In the basic region, increasing the concentration of NH_4F appreciably raised the ratio D in extraction, whereas in stripping, the ratio was little affected by differences in NH_4F concentration. Separation of Tc(V11) from uranium (V1) was studied through experiments in coprecipitation of Tc(V11) with ammonium diuranate. This coprecipitation procedure proved to provide the most satisfactory means of separating Tc(V11) from U(V1) in solution.

VOLATILIZATION OF Tc(VII) FROM SIMULATED REPROCESSING SOLUTIONS

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Reprocessing of spent nuclear fuel includes several evaporation and concentration processes of nitric acid solutions containing fission products(FPs). We have been examining volatilization behavior of some FPs in the evaporator and have already reported that the purification factor (PF = molarity in a concentrate / molarity in a distillate) of 10^4 to 10^5 [1] was obtained for ruthenium and technetium by the equilibrium distillation using the Othmer-type equipment. In this study, we measured the PF and vapor pressure of technetium during a continuous distillation under the same condition as that of the actual reprocessing evaporator in order to confirm the PF previously obtained and to determine the thermodynamic properties of the gas-liquid transfer reaction of technetium.

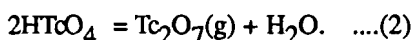
Continuous distillations of HTcO_4 solutions were carried out with constant distillation rate and with constant solution composition in an equipment. Sample solutions(10m/l) were prepared by dissolving 0.0023-0.023mol/l of HTcO_4 into 0.1mol/l perchloric acid or 2-13.5mol/l nitric acid. The temperature range is from 333.15 to 363.15K. Technetium molarity in a distillate was measured by ICP-MS (Inductively Coupled Plasma-Mass Spectrometer) which can detect 5×10^{-9} g/l of technetium.

The PF obtained was 10^4 to 10^5 in the experimental range, which agreed well with the previous report[1]. The almost all of the dissolved technetium would form the heptavalent species, HTcO_4 , because the distillation result for 2 mol/l nitric acid solution was very similar to that in perchloric acid solution which was much more oxidative than the nitric acid solution. In order to determine gas-liquid transfer mechanism, the vapor pressure of the technetium was calculated from PF.

The obtained vapor pressure of technetium could be described as;

$$P(\text{Tc}) = K \cdot [\text{HTcO}_4]^2 / a_w, \dots(1)$$

where $P(\text{Tc})$, K , $[\text{HTcO}_4]$ and a_w are vapor pressure of technetium, apparent equilibrium constants, molarity of HTcO_4 and activity of water in sample solution, respectively. This equation suggests that the gas-liquid transfer reaction is;



The change of enthalpy (ΔH) and entropy (ΔS) during the gas-liquid transfer of technetium were calculated from the temperature dependence of K . The evaluated values of ΔH and ΔS are 82.3 kJ mol^{-1} and $205.4 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$, respectively.

[1] Y. Hirose *et al.*, "Removal behavior of Ru and Tc in acidic liquid waste evaporators", Fall Meeting of the Atomic Energy Soc. Jpn., (Fukuoka), K58, p.682 (1991).

Acknowledgement;

This work is supported by Nuclear Fuel Division, Atomic Energy Bureau, Science and Technology Agency of Japan.

BASIC COORDINATION CHEMISTRY OF TECHNETIUM

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The transition element technetium having the electronic ground state configuration $[\text{Kr}]4d^65s^1$ tends to form coordination compounds and occurs in the oxidation states from +7 to -1. Tc(VII) is represented by $[\text{TcO}_4]^-$ and the hydrido complex $[\text{TcH}_9]^{2-}$ which exhibits the maximum coordination number in technetium chemistry. Recently this oxidation state was moreover exemplified by the binuclear nitrido-Tc(VII)-hydrazido(2-) core and the hydrotris(1-pyrazolyl) borato-trioxotechnetium (VII). The highly reactive $[\text{TcO}_4]^{2-}$ and the notably stable $[\text{TcN}]^{3+}$ core mainly represent the +6 state. A unique example of a Tc(V)/(Tc(VI) mixed-valence species is the catechol complex with hydrazido ligands $[\text{Tc}_2(\text{NNPh}_2)_2(\text{C}_6\text{Cl}_4\text{O}_2)_4]^-$. Pentavalent Tc is exemplified by the dodecahedral $[\text{Tc}(\text{diars})_2\text{Cl}_4]^+$ exhibiting the coordination number 8 and numerous complexes containing the $[\text{TcN}]^{2+}$, trans- $[\text{TcO}_2]^+$ or $[\text{TcO}]^{3+}$ core, the latter appearing in highly significant radiopharmaceuticals. The hexahalogeno complexes and their derivatives are simple representatives of the +4 state and octahedral coordination. Very recently a novel oxalato complex of Tc(IV), centred by the $\text{Tc}(\mu\text{-O}_2)\text{Tc}$ moiety, was synthesized. Tc(III) is frequently exemplified in octahedral complexes formed with different ligands, whereas seven-coordinate compounds are $[\text{TcCl}_3(\text{CO})(\text{PMe}_2\text{Ph})_3]$, the xanthate $[\text{Tc}(\text{PPh}_3)(\text{S}_2\text{COC}_4\text{H}_9)_3]$ and the boron-capped Tc-dioximes. $[\text{Tc}_2\text{Cl}_8]^{2-}$ and $[\text{Tc}_2\text{Cl}_8]^{3-}$ revealed multiple metal to metal bonds. The number of well-defined Tc(II) complexes is relatively low. Examples are $[\text{TcX}_2(\text{diars})_2]$, the analogous diphosphines and the chlorophosphonite $[\text{TcCl}_2(\text{C}_6\text{H}_5\text{P}(\text{OC}_2\text{H}_5)_2)_4]$. Tc(I) is represented for instance by the myocardial agent hexakis(2-methoxy-isobutyl-isonitrile)technetium cation, the $[\text{Tc}(\text{CN})_6]^{5-}$ and the dibenzene-technetium cation. $\text{Na}[\text{Tc}_3(\text{CO})_9(\text{OCH}_3)_4]$ is a novel and unique cubane-type cluster of Tc(I). The structurally characterized $\text{Tc}_2(\text{CO})_{10}$ and the rather undefined $[\text{Tc}(\text{CO})_5]^-$ are regarded as examples for Tc(0) and Tc(-1), respectively.

The explanation of magnetic moments is based on crystal field consideration showing technetium to form low-spin compounds. There is some evidence that technetium complexes are thermodynamically less stable and kinetically more labile than the corresponding complexes of rhenium.

TECHNETIUM COMPLEXES WITH THIOETHER LIGANDS

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Intensive studies of technetium/S-donor ligand systems have shown that with thio-
lates preferably anionic oxotechnetium(V) complexes are formed. The use of thio-
ethers may provide novel complexes with technetium also in low oxidation states.
Particularly when combined with suitable co-ligands thioethers are expected to give
complexes of well balanced charge and lipophilicity, which are important for radio-
pharmaceutical design.

Another interesting aspect is the relation to the well-studied Tc/phosphine
chemistry, which motivates us to study analogies and differences in the chemistry as
well as the radiopharmacology of Tc/P and Tc/-S- compounds.

Here we describe new classes of technetium complexes with bi- and tetradentate
thioethers of the type $R-CH_2CH_2-(S-CH_2CH_2-S-CH_2CH_2)_n-R$ ($n=1$: "S₂", $R=H$,
OH; $n=2$: "S₄", $R=H$, ethyl) and thiacycrown ethers.

Oxotechnetium(V) complexes, which contain single bonded oxygen in trans position
to the Tc=O core, $[TcO("S_2")Cl_2]_2O$ and $[Tc("S_2-O-")Cl_2]$, are formed with
bidentate thioethers ("S₂") and $TcOCl_4^-$ as precursor.

Cationic nitridotechnetium(V) complexes of the general formulation
 $[TcNCl(thiacycrown)]^+$ have been obtained by ligand exchange reaction of thiacycrown
ethers with $TcNCl_4^-$.

Representatives of both new classes of complexes have been characterized by X-ray
structural analysis.

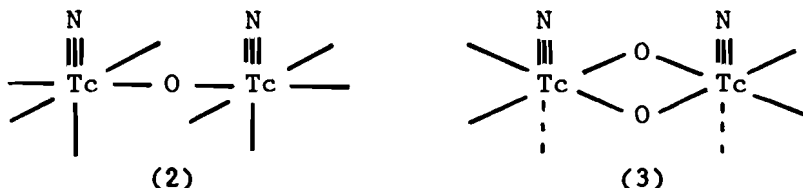
Cationic Tc(III) complexes $[Tc("S_4")(SR')_2]^+$ were prepared by reduction of
 ^{99}Tc -pertechnetate in the presence of both a tetradentate thioether ("S₄") and a
monodentate thiole ($R'SH$, $R'=aryl$, alkyl). The X-ray crystal structure analysis
of $[Tc("S_4")(SR')_2]PF_6$ ($R=ethyl$, $R'=phenyl$) showed that Tc(III) is centred in
a heavily distorted octahedron with the thiolate ligands being coordinated in cis-
configuration. The combination of tetrathiaalkanes with monodentate thiolate li-
gands gives full scope for structural alterations.

MONOMER, μ -OXO DIMER, DI(μ -OXO) DIMER INTERCONVERSION OF
NITRIDOTECHNETIUM(VI) COMPLEXES IN ACID SOLUTION

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UV-Vis and ESR spectroscopy have been used to study the behaviour of $\text{Cs}_2[\text{TcNCl}_5]$ and the hydrolysis product $[\{\text{TcN}(\text{OH})(\text{OH}_2)\}_2(\mu\text{-O})_2](1)$ in concentrated and aqueous solutions of a variety of acids ranging from the very weakly coordinating $\text{CF}_3\text{SO}_3\text{H}$ to the coordinating HX ($\text{X} = \text{F}, \text{Cl}, \text{Br}$) and H_3PO_4 or $\text{H}_4\text{P}_2\text{O}_7$. The paramagnetic monomeric $\text{Tc}^{\text{VI}}\text{N}^{3+}$ (d^1) forms are readily identified by ESR spectroscopy and the diamagnetic dimeric μ -oxo ($\text{Tc}_2\text{N}_2\text{O}^{4+}$) (2) and di(μ -oxo) ($\text{Tc}_2\text{N}_2\text{O}_2^{2+}$) (3) forms by their UV-Vis spectra.



For solutions of $\text{Cs}_2[\text{TcNCl}_5]$ the form of $\text{Tc}^{\text{VI}}\text{N}$ and the rate of conversion of monomer \rightarrow (2) \rightarrow (3) is dependent on the presence of Cl^- and the concentration and complexing ability of the acid, with the monomeric form being favoured by acids of greater complexing power. For solutions of (1) the reverse order of conversion is observed. In 1M $\text{CF}_3\text{SO}_3\text{H}$, MeSO_3H and *p*-toluenesulphonic acid, (1) is converted to the di(μ -oxo) aqua cation $[\{\text{TcN}(\text{OH}_2)_3\}_2(\mu\text{-O})_2]^{2+}$ while in 7.5M $\text{CF}_3\text{SO}_3\text{H}$ it is proposed that the predominant form is the μ -oxo aqua dimer $[\{\text{TcN}(\text{OH}_2)_4\}_2(\mu\text{-O})]^{4+}$. In H_2SO_4 and the phosphorus oxo acids the aqua cations are coordinated by the acid anions. The monomeric aqua cation $[\text{TcN}(\text{OH}_2)_5]^{3+}$ does not appear to be a viable species, as is also the case for $\text{MoO}^{3+}(\text{aq})$, and spontaneously isomerises in 7.5M $\text{CF}_3\text{SO}_3\text{H}$. In anhydrous $\text{CF}_3\text{SO}_3\text{H}$ or H_2SO_4 monomeric $\text{Tc}^{\text{VI}}\text{N}$ with CF_3SO_3^- or HSO_4^- coordination is observed. A characteristic feature of the UV-Vis spectra of monomeric $\text{Tc}^{\text{VI}}\text{N}$ is a strong absorption at 266-300 nm assigned to N to Tc charge transfer.

EXAFS and UV-Vis studies have shown that in $>3\text{M}$ HCl the predominant species is $[\text{TcNCl}_4]^-$ while in 1M HCl $[\text{TcNCl}_4]^-$ exists in equilibrium with $[\{\text{TcNCl}_3(\text{OH}_2)\}_2(\mu\text{-O})]^{2-}$ or $[\{\text{TcNCl}_4\}_2(\mu\text{-O})]^{4-}$, for which the Tc...Tc distance indicates a linear Tc-O-Tc system. Slow addition of HCl to a solution of (1) in MeSO_3H containing AsPh_4Cl has resulted in the isolation of $(\text{AsPh}_4)_2[\{\text{TcNCl}_2\}_2(\mu\text{-O})_2]$, the structure of which has been determined by X-ray crystallography.

NOVEL TECHNETIUM AND RHENIUM COMPLEXES WITH
MULTIDENTATE NITROGEN DONOR LIGANDS

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The synthesis and characterization of technetium and rhenium complexes with multidentate unsaturated nitrogen donor ligands were investigated.

The reaction of pertechnetate with 1,2-diaminobenzene (H_2pda) in the presence of the reducing agent sodium dithionite in alkaline aqueous solution led to the formation and isolation of $(n-Bu_4N)[TcO(pda)_2][1]$. If the reaction is performed without reducing agent in methanol, the compound $[Tc(pda)_3][TcO_4][2]$ is formed. The X-ray crystal structures of both complexes will be discussed. Complex [2] represents the first tris-bidentate cationic complex of technetium to be structurally characterized, and it completes the series of complexes of the type $Tc(L^{\wedge}L)_3$, which have now been found in all oxidation states from +3 to +7. Analogous complexes with diaminomaleonitrile will also be discussed.

Complexes of the general formula $MOCl_2[(C_5H_4N)_2C(O)(OR)]$ ($M=Tc, Re$; $R=H, Et$) were prepared by the reactions of $(n-Bu_4N)[TcOCl_4]$ and trans- $ReOCl_3(PPh_3)_2$ with di-2-pyridylketone (DPK) in ethanol ($R=Et$) under nitrogen and in benzene, containing trace amounts of water, in air ($R=H$). Spectroscopic evidence suggests that the coordinated DPK ligand has undergone addition of ethanol and water at the carbonylic carbon atom, and that the $(C_5H_4N)_2C(O)(OR)$ moiety acts as a uninegative, tridentate N,O,N-donor ligand. The X-ray crystal structure of $ReOCl_2[(C_5H_4N)_2C(O)(OH)]$, as well as that of related compounds, will be present.

MULTIPLE TECHNETIUM-TECHNETIUM BONDS

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This communication is concerned with the analysis of experimental and theoretical results on the chemistry, electronic and molecular structure, and other physicochemical properties of compounds with multiple Tc-Tc bonds, including compounds of a new class - polynuclear clusters with a system of delocalized multiple M-M bonds. Most of the results discussed have been obtained in the group headed by the author of this communication.

By its position in the Periodic Table technetium is expected to have strong cluster forming properties, i.e., it has a tendency to form bi- and polynuclear complexes with M-M bonds of different formal multiplicity. The increased ability of Mo, W, and Re to form binuclear acidocomplexes with multiple M-M bonds suggests the presence of a similar ability for technetium. However, the available literature data [1, 2] were, on the one hand, scanty and rather unclear in terms of the generally-accepted theoretical concepts and, on the other hand, allowed one to suggest that technetium had "anomalous" cluster forming properties and cluster forms [3].

These "anomalous" properties are: increased ability of technetium bi- and polynuclear clusters to form "electrosuperfluous" systems with multiple M-M bonds, the stabilization of these systems in the case of the uneven number of metallic electrons, the formation of octahedral clusters with unusual ligand distortion, the appreciable shortening of M-M bonds in $[\text{Tc}_2\text{Cl}_6]^{2-}$ and some other properties.

The communication will show that these technetium properties are due to a decrease in the effective charge on its atoms in formation of M-M bonds resulting from the increased ability of their outer diffusion 5s(5p)-AO's to additionally bond the metal atoms into a cluster. It was illustrated by means of SCF- X_α -SW and EHT calculations, X-ray photoelectron, X-ray emission and ESR spectroscopy [4-6].

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EPR SPECTROSCOPY OF TECHNETIUM COMPOUNDS

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Electron Paramagnetic Resonance spectroscopy is a favourable spectroscopic method to study coordination compounds of technetium in the oxidation states „+2“ and „+6“, corresponding to the electronic configurations „d⁵-low-spin“ and „d¹“, both having one unpaired electron. This enables the observation of EPR spectra at convenient temperatures (room-temperature down to liquid nitrogen temperature). The information which can be derived from the spectra can be used to discuss structure and bonding properties of the compounds under study as well as to evaluate chemical reactions in which Tc(II) or Tc(VI) compounds are involved.

The application of EPR spectroscopy on chemical reactions will be demonstrated on Tc(II) nitrosyl and thionitrosyl complexes of the general formula $[\text{Tc}(\text{NY})\text{X}_{4/5}]^{(-/2-)}$ ($\text{X} = \text{Cl}, \text{Br}, \text{NCS}$; $\text{Y} = \text{O}, \text{S}$) and the Tc(VI) nitrido complexes $[\text{TcNX}_4]^-$ ($\text{X} = \text{Cl}, \text{Br}$) which all undergo ligand exchange reactions in the equatorial coordination sphere. Additionally, the thermal decomposition of thionitrosyl species will be regarded which finally yields nitrido compounds.

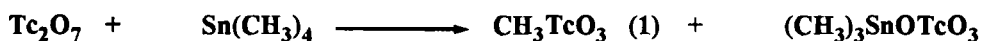
The application of EPR on problems of structural chemistry and the detailed evaluation of the electronic situation in paramagnetic compounds will be discussed on Tc(VI) nitrido and oxo compounds and Tc(II) cations of the general formula $[\text{Tc}(\text{TMP})_4(\text{L})_2]^{2+}$ ($\text{TMP} = \text{trimethylphosphite}$, $\text{L} = \text{thiourea}$ or selenourea). The results of modern Double Resonance experiments (ENDOR and ESEEM) are involved as well as computer simulation of spectral parameters.

