Inst., 4, 13 (1940).
150. G. A. Abramov and L. N. Lozhkin, Trudy Leningrad. Politekh. Inst., 4, 36 (1940).
151. G. A. Abramov and A. A. Kostyukov, Zhur. Prikl. Khim., 22, 578 (1949).
152. A. F. Alabyshev, Zhur. Fiz. Khim., 20, 558 (1947).
153. P. Drossbach, Z. Elektrochem., 40, 180, 370 (1934).
154. S. V. Karpachev and O. Poltoratskaya, Zhur. Fiz. Khim., 6, 966 (1935).
155. A. I. Bukhbinder, Trudy Leningrad. Politekh. Inst., No. 188, 115 (1957).
156. T. Yanagase and G. Derge, J. Electrochem. Soc., 103, 303 (1956).
157. J. F. Duncan, Nature, 179, 187 (1957).
158. L. N. Antipin, Zhur. Fiz. Khim., 29, 1668 (1955).
159. L. N. Antipin and I. Niderkorn, Zhur. Prikl. Khim., 28, 577 (1956).
160. L. N. Antipin, "Trudy IV Soveshchaniya po Elektrokhimii" (Proceedings of the IVth Conference on Electrochemistry), Izd. Akad. Nauk SSSR, p. 345.
161. L. N. Antipin and Yu. B. Kholmanskikh, Zhur. Fiz. Khim., 31, 456 (1957).
162. L. Sucki, Bull. Acad. polon. Sci., Ser. Sci. chim., geol., geog., 3, 5, 743 (1957).
163. L. Sucki, Zhur. Fiz. Khim., 32, 1785 (1958).
164. L. Sucki, Zhur. Fiz. Khim., 32, 1393 (1958).
165. M. V. Smirnov and N. Ya. Chukreev, Zhur. Fiz. Khim., 32, 2165 (1958).
166. K. P. Batashov and M. M. Vetyukov, Trudy Leningrad. Politekh Inst., 2, 62 (1951).
167. A. I. Belyaev, "Referaty Dokladov VIII Mendeleevskogo S'ezda" (Abstracts of Reports to the VIIIth Mendeleev Congress), No. 13, 1959, p. 121.

Berezniki Section,
All-Union Aluminium-Magnesium Institute

TECHNETIUM — ELEMENT 43

A. N. Murin, V. D. Nefedov,
Yu. A. Ryukhin, and M. A. Toropova

CONTENTS

History of discovery 107
Identification of the isotopes of element 43 108
Possible natural occurrence of radioactive technetium isotopes 109
Electronic configuration and valence states of technetium 110
Elemental technetium 110
Properties of metallic technetium 111
Compounds of technetium(VII) 111
Compounds of technetium(VI) 113
Compounds of technetium(V) 113
Compounds of technetium(IV) 113
Compounds of technetium in +3, +2, +1, and -1 oxidation states 113
Methods for the isolation of radioactive technetium isotopes 114
Applications of technetium 114

HISTORY OF DISCOVERY

In 1871 Mendeleev predicted the existence of the element with atomic number 43, which he called "ekamanganese", and determined its position in the Periodic System[1]. However, the element remained unknown for a long time. Numerous attempts to find it in nature, based on its presumed analogy to manganese and certain platinum metals, were unsuccessful[2-13]. A typical example is the work of Ogawa[8] who claimed to have isolated a new element from molybdenite, thorianite, and certain other minerals. This "new element" had many of the properties predicted for element 43. Ogawa called it "nipponium" and described the properties of several of its compounds.

In 1925 Noddack and Tacke[12] announced the discovery, from X-ray spectroscopic data, of element 43 for which they proposed the name "masurium". The data given below show that the X-ray lines which they ascribed to element 43 approximately correspond to calculations from Moseley's relation with allowance for the screening constant.

	$K_{\alpha 1}$	$K_{\alpha 2}$	$K_{\beta 1}$
Observed wavelength, Å	0.672	0.675	0.601
Calculated wavelength, Å	0.6734	0.6779	0.6000

The relative intensity of the masurium and rhenium lines suggested identical content of both elements in the specimens studied*. From its position in the Periodic System, Noddack described some of the physical and chemical properties of masurium. He suggested that it should have an atomic weight between 98 and 99, density of 11.5, and melting point of 2300°. Its lower oxides (MaO, Ma_2O_3, MaO_2) should be yellow in colour and probably insoluble in acids. The higher oxides (MaO_3 and Ma_2O_7) should be lightly coloured and on reaction with water should yield acids analogous to manganic and permanganic.

About a year later Prandtl[13] proved Noddack's results to have been erroneous. Thus for a long time there has been no reliable experimental proof of the existence of stable isotopes of element 43, although evidence from nuclear physics suggests that such stable isotopes should exist[14].

Various nuclear reactions appear to be the only source of technetium. The element was first prepared in 1937 by Segrè and Perrier[15] by the bombardment of molybdenum nuclei with deuterons. Since this was the first preparation of an artificial element, Segrè and Perrier called it "technetium"**. Later many other nuclear reactions leading to the formation of various isotopes of this element studied.

At present nuclear fission of uranium is the principal source of technetium in relatively large quantities[17]. One of the most long-lived isotopes of technetium, ^{99}Tc, is formed in the nuclear reactor, among other products. The

* Later Noddack showed that the lines of masurium are much weaker than those of rhenium.

** From τεχνητδς "artificial" (Ed. of Translation).

TABLE 1. Technetium isotopes 1161.

Mass number	Type of decay*	Half-life	Energy of radiation, MeV		Mode of formation
			β	γ	
92	EC, β^+	4.5 min	4.1	1.3	$^{92}Mo(d, 2n)^{92}Tc$
93*m*	EC, IT	45 min		0.39	$^{92}Mo(d, n)^{93m}Tc$
93	EC, β^+	2.7 h	0.8	1.3	$^{92}Mo(d, n)^{93}Tc$
94	β^+ (75%) EC (25%)	53 min	2.4	0.87 (98%), 3.27 (2%)	$^{94}Mo(p, n)^{94}Tc$; $^{94}Mo(d, 2n)^{94}Tc$ $^{94}Ru \xrightarrow{\beta^+} {}^{94}Tc$
95*m*	EC(96%) β^-(0.2–0.6%) IT(3%)	60 days	0.4	0.039	$^{92}Mo(a, p)^{95m}Tc$; $^{95}Mo(p, n)^{95m}Tc$; $^{95}Mo(d, 2n)^{95m}Tc$; $^{95}Ru(n, p)^{95m}Tc$
95	EC	20 h		0.93 (5%), 1.07 (5%), 0.76 (90%)	$^{95}Mo(p, n)^{95}Tc$; $^{95}Mo(d, 2n)^{95}Tc$; $^{92}Mo(a, p)^{95}Tc$; $^{94}Mo(d, n)^{95}Tc$; $^{95}Ru \xrightarrow{\beta^+} {}^{95}Tc$
96*m*	IT	52 min		0.034	$^{96}Mo(p, n)^{96m}Tc$
96	EC	4.2 days		0.238, 0.312, 0.415 0.560, 0.771, 0.806 0.842, 1.078, 1.119 1.187	$^{93}Nb(a, n)^{96}Tc$; $^{95}Mo(d, n)^{96}Tc$; $^{96}Mo(d, 2n)^{96}Tc$
97*m*	IT	90 days		0.096	$^{97}Mo(d, 2n)^{97m1}Tc$; $^{97}Mo(p, n)^{97m}Tc$; $^{97}Ru \xrightarrow{EC} {}^{97m}Tc$; $^{96}Mo(d, n)^{97m}Tc$
97	EC	> 10^4 years			$^{97}Mo(d, 2n)^{97}Tc$; $^{97m}Tc \xrightarrow{IT} {}^{97}Tc$
98	β^-, EC	> 10^5 years	2.1	0.2, 0.86	$^{98}Mo(p, n)^{98}Tc$
99*m*	IT	6 h		0.0020 ± 0.0001 0.1403 ± 0.0005 0.1423 ± 0.0005	$^{99}Mo \xrightarrow[67\ min]{\beta^-}$ 87% → ^{99m}Tc; $^{99m}Tc \xrightarrow{IT}$ 13% → $^{99}Tc \xrightarrow{\beta^-} {}^{99}Ru$; $^{99}Ru(n, p)^{99m}Tc$
99	β^-	2.12 × 10^5 years	0.293	No γ	$^{99m}Tc \xrightarrow{IT} {}^{99}Tc$; U(fission)$^{99}Tc$
100	β^-	15.8 – 17.5 sec	2.4	0.6	$^{100}Mo(p, n)^{100}Tc$
101	β^-	14.3 – 16.5 min	1.2	0.3	$^{100}Mo(d, n)^{101}Tc$; $^{102}Ru(\gamma, p)^{101}Tc$; $^{103}Rh(\gamma, 2p)^{101}Tc$
102	β^-	25 sec			U(fission) ...
104	β^-	3.8 ± 0.2 sec			
105	β^-	short			
107	β^-	1.5 sec			

* EC—orbital electron capture; IT—isomeric transition; β^+—positron emission; β^-—negatron (negative β^- particle) emission.

yield of the isotope in the fission of uranium-235 induced by thermal neutrons is approximately 6.2%. Hahn's rough calculations show that the production of 10^4 g of plutonium in a uranium reactor is accompanied by the accumulation of approximately 150 g of ^{99}Tc together with other fission products[18]. According to other data a 10^5 kW reactor produces approximately 2.5 g of technetium in 24 h†. The power of this reactor corresponds to a production of approximately 100 g of plutonium in 24 h. Hence the preparation of 10 kg of plutonium leads to the formation of approximately 250 g of technetium. The total quantity of technetium obtained in various plutonium-producing plants apparently amounts to tens or even hundreds of kilograms: the chemistry of technetium can therefore be investigated as thoroughly as that of many other elements.

Up to the present 19 isotopes and nuclear isomers of technetium have been synthesised. The methods used and some of the characteristics of the nuclei are given in Table 1.

Interesting work has been done on the effect of electron density[19-21], pressure[22], and temperature[23], on the fission constant (λ) of ^{99}Tc.

IDENTIFICATION OF THE ISOTOPES OF ELEMENT 43

The activity arising on irradiation of molybdenum with deuterons and neutrons has been assigned to element 43 by means of chemical[24-28] and other methods[29]. Chemical identification consists in observing the behaviour of radioactive isotopes during the separation of carrier elements introduced into the irradiated solution. If the activity follows a particular carrier element, it must be associated with a radioactive isotope of this element or its close analogue.

† The quantity of technetium obtainable by irradiating Mo with deuterons is approximately 10^{-10} g.

The following method has been used for the chemical identification of element 43 prepared by the Mo (d, n) Tc reaction. The surface of the irradiated molybdenum target was dissolved in a mixture of nitric and hydrochloric acids, and the solution was evaporated to dryness. The residue was dissolved in water containing a few drops of concentrated ammonia and the resulting solution was divided into several portions. The (d, n) reaction might have formed radioactive isotopes of zirconium, niobium, tantalum, and ruthenium either in the main reaction with the target element or in side reactions with the target element and impurities. Hence the number of carriers required was limited to those elements and rhenium, which was used as the closest analogue of element 43 available.

Zirconium sulphate was added to the first part of the solution and the zirconium was precipitated as ZrO_2 with ammonia. The precipitate was found to be completely inactive. The second part of the solution was treated with an alkaline solution of tantalate and Ta_2O_5 was precipitated with dilute sulphuric acid. Again the precipitate proved inactive. Potassium perrhenate was added to the third part of the solution and the molybdenum present was precipitated as the 8-hydroxyquinoline complex. The precipitate contained only a small part of the activity which was completely lost on reprecipitation. Hence, appreciable quantities of radioactive molybdenum isotopes were also absent from the irradiated target. These results suggest that the activity in the target might have been due either to technetium or ruthenium isotopes. To distinguish between those two possibilities, rhenium sulphide was precipitated from the filtrate remaining after the removal of the molybdenum. The precipitate was dissolved in 5% sodium hydroxide and the hot solution was treated with an excess of hydrogen peroxide. A ruthenium salt was then added, the solution was acidified with dilute sulphuric acid, and the perrhenate was precipitated with nitron. The activity passed quantitatively into the precipitate. This constitutes a proof that irradiation of molybdenum does, in fact, lead to the formation of isotopes of element 43.

Later some technetium isotopes were identified by means of specific filters, the method being based on characteristic X-ray absorptions observed during isomeric transitions in specially selected substances[29].

Recently Spitsyn and Kuzina[30] isolated technetium from molybdenum trioxide irradiated with thermal neutrons in a nuclear reactor and identified ^{99}Tc by chemical, radiometric, and spectroscopic methods. The spectroscopic determination was made in a glass three-prism spectrograph in a camera (f = 1300 cm) with automatic collimation. The spectrum obtained on combustion of the specimen contained characteristic technetium lines.

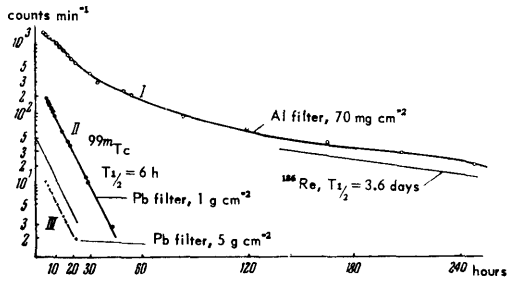
POSSIBLE NATURAL OCCURRENCE OF RADIOACTIVE TECHNETIUM ISOTOPES

Detailed investigation of the properties of the artificially produced technetium, and in particular the thorough study of its emission spectrum carried out in 1950 by Meggers and Scribner[31], allowed a further search for this element in nature to be undertaken. In 1951 Moore suggested that certain weak lines in the solar spectrum might be due to ionised technetium[32]. A year later Merrill[33], using the 100 inch telescope, obtained spectra of young stars containing technetium lines. These results suggest that technetium is synthesised in S-type stars.

From a thorough investigation of the solar spectrum (lines at 3195–3125 Å and 3298–3286 Å) Hibenet *et al.*[34] found that the technetium content in the sun amounts to $2.1 \times \times 10^{-11} - 2.6 \times 10^{-11}$ [the units are not given in the Russian text (Ed. of Translation)]. Herr[35] described an attempt to find naturally occurring long-lived technetium isotopes. Rhenium-containing molybdenum minerals were processed to yield approximately 370 g of molybdenite with 0.3% of rhenium. A technetium-containing rhenium fraction was obtained by distilling the material with $HClO_4$. To avoid losses of technetium, all operations were carried out in the presence of a short-lived radioactive technetium isotope as a tracer: $As(C_6H_5)_4ReO_4.As(C_6H_5)_4TcO_4$ was precipitated from the rhenium fraction. As much rhenium as possible was then removed by repeated distillation from $HClO_4$ and precipitation from 9 N hydrochloric acid with hydrogen sulphide. From the solution, which was markedly enriched with technetium (the technetium was still present, however, in virtually tracer quantity), approximately 1.5 mg of copper sulphide was precipitated. The sulphide with the coprecipitated technetium was subjected to neutron irradiation in a reactor (neutron flux 1.2×10^{12} neutron cm^{-2} sec^{-1}). Particular interest attaches in this connection to the ^{99m}Tc nuclear isomer of technetium (half-life 6.6 h). Observation in the irradiated solution of an activity corresponding to this half-life would constitute evidence that ^{99m}Tc was present and was formed as a result of neutron capture by the nucleus of ^{98}Tc. However, it was necessary to bear in mind that ^{99m}Tc might have arisen also through neutron capture by ^{98}Mo and subsequent fission of ^{99}Mo:

$$^{98}\mathrm{Mo}(n, \gamma)^{99}\mathrm{Mo} \xrightarrow{\beta^-} {}^{99m}\mathrm{Tc}.$$

Control experiments with much greater amounts of molybdenum showed that, in analogous conditions, the (n, γ) reaction can lead only to a very small ^{99m}Tc activity.



Although thorough chemical purification of the irradiated specimen excluded the possibility of the presence of molybdenum, the activity corresponding to ^{99m}Tc was nevertheless found. Curve I in the Figure shows the change with time of the activity obtained after 9 h irradiation in a reactor and measured using a 70 mg cm^{-2} aluminium filter. The curve is non-linear throughout its length and reveals the presence of a long-lived component with half-life corresponding to ^{186}Re. The purification used had not therefore

completely removed all the rhenium. Curves *II* and *III* show the change in the activity measured with lead filters, and the observed half-life is very close to that of ^{99m}Tc. This activity may be ascribed to tracer quantities of ^{99m}Tc formed as a result of neutron capture by ^{98}Tc present in very small quantities in the irradiated specimen.

In 1956 Boyd and coworkers[36] carried out a search for technetium in various minerals using spectrochemical, radioactivation, and mass-spectrometric methods. The results (Table 2) show that technetium is present in some minerals in vanishingly small quantities. The authors suggest the technetium is formed in the earth's crust, on the one hand, by the radioactivation of molybdenum, niobium, and ruthenium with hard cosmic rays, and on the other, by spontaneous uranium fission.

TABLE 2. Technetium content in some materials.

Specimen	Method of determination	Technetium content, g kg^{-1}
MoS_2 (Climax, Colorado)	spectroscopic	$< 4 \times 10^{-10}$
Pure $KReO_4$	"	$< 8 \times 10^{-*}$
Pure $KReO_4$	"	$< 8 \times 10^{-9}$
MoS_2 (Nevada)	"	$< 1.5 \times 10^{-8}$
MoS_2 (Miami, Arizona)	spectrophotometric	$< 1.8 \times 10^{-7}$
MoS_2 (Miami, Arizona)	activation	$< 10^{-9}$
MoS_2 (Miami, Arizona)	spectroscopic	$< 1.7 \times 10^{-9}$
MoS_2 (Miami, Arizona)	activation	$\sim 8.3 \times 10^{-11}$
MoS_2 (Nevada)	"	1.3×10^{-10}
Osmium-iridium concentrate	spectroscopic	$< 1.6 \times 10^{-8}$
Volatile Mo combustion products	"	$< 1.3 \times 10^{-8}$
Yttrotantalite (West Africa)	mass-spectrometric	$< 6 \times 10^{-11}$
Iron-nickel meteorite	spectroscopic	$< 4.5 \times 10^{-10}$

* [Value not given in Russian text. (Ed. of Translation)].

ELECTRONIC CONFIGURATION AND VALENCE STATES OF TECHNETIUM

The spectrum of the neutral technetium atom has not so far been interpreted. It is probable that the electronic configuration of technetium atoms in the ground state is $4s^24p^64d^55s(^6D_{9/2})$ or $4s^24p^64d^55s^2(^6S_{5/2})$.[37]

Since the properties of technetium are similar to those of rhenium, the chemistry of which is known in some detail, technetium may be expected to exhibit valence states +7, +6, +5, +4, +2, and -1. At the present time the oxidation states established experimentally are -1 (doubtful), 0, +2, +4, +5, +6, and +7.[37] The most characteristic and stable valence state is +7.

ELEMENTAL TECHNETIUM

Flagg and Bleidner[38] appear to have been the first to prepare invisible films of metallic technetium. A molybdenum plate was irradiated with deuterons, dissolved in aqua regia, and the solution was evaporated to dryness with an excess of ammonia. The evaporation with ammonia was repeated until the MoO_3 precipitate became perfectly white. It was dissolved in 15 *N* ammonia solution, which was then acidified with hydrochloric acid and treated with ammonium acetate. The solution was heated to boiling and molybdenum was precipitated with a tenfold excess of 1 *N* silver nitrate. The precipitate of Ag_2MoO_4 was filtered off and washed with 0.5% silver nitrate. The excess of silver nitrate was then removed from the filtrate by precipitation with NH_4I, aqua regia was added to the filtrate, and the mixture heated with simultaneous addition of nitric acid. Finally, concentrated sulphuric acid was added, the solution was heated until the appearance of heavy fumes, diluted with distilled water, and electrolysed. An invisible radioactive film was obtained on the electrode surface.

The first "visible" specimens of technetium compounds were obtained by Parker and coworkers[39], who isolated it in milligram quantities from uranium fission products by means of remote-manipulation methods. A rod of irradiated uranium was dissolved in 30% hydrochloric acid. The UCl_4 formed was oxidised with 30% hydrogen peroxide to UO_2Cl_2, the excess of H_2O_2 being removed by treatment with liquid bromine. The uranyl chloride solution was treated with $PtCl_2$ and technetium sulphide was coprecipitated with PtS by hydrogen sulphide. The sulphide precipitate was dissolved in a mixture of 30% hydrogen peroxide and 19% ammonia, and then evaporated to dryness. The pink precipitate obtained contained ammonium pertechnate. Further separation was effected by distilling Tc_2O_7 from 18 *N* sulphuric acid. Later studies on the preparation of macroquantities of technetium itself and its compounds are based on this work.

Metallic technetium, approximately 100 μg, was obtained in 1948 by Fried[40], and then in fractions of a gram by many other investigators[41-43]. Fried used very pure ammonium pertechnate, NH_4TcO_4, as the starting material. A hot solution of ammonium pertechnate in 4 *N* hydrochloric acid (technetium concentration 1 mg ml^{-1}) was placed in a conical micro(test-tube) and hydrogen sulphide was passed in. The slowly formed dark-brown precipitate of technetium sulphide (Tc_2S_7) was separated by centrifugation, thoroughly washed, and dried in a vacuum at room temperature. The sulphide was then placed in a quartz capillary; this was joined to an apparatus which provided an atmosphere of hydrogen over the heated specimen and also permitted the removal of volatile and gaseous reduction products. Successive treatment of Tc_2S_7 with hydrogen at 1100° followed by the removal of the volatile products gave the first macrospecimen of metallic technetium. Mooney confirmed, from X-ray diffraction data, that the product was in fact the element[44]. When large quantities of technetium from fission products became available, another group of investigators[45] obtained 0.6 g specimens of spectroscopically pure technetium. The starting material was an isomorphous mixture $As(C_6H_5)_4ClO_4.As(C_6H_5)_4TcO_4$. The precipitate, which is extremely stable to the action of the usual reagents, was decomposed with a mixture of concentrated sulphuric and perchloric acid. About 0.2 g of technetium [initially present in 3–4 g of $As(C_6H_5)_4ClO_4$], dissolved in 1000 ml of concentrated sulphuric acid, was electrolysed for 24 h in a cell with a large platinum cathode (current density 10 mA cm^{-2} at 2–3 V). The black precipitate formed as a result of electrolysis was transferred to a glass distillation apparatus and dissolved in a mixture of 5 ml each of concentrated nitric, perchloric, and sulphuric acids. After the initially very rapid dissolution

ceased, the technetium was distilled from perchloric acid as Tc_2O_7 into dilute ammonia solution. The distillate was acidified with hydrochloric acid, treated with bromine water, and then technetium sulphide was precipitated; its coagulation was accelerated by heating on a water-bath. The freshly precipitated technetium sulphide readily dissolved in a mixture of NH_4OH and H_2O_2. The mixture of $(NH_4)_2SO_4 + NH_4TcO_4$ formed on evaporation of the solution was reduced with hydrogen in a platinum boat. The first stage was carried out at low temperature to avoid loss of technetium through sublimation of the lower oxides. In the final stage at 500°–600°, $(NH_4)_2SO_4$ sublimed off and very pure specimens of metallic technetium were obtained.

PROPERTIES OF METALLIC TECHNETIUM

Metallic technetium is a silver-brown* mass, tarnishing in moist air. X-Ray diffraction studies [46-48] have established that metallic technetium has a hexagonal close-packed structure, fully analogous to the neighbouring elements — rhenium, ruthenium, and osmium. The unit cell contains two atoms and has the following parameters: $a = 2.735 \pm \pm 0.001$ Å; $c = 4.391 \pm 0.0001$ Å. The density calculated from X-ray diffraction data (on the assumption that the atomic weight is 99) is 11.487 g cm^{-3}. The atomic weight determined from chemical analysis of milligram quantities of Tc_2O_7 was found to be 98.8 ± 0.1,[45] in fair agreement with the mass-spectrographic determination (98.813). The melting point of technetium should be about 2300°. Among other physical properties the comparatively recently established superconductivity of technetium is noteworthy [49]. The critical temperature (the temperature at which superconductivity becomes apparent) for elemental technetium is highest among those known for elements (T_{cr} = 11.2°K). The superconductivity was studied with ^{99}Tc specimens of high purity (99.9%). The paramagnetic susceptibility is $2.5 \times \times 10^{-6}$ g^{-1} at 102°K, 2.7×10^{-6} g^{-1} at 298°K, and $2.9 \times \times 10^{-6}$ g^{-1} at 780°K, *i.e.* it is much greater than for rhenium [50]. One of the most interesting nuclear properties of ^{99}Tc is its very low capture cross-section for thermal neutrons.

According to Fried's data [40], subsequently confirmed by Cobble *et al.* [45], metallic technetium does not dissolve in cold or hot concentrated or dilute hydrochloric acid. Unlike metallic rhenium it does not appreciably dissolve in a mixture of hydrogen peroxide and aqueous ammonia. The metal readily dissolves in aqua regia and in nitric acid. On combustion in oxygen, technetium yields a pink oxide, Tc_2O_7, which is volatile at 300°. Elemental technetium reacts with much greater difficulty with chlorine than does rhenium.

Although the specific activity of pure technetium is small (17 mc mg^{-1}), it can on occasion present a serious radiation hazard. Its dry preparations give a radiation dose at the surface of 10 r h^{-1} per 100 mg. Fortunately the radiation from technetium (β-particles with maximum energy of 300 keV) is almost completely absorbed by the walls of the usual chemical ware. Data on the specific radiological toxicity of technetium are not at present available.

COMPOUNDS OF TECHNETIUM(VII)

The +7 oxidation state is the most stable and characteristic one of technetium. This state arises as a result of direct high-temperature oxidation of technetium with oxygen and also when its solutions are treated with reagents such as nitric acid, aqua regia, etc. [51] The existence of the heptavalent state, and in particular of the pertechnate ion, was established in the early stages of the study of the chemistry of technetium from purely radiochemical investigations. The presence of heptavalent technetium in solutions is also indicated by its coprecipitation with perrhenates and perchlorates. Segrè *et al.* [27], studying the possibility of the separation of technetium from its closest analogue, rhenium, determined the crystallisation coefficient* for the $KReO_4-KTcO_4-H_2O$ system. The experiments were carried out as follows. To a solution of $KReO_4$ a definite quantity of a technetium solution was added. The mixture was partly evaporated at a constant temperature, until crystals appeared, and then the activity of the crystals and the mother liquor was determined. The mean value of the crystallisation coefficient was found to be 2.6; however, the values obtained from separate experiments varied between 2.2 and 3.7. The considerable scatter was apparently due to insufficiently defined experimental conditions and to the imperfect technique of the measurements. Similar experiments made with caesium perrhenate as the macrocomponent yielded a crystallisation coefficient of 0.75. Other possible carriers for heptavalent technetium (the pertechnate ion) are thallium, nitron, and tetraphenylarsonium perrhenate [45].

It is probable that, like rhenium, technetium distils as Tc_2O_7, formed by dehydration of $HTcO_4$. The high volatility of technetium(VII) has been observed in various experiments: (a) after deuteron bombardment of a target made from compressed molybdenum trioxide with added rhenium, technetium sublimes together with Re_2O_7 when the mixture is heated to 550° in a stream of oxygen, the MoO_3 remaining in the target [15]; (b) when a mixture of technetium and rhenium is distilled from concentrated perchloric acid, technetium appears in the first fraction, whereas rhenium distils only in the last fractions; (c) in the distillation from hot concentrated sulphuric acid solutions technetium volatilises showly, whereas rhenium distils over quickly and quantitatively. When such solutions are treated with a strong oxidising agent (for example potassium dichromate), technetium volatilises more rapidly and more fully than rhenium [52,53].

Chromatography of very dilute solutions of technetium [38] has shown that it is present in anionic form in $H_2SO_4 + HNO_3$ solutions. When such solutions are passed through a column of "acid" alumina (known to absorb anions) technetium is fully absorbed; but it is not absorbed on "basic" alumina which is known to absorb cations. When solutions of technetium are treated with certain reducing agents (HCl, $SnCl_2$, etc.), definite changes in its chromatographic behaviour take place. These changes (decrease in the absorption on "acid" alumina and increase in the absorption on the "basic" form) may be related to the reducing action of these reagents, *i.e.* to a transition from the anionic to cationic form of technetium.

Hall and Johns [54] studied the ion exchange of technetium(VII) in very dilute solutions on IRA-400 anion-exchange resin. In alkaline solution, technetium, like molybdenum, is retained on the resin; when molybdenum is eluted with 10% sodium carbonate or 1 *N* $K_2C_2O_4$, technetium remains on the resin, but can be subsequently eluted with 0.5 M solution of sodium thiocyanate. These data show that in

* Boyd [J. Chem. Educ., 36, 3 (1959)] states that technetium is a silver-*grey* mass (Ed. of Translation).

* This was termed the 'partition coefficient between solution and solid salt' by the original authors (Ed. of Translation).

very dilute acid solutions technetium is present as the anion TcO_4^-.

The redox potential for the process $Tc \rightarrow TcO_4^-$ has been calculated from the results of experiments on cathodic reduction in very dilute oxidised solutions of technetium and from a comparison with the standard redox potentials for the processes $Mn \rightarrow MnO_4^-$ and $Re \rightarrow ReO_4^-$. The resulting potential, -0.41 V, lies between -0.78 (standard redox potential for the reaction $Mn + 4H_2O = MnO_4^- + 8H^+ + 7e$) and -0.15 (standard redox potential for the reaction $Re + 4H_2O = ReO_4^- + 8H^+ + 7e$). [38,55].

The studies of Boyd and coworkers [41] on macroquantities of technetium have produced quite convincing evidence of the existence of the higher oxide Tc_2O_7 and the corresponding acid, $HTcO_4$. Fried [40], who first studied the combustion of metallic technetium, suggested that the oxide formed has the formula TcO_3. However, later studies showed that the formula is Tc_2O_7. In these experiments, Boyd [41] burnt a quantity of metallic technetium in dry oxygen at 400°–600°. The light, yellow hygroscopic oxide formed (m.p. 113° ± ± 0.1°) was purified by sublimation in a quartz tube. A definite quantity was dissolved in water and titrated potentiometrically with 0.05 M ammonia solution. The curves obtained were characteristic of strong monobasic acids. The neutralised solution was evaporated to dryness in a platinum dish at 95° and the residue weighed. Results of two such experiments are summarised in Table 3. It is interesting that, as shown by X-ray diffraction studies, the oxide is not isomorphous with the analogous rhenium compound.

In further experiments Boyd and coworkers [41] isolated a hydrate of Tc_2O_7 and established its composition. A 1 M aqueous solution of Tc_2O_7 was slowly evaporated at room temperature over concentrated sulphuric acid. The solution became first yellow, then dark yellow, dark red, and finally dark-red hygroscopic crystals separated. These, on being left in air, avidly absorbed water. It was suggested that the crystals were of the hydrate $Tc_2O_7.H_2O$. A solution containing an exact quantity of the hydrate was neutralised with ammonia, evaporated, dried, and the weight of the residue (NH_4TcO_4) determined. The results of the analysis of the yellow-red substance obtained on evaporation of an aqueous solution of Tc_2O_7 at constant temperature are given in Table 4, which shows that the composition of the dark-red crystals corresponds to the formula $Tc_2O_7.H_2O$ or, in other words, to "anhydrous $HTcO_4$". Thus, unlike the colourless perrhenic acid, the corresponding acid of technetium is intensely coloured. The form of the potentiometric titration curves shows that pertechnic acid is a fairly strong monobasic acid..

TABLE 3.

Wt. of ppt., mg	No. of milliequiv. expected for Tc_2O_7	No. of milliequiv. expected for TcO_3	Milliequiv. of OH^- required for neutralisation
157.7	1.017	2.146	1.019
70.11	0.4524	0.9538	0.4561
milliequiv. of NH_4TcO_4 obtained			1.020
			0.4564

TABLE 4.

Wt. of Tc_2O_7 hydrate, mg	Wt. of NH_4TcO_4 formed, mg	Mol. wt. of hydrate	Tc_2O_7 : H_2O
98.1	108.5	327.4	0.97
98.5	108.5	328.6	1.02

Some salts of pertechnic acid have been obtained in weighable quantities. For example, ammonium pertechnate (NH_4TcO_4) may be obtained by direct neutralisation with ammonia and evaporation of an aqueous solution of Tc_2O_7, or by evaporation of a solution obtained by dissolving Tc_2S_7 in a mixture of NH_4OH and H_2O_2. Pure NH_4TcO_4 is a crystalline non-hygroscopic pink substance which shows no signs of decomposition on heating at 100° for several hours. The salts NH_4TcO_4, $KTcO_4$, and $AgTcO_4$ have the structure of the $CaWO_4$ type [47]. Aqueous solutions of pertechnate absorb intensely in the ultra-violet, which fact may be used for the quantitative determination of technetium. At wavelengths of 2470 Å and 2890 Å, Beer's law holds up to 10^{-3} M concentrations of pertechnate ions. It is possible to determine in this way as little as 10^{-8} g of technetium [41].

The reduction of pertechnate ions in very dilute solutions with various reagents has been studied [27]. Zinc, tin, nickel, lead, mercury, and copper in sulphuric acid solutions, and a 1 : 1 mixture of concentrated hydrochloric acid and 20% stannous chloride solution lead to quantitative precipitation of technetium. This shows that the TcO_4^- ion is reduced either to free technetium or to an insoluble oxide.

The preparation of weighable quantities of pure Tc_2O_7 and $HTcO_4$ allowed their thermodynamic properties to be investigated; they are of considerable interest for the more profound understanding of the chemistry of the elements in the second subgroup of Group VII in the Periodic System. The vapour pressures of $HTcO_4$ and its solutions have been determined. The vapour pressures over solid and liquid Tc_2O_7 at 20° are 0.65 and 1.0 mm Hg respectively. The variation of the vapour pressure of the solid and liquid technetium oxide can be expressed by the following equations:

$$\log P \text{ (mm)} = -\frac{7.969}{T} - 8.97 \log T + 41.11,$$

$$\log P \text{ (mm)} = -\frac{6264}{T} - 12.59 \log T + 48.36.$$

When hydrogen sulphide is passed through acid solutions of pertechnates, technetium(VII) sulphide is formed. Parker and coworkers [39] found that technetium sulphide may be coprecipitated with carriers (rhenium and copper) from 100 ml of solution acidified with aqueous hydrochloric acid (0.4–5 *N* HCl). This was studied in detail in an examination of the dependence of the precipitation of microquantities of technetium on time and on the concentration of hydrochloric acid [24]. There are also indications that technetium sulphide may be precipitated from ammonia solutions. Technetium sulphide is often the end-product in general schemes for the purification and concentration of the element.

The sulphide readily dissolves in a cold mixture of ammonia and hydrogen peroxide, yielding a light-green solution. It is also soluble in cold ammonia itself, like Re_2S_7. Somewhat unexpectedly, Tc_2S_7 is insoluble in ammonium polysulphide solution despite the fact that the latter contains an excess of NH_4OH. Further studies with weighable quantities of the material should explain these results.

When a solution of $KTcO_4$ in 18 M H_2SO_4 is treated with 12 M HCl, TcO_3Cl is formed; this can be extracted with carbon tetrachloride, chloroform, or hexane[56]. Another oxyhalide of technetium, TcO_3F, is formed when $HTcO_4$ or Tc_2O_7 reacts with UF_4.[57] Technetium(VII) can be readily reduced to lower oxidation states with hydrochloric acid, thiocyanate[58], and anion-exchange resins[59].

COMPOUNDS OF TECHNETIUM(VI)

The existence of technetium(VI) has been revealed by polarographic studies[60]. Polarography of alkaline (2 *N* NaOH) solutions of heptavalent technetium has revealed waves corresponding to the reduction of technetium(VII) to technetium(VI) and of technetium(VI) to technetium(II). Furthermore, the hexavalent state arises in the reduction of heptavalent technetium with "mild" reducing agents (for example hydrazine hydrate) in alkali in the cold, and in the irradiation of molybdenum blue with neutrons. Technetium(VI) is not extracted with ketones and pyridine and is not appreciably coprecipitated with ferric hydroxide. However, it is quantitatively coprecipitated with the 8-hydroxyquinoline complex of molybdenum and with silver and lead molybdates.

Comparison of the standard redox potentials of the MnO_4^{2-}/MnO_4^- and ReO_4^{2-}/ReO_4^- systems in alkali solutions, -0.567 and 0.7 V, suggests that under analogous conditions the potential of the TcO_4^{2-}/TcO_4^- system should be about 0.2 V. This indicates that in alkaline solutions technetium(VI) should be relatively stable. However, according to Boyd[67], technetium(VI) in aqueous solutions should disproportionate to the (IV) and (VII) states. These processes should be faster, the lower the alkalinity of the solution, and in fact, when an alkaline solution of technetium(VI) is diluted so that the alkali concentration falls to 0.02–0.05 *N*, disproportionation does take place. At equilibrium, the ratio of the +7 and +4 forms is 2 : 1, whereas the +6 form has almost completely disappeared. The disproportionation apparently takes place similarly to that of manganese and rhenium:

$$3TcO_4^{2-} + 2H_2O \rightleftharpoons 2TcO_4^- + TcO_2 + 4OH^-.$$

COMPOUNDS OF TECHNETIUM(V)

The existence of technetium in the +5 state of oxidation can only be inferred from polarographic studies of technetium(VII) solutions. Polarographic reduction of technetium(VII) in 1 M solution of hydrochloric acid yielded two waves, one of which was due to the reduction of technetium(VII) to technetium(V).[33] When TcO_4^- is reduced in 6–8 M HCl at 100°, technetium in the +5 state is formed during the first 2 h, and can be extracted with xylene (partition coefficient > 30)[62].

COMPOUNDS OF TECHNETIUM(IV)

The existence of technetium compounds in the +4 state of oxidation has been established with certainty. The first evidence of this was obtained in experiments with sub-microquantities of technetium, which showed that the element is quantitatively precipitated with platinum(IV) sulphide from acid solutions (0.25–11 M H_2SO_4). The behaviour of very small quantities of technetium in acid solutions is very reminiscent of the behaviour of manganese dioxide. Like rhenium[63], technetium(IV), in the presence of the thiocyanate ion, is extracted with ethyl ether from 3 *N* hydrochloric acid; the species extracted appears to be the complex ion $Tc(SCN)_6^{2-}$.

In 1953 Cobble and coworkers[64], using microquantities of technetium, developed a number of methods for the preparation of the dioxide. TcO_2 is obtained when aqueous solutions of NH_4TcO_4 are reduced with zinc and hydrochloric acid or by pyrolysis of NH_4TcO_4. According to Nelson and coworkers[50], the product obtained by the reduction of ammonium pertechnate with zinc and hydrochloric acid has the composition $TcO_2 . 1.6H_2O$. The composition and structure of the oxide obtained by pyrolysis were established by chemical and X-ray analyses. Technetium dioxide can also be obtained by the electrolytic reduction of technetium(VII) at a platinum electrode[60] in alkaline solution.

Compared with the analogous oxides of manganese and rhenium, technetium dioxide is more stable to heat. Whereas MnO_2 loses oxygen at high temperatures to form MnO, and ReO_2 disproportionates to Re and Re_2O_7, TcO_2 volatilises without decomposition. On heating to 300°, $TcO_2 . 1.6H_2O$ is completely dehydrated, and at 900°–1100° the anhydrous TcO_2 distils. X-Ray analysis of the distillate has shown it to be identical with the TcO_2 obtained by pyrolysis of $HTcO_4$.

Technetium dioxide reacts with chlorine on heating to 300°, yielding readily hydrolysable products which can be separated by distillation. In oxygen or in air the dioxide is oxidised to Tc_2O_7.

Using macroquantities of technetium, Nelson[50] obtained another compound of technetium(IV), K_2TcCl_6, by reducing ammonium pertechnate with potassium iodide in hydrochloric acid solution. X-Ray analysis has shown that the compound has a cubic lattice and is isomorphous with the analogous rhenium compound. It hydrolyses in more acid solutions than the rhenium analogue, yielding hydrated technetium dioxide, $TcO_2.2H_2O$.

Technetium(IV) chloride was obtained by allowing carbon tetrachloride to react with Tc_2O_7 at 400°, the yield being 79%. $TcCl_4$ consists of fine, blood-red, easily hydrolysable crystals[65]. It is interesting that under these conditions rhenium yields $ReCl_3$ and $ReCl_5$. Thus in this respect technetium resembles more closely manganese than rhenium. Furthermore, $TcCl_4$ can be readily obtained in the pure state, showing it to be more stable than $MnCl_4$.

COMPOUNDS OF TECHNETIUM IN +3, +2, +1, and -1 OXIDATION STATES

Compounds of technetium(III), predicted by Noddack[12], are completely unknown although rhenium(III) compounds have been studied in some detail.

The evidence for the existence of technetium(II) is unreliable. Indications of its existence come from polarographic studies and from studies on the coprecipitation of technetium with divalent-metal sulphides (copper and cadmium)[66].

There appear to be no data at present on the existence of technetium(I). The corresponding rhenium compounds are obtained by reducing a dilute solution of perrhenic acid with zinc and hydrochloric acid. The black precipitate formed is soluble in nitric acid and bromine water, its composition corresponding to $Re_2O.H_2O$.

The evidence for the existence of technetium in the -1 state of oxidation comes so far only from polarographic studies[67]. However, the corresponding rhenium compounds have been studied and isolated in a fairly pure state.

METHODS FOR THE ISOLATION OF RADIOACTIVE TECHNETIUM ISOTOPES

The methods at present available for the isolation of technetium isotopes from fission products or from cyclotron targets can be divided into the following principal classes.

1. Extraction[35,39,68-73].
2. Chromatographic[54,74-80].
3. Distillation[15,52,53,81].
4. Electrochemical[82].

The method described by Tribalat[68] for the separation of technetium from uranium-fission products is an example of the extraction methods. Irradiated uranium oxide is dissolved in dilute H_2SO_4, the solution is treated with ammonium persulphate, and the elemental iodine formed is extracted with toluene. The aqueous solution is boiled, neutralised with $(NH_4)_2CO_3$, and again treated with ammonium persulphate. Technetium(VII) is then extracted with a chloroform solution of tetraphenylarsonium chloride. Radiochemically-pure technetium preparations are obtained in this way.

Chromatographic methods for the isolation of technetium have found wide application recently. A method using anion-exchange resins, IRA-400 and others has been described[54]. Neutron-irradiated metallic molybdenum is dissolved in 10% NaOH in the presence of 30% H_2O_2. Under these conditions technetium is present as sodium pertechnate. The excess of H_2O_2 is removed by boiling, and the solution is passed through a chromatographic column filled with Amberlite IRA-400 resin in perchlorate form. Molybdenum can be eluted from the column with 10% NaOH, technetium being firmly held by the resin under these conditions. It can be subsequently eluted with ammonium thiocyanate solution. Kuzina and Spitsyn[83] have described a chromatographic purification of technetium concentrates isolated from neutron-irradiated MoO_3. Technetium is purified by passing the concentrate in nitric acid solution (pH 2) through KU-2 cation exchanger.

Methods based on the distillation of technetium oxide at 550°, or of technetium(VII) from H_2SO_4 in a weak current of air, are very convenient in a number of cases. Lincober and coworkers[52] and Glendenin[53] isolated technetium by distillation from perchlorate solution. To remove traces of molybdenum, the distillation was repeated several times. However, ruthenium, as RuO_4, also distils from perchlorate solution, but can be separated from the distillate by reduction with alcohol which precipitates a mixture of ruthenium(III) and ruthenium(IV) oxides which are sparingly soluble and do not entrain technetium(VII).

An electrochemical method for the isolation of technetium has been described by Barrett[82].

Methods for the separation of technetium from its closest analogue, rhenium, have considerable importance since the latter is often used as a carrier for technetium. The following methods are at present available.

1. A mixture of Tc and Re metals or sulphides is distilled in a stream of chlorine as the chlorides. Rhenium is distilled from the product at 300° in a vacuum, and technetium chloride decomposes, the metal remaining in the residue[84].
2. Technetium and rhenium can be separated by virtue of the fact that technetium sulphide is soluble in 9 *N* HCl, whereas rhenium sulphide is not. Repeated precipitation of Re_2S_7 with hydrogen sulphide from 9 *N* HCl leads to complete separation.
3. In a convenient chromatographic method[74], the sulphides of rhenium and technetium are dissolved in ammonia and the solution is passed through a Dowex-2 (sulphate form) column. Both elements are retained on the resin, but technetium can be eluted with 0.1 M ammonium thiocyanate solution at pH 8.3–8.5.
4. Technetium can be separated from rhenium, as TcO_2, by electrochemical reduction at a platinum cathode at 1.1 V. The concentration of technetium should not exceed 10^{-4} M and must be lower than that of rhenium[60].
5. For the separation of small quantities of radioactive technetium and rhenium isotopes, a method based on the different stabilities of the phthalocyanine complexes of the two metals is used.

APPLICATIONS OF TECHNETIUM

As already mentioned, the most long-lived technetium isotope (^{99}Tc) has an extremely low neutron-capture cross-section. This, together with its exceptional stability to corrosion, makes metallic technetium suitable for use in the construction of reactors[85] (at present this is being done). In view of its corrosion inhibiting properties [for iron and steel (Ed. of Translation)], it may find application in the manufacture of precision instruments[61]. It is also very probable that technetium may be employed as a semiconductor.

1. D.I. Mendeleev, Zhur. Russ. Fiz.-Khim. Obshch., 1, 60 (1869).
2. S. Kern, Chem. News, 36, 4 (1877).
3. H. Rong, Chem. News, 72, 217 (1895).
4. R. Hermann, J. prakt. Chem., 38, 91 (1846).
5. R. Hermann, Bull. Soc. imp. de Moscow [2], 15, 105 (1877).
6. M. P. Barriere, Chem. News, 74, 159 (1896).
7. B. Shapleigh, J. Franklin. Inst., 144, 68 (1897).
8. M. Ogawa, J. Chem. Soc., II, 94, 952 (1908).
9. B. Skrobal and R. Artmon, Chem.-Ztg., 33, 143 (1909).
10. G. G. Boucher, Chem. News, 76, 99 (1897).
11. F. G. Ruddoer, Chem. News, 76, 118 (1897).
12. W. Noddack and I. Tacke, Naturwiss., 13, 5671 (1925).
13. W. Prandtl, Z. angew. Chem., 40, 561 (1927).
14. V. I. Gol'danskii, "Novye Elementy v Periodicheskoi Sisteme D. I. Mendeleeva" (New Elements in Mendeleev's Periodic System), Gostekhteoret., Moscow, 1955, p. 89.
15. C. Perrier and E. Segrè, J. Chem. Phys., 5, 712 (1937).
16. D. Strominger, J. M. Hollander, and G. T. Seaborg, Rev. Mod. Phys., 30 [2], 585 (1958).

17. E. E. Motta, G. E. Boyd, and Q. V. Larson, Phys. Rev., 72, 1270 (1947).
18. O. Hahn, Helv. Chim. Acta, 36, No. 77, 608 (1953).
19. K. Bainbridge, M. Goldhaber, and E. Wilson, Phys. Rev., 84, 1260 (1951).
20. K. Bainbridge, T. Kenneth, M. Goldhaber, and E. Wilson, Phys. Rev., 90, 430 (1953).
21. B. S. Dzhelepov and O. E. Kraft, Vestnik Leningrad. Gos. Univ., Ser. Mat. Fiz. Khim., No. 3, 97 (1955).
22. R. A. Porter and W. I. McMillan, Phys. Rev., 117, No. 3, 795 (1960).
23. D. H. Byers and R. Stump, Phys. Rev., 112, 77 (1958).
24. E. Jacobi, Helv. Chim. Acta., 31, 2118 (1948).
25. C. Perrier and E. Segrè, Nature, 159, 24 (1947).
26. E. Segrè and C. S. Wu, Phys. Rev., 57, 552 (1940).
27. C. Perrier and E. Segrè, J. Chem. Phys., 7, 155 (1939).
28. H. Hoelemann, Z. anorg. Chem., 211, 195 (1933).
29. G. T. Seaborg and E. Segrè, Phys. Rev., 55, 808 (1939).
30. V. I. Spitsyn and A. F. Kuzina, Atomnaya Energiya, 5, No. 2, 141 (1958).
31. W. F. Meggers and B. F. Scribner, J. Res. Nat. Bur. Stand., 45, 476 (1952).
32. C. E. Moore, Science, 114, 59 (1951).
33. P. W. Merrill, Science, 115, 484 (1952); Astrophys. J., 116, 2166 (1952).
34. H. Hibenet, C. Jager, and S. Z. Zwann, Ext. Mém. Soc. roy. sci. Liége, 1953, Ser. 4, N 13, Fasc. 3, 471.
35. W. Herr, Z. Naturforsch., 9A, 907 (1954).
36. G. E. Boyd, Q. V. Larson, and O. V. Anders, J. Phys. Chem., 60, 707 (1956).
37. A. C. Wahl and N. A. Bonner, "Radioactivity Applied to Chemistry" (Translated into Russian), Inostr. Lit., Moscow, 1954, p. 150.
38. J. Flagg and W. J. Bleidner, J. Chem. Phys., 13, 269 (1945).
39. G. W. Parker, J. Reed, and J. W. Rugh, U. S. Atomic Energy Commission, Document 2043 (1949).
40. S. Fried, J. Amer. Chem. Soc., 70, 442 (1948).
41. G. E. Boyd, J. W. Cobble, G. M. Nelson, and W. T. Smith, J. Amer. Chem. Soc., 74, 556 (1952).
42. R. Mooney, Phys. Rev., 72, 1269 (1947).
43. G. E. Boyd, Q. V. Larson, and E. E. Motta, J. Amer. Chem. Soc., 82, N4, 809 (1960).
44. R. Mooney, Acta Cryst., 1, 161 (1948).
45. J. W. Cobble, C. M. Nelson, G. W. Parker, W. T. Smith, and G. E. Boyd, J. Amer. Chem. Soc., 74, 1852 (1952).
46. L. Burkhart, W. Peed, and B. Saunders, Phys. Rev., 73, 347 (1949).
47. P. Marmier, J. Blaser, P. Preiswerc, and P. Scherrer, Helv. Phys. Acta, 22, 155 (1949).
48. G. Rogosa and W. Peed, Phys. Rev., 100, 1763 (1955).
49. J. G. Daunt and J. W. Cobble, Phys. Rev., 92, 507 (1953).
50. C. M. Nelson, G. E. Boyd, and W. C. Smith, J. Amer. Chem. Soc., 76, 348 (1954).
51. Yu. B. Gerlit, F. I. Pavlotskaya, and S. S. Rodin, Khim. Nauka i Prom., 4, No. 4, 465 (1959).
52. D. L. Lincober and W. H. Sulliwan, Nat. Nuclear Energy Ser., Div. P. P. R., "The Fission Products", Book III, 1951, p. 778.
53. L. E. Glendenin, Nat. Nuclear Energy Ser., Div. P. P. R., "The Fission Products", Book III, 1951, p. 1936.
54. N. F. Hall and D. H. Johns, J. Amer. Chem. Soc., 75, 5787 (1953).
55. J. C. Hackney, Chem. Educ., 28, N4, 186 (1951).
56. R. Rusey and O. Larson, U. S. Atomic Energy Commission, Document ORNL-2584 (1958).
57. J. Sites, C. Baldock, and L. Gilpatrick, U. S. Atomic Energy Commission, Document ORNL-1327 (1952).
58. S. Tribalat and J. Beydon, Analyt. Chim. Acta, 8, 22 (1953).
59. R. M. Sen, Sarmo, E. Anders, and J. Miller, J. Phys. Chem., 63, 559 (1959).
60. L. B. Rogers, J. Amer. Chem. Soc., 71, 1507 (1949).
61. G. H. Cartledge, J. Phys. Chem., 59, 979 (1955).
62. E. Crouthamel, Analyt. Chem., 29, 1756 (1957).
63. A. Melaven and K. Whetsel, Detroit Meeting of Amer. Chem. Soc., April, 1950, Abstracts, p. 13.
64. J. W. Cobble, W. T. Smith, and G. E. Boyd, J. Amer. Chem. Soc., 75, 5777 (1953).
65. K. Knox, S. Tyree, R. Srivastava, V. Norman, J. Bassett, and J. Holloway, J. Amer. Chem. Soc., 79, 3358 (1957).
66. P. Thompson, U. S. Atomic Energy Commission, Document ORNL-2453 (1958).
67. G. E. Boyd, Q. V. Larson, and E. E. Motta, U. S. Atomic Energy Commission, Document AECD-2151 (1948).
68. S. Tribalat, "Rhenium et Tecnetium", Paris, 1957.
69. S. Tribalat and J. Beydon, Analyt. Chim. Acta, 6, 96 (1952).
70. M. S. Fadeeva, O. N. Pavlova, and V. V. Bakunina, Zhur. Neorg. Khim., 3, 165 (1958).
71. V. D. Nefedov and M. A. Toropova, Zhur. Neorg. Khim., 3, 178 (1958).
72. G. E. Boyd and Q. V. Larson, U. S. Atomic Energy Commission, Document ORNL-2284 (1958).
73. G. E. Boyd and Q. V. Larson, U. S. Atomic Energy Commission, Document ORNL-2159 (1956).
74. R. W. Atteberry and G. E. Boyd, J. Amer. Chem. Soc., 72, 4805 (1950).
75. E. H. Hoffman, F. L. Oswalt, and L. A. Williams, J. Inorg. Nuclear Chem., 3, 49 (1956).
76. D. I. Ryabchikov and L. V. Borisova, Zhur. Anal. Khim., 13, 155 (1958).
77. K. Kraus and F. Nelson, "Proceedings of the Internation Conference on the Peaceful Uses of Atomic Energy, Geneva, 1955", Vol. 7, 1956, p. 113.
78. G. E. Boyd and Q. V. Larson, J. Phys. Chem., 24, 1100 (1952).
79. M. Lederer, Analyt. Chim. Acta, 12, 146 (1955).
80. M. Levi and M. Lederer, J. Inorg. Nuclear Chem., 4, 381 (1957).
81. C. L. Rulfs and W. Meinke, J. Amer. Chem. Soc., 74, 235 (1952).
82. P. T. Barrett, Proc. Roy. Soc. (London), 218A, 104 (1953).
83. A. F. Kuzina and V. I. Spitsyn, Zhur. Neorg. Khim., 5, 1006 (1960) [Rus. J. Inorg. Chem., 482 (1960)].
84. J. Beydon and L. Papineau, Compt. rend., 238, 791 (1954).
85. Science, News Letter, 67, 117 (1955).

Zhdanov Leningrad State University