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Klaus Schwochau

Technetium
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Preface

The artificial radioelement of atomic number 43, technetium, is frequently considered to be a curiosity in inorganic chemistry. However, more than five decades ago, when sufficient quantities of the long-lived nuclide $^{99m}$Tc with a half-life of $2.13 \times 10^5$ a became available, investigations of its chemistry and physics soon confirmed technetium to be a true second-row transition element, filling the gap in the periodic system between manganese and rhenium. Technetium received much attention in fundamental inorganic chemistry studies at research institutions and universities. At present, the enormous number of technetium compounds, that have been isolated and characterized, documents the extensive research performed in technetium chemistry. Its rapid expansion was primarily spurred by the world-wide intention to develop technetium radiopharmaceuticals of high diagnostic efficacy labeled with the $^{99m}$Tc isomer with a physical half-life of six hours. Over 80% of all radiopharmaceuticals now used in clinics are labeled with $^{99m}$Tc.

This monograph represents the present status of technetium chemistry and technetium radiopharmaceuticals. It is intended for use as a handbook and a text book for inorganic and nuclear chemists, nuclear pharmacists and nuclear medicine physicians. First discussed are the discovery and occurrence of technetium, its nuclides, fundamental and analytical aspects, and its uses. Technetium chemistry is focused on in discussions of synthesis, properties, and structures of individual technetium compounds. Complex compounds are treated in the sequence of Tc oxidation states in most of part A. Part B is concerned with synthesis, composition, and structure of $^{99m}$Tc radiopharmaceuticals currently used for diagnostic organ and tumor imaging, and with future prospects, including imaging of hypoxic tissue, receptor binding, and dopamine transporters. Concluding tables are provided to summarize the chapters. Each chapter terminates with the pertinent literature. Acronyms and abbreviations used in both parts of this book are listed in the appendix.

I am grateful to the late Prof. Dr. W. Herr for drawing my attention as early as the late 1950s to the artificial element technetium. I would like to express my cordial gratitude on this occasion to all my former co-workers in technetium chemistry, in particular to Dr. L. Astheimer, Mr. K. H. Linse, Dr. H. J. Schenk, Dr. H. H. Pieper, and Dr. J. Hauck. My sincere thanks are due to Prof. Dr. K. H. Lieder, Darmstadt, for his interest in this book. I would further like to thank the staff on the Central Library of the Research Center in Juelich, Germany, for actively supplying the relevant literature. Finally, my thanks are extended to the publishers for their friendly cooperation. All criticisms of this book brought to my attention will be gratefully acknowledged.

Juelich, December 1999

Klaus Schwochau
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A. Chemistry
1 Introduction

Element 43 in the seventh subgroup of the periodic system, technetium, is the lowest atomic number radioelement. Stable, non-radioactive isotopes do not exist according to Mattauch's rule. Technetium isotopes can be produced artificially by nuclear processes. Long-lived isotopes are $^{97}\text{Tc}$ ($2.6 \cdot 10^6$ a), $^{98}\text{Tc}$ ($4.2 \cdot 10^6$ a) and $^{99}\text{Tc}$ ($2.1 \cdot 10^5$ a). The spectroscopic discovery of technetium in several fixed stars provided the first proof of stellar synthesis of heavy nuclides. Traces of $^{99}\text{Tc}$ occur in the earth's crust where they arise mainly from spontaneous fission of $^{238}\text{U}$.

Among the long-lived isotopes, $^{99}\text{Tc}$ is the only one which is obtained in weighable amounts. It is formed in high yield by the fission of $^{235}\text{U}$, and quantities of the order of kilograms can be isolated from nuclear reactor fission product waste solutions. Because of the relatively low specific activity of 17 $\mu\text{Ci/mg}$ (629 kBq/mg) and the weak $\beta^-$-radiation ($E_{\text{max}}=0.29$ MeV), the laboratory handling of $^{99}\text{Tc}$ needs no special radiation protection.

The chemical behavior and the coordination chemistry of this second row transition element closely resemble those of the homologous element rhenium, however, detailed investigations also revealed many distinct differences. The critical temperature of superconductivity of technetium metal is remarkably high at 8.2 K. Specific catalytic properties of technetium have been demonstrated. The effectiveness of pertechnetate ions in inhibiting the corrosion of steel is noteworthy. Pertechnetate is a weakly oxidizing agent, although somewhat stronger than perrhenate. Because of the almost equal ionic radii of technetium and rhenium, their analogous compounds frequently exhibit isostructural lattices. Alkali pertechnetates are the thermally most stable compounds of technetium; $\text{KTcO}_4$ boils without decomposition at $-1000^\circ\text{C}$.