NEW ORGANOMETALLIC COMPLEXES OF TECHNETIUM IN ITS HIGH AND LOW OXIDATION STATES

By Roger Alberto

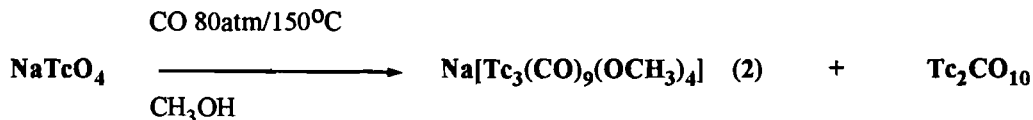
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Chemistry of technetium is best developed in its medium oxidation states +III, +IV and +V resulting in a profound knowledge about coordination chemistry and chemical behaviour. We tried different approaches to expand this knowledge also to high and low oxidation states. Special interest was put on the comparison between the reactivity of rhenium and technetium. With the synthesis of the very volatile compound **1** we could characterize for the first time a high valency organometallic Tc-compound.



Although the synthesis follows that of the rhenium compound, subsequent chemical reactions with **1** proved that the difference in reactivity between the two elements is not only gradual as would be predicted but fundamental. Catalytic oxidation of alkenes, for example, results stereospecifically in *cis*-dihydroxy compounds.

As well as the oxidation state +VII the state +I opens a wide variety of new compounds and reactions. For the synthesis of carbonyl complexes as useful educts for low valent chemistry we investigated low pressure carbonylation of pertechnetate. Under moderate conditions the first fully characterized Tc(I) cluster **2** is formed which proved to be a reactive educt for easy formation of carbenes and other organometallic compounds.



Whereas Tc chemistry usually mirrors that of rhenium the synthesis and properties of **2** initiated our efforts to investigate analogous Re chemistry, as this kind of complex was not previously known.

STRUCTURE AND PHYSICOCHEMICAL PROPERTIES OF NEW TECHNETIUM COMPLEXES

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The topic of this report is the analysis of the data about electronic and molecular structures and physicochemical properties (stability in water solutions, optical spectra, magnetic and some other properties) of Tc coordination compounds investigated recently in the Institute of Physical Chemistry. The most important types of the Tc coordination compounds under consideration are pertechnetates and hexachlorotechnetates(IV) with organic and inorganic ligands, bi- and polynuclear clusters with metal-metal bonds of different multiplicity, carbonyl complexes. The main attention is paid to structurally characterized compounds. For the majority of the compounds the electronic structure has been investigated by EHT technique. Crystallographic data for some of the compounds are as follows.

[Tc(CO)₃Cl]₄: cubic, space group I $\bar{4}$ 3m, $a = 10.322(3)$ Å, $R = 0.021$. The neutral tetranuclear complex with crystallographic T_d symmetry has interatomic distances Tc-C 1.93 Å, Tc-Cl 2.559 Å, C-O 1.13 Å. Both Tc...Tc distance of 3.840 Å and the results of EHT calculations show the absence of a direct Tc-Tc interaction in this complex.

[Tc(CO)₃Br·en]: monoclinic, space group P2₁/n, $a = 7.013(2)$, $b = 13.177(8)$, $c = 10.736(5)$ Å, $\beta = 101.73(3)^\circ$, $R = 0.045$. The coordination polyhedron of Tc is a distorted octahedron with Br atom in *trans*-position to one of carbonyls (the symmetry of the complex is C_s). The main interatomic distances are Tc-Br 2.64 Å, Tc-N 2.22 Å, C-O 1.15 Å and Tc-C 1.89 Å (the last two distances being equal for all three CO groups, showing the absence of a *trans*-influence). The possible isomer of this complex has Br and N atoms in *trans*-positions.

[Tc₂(μ-CH₃COO)₄][TcO₄]₂: monoclinic, space group P2₁/n, $a = 8.324(1)$, $b = 7.826(1)$, $c = 14.644(4)$ Å, $\beta = 101.81(2)^\circ$, $R = 0.037$. The main interatomic distances for the cationic part of the centrosymmetric neutral complex are Tc-Tc 2.149 Å, Tc-O(acet) from 2.00 to 2.03 Å. The distances Tc-O in TcO₄ group are 1.68 Å for terminal O atoms and 1.73 Å for the bridging one which occupies the axial position in the cation with Tc-O distance of 2.15 Å.

[Fe(C₅H₅)₂][TcO₄]: trigonal, space group P3₁21, $a = 8.967(3)$, $c = 12.464(7)$ Å, $R = 0.058$. Both Tc and Fe occupy positions on two-fold axes. The mean interatomic distances are Tc-O 1.69 Å and Fe-C 2.04 Å.

[Fe(C₅H₅)₂]₄(H₁₁O₅)[TcCl₆]₃: monoclinic, space group P2₁/c, $a = 14.918(6)$, $b = 11.448(2)$, $c = 19.915(4)$ Å, $\beta = 91.96(2)^\circ$, $R = 0.044$. The mean interatomic distances are Tc-Cl 2.34 Å and Fe-C 2.05 Å.

[Fe(C₅H₅)₂]₃[TcCl₆]₄: hexagonal, space group P6mm, $a = 15.34$, $c = 12.70$ Å. The main interatomic distances in the anion are Tc-Tc 2.17 and 2.67 Å, Tc-I 2.71 (terminal), 2.61 (bridging) and 3.27 Å (ionic).

A preliminary investigation of the red form of technetium acid has given the triclinic cell with $a = 11.26$, $b = 12.87$, $c = 14.16$ Å, $\alpha = 71.0$, $\beta = 69.1$, $\gamma = 74.1^\circ$.

The influence of a number of factors on the main interatomic distances in Tc complexes has been considered. The most important factors are the formal oxidation state and effective charge of Tc atoms, the chemical nature of ligands and cations. For some compounds a statistical disordering of structure has been found.

ASPECTS OF THE CHEMISTRY OF TECHNETIUM PHOSPHINE COMPLEXES

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The chemistry of technetium complexes containing tertiary phosphine ligands is now well developed. The research leading to this situation has been conducted with the goals of both elucidating the intricate and diverse chemistry of technetium, and then also applying this chemistry to the design and development of ^{99m}Tc radiopharmaceuticals. As a result of these efforts, there are now at least two ^{99m}Tc -phosphine radiopharmaceuticals in commercial development.

Early studies with the prototypical bidentate phosphine ligand DMPE (1,2-bis(dimethylphosphino)ethane) established that stable complexes of Tc(V), Tc(III) and Tc(I) can be readily prepared: $[\text{Tc}^{\text{VO}}_2(\text{DMPE})_2]^+$, $[\text{Tc}^{\text{III}}\text{Cl}_2(\text{DMPE})_2]^+$ and $[\text{Tc}^{\text{I}}(\text{DMPE})_3]^+$. In addition, the corresponding Tc(II) complexes $[\text{Tc}^{\text{II}}\text{Cl}_2(\text{DMPE})_2]^0$ and $[\text{Tc}^{\text{II}}(\text{DMPE})_3]^{2+}$ can be easily generated by chemical or electrochemical means. This facile redox reactivity of the lower oxidation state Tc-phosphine complexes has serious biochemical consequences. The biodistribution of ^{99m}Tc complexes is strongly dependent upon their formal charge; for example, cationic complexes accumulate in the heart but cannot pass the blood-brain barrier (BBB), whilst neutral complexes do not accumulate in the heart but can pass the BBB. Redox reactions which occur in vivo complicate the situation, but also raise the possibility of designing ^{99m}Tc imaging agents which function because of their redox reactivity. For example, it should be possible to design a neutral $^{99m}\text{Tc}(\text{II})$ complex which crosses the BBB and then undergoes oxidation within the brain to a cationic $^{99m}\text{Tc}(\text{III})$ species which is trapped in the brain sufficiently long to allow tomographic imaging.

Extensive studies have shown that the Tc(III/II) redox potential can be precisely controlled by varying (a) the number of coordinated phosphine ligands (the more coordinated phosphines, the easier it is to reduce Tc(III) to Tc(II)), (b) the nature of other ligands coordinated to technetium (e.g., replacing a halo ligand by a thiolato ligand makes the Tc(III)-phosphine complex much more difficult to reduce), and (c) the pendant groups attached to the phosphorus ligand (e.g., complexes of phenyl substituted phosphine ligands are more easily reduced than are their methyl substituted analogs). These principles have been used to design cationic $^{99m}\text{Tc}(\text{III})$ -phosphine complexes suitable for myocardial perfusion imaging, one of which is now in commercial development.

CHEMICAL SENSORS FOR RADIOPHARMACEUTICAL IMAGING AGENTS

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Radiopharmaceuticals are used in nuclear medicine to image specific organs for the purpose of diagnosis. In many instances the composition of the injected radiopharmaceutical is known, but the chemical form of the agent that is actually responsible for the image may be an altered form due to *in vivo* reaction. Sensors are being developed for imaging agents to determine the chemical form of the agent that provides the image of the organ. Since many imaging agents are electroactive and absorb light in the UV-visible range, both electrochemical and optical sensors are being developed. The optical sensors are based on the measurement of absorbance with a fiber optic. The electrochemical sensors are based on polymer modified electrodes at which the agent is detected by voltammetry. The polymer film is expected to serve several functions: (a) To improve detection limit by extracting the imaging agent from the sample and enhancing its concentration at the electrode surface. (b) To improve selectivity in a biological matrix by rejecting some possible electroactive interferents. (c) To retard electrode fouling by surfactants in the biological matrix. A prototype sensor that consists of a carbon electrode modified with a cation exchange polymer, Nafion gel, has been developed for $\text{Re}(\text{DMPE})_3\text{CF}_3\text{SO}_3$, where $\text{DMPE} = 1,2\text{-bis}(\text{dimethylphosphino})\text{ethane}$. This compound is a non-radioactive analog of the $\text{Tc}(\text{DMPE})_3^+$ radiopharmaceutical that shows uptake in the heart. The electrochemistry of the rhenium complex at a Nafion gel modified electrode is a single, well-defined redox couple located at 0.062 V. However, peak currents for cyclic voltammetry and differential pulse voltammetry show an enhancement of up to 100x (compared to bare electrodes) for 10^{-6} M solutions due to partitioning of the complex into the Nafion gel coating. Thus, Nafion gel is a promising candidate for surface modification of electrodes for the detection of cationic imaging agents.

**o-TOLUENEBORONIC ACID ADDUCTS OF TECHNETIUM TRIS(DMG):
SYNTHESIS, STRUCTURE ANALYSIS AND CHARACTERIZATION**

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Monocapped boronic acid adducts of technetium tris(dioxime)(BATO), now attract more and more attention owing to their potential usage in radiopharmaceutics. A large number of BATOs have been prepared and characterized. We recently synthesized BATO complex, $\text{TcCl}(\text{dmg})_3\text{BC}_6\text{H}_4\text{CH}_3$, determined its crystal structure and studied its ^1H NMR, IR and UV/Vis spectra.

The complex was prepared by template reaction reported in literature. The crude product was recrystallized from CH_2Cl_2 /hexane/ligroin mixture, yielding red -brown single crystals.

The ^1H NMR indicates a singlet(6H) at 2.39ppm, a singlet (12H) at 2.44ppm , a singlet(3H) at 2.49ppm, a singlet(4H) at 7.25ppm.

The IR shows that the stretching vibration of $>\text{C}=\text{N}-$ shifted to $\nu=1635\text{cm}^{-1}$ from $\nu=1697\text{cm}^{-1}$ in free dimethylglyoxime.

The UV/Vis contains four peaks ($\lambda=230, 325, 382, \text{ and } 458\text{nm}$), while the $(\text{OH})_2\text{BC}_6\text{H}_4\text{CH}_3$ has only three peaks($\lambda=202, 215 \text{ and } 272\text{nm}$). The latter two absorptions in the complex may be assigned as $\text{Tc}(\text{II})d-d$ transition peaks.

A $0.15 \times 0.20 \times 0.30\text{mm}^3$ crystal was used for structural analysis. Data were collected with a Siemens R3m/V four-circle diffractometer using the $\theta - 2\theta$ scan technique with $\text{Mo K}\alpha$ radiation and a graphite monochromator. A total of 4579 independent diffractions were collected. Among them 3577 observed diffractions ($F > 6.0\sigma(F)$) were taken for the least-square fitting. The final value of R is 0.044.

The crystal is triclinic with space group $P\bar{1}$. The cell parameters are: $a=8.581(1)\text{\AA}$, $b=11.996(3)\text{\AA}$, $c=13.364(4)\text{\AA}$, $\alpha=96.71(2)^\circ$, $\beta=92.14(2)^\circ$, $\gamma=108.24(2)^\circ$, $V=1293.6(5)\text{\AA}^3$, $Z=2$, $d(\text{calc.})=1.595\text{g/cm}^3$.

One molecule of CH_2Cl_2 is assumed to be present in each cell according to the site disorder and apparent temperature factors. This assumption is also supported by experimental determination of its density ($d(\text{Exp.})=1.594\text{g/cm}^3$) by flotation method.

The coordination polyhydal of this complex can be described as a capped triangle prism. The bond lengths(in \AA) are as follows: $\text{Tc}-\text{Cl}$ 2.410(2), $\text{Tc}-\text{N}(1\text{B})$ 2.046(4), $\text{Tc}-\text{N}(2\text{B})$ 2.077(5), $\text{Tc}-\text{N}(3\text{B})$ 2.052(4), $\text{Tc}-\text{N}(1\text{F})$ 2.132(4), $\text{Tc}-\text{N}(2\text{F})$ 2.070(5), $\text{Tc}-\text{N}(3\text{F})$ 2.128(4). The structure is very similar to those of other known BATOs.

The Design and Properties of ^{99m}Tc -Chelates for Brain Perfusion Imaging

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Because ^{99m}Tc exhibits favorable physical properties and it is readily available, it will remain the most widely used radionuclide in clinical nuclear medicine for the foreseeable future. Coupling the ideal imaging properties of ^{99m}Tc with the introduction of new high resolution, high sensitivity imaging instrumentation, the utility of ^{99m}Tc radio-pharmaceuticals for brain perfusion imaging will increase dramatically over the next decade. ^{99m}Tc -chelates currently used or under consideration as brain perfusion imaging agents are small, neutral and lipophilic. In addition to these general characteristics, other structural requirements are necessary to facilitate efficient extraction of ^{99m}Tc -chelates from the blood into living cerebral tissue. For example, the two most widely used chelates in humans for regional cerebral blood flow (rCBF) imaging (^{99m}Tc -d,l-HMPAO and ^{99m}Tc -l,l-ECD) contain the TcO^{+3} core and have minimal sites on the chelate for hydrogen bonding.

A high degree of long-term cerebral retention of ^{99m}Tc after extraction of the tracer in brain is also an important characteristic of potential rCBF imaging agents. Various mechanisms for efficient intracellular trapping have been shown to be effective for providing retention of ^{99m}Tc in brain including conversion of the lipophilic chelate to a hydrophilic species, chelate dissociation and high affinity cellular binding of the intact chelate. To complicate matters, the rate and duration of intracellular trapping of ^{99m}Tc is often highly sensitive to chelate stereochemistry.

Clearly, the design of effective new ^{99m}Tc -rCBF agents is challenging since the chelates (drug product) must satisfy the stringent *in vivo* localization properties described above, as well as being able to be readily formed in high radiochemical yields with good stability in aqueous solutions.

STABILITY OF ISOMERS OF ^{99m}Tc -HMPAO AND COMPLEX OF ^{99m}Tc -CBPAO BASED ON CNDO/2 METHOD

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It is well know that 3,6,6,9-tetramethyl 4,8-diazaundecane-2,10-dione dioxime (HMPAO) is now widely used in nuclear medicine as a potential brain imaging agent. The isomers of ^{99m}Tc -HMPAO reveal dramatical differences of biodistribution in brain uptake and retention that may be caused by structural configuration and various stability of isomers. In this paper, we use three indicators to describe the stability of isomers and complex of ^{99m}Tc -CBPAO based on corn packing model or CNDO/2 method.

The computed results indicated that the order of stability of isomers is as follows: meso-2- ^{99m}Tc -HMPAO > ^{99m}Tc -d,1-HMPOAO > meso 1- ^{99m}Tc -HMPAO. After cyclation of d, 1-HMPAO, the stability of ^{99m}Tc -d, 1-CBPAO is increased rapidly. This study reveal structural features that may be useful to account for disparate pharmacokinetic of the meso and d,1-HMPAO ^{99m}Tc -radiopharmaceuticals.

comparison of SAS values, formation energies and total energy of system

d,1-HM-PAO meso 1-HMPAO meso 2-HMPAO d,1-CB-PAO

NETCHARGE DISTRIBUTION

Tc:	0.978	0.875	1.081	1.577
O :	-0.114	-0.162	-0.163	-0.469
N ₁ :	-0.236	-0.440	-0.241	-0.176
N ₂ :	-0.176	-0.205	-0.301	-0.007
N ₃ :	-0.059	-0.080	-0.405	-0.411
N ₄ :	-0.321	-0.060	-0.008	-0.200

FORMATION ENERGY

0.4575	0.4209	0.6312	0.7563
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TOTAL ENERGY OF SYSTEM

-179.44320	-178.5840	-180.3409	—
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SAS VALUES

0.9140	0.9114	0.9147	—
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THE CHEMISTRY AND PHYSICAL PROPERTIES OF LIPOPHILIC RHENIUM DI AMINO DI THIOL COMPLEXES .

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The similarity of the chemistry of Technetium and Rhenium have, in the light of recent interest in ^{186}Re and ^{188}Re as radiotherapeutic isotopes, been utilised to transfer the knowledge and expertise obtained in research on Technetium radiopharmaceuticals to the field of Rhenium based therapeutic agents. The Di-amino-di-thiolate ligands have proved to be some of the most stable and useful for technetium and recent work¹ has shown that they are useful for rhenium as well.

