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Present State of the Chemistry of Technetium

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We review recent work in the Soviet Union and abroad on the chemistry and technology of technetium which allows the properties of this element to be discussed in the light of Mendeleev's Periodic Law. A section outlining the history of the discovery of technetium is included because of the many inaccuracies in the published accounts of the search for this element. 129 references.

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I. INTRODUCTION

The rapid development of nuclear energy has highlighted the problems associated with the treatment of nuclear fuels, including the regeneration of uranium and plutonium and the extraction from the waste products of the nuclear industry of valuable isotopes for use in various technological processes.

Among the most interesting fission products of uranium is the isotope technetium-99, the first artificially radioactive element, found in nature in insignificant amounts. It can be prepared from waste products of the atomic energy industry[1,2]. Technetium has some unique superconducting[3], anti-corrosion[4,5], and catalytic properties[6,7], as well as a high melting point (2200°C)[8] and boiling point (4700°C),[9] and therefore it offers a number of possibilities as a new technological material for refractory, corrosion-resistant, and superconducting structures.

Table 1. Unit cell parameters of technetium and rhenium compounds.

Compound	Cell parameter, A	Reference
$K_2[TcCl_6]$	$a=9.89$	12
$K_2[ReCl_6]$	$a=9.84$	12
$[TcO_2Py_4]Cl\cdot 2H_2O$	$a=14.40$; $b=12.34$; $c=15.06$	13
$[ReO_2Py_4]Cl\cdot 2H_2O$	$a=13.95$; $b=12.04$; $c=15.04$	13
$[ReO_2Py_4]Cl\cdot 2H_2O$	$a=13.592$; $b=11.973$; $c=15.55$	14
$K_3[Tc(CN)_6]$	$a=12.106$	15
$K_3[Re(CN)_6]$	$a=12.033$	15
K_2TcH_9	$a=9.64$; $c=5.56$	16–18
K_2ReH_9	$a=9.607$; $c=5.508$	16–18

The study of the properties of technetium—a transition element with an unfilled outer electronic *d*-shell—should help to clarify the nature of its chemical bonding. Technetium, like its subgroup and period analogues, forms a multiplicity of structurally unusual complexes which are difficult to synthesise because of their low stability and also because of the radioactivity of the element. In addition to the classical tetrahedral and octahedral structures we find technetium compounds obeying new structural rules, such as the cluster compounds (binuclear complexes)[10,11].

Structural studies of technetium and rhenium compounds have shown that the unit cell of technetium compounds is larger than that of the isostructural rhenium compounds, although the technetium atom is smaller than the rhenium atom (Table 1). This effect can be ascribed to the higher ionicity of the technetium–ligand bond as compared to the rhenium–ligand bond in which the covalent contribution is predominant.

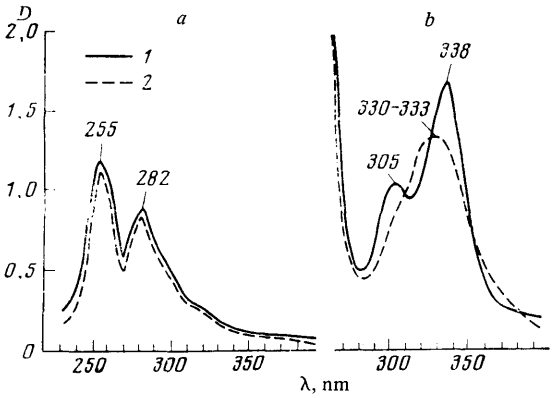


Figure 1. Time changes of absorption spectra: *a*) $(PyH)_2[ReCl_6]$, *b*) $(PyH)_2[TcCl_6]$; *1*) freshly made compound, *2*) after 1 day.

The rhenium compounds are more stable in solution, as shown by a spectrophotometric study[19] of the complexes $(PyH)_2[ReCl_6]$ and $(PyH)_2[TcCl_6]$ (Fig. 1).

Technetium belongs to a group of elements showing strongly developed complex-formation properties[20]. Its ability to form coloured complexes with high molar extinction coefficients has been exploited in the analytical chemistry of the element (Fig. 2).[2] Methods of extracting technetium from industrial solutions, of purifying it from radioactive and stable elements, and of preparing it in a

metallic form have all been based on complex formation. Thus the chemistry of technetium is essentially the chemistry of its complexes, but unlike the "typical" complex-forming elements of the platinum group, technetium forms relatively unstable compounds, resembling rhenium in this respect. Nevertheless it has been shown experimentally that technetium compounds can exist (under certain conditions) both in solution and in the solid state.

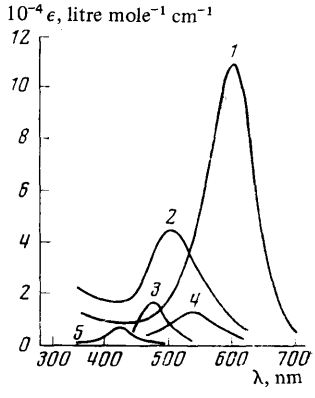


Figure 2. U. v. spectra of technetium complexes with: *1*) Methyl Violet, *2*) thiocyanate, *3*) α-benzildioxime, *4*) α-furyldioxime, *5*) 1,2-dioxime.

This review aims to discuss the properties of technetium in relation to those of its nearest period and group analogues: no attempt is made to describe in detail all the published work on the chemistry of technetium, which includes over 1000 publications.

II. HISTORY OF THE DISCOVERY OF TECHNETIUM

The existence of element "43" was predicted by Mendeleev on the basis of his Periodic Law[21]. Several workers claimed to have discovered an analogue of manganese, and even proposed new names for it: ilmenium (Hermann, 1846),[22] devium (Kern, 1877),[23] lucium (Barriere, 1896),[24] and nipponium (Ogawa, 1908).[25]

In 1925 Noddack, Tacke, and Berg[26] described the physical properties of eka-manganese by interpreting the properties of its neighbouring elements in the Periodic Table. They made a comprehensive study of the X-ray spectra of various ore concentrates including those of the platinum minerals (columbite etc.). They claimed to have obtained a preparation containing 0.5% of eka-manganese, for which they proposed the name masurium. Their claim was soon refuted by Prandtl[27]: however, the element rhenium was discovered during the search for element "43"[26]. In 1927 Zvyagintsev and coworkers re-examined a range of platinum minerals and concluded that element "43" was absent[28].

Work on the structure and properties of the atomic nucleus led to the suggestion that elements which had not yet been discovered in Nature were unstable and could be obtained only by synthesis. By using the arguments of the Periodic Law, and by applying recent developments in atomic physics (atomic reactors and accelerators), Perrier and Segre[29,30] were able to prepare technetium after 70 years' unsuccessful attempts to discover the element in Nature. These workers demonstrated the possibility of preparing elements artificially by transmutation.

The first minute quantities of the element (~ 10^{-10} g) were prepared in the Berkeley cyclotron by the reactions

$$^{92}_{42}\mathrm{Mo}\,(d,\ n)^{93}_{43}\mathrm{Tc};\quad ^{92}_{42}\mathrm{Mo}\,(d,\ 2n)^{92}_{43}\mathrm{Tc}$$

In 1938 Seaborg discovered the long-lived isotope ^{99}Tc, which was later isolated from uranium fission products by Segre and coworkers[30].

16 technetium isotopes are now known, with masses ranging from 92 to 107, and 6 isomers[31]. All the technetium isotopes are radioactive, as expected from the Shchukarev–Mattauch rule.

The possibility of finding primary technetium in the earth's crust is excluded by the half-lives of the technetium isotopes. The small trace of technetium (10^{-9} g per kilogramme) detected[32] in pitchblende is the result of spontaneous fission of uranium; traces of technetium may be present in other minerals through the interaction of cosmic neutrons with molybdenum, ruthenium, or niobium.

Thus the primary technetium which existed in Nature several billion years ago when the Earth was formed has now disappeared by radioactive decay. If any technetium exists at present it has been formed by secondary nuclear reactions on the Earth. However, weak lines of ionised technetium have been detected in the Sun's spectrum[33] and in that of some of the younger stars[34,35]. The presence of technetium in some stars in amounts comparable with that of its analogues suggests that technetium is being formed in stars at the present time. This observation is of the utmost importance to the cosmological theory of the development of the chemical elements, which denies the hypothesis of pre-stellar formation of the elements and states that stars are continuously active "factories" of chemical elements.

III. SOURCES AND METHODS OF PREPARATION

The knowledge that technetium is a transition element able to form a variety of complexes enables us to develop methods of preparing the element.

Technetium-99 at present is obtained from the fission products of uranium-235, among which it was first detected by Hahn and Strassmann[36] in 1939. It can also be produced by the action on slow neutrons on molybdenum:

$$^{98}_{42}\mathrm{Mo}\,(n,\gamma) \rightarrow {}^{99}_{42}\mathrm{Mo} \xrightarrow[T_{1/2}=6.7\ \mathrm{h}]{\beta,\gamma} {}^{99}_{43}\mathrm{Tc} \xrightarrow[T_{1/2}=6.1\ \mathrm{h}]{\text{i.p., }\bar{e},\gamma} {}^{99}_{43}\mathrm{Tc} \xrightarrow[T_{1/2}=2.12\cdot10^{5}\ \mathrm{years}]{\beta} {}^{99}_{44}\mathrm{Ru}_{\text{stable}}$$

It is very difficult to obtain a high yield of technetium-99 from this source. Thus, irradiation of 1 kg of molybdenum for 1 year in a flux of ~ 8×10^{13} neutrons cm^{-2} s^{-1} yields approximately 60 mg of Tc.[37]

The technetium can be isolated from this source by various methods, which can be classified in the following order of effectiveness: extraction, ion exchange, precipitation, distillation, electrodeposition. Under industrial conditions combined methods are often used: for example, precipitation and extraction, ion exchange and extraction, etc.

Technological methods of preparing technetium from solutions used in the atomic energy industry have been developed over a number of years both in the Soviet Union and abroad. We shall mention only those which have

yielded appreciable amounts of technetium[38-42]. Among the foreign developments the most interesting is the American technology for the isolation of technetium during the treatment of uranium hexafluoride in a gaseous diffusion plant[39,40]. The method depends on the similarity in physicochemical properties of the two volatile compounds (uranium and technetium hexafluorides) formed during the fluorination of uranium being regenerated. The two fluorides are separated by a sorption method and the technetium is finally purified by extraction.

The isolation of technetium from industrial atomic energy solutions is a complex technological problem, with special emphasis on the problem of waste solutions. Any increase in the volume of these solutions as a result of additional treatments aimed at concentrating the technetium must be avoided. Only the sorption technology in conjunction with ion exchange can satisfy this requirement.

Ion-exchange methods of concentrating technetium by the use of highly basic resins have been patented[41,42]; the eluent is nitric acid, and the product is purified by extraction with ethyl methyl ketone. The ion-exchange method has been developed and applied also in the Soviet Union, in conjunction with acetone extraction and precipitation as technetium heptasulphide[2,38]. An important advantage of ion exchange over all other methods of separating technetium is its ability to separate technetium from ruthenium. Both high-basicity and low-basicity organic resins have been shown[38-44] to be usable, in a variety of chemical compositions and structures.

Treating the ion-exchange properties of technetium in the light of the periodic classification of the elements we note that the perrhenate ion and the pertechnetate ion are both readily adsorbed by anion exchange resins over a wide range of solution pH. The permanganate ion is reduced by these resins, and therefore ion exchange is not applicable in the presence of manganese(VII). Manganese(II) is adsorbed to a moderate extent by cation exchange resins.

The selectivity of the resins towards the $[TcO_4]^-$ ion arises partly from the properties of the resins themselves and partly from the special structure of the ion, its tendency towards complex formation, and its low degree of hydration.

IV. CHEMICAL PROPERTIES

The structure of the outer electron shells of the technetium atom, whose configuration is given as $4d^65s^1$ (S 9/2)[45,46] or $4d^55s^2$ (S 5/2)[47,48], is responsible for the properties of the element as a transition metal of the second series of the d group (Zr, Nb, Mo, Tc, Ru, Rh, Pd, and Ag).[49] This electronic structure makes possible several oxidation states, from +7 to −1, and it explains the tendency towards disproportionation, hydrolysis, hydride formation, formation of compounds with metal–metal bonds, and complex formation, all of which play an important part in the chemistry of the element.

The chemical properties of technetium are similar to those of rhenium, but they are quite different from those of manganese in spite of some analogy in the stereochemistry of several of their compounds: the oxo-anions $[MO_4]^-$, $[MO_4]^{2-}$, the oxides M_2O_7, MO_2, the hexa-halogen complexes $[MX_6]^{2-}$, and the π-complexes $[M(CN)_6]^{5-}$, $M_2[CO]_{10}$, $M[CO]_5Cl$. However manganese tends to favour the lower oxidation state+2, which is more stable than manganese(VII), d^0, as a result of the configuration involving unpaired spins with a d^5 electronic shell. Manganese(II), d^5, occurs mainly in a series of high-spin complexes and in simple cationic compounds, usually with an ionic bond. In the heptavalent state manganese is unstable, and behaves as a strong oxidising agent. On the other hand technetium and rhenium typically adopt the heptavalent d^0 state with a weak tendency towards reduction, as shown by their standard redox and ionisation potentials:

Redox potentials, V		Ionisation potentials, eV (Ref.5)	
$[MnO_4]^-/MnO_2$	−1.695(Ref.50)	Mn	122
$[TcO_4]^-/TcO_2$	−0.738(Ref.51)	Tc	95
$[ReO_4]^-/ReO_2$	−0.510(Ref.52)	Re	79

This difference between the properties of technetium and rhenium is explained by the difference between the electronic shells of these elements. The main feature of the 4d shell of the technetium atom, and also of the 5d shell of its nearest analogue, rhenium, is that the electrons in these shells are much further from the nucleus than the electrons in the 3d shell of manganese. As a result the interaction between the positive nucleus and the outer electrons is much weaker, the pairing of the electrons is enhanced, and the splitting of the levels by the ligand field is increased, leading to the formation of the characteristic low-spin complexes of technetium and rhenium. Manganese forms high-spin complexes as a rule. Typical of these are the halogen o-phenylene-bis-dimethyldiarsine complexes of Tc(II), $[TcDiars_2Hal]^0$,[54] with the d^5 configuration, spin paired with μ_{eff} = 1.9–2.1 μ_B, corresponding to the presence of one unpaired electron. The analogous complex of manganese(II) is a spin-free complex. The low-spin complexes of Mn(II) with one unpaired electron, of composition $[Mn(CN)_6]^{4-}$ and $[Mn(CN)_5NO]^{3-}$, are exceptional in the chemistry of manganese; the Mn(III) complex $[Mn(CN)_6]^{3-}$ with two unpaired electrons is also known[49]. In all these complexes the pairing of the electrons is governed by a strong ligand field.

The partly filled d-shell and the presence of "spare" electrons (not involved in bond formation with the ligand) in increasing numbers as the oxidation state of technetium and rhenium decreases tend to favour the interaction between electrons of the metal atoms and the formation of metal–metal bonds. Rhenium and technetium begin to display a tendency to form compounds of this type when in the oxidation state +4 (as ReO_2 and TcO_2).[55]

It has been reported that aquo-ions do not play a significant part in the chemistry of technetium and rhenium[49], although they are characteristic of manganese and of the whole of the first group of transition elements. However more recent work[56,57] has shown that aquo-complexes are formed by rhenium and technetium in the oxidation states +2, +3, and +4. In the highest oxidation state Tc(VII), having the d^0 configuration, forms complexes with a coordination number of 4 as the $[TcO_4]^-$ ion, analogous not only to manganese(VII), $[MnO_4]^-$, and rhenium(VII), $[ReO_4]^-$, but also to chlorine(VII), $[ClO_4]^-$, iodine(VII), $[IO_4]^-$, bromine(VII), $[BrO_4]^-$, ruthenium(VII), $[RuO_4]^-$, and neptunium(VII), $[NpO_4]^-$.[49,58,59]

Studies by vibrational spectroscopy have shown that a tetrahedral ion such as $[TcO_4]^-$ with a T_d point symmetry is stable in aqueous solution[63], but undergoes changes in crystalline compounds[62,64,65]. The nature of the cation has a strong influence on the structure of the anion, as shown by an analysis[62] of the vibrational spectra of pertechnetates, according to which the crystal field decreases as the ionic radius of the cation increases.

Pertechnetic acid forms dark red, hygroscopic crystals of composition $H[TcO_4]$.[68] The structure of this compound has not yet been established, and it is not known whether the anhydrous acid corresponds to the stereochemical composition $Tc_2O_7.H_2O$ or $HTcO_4$: it would be

interesting to resolve this question. The acid strength of Group VII elements falls on going from the main subgroup to the secondary subgroup. It is known that $H[ClO_4]$ is a very strong acid in aqueous solutions, and that the oxidising power of perchlorates is higher than that of permanganates; $H[MnO_4]$ has an acid strength comparable to that of HCl, and $H[TcO_4]$ is weaker than these acids but stronger than $H[ReO_4]$.

All three acids $H[ReO_4]$, $H[TcO_4]$, and $H[MnO_4]$, like their isostructural acid $H[ClO_4]$, form sparingly soluble salts with the cations Tl^{3+}, Cs^+, nitronium, tetraphenylarsonium $[(C_6H_5)_4As]^+$, and tetraphenylphosphonium $[(C_6H_5)_4P]^+$. The salts of all four acids are isomorphous.

Alkali metal and ammonium pertechnetates crystallise in the scheelite structure (tetragonal system), but $Cs[TcO_4]$ is rhombic, like $Tl[TcO_4]$ (D_{2h}^{16}–P_{nma}, $z = 4$, the so-called pseudo-scheelite type)[60,61].

Pertechnetates (like perrhenates) are colourless in solution, unlike the salts of permanganic acid which have a violet–red colour: the chromophoric power decreases steeply from Mn to Tc and Re. The colour of the pertechnetates of some organic cations (berberinium, Methyl Violet) is due to the chromophoric properties of the cations themselves.

An interesting property of pertechnetates is the formation of crystal hydrates as the cation changes from the Group I metals to metals of Groups II and III. The solubility along the subgroups decreases as the ionic radius of the cation increases ($K[TcO_4]$ 2.130 g/100 g, $Cs[TcO_4]$ 0.412 g/100 g of solution).[47]

The following compounds of technetium(VII) have been synthesised in recent years: $Pr[TcO_4]_3$, $Pr[TcO_4]_3.4H_2O$, $Pr[TcO_4]_3.3H_2O$, $Nd[TcO_4]_3.4H_2O$;[66] $Ba_3[TcO_5]_2$, $Sr_3[TcO_5]_2$, $Ca_3[TcO_5]_2$, $Ba[TcO_4]_2$, $Sr[TcO_4]_2$, $Ca[TcO_4]_2$, $Ba_5[TcO_6]_2$, $Sr_5[TcO_6]_2$, $Ca_5[TcO_6]_2$, $Ba[Na_{0.5}Tc_{0.5}]O_3$, $Sr[Na_{0.5}Tc_{0.5}]O_3$, $Ba[TcO_4]_2.2H_2O$, $Sr[TcO_4]_2.2H_2O$, $Ca[TcO_4]_2.2H_2O$, $Ca[TcO_4]_2.H_2O$, $Sr[TcO_4]_2.H_2O$.[67]

The Group VII elements of the main subgroup behave as non-metals in both the higher and the lower oxidation states, whereas the elements of the secondary subgroup (Mn, Tc, Re) show definite metallic properties in the lower valence states but retain their non-metal character in the heptavalent state. The elements of this subgroup, unlike those of the main subgroup, show a great deal of similarity with elements in the same period.

The oxide Mn_2O_7 is a dark green oily liquid; Tc_2O_7 and Re_2O_7 are orange–yellow crystalline compounds. Their relative stabilities are indicated in Table 2. Tc_2O_7 crystallises in the orthorhombic system with lattice parameters $a = 13.756$, $b = 7.439$, and $c = 5.617$ ($z = 4$). A full X-ray diffraction analysis of this oxide[69] has shown that the centro-symmetrical Tc_2O_7 molecule has a tetrahedrally coordinated metal atom and a linear Tc–O–Tc bond. The structure of technetium heptoxide is more similar to the layer structure of CrO_3, RuO_4, and OsO_4 than to the polymeric layer structure of Re_2O_7. The Tc_2O_7 lattice is not isostructural with the Re_2O_7 lattice. The compound Tc_2O_7 is weakly paramagnetic. It is readily soluble in dioxan, and it forms $H[TcO_4]$ when dissolved in water[68].

The oxyhalides of technetium(VII), TcO_3F[72] and TcO_3Cl,[73] have both practical and scientific interest. The latter has not been isolated in a pure form.

An important role in the technological separation of technetium is played by the heptasulphide Tc_2S_7, a dark brown sparingly soluble compound precipitated from 2–4 *N* solution of HCl or H_2SO_4,[2,74] unlike rhenium sulphide, which is obtained from more concentrated acid solutions. This property of technetium is related to its reduction to lower oxidation states, whose sulphides are soluble in mineral acids. In this respect technetium is similar to manganese.

Technetium(VI) exists in both cationic and anionic forms. The most stable are the fluorine and chlorine compounds $TcCl_6$,[75] TcF_6,[76] $TcOF_4$,[77] and $TcOCl_4$.[73,78]

Table 2. Physicochemical properties of oxides[53].

Oxide	Heat of formation from the elements, kcal mole^{-1}	Melting point, °C	Thermal behaviour
Mn_2O_7	177	6	Decomposes explosively at 90°C
Tc_2O_7	266	120	Decomposes at 260°C and sublimes
Re_2O_7	296	296	Boils without decomposition at 362°C

Astheimer and Schwochau[79] have reported a coulometric synthesis of oxygen-containing complexes of technetium(VI), rhenium(VI), and manganese(VI) with an organic cation, using the controlled potentials $E_{\frac{1}{2}} = 1.74$, 2.3, and 0.6 V respectively. They obtained complexes of composition $[(CH_3)_4N]_2MO_4$, crystallising in the cubic system with lattice parameters $a = 11.20$ Å (Tc), 11.35 Å (Re), and 11.09 Å (Mn).

The formation of Tc(VI) had been observed previously[2] during coulometric treatment of a weakly acid solution of Tc(VII) (1 *M* KCl + 4×10^{-4} *M* HCl + 0.9×10^{-5} *M* NH_4TcO_4). The u.v. absorption spectrum of the solution was shown to have a maximum at 231 nm.

By comparing the properties of the technetates, manganates, and rhenates we conclude that the six-valent state of all three analogues (Tc, Mn, and Re) is unstable and undergoes disproportionation by the reaction

$$3M\,(VI) \rightarrow 2M\,(VII) + M\,(IV).$$

The electronic structure of the manganate and rhenate is still unknown, and therefore we cannot predict their properties from the ligand field theory because of the excessive overlap of the metal and oxygen orbitals[49]. No attempt has been made to describe the properties of the technetate ion in terms of its electronic structure.

Derivatives of pentavalent technetium, like those of technetium(VI), are known in the form of cationic and anionic complexes. The most stable are the halogen compounds[77] TcF_5, $NaTcF_6$, and $KTcF_6$, isostructural with the corresponding ruthenium salts but different from the rhenium salts.

Compounds of the anion $[TcO_4]^{3-}$ have not been prepared, though the manganese analogues are known (prepared by thermal decomposition of the permanganate). Rhenium(V) forms both tetrahedral ions with a coordination number of 4, $[ReO_4]^{3-}$, and ions of composition $[Re_2O_7]^{4-}$ and $[ReO_3]^-$.[80]

The synthesis of the following complexes has been reported: technetium oxide tribromide $TcOBr_3$,[75] technetium oxide trichloride $TcOCl_3$,[78,81] and tetrachlorodi-*o*-phenylene-bis-dimethylarsinetechnetium chloride $[TcDiars_2Cl_4]Cl$.[82] Technetium is eight-coordinated in the latter complex.

The reaction between the $[TcO_4]^-$ ion and concentrated hydrochloric acid is very interesting. This reaction clearly illustrates the position of technetium in the

Periodic Table. Thus, Mn(VII) in the form of the $[MnO_4]^-$ ion is reduced to Mn(II), $[ReO_4]^-$ does not react with HCl, and the $[TcO_4]^-$ ion reacts with HCl to give the complex ion $[TcCl_6]^{2-}$ as the final product[2,83-85]. This anion can be obtained at room temperature[19].

The reduction of the $[TcO_4]^-$ ion by hydrochloric acid has been studied in detail, and shown to involve an intermediate step: the formation of Tc(V). The compounds $(NH_4)_2[TcOCl_5]$,[83] $K_2[TcOCl_5]$, and $K_2[TcO(OH)Cl_4]$ [84] have been isolated in a solid crystalline form. The absorption band of the $[TcO(OH)Cl_4]^{2-}$ anion in the u.v. spectrum is shifted towards longer wavelengths, showing that the hydrolysed compound is less stable than the $[TcOCl_5]^{2-}$ complex anion (Fig. 3).

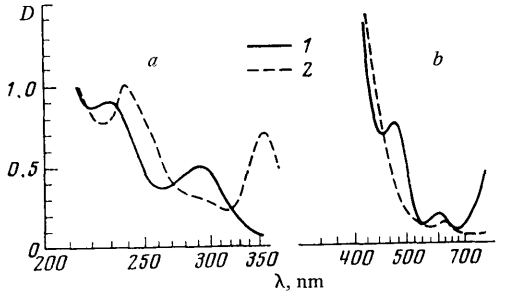
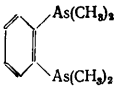


Figure 3. Adsorption spectra in (*a*) the u.v. and (*b*) the visible region of: *1*) $K_2[TcOCl_5]$, *2*) $K_2[TcO(OH)Cl_4$.

The effect of an organic ligand on the stability of technetium(V) compounds has been demonstrated by the synthesis of dioxotetrapyridinetechnetium chloride TcO_2Py_4Cl [19] and tetrachlorodi-*o*-phenylene-bis-dimethylarsinetechnetium perchlorate $[TcDiars_2Cl_4]ClO_4$.[54] The latter contains no unpaired electrons ($\mu_{eff} = 0.7\ \mu_B$), as expected from its formula with a coordination number of eight. This coordination allows the use of the chelating arsine group of *o*-phenylene-bis-dimethylarsine



which is widely used as a ligand in transition metal complexes (including technetium compounds).

The compounds $[TcO_2Py_4]Cl$ and $[TcO_2Py_4]Cl.2H_2O$,[19] which are isostructural with the analogous rhenium compounds $[ReO_2Py_4]Cl$ and $ReO_2Py_4Cl.2H_2O$,[86] are formed in neutral solution. The powerful stabilising effect of the water of crystallisation in these compounds has been demonstrated by i.r. spectral studies[19].

The compounds of technetium(IV) have been investigated most fully because in this valence state the *d*-shell is half full and as a result the complexes are structurally stable[87]. A series of stable technetium compounds with the formula $[TcHal_6]^{2-}$, analogous to the manganese, rhenium, platinum, molybdenum, and tungsten compounds, is known. The anion of the salts of hexachlorotechnetic acid, $[TcCl_6]^{2-}$, is a regular octahedron with a halogen atom at each apex and a technetium atom at the centre. The octahedra of the crystalline salt are located at the corners and at the face centres of an elementary cubic cell, with cations at the centres of eight octants[88-92].

These compounds are spin-free, and are strongly paramagnetic. In the presence of an inorganic cation their magnetic moment is strongly temperature dependent[12,93] (Table 3).

Table 3. Magnetic properties of technetium(IV) compounds.

Compound	*T*, K	μ_{eff}, μ_B
$K_2[TcCl_6]$	78—398	2.93—3.88
$(PyH)_2[TcCl_6]$	84.7—289	3.97—3.97
$(ChH)_2[TcCl_6]$	78—291	3.78—3.78

Hexachlorotechnetic acid, which was recently synthesised by the present writers, is a typical member of the class of technetium complexes containing the $[TcHal_6]^{2-}$ anion. A structural study of this compound[94] has shown that the phase $H_2[TcCl_6].9H_2O$ crystallises in the triclinic system. This low symmetry is due to the hydrogen bonds of the water molecules, which distort the $[TcCl_6]^{2-}$ octahedron (Fig. 4), whereas the ionic forces acting on the structural units in the alkali metal salts tend to preserve the octahedral structure of the anion[92].

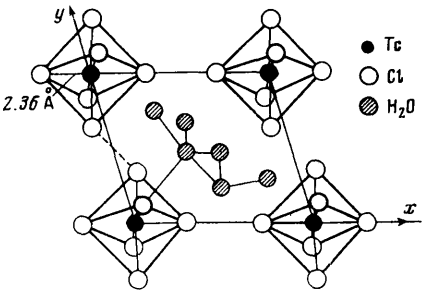


Figure 4. Projection of the $H_2[TcCl_6].9H_2O$ structure on the *xy* plane.

A comparative study of the salts of hexachlorotechnetic acid with inorganic cations ($K_2[TcCl_6]$, $Na_2[TcCl_6]$, $(NH_4)_2[TcCl_6]$) and with organic cations ($(PyH)_2[TcCl_6]$, $(ChH)_2[TcCl_6]$, $(DpH)_2[TcCl_6]$) has shown that the latter crystallise in a low-symmetry system, whereas the former have a cubic structure[88,90-92]. The magnetic moments of $(PyH)_2[TcCl_6]$ and $(ChH)_2[TcCl_6]$ are independent of temperature (Table 3). It is thought[93] that the decreased exchange interaction in the complexes with organic cations gives rise to some measure of diamagnetism.

The thermal stability of the $[TcCl_6]^{2-}$ anion is not very high: the compound $(NH_4)_2[TcCl_6]$ begins to decompose at 350°C; the decomposition is rapid at 420°C, and is complete at 535°C, with formation of the metal without intermediate steps (Fig. 5).

In dilute acid solutions the $[TcHal_6]^{2-}$ anion is readily hydrolysed. Formation of the monaquo- and diaquochloro-complexes $[TcCl_5(H_2O)]^-$ and $[TcCl_4(H_2O)_2]^0$ has been confirmed by paper chromatography[57]. A binuclear complex of composition $K_4[Tc_2OCl_{10}]$ has been synthesised[47]; the alternative formula $K_2[Tc(OH)Cl_5]$ has been suggested for this compound[97].

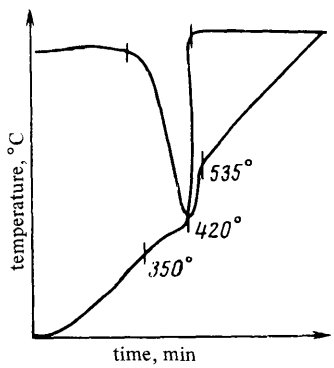


Figure 5. Thermogram of $(NH_4)_2[TcCl_6]$.

The compound TcO_2 is fairly stable and can exist in a hydrated and a non-hydrated form. Technetium dioxide TcO_2, like the analogous rhenium compound, crystallises in the monoclinic system with a metal–metal bond length of 2.5 Å. The technetium (or rhenium) atoms lie at the centres of oxygen octahedra[55]. These compounds are weakly paramagnetic. Unlike the rhenium and manganese dioxides, technetium dioxide can be sublimed in a vacuum without decomposition at 900–1100°C,[12] but it decomposes to the metal at 600°C in a stream of CO (0.75% CO).[71]

Compounds of tervalent technetium were known only in solution for a long time. They were detected during polarographic reduction of the $[TcO_4]^-$ ion at a dropping mercury cathode[2,119], and in micro-cocrystallisation experiments[95], but the pure compounds were not isolated.

Technetium(III) compounds have been obtained more recently. Like rhenium(III) and manganese(III), technetium(III) forms complexes, but only manganese(III) has yielded a large number of simple compounds. Simple compounds of rhenium(III) and manganese(III) are not known. Among the known compounds of technetium(III) are the complexes with *o*-phenylene-bis-dimethyldiarsine of composition $[TcDiars_2Hal_2]Cl$,[54] which were successfully obtained on the theory that spin-paired technetium complexes in low states of oxidation are favoured by the use of ligands having a strong field, such as *o*-phenylene-bis-diarsine.

However it was shown more recently that compounds of technetium in a low oxidation state can be obtained with a ligand as simple as the Cl^- ion. The very interesting compounds of the octachloroditechnetate ion $[Tc_2Cl_8]^{3-}$, with a metal–metal bond and an oxidation number of 2.5, have been synthesised by two methods. In the first method[10] zinc was used to reduce the pertechnetate ion in concentrated HCl solution, whereas the second method uses molecular hydrogen under pressure[11]. Both methods yield binuclear complexes consisting of a slightly distorted tetragonal prism with chlorine atoms at the corners and two technetium atoms within the prism (Fig. 6). The anions are held by a weak Tc–Cl bond 3.54 Å long. Water molecules are not accommodated in the inner sphere of the $K_3[Tc_2Cl_8].2H_2O$ complex. The Tc–Tc distance is 2.14 Å, as compared to 2.73 Å in metallic technetium[96]. The octachloroditechnetate ion $[Tc_2^{2.5+}Cl_8]^{3-}$ and the octachlorodirhenate ion $[Re_2^{3+}Cl_8]^{2-}$ belong to the same structure type of binuclear complexes, with D_{4h} symmetry, but they have different states of oxidation. The analogous technetium(III) binuclear complex, with the anion $[Tc_2Cl_8]^{2-}$, has recently been prepared[128].

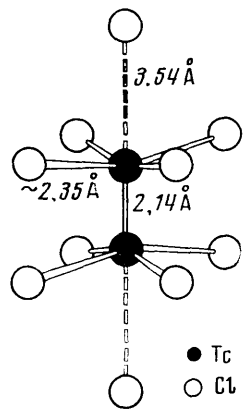


Figure 6. Structure of $[Tc_2Cl_8]^{3-}$ complex (cluster) anion.

Tc(II) is known to form a halogen-diarsine complex of octahedral structure, analogous to the rhenium and manganese complexes of composition $[MDiars_2Hal_2]^0$.[54] The d^5 electronic configuration, corresponding to a valence state of two, is theoretically a stable configuration. However only the Mn(II) compounds are spin-free, whereas the Tc(II) and Re(II) complexes have a spin-paired configuration with one unpaired electron.

Eakins and coworkers[10] have isolated a complex of composition $[Tc^{2+}(NH_2OH)_2(NH_3)_3]Cl_2$, dihydroxylaminetriamminetechnetium dichloride, which has no analogues among the manganese and rhenium compounds and has not yet been characterised physicochemically. This compound can form stable aqueous solutions.

Using the CN^- ion as a strong-field ligand, Herr and Schwochau[98] obtained the diamagnetic cyano-complex of univalent technetium $K_5[Tc(CN)_6]$, isomorphous with the known rhenium and manganese analogues.

The binuclear carbonyl $Tc_2(CO)_{10}$ has been synthesised[99] and shown to have a distorted octahedral structure[100]. In carbon tetrachloride solution this compound reacts with halogens to give pentacarbonyls and tetracarbonyls by the reaction

$$Tc_2(CO)_{10} + Hal_2 \rightarrow 2Tc(CO)_5Hal \xrightarrow[100°C,\ 1000\ atm]{} [Tc(CO)_4Hal]_2 + 2CO$$

The dibenzenetechnetium complex cation $[(C_6H_6)_2Tc]^+$,[101] formed by the β-decomposition of $^{99}Mo(C_6H_6)_2$, and the diamagnetic bis-dicyclopentadienyltechnetium $[Tc(C_5H_5)_2]_2$, consisting of golden yellow crystals unstable in air[102], have been reported. The latter is an analogue of the complex $ReH(C_5H_5)_2$,[103,104] which has a Re–H bond: although

this bond is absent in the technetium compound, the bond between the ring and the metal is similar in the compounds $[Tc(C_5H_5)_2]_2$ and $ReH(C_5H_5)_2$, and it differs from the metal–ring bond in the paramagnetic $MnH(C_5H_5)_2$ complex[105].

Metallic technetium is a dark grey powder which acquires a silvery sheen when heated to 1000°C. It is similar to rhenium, molybdenum, and platinum in external appearance, unlike manganese, which is similar to iron. The physical and mechanical properties of metallic technetium have been studied in our laboratory[106]: the metal can be formed into rods, tape, foil, and wire by cold working, with recrystallising anneals. Its cold working properties are better than those of many familiar metals. The highest strength is obtained by cold working, the highest ductility by annealing at 1000°C. The thermal expansion coefficient at right angles to the rolling direction is 8.9 (sic.).

Metallic technetium crystallises in the hexagonal system and is close-packed. Each atom is surrounded by twelve nearest neighbours at a distance of 2.73 Å. Important new information on the structure of technetium was obtained[107] in a study of sputtered thin films of the metal. Technetium films less than 150 Å thick consist of a new modification, stable at room temperature, with a face-centred cubic structure (lattice parameter $a_0 = 3.68 \pm 0.05$ Å).

Studies of the physical properties of metallic technetium[3,108] showed that this metal is superconducting, like rhenium but unlike manganese. For technetium $T_{cr} = 8.2$ K[108]. The neighbours of technetium and rhenium in the Periodic Table (ruthenium and osmium respectively) also show superconducting properties. Technetium is one of the refractory metals (m.p. = 2200°C).[8]

The chemical activity of metallic technetium is lower than that of manganese but somewhat higher than that of rhenium. In the electromotive force series technetium lies to the right of hydrogen and copper, and (like rhenium) it is not attacked by HCl, whereas manganese lies to the left of hydrogen—between magnesium and zinc—and reacts readily with water and acids. At elevated temperatures technetium reacts with chlorine, fluorine, and carbon. The metal burns in oxygen, forming Tc_2O_7. It is easily oxidised by aqua regia and by nitric acid (with formation of $H[TcO_4]$), and it is also oxidised by solutions of hydrogen peroxide, bromine water, and sulphuric acid.

Technetium(VII) exists as the $[TcO_4]^-$ ions in aqueous solutions over a wide range of solution acidity or alkalinity. The $[TcO_4]^-$ ion, like its analogues, has the stable tetrahedral configuration. In aqueous solution the $[TcO_4]^-$ ion is strongly absorbing in the u.v. region; its spectrum is similar to those of the isoelectronic forms $[ReO_4]^-$, $[RuO_4]^-$, and $[MnO_4]^-$.

There are many published reports of the tendency of technetium(VII) to be reduced to lower valence states by various reducing agents: hydrazine, hydroxylamine, and ascorbic acid. These reactions have been studied by spectrophotometric, paper chromatography, and polarographic methods[129]. Technetium(VII) is reduced by hydrochloric acid solutions. In concentrated hydrochloric acid the first step of the reduction is instantaneous, with formation of technetium(V) oxide chloride $[TcOCl_5]^{2-}$, which is slowly converted into $[TcCl_6]^{2-}$. An additional reducing agent—hydrogen—is needed for more complete reduction, which can be achieved by electrochemical reduction methods or by autoclave techniques.

The $[TcO_4]^-$ ion can be extracted[95,109–117] by various organic solvents from acid, neutral, or alkaline solutions. Alcohols, ethers, ketones, and nitrogen- and phosphorus-containing organic compounds have been used successfully. Technetium(VII) is extracted as solvated pertechnetic acid in the form of complex salts. The $[TcO_4]^-$ ion can form ionic associations containing large organic cations such as tri- and diphenylguanidinium, tetraphenylarsonium, and tetraphenylphosphonium, which are easily extracted by non-polar solvents (chloroform, Chlorex, etc.). The mechanism of extraction in this case depends on the high solubility of the association in the non-polar solvent. Cyclohexanol, cyclohexane, tributyl phosphate, trioctylphosphine oxide, and trioctylamine can extract the $[TcO_4]^-$ ion from acid solution[109]. The following reactions occur during extraction with amines and tributyl phosphate:

$$[R_4NNO_3]_{org} + [TcO_4]^- \rightleftarrows [R_4NTcO_4]_{org} + NO_3^- ,$$

$$H^+ + NO_3^- + n(H_2O) + n[TBP] + TcO_4^- \rightleftarrows HTcO_4(H_2O)_n \cdot (TBP)_n + NO_3^- .$$

An interesting extraction scheme involves trimethyloctylammonium chloride[117] and pyridine[114]. A detailed study[116] of the extraction of technetium(VII) from alkaline solutions by quinoline and by pyridine derivatives (2-methylpyridine, 2,4-dimethylpyridine, 2-methyl-5-ethylpyridine) has shown that the distribution coefficient of technetium in these solvents is much higher than in pyridine. However the use of 2-methylpyridine as an extractant for technetium is limited in practice by the high solubility of this compound. Extraction methods continue to be the most widely used in the technology of technetium separation at the refining stage.

Polarographic studies of the oxidation–reduction reactions of oxygen-containing anions of the Group VII elements yield a great deal of information on the reactivity of these species and on their oxidation state in solution. Many papers have already been published on this topic. The earliest work[118] gave contradictory results, but a later paper[119] showed that the $[TcO_4]^-$ ion is reduced to Tc(IV) at a dropping mercury electrode in neutral solution. Sharp reduction waves are not obtained in strongly acid solutions, and in alkaline solutions a two-electron reduction process is observed, with formation of Tc(V). Similar results were obtained by other workers[120–123].

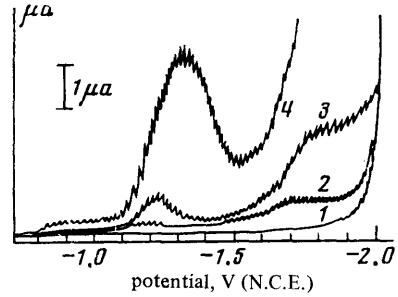


Figure 7. Catalytic waves on the polarograms of the $[TcO_4]^-$ ion in neutral NH_4TcO_4 solution; base electrolyte 1 *M* KCl + 0.01% gelatine, technetium concentration: *1*) 0, *2*) 4.3×10^{-6}, *3*) 8.6×10^{-6}, *4*) 2.5×10^{-5} *M* NH_4TcO_4.

The electrochemical reduction of the $[TcO_4]^-$ ion at a dropping mercury electrode was studied[119–123] over a wide range of acidity and alkalinity, and the following general features were noted. Reduction of the $[TcO_4]^-$ ion is by

the diffusion and catalytic mechanism, irrespective of the nature of the base electrolyte and of different media. The polarograms show maxima due to the fast evolution of hydrogen on metallic technetium. The height of the waves showing these maxima is greater than the current corresponding to the maximum possible (eight-electron) reduction (Fig. 7). These waves are similar to the catalytic waves in the polarograms given by rhenium [124,125]. The hydrogen maxima have been ascribed[124] to a lowering of the hydrogen overvoltage upon the formation of the rhenide (Re^-) ion. According to Zhdanov and coworkers[123] metallic technetium is formed by the reduction of $[TcO_4]^-$.

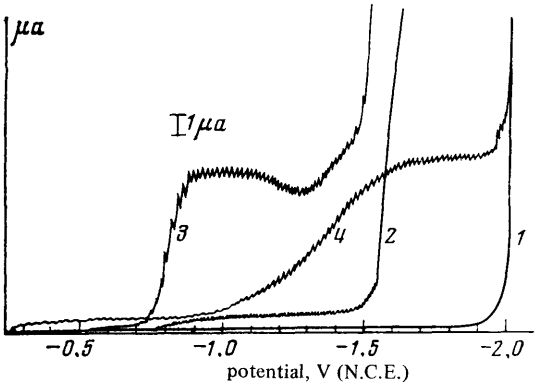


Figure 8. Effect of hydrogen peroxide on the polarogram of the $[TcO_4]^-$ ion in alkaline solution. Composition of solutions: *1*) base electrolyte 0.58 *M* HCl + 0.3 M KOH + 0.01% gelatine, *2*) base electrolyte + 8.0×10^{-5} *M* NH_4TcO_4, *3*) base electrolyte + 8.0×10^{-5} *M* NH_4TcO_4 + 8.1×10^{-4} *M* H_2O_2, *4*) base electrolyte + 8.1×10^{-4} *M* H_2O_2.

Catalytic waves occur in all media, and are independent of the nature of the base electrolyte with the exception of ammoniacal solutions in which the waves disappear[122]. Catalytic currents are produced also by the interaction of an oxidising agent with the products of electrochemical reduction of technetium. This type of wave is observed only in alkaline peroxide solutions (curve *3* of Fig. 8). A comparative study of the polarograms of $[MO_4]^-$ ions of the three analogues rhenium, technetium, and manganese has shown[118,126,127] that the electrochemical behaviour of the three elements is quite different during reduction at a dropping mercury electrode.

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In conclusion we note that technetium is among the most interesting of all the elements from the standpoint of its chemical properties. It exhibits many valence states, it is readily converted from one state into another, and it can exist in solution in different valence states at the same time. The other important properties of this element are its tendency towards disproportionation, complex formation, and hydrolysis.

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