The coordination chemistry involves the oxidation states from +7 to −1. Coordination numbers from 4 to 9 are known. Crystal field considerations and magnetic susceptibility measurements show that technetium forms low-spin compounds. Dinuclear complexes frequently display metal to metal bond character. There is some evidence that technetium complexes are thermodynamically less stable and kinetically more reactive than the corresponding complexes of rhenium. A multitude of coordination compounds of technetium has been synthesized and unambiguously characterized. Investigations of the complex chemistry have been enormously stimulated by the development of $^{99m}\text{Tc}$ radiopharmaceuticals.
The first conclusive experimental evidence for element 43 was given by Perrier and Segrè in 1937 [1]. This discovery was a consequence of the invention of the cyclotron. A plate of natural molybdenum irradiated over a period of some months by a strong deuteron beam in the Berkeley cyclotron was presented by E. O. Lawrence of the University of California to E. Segrè at the Royal University of Palermo, Italy. The molybdenum plate showed strong radioactivity due to more than one nuclide with a half-life of months. In a cooperation of E. Segrè with C. Perrier, of the same university, a chemical investigation of the activity ruled out any radioactive isotopes of zirconium, niobium, molybdenum or ruthenium, and revealed that the activity arose from nuclides of the missing element cokamanganes of the atomic number 43 [2]. The metastable isomers $^{95m}\text{Tc}$ and $^{97m}\text{Tc}$ had been produced by the nuclear reactions:

$$^{94}_{42}\text{Mo}(d,n)^{95m}\text{Tc} \quad t_{1/2} = 61\text{d}$$

and

$$^{96}_{42}\text{Mo}(d,n)^{97m}\text{Tc} \quad t_{1/2} = 91\text{d}$$

Using concentrated fractions of these isomers, Perrier and Segrè were able to demonstrate by coprecipitations, for instance with sulphides of manganese and rhenium or with $\text{TlReO}_4$, that the element produced bore the closest resemblance to rhenium. Other experiments showed the radioactivity to volatilize with rhenium in an oxygen flow at 550°C [2]. They could already identify several chemical properties of this artificial element [3]. In 0.4 to 5 M hydrochloric acid solution the sulphide precipitation was complete in the presence of rhenium or platinum as a carrier, but in 10 M hydrochloric acid only a very small fraction of the total activity precipitated, in contrast to the precipitation of $\text{ReO}_3$. In considering the possibility of separating element 43 and rhenium, Perrier and Segrè tried to determine partition coefficients of the radioactivity between aqueous solutions and crystals of $\text{KReO}_4$ and $\text{CsReO}_4$. They found a partition coefficient of the activity for $\text{KReO}_4$ of 2.6 and for $\text{CsReO}_4$ of 0.75 in agreement with the lower solubility of $\text{CsTcO}_4$ as compared to $\text{KTeO}_4$ [3]. In 1947 the discoverers proposed for element 43 the name "technetium" derived from the Greek word τεχνητός meaning artificial, in recognition of the fact that technetium was the first artificially made element, and they suggested the corresponding chemical symbol "Tc" [4]. Prior to the naming, Segrè and Wu [5] detected a 6 h activity of element 43, obviously $^{99m}\text{Tc}$, by extraction of $^{99}\text{Mo}$, a neutron fission product of $^{235}\text{U}$.
2.1 References

3 Natural occurrence

3.1 Primordial technetium

In 1869 Mendeléev [1] predicted the existence of an element of atomic weight 100 occupying the vacant space between molybdenum and ruthenium in his Periodic System. He named this element provisionally “ekamanganese” corresponding to its position below manganese. In 1913 and 1914 Moseley [2,3] found the atomic number of elements in the Periodic System to be directly proportional to the square root of the frequency of their K or L X-ray emission and thus derived a vacant space for the atomic number 43 in addition to 61(Pm) and 75(Re). These indications of Mendeléev and Moseley stimulated numerous attempts to demonstrate the occurrence of element 43 [4,5] and the other elements lacking in nature.

In this context the systematic investigations of Noddack and Tacke [6] as well as Berg and Tacke [7] should be mentioned. It was not unexpected that when they announced in 1925 the discovery of element 75 “dvimanganese”, later called rhenium, they also claimed to have detected element 43 by X-ray spectroscopy in concentrates of the minerals sperrylite (PtAs$_2$), gadolinite [Be$_2$Y$_2$Fe(SiO$_4$)$_2$O$_2$], and columbite [(Fe,Mn)(NbO$_3$)$_2$]. The wavelengths of the X-ray lines interpreted as $K\alpha_1, K\alpha_2$, and $K\beta_1$ showed good agreement with the calculated wavelengths. Noddack, Tacke, and Berg named the alleged element 43 “masurium”, commemorating the former East Prussian district of Masuria. Whereas I. Noddack (née I. Tacke) and W. Noddack [8] succeeded in isolating about 2 mg of rhenium, they could not concentrate and isolate element 43. Because no further evidence for the existence of masurium in the earth’s crust was submitted, their claim to discovery was finally not accepted.

In 1934 Mattauch’s rule on the stability of atomic nuclei was published [9]. Mattauch pointed out that $\beta$-stable isobar pairs do not exist when they differ only by one atomic number unit and ruled out the existence of stable isotopes of element 43. Nevertheless, the primordial occurrence of long-lived isotopes in the earth’s crust could not be excluded [10], thus the search for element 43 continued. Herr [11] exposed concentrates of rhenium-rich molybdenites (MoS$_2$), from which Mo was separated, to an intense neutron bombardment and observed a 6 h activity of $^{99m}$Tc. This activity supposedly resulted from the reaction $^{98}$Tc(n,γ)$^{99m}$Tc indicating the occurrence of $^{98}$Tc in these ores. However, taking into account neutron reactions with possible contaminations ($^{96}$Mo, $^{99}$Tc, $^{99}$Ru, $^{235}$U) of the concentrates, the occurrence of $^{98}$Tc could not be demonstrated conclusively. Similar investigations were carried out by Alperovitch and Miller [12] who claimed the detection of $^{98}$Tc in columbites, yttrotantalites [(Y,Ce)$(Ta,NbTi)O_6$] and a thortveitite [(Y,Sc)$_2$(Si$_2$O$_7$)]. Anders (Alperovitch) et al. [13] extended the search for $^{98}$Tc by neutron activation analysis mainly of the same minerals, but of different locality...
and stated strong evidence for the existence of $^{98}\text{Tc}$ in nature. In the same year Boyd and Larson [14] published a report on the occurrence of technetium in the earth's crust after a thorough search in a variety of terrestrial substances including molybdenite and yttro tantalite. They used different analytical methods of high sensitivity such as isotopic dilution, mass spectrometry, neutron activation analysis, emission spectroscopy, spectrophotometry, and polarography, but they failed to reveal any traces of technetium in the samples analyzed. In addition, Herr et al. [15] could not detect in Precambrian columbite, gadolinite, and tantalite any enrichment of the isotopes $^{97}\text{Mo}$, $^{98}\text{Mo}$ and $^{98}\text{Ru}$ as potential decay products of $^{97}\text{Tc}$ and $^{98}\text{Tc}$, respectively. Boyd et al. [16] produced the long-lived isotopes $^{97}\text{Tc}$, $^{98}\text{Tc}$, and $^{99}\text{Tc}$ by bombarding molybdenum metal with 22 MeV protons for 270 days and identified some amounts by mass spectrometry for the first time. The half-life of these isotopes was found to be considerably less than $10^8$ a [14, 17], thus excluding the presence of primordial technetium in the earth's crust given the formation of the earth approximately $4.5 \cdot 10^9$ a ago.

3.2 Non-primordial technetium

Nevertheless, the earth's crust contains technetium. $^{99}\text{Tc}$ is predominantly formed by spontaneous fission of $^{238}\text{U}$ and is also produced by neutron induced fission of $^{235}\text{U}$. The first isolation of naturally occurring technetium was reported by Kenna and Kuroda [18, 19], who separated about $10^{-3}$ μg of $^{99}\text{Tc}$ from 5.3 kg of Belgian Congo pitchblende. The ore contained 42.2 wt% U, 0.37 wt% Mo, 0.17 wt% Cu, 0.03 wt% Cl, less than 0.00004 wt% Ru, and 0.000002 wt% Re. Three technetium fractions were isolated from 2.0, 1.3 and 2.0 kg of pitchblende, respectively. The samples were dissolved in dilute nitric acid. Lead was precipitated as the sulphate and H$_2$S was passed through the filtrate. The precipitate was dissolved in ammoniacal hydrogen peroxide and excess peroxide was removed by boiling. The pH was kept at 8 or higher. To remove the bulk of the cations, the neutralized solution was passed through a cation exchange column. Copper and molybdenum were removed from the evaporated solution by precipitation with x-benzoin-oxime. Pertechnetate and perrhenate were extracted from the 5 M NaOH solution. After re-extraction into the aqueous phase, a few mg of copper were added to act as a carrier and sulphides again precipitated, filtered and dissolved. The solution was evaporated, the pH adjusted to 7, pertechnetate and perrhenate adsorbed on an anion exchange column and eluted with 0.25 M perchlorate. Finally, again copper carrier was added to the technetium fraction, the acidity adjusted to 2 N, and sulphides were precipitated [20].

The activity of the precipitate was counted with a low-background $\beta^-$-counter, with a background of about 0.7 counts per min. The observed activity measured in the precipitate per kg ore was 1.8, 1.7 and 2.1 counts per min for the three pitchblende samples, respectively. The average half-thickness value of $7 \pm 1$ mg/cm$^2$ aluminum was in agreement with the accepted half-thickness value of 7.2 mg/cm$^2$ Al for $^{99}\text{Tc}$. The atomic ratio $^{99}\text{Tc}/^{238}\text{U}$ in pitchblende was found to be fairly conformable with the
$^{99}\text{Mo}/^{238}\text{U}$ ratio, indicating that the $^{99}\text{Tc}$ in pitchblende was predominantly produced by the spontaneous fission of $^{238}\text{U}$ [19].

Some billion years ago natural nuclear reactors must have operated and generated $^{99}\text{Tc}$ as a high yield fission product by induced fission of $^{235}\text{U}$ with slow neutrons. The relics of a natural reactor were discovered in 1972 at the Oklo uranium mines in the Republic of Gabon, Africa. The Oklo phenomenon occurred 1.72 billion years ago and produced a greater amount of $^{99}\text{Tc}$ than detected in other uranium ores [20]. Ruffenach et al. [21] reported values of integrated flux of thermal neutrons for the Oklo uranium ores of up to $1.32 \cdot 10^{21}$ n \cdot cm$^2$ and a $^{235}\text{U}/^{238}\text{U}$ atomic ratio down to 0.00410, compared to 0.00725 in normal natural uranium. If the fission yield of $^{99}\text{Tc}$ amounts to around 6 atom $\%$, $0.315 \cdot 0.06 = 0.019$ atom $\%$ of $^{235}\text{U}$ should have been converted to $^{99}\text{Tc}$, corresponding to about 0.2 mg of $^{99}\text{Tc}$ per kg of a uranium ore containing 37 wt$\%$ uranium. However, since the half-life of $^{99}\text{Tc}$ is $2.13 \cdot 10^5$ a, the isotope completely decayed to $^{99}\text{Ru}$. The considerably higher abundance of $^{99}\text{Ru}$ in Oklo uranium ores was proved by Frejacques et al. [22].

### 3.3 Technetium in stars

Soon after the publication of the first and second atomic emission spectrum of technetium by Meggers and Scribner [23], Moorc [24] looked for technetium lines in the spectrum of the sun. The evidence for the presence of Tc$^+(\text{TcII})$ rested chiefly on the one unblended solar line at 3195.230 Å. Later, this suggestion was shown to be erroneous [25, 26, 27]. However, in 1952 Merrill [28, 29] detected neutral technetium, (TcI) absorption lines at 4031, 4238, 4268, and 4297 Å in S-type stars. The highest intensity lines were identified in the stars R Geminorum, R-Andromeda, and AA Cygni. Stellar spectra of type S are characterized by bands of zirconium oxide and by relatively strong lines of heavy metals such as zirconium and barium. Some years later Merrill [30] also observed TcI-lines in the N-type stars TX Piscium and U Hydrae. Moreover, also M-type stars showed TcI-lines. Stars of S-, N- and M-type are relatively cold, having surface temperatures of around 3000 K. The discovery of technetium in numerous stars was of great significance to cosmological theories [31]. Considering the half-life of $2.6 \cdot 10^6$ a of $^{97}\text{Tc}$ and $2.1 \cdot 10^5$ a of $^{99}\text{Tc}$, the isotopes which have been discussed to be produced in stars [32], the existence of technetium at the surface of stars is one of the strongest supports for the idea of nucleosynthesis of heavy elements by slow neutron capture (s-process) [33]. The time scale for neutron capture in the s-process is much longer than that for $\beta$-decay [34].

### 3.4 References

3.4 References

[10] H. Jensen, Naturwissenschaften 26, 381 (1938)
[29] P. W. Merrill, Science 115, 484 (1952)
4 Artificial occurrence

Among the long-lived technetium isotopes only the $\beta$-emitter $^{99}$Tc with a half-life of $2.13 \cdot 10^5$ a is obtained in weighable amounts, either by neutron irradiation of highly purified natural molybdenum or by induced fission of $^{235}$U with thermal neutrons. Because of the high fission yield of 6.13 atom%, appreciable quantities of $^{99}$Tc can be isolated from uranium fission product mixtures. Nuclear reactors with a power of 3500 MW$_{th}$ produce about 100 g of $^{99}$Tc per day or 6 TBq ($\sim 10$ kg) $^{99}$Te/GW$_{th}$ per year.

The total stratospheric fallout of $^{99}$Tc from nuclear weapons testing was estimated at 140 TBq [1, 2]. The fission of $^{235}$U and $^{239}$Pu in nuclear weapons test explosions produce $^{99}$Tc, which is oxidized to Tc$_2$O$_7$ in the presence of atmospheric oxygen at the high temperatures prevalent during the explosions. Tc$_2$O$_7$ reacts with water vapor to give pertechnetic acid. Radioactive fallout is very low at present as a consequence of international agreements banning nuclear weapons tests in the atmosphere [3]. The Chernobyl accident in 1986 liberated about 0.75 TBq of $^{99}$Tc [2].

Releases of $^{99}$Tc from nuclear power plants are low during normal operation. About 1 MBq $^{99}$Tc per year is released from a 1000 MW$_{e}$ reactor. With an operational experience of 6000 reactor years and a mean reactor capacity of 700 MW$_{e}$, the total calculated release of $^{99}$Tc is only 4.2 GBq [2].

The short-lived $^{99m}$Tc ($t_{1/2} = 6.0$ h) is used as an organ imaging radioisotope in radiopharmaceuticals in nuclear medicine. $^{99m}$Tc is produced in commercial generators and decays by $\gamma$-emission to the $^{99}$Tc ground state. Per medical investigation 20 to 1000 MBq $^{99m}$Tc is applied. This radionuclide has shown the greatest increase in usage during the past two decades. However, the activity of $^{99m}$Tc formed by decay of $^{99m}$Tc is negligible as calculated from the ratio of the decay constants $\lambda(99mTc)/\lambda(99mTc)=3.2 \cdot 10^{-9}$.

The most important source of artificially occurring $^{99}$Tc is the nuclear fuel cycle. The total electricity generated by nuclear power stations over the world until the end of 1980 was 419 GW$_e$ years [4]. Assuming that some 10% of the fuel, from which this electricity has been produced, is reprocessed and that all the $^{99}$Tc liberated by reprocessing was discharged before the end of 1980, an activity of about 825 TBq was released. After 1980 reprocessing was improved to reduce emissions. It is estimated that the $^{99}$Tc discharge is only about 10% of that, released up until 1980, i.e. 68 TBq corresponding to 343 GW$_e$ years up to 1983 and 234 TBq corresponding to 1187 GW$_e$ years [5] until the end of 1993. The total global discharge of $^{99}$Tc by the nuclear fuel cycle would be on the order of 1130 TBq up till the end of 1993. Summarizing the radioactivity of the relevant artificial $^{99}$Tc sources over the world would result at present in around $1.3 \cdot 10^3$ TBq, equivalent to more than 2 t of $^{99}$Tc.
4.1 Technetium in the nuclear fuel cycle

The description of technetium production in the nuclear fuel cycle and technetium release to the environment is based on a light-water reactor (LWR) designed to produce 800 MW of years [6]. The lifetime of this model reactor is considered to be 30 years. The difference in the amounts of $^{99}$Tc formed in spent fuel in the pressurized water reactor (PWR) and the boiling water reactor (BWR) appears to be negligible.

35 metric tons of uranium are assumed to be the annual feed of new fuel. The $^{235}$U enrichment in the fresh fuel is supposed to be 3.2 wt%, in the spent fuel 0.84 wt%. Technetium isotopes of mass numbers greater than 99 have half-lives of less than 20 min and thus have decayed during storing of the fuel elements for 150 days after discharge from the reactor. As compared to $^{99}$Tc the production of the long-lived isotopes $^{97}$Tc and $^{98}$Tc by thermal neutron fission can be neglected. $^{99}$Tc is by far the dominant technetium isotope occurring in the nuclear fuel cycle [4]. It is also formed in high yield (atom%) from thermal neutron fission of $^{233}$U(4.8) and $^{239}$Pu(5.9), and fast neutron fission of $^{238}$U(6.3), and $^{232}$Th(2.7). All of these sources may contribute to the accumulated inventory of $^{99}$Tc. The specific radioactivity of $^{99}$Tc normalized to fuel with a burnup of 33,000 MWd (therm) per ton of uranium is calculated to be about 14.5 Ci/t [6] corresponding to 0.85 kg of $^{99}$Tc/t of uranium.

The reprocessing procedure for recovering uranium from spent fuel elements is a chemical technique known as the Purex (plutonium and uranium recovery by extraction) process [7]. The fuel elements are cut into small pieces for dissolution in 7.5 M HNO$_3$. The dissolution is normally incomplete. An amount of small metallic particles containing Mo, Ru, Rh, Pd, and Tc is not dissolved [8] and discharged as highly active waste [9]. Technetium, assumed to be produced during fission in its elemental state, is converted to TcO$_4$-$^-$. The aqueous nitric acid liquid containing the dissolved burned-up fuel is processed through a series of solvent extractions [6].

The solvent extraction of TcO$_4$ by tributyl phosphate (TBP) in n-dodecane was studied over a wide range of concentrations of TBP, HNO$_3$, NH$_4$NO$_3$, and uranium, and as a function of temperature [7, 10]. The extraction was found to proceed via the compound H$_2$TeO$_4$·3TBP [10]. Increasing TBP concentration from 10 to 80 vol% results in a rise of the TcO$_4$ distribution coefficient $D_{Tc}$ of almost three orders of magnitude. For any given TBP concentration $D_{Tc}$ increases with increasing nitric acid concentration until a maximum is reached at 0.6 M HNO$_3$. There is almost no extraction of TcO$_4$ in the absence of HNO$_3$. The reason for the increase of $D_{Tc}$ up to 0.6 M HNO$_3$ appears to be the reduced dissociation of HTeO$_4$. Above 1.0 M HNO$_3$ D$_{Tc}$ decreases rapidly due to competition of a complex formation of HNO$_3$ with TBP. When, by addition of UO$_2$(NO$_3$)$_2$, the aqueous phase is 0.1 M in UO$_2$(NO$_3$)$_2$, $D_{Tc}$ is substantially increased by some orders of magnitude at HNO$_3$ concentrations lower than 0.1 M. Apparently, the extracted compound formed is UO$_2$(NO$_3$)(TcO$_4$)·2TBP [7, 9, 10]. In the temperature range from 25 to 60 °C $D_{Tc}$ was found to decrease steadily as the temperature is increased (Fig. 4.1.A).

After extraction of pertechnetate with TBP in n-dodecane, the uranium in the cycle may contain about 0.1 wt% of technetium which originally occurred in the spent fuel [6, 7, 11]. Because of restrictions on impurities of recycled uranium, it is required that the
concentration of $^{99}$Tc in uranium is only about 4 ppm. The assumption of 4 ppm $^{99}$Tc in uranium implies that in 35 t of recovered uranium 0.14 kg of $^{99}$Tc returns to the fuel for any year, while around 30 kg of $^{99}$Tc enters the high level waste [6]. The release of $^{99}$Tc from the reprocessing plant to the atmosphere may be assessed by using a so-called confinement factor. If technetium is released during the dissolution of spent fuel elements in 7.5 M HNO$_3$, volatile compounds formed would predominantly be Te$_2$O$_7$ and HTcO$_4$. However, these and other volatile products would be almost quantitatively stripped by gas scrubbers containing oxidizing agents dissolved in alkaline water and would form non-volatile pertechnetate. It can be expected that the $^{99}$Tc cycled through the uranium reprocessing plant remains almost completely in the process streams and does not escape. A confinement factor of $10^8$ was selected due to resemblances in the chemical properties and volatility of technetium and ruthenium compounds [6]. Applying this factor to the total amount of $^{99}$Tc of almost 30 kg, formed per year in the model reactor, yields a source term for reprocessing of only 0.3 mg of $^{99}$Tc released to the atmosphere.

For operation of the model reactor, the input of uranium to the model plant converting UO$_2$ to UF$_6$ is assumed to be 182 t of natural uranium which is processed to about 270 t of UF$_6$. 13.2 wt% of 270 t of UF$_6$ is from uranium recycled back to the system. As mentioned above, 0.14 kg of $^{99}$Tc per reactor year is returned with uranium to the fuel cycle, where it reacts with fluorine to give TeF$_6$. An estimate of the source term for $^{99}$Tc released to the atmosphere and to water can be formed by assuming that TeF$_6$ is released to each pathway in the same fraction of fluoride appearing in the effluent to the total fluoride used in the process [6]. The total amount of fluoride used in the model plant for fluorination is at least 270 t of UF$_6$ minus 182 t of uranium, i.e. 88 t. Releases of fluoride to water account for 0.22 t and to the atmosphere for 0.11 t per model reactor year. Consequently, it may be assumed that the fraction 0.22/88 of

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**Fig. 4.1.A** $D_{Te}$ as a function of HNO$_3$ concentration and temperature at a TBP concentration of 30 vol% in n-dodecane [7].
0.14 kg $^{99}$Tc, i. e. 0.35 g is released to water and 0.11/88 of 0.14 kg $^{99}$Tc, i. e. 0.175 g, to the atmosphere [6].

Significant amounts of $^{99}$Tc are known to accumulate in the cascades of the gaseous diffusion enrichment plants as TcF$_6$. Emission of $^{99}$Tc to the atmosphere result from its presence in the effluent of the cascades, but the major source are liquids used for equipment decontaminations. The relatively light TcF$_6$ moves toward the product end of the diffusion cascade rather than to the tails end. It can be separated from the UF$_6$ stream by using more or less efficient magnesium fluoride traps. $^{99}$Tc may be removed from aqueous decontamination solutions by precipitation or ion exchange techniques [6]. Quantitative data are not available from which a confinement factor for $^{99}$Tc can be calculated, therefore several assumptions are made. 50 wt% of the $^{99}$Tc entering the model enrichment plant may follow the $^{235}$U enriched UF$_6$, that is 70 g, while 40 wt% are assumed to remain with tails. 10 wt% of $^{99}$Tc (14 g) may escape to the environment. According to some data concerning release of $^{99}$Tc to water and air during gaseous diffusion enrichment of uranium in the United States [6], the mean source term ratio of water/air is around 40. Thus, per year, about 97.5 wt% of 14 g $^{99}$Tc, i. e. 13.65 g, may enter the water pathway and 2.5 wt%, i. e. 0.35 g enter the atmosphere in the model enrichment plant.

The UF$_6$, enriched to 3.2 wt% $^{235}$U constitutes the feed material to the model fuel fabrication plant. UF$_6$ still contains around 70 g of $^{99}$Tc. 52 t UF$_6$ per model reactor year are converted to 40 t of UO$_2$ by hydrolysis of UF$_6$, precipitation of (NH$_4$)$_2$U$_2$O$_7$, calcination to UO$_3$, and hydrogen reduction to UO$_2$. During these chemical processes TcF$_6$ may be partially converted to Tc$_2$O$_7$ and vaporized at elevated temperature. To calculate an upper limit for $^{99}$Tc release, it may be assumed that 50 wt%, i. e. 35 g of $^{99}$Tc, is carried through the process and remains with the UO$_2$ probably in the form of TcO$_2$. An estimate of source terms for the environment can be made by assuming that TcF$_6$ is released to water and to the atmosphere in the same fraction as UF$_6$ [6]. Thus, per year, 99.9 % of the remaining 50 wt% of $^{99}$Tc, i. e. 34.96 g, may enter the liquid waste stream and only 0.1 wt%, i. e. 0.35 mg, the atmosphere in the model fuel fabrication plant.

Fission products including $^{99}$Tc are separated from uranium during reprocessing and retained in liquid tanks for solidification by calcination or glassification [12]. We will consider the glassification process as a model [6]. It is assumed that the model reactor creates 2 m$^3$ of solidified high-level waste per year, and that there are no liquid wastes associated with the solidification process. As mentioned above around 30 kg per year of $^{99}$Tc is expected in the high-level radioactive waste residue which may release about 0.3 mg of $^{99}$Tc to the atmosphere by solidification, assuming again a confinement factor of $10^8$ as for reprocessing [6]. The solidified high-level waste containing $^{99}$Tc will be transferred to a geologic repository. If it is assumed that no breach of the containment occurs, the amount of $^{99}$Tc released to the atmosphere per year during the waste storage appears to be negligible.

Significant source terms assessed for $^{99}$Tc releases to the environment during the different processes of the nuclear fuel cycle are summarized in Table 4.1A [6]. The amounts expected to be released per year were calculated on the basis of the model reactor defined at the beginning of Section 4.1. The total release via effluent water
appears to be two orders of magnitude higher than the release to the atmosphere. Among the processes releasing $^{99}$Tc to water, fuel fabrication and enrichment are by far the most important sources. In order to reduce the concentration of $^{99}$Tc in aqueous discharges, a strong-base ion-exchange resin was suggested to bind TcO$_4^-$ [13].

Table 4.1.A Assessment of annual $^{99}$Tc releases to the environment during nuclear fuel cycle processes. The assessment is based on the model reactor defined in the text [6].

<table>
<thead>
<tr>
<th>Process</th>
<th>Release of $^{99}$Tc (g/a(MBq/a))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Atmosphere</td>
</tr>
<tr>
<td>Reprocessing</td>
<td>$3 \cdot 10^{-4}$ (0.189)</td>
</tr>
<tr>
<td>Production of UF$_6$</td>
<td>$1.75 \cdot 10^{-1}$ (110)</td>
</tr>
<tr>
<td>Enrichment</td>
<td>$3.5 \cdot 10^{-1}$ (229)</td>
</tr>
<tr>
<td>Fuel fabrication</td>
<td>$3.5 \cdot 10^{-2}$ (22)</td>
</tr>
<tr>
<td>High-level waste solidification</td>
<td>$3 \cdot 10^{-4}$ (0.189)</td>
</tr>
<tr>
<td>Total</td>
<td>$5.6 \cdot 10^{-1}$ (352)</td>
</tr>
</tbody>
</table>

After glassification of the high-level radioactive waste, technetium appears to occur mainly in the chemical form of TcO$_2$ [7]. In a dry repository no chemical changes of the solidified waste are expected for a long time. However, any contact with aqueous solutions may alter the situation drastically by initiation of chemical reactions (Fig. 4.2.A) depending on the composition of the solution, the pH, redox potential and temperature [14]. The containment is assumed to resist corrosion by aqueous solutions no longer than about one hundred years [7]. Thereafter the radioactive waste is subject to water leaching, and silicates formed by glassification will be exposed to hydrolysis. In the presence of oxygen and water, TcO$_2$ will be oxidized to easily soluble TcO$_4^-$. This oxidation is expected to be enhanced radiolytically, particularly in salines [15, 16].

Fig. 4.2.A Dissolution of TcO$_2$ under anaerobic and aerobic conditions (3 mg TcO$_2$, 100 ml 0.1 M NaNO$_3$, 20 °C, pH 5.7 [14].
4.2 Technetium in the environment

We discussed the sources of artificial occurrence of $^{99}$Tc at the beginning of this chapter and demonstrated that the nuclear fuel cycle is the predominant source of $^{99}$Tc in the environment. Other, much less important, sources are the fallout from nuclear weapons testing, the Chernobyl accident, nuclear power production and the radio-pharmaceutical use of the metastable $^{99m}$Tc decaying to ground state $^{99}$Tc. The natural occurrence of $^{99}$Tc formed in the earth’s crust by spontaneous fission of $^{238}$U and neutron-induced fission of $^{235}$U in uranium ores are negligible.

Taking into account the kind of sources and the chemistry of technetium, $^{99}$Tc will be released to the environment as pertechnetate. Its behavior in the environment attracted much attention during the last two decades due to the long physical half-life of $^{99}$Tc and the solubility and mobility of $^{99m}$TcO$_4^-$ in aquatic systems. Considerable effort has been made to understand the long-term biogeochemical behavior of $^{99}$Tc, its transfer in food chains and the mechanisms controlling its mobility in diverse environments [17].

4.2.1 Retention in soils, sediments, and rocks

The pertechnetate ion will not likely be sorbed in significant amounts by soils and suspended bottom sediments of predominantly negative charge, but will be highly mobile in soils and waters and thus available for uptake in biota. The $^{99}$Tc level in soil down to a depth of 25 cm was estimated in 1979 to be $10^{-14}$ g/g of soil [18]. This concentration was calculated from the known relative fission yield and the measured levels of $^{90}$Sr and $^{137}$Cs in soil, assuming that these fission products from nuclear bomb tests have nearly the same retention rates in soil.

Early sorption studies encompassed 22 soil types collected in Oregon, Washington, and Minnesota and used a batch equilibration technique. Distribution coefficients $K_d$ for $^{95m}$TcO$_4^-$ were determined; this is defined as the ratio at equilibrium of the quantity of pertechnetate sorbed per gram of soil to solute per ml of solution. The $K_d$ values for $^{95m}$TcO$_4^-$ ranged from 0.007 to 2.8, demonstrating the potential for accumulation in certain soils [19]. The sorption was directly correlated with increased organic carbon content and inversely correlated with increased pH. It appears that the positive charge on soil organic colloids is an important factor governing technetium retention. As pH decreases, positive charge may be expected to increase with decreased ionization of acidic groups and increased protonation of basic groups. In addition, $K_d$ values were correlated with cation exchange capacity [19].

Recently, distribution coefficients $K_d$ for $^{95m}$Tc in Canadian Shield lake sediments were determined under oxic and anoxic conditions in a laboratory study. Untreated Winnipeg River water was used. For the oxic treatment, sediment and water were shaken for 24 h, spiked with 932 Bq of $^{95m}$Tc and then shaken for another 48 h. The anoxic treatment involved purging with N$_2$ gas. The pH of the solution under oxic conditions was 6.7, under anoxic conditions 5.8. Under oxic conditions and the presence of 1, 10 or 50 wt% organic sediment, a mean of 98.5, 89.7 and 48.1 %, respectively, of $^{95m}$Tc remained in solution, corresponding to distribution coefficients of 4.3, 6.9, and
13.0 kg for the organic sediment. Under anoxic conditions the mean values were 96.7, 0.8, and 6.2 % of $^{95m}$Tc in solutions, corresponding to $K_d$ values of 14, 9200, and 210 I·kg$^{-1}$, respectively. Consequently, considerable quantities of technetium may be sorbed to the sediment under the anoxic conditions expected for Canadian Shield lake sediments [20].

Investigations on the sorption of $^{99}$TcO$_4^-$ by soils revealed that about 98 % of the added pertechnetate was sorbed within a period of 2 to 5 weeks at 25°C by 8 of 11 soils with a wide range of physical and chemical properties such as texture, pH, organic matter, free iron oxide content and cation exchange capacity. The slow kinetics observed and the insignificant reduction of $^{99}$Tc sorption by addition of excess of Cl$^-$ or H$_2$PO$_4^-$ tend to rule out anion exchange as the sorption mechanism. The lack of sorption exhibited by the low organic matter soils and the reduction in sorption following H$_2$O$_2$ digestion of the soils suggested a role for the living and/or non-living organic fraction of the soil. Sterilization of the previously sorbing soils by steam eliminated the sorption ability, indicating a microbial role in the sorption process [21].

Concentrations of $^{99}$Tc caused by global fallout in the surface layer (< 20 cm) of paddy field soil samples in Japan collected in 1991 and 1992 near Ogata, Omagari, Morioka, Imari, and Kawazoe were measured by inductively coupled plasma mass spectrometry (ICP-MS). On a dry weight basis the $^{99}$Tc concentrations ranged from 0.02-0.11 Bq per kg soil. The activity ratios of $^{99}$Tc/$^{137}$Cs varied from 2.0·10$^{-3}$ to 5.2·10$^{-3}$. The theoretical activity ratio is about 3.0·10$^{-4}$. The mechanism of $^{99}$Tc accumulation in paddy fields may be explained by the reduction of TcO$_4^-$ under the reducing conditions of paddy field soil [22].

The soil chromatographic movement of $^{99}$Tc through 41 selected Minnesota soils was studied to determine the short-term dynamic behavior of technetium under aerobic conditions over a wide range of physical and chemical soil properties. Under aerobic conditions $^{99}$Tc occurs as TcO$_4^-$. Its movement was characterized by the chromatographic parameter $R_t$. Reduced $R_t$ values were statistically related to elevated levels of soil organic matter. Complexation of $^{99}$Tc by organic matter appeared to be weak. Pertechnetate exhibited greater retention than $^{95m}$Tc which may be attributed to a weak binding of TcO$_4^-$ by organic matter [23].

The sorption of $^{95m}$TcO$_4^-$ on diverse soils under strictly aerobic conditions was extended to samples collected throughout the United States at locations in the states of Washington, Oregon, Colorado, Illinois, and Minnesota under arid, semi-arid and humid climates and under sagebrush, grassland, pasture land, agricultural and forest vegetation. Soils developed primarily under grassland-shrub vegetation and arid to semi-arid conditions sorbed less than 5.7 % $^{95m}$Tc from solutions after 48 h equilibration. In contrast, soils developed in forests and marshlands under humid and subhumid conditions exhibited up to 31 % sorption of $^{95m}$Tc over the same period. The forest-marshland soils were characterized by higher organic carbon content and contents of amorphous iron and aluminum compounds as well as lower pH values than the grassland-shrub soils. In all soils at the 48 h equilibration time, sorption was strongly correlated to organic carbon, total nitrogen, extractable iron and aluminum, several clay and silt fractions and low pH. After 1050 h of equilibration the carbon and nitrogen components significantly increased the technetium sorption [24].