A series of model Rhenium complexes based on this ligand were prepared to investigate the feasibility of this ligand system for radiotherapeutic applications such as radioimmunotherapy when using ^{186}Re and ^{188}Re as the label. The complexes $\text{ReO}[\text{TE-DADT}]$, $\text{ReO}[\text{TEDM-DADT}]$ and $\text{ReO}[\text{HM-DADT}]$ were prepared and showed similar chemical and physical properties to each other but exhibited some variance with their Tc analogue; notably a reduced solubility range .

The previously made complex $\text{ReO}[\text{NMeTM-DADT}]^1$, while also showing poor water solubility, exhibited higher lipophilicity than the other Re complexes and showed differences in physical properties; notably a shift in the Re-O stretch frequency and lowered melting point. A range of Re complexes which possess longer N-alkyl side chains ($\text{ReO}[\text{N-Hexyl-TM-DADT}]$, $\text{ReO}[\text{N-Octyl-TM-DADT}]$, $\text{ReO}[\text{N-Decyl-TM-DADT}]$ and $\text{ReO}[\text{N-Myristyl-TM-DADT}]$) were prepared. These complexes showed increasing lipophilicity and lowering melting point with increasing chain length although labelling yields also decreased with length of chain. The Re-O stretch wavenumber was the same as the N-Methyl complex.

An X-ray crystal study showed that the $\text{ReO}[\text{TE-DADT}]$ complex has strong hydrogen bonding between the single remaining amine proton and the oxygen atom of an adjacent complex, forming dimeric structures in lattice. In comparison crystals of $\text{ReO}[\text{N-Hexyl-TM-DADT}]$ showed no hydrogen bonding. This absence helps explain the improved lipophilicity and difference in Re-O stretch wavenumber between the N-substituted and unsubstituted complexes.

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USE OF TECHNETIUM-99m IN PULMONARY NUCLEAR MEDICINE

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Nuclear Medicine cannot survive without technetium-99m (Tc-99m). Practically all radiopharmaceuticals currently in use are tagged with Tc-99m. Pulmonary Nuclear Medicine is no exception. Since elaboration of Iodine-131 tagged macroaggregated human serum albumin (HSA)(I-131 MAA) by Taplin in 1963, this agent had been widely used for perfusion lung imaging for detecting pulmonary embolism. By 1970, however, I-131 was replaced by Tc-99m because of the latter's favorable characteristics; gamma-energy of 140 kev, 6 hrs half-life, easy milking system from Molybdenum-99 cow and simple labeling using kit products. In a country like Japan where the incidence of pulmonary embolism is low, pulmonary perfusion studies have been used as a means to assess regional lung function. Trials were made to develop methods to study the distribution of ventilation or inhaled tracer materials in the lungs. Radioactive gases like Xenon-133 and Krypton-81m were used but radioaerosols especially of Tc-99m tagged HSA, DTPA, and so on were applied to the study of ventilation distribution. Due to the inherent size the distribution of inhaled radioaerosols in the lungs is not necessarily the true picture of ventilation distribution, but can serve as its substitute and help differentiate underlying obstructive airways disease as well. The knowledge whether or not the areas with perfusion defect are ventilated is vital to the diagnosis of pulmonary embolism. In addition to evaluating ventilatory status in the lungs, radioaerosols can be used for studying nonrespiratory lung function such as mucociliary clearance mechanisms and pulmonary epithelial permeability. Using nonabsorbable but biodegradable aerosols like Tc-99m HSA, mucociliary clearance in vivo has been quantitatively and qualitatively elucidated and visualized with "radioaerosol inhalation lung cine-scintigraphy". Mucociliary clearance in pathologic states has been revealed to show protean disturbances in mucus transport which should have something to do with pathogenesis of infections. Smokers and patients with interstitial lung diseases show increased pulmonary epithelial permeability. One of the recent advances in the application of Tc-99m is the development of "Technegas". It sounds like a gas but is actually a mixture of Tc-99m tagged carbon particulates the maximum size of which is 200 nm but the majority far smaller in size. Application of "Technegas" will be also discussed.

THE CLINICAL UTILITY OF BRAIN PERFUSION SPECT USING Tc-99m HMPAO

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The clinical value of measuring regional brain perfusion has been recognized. Local variations in perfusion are associated with many brain diseases such as stroke, tumors, epilepsy, dementia, and psychiatric illness, and any technique which provides an image of brain perfusion is of particular interest. Radionuclide tracers have been used for this purpose for many years, but it is only recently that potential for three-dimensional imaging of brain perfusion on a routine diagnostic basis has come close to being realized.

Several tracers for evaluating brain perfusion have been developed for a Single Photon Emission Computed Tomography (SPECT) technique that uses conventional gamma ray production and detection. Of these tracers, Tc-99m hexamethylpropylene amine oxime (Tc-99m HMPAO) has several advantages over other tracers. The proper energy of Tc-99m to a gamma camera and relative high dose result in good image quality. It is readily available even in an emergency case because of its kit form for Tc-99m labeling. A distribution pattern of the tracer is determined in a short period and kept for a long time after intravenous injection. This property is quite useful for the evaluation of perfusion changes during interventional studies of short duration. We applied this property to investigate perfusion changes during the artificial carotid artery occlusion and to evaluate drug effects, e.g., acetazolamide or haloperidol on regional brain function. We combined a perfusion study during the intervention with that at baseline as a consecutive study. This combination enabled us to perform the whole study within 35 min and to obtain identical slices to compare the results at baseline and during the intervention with little motion artifact of the patient's head.

It has been reported that one of disadvantage of the tracer is the practical difficulty in determining cerebral blood flow values. However we recently developed a non-invasive, simple method for the quantitative evaluation of brain perfusion. In this approach graphical analysis was employed for the evaluation of the unidirectional influx constant of the tracer from the blood to the brain. This technique is easy to apply as an adjunct to SPECT without any blood sampling and may be helpful in the quantitative evaluation of brain perfusion in routine clinical studies.

CURRENT STATUS AND TREND IN DEMAND OF Tc-99m RADIOPHARMACEUTICALS IN JAPAN

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About 20 years have passed since the official approval of ^{99}Mo - $^{99\text{m}}\text{Tc}$ generator as radiopharmaceuticals in Japan. In accordance with the consequent development of new ligands for labeling and expansion of diagnostic field, $^{99\text{m}}\text{Tc}$ -radiopharmaceuticals have on the increase in number of the items and the consumption amount.

^{99}Mo - $^{99\text{m}}\text{Tc}$ generator is the type which is supplied and used on the most largest scale. The total yearly supply of the product from four manufacturers/importer has amounted to 177.8 TBq in 1991, furthermore showing a tendency to increase in demand. Twelve types of cold kits distinguished by diagnostic use are being supplied for labeling use, with about 320,000 vials recorded as consumption amount in 1991.

On the other hand, "ready-to-inject" form can be pointed out as a characteristic form in domestic supply to hospitals after $^{99\text{m}}\text{Tc}$ -labeling and quality tests by manufacturers. The wide-scale diffusion is attributed to the various advantages welcomed by users, e.g. exposure reduction, assured quality and simplified usage. Moreover, continuous introductions of new products in the form (currently eight items on the market) are contributing to increase in demand, with the growth rate of more than 20% per year. Thanks to the product line, the supply amount reached about 92 TBq in the year of 1991, and the increase will likely continue in the future.

Currently in Japan, as far as the source of ^{99}Mo is concerned, the domestic production/supply system is not established, and the situation is considered one of the controversial issues to be improved, in securing the stable supply of $^{99\text{m}}\text{Tc}$ -radiopharmaceuticals.

In the field of image diagnosis, technical improvement and expansion of competitive modalities such as CT, MRI, US are found to be remarkable. However, nuclear medicine procedures using radiopharmaceuticals including Tc-99m compounds are inevitable for diagnoses, taking advantage of the character as "in vivo RI tracer" or catching regional physiological/biochemical-function changes based on dynamics, and further development toward the course is expected.

1-P-1

(n,n') PRODUCTION OF ^{99m}Tc BY ^{252}Cf FISSION NEUTRONS

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Activation technique was employed to determine the average cross section of $^{99}\text{Tc}(n,n')^{99m}\text{Tc}$ reaction for fast-neutron spectrum of spontaneous fission of ^{252}Cf by two different gamma-spectrometric method. One of the measurements was relative to that of the known cross-section value of $^{115}\text{In}(n,n')^{115m}\text{In}$ reaction, the other one was absolute. The measured values are 141 ± 21 mb and 137 ± 18 mb for the relative and absolute measurement, respectively.

INTEGRAL CROSS SECTION OF THE $^{99}\text{Tc}(\gamma, \gamma')^{99\text{m}}\text{Tc}$ REACTION
AT 4 MeV

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The $^{99\text{m}}\text{Tc}$ production was studied with the aid of photoexcitation by a 4 MeV endpoint energy bremsstrahlung from the linac of the Institute of Isotopes, Budapest. The intensity of the γ -flux was monitored by disc-shaped natural indium plates, placed in front of and behind the small cylindrical aluminium holders containing TcO_2 samples in a powder form. Isomeric activities were measured through the 140 keV γ -line by a Ge spectrometer.

The integral cross section at 4 MeV was found to be 63.3 ± 7.1 μbMeV , which can be considered reasonable compared to the corresponding value of 55.3 μbMeV established for the $^{115}\text{In}(\gamma, \gamma')^{115\text{m}}\text{In}$ reaction.

We also attempted the photoexcitation of $^{99\text{m}}\text{Tc}$ by irradiation with γ -rays from a 1.5×10^{15} Bq ^{60}Co source, but no isomeric activity could be observed. This renders the first activation level to lie between 1.33 and 4 MeV.

^{95}Tc AND ^{96}Tc PRODUCTION BY (γ, xn) REACTIONS

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The $^{99}\text{Tc}(\gamma, 3n)^{96}\text{Tc}$ and $^{99}\text{Tc}(\gamma, 4n)^{95}\text{Tc}$ reactions were studied by irradiation of target ^{99}Tc with bremsstrahlung from the linear electron accelerator at the Tohoku University, up to 50 MeV γ -energy. The resulting ^{96}Tc (4.3 d) and ^{95}Tc (20 h) activities were determined by γ -spectrometry, measuring the 813, 1127 keV, as well as the 766, 1074 keV photopeaks, respectively. Metallic copper and gold foils were used as flux monitors in front of and behind the samples. Their measured radioactivity was utilized for normalizing bremsstrahlung flux calculations, in order to determine reaction cross sections.

Cross sections were also determined theoretically performing calculations in the framework of a neutron cascade evaporation model. Above the $(\gamma, 3n)$ and $(\gamma, 4n)$ threshold energies the neutron emission channel was supposed to be the only open channel for deexcitation following photoabsorption. The preequilibrium contribution was considered negligible. The experimental results obtained for integrated cross section at 30 and 50 MeV fit reasonably well the calculated curves.

NUCLEAR REACTIONS OF ^{99}Tc WITH FISSION NEUTRONSI. Yamagishi, M. Kubota, T. Sekine*, K. Yoshihara*Department of Fuel Safety Research, Japan Atomic Energy
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The cross-sections of the (n,n') , (n,p) and (n,α) reactions of ^{99}Tc have been reported by several workers for 14 MeV neutrons. However, the nuclear data of ^{99}Tc are not satisfactory for the fission neutron induced reactions. In the present study, the integral cross-sections of these reactions of ^{99}Tc were determined by means of the activation method with fission neutrons.

^{99}Tc , in the chemical form of ammonium pertechnetate, was purchased from Amersham International. Various amounts (0.3~5mgTc) of the ^{99}Tc stock solution were taken on filter papers and quartz tubes, and evaporated to dryness. These targets were irradiated for 20 minutes with the JRR-4 reactor at our institute. The activity was measured by a pure Ge detector connected to a 4096 channel pulse height analyzer.

The direct γ -ray spectrometry for the irradiated filter type target showed major peaks at 140, 137 and 155 keV of $^{99\text{m}}\text{Tc}$, ^{186}Re and ^{188}Re , respectively. The activities of these nuclides increased proportionally with the amount of ^{99}Tc taken on filter paper. Standard Re target was irradiated at the same time to determine the amount of Re in the Tc target. The molar ratio of Re to Tc in the Tc stock solution was found to be 8.63×10^{-5} . The activity ratio of ^{186}Re to ^{188}Re produced in the Re target was in agreement with that in the Tc target.

^{99}Tc irradiated on quartz tube was dissolved in HNO_3 . ^{99}Mo produced by the (n,p) reaction was extracted completely from the HNO_3 solution with diisodecylphosphoric acid. The γ -ray spectrometry for the organic phase showed decisive evidence of the presence of the 181 and 740 keV peaks of ^{99}Mo . Furthermore, the peaks of ^{96}Nb were observed in the same γ -ray spectrometry.

The activities of $^{99\text{m}}\text{Tc}$, ^{99}Mo and ^{96}Nb produced with fission neutrons were 3.38×10^5 , 3.9 and 0.85 Bq/mg ^{99}Tc , respectively. Assuming the fast neutron flux at the irradiation site of 1.2×10^{13} /cm²/s, the following cross-sections were obtained

$$\begin{aligned} {}^{99}\text{Tc}(n,n'){}^{99\text{m}}\text{Tc} & 0.123 \pm 0.008 \text{ barn} \\ {}^{99}\text{Tc}(n,p){}^{99}\text{Mo} & (1.53 \pm 0.04) \times 10^{-5} \text{ barn} \\ {}^{99}\text{Tc}(n,\alpha){}^{96}\text{Nb} & (1.19 \pm 0.06) \times 10^{-6} \text{ barn.} \end{aligned}$$

These values should be corrected for the fast neutron flux obtained from monitoring reactions of several threshold detectors.

DETERMINATION OF TECHNETIUM-99 IN ENVIRONMENTAL SAMPLES BY INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY

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[Introduction]

Inductively Coupled Plasma Mass Spectrometer (ICP-MS) is a powerful apparatus for ultra sensitive trace analysis, and has several superior characteristics, e.g., extremely low detection limit, short measuring time and easy qualification and quantity of ultra trace elements. This research has considered about the determination of Technetium-99 (Tc-99) in environmental samples by ICP-MS.

[Development of Determination Method by ICP-MS]

Environmental samples like soils contain much amount of matrix elements. Thus, the organic matrix was eliminated by ashing at 450°C for 20 hours, and inorganic matrix elements were eliminated by the iron hydroxide coprecipitation method and anion exchange method.

Fig.1-a) shows the mass spectrum of a sample solution by ICP-MS. The solution was prepared by the solvent extraction method using tri-iso-octylamine (TIOA). The figures indicate the interference by Ru-99, whose mass number is the same as Tc-99, on the basis of the results from the relative abundance of naturally occurring isotopes. Then, the decontamination factor (D.F.) test using Ru-106 was conducted, and the result of this test is shown in Table 1.

The values in the table show that the solution, extracted by cyclohexanone from the potassium carbonate alkaline solution, gets higher D.F. value, i.e., 1.9×10^5 . Thus, the cyclohexanone extraction method was selected as a Ru-99 eliminating method.

Fig.1-b) present the spectrum by ICP-MS of the solution after the elimination of Ru by solvent extraction method using cyclohexanone. This spectrum shows that Ru could be completely eliminated from the sample solution, due to no peak on the position for the substance of mass number 101.

[Conclusion]

In comparison with conventional determination methods, it has been identified that ICP-MS was able to lower modified the detection limit by 1/10 to 1/100, and the total time required through all analytical processes was shortened to be one half of that by the method without using ICP-MS.

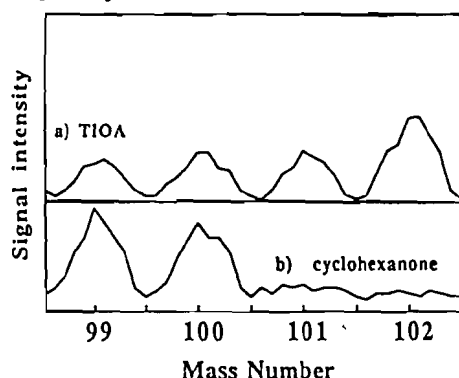


Fig.1 Mass spectra of soil sample solution

- a) Tc-99 was extracted with TIOA
- b) Tc-99 was extracted with cyclohexanone

Table 1 Decontamination Factors for Ru-106

separation method	D. F. of Ru-106
Anion exchange (NO_3^- media)	220
Solvent extraction	
TIOA - 1M HNO_3	11.1
TBP - 0.1M HNO_3	34.9
$\text{C}_6\text{H}_{10}\text{O}$ - 1M HNO_3	9.9
$\text{C}_6\text{H}_{10}\text{O}$ - 1M HNO_3^*	74.6
$\text{C}_6\text{H}_{10}\text{O}$ - 1M K_2CO_3	726
$\text{C}_6\text{H}_{10}\text{O}$ - 1M K_2CO_3^*	1.9×10^5
Coprecipitation on TPAC	27.7

* Oxidation before extraction

ANALYTICAL PROCEDURE FOR TECHNETIUM-99
IN SEAWATER BY ICP-MS

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Analytical procedure for determining ^{99}Tc concentration in seawater was developed. Pre-concentration of ^{99}Tc is necessary because quite low ^{99}Tc concentration is expected in seawater except near re-processing plants. The pre-concentration of ^{99}Tc from a large volume of seawater was carried out as described below.

The ^{99}Tc in seawater was co-precipitated with iron hydroxide after reduction Tc(VII) to Tc(IV) . Almost complete reduction was achieved by $\text{K}_2\text{S}_2\text{O}_5$ at pH 4 and co-precipitation of ^{99}Tc with iron hydroxide was quantitative at pH 9. The iron hydroxide with ^{99}Tc was dissolved with acid and the iron was used repeatedly as co-precipitater. The ^{99}Tc was successively accumulated from seawater on the same iron. No loss of ^{99}Tc and no reduction of ^{99}Tc recovery was observed.

Linear relationship was found between ^{99}Tc concentrations and counts in mass 99 of the ICP-MS (YOKOGAWA, PMS-2000) in the range from 0 to 15 ppt, which would encounter in the analysis of environmental samples. Separation of ^{99}Tc from other elements is necessary for reliable measurement because background counts in mass 99 varies depending upon the purification of samples. Isolation of Ru from samples is required because Ru has an isotope of mass 99. The ^{99}Tc co-precipitated on the iron hydroxide was oxidized to TcO_4^- (VII) and the large amount of iron was eliminated by precipitation. The ^{99}Tc in the solution was co-precipitated again on a small amount of iron hydroxide to reduce sample volume. Finally the ^{99}Tc was recovered as TcO_4^- and evaporated to dryness. The residue was dissolved in 5M NaOH, and the ^{99}Tc was extracted 2 times with MEK (methyl ethyl ketone). After removed the MEK by evaporation, the ^{99}Tc was dissolved in 1N HNO_3 , and passed through an anion-exchange column, Dowex 1X8. After washing the column with 1N HNO_3 , the ^{99}Tc was eluted with warmed 16N HNO_3 . The eluate was evaporated to dryness and dissolved in 1N HNO_3 . The ^{99}Tc was purified by cation-exchange resin and evaporated to dryness. Finally the ^{99}Tc was dissolved in 1N HNO_3 and subjected to measurement by ICP-MS.

The recovery of ^{99}Tc from seawater was almost quantitative; more than 98% was confirmed for 7 repeats. Overall recovery by above procedure was around 60%. In sample analysis $^{95\text{m}}\text{Tc}$ tracer would be available for evaluating recovery of ^{99}Tc .

SEPARATION PROCEDURE FOR DETERMINATION OF TECHNETIUM-99 IN SOIL BY ICP-MS

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Since technetium-99 is thought to be accumulating in soil, its concentration there should be determined for dose assessment. In previous studies, ^{99}Tc in soil was leached by acid reagents. Although most of the nuclide could be dissolved by this procedure, other elements could also be dissolved. Which interfered with chemical purification of technetium. In our study, a separation method for ^{99}Tc in soil was studied. Technetium was separated from incinerated soil by volatilization, i.e. by combustion of the sample and trapping of the element in solution. After carrying out the separation steps, ^{99}Tc in the final solution was measured by inductively coupled plasma mass spectrometry (ICP-MS). Recently, ICP-MS has attracted attention for its capability to determine trace elements in environmental samples. Some reports also noted it was applicable to determination of ^{99}Tc in the environment, with high sensitivity.

Samples were collected of rice paddy soils in Akita City and Ohgata Village and of unploughed soil in Tsukuba City, then they were air-dried. After incinerating each soil, the sample was put into a combustion apparatus. Oxygen gas was passed through the sample and the ovens were heated to 950°C . During heating, technetium was evaporated from the sample and collected in a trap filled with K_2CO_3 solution. The solution was transferred into a separatory funnel. After addition of cyclohexanone, the solution was shaken to extract technetium into the organic layer. Ruthenium, which has an isotopic abundance of 12.7% at mass of 99, was almost completely decontaminated in the organic layer. This layer was transferred to another separatory funnel. Deionized water ($>17.8\text{M}\Omega$) and carbon tetrachloride were added and the solution was shaken to extract technetium into the aqueous layer. Each step of the solvent extraction was carried out twice. Acidity of the solution containing technetium was adjusted to 5% HNO_3 . This solution was subjected to ICP-MS (YOKOGAWA, PMS-2000). Chemical recovery of technetium was obtained by using soil contaminated with $^{95\text{m}}\text{Tc}$ ($T_{1/2}=61\text{d}$). The ^{137}Cs level in soil was measured by gamma-ray spectroscopy (Seiko EG&G Ortec) for comparison.

Total recovery of this method was 52–64%. The recovery of technetium at the step separating it from the soil by volatilization was 57–71%. For extraction and back-extraction steps by organic solvents the recovery was more than 95%, because hardly any elements which interfere with technetium purification were contained in the trap solution. Activity ratio of $^{99}\text{Tc} / ^{137}\text{Cs}$ was $3.8 \times 10^{-2} - 3.7 \times 10^{-3}$, though the theoretical fission ratio was 1.4×10^{-4} .

CONCENTRATION OF TECHNETIUM-99 IN MARINE ALGAE AND SEAWATER

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Technetium-99 is produced by the fission of uranium, thorium-232 and plutonium-239 with high yield and exists in terrestrial and marine environment as a consequence of the explosion of nuclear bomb tests and of disposals of waste from reprocessing plants. Although the concentrations of technetium-99 in seawater and algae in the north Atlantic Ocean was determined, those in the Pacific Ocean were very few.

The method for the determination of low level technetium-99 in seawater and algae was developed by radioisotope tracer experiment using technetium-95m. Technetium was pre-concentrated from seawater by anion exchange resin, Bio-rad AG1-X8, Cl-form, and was desorbed from the resin by mixing with equal volume of 30% tri-n-octylamine (TOA):xylene solution and nitric acid solution. The organic phase was separated and another 30% TOA:xylene solution was added to the resin and was mixed again. This process was repeated 3 times and all the organic phases were combined and transferred into another separatory funnel. Technetium was stripped from the organic phase by shaking with 5M sodium hydroxide solution, then the aqueous phase was shaken with 2-butanone, which was then removed by rotary evaporator. The residue was dissolved in 0.6N sulfuric acid solution, to which 20mg of cupric ion was added as a co-precipitation carrier. The solution was heated to 80° - 90°C and saturated solution of thioacetamide was added drop by drop with constant agitation for 2 hours till a black precipitate was formed and was coagulated. The precipitate was then filtered by Toyo No. 5C filter paper. Then, the sample was transferred into plastic test tube and was dissolved by diluted ammonium hydroxide and one drop of hydrogen peroxide to estimate the chemical yield by counting gamma ray of technetium-95m.

Algae was reared in an aquarium in which technetium-95m was inoculated. After the algae concentrated the activity it was transferred to a beaker and was mineralized by heating with conc. nitric acid solution. Loss of the activity was not observed in this process. The acidity of the solution was adjusted to 2N nitric acid solution and technetium was extracted by 30% TOA:xylene solution. The rest of the analytical procedures were the same as that of seawater. Overall yield of the tracer experiment was estimated 70%, and error was within 10%.

The concentration of technetium-99 varied from 50 - 2,000mBq/kg. wet for brown algae collected at Nakaminato-shi, Ibaraki, and that of seawater varied from below the detection limit, 10mBq/m³, to 200 mBq/m³. Beta-ray of technetium-99 was measured by beta-spectrometer PICOBETA PBS-1, Fuji Electric.

TRANSFER FACTORS OF TECHNETIUM FROM SOIL TO VEGETABLES

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Laboratory experiments on the transfer of technetium from soil to edible parts of vegetables have been carried out.

Vegetables such as cabbage, Chinese cabbage, carrot, sweet potato and tomato were cultivated in pots containing soil (Andosol) spiked with a ^{95m}Tc tracer (TcO_4). The transfer factor of technetium is defined as "concentration of the technetium per unit weight of plant sample at the time of the harvest (Bq g^{-1} , dry weight)" divided by "concentration of the technetium per unit weight of dry soil (Bq g^{-1} , dry weight)." The transfer factors of technetium for cabbage and Chinese cabbage depended on the position of leaves. The outer part showed higher concentration of technetium than the inner part. Range of the transfer factors of inner and outer parts for edible part of cabbage was 0.3 to 4.5 (dry weight basis) and that of Chinese cabbage was 0.2 to 2.8 (dry weight basis).

In the case of carrot, the transfer factors for root (edible part) was 1.4 - 1.9 (dry weight basis), while the values of the leaves were 41 - 128 (dry weight basis). It was suggested that the Tc concentration in the leaves was higher than that in the other part of the plant.

For tomato, the concentration factors obtained in the experiment were 0.1 - 0.5 (dry weight basis) for edible part (fruit) and 57 - 135 (dry weight basis) for leaves. A similar tendency was also found in the case of sweet potato. The concentration factors were 0.1 (dry weight basis) for edible part (tuber) and 15 - 19 (dry weight basis) for leaves. It can be explained that the transpiration of water from the leaves may promote the accumulation of technetium into the leaves. The lower concentration factors obtained in the inner parts of the cabbage and Chinese cabbage might be caused by the leaf age and the lower transpiration rate due to head formation.

COMPLEXATION OF TECHNETIUM WITH HUMIC ACID

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The complexation of technetium with humic acid, which was extracted from one of the Gorleben groundwaters in northern Germany, was investigated in order to give a basic information on the migration behavior of technetium in a natural aquifer system. It was found that technetium humate was produced as a brownish-black precipitate by addition of Sn^{2+} as a reductant to a mixture solution of pertechnetate (ca. $10^{-4} \text{ mol L}^{-1}$) and humic acid (ca. $10^{-3} \text{ eq L}^{-1}$) at pH 4 in $0.1 \text{ mol L}^{-1} \text{ NaClO}_4$. This precipitate could be distinguished from the TcO_2 , which is stoichiometrically precipitated by the Sn^{2+} reduction of pertechnetate even in the absence of humic acid, with respect to the dissolution behavior. Almost complete redissolution was observed for the technetium humate with increasing pH (up to 11) but not observed for TcO_2 . By means of gel permeation chromatography with a Sephadex G-15 column, more than 96 % of Tc was found in a pertechnetate fraction and only a few percent of Tc was found in an eluate of humic acid. Spectrophotometric analysis also showed the formation of pertechnetate again in the solution. It was suggested that the formed technetium humate is not stable for higher pH and is decomposed to form pertechnetate. The produced amount of technetium humate linearly increases with the added amount of Sn^{2+} with a slope of ca. 0.5, showing that the valence state of technetium is 3+. With decrease of the concentration of humic acid in the solution, the formation of TcO_2 became prominent.

DETERMINATION OF TECHNETIUM BY LASER INDUCED PHOTOACOUSTIC SPECTROSCOPY COUPLED WITH A WAVE-LENGTH SHIFTER METHOD

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Detection of the radioactive nuclide with a long half-life, ^{99}Tc , is an important problem from the view-point of global pollution, because it is accumulating with nuclear reactor operation.

Laser induced photoacoustic spectroscopy is known to be effective in determination of actinide elements in micro amounts. In this study the LPAS method was applied to the case of ^{99}Tc coupled with complexation of Tc with thiourea(tu) or thiocyanate ion.

The complexation procedure was adopted to shift a uv absorption peak of pertechnetate to the visible region.

Photoacoustic signals due to the absorption peaks of $[\text{Tc}(\text{tu})_6]^{3+}$ or $[\text{Tc}(\text{NCS})_6]^{2-}$ were analyzed by using a Fast Fourier Transform (FFT) system. The quantitative detection of ^{99}Tc could be easily performed down to the 10^{-8} M concentration for $[\text{Tc}(\text{tu})_6]^{3+}$. This is about 1000 times more sensitive than ordinary colorimetric analysis. Improvement of the sensitivity is in progress.

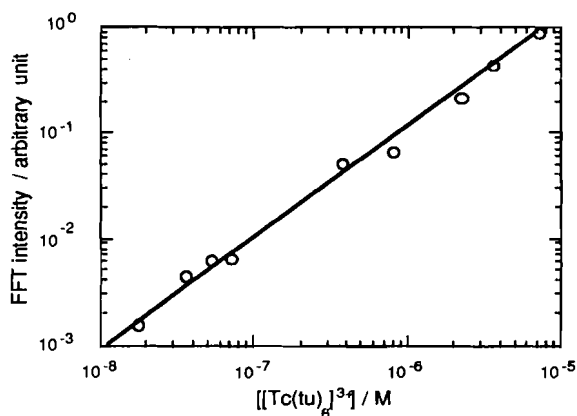


Fig. FFT intensity of photoacoustic signals
at 500nm vs. concentration of $[\text{Tc}(\text{tu})_6]^{3+}$.

THE METHOD FOR TECHNETIUM-99 (Tc-99) ANALYSIS AND ITS
APPLICATION TO HUMAN TISSUES

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Tc-99 is expected to be one of the important nuclides for the collective dose on a long-term scale. The dose contributions come from fallout of nuclear weapon tests and the enhanced total nuclear fuel cycles. The objective for estimation of the exposure from a given source is the determination of the dose distribution to the affected population. In this paper a method was investigated in which Tc-99 in human tissues was determined by gas-flow proportional counting.

The fresh tissue samples were gradually ashed from 100°C to 450°C, and then carbonized in electric furnaces at 550°C to 600°C for 30 to 60 min. Oxalic acid was used to accelerate the ashing speed. The ashed samples were dissolved in 100 ml of 3M H₂SO₄ and the Tc was oxidized to the heptavalent state by boiling for 20 min with 10 g of K₂S₂O₈ and 1 ml of H₂O₄, about 10 μ Ci of Tc-99m isotope was added as a tracer for the determination of chemical yield. The samples were cooled, filtered and rinsed with 3M H₂SO₄. After this, the solution was transferred to a 250 ml separating funnel, 1.0 ml of HF and 10 ml of TBP were added and funnel was shaken for 2 min to extract the Tc into TBP. The phases were allowed to separate for 15 min the aqueous and organic phase washed with 25 ml of 3M H₂SO₄, then 30 ml of xylene was added to dilute the organic phase in order to make back-extraction. The Tc was back-extracted with 15 ml 2M NaOH and the solution was transferred to an electrodeposition cell, Tc was electroplated onto a stainless steel disk 1 inch diameter at 0.3 A for 2 hours. H₂SO₄ was added, the pH was adjusted to 6-8. On completing of the electrodeposition, the electrolyte was discharged and the disc dried on a hot plate.

The concentration of Tc-99 in the samples was measured by pico-beta (Fuji Electric Co., Japan) and Low background beta spectrometer (Aloka Co., Japan). The counting efficiency of the detectors was approximately 4.5% for the former and 15% for the latter, respectively. The counting time was about 3000 min. The autopsy tissues were collected from the Hospital of Niigata Prefecture Institute for Cancer Research. The samples selected for analysis consist of liver and kidney. The average chemical recovery of the Tc-99 in liver samples and kidneys was $74.2 \pm 3.134\%$ ($n = 6$), and $74.7 \pm 2.8\%$ ($n = 2$) respectively. This method will give adequate recoveries for the determination of trace amounts of Tc-99 in biological samples, allowing background activity to be kept at very low levels.

TRANSPORT OF Tc AND Re THROUGH A SUPPORTED LIQUID MEMBRANE

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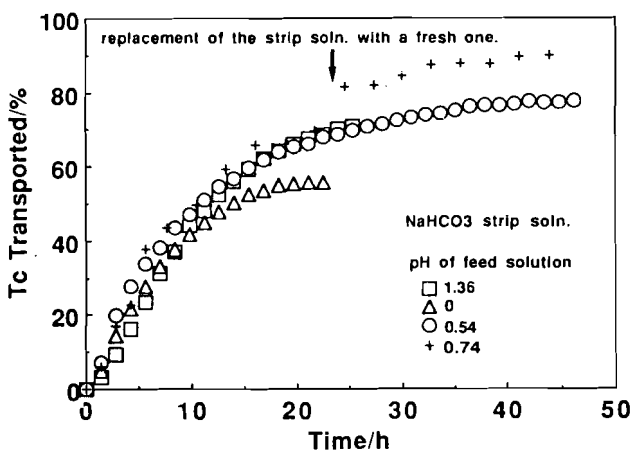
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Separation of metal ions by means of supported liquid membranes is now being viewed with keen interest as an efficient analytical tool. The method is considered to be especially suitable for preparation of radioactive tracer solutions because of (i) the simplicity of operation leading to facile automation, (ii) the feasibility of concentrating tracers into a small volume of a solution, and (iii) the necessity of a far smaller amount of extractants than conventional solvent extraction and reversed-phase liquid chromatography, resulting in little organic radioactive waste. This paper describes successful transport of Tc and Re from acid solutions to alkaline solutions by means of a TBP-decalin membrane supported on a microporous polytetrafluoroethylene sheet.

Tc* and Re* produced in the Au target irradiated with a 135-MeV/nucleon ^{14}N beam were used as tracers. After chemical treatment of the target, a solution containing Tc*(VII) and Re*(VII) was used as a feed solution which was $0.12 \text{ mol dm}^{-3} \text{ NaCl}$ and $0.04 \text{ mol dm}^{-3} \text{ NaNO}_3$. The microporous polytetrafluoroethylene sheet used as the support for TBP-decalin was Fluoropore FP-045 (Sumitomo Electric Ind.) with an average pore size of $0.45 \mu\text{m}$, 75 % porosity, and 0.08 mm thickness. A 24 mm ϕ supported liquid membrane was prepared by impregnating the sheet with a TBP-decalin (3:1) solution. Distilled water or $0.5 \text{ mol dm}^{-3} \text{ NaHCO}_3$ was used as a strip solution. The supported liquid membrane was fixed at the bottom of a Teflon vessel with a Teflon ring. The feed solution in the outer vessel was stirred at 400 rpm with a magnetic stirrer. The strip solution was circulated at the rate of $3 \text{ cm}^3 \text{ min}^{-1}$, a given portion of the circulating solution being trapped in a Teflon vessel put on a pure-Ge detector for measurement of γ -rays. Measurement of 5000 s duration for the strip solution was automatically repeated, and the γ -ray spectra obtained were recorded on a disk.

The transport behavior of Tc and Re was found to be almost the same. The NaHCO_3 solution turned out to be better than the distilled water as a strip solution because of enhancement of the transport. Thereafter, the NaHCO_3 solution was used as a strip solution. Only slight difference in the initial transport rates of Tc was observed for the feed solutions at pH 0 - 1.36 as shown in the Figure. However, the transport of Tc from the feed solution at pH 0 showed saturation soon after beginning of permeation. Transport of Tc from the feed solution at pH 0.54 increased gradually with time. The step at 24 h observed for the feed solution at pH 0.74 was caused by the replacement of the strip solution with a fresh solution.

In conclusion, both Tc(VII) and Re(VII) can be concentrated from a dilute solution by means of a supported liquid membrane of TBP-decalin.



Transport of Tc from feed solutions at pH 0 - 1.36

SENSITIVITY ENHANCEMENT OF PVC MEMBRANE BASED PERRHENATE ION-SELECTIVE ELECTRODE BY ATTACHING ANIONIC POLYELECTROLYTE SOLUTION LAYER

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Pertechnetate and technetium complexes have been used as imaging reagents in radiopharmaceutical fields. A γ -ray camera has been used for detection of radioactivity of the reagents. A sensor for pertechnetate and technetium complexes is expected to be a useful to study of metabolism of the imaging reagents in vivo because of its advantage capable to detect at a small area. In this paper, we described the fabrication of a perrhenate ion-selective electrode (ISE) as a model of pertechnetate ISE because of similarity of chemical properties of both ions. Unfortunately detection limit of a perrhenate ISE reported so far is not so high, it is almost around 10^{-6} M. The main purpose of this study is to enhance the sensitivity by examining an ion exchanger and plasticizer as well as by attaching an anionic polyelectrolyte solution layer on the surface of the ISE membrane.

The perrhenate ISE based on a plasticized poly(vinyl chloride) (PVC) membrane containing an ion-pair of perrhenate ion with a hydrophobic quaternary ammonium ion was fabricated and its performance was examined with respect to selectivity, sensitivity, response time, pH effect etc. Tridecylhexadecylammonium (TDHA), trioctylmethylammonium etc. were examined as an ion-exchanger. Effect of plasticizer on the performance of the electrode was examined by using o-nitrophenyl octyl ether (NPOE), o-nitrophenyl phenyl ether, di(2-ethylhexyl) phthalate etc. As the results, the electrode using TDHA and NPOE as the ion exchanger and the plasticizer, respectively, showed the best performance with the lower detection of 3×10^{-7} M. The potential of the electrode was almost independent of pH in the range pH 2-10. The interference from some common anions such as Cl^- , Br^- , NO_3^- ion etc. was negligibly small against the potential response of the electrode. The response time of the electrode was less than 30 sec for the concentration change by 10-fold from 10^{-5} M ReO_4^- ion.

In order to improve the lower detection limit of the electrode, an aqueous solution layer of an anionic polyelectrolyte, a poly(diallyl dimethyl ammonium) chloride (PDDAC, $M_n=240,000$) was attached to the surface of the PVC membrane of the electrode by covering with a dialysis membrane (molecular weight cut-off; 12,000-14,000), where PDDAC cannot permeate into a sample solution. The perrhenate ion in the sample solution is concentrated into the PDDAC solution layer by ion exchange reaction. This electrode with preconcentration function shows linear response down to 10^{-9} M ReO_4^- with the slope of 10 mV/decade from 10^{-7} M. The response time of the electrode was about 6-10 min, and it was longer than the electrode without PDDAC layer. This is probably controlled by a mass transfer rate of perrhenate ion from the sample solution into the PDDAC layer through the dialysis membrane.

ADSORPTION MECHANISM OF PERTECHNETATE ON ANION EXCHANGE RESIN

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It is well known that pertechnetate can strongly adsorbed on an anion exchange column and its behavior is compared with those of perhenate and perchlorate. However, quantitative explanation for the adsorption mechanism of pertechnetate has not yet been established.

In order to clarify precisely the adsorption behavior of pertechnetate on an anion exchange resin, Dowex 1-X8, distribution ratio was determined as a function of the concentration of hydrogen ion in various acids such as hydrochloric acid, nitric acid and perchloric acid. Similar study was also carried out in sodium hydroxide solution. Thus, fundamental parameters controlling the adsorption mechanism of pertechnetate could be evaluated. Furthermore, thermodynamical consideration was done by the analysis of the temperature dependence of distribution ratio. The distribution ratio of pertechnetate decreases in the order $\text{OH}^- > \text{Cl}^- > \text{NO}_3^- > \text{ClO}_4^-$.

ADSORPTION BEHAVIOR OF OXYANIONS (MO_4^- , $\text{M}=\text{Tc}$, Re , Cl) ON NON-IONIC MACRO-RETICULAR COPOLYMER AND ACTIVATED CARBON FIBER

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Non-ionic macro-reticular (MR) copolymer and activated carbon have been reported to be effective adsorbents for a number of organic materials in aqueous solutions, but not enough attention has been on the adsorption of inorganic substances. Adsorption of various radionuclides on the MR copolymer could be effected if they were converted to organic salts by treating them with suitable organic ligands. In addition, those materials have particularly high distribution ratio (K_d) for MCl_4^- ($\text{M} = \text{Fe}$, Ga and Au) type anions in aqueous solutions above $6 \text{ mol} \cdot \text{dm}^{-3}$ HCl without any other organic ligands. Such peculiar adsorption is similar to those on cation exchange resins obtained by Kraus et al.

In the present work, the adsorption behavior of MO_4^- ($\text{M} = \text{Tc}$, Re , Cl) type anions in aqueous solutions on a non-ionic MR copolymer (Amberlite XAD-7) and a novoloid-based activated carbon fiber (Kynol ACF-1605-15) were studied. The retention of the oxyanions was studied under static conditions (batch method). The solutions of oxyanion in 0.01 – $10 \text{ mol} \cdot \text{dm}^{-3}$ HCl , LiCl , HNO_3 or LiNO_3 were shaken with the adsorbents for 2 hours, and then the concentrations of substance in the supernatant were determined with GM-counter (Tc), PIXE method (Re), spectrophotometer (Re) and ion-chromatography (Re and Cl).

Maximal K_d values with Tc , Re and Cl were obtained $\sim 10^5$, $> 10^5$ and $\sim 10^4$ for ACF, and $\sim 10^2$, $\sim 10^2$ and ~ 10 for XAD-7 at $0.01 \text{ mol} \cdot \text{dm}^{-3}$ in acidic media, respectively. On the other hand, K_d values fell into < 10 in alkaline media. The application for radiochemical analysis was also studied.

SOLUBILITY, SPECIATION AND CYCLING OF Tc IN NATURAL WATERS
UP TO 300°C.

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ABSTRACT

Technetium speciation and solubilities have been calculated as a function of temperature at different chemical conditions. A comparison is made between the redox properties of Tc and Fe, and the consequences for the turnover of technetium in natural cycles is discussed.

This is based on a thermodynamic data base for solid compounds and aqueous species of technetium. Equilibrium constants have been calculated from this data base for the temperature range 0 to 300°C. For aqueous species, the temperature extrapolation procedure is the revised Helgeson-Kirkham-Flowers model, while for solid compounds, heat capacity integration is used.

The data base contains a large amount of estimated data. The formation equilibrium constants of chloro complexes of Tc(V) and Tc(IV), whose existence is well established, has been estimated, as well as the majority of entropy and heat capacity values.

CHARACTERIZATION OF INTERACTION OF TECHNETIUM (VII) WITH URANIUM (IV) IN SOLUTIONS OF MINERAL ACIDS

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To model U, Np and Pu separation in extraction technology of nuclear fuel reprocessing data are needed on the kinetics of Tc(VII) - U(IV) reaction. In perchloric acid solution its products are Tc(IV) and U(VI); the reaction is not complicated by nitrate-ion oxidation of Tc(IV) and its rate is described as:

$$-d[U(IV)]/dt = k[U(IV)][Tc(VII)]/[H^+], \quad (1)$$

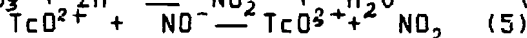
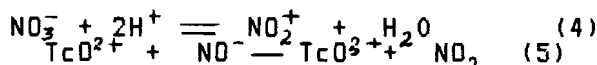
where $k = 6.75 \pm 0.14 \text{ min}^{-1}$ at 25°C and the solution ionic strength $\mu = 2$. In solution of HCl the reaction follows the same equation; the rate constant being $k = 2.41 \pm 0.14 \text{ min}^{-1}$ under the same conditions. In both media the activation energies are close: $E = 98.3 \pm 1.2$ and $99.3 \pm 5.4 \text{ kJ} \cdot \text{M}^{-1}$. Due to two opposite reaction proceeding in solution of HNO_3 reduction of Tc(VII) to Tc(IV) by U(IV) and oxidation of Tc(IV) by nitric acid, reaction of nitrate-ion oxidation of U(IV) is catalyzed by technetium ions. At concentration of HNO_3 more than 3M the reaction is the zero order relatively to U(IV) and is the first order relatively to catalyzer, i.e., Tc-ions, and under conditions of variable ionic strength the general equation of rate takes the form:

$$-d[U(IV)]/dt = k_1[Tc] + k_2[Tc][HNO_3]^2, \quad (2)$$

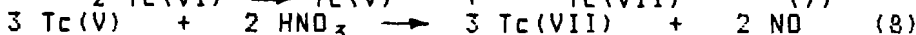
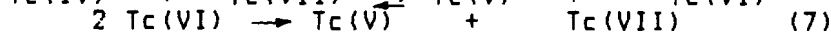
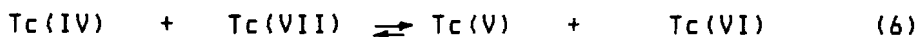
where $k_1 = 0.475 \pm 0.056 \text{ min}^{-1}$ and $k_2 = 0.149 \pm 0.006 \text{ M}^{-2} \text{ min}^{-1}$ at 41°C . At concentration of HNO_3 less than 3M the reaction is conformed to the same equations except for its initial step during which oxidation of U(IV) is autoaccelerated. At constant ionic strength of solution U(IV) is oxidized according to the equation:

$$-d[U(IV)]/dt = k_1[Tc] + k_2[Tc][H^+]^2[NO_3^-], \quad (3)$$

where $k_1 = 0.68 \pm 0.18 \text{ min}^{-1}$ and $k_2 = 4.16 \pm 0.17 \cdot 10^{-2} \text{ M}^{-3} \text{ min}^{-1}$ at 40°C and $\mu = 5$. The activation energy is $E = 115 \pm 6 \text{ kJ} \cdot \text{M}^{-1}$. Taking into account the second order of the reaction relatively to H^+ -ions and the first order relatively to NO_3^- -ions one can assume that the slow step of the main reaction course controlled by the rate constant k , is realized through the interaction between Tc(IV) (TcO^{2+} -ions) and nitronium ions NO^+ , which can be expressed as



The autocatalytic path of the reaction controlled by the rate constant k is realised with the participation of the slow step of reproporionality of Tc(V):

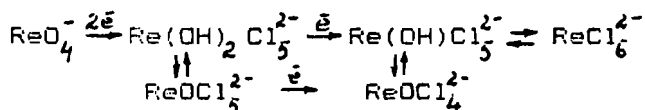


SPECIFIC FEATURES OF KINETICS AND MECHANISM OF REDUCTION
OF RHENIUM (VII) BY TIN (II)

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The ^{186}Re radiopharmaceutical (or ^{188}Re) preparations require the reduction of perrenate by a reducing agent in HCl solution. Stannous chloride is the compound which has been the most widely used for this purpose. In this respect the data on stoichiometry and kinetics of reaction between Re(VII) and Sn(II) are interested. Mechanism of interaction of Re(VII) with Sn(II) is complicated by including a lot of successive and parallel Re(V)-Re(IV) oxidation-reduction, aquation-anation reactions. The total scheme of reactions may be described as:



The first reaction in the scheme is the fast reduction of Re(VII) by Sn(II) to yield Re(V). Originally formed ions $\text{Re(OH)}_2\text{Cl}_5^{2-}$ are reduced by excess stannous chloride to Re(IV) as ions Re(OH)Cl_5^{2-} with rate controlled by the zero-order dependence on stannous chloride concentration equation:

$$-d[\text{Re(V)}] / dt = k_1 [\text{Re(OH)}_2\text{Cl}_5^{2-}] / [\text{H}^+],$$

where $k_1 = (9.0 \pm 0.2) \cdot 10^{-2} \text{ M min}^{-1}$ at 40°C and ionic strength $\mu=2$. At the same time the dehydration reaction of ions $\text{Re(OH)}_2\text{Cl}_5^{2-}$ is without valency change of Re(V) and with the rate constant $k_2 = 8.2 \cdot 10^{-2} \text{ min}^{-1}$ at 25°C and 4M HCl. It has been found that as the acidity is increased the reaction accelerates. Formed ions ReOCl_5^{2-} react with Sn(II) to yield Re(IV)-ions ReOCl_4^{2-} , the reaction rate conformed to equation:

$$-d[\text{Re(V)}] / dt = k_3 [\text{ReOCl}_5^{2-}] [\text{Sn(II)}] / [\text{HCl}],$$

where $k_3 = 4.52 \pm 0.18 \text{ min}^{-1}$ at 25°C and variable ionic strength. The activation energy is $47.6 \pm 0.8 \text{ kJ M}^{-1}$. Ions ReOCl_4^{2-} are stable in solution HCl of middle acidity (4M), however with increase in acidity the ions turn into ions Re(OH)Cl_5^{2-} by anation reaction with rate constant $k_4 = 8.0 \cdot 10^{-2} \text{ min}^{-1}$ at 25°C and 11.3M HCl. At last at elevated temperature ions Re(OH)Cl_5^{2-} join Cl^- -ions slowly, forming ions ReCl_6^{2-} with rate controlled by constant $k_5 = 3.6 \cdot 10^{-2} \text{ min}^{-1}$ at 90°C and 11.3M HCl. The reaction become slower with decreasing of HCl concentration and become reverse at slight acidity (hydrolysis ReCl_6^{2-} -ions is proceeded). Mechanism for the separate reaction in the system is proposed.

BEHAVIOR OF TECHNETIUM-CYCLOPENTADIENYL COMPLEXES IN NUCLEAR RECOIL IN γ -IRRADIATED RUTHENOCENE AND ITS β -CYCLODEXTRIN INCLUSION COMPOUND

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High energy gamma ($E_{\gamma\text{max}} = 50 \text{ MeV}$) irradiation of ruthenocene produced technetium isotopes $^{99\text{m}}\text{Tc}$ and ^{95}Tc by $^{100}\text{Ru}(\gamma, p)^{99\text{m}}\text{Tc}$ and $^{96}\text{Ru}(\gamma, n)^{95}\text{Ru}$ (EC, β^+) ^{95}Tc processes. Chemical behavior of technetium cyclopentadienyl complexes Tc-Cp formed in ruthenocene was compared with that of Tc-Cp complexes in ruthenocene- β -cyclodextrin inclusion compound. Silica gel chromatographic separation showed the presence of two chemical species which were consistent with TcCp_2H (A) and TcCp_3 (B). Interestingly, the A-peak was smaller than the B-peak in ruthenocene while A was larger than B in ruthenocene- β -cyclodextrin inclusion compound as shown in Fig. 1 and 2. This remarkable contrast shows effects of inclusion with cyclodextrin in the reaction zone. The following mechanisms are argued for the formation of A and B.

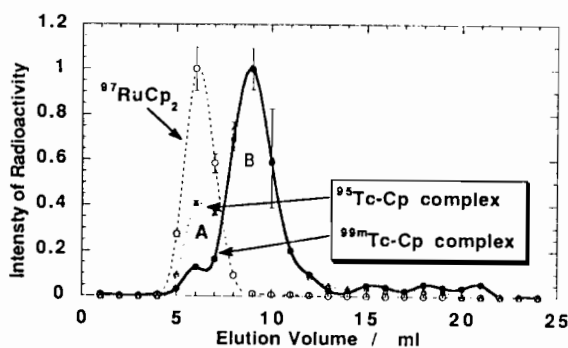
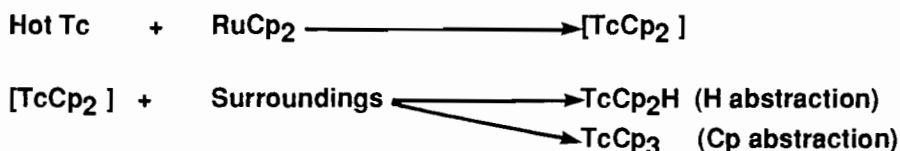


Fig.1 Elution Curve of γ -Irradiated RuCp_2

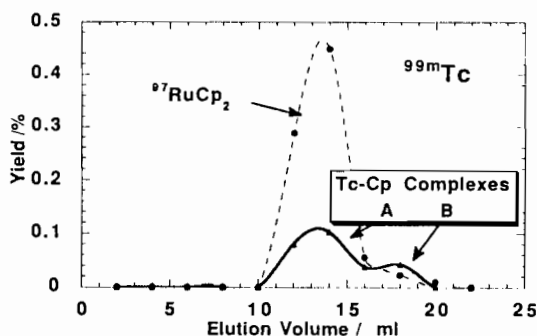


Fig.2 Elution Curve of γ -Irradiated RuCp_2 - β -CD

Recoil Behaviours of Central Metal Atoms in Tris-bipyridineruthenium(III) Chloride

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We have been investigating the recoil behaviours of central metal atoms in the solid phase of metal complexes with the large organic ligand. In this study we have chosen tris-bipyridineruthenium(III) chloride of chlorophyll-like functional substance.

The compound prepared by us from ruthenium(III) chloride and 2,2'-bipyridine was purified and subjected to thermal neutron irradiation and bremsstrahlung irradiation of max. 60MeV at very low temperatures. After the irradiation, the sample was dissolved in water containing Ru(III) carriers and passed through a cation exchanger column of Na-type Sephadex SP-C25.

In both irradiations, at first colorless part with rather strong activity was eluted with water (Fract. A) and later orange fraction eluted out with 0.2M NaCl (Fract. R) which was found to correspond to the complex part from its absorption spectrum and the observation with ^{103}Ru -labelled complex. The rest colored part was not eluted out in even higher concentration of NaCl. In Fract. A, Ru nuclides showed 40-50% radiochemical yields in thermal neutron irradiation and 20-30% of those in bremsstrahlung irradiation both at dry-ice temperature. In Fract. R, Ru nuclides showed a few % of retention in thermal neutron irradiation, while much less 1-2% in bremsstrahlung irradiation at dry-ice temperature. The Fract. A was passed through the anion exchanger column and no activity was found in the effluent, which implies the species of Ru in Fract. A was anionic.

In photonuclear reaction, ^{95}Tc and ^{99m}Tc were found to be formed. In Fract. A, Tc nuclides showed 70-90% radiochemical yields while in Fract. R, 1-2%.

In all the cases isotopic effects were not remarkable. Tc nuclides thus formed suggested the formation of the similar complex compound to ruthenium(III).

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Re(V) AND Re(VII) COMPLEXES OF TETRAKIS(PYRAZOL-1-YL)BORATE

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The poly(pyrazol-1-yl) borate ions, $[\text{RB}(\text{pz}^*)_3]^-$ ($\text{pz}^* =$ pyrazolyl-1 group; $\text{R} = \text{H}$, alkyl, aryl, pz) are nitrogen donor ligands that have been used extensively as stabilizing ligands for d and f transition elements¹.

With the metals of the group 7 (Mn , Tc , Re) poly(pyrazol-1-yl)borate complexes are known with the ligands $[\text{HB}(\text{pz})_3]^-$ and $[\text{HB}(3,5\text{-Me}_2\text{pz})_3]^-$ ²⁻⁴. The ligand $[\text{B}(\text{pz})_4]^-$, that usually coordinates in a tridentate fashion but, that can also work as bis-bidentate, has been much less used in coordination chemistry studies. For group 7 and with this ligand were only described complexes of the type $\text{Mn}[\text{B}(\text{pz})_4](\text{CO})_2(\text{L})$ ($\text{L} = \text{P}(\text{OMe})_3$, $\text{P}(\text{OPh})_3$, PMe_3)⁵.

In this work we report the synthesis and characterization of the Re (VII) complex $[\text{B}(\text{pz})_4]\text{ReO}_3$ and of the Re (V) complex $\text{ReOCl}_2[\text{B}(\text{pz})_4]$. The complex $[\text{B}(\text{pz})_4]\text{ReO}_3$ was synthesized by reacting Re_2O_7 with $\text{K}[\text{B}(\text{pz})_4]$ in THF, while $\text{ReOCl}_2[\text{B}(\text{pz})_4]$ was obtained by reduction of $[\text{B}(\text{pz})_4]\text{ReO}_3$ with PPh_3 in presence of $(\text{CH}_3)_3\text{SiCl}$ in THF.

The characterization of the complexes involved C, H, N, analysis, laser desorption FTICR-MS, IR, ^1H and ^{13}C -NMR, giving results coherent with the proposed formulas.

Till now, no X-ray structural analysis has been undertaken for the above referred complexes. However, the ^1H and ^{13}C NMR spectra are consistent with C_{3v} and C_∞ symmetries for $[\text{B}(\text{pz})_4]\text{ReO}_3$ and $\text{ReOCl}_2[\text{B}(\text{pz})_4]$ respectively, as well as with a static behaviour in solution at room temperature for both complexes.

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INVESTIGATION OF PHASE TRANSITIONS AND SOME OTHER PHYSICO-CHEMICAL PROPERTIES OF PERTECHNETATES AND PERRHENATES

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Physico-chemical properties of a large number of pertechnetates and perrhenates has been determined. All DSC measurements were carried out at Mettler TA 3000 System (Switzerland); Thermography was fulfilled using derivatograph Q-1500D, system F.Paulik - J.Paulik - L.Erdey (Hungary). The solubility was determined gravimetrically or radiometrically.

Here we give some data on a number of new phase transitions found (all transitions are endothermic, later on are given in brackets: the temperature of phase transition, t, K ; the heat of phase transition, $Q, kJ/mol$). Of most interest are the following transitions: $KReO_4$ (808; 0.1), $KTcO_4$ (753; 5.2), Bu_4NTcO_4 (345; 19.0), Bu_4NReO_4 (371; 7.3), $[cyclo-(CH_2)_6NH_2]ReO_4$ (227; 2.24). Also estimated are the heats of known phase transitions in $CsReO_4$ (402; 0.25), $CsTcO_4$ (420; 0.86), Et_4NReO_4 (309; 11.6), Et_4NTcO_4 (318; 5.0). For a number of substances, also, the melting heats were measured: $KTcO_4$ (815; 28.4), Bu_4NReO_4 (500; 13.8), Bu_4NTcO_4 (508; 20.9).

The nature of phase transitions in the substances being sheelites and pseudo-sheelites at room temperature is discussed.

The solubility value for morpholinium perrhenate was measured at room temperature as 0.48 mol/l, and for tetrabutylammonium perrhenate as $5.08 \cdot 10^{-3}$ mol/l. The solubility values for some pertechnetates were also obtained: $NaTcO_4 \cdot 4H_2O$ (1.42 mol/l at 20 °C, 1.77 mol/l at 90°C), ND_4TcO_4 (0.4 mol/l). The solubility value for Tc_2S_7 was estimated as $6.09 \cdot 10^{-4}$ mol/l.

TECHNETIUM AND RHENIUM OXO AND HALOGENIDE COMPLEXES WITH FERRICINIUM CATIONS

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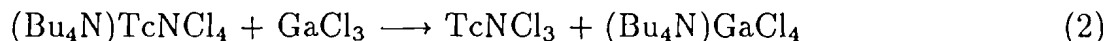
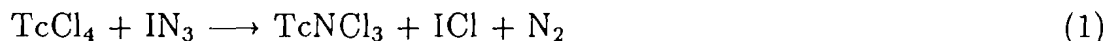
The following new compounds have been obtained and identified: $[\text{Fe}(\text{C}_5\text{H}_5)_2][\text{TcO}_4]$ (1), $[\text{Fe}(\text{C}_5\text{H}_5)_2]_4[\text{H}_3\text{O}(\text{H}_2\text{O})_4]_2[\text{TcCl}_6]_3$ (2), $[\text{Fe}(\text{C}_5\text{H}_5)_2]_3[\text{Tc}_6\text{I}_{14}]$ (3), $[\text{Fe}(\text{C}_5\text{H}_5)_2]_3[\text{Tc}_6\text{Cl}_{14}]$ (4), $[\text{Fe}(\text{C}_5\text{H}_5)_2]_2[\text{Tc}_8\text{Br}_{14}]$ (5), $[\text{Fe}(\text{C}_5\text{H}_5)_2]_2[\text{Re}_2\text{Br}_8]$ (6). Compounds (1 - 2) were obtained by evaporating of the suspension of powder ferrocene in water or in hydrochloric acid with 1 M solutions of pertechnetate or hexachlorotechnetium(IV) acid. Compounds (3 - 6) were obtained by carrying out exchange reactions in acetone solutions of related technetium complexes with tetrabutylammonium cations. All the compounds obtained are insoluble in water and organic solvents, stable in air, poorly crystallizable, and as a rule, X-ray amorphous black powders. We succeeded in obtaining single crystals only for compounds (1 - 3). The structures of all other compounds have been verified by indirect methods using a comparative analysis of IR and X-ray photoelectron spectroscopic data for compounds with a similar composition but with the known structure. All the compounds considered are built of complex or cluster technetium- or rhenium-containing anions and ferricinium cations. The direct covalent or other localized bonds between the anions and cations are absent. The magnetic properties of the compounds obtained were investigated by the Faraday technique in the temperature range 78 - 300K. All the compounds are "superparamagnetics" with strong antiferromagnetic intermolecular exchange interactions. All the compounds, except for (5), have ESR spectra with complicated very wide signals at $g_{\text{eff}} \sim 2$. All the compounds are semiconductors with a weak temperature dependence of conductivity. The Mossbauer ^{57}Fe spectra have a tendency to broaden with decreasing temperature to 78K and 4K; two doublets are identified in them which corresponding to ferricinium and ferrocenium formal oxidation state of iron atoms. After cooling to $\sim 80\text{K}$ structural or electronic nonequivalence of iron, technetium's or ligands begins to appear, which is reflected in their X-ray photoelectron and Mossbauer spectra. The low temperatures X-ray photoelectron spectra of the compounds (2, 4, 5) are absent, but unusual high binding energy electron emission in this case takes place.

THE SYNTHESIS OF TcNCl_3 ; NEW APPROACHES TO TcNCl_4^-

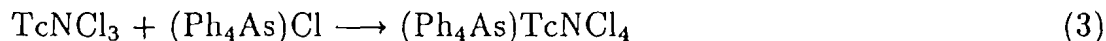
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The neutral technetium nitride chloride TcNCl_3 can be prepared from TcCl_4 and IN_3 (equ. 1) in CCl_4 suspension. The same product is formed during the reaction of $(\text{Bu}_4\text{N})\text{TcNCl}_4$ with GaCl_3 in CH_2Cl_2 according to equ. 2.



TcNCl_3 is a very moisture-sensitive black-brown powder. The infrared spectrum of the compound suggests a polymeric structure which is very similar to that of the neutral molybdenum nitride chloride. The TcNCl_3 units are connected by Tc-N-Tc and TcCl_nTc bridges according to the low frequency of the TcN stretch (1018 cm^{-1}) and Tc-Cl vibrations due to terminal chlorides ($320 - 400 \text{ cm}^{-1}$) and Tc-Cl-Tc bridges (240 cm^{-1}). TcNCl_3 is insoluble in CH_2Cl_2 ; the addition of $(\text{Ph}_4\text{As})\text{Cl}$, however, results in a marked solubility. In accordance with equ. 3, the well-known $(\text{Ph}_4\text{As})\text{TcNCl}_4$ is formed, which was isolated in form of red crystals and characterized by its EPR and IR spectra.



Other new approaches to obtain the nitridotechnetium(VI) anion TcNCl_4^- are given with the reactions of TcOCl_4^- with NCl_3 or the trimethylsilyl protected benzamidine $(\text{Me}_3\text{Si})_2\text{N}(\text{Ph})\text{CN}(\text{Me}_3\text{Si})$. The latter compound is completely destroyed during the reaction to yield the nitrido ligand, benzonitrile, hexamethyldisilane and hexamethyldisiloxan.

THE SYNTHESIS OF NEW Tc(IV) COMPLEXES FROM TcCl₄

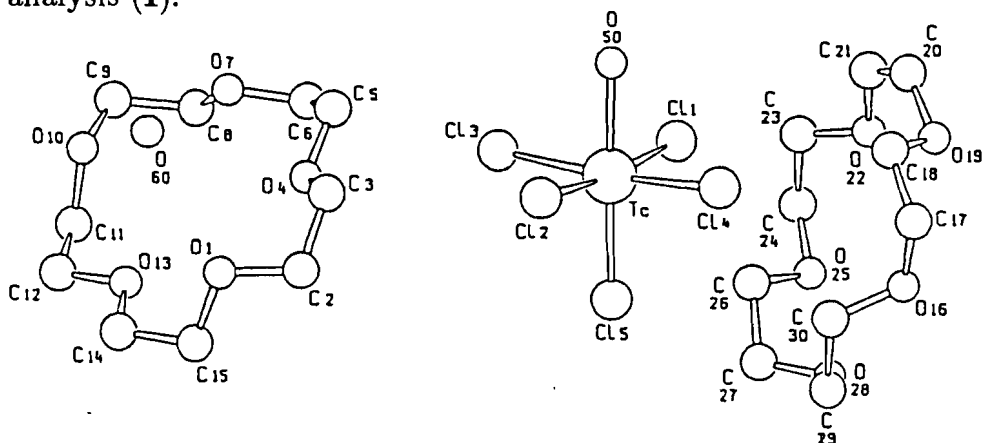
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Due to the low solubility of the polymeric technetium tetrachloride in the most common solvents, this compounds is only rarely used as starting material in synthetic procedures.

In acetonitrile or isocyanides, however, TcCl₄ as well as TcBr₄ (which can be obtained from the slow reaction of TcCl₄ with trimethylsilylbromide) dissolve to yield complexes of the general formula [Tc(halide)₄(L)₂]. After carefull removing of the solvents yellow (Cl) and red (Br) crystalline products can be isolated. The infrared spectra of the compounds suggest *cis*-coordination.

After addition of crown ethers, TcCl₄ dissolves rapidly in CH₂Cl₂ forming a yellow solution from which yellow and a small amount of red crystals (about 15 per cent) could be isolated. Whereas mass spectrometric studies on the red compound gives reference to the formation of a cationic crown ether complex of the composition [Tc(crown)Cl₂]⁺, in the yellow main product technetium is not coordinated by the crown ether, but contain the anion [TcCl₅(H₂O)]⁻. The crystals have the composition [TcCl₅(H₂O)][[crown(H₃O)][crown]] as was confirmed by X-ray structure analysis (I).



PREPARATION AND EVALUATION OF CATIONIC, LOW OXIDATION STATE
TECHNETIUM
O-PHENANTHROLINE COMPLEXES

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o-Phenanthroline (phen) is a frequently used ligand for the chelation of transition elements including technetium. Most of the Tc(phen) chelates described till now contain o-phenanthroline in mixed ligand complexes. Recently, Breikss et al. (1990) obtained $[\text{Tc}(\text{phen})_3]^+$ by reaction of $[\text{TcCl}_6]^{2-}$ with phenanthroline and zinc, while Archer et al. (1990) reported the synthesis of $[\text{Tc}(\text{phen})_3]^{2+}$ from reaction of $[\text{TcCl}_3(\text{MeCN})(\text{PPh}_3)_2]$ with phenanthroline. Both phenanthroline complexes were scarcely characterized.

Following the hypothesis that cationic complexes tend to accumulate in the myocardium, both $[\text{}^{99\text{m}}\text{Tc}(\text{phen})_3]^+$ and $[\text{}^{99\text{m}}\text{Tc}(\text{phen})_3]^{2+}$ appear to be a promising basis to develop new myocardial agents. However, a practical requirement would be a one-stage synthesis of the chelates starting with pertechnetate.

We prepared $[\text{Tc}(\text{phen})_3]^+$ by electrochemical reduction of pertechnetate dissolved in a mixture of saline and ethanol containing o-phenanthroline. The reduction was performed in an argon atmosphere at pH 3 under the controlled potential of 1.0 volt vs the saturated Ag/AgCl electrode. After extraction of excess ligand with dichloromethane $[\text{Tc}(\text{phen})_3]\text{PF}_6$ was precipitated as a purple crystalline solid, purified by dissolution in nitromethane and reprecipitation. The complex salt proved to be soluble and rather stable in acetonitrile and nitromethane. Conductivity measurements in nitromethane confirmed the presence of a 1:1 electrolyte. Cerimetric titrations indicated the oxidation state +1 of technetium.

$[\text{Tc}(\text{phen})_3]^{2+}$ was synthesized in a solution of 2-propanol and water by reduction of pertechnetate with borohydride in the presence of excess o-phenanthroline. The chelate was purified by HPLC. In the positive FAB mass spectrum the prominent peak at 319.5 m/z could be attributed to the dipositively charged cationic complex of divalent technetium. Magnetic susceptibility measurements resulted in the effective magnetic moment of 1.89 B.M which is in good agreement with the spin-only moment for one unpaired electron of the d^5 configuration of Tc(II) in an octahedral ligand field. For biodistribution evaluation in mice $[\text{}^{99\text{m}}\text{Tc}(\text{phen})_3]^{2+}$ was obtained with a radiochemical purity of 92.5%. The rather hydrophilic complex was predominantly excreted by the kidneys. The low blood retention yielded a heart/blood ratio of 4.2 at 100 min post-injection.

REACTIONS OF TECHNETIUM(III)-THIOUREA DERIVATIVE COMPLEXES WITH PYRIMIDINE DERIVATIVES

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The ligand substitution reactions of hexakis(substituted thiourea)technetium(III) ion [thiourea (tu), N-methylthiourea (Me-tu), N,N'-dimethylthiourea (Me-tu-Me), N,N'-diethylthiourea (Et-tu-Et)] with pyrimidine derivatives [4,6-dimethylpyrimidine-2-thione (Hdmpt), 4-methylpyrimidine-2-thione (Hmpt), pyrimidine-2-thione (Hpt), 4,6-dimethylpyrimidine-2-one (Hdmpo), pyrimidine-2-one (Hpo)] were investigated by means of solvent extraction. The extraction behavior was strongly affected by the difference of ligands. Technetium was extracted into the organic phase more than 95 % of the initial concentration using pyrimidine-2-thione derivatives, but was hardly extracted using pyrimidine-2-one derivatives.

Pyrimidine-2-thione, HL, exists mainly in three forms in aqueous solution; $\text{H}_2\text{L}^+ \rightleftharpoons \text{HL} \rightleftharpoons \text{L}^-$. From the effect of pH on apparent rate constant, it can be concluded that $[\text{Tc}(\text{sub-tu})_6]^{3+}$ reacts competitively with L^- and HL in this extraction system. The rate constants k_1 (substitution reaction between $[\text{Tc}(\text{sub-tu})_6]^{3+}$ and L^-) and k_2 ($[\text{Tc}(\text{sub-tu})_6]^{3+}$ and HL) were determined by the non-linear least squares method. The obtained rate constants were in the order $\text{Hpt} < \text{Hmpt} < \text{Hdmpt}$ and $[\text{Tc}(\text{tu})_6]^{3+} < [\text{Tc}(\text{Me-tu})_6]^{3+} \sim [\text{Tc}(\text{Et-tu-Et})_6]^{3+} < [\text{Tc}(\text{Me-tu-Me})_6]^{3+}$. A linear relationship between the rate constants and the acid dissociation constants of corresponding conjugate acid of pyrimidine-2-thione was found. The k_1 value for $[\text{Tc}(\text{Me-tu-Me})_6]^{3+}$ was more than 50 times as large as that for $[\text{Tc}(\text{tu})_6]^{3+}$.

The extracted technetium complex was characterized by elemental analysis and infrared spectroscopy. This complex can be considered $\text{Tc}(\text{dmpt})_3$ which was formed by the ligand substitution between $[\text{Tc}(\text{tu})_6]^{3+}$ and Hdmpt.

FORMATION OF Tc(III) COMPLEXES WITH POLYAMINOPOLYCARBOXYLIC ACID

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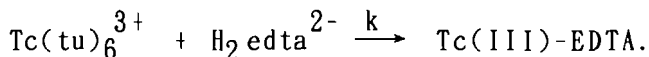
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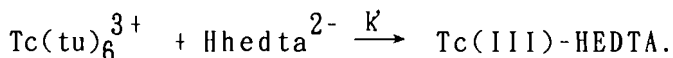
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The addition of EDTA or HEDTA¹⁾ to Tc(tu)₆^{3+ 2)} solution changes the color of solution from red-orange to light brown. The results of electrophoresis indicate that neutral (EDTA, HEDTA) and cationic (HEDTA) complexes are synthesized by ligand substitution reaction. The yields of [Tc-EDTA]⁰, [Tc-HEDTA]⁺ and [Tc-HEDTA]⁰ in reaction mixture are 71.2±1.9%, 43.0±1.0% and 21.0±2.0% based on Tc. The UV-Vis spectra of these complexes give two absorption maxima, at 368 nm and 470 nm with the molar absorption coefficients (ε) of 4400±40 and 2100±50 ([Tc-EDTA]⁰), 377 nm and 493 nm with ε = 2100±50 and 1740±70 ([Tc-HEDTA]⁺), 373 nm and 487 nm with ε = 2800±70 and 1300±50 ([Tc-HEDTA]⁰) respectively. Elemental analysis and IR spectroscopy suggest that they include one or two tu molecules as ligand. Consequently, their composition can be concluded as [Tc(tu)Hedta]⁰, [Tc(tu)₂Hhedta]⁺ and [Tc(tu)hedta]⁰.

In both cases of edta and hedta, the reaction rate increase with an increase in pH, though precipitates appear gradually at high pH. Dependence of the reaction rate on hydrogen ion concentration suggests that the principal reaction of Tc(tu)₆³⁺ with edta is considered to be



In the same manner the reaction with hedta is considered to be



These rate constants k and k' at 25 °C were determined as

$$k = (2.1 \pm 0.2) \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}, k' = (3.2 \pm 0.3) \times 10^{-1} \text{ M}^{-1} \text{ s}^{-1}$$

1) N-(2-hydroxymethyl)ethylenediamine-N,N',N'-triacetic acid

2) hexakis(thiourea)technetium(III)

SYNTHESIS AND CHARACTERIZATION OF TECHNETIUM(V) NITRIDO CORE β -DIKETONE COMPLEXES

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New Technetium nitrido complexes with β -diketone ligands (acac, bza, dbm, and dpm) were prepared by ligand substitution reactions of $\text{TcNCl}_2(\text{PPh}_3)_2$. The latter has been prepared by the reaction of pertechnetate and sodium azide or S-methyldithiocarbazate in the presence of triphenylphosphine. The complex was characterized by paper chromatography, electrophoresis, RP-HPLC, UV-Visible and IR spectroscopy, and elemental analysis.

Electrophoresis results show that all the complexes have no charge. In the ir spectra the common bands to the most metal β -diketone are found to be $1512\text{-}1517\text{ cm}^{-1}$ ($\nu(\text{C}=\text{O}) + \nu(\text{C}-\text{C})$); $1431\text{-}1486\text{ cm}^{-1}$ ($\delta(\text{C}-\text{H}) + \nu(\text{C}-\text{C})$). The $\nu(\text{Tc}\equiv\text{N})$ is found in the range $1043\text{-}1045\text{ cm}^{-1}$ for all the complexes. The almost identical spectra of the four complexes in uv/vis and ir indicate that the complexes are analogous in composition and molecular structure. The above results are ascribed to the formation of neutral complexes $\text{TcN}(\beta\text{-diketone})_2$.

PREPARATION OF ^{99m}Tc NITRIDO β -DIKETONE RADIOPHARMACEUTICALS

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In general, technetium-99m compounds as potential radiopharmaceuticals in nuclear medicine could be characterized as anionic complexes which are excreted via the urinary or hepatobiliary system, neutral ones which are able to cross the brain blood barrier, and cationic ones which accumulate in myocardium.

In this paper the preparation and characterization of neutral, lipid-soluble technetium-99m complexes with β -diketone (acac, bza, dbm, dpm) containing $\text{Tc}^{\text{V}} \equiv \text{N}$ core are reported. The complexes were synthesized by two methods, i.e. (a) by reacting $^{99m}\text{TcNCl}_4^-$ with triphenylphosphine in the presence of β -diketone ligand, while $^{99m}\text{TcNCl}_4^-$ was prepared by reduction of pertechnetate with sodium azide in concentrated HCl. (b) by reacting of pertechnetate with the S-methyl ester of dithiocarbazic acid in the presence of HCl, triphenylphosphine, and β -diketone ligand.

The complex was characterized by means of electrophoresis, paper chromatography, and RP-HPLC. The result was compared to that of ^{99}Tc Nitrido β -diketone complex. Cyclohexane/water and octanol/water partition coefficients of the complexes were determined by activity measurements. Solution studies show the complexes to be neutral, lipid-soluble tracers.

OCCURRENCE AND NATURE OF DIFFERENT Tc(V) AND Re(V) COMPLEXES WITH MERCAPTO/AMIDE LIGANDS

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Mercaptoamino acids and mercaptopeptides, such as mercaptoacetyltriglycine (MAG₃), are important ligands for technetium in radiopharmaceutical research. The subtle interplay of S, N and O-donor atoms in varying ligand structures may give rise to a diversity of occurring Tc complexes.

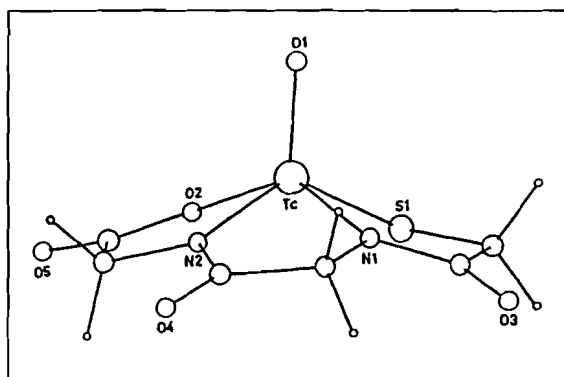
In order to elucidate the nature of intermediates and products in dependence on ligand alteration and molar metal/ligand ratio, complex formation of Tc and Re with MAG₃, MAG₂, MAG₂ ester, MAG₁ and MAG₁ ester has been studied.

At ligand excess, formation of the well-known [TcO(MAG₃)]¹⁻ complex proceeds via 1:4 and 1:2 intermediates and indicates a dominant role of the S-donor atom in the initial attack of the ligand onto the Tc(V) oxo core.

Shortening of the peptide chain length in the ligand molecule is expected to make 1:2 complexes the main products,

unless the carboxylic group becomes involved in the coordination sphere. Such an involvement is seen with MAG₂.

X-ray structure analysis of AsPh₄[TcO(MAG₂)] showed that the square-pyramidal structure contains the carboxylate-O in the equatorial plane.

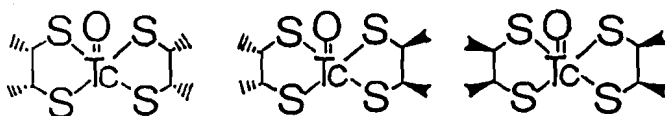


Unlike MAG₂, its methyl ester as well as MAG₁ mainly lead to 1:2 complexes beside 1:4 species. The methyl ester of MAG₁ only forms an 1:4 complex.

UNUSUAL ISOMERIZATION OF Tc AND Re-DMSA COMPLEXES

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Our early studies in the late 70's already showed that Tc(V)oxo complexes of the formula $[\text{TcOL}_2]^+$, where L = *meso* or *racemic* DMSA, exist as stable compounds, which usually occur as mixtures of at least three isomers, and display an interesting influence of the stereoisomeric form on the biodistribution.



syn-exo

anti

syn-endo

The model complexes were not only helpful in studying the phenomenon of bone affinity but have offered a possibility to identify the chemical nature of tumour-affine, so-called pentaent $^{99\text{m}}\text{Tc-}meso\text{-DMSA}$.

Detailed investigations on the individual isomers has revealed an unexpected reactivity, in form of isomerization, of bidentate ligands at the Tc/Re core. Isomerism of M=O complexes may occur due to different orientation of the substituents, such as COOH , at the ligand with respect to the oxo group.

Two kinds of conversion of isomers have been observed:

- Each of the ligand changes its arrangement in the complex, so that the initial orientation of the substituents is altered from exo to endo or vice versa. When stereochemically pure isomers, separated by HPLC, are allowed to stand in solution, they quickly convert to give a mixture of isomers again. The rate of isomerization is different for each isomer and the final composition of the mixture depends on the nature of the solvent.
- The coordinated ligand itself changes its configuration as seen in the conversion of *meso* to *racemic* DMSester in solution of sodium hydroxide, ammonia, or amines.

The initial studies have been extended to nitridotechnetium complexes and rhenium. The complexes were prepared both by ligand substitution reaction and by direct reduction methods. Mixtures of isomers as well as isolated stereochemically pure compounds were identified by ^1H NMR spectroscopy.

TECHNETIUM(III) COMPLEXES WITH TETRADENTATE THIOETHER LIGANDS: PREPARATION AND PRELIMINARY BIOLOGICAL EVALUATION

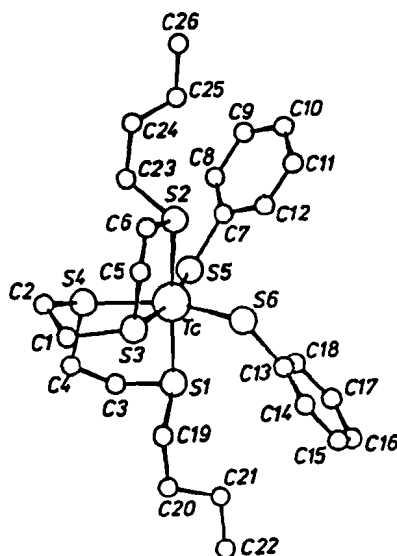
H.J. Pietzsch, S.Seifert, R. Syhre, H. Spies and B.Johannsen

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First representatives of a new class of technetium complexes with open-chain thioether ligands have been synthesized and evaluated in animal experiments.

Reduction of TcO_4^- in the presence of both a tetradentate thioether $\text{RS-CH}_2\text{CH}_2\text{-S-CH}_2\text{CH}_2\text{-S-CH}_2\text{CH}_2\text{-SR}$ ("S₄", R = , Et, n-Bu) and a monodentate thiole (R'SH , R' = Et, n-Pr, i-Pr, n-Bu, phenyl, p-CH₃O-phenyl) gives Tc(III) complexes $[(\text{Tc}(\text{"S}_4\text{"})(\text{S'R})_2)]^+$, which were isolated as PF_6^- salts.

The X-ray crystal structure analysis of one representative (R = n-butyl, R' = phenyl) showed that the metal is centred in a heavily distorted octahedron with the thiolate ligands being coordinated in cis-configuration.



For biodistribution studies, complexes were prepared at carrier-added level (10^{-4} mol/l ^{99}Tc) and characterized by HPLC and TLC.

Animal studies were performed in male wistar rats (150g BW, i.v.).

The biodistribution of all complexes are similar with high hepatobiliary rate. For some representatives significant myocardial uptake was found.

HIGH PERFORMANCE ION EXCHANGE CHROMATOGRAPHY OF ^{99m}Tc LABELED HUMAN SERUM ALBUMIN USING A MACROMOLECULAR Sn(II) COMPLEX.

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We previously reported that N-methylpyridinium polymer (4VP) developed as a column packing for high performance ion exchange chromatography (HPIEC) could resolve human serum albumin components such as mercaptoalbumin (HMA) and nonmercaptoalbumin (HNA).¹⁾ In this study, the characteristics of this column were applied to the HPIEC analysis of ^{99m}Tc labeled human serum albumin (^{99m}Tc -HSA).

N-methylpyridinium polymer cross-linked with ethylene glycol dimethacrylate was packed into a 250 X 4 mm (i.d.) column. The labeled compound was eluted using a gradient from the initial buffer (solution A) of 0.05 M tris (hydroxy methyl) aminomethane (Tris)-HCl buffer (pH 7.0) to the final buffer (solution B) consisting of solution A containing 0.5 M sodium chloride at a flow rate of 0.5 ml/min. HMA, HNA conjugated with cysteine and a disulfide dimer of HSA (HDA) were prepared by the method of Sogami et al.²⁾

A macromolecular Sn(II) complex (R-Sn)³⁾ was used as the solid phase reductant in order to minimize contamination of resulting preparations by Sn(II) and this method simplified the reducing process. Albumin (3.5 mg) was dissolved in 0.5 ml of 0.01 M HCl-0.1 M NaCl and 2.5 mg of R-Sn (1.8 mmol Sn/g-resin) was added. After 5 min, 0.4 ml (14.8 MBq) of $^{99m}\text{TcO}_4^-$ in saline was added and the mixture was shaken at room temperature for 30 min. The sulfhydryl content of HSA, HMA, HNA, and HDA used in ^{99m}Tc -labeling was 0.48, 0.94, 0.04, and 0.09 (mol/mol-albumin), respectively. The labeling efficiency of HNA, which was determined by TLC method, was the lowest (77%) among the albumins tested, but the other albumin components were labeled in high efficiency (>90%). These ^{99m}Tc -labeled albumins were also examined by PAGE, and the radioactive bands coincided with the band stained with CBB.

HSA is comprised of HMA, HNA, and some polymerized albumin (mainly HDA). There were five major peaks at 25, 26, 28, 29 and 32 min in a radiochromatogram of ^{99m}Tc -HSA prepared from this HSA. The retention times of four peaks (25, 26, 28, and 29 min) differed from those of albumin in the UV chromatogram and only the last peak at 32 min coincided with that of polymerized albumins. ^{99m}Tc -HMA showed a similar radiochromatographic profile to that of ^{99m}Tc -HSA. However, there were indistinct peaks in the ^{99m}Tc -HNA radiochromatogram. To elucidate the effect of HMA in the labeling of HSA with ^{99m}Tc , HSA was labeled with ^{99}Tc that is applicable to this experiment in a stoichiometric scale. The UV chromatogram of ^{99}Tc -HSA showed a decreased HMA peak and no change in that of HNA. This implies a selective, high reactivity of HMA for technetium. It is concluded that HPIEC using the 4VP column presented here would be applicable as an analytical method for ^{99m}Tc -HSA.

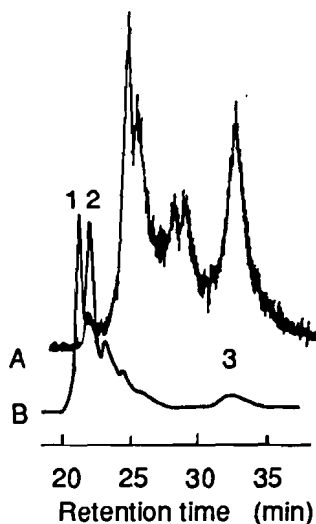


Fig.1. Chromatograms of ^{99m}Tc -HSA. Peaks: 1, HMA; 2, HNA; 3, polymerized albumin. Detection: A, radioactivity; B, absorbance (280 nm)

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- 2) M. Sogami, S. Nagaoka, S. Era, and et al., *Int. J. Peptide Protein Res.*, **24**, 96(1984).
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DEVELOPMENT OF ^{99m}Tc -GALACTOSYL HUMAN SERUM ALBUMIN DIETHYLENE TRIAMINE PENTAACETATE(^{99m}Tc -GSA) AS A HEPATIC FUNCTIONAL IMAGING AGENT

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1. Introduction

It is well known that the majority of blood proteins except for HSA(human serum albumin) is glycoprotein and catabolized by liver upon desialization of sugar chain terminals. The uptake of asialoglycoprotein(ASGP) into liver is mediated by the specific receptor for ASGP expressed on the sinusoidal cell surface of hepatocyte. The activity of ASGP receptor has been correlated with the extent of hepatic disorders. ^{99m}Tc -GSA was designed to behave like ASGP in blood and to provide an information on the hepatic functional reserve by scintigraphic analysis of ^{99m}Tc -GSA uptake kinetics.

2. Synthesis of GSA and labeling with Tc-99m

GSA was synthesized by coupling galactose and bifunctional chelator, DTPA, to HSA. Coupling molar ratio of galactose was finally fixed Gal/HSA = 30~40/1 to compete well with naturally existing ASGP. DTPA coupling ratio was kept below 7(DTPA/HSA = 4~7/1) to prevent the non-specific liver uptake.

GSA was labeled with ^{99m}Tc using SnCl_2 as a reducing agent. The radiochemical purity(RCP) of ^{99m}Tc -GSA in saline solution was influenced by the concentration of GSA, SnCl_2 and pH. DTPA facilitated the radiochemical stability of ^{99m}Tc -GSA required for the production of prelabeled injectable. The RCP of ^{99m}Tc -GSA used in further studies was ca. 95 % and free from ^{99m}Tc -Sn-colloid.

3. In vivo behavior of ^{99m}Tc -GSA in normal animals

The biodistribution of ^{99m}Tc -GSA was studied in normal Sprague-Dawley rats injected intravenously with 330 $\mu\text{g/kg}$ of ^{99m}Tc -GSA. 10 min after the injection, 92.4 % of injected radioactivity was found in liver, which proved high potential of ^{99m}Tc -GSA as in vivo hepatic imaging agent. 74.8 % was excreted then hepatobiliary into feces 48 hr after injection. Imaging study was also carried out in normal Japanese white rabbits with the dose of 330 $\mu\text{g/kg}$ using γ -camera(Toshiba GCA-90B). Liver uptake reached maximum ca. 7 min after i.v. injection and kept constant for 7 min thereafter. No accumulation in spleen or bone marrow was observed throughout the imaging study.

The dose dependence of ^{99m}Tc -GSA clearance from blood was studied in rats by increasing the dose from 0.25 to 10 mg/kg. The initial removal rate of ^{99m}Tc -GSA was strongly dependent on dose and the Lineweaver-Burk plot gave $V_{\text{max}} = 17.3 \mu\text{g GSA/min per g wet liver}$ for ^{99m}Tc -GSA with Gal/HSA = 40/1 and 15.7 $\mu\text{g GSA/min per g wet liver}$ for that with Gal/HSA = 31/1, respectively.

EVALUATION OF HYDROXAMAMIDE-BASED LIGAND AS A CHELATING MOIETY FOR ^{99m}Tc RADIOPHARMACEUTICALS

M. Nakayama, H. Saigo, K. Ozeki, K. Harada and A. Sugii

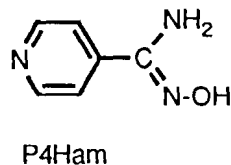
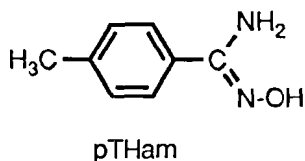
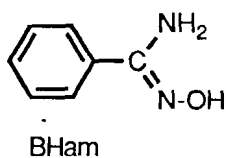
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The study on a coordination site capable of binding ^{99m}Tc is essential for the development of novel ^{99m}Tc labeled functional imaging agents. In this study, the hydroxamamide (or amidoxime) derivatives with different substituents are prepared and the effectiveness of the hydroxamamide group as a coordination site for the formation of ^{99m}Tc chelate is evaluated.

A hydroxamamide group contain a nitrogen and an oxygen as donor atoms, and can be easily introduced by the simple reaction of nitriles with hydroxylamine. Benzohydroxamamide (BHam), p-toluhydroxamamide (pTHam) and pyridine-4-hydroxamamide (P4Ham) used in this study were respectively prepared from the benzonitrile, p-tolunitrile, and 4-cyanopyridine. The yield of ^{99m}Tc complex was determined by TLC using cellulose strips.

The TLC system was suitable for evaluating the affinity of each ligand for ^{99m}Tc because this method was able to resolve clearly both $^{99m}\text{TcO}_4^-$, the reduced hydrolyzed form of ^{99m}Tc , and the new ^{99m}Tc complex. When formation of the ^{99m}Tc complexes was examined using a 5×10^{-4} M ligand solution, all three ligands reached high yield over a wide pH range. The high yield of each complex obtained at a low pH indicates that the hydroxamamides have the capability of forming stable complexes with ^{99m}Tc . Although the yield of each complex tended to decrease slightly with a decrease in the ligand concentration, they achieved yield still over 80%, even in a 5×10^{-7} M ligand solution at pH 9.5. The high stability of each complex was confirmed by TLC analysis after the solutions had been let to stand for 12 h at room temperature. The results demonstrated that the hydroxamamide group was an effective chelation site for binding ^{99m}Tc . The solvent extraction experiment showed that the ^{99m}Tc -P4Ham was the most hydrophilic complex and the lipophilicity increased in the order of ^{99m}Tc -P4Ham, ^{99m}Tc -BHam, and ^{99m}Tc -pTHam.

These complexes showed similar distribution patterns in the mice, with some differences in the clearance from excretory organ. ^{99m}Tc -pTHam showed the slowest blood clearance, but ^{99m}Tc -P4Ham cleared from the blood into the urine with transient concentration in the kidneys, since the cumulative 12 h urinary excretion was 64% of the injected dose. Although ^{99m}Tc -BHam showed a similar blood clearance pattern to ^{99m}Tc -P4Ham, the radioactivity cleared through the liver, moving rapidly toward the gallbladder and intestines, and only 10% of the administered dose appeared in the urine at 12 h after injection. The biodistribution of all three hydroxamamide-based ^{99m}Tc -complexes provide an indirect indication of their *in vivo* stability, since each ^{99m}Tc -hydroxamamides presented independent distribution pattern, and reinforced by the low level of radioactivity in the stomach. The singularity presented by each ligand with substituent suggest that the hydroxamamide-based ligand can serve as a basic structure for the binding of ^{99m}Tc , with good *in vitro* as well as *in vivo* stability, offering good alternatives for attaching other substituents to provide variable biolocalization properties as desired. Finally, the very easy and simple synthesize pathway of the hydroxamamide-based ligand offers a good potential for the design of new ^{99m}Tc -radiopharmaceuticals.



TECHNETIUM-99m PHYTATE AND GALLIUM-67 CITRATE
SCINTIGRAM IN LIVER CANCER-BEARING RATS.

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Technetium-99m is widely available and has a number of properties suggesting that it might be an ideal radionuclide as a chemical label for external scanning.

Technetium-99m phytate is an excellent liver scanning agent. After intravenous injection, technetium-99m phytate becomes a microcolloid, which undergoes reticuloendothelial localization in liver.

Technetium-99m phytate and gallium-67 citrate liver scans of rat model with chemical(Me-DAB)-induced hepatocarcinoma are presented. In rats the in vivo distribution was assessed by scintigraphy using γ camera unit.

Rats were given 37MBq(in 0.5ml) of technetium-99m phytate or 3.7MBq of gallium-67 citrate through a tail vein after they had been anesthetized with intraperitoneal pentobarbital. Anterior scans were obtained with each rat lying supine on the face of a scintillation camera(shimazu's γ camera) with a pinhole collimator.

Most of ^{99m}Tc -phytate found in normal area of liver 3 hour after injection in rats, and a small quantity of radioactivity was found in the tumor area of liver in hepatocellularcarcinoma-bearing rats.

On the other hand, in rats with induced liver-cancer, the uptake of ^{67}Ga -citrate in tumor area of liver was increased as compared with normal host liver tissue 78 hours after intravenous injection.

TECHNETIUM-99m LABELING ON MONOCLONAL ANTIBODIES VIA N, N' -ETHYLENE-BIS-L-CYSTEINE

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A newly developed excellent kidney imaging agent N, N' -ethylene-bis-cysteine (EC) has been used as a bifunctional chelating agent for Tc-99m labeling of monoclonal antibodies. EC is a chelator of diaminedithiol type (N_2S_2) containing two carboxyl groups which enable it to conjugate antibody protein. The merits of employment of EC are simple synthetic procedure, strong chelation toward Tc and rapid in vivo clearance.

New conjugating agents N-hydroxyl-1,4- epoxy-cyclohex-5-ene-2,3-dicarboxylimide (HONCE) and 1-ethyl-3-(3-dimethylamino-propyl) carbodiimide (EDC) were used to activate the carboxyl groups of EC, and thereby accomplish the conjugation to antibodies. A conjugation yield of 30-40% was obtained. The experimental condition including conjugating agent quantity, C/P ratio, antibody concentration, pH value and reaction time were optimized for the best conjugation performance. Tc-99m labeling was then completed after conjugation.

More than of 90% of activity retained in the labeled complex Ab-EC-Tc-99m after incubation in DTPA solution for 16h. The studies of biodistribution and tumor localization in mice of the label are ongoing.

SYNTHESIS AND CHARACTERIZATION OF A NEW ^{99g}Tc TECHNETIUM (V)
COMPLEX WITH 2-THIOHYDANTOIN

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Assiut University, Egypt

A new ^{99g}Tc Technetium (V) complex with 2-thiohydantoin ligand was prepared by the direct reduction of pertechnetate with dithionite in the presence of excess ligand, and in alkaline medium. The complex obtained was characterized by i.r., U.V.- visible spectroscopy. Separation by HPLC on Lichrosorb-Rp.18 column yielded one chromatographically pure peak due to the complex using methanol water 60 : 40 as mobile phase. The deep orange solution of the complex exhibits characteristic, and intensive band at 450 nm. I.R. spectrum of the complex showed the presence of $\text{Tc}=\text{O}$ stretch. The complex is soluble in water and could be of help in developing new perfusion imaging technetium agents for clinical studies.

TECHNETIUM-ASPIRIN LIKE MOLECULE COMPLEXES

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Technetium-aspirin and Technetium-aspirin like molecule complexes, i.e. N-acetylanthranilic acid, NAA, acetylthiosalicylic acid, ATS, were prepared. The structure of NAA has been decided through CNDO-CI calculations, in addition to the calculation of ionization potential, 11,899 eV, and electron affinity, 1.992 eV.

The electronic absorption spectra of the TC-L complexes have been scanned in EtOH as a solvent. The electronic absorption spectra of Tc(V)-Asp and Tc(V)-ATS complexes have two characteristic bands at 450 and 600 nm but the Tc(V)-NAA spectrum has one characteristic band at 450 nm. Mo-ATS complex was prepared and its electronic absorption spectrum is comparable with the Tc(V)-ATS complex spectrum.

Stoichiometry of the complexes formed between Tc(V) and the other ligands (L) were determined in their solutions from their electronic absorption spectra using the molar ratio method and it has been concluded that the ratio is 1:2 Tc-L. IR spectra of the three types of complexes showed an intensive absorption band at 980 cm^{-1} which can be attributed as $\nu(\text{TC}=\text{O})$ stretching. Extension of our studies are in progress.

RADIOCHEMICAL PROPERTIES AND ELECTRONIC STRUCTURE
OF $^{99m}\text{TcO-HMPAO}$

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Complexon HMPAO was synthesized from 1,3-diaminopentane and diacetyl monoxime according to /1/. The recrystallization from ethylacetate was used to isolate d,l-isomer being the main one for diagnostic. The structure of d,l-form was characterized by NMR spectra. Each vial of the kit for $^{99m}\text{TcO-HMPAO}$ preparation contains complexon SnCl_2 , tartaric acid and NaCl. The combination of three chromatographic systems was used for determination of radiochemical composition. With the use of these chromatographic systems the percentage of TcO_4^- , reduced hydrolyzed technetium, primary lipophilic and⁴ secondary hydrophilic complexes were determined.

The quantum-chemical calculations of the electronic structure of Tc complexes with d,l- and meso-forms of HMPAO were carried out by extended Huckel method with self-consistent atomic charges. The influence of the proton dissociation with formation of O-H-O intramolecular bond upon the valent molecular orbitals (MO) was investigated. In all cases studied three approximately degenerate MO with one unpaired electron have appeared near the occupation border. Two of them are mainly metal in character and the last one is the MO of ligands. This makes it possible for Tc-complex easily to change the metal spin and oxidation states.

The comparative analysis of the electronic properties was carried out for TcO_4^- , TcO-PAO , TcO-HMPAO .

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THE INFLUENCE OF L-CYSTEINE ON THE RADIOCHEMICAL PURITY AND PROPERTIES OF THE COMPLEX Tc-99m-MIBI

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Complex copper(I) salt of methoxy isobutyl isonitrile (MIBI) and fluoborate is the base of the well-known radiopharmaceutical (RP) nowadays. Additionally tin dichloride, mannitol, citric acid and L-cysteine are included in the kit composition. In the present work the influence of the kit components on the radiochemical composition and biological behaviour of RP was studied. Thin layer chromatography was used for the control of radiopharmaceutical composition. The alumina (Alufol) was used as a carrier, ethanol served as a solvent.

It was found that the L-cysteine exclusion from RP-composition does not allow to obtain the necessary complex. The index of radiochemical purity (RCP) becomes too low (less than 1%). The usage of aminoacids without SH-group in molecule also decreases the index of RCP (less than 10 %). On the other hand the usage of a compound containing SH-group (such as DMSA for example) allows to obtain the necessary effect.

The experimental results obtained by NMR and gamma-resonance spectroscopy allow to conclude that compounds containing SH-group in molecule take part in the multi-step reduction of technetium with the following incorporation in the coordinated sphere of the complex.

PRODUCTION OF Tc-99m - GENERATORS IN RUSSIA

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The new designed models of Tc-99m generators (GT-2M and the latest model GT-3) are produced in the Institute of Physics and Power Engineering (Obninsk, Russia) since 1989. The AM-reactor of the first APS-1 is used for Mo-99 production. Irradiation of the target is carried out with a neutron flux of $1,1 \cdot 10^{13} \text{ n/cm}^2 \text{ s}$ in the open channels with a water circulation. Fuel composition contains UO_2 , MgO , Mg . A combination of extraction and extractive chromatography is used for Mo-99 sorption.

A generator loading section includes all technological process connected with preparation of sterile and pyrogen-free vials, solutions and sorbents. A chromatographic column filled with layers of silica, modified manganese oxide and alumina is used for Mo-99 sorption. Tc-99m is eluted with 5 ml of saline into a vacuum vial. The elution efficiency is higher than 80%.

The generators are produced with 6, 8, 11, 19 GBq Tc-99m activity on the delivery date. Nowadays 8000 generators per year are manufactured in Russia, what satisfy the requirements completely. However, if it will be necessary the technology of generator production is allowed to increase the output considerably.

CRITICAL TEMPERATURE OSCILLATIONS FOR THIN FILMS OF TECHNETIUM AT VARIOUS THICKNESS OF CARBON COVERING.

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The critical temperature T_c of technetium thin films covered with the diamond-like carbon layer have been investigated. The set of the technetium films with different covering thickness d_c is prepared at the same vacuum cycle by ultrahigh vacuum ion sputtering. Carried out earlier experiments showed that these carbon films possess number of unique properties: they became continuous beginning with some mono layers of thickness, the amorphous structure is observed and their properties are closed to diamond ones. The thickness of technetium films d was $50 \div 300 \text{ \AA}$. It proved to be that $T_c(d_c)$ dependence have nonmonotonic, oscillating character: at $d_c = 5 \text{ \AA}$ $T_c(d_c)$ displays the maxima, and at $d_c = 10 \text{ \AA}$ - minima. The oscillation amplitude decreases according to law closed to $1/d$ dependence and its value is near 5% for $d = 100 \text{ \AA}$.

SUPERCONDUCTING PROPERTIES AND STRUCTURE OF THE THIN-FILM SAMPLES OF TECHNETIUM AND TECHNETIUM-CARBON SYSTEM

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The thin-film samples of technetium and technetium-carbon system have been prepared by ultrahigh vacuum ion sputtering. The carbon concentration x and film thickness d varies over wide ranges, $0 < x < 70$ at.%, $d = 30 \div 1000$ Å. The phase transformations during the annealing have been studied by TEM and ED, each phase is characterized by measuring superconducting critical temperature T_c and critical magnetic field H_c .

It turns out that there are new phases in technetium based films, which are absent in bulk material. Thus, in technetium films at room temperature for $d < 100$ Å the cubic phase is realized and only for $d > 150$ Å the usual HCP structure is observed. For technetium-carbon system with $d > 300$ Å and $x < 12$ at.% fresh samples represent supersaturated solid solution of carbon into technetium, and for $x > 12$ at.% they are in amorphous state with crystallite size < 10 Å. For these amorphous samples two phase transformations have been observed at $T_1 = 500^\circ\text{C}$ and $T_2 > 600^\circ\text{C}$. At $T = T_1$ the phase with the primitive cubic cell is formed, while at $T = T_2$ this phase turns into HCP phase of carbon solid solution in technetium with solubility limit over 40 at.%. T_c raises sharply for cubic phase up to $T_c = 14 \div 15$ K and falls down to 3 K after the second transition. For cubic phase the high values of H_c have been obtained with derivative $dH_c/dt = 24$ kOe/K near T_c .

APPLICATION OF THE TECHNETIUM-99 FOIL FOR THE DEFECTOSCOPY OF LIGHT MATERIALS

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Technetium - silver-gray metal similar in appearance to manganese and rhenium is close to them by chemical behavior. Its corrosion properties are close to the properties of noble metals.

Under ordinary conditions in the air Tc metal does not lose its lustre and even two year exposure in sea water didn't result in the loss of metal brightness. At the same time heating of Tc metal in the air to temperatures higher than 300°C results in its oxidation with formation of highly volatile oxides. Technetium is hard durable heavy metal ($\rho=11.49 \text{ g/cm}^3$, $p=100 \text{ MPa}$, $\sigma=40\%$, $HV_{10}=1100$), yielding to reviting.

Its firmness after volling is 3000-4000 MPa ($HRC=6-8$), which is comparable to the hardness of low-alloy steel or titanium. Thus, at the direct contact with Tc radioactive contamination is practically impossible. Another advantage of this material is even distribution of radioactive element along the surface of emitter. Being pure β -emitter with a long half decay period ^{99}Tc can be used as a safe source of ionizing radiation.

Optimum parameters of the radiator allow its successful use in metrology, β -radiography, particularly in defectoscopy of light materials, such as paper and fabric.

Procedure of calculation of time of exposure in radiography has been developed on the base of data on the interaction of electrons airrent from the radiator with electron sensitive (photo and XR) layers. In order to use this procedure you should know sencitometrical characteristics of electroresistive layers and of some of the objects parameters: width, electron adsorption coefficient. Sencitometrical characteristics have been calculated (computed) through the analysis of characteristical curred (crooked) layers exposed by the radiographic images of water marks with preprogrammed characteristics. If found its utilization in pallography, archivistics, polygraphy and criminalistics.

EFFECT OF TRITIUM ON HYDROGEN-ISOTOPE EXCHANGE REACTION IN A HETEROGENEOUS SYSTEM

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In order to reveal the effect of tritium (^3H or T) on hydrogen-isotope exchange reaction, the exchange reaction between one of inorganic or organic compounds and one of tritiated compounds was observed in gas-solid or liquid-solid system [1,2]. The rate constants for the unlabeled materials used were obtained with both the data obtained and the A'' -McKay plot method [3,4]. It can be considered that the rate constants indicate the reactivities of the materials.

Though the ratio of number of T atoms to that of ^1H atoms in rain water is about $1 \times 10^{-18} : 1$, the atmospheric concentration of T is believed to gradually increase with the increased use of both nuclear fusion and the reprocessing plant for spent nuclear fuel. Further, hydrogen atom is important in biological system. Accordingly, behavior of T needs to be clarified, urgently.

For gas-solid reaction, the following equality has been obtained by comparing the rate constants at 70°C :

$$\begin{aligned} &(\text{PVA}_{500}):(\text{PVA}_{2000}):(\text{succinic acid}):(\text{BaHPO}_4):(\text{anisic acid}) \\ &= 1.3 : 1.0 : 0.20 : 0.063 : 0.011 \end{aligned}$$

For liquid-solid reaction, the following equality has been obtained in a similar manner as above.

$$\begin{aligned} &(\text{ethanol}):(\text{acetic acid}):(\text{phenol}):(\text{benzoic acid}):(\text{aniline}) \\ &= 13 : 11 : 5.2 : 4.6 : 2.8 \end{aligned}$$

From the above mentioned and previously obtained [5], it has been quantitatively clarified that the effect of T on the exchange reaction is changed with (1) the degree of polymerization of the material, (2) the kind of the functional group in the material, (3) the reaction-system (e.g., gas-solid or liquid-solid system).

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