TECHNETIUM

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Introduction

HISTORY OF THE DISCOVERY OF TECHNETIUM

At the end of the first quarter of the twentieth century, elements with atomic numbers 43, 61, 85, and 87 were lacking in the periodic system of elements. The existence of these elements had been predicted by the original discoverer of the Periodic Law, D. I. Mendeleev. These elements included analogs of manganese, which he named eka-manganese and dvi-manganese (*1*). The element ilmenium, the discovery of which was announced in 1846 by Hermann (*2*), was known at that time. Because of some of its properties, including the atomic weight (about 104), ilmenium seemed entitled to occupy the place of eka-manganese. Mendeleev, however, on the basis of a thorough analysis of the properties of eka-manganese resulting from the Periodic Law, expressed doubts about the genuineness of the discovery of ilmenium. Later studies confirmed his point of view.

In 1877, Kern announced his discovery of an element resembling manganese in properties and called it davium in honor of the English chemist, Davy. Davium gave a reaction with the thiocyanate ion, that today is an analytical reaction for rhenium. Kern suggested at first that davium should occupy the place of eka-manganese, but later, after determining its atomic weight (about 154), held that davium is analogous to dvi-manganese (*3*). Davium as well as lucium, which was discovered by Barriere in 1896, turned out to be false elements and completed the "black list" of failures in inorganic chemistry (*4*).

Failure also befell Ogawa, who in 1908 announced the isolation of an element that he named "nipponium" from the minerals thorianite and molybdenite (*5*). This element had an atomic weight of 100 and in some of its reactions resembled manganese.

The series of errors allowed to creep into the discovery of new elements forced researchers to evaluate the results of their experiments more critically.

Only in 1925 did the German chemists Noddack, Tacke, and Berg publish a report (*6*) on the discovery of new elements called masurium (eka-manganese) and rhenium (div-manganese). This discovery was the result of logical premises and conclusions and improvements in methods. Since the neighbors of element 43 are molybdenum and ruthenium, the search for this element was concentrated on minerals—columbites and tantalites—instead of manganese ores. From columbites the German scientists obtained a concentrate containing about 0.5 % masurium and about 5 % rhenium. They established the presence of these two elements on the basis of the X-ray lines K_{α_1}, K_{α_2}, and K_{β_1} (for masurium) and L_{α_1}, L_{α_2}, L_{β_1}, and L_{β_2} (for rhenium).

Repeated experiments by Noddack and others confirmed the discovery of rhenium, but not masurium (*7–9*). In 1927, 100 mg of rhenium had already been isolated (*10*).

The development of nuclear physics and radiochemistry was the precondition for the discovery of eka-manganese. Studies of the structure and properties of atomic nuclei led to the conclusion that elements not observed in nature are unstable, and can therefore be obtained only by synthesis from other elements.

In 1937 the Italian physicists Perrier and Segrè first obtained trace amounts of element 43 (about 10^{-10} g) by bombarding molybdenum with deuterons in a cyclotron via the reaction Mo(d,n) (*11*). The new element was given the name technetium. It was the first chemical element artificially created by man. Its name was officially confirmed at a convention of chemists held on September 2–5, 1949, in Amsterdam.

A study of the physicochemical properties of technetium revealed that its stability in the heptavalent state is greater than that of manganese, and less than that of rhenium. The new element coprecipitated with rhenium as the sulfide in 6 *N* HCl, but remained in solution in 10 *N* HCl.

When moist gaseous HCl was passed through a mixture containing rhenium and technetium in 80 % H_2SO_4, after 1.5 hours at 180°–200° all the rhenium distilled over, whereas technetium remained in the H_2SO_4.

Despite the fact that the chemical properties of the new element were studied on unweighable amounts, Perrier and Segrè were able to establish the similarity between technetium and rhenium and, to a somewhat lesser extent, manganese. Many other nuclear reactions leading to the formation of various isotopes of this element were investigated later.

At the present time the main source of relatively large amounts of technetium is its recovery from a mixture of the fission products of uranium (*12*).

In a nuclear reactor, one of the longest-lived isotopes of technetium, Tc^{99}, is formed together with other fission products. The yield of this isotope from the fission of U^{235} produced by thermal neutrons is approximately 6.2 %. According to the rough calculations of Hahn, the production of 10^4 g of plutonium in a uranium reactor results in the accumulation of approximately 150 g of Tc^{99} along with other fission products (*13*).

There are also other data according to which 100 g of plutonium and 2.5 g of technetium are obtained per day in a reactor operating at a power level of 10^5 kw. Thus, for every 10 kg of plutonium 250 g of technetium is formed under these conditions.

The total quantity of this element, formed as a result of the operation of the numerous reactors producing nuclear fuel (plutonium), is apparently measured in tens or even hundreds of kilograms.

It follows that technetium ceases to be an element unavailable to researchers. The chemistry of technetium can be studied just as well as that of other elements, and for this reason this element is finding increasingly extensive practical applications.

TECHNETIUM IN NATURE

All the isotopes of technetium are radioactive. Numerous attempts to detect technetium in the earth's crust have failed. If the half-life of a radioactive element exceeds 150 million (1.5×10^8) years, it should have been preserved until the present time in at least trace amounts.

In the 1930's the half-lives of the technetium isotopes were still unknown, and therefore the question whether these isotopes had decayed during past geological epochs remained unanswered. Detailed investigations of the properties of technetium obtained artificially, particularly a thorough study of the emission spectrum performed in 1950, provided a justification for further attempts to find this element in nature.

In 1951 Charlotte Moore published a sensational report (*14*) on the possible presence of technetium on the Sun. A year later the astrophysicist P. W. Merrill detected technetium in the atmosphere of certain stars (S and M classes) (*15*). By the time of these discoveries, the half-lives of technetium isotopes had been determined.

Since the half-life of the longest-lived technetium isotope is slightly over 2×10^6 years, it should have decayed completely on the Sun. Indeed, some scientists dispute the possibility of the presence of technetium on the Sun.

The presence of technetium on stars was also confirmed by other researchers (*16*); in some stars, the amount of technetium differs only slightly from the content of the neighboring elements. To account for this fact, it is necessary to assume that technetium is being formed on the stars at the present time as well. This fact is of great significance for the development of the theory of the origin of chemical elements. It refutes numerous theories of prestellar formation of elements and shows that stars are continually operating "factories" of chemical elements. On the basis of the presence of technetium on stars, Jordan (*17*) called technetium the "touchstone" of cosmogonic theories.

Following Moore's report on the possible existence of technetium on the Sun, the search for primary technetium on earth began again. This search is discussed in particular in the work of Herr, published in 1954 (*18*). For his study he selected samples of molybdenum blende from Norway and South Africa characterized by a high rhenium content. By decomposing the mineral, Herr obtained a rhenium concentrate (370 g of molybdenum blende with 0.3% rhenium content). Distillation with perchloric acid isolated the technetium-rhenium fraction from the concentrate.

In order to avoid unaccounted for losses of technetium, all the operations were carried out in the presence of a short-lived isotope of radioactive technetium, which served as a tracer for the processes of separation and isolation of this element. Ph_4AsReO_4 and Ph_4AsTcO_4 were then precipitated from the rhenium fraction. To achieve the fullest possible removal of rhenium, multiple distillations from $HClO_4$ were carried out, and the rhenium was precipitated with hydrogen sulfide from 9 *N* HCl. From the solution obtained, enriched with technetium (the quantity of technetium was practically unweighable), 1.5 mg of copper sulfide was precipitated. The copper sulfide containing occluded technetium was exposed to a neutron flux of 1.2×10^{12} n/(cm^2 sec) in a reactor.

The detection of an isotope with a half-life of 6 hours would make it possible to conclude that this isotope is Tc^{99m}, formed by the capture of a neutron by a Tc^{98} nucleus according to the reaction:

$$Tc^{98}(n,\gamma)Tc^{99m} \xrightarrow[\text{6.0 hours}]{\text{isomeric transition}} Tc^{99}$$

It was kept in mind in these experiments that Tc^{99m} could also be formed as a result of the activation of Mo^{98} and subsequent decay, as follows:

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

Despite the fact that a thorough chemical purification excluded the presence of molybdenum in the irradiated sample, after the irradiation an impurity was detected that decayed with a half-life of 6.6 hours.

The curve of Fig. 1 shows the change in activity of a sample obtained by a 9-hour irradiation in the reactor; the measurements were made with an aluminum filter having a thickness of 70 mg/cm^2. The curve is nonlinear and indicates the presence of a long-lived component with a half-life corresponding to Re^{186}. Thus, the purification method employed did not result in complete removal of the rhenium impurity. The radioactive decay of the sample, measured with a lead filter, is shown in curves 2 and 3. The decay observed occurs with a half-life that is very close to that of Tc^{99m}. This activity can be attributed to the radiation of unweighable quantities of Tc^{99m}, formed by the capture of a neutron by one of the technetium isotopes, Tc^{98}, present in the irradiated sample in very small amounts.

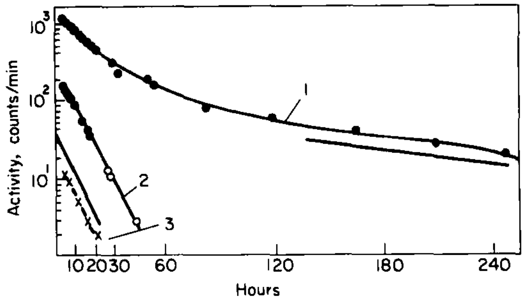


FIG. 1. Activation analysis of technetium fraction isolated from molybdenite. Change of radioactivity during measurement: (1) with aluminum filter 70 mg/cm^2 thick ($T_{1/2}$ = 3.6 days, Re^{186}), (2) with lead filter 1000 mg/cm^2 thick ($T_{1/2}$ = 6 hr, Tc^{99m}), (3) with lead filter 5000 mg/cm^2 thick ($T_{1/2}$ = 6 hr, Tc^{99m}).

In 1955 Alperovitch and Miller reported the discovery of primary Tc^{98} in various minerals, for instance columbite *(19)*. According to their data, a combination of coprecipitation, distillation, and ion exchange enabled them to isolate a minute quantity of technetium. After irradiation with neutrons, they observed the γ-radiation of Tc^{99m}. Similar results were obtained for many samples.

It should be noted that some isotopes interfere with the activation analysis, for Tc^{99} is formed when neutrons act upon Mo^{98}, Tc^{98}, and Ru^{99}. These results were confirmed by Anders *et al.* *(20)*. The method of isolating technetium was analogous to that used in the preceding study.

In 1956 Boyd and Larson *(21)* made a thorough search for technetium in various minerals, using spectrochemical, activation, and mass-spectrometric methods. The results of this study are shown in Table I. Technetium was isolated by precipitation and ion exchange. Of the samples studied, only two gave positive results. As was shown later, one of them was contaminated with Tc^{99}, and the other with Re.

TABLE I

DETERMINATION OF TECHNETIUM CONTENT IN VARIOUS SUBSTANCES

Substance	Method of determination	Technetium content (g/kg)
MoS_2 (Climax, Colorado)	Spectrochemical	$< 4 \times 10^{-10}$
$KReO_4$, pure	Spectrochemical	$< 8 \times 10^{-9}$
MoS_2 (Nevada)	Spectrochemical	$< 1.5 \times 10^{-9}$
MoS_2 (Miami, Arizona)	Spectrometric	$< 1.8 \times 10^{-7}$
MoS_2 (Miami, Arizona)	Activation	$< 10^{-9}$
MoS_2 (Miami, Arizona)	Spectrochemical	$< 1\ 7 \times 10^{-9}$
MoS_2 (Miami, Arizona)	Activation	8.3×10^{-11}
MoS_2 (Nevada)	Activation	1.3×10^{-10}
Osmium-iridium concentrate	Spectrochemical	$< 1.6 \times 10^{-8}$
Volatile products of molybdenum roasting	Spectrochemical	$< 1.3 \times 10^{-8}$
Yttrotantalite (western Africa)	Mass-spectrometric	$< 6 \times 10^{-11}$
Iron-nickel meteorite	Spectrochemical	$< 4.5 \times 10^{-10}$

Furthermore, it was found that the half-life of the long-lived Tc^{98} is approximately 1.5×10^6 years, which completely excludes the occurrence of primary technetium in the earth's crust.

For this reason, Boyd *et al.* suggested that, if technetium does exist on earth, it is of secondary origin and results from the activation of Mo, Nb, and Ru by hard cosmic radiation and from the spontaneous fission of uranium.

This point of view is also held by Parker and Kuroda (*22*), who found that 10^{-14} curie of Mo^{99} is at equilibrium with 1 g of U^{238} due to the spontaneous decay of the latter.

In subsequent studies, Kuroda *et al.* (*23–27*) established more precisely the relative proportions of the short-lived fission fragments of U^{238}. The investigations showed that 1 kg of pitchblende (50% U) at equilibrium contains 2.5×10^{-10} g of Tc^{99} (10.5 disintegrations/min).

The first isolation of an appreciable amount of natural technetium was achieved in 1961 by Kenna and Kuroda (*28*). Having processed about 5.3 kg of pitchblende mined in the Congo, they obtained three samples with a total content of 1×10^{-9} g of Tc^{99}, which is in good agreement with the calculated data.

I. Nuclear Properties of Technetium

A. INTRODUCTION

The unsuccessful attempts to discover element 43 prior to its artificial preparation by Perrier and Segrè were explained by the absence of this element in appreciable quantities in nature. This is because technetium has only radioactive isotopes with relatively short half-lives. The search for natural technetium posed the question of the stability of its isotopes. This was the subject of several theoretical studies (*29–32*). On the basis of general principles of nuclear structure, it was shown that all the isotopes of technetium (nuclear charge $Z = 43$) should be unstable, although some of them may have very long half-lives. Indeed, for odd Z's, a necessary although insufficient condition of nuclear stability is the presence of an even number of neutrons N.

Analysis of the curves of nuclear stability (see *30–32*) shows that only isotopes with atomic weight $A = 97$ and 99 should be stable. However, according to the Shchukarev-Mattauch rule, no two stable isobars exist whose nuclear charges differ only by unity. This rule is a good reflection of the general principles of the isotopic composition of various elements, although there are some exceptions (Cd^{113} and In^{113}; In^{115} and Sn^{115}; Te^{123} and Sb^{123}).

TABLE II

Isotopes of Molybdenum, Technetium, and Ruthenium[a]

	Mass number								
Element	94	95	96	97	98	99	100	101	102
Mo	S	S	S	S	S	β^-	S	β^-	β^-
Tc	EC	EC	EC	EC	β^-	β^-	β^-	β^-	β^-
Ru	EC β^+	EC β^+	S	EC	S	S	S	S	S

[a] S = stable; EC = electron capture.

The nuclear charge and atomic weight of technetium (about 99) determines its position in the periodic system between molybdenum (95.94) and ruthenium (101.07). When all the known stable isotopes of these elements are tabulated (Table II), it is seen that, in the interval corresponding to the atomic weight of technetium, there is no reason to expect the existence of stable isotopes of this element.

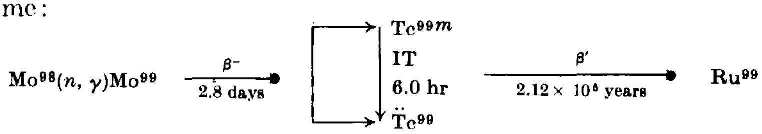
Segrè (*29*) also showed that the half-life of Tc^{98} should be relatively appreciable. Subsequently, the conclusions regarding the relative stability of technetium isotopes Tc^{97}, Tc^{98}, and Tc^{99} were confirmed experimentally. This is indicated by the longest half-lives of these isotopes and their position in a certain transition zone between two types of decay (positron or electron capture or β^- decay).

B. ISOTOPES OF TECHNETIUM

Sixteen isotopes of technetium with mass numbers from 92 to 107 and six isomers are known (Table III) at the present time.

A systematization of the β decay of some of them is given in the studies of Everling (*53*), Kienle and others (*38*, *54*, *55*). The majority of technetium isotopes are formed by the irradiation of a molybdenum target with deuterons or protons, or molybdenum or ruthenium targets with neutrons. The capture cross sections for irradiation of natural molybdenum with 10.2-MeV deuterons are given in Table IV (*56*).

Among the short-lived technetium isotopes, those of greatest practical importance are the isomers Tc^{95m} (60 days), Tc^{97m} (90.5 days), and Tc^{99m} (6.0 hours). The first two isomers are obtained by deuteron or proton irradiation of molybdenum, and Tc^{99m} is formed by irradiating molybdenum with neutrons in a reactor. At the same time, the Mo^{98} isotope (whose content in the natural mixture is 23.78%), is transmuted into Mo^{99} by capturing a neutron (the capture cross section of this reaction is 0.13 barn). As Mo^{99} decays further, first the short-lived isomer Tc^{99m} and then the long-lived isotope Tc^{99} are formed, in accordance with the scheme:



Usually, molybdic trioxide MoO_3 is irradiated. The radioactivity of $Mo^{99}O_3$, induced by the neutron irradiation, may be calculated from the equation

$$A = 3.48 \times 10^{-12} \Phi (1 - e^{-0.248t}) \qquad (1)$$

where A is the radioactivity of MoO_3, $\mu C/g$; Φ is the neutron flux, $n/(cm^2\ sec)$; and t is the irradiation time, days.

Practically, the irradiation time in a reactor usually does not exceed one to two half-life periods of Mo^{99}, i.e., 3–6 days. Commercial radioactive preparations of Mo^{99} (usually in the form of molybdic trioxide) have a specific activity of approximately 10 $\mu C/g$, the activities of the daughter Tc^{99m} and Mo^{99} being approximately equal.

Owing to the absence of stable isotopes, technetium is isolated from molybdic trioxide without a carrier, and its specific activity may be very high. Tc^{99m} has also been obtained recently from the fragment product Mo^{99} (*57*).

The precursors of the Tc^{95m} and Tc^{97m} isomers are stable molybdenum isotopes, whereas Tc^{99m} is formed as a result of the radioactive decay of the relatively longer-lived Mo^{99}. The latter characteristic of Tc^{99m} can

TABLE III

TECHNETIUM ISOTOPES (*33–36*)

Mass number	Half-life	Type of radioactive decay[a]	Particle energy (MeV)		Reaction of isotope production	Reference
			β	γ		
92	4.3 min	β^+, EC	4.1	1.3	Mo(p,n) Mo($d,2n$)	
93*m*	43.5 min	EC (18%)	—	0.39 (82%)	Mo(d,n)	(*37*)
		IT (82%)	—	2.66 (18%)		
93	2.7 hr	EC (~ 85%)	0.82 (~ 13%)	0.86 (2.6%)	Mo(d,n)	(*37*)
		β^+ (~ 15%)	1.67 (~ 2%)	1.35 (60%)		
				1.49 (30%)	Mo(p,γ)	
				2.03 (0.35%)		
94*m*	52.5 min			2.44 (0.3%)		
		EC (21%)	0.56 (1%)	0.874 (73%)	Mo($d,2n$)	(*37, 38*)
		IT (24%)	2.41 (54%)	1.85 (11%)		
		β^+ (55%)		2.73 (1%) 3.27 (~ 1%)	Nb($\alpha,3n$)	(*39*)
94	293 min	EC (93%)	0.9 (2%)	0.705 (100%)	Mo(p,n)	
		β^+ (7%)	2.41 (5%)	0.846 (72%)	Mo($d,2n$)	(*40*)
				0.874 (100%)	Ru^{94} $\xrightarrow{\beta^+}$ Nb($\alpha,3n$)	(*39*)
95*m*	60 days	IT (~ 4%)	0.477 (< 1%)	0.039 IT		
		EC	0.68 (< 1%)	0.204 (71%)	Mo($d,2n$)	(*41–43*)
		β^+?		0.256 (~1%) 0.584 (40%) 0.617 (2%) 0.788 (13%) 0.822 (8%) 0.837 (29%) 1.042 (4%)		
95	20 hr	EC	—	0.205 (1%) 0.680 (2%) 0.765 (82%) 0.84 (10.5%) 0.93 (1.7%) 1.06 (4%)	Mo($d,2n$)	(*37, 42*)
96*m*	52 min	IT	—	0.034	Mo(p,n) Mo($d,2n$)	

TABLE III—*cont.*

TECHNETIUM ISOTOPES (*33–36*)

Mass number	Half-life	Type of radioactive decay^a	Particle energy (MeV)		Reaction of isotope production	Reference
			β	γ		
96	4.3 days	EC	—	0.310 (4%)	Nb(α,n)	
				0.770 (100%)	Mo($d,2n$)	(*44*)
				0.800 (86%)	Mo(d,n)	(*43, 44*)
				0.840 (100%)	Mo(p,n)	
				1.115 (15%)	Ru(n,p)	
97*m*	90.5 days	EC	—	0.090	Mo($d,2n$)	(*42*)
				0.099	Mo(p,n)	
					Mo(d,n)	(*42*)
					Ru(EC)	
97	2.6×10^6 years	EC	—	—	Mo($d,2n$)	
					Tc^{97m} (IT)	(*45*)
98	1.5×10^6 years	β^-	0.30	0.74	Ru(n,p)	(*45*)
		γ		0.65	Mo(p,n)	(*46*)
					Mo(d,n)	
99*m*	6.0 hr	IT	—	0.002 (1.4%)	$\mathrm{Mo}^{99} \xrightarrow{\beta^-}$	
				0.140 (1.4%)	Ru(n,p)	
				0.142 (98.6%)	Th(ϕ)	
99	2.12×10^5 years	β^-	0.292	—	U(ϕ)Mo $\xrightarrow{\beta^-}$	
					Tc (IT)	
					U(ϕ)	
					$\mathrm{Mo}^{99} \xrightarrow{\beta^-}$	
100	15.8 sec	β^-			U(ϕ)Mo $\xrightarrow{\beta^-}$	
		γ	2.20	0.542	Mo(n,p)	
			2.88	0.60	Tc(n,γ)	(*21*)
			3.38	0.71	$\mathrm{Ru}^{103}(n,\alpha)$	(*47*)
				0.81		
				0.89		
				1.01		
				1.14		
				1.31		
				1.49		
				1.80		
101	14.3 min	β^-	1.4	0.307	Mo(d,n)	
		γ			Ru(γ,p)	
					U(ϕ)Mo $\xrightarrow{\beta^-}$	
					Ru(n,np)	(*48*)
					U(d,ϕ)	(*49*)
102	4.5 min	β^-	2	0.473	Ru(n,p)	
		γ		< 0.662	U(d,ϕ)	(*48*)
	(5 sec)	β^-	4.2			
103	50 sec	β^-	2.0	0.135; 0.215	Ru(n,np)	(*48*)
		γ	2.2	0.350	U(ϕ)	(*38, 50*)

TABLE III—*cont.*

TECHNETIUM ISOTOPES (*33–36*)

Mass number	Half-life	Type of radioactive decay[a]	Particle energy (MeV) β	Particle energy (MeV) γ	Reaction of isotope production	Reference
104	18 min	β^-	1.8	0.36	Mo(d,xn)	
		γ	2.4	0.89	Ru(d,xn)	(*38, 51*)
			3.3	2.5	Mo($d,\alpha xn$)	
				3.5		
				4.05	Ru(n,p)	(*48*)
					U(ϕ)Mo $\xrightarrow{\beta^-}$	(*38, 51*)
105	7.7 min	β^-	3.4	0.110	U(ϕ)	
	(10 min)	γ			U(ϕ)Mo $\xrightarrow{\beta^-}$	
(107)	< 1 min	—	—	—	U(ϕ) $\cdots$	(*52*)
					Ru $\rightarrow$	

[a] IT = isomeric transition.

be utilized for its preparation by the "milking" method, which is steadily gaining in importance in the case of short-lived isotopes. Essentially, the method consists in separating the short-lived daughter isotope from the relatively longer-lived mother isotope, which remains in the liquid or solid phase. The phase containing the mother isotope may serve as a kind of isotope generator for a periodic recovery of the daughter isotope. A diagram of the operation of such a generator is shown in Fig. 2. The activity of technetium in molybdenum regains its maximum in 21 hours. However, after 2, 4, and 10 hours one can already extract, respectively, 26, 46, and 79 % of the maximum. The generator retains an acceptable activity of Mo^{99} and Tc^{99m} for about 2 weeks. The methods used for separating technetium from molybdenum are described in Section IV.

TABLE IV

CROSS SECTION OF CAPTURE OF DEUTERONS (10.2 MeV) BY MO ISOTOPES

Stable Mo isotope	Capture cross section (barns)	Tc isotope formed	Stable Mo isotope	Capture cross section (barns)	Tc isotope formed
Mo^{95}	1.00	Tc^{95m}	Mo^{97}	2.4	Tc^{97m}
Mo^{95}	13.3	Tc^{95}	Mo^{98}	12	Tc^{98}
Mo^{96}	3.3	Tc^{96m}			

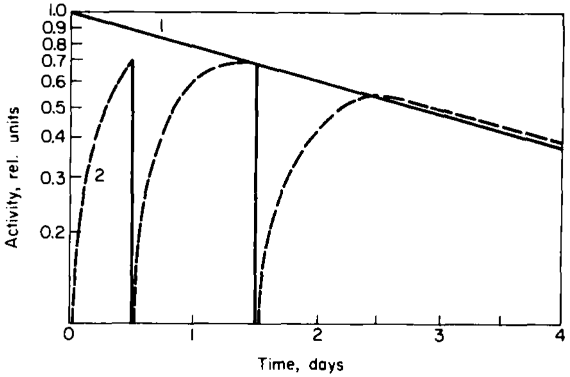


FIG. 2. Diagram of operation of Tc^{99m} generator: (1) change of activity of Mo^{99}, (2) accumulation of Tc^{99m} in Mo^{99} after 12 and 24 hours.

A large amount of technetium isotopes, mainly heavier ones, is formed by the fission of uranium, thorium, or plutonium either directly, or via the mother isotopes of molybdenum. Thus, according to the data of Katcoff (*58*), during the fission of U^{235} in a reactor the yield of the various technetium isotopes is approximately 1–6 % (Table V).

TABLE V

YIELD OF TECHNETIUM ISOTOPES FROM FISSION OF U^{235}

Technetium isotope :	Tc^{99}	Tc^{101}	Tc^{102}	Tc^{103}	Tc^{104}	Tc^{105}	Tc^{107}
Yield (%) :	6.06	5.6	4.3	3.0	1.8	0.9	0.19

The main isotope, Tc^{99}, is formed in one of the highest yields during the fission of other fissionable materials as well (Table VI).

A general equation describing the accumulation of Tc^{99} in a reactor, and allowing for the fission of U^{235} and for the Pu^{239} and Pu^{241} which are formed, has been proposed by Kir'yanov *et al.* (*59*):

$$N_{\mathrm{Tc}} = \frac{A}{6.02 \times 10^{23} \times 100(\sigma_c^{235} - \sigma_\gamma^{\mathrm{Tc}})} \ \mathrm{mg/kg\ U} \qquad (2)$$

where

$$A = 99 \times 10^3 \times \mathrm{No}^{235}\, \sigma_f^{235}(1+\beta)\, \delta^{\mathrm{Tc}}[1 - \mathrm{e}^{-(\sigma_c^{235} - \sigma_\gamma^{\mathrm{Tc}})\Phi t}]\, \mathrm{e}^{-\sigma_\gamma^{\mathrm{Tc}}\Phi t}$$

No^{235} is the content of U^{235} nuclei in 1 kg of uranium; σ_c^{235}, σ_f^{235} are the capture and fission cross sections for U^{235}; $\beta(A^{239,\,241}/A^{235})$ is the ratio of the number of fissions of Pu^{239} and Pu^{241} to the number of fissions of

TABLE VI

YIELD OF Tc^{99} (Mo^{99}) DURING FISSION (*58*)

Isotope undergoing fission	Neutron energy	Yield (%)	Isotope undergoing fission	Neutron energy	Yield (%)
U^{233}	Thermal	4.8	U^{235}	Thermal	6.06
Pu^{239}	Thermal	5.9	U^{238}	Fast neutrons	6.3
Pu^{239}	Fast neutrons	5.9	Th^{232}	Fast neutrons	2.7
U^{235}	14 MeV	5.17	Th^{232}	8 MeV	3.1

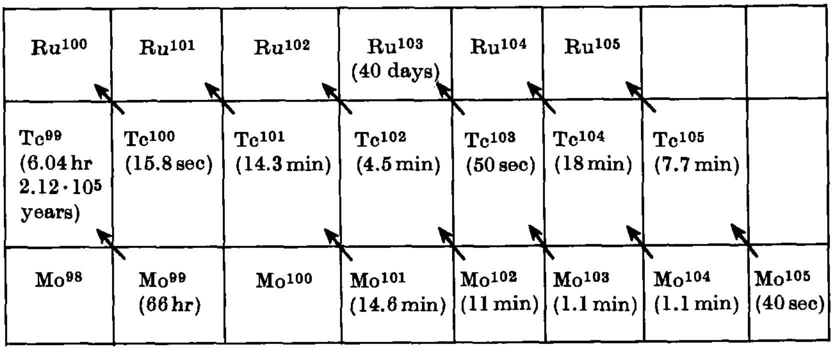
U^{235}; δ^{Tc} is the yield of technetium during fission (assumed equal for Pu^{239}, Pu^{241}, and U^{235}); and Φt is the total neutron flux.

This formula agrees well with the results obtained from analyses of fuel elements of the First Atomic Power Station. However, all the remaining technetium isotopes obtained in the reactor are short-lived, and their rapid recovery is difficult. For this reason, in order to obtain such isotopes, small amounts of uranium are irradiated with deuterons or neutrons, and use is made of methods that permit a rapid isolation of the technetium or molybdenum isotopes (*60, 61*). Molybdenum and technetium isotopes obtained as a result of fission and their nuclear transformations are shown in Table VII.

The methods of recovering technetium are described in more detail in Sections IV and V. Let us mention only that these methods can be

TABLE VII

TECHNETIUM AND MOLYBDENUM ISOTOPES FORMING DURING FISSION



Ru^{100}	Ru^{101}	Ru^{102}	Ru^{103} (40 days)	Ru^{104}	Ru^{105}		
Tc^{99} (6.04 hr $2.12 \cdot 10^5$ years)	Tc^{100} (15.8 sec)	Tc^{101} (14.3 min)	Tc^{102} (4.5 min)	Tc^{103} (50 sec)	Tc^{104} (18 min)	Tc^{105} (7.7 min)	
Mo^{98}	Mo^{99} (66 hr)	Mo^{100}	Mo^{101} (14.6 min)	Mo^{102} (11 min)	Mo^{103} (1.1 min)	Mo^{104} (1.1 min)	Mo^{105} (40 sec)

considerably simplified in nuclear investigations, since frequently a quantitative yield is not required and only a relative purity of the products and their rapid isolation from the irradiated mixture are necessary. Occasionally the isolation of technetium can be dispensed with altogether, as is evident from reference (*39*), if the nuclear characteristics of the investigated isotope differ markedly from the nuclear characteristics of possible impurities. Usually the nature of the products formed can be predicted from the energy of the particles bombarding the target and from the target material. However, in a rigorous identification of the products of nuclear reactions, it is necessary to use other physical and chemical methods as well. Chemical identification in the case of trace amounts of elements consists in selecting appropriate carrier elements,

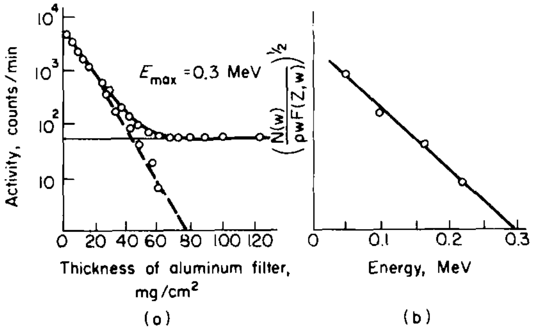


FIG. 3. Identification of Tc^{99} by its β radiation: (a) absorption of β particles in aluminum, (b) determination of maximum energy by means of β spectrometer.

and then comparing the behavior of the radioactivity of the trace component with the behavior of the carrier element during the chemical operations. Such a method was used with element 43 when the latter was prepared by irradiating a molybdenum target with deuterons (*11, 62, 63*). After the irradiation and dissolution of the target in a mixture of nitric and hydrochloric acids, other radioactive isotopes formed by the (*d,xn*) reaction could have been present in the solution obtained. These isotopes could have belonged to the closest neighbors of molybdenum (zirconium, niobium, and ruthenium) or to activated impurities of the target.

Because of the lack of stable technetium isotopes in nature, an analog of technetium, rhenium, was used as the carrier. The acid solution was evaporated to dryness, and the residue was dissolved in water made alkaline with ammonia. As carriers, salts of zirconium, tantalum, and potassium perrhenate along with the molybdate were added to various portions of the solution. The precipitation of zirconium as ZrO_2, tantalum as Ta_2O_5, and molybdenum as the hydroxyquinolate showed, according to radioactivity measurements, that the presumable element 43 is occluded to a slight degree only by molybdenum hydroxyquinolate, and is completely removed from the latter by reprecipitation. Consequently, the target did not contain radioactive isotopes of zirconium, tantalum, and molybdenum in detectable amounts. The separation of the presumable ruthenium and element 43 together with the carrier rhenium was achieved by precipitating rhenium sulfide from the filtrate after the precipitation of molybdenum.

Rhenium sulfide was dissolved in an alkaline solution of hydrogen peroxide and, after addition of ruthenium to the solution obtained, nitron perrhenate was precipitated. The radioactivity was quantitatively eliminated from the solution and passed into the precipitate; hence, it could be ascribed to the isotope of an element similar in chemical properties to rhenium, i.e., technetium. The chemical methods of identification were soon supplemented by Seaborg and Segrè, who used the method of characteristic filters for technetium (*64*).

The physical characteristics of technetium have now been adequately studied, and are therefore widely employed by researchers today for the identification of technetium isotopes. Such identification can be performed on the basis of spectroscopic, mass-spectroscopic, and spectrophotometric data, the character and energy of the radiation, and the half-life. An example of a study that has made ample use of these techniques is the work of Spitsyn and Kuzina (*65*), who identified Tc^{99} by means of radiometric and spectral methods.

Figure 3 shows the absorption curve of Tc^{99} β-radiation in aluminum (*66*) for identifying Tc^{99} from the maximum energy of β-radiation (0.292 ± 0.003) (*67*), and the determination of the maximum energy of Tc^{99} β-radiation with a β-ray spectrometer (*59*).

II. Physical Properties of Technetium

Elemental technetium is a silver-gray metal, which, like rhenium, ruthenium, and osmium, crystallizes in a hexagonal system with close packing. The unit cell contains two atoms with a radius of 1.358 Å (*68*). A study of the change in electrical resistance of technetium at pressures up to 30,000 kg/cm^2 and shear measurements at pressures up to 60,000 kg/cm^2 show that no appreciable changes occur in its crystal structure (*69*). The compressibility coefficient of technetium has also been calculated and found to be 0.27 mbar^{-1} (*70*). The atomic weight, determined chemically (from the composition of the oxide Tc_2O_7), is 98.8 ± 0.1 (*71*), which is in good agreement with the value 98.913 obtained by direct mass-spectrometric determination (*72*), and with the value 98.911 determined from the mass of the Ru^{99} isotope and energy of the β decay of Tc^{99} (*73*). The melting point of technetium was predicted theoretically (2257°C) by Szabo and Lakatos (*74*) and determined experimentally by Anderson *et al.* (*75*). Its value, 2200 ± 50°C, distinguishes technetium from rhenium to a certain extent and brings it closer to manganese, since technetium melts at a temperature below the melting points of the succeeding elements. The boiling point of technetium lies around 4700°C (*36*). The temperature dependence of the vapor pressure of technetium is shown in Table VIII. According to X-ray structural analysis data and assuming that its atomic weight is 99, the density of technetium is 11.487 g/cm^3 (*67*).

TABLE VIII

Vapor Pressure of Technetium at Various Temperatures

Temperature: (°C)	1567	1797	1930	2090	2270	2800	3100	3500	4100	4700
Vapor pressure of technetium, (mm Hg)	10^{-8}	10^{-6}	10^{-5}	10^{-4}	10^{-3}	10^{-1}	1	10^{1}	10^{2}	760

At low temperatures, technetium possesses the property of superconductivity. The critical temperature (11.2°K) (*76*) is the highest for the elements. Another value (8.22°K) is given in a later work by Picklesimer and Secula (*77*) for the massive metal of 99.995% purity. A still higher critical temperature is displayed by alloys of technetium with molybdenum (*78*). Technetium is weakly paramagnetic, but much more so than rhenium. Its paramagnetic sensitivity per gram is $270 \cdot 10^{-6}$ c.g.s. at 298°K and $290 \cdot 10^{-6}$ c.g.s. at 780°K (*79*). The neutron capture cross section of the Tc^{99} isotope is small (*21*) and decreases with increasing neutron energy (*80*).

Over 2000 lines of the optical spectrum of technetium in the wavelength range 2200–9000 Å have now been determined. Many of them are used for spectral determinations and identification of technetium (*81*). They include lines of sufficient intensity for identification of technetium with a sensitivity of 10^{-7} g (*21*). Characteristic spectra of X-radiation also have been obtained that are in good agreement with the position of technetium in the periodic system on the basis of Moseley's law (*82*).

TABLE IX

PHYSICAL PROPERTIES OF MANGANESE, TECHNETIUM, AND RHENIUM (*36*)

Physical property	Mn	Tc	Re
Atomic number	25	43	75
Atomic weight	54.938	98.913	186.31
Atomic radius, Å	1.306	1.358	1.373
Crystal lattice parameters, Å	$a = 8.896$ (α-Mn)	$a = 2.735$ $c = 4.391$	$a = 2.755$ $c = 4.449$
Density, g/cm^3	7.30	11.487	21.02
Melting point, °C	1244	2200 ± 50 (*75*) 2140 ± 20 (*87*)	3170
Boiling point, °C	2120	(4700)	5870
Critical point, °K	—	11.2; 8.8	2.42
Electronic work function, eV	3.95	(4.4)	4.8
Ionization potential, V	$U_1 = 7.432$ $U_2 = 15.64$ $U_3 = 33.69$	7.23 14.87 31.9	7.87 16.6 (26)
Magnetic susceptibility at 25°C, × 10^{-6} c.g.s.	527	270	69
Frequency of nuclear magnetic resonance for field of 10^{-4} gauss, Mc	10.553	9.583	9.586 (Re^{185}) 9.684 (Re^{187})
Relative sensitivity			
At constant field	0.178	0.376	0.133 (Re^{185}) 0.137 (Re^{187})
At constant frequency	2.89	7.43	2.63 (Re^{185}) 2.65 (Re^{187})
Magnetic moment, nuclear magnetons	3.4610	5.6572	3.1437 (Re^{185}) 3.1760 (Re^{187})
Electronic quadrupole moment, $e \times 10^{-4}$ cm^2	0.5	0.3	2.8 (Re^{185})
Main lines of optical spectrum and their relative intensities, Å	4034.49 (250) 4033.07 (400) 4030.75 (500) 2605.69 (100) 2593.73 (200) 2576.10 (300)	4297.06 (500) 4262.26 (400) 4238.19 (300) 4031.63 (300) 3636.10 (400) 3466.29 (250)	5270.96 (200) 4889.14 (100) 3725.76 (100) 3464.73 (350) 3460.46 (500) 3451.88 (200)
Main lines of X-ray Spectrum, Å	$K_{\alpha_1} = 209.75$ $K_{\alpha_2} = 210.15$ $K_{\beta_1} = 190.62$	$K_{\alpha_1} = 673.57$ $K_{\alpha_2} = 677.90$ $K_{\beta_{1,3}} = 600.20$ $K_{\beta_{2,4}} = 588.99$	$L_{\alpha_1} = 1429.97$ $L_{\alpha_2} = 440.96$ $L_{\beta_1} = 1236.03$ $L_{\beta_2} = 1204.15$
Half-life	Stable	2.12 × 10^5 years	6.2 × 10^{10} years (Re^{187})
Neutron capture cross section, barns:			
(n,γ) reaction	10.7	20 ± 5	48.7
(n,n') reaction	—	0.009	—

The literature contains no data on liquid and gaseous elemental technetium, with the exception of data on the vapor pressure. Only the value of the entropy (43.3 cal/mole at 25°C) (*83*) is known for gaseous technetium, and it has been established that the $Tc^{+}_{(gas)}$ ion is formed in the mass spectrometer during thermal ionization or electron bombardment (*84*). The electronic work function, calculated from the dependence of the atomic number Z, is equal to 4.4 eV (*85*), and the ionization potential is equal to 7.23 V (*86*). The basic physical properties of technetium are listed in Table IX, where they are compared with the analogous properties of rhenium and manganese. The data pertain to the principal technetium isotope Tc^{99}

III. Chemical Properties of Technetium

A. ELEMENTAL TECHNETIUM

Technetium is located in Group VII of the Periodic Table and is an analog of manganese and rhenium. From the similarity of the properties of technetium and rhenium, whose chemistry has been sufficiently studied, technetium could have been expected to have several valences from +7 to −1. All of these have now been established experimentally.

The most stable and characteristic oxidation state of technetium is the heptavalent one. It arises from direct oxidation of technetium by oxygen and other oxidants. Another stable oxidized form of technetium is the tetravalent state. The remaining valence states are found only in the form of various complex compounds. Compounds with valences less than 4 oxidize readily, and technetium changes to the tetra- and heptavalent state, whereas compounds of penta- and hexavalent technetium have a tendency to disproportionate, as follows:

$$3Tc^{5+} \rightarrow 2Tc^{4+} + Tc^{7+}$$

$$3Tc^{6+} \rightarrow Tc^{4+} + 2Tc^{7+}$$

The compounds of technetium known at the present time and its properties in the elemental state are examined below. In its chemical and physical properties, technetium is closer to rhenium than to manganese. This results from a phenomenon similar to the lanthanide contraction, which can be observed in the analog pairs Zr-Hf, Nb-Ta, and Mo-W. In the ground (unexcited) state, the atoms of technetium have the following electron configuration: $4s^2 4p^6 4d^6 5s$ $(S_{9/2})$ (*88, 89*). However, in some surveys (*90, 91*) an electronic structure of the type $4s^2 4p^6 4d^5 4s^2$ $(S_{5/2})$, similar to the electronic structures of manganese and rhenium, is given for technetium. Although the chemical properties of metallic technetium repeat those of elemental rhenium in many respects, they differ markedly from them in many cases.

Metallic technetium slowly tarnishes in moist air (*92*), but does not change in dry air (*93*). It dissolves in acids that are oxidants: nitric acid, aqua regia, and concentrated sulfuric acid. Metallic technetium dissolves in bromine water and also in neutral and alkaline solutions of hydrogen peroxide (*94*), which contradicts the data of earlier reports (*92*, *95*). The solution rate of technetium in hydrogen peroxide is apparently affected greatly by the condition of the metal surface and the presence of impurities. Under analogous conditions, metallic rhenium also dissolves readily.

Technetium burns in oxygen, forming the higher oxide Tc_2O_7 (*96*). At high temperatures, technetium reacts with chlorine and fluorine, and at 700°–1100° with carbon to form the carbide TcC (*97*). Technetium carbide is a compound with a face-centered lattice ($a = 3.982$ Å) and a density of 11.5 g/cm^3.

B. TECHNETIUM OXIDES

The existence of two technetium oxides, the volatile Tc_2O_7 and the relatively involatile TcO_2, has now been firmly established. The combustion of technetium in excess of oxygen at 500° yields Tc_2O_7 as the only product (*96*, *98*). The compound obtained can be readily purified by repeated sublimations. At room temperature, Tc_2O_7 is a light-yellow crystalline substance soluble in water and dioxane. In air, the crystals avidly absorb water, dissolving into a red liquid. The melting point of Tc_2O_7 is 119.5°, and the boiling point is 310.5°.

Thus, Tc_2O_7 exists as a liquid over a relatively large temperature interval as compared with Re_2O_7, whose melting and boiling points are, respectively, 300° and 360°.

The vapor pressure of Tc_2O_7 at various temperatures is shown in Table X and obeys the following equations:

$$\text{For solid } Tc_2O_7,\ \log p = 18.279 - \frac{7205}{T} \pm 8\%$$

$$\text{For liquid } Tc_2O_7,\ \log p = 8.999 - \frac{3571}{T} \pm 1\% \qquad (99)$$

It is interesting to note that solid Tc_2O_7 conducts electric current, whereas liquid Tc_2O_7 does not. This behavior of Tc_2O_7 does not correspond to that of Re_2O_7 (*91*). X-ray diffraction has shown that crystalline Tc_2O_7 has a symmetry of a lower order than Re_2O_7 and is not isomorphous with it (*91*). Technetium heptoxide possesses a weak diamagnetism (*39*), is a stronger oxidant than Re_2O_7, and is readily reduced by vapors of organic substances (including vacuum stopcock grease).

When Tc_2O_7 dissolves in water, a colorless solution is formed which, when slowly evaporated over concentrated sulfuric acid, turns yellow at first, then dark yellow, dark red, and finally dark red hygroscopic crystals separate. The chemical composition of these crystals has shown that they are a hydrate of the composition $Tc_2O_7 \cdot H_2O$, i.e., anhydrous pertechnetic acid $HTcO_4$ (*96*). Many attempts have been made to obtain oxides of hexavalent technetium TcO_3. Thus, Fried and Hall reported that they obtained a volatile dark red oxide by reacting oxygen with metallic technetium at 400°–1000°. Chemical analysis of two samples of this compound led to the formula $TcO_{3.05}$. However, subsequent studies did not confirm this (*99*), and the question of the existence of TcO_3 has remained unanswered.

TABLE X

TEMPERATURE DEPENDENCE OF SATURATED Tc_2O_7 VAPOR

Pressure (mm Hg):	0.1	1	10	100	760
Temperature (°C):	100.5	123.6	173.2	237.0	310.5

Another stable oxygen compound of Tc is the dioxide TcO_2. It does not form by a direct reaction between metallic technetium and oxygen, but can be readily obtained by indirect means. The first sample of TcO_2 was obtained by Rogers (*101*) in the form of a greenish black precipitate by electrolyzing a solution of pertechnetate in 2 *N* NH_4OH. Technetium dioxide can also be obtained by reduction of aqueous solutions of pertechnetates with zinc and hydrochloric acid, by pyrolysis of ammonium pertechnetate (*99*), and by hydrolysis of K_2TcCl_6 (*79*). According to chemical analysis data, the hydrated dioxide has the composition $TcO_2 \cdot 2H_2O$. This compound is weakly paramagnetic. On heating to 300° in a vacuum, $TcO_2 \cdot 2H_2O$ dehydrates completely, and, at 900°–1100°, sublimation of TcO_2 takes place (*79*). Like ReO_2, anhydrous black TcO_2 crystallizes in the manner of MoO_2 and has a density of 6.9 g^2cm^3 (*102*). Technetium dioxide is stable in air at room temperature but is readily oxidized by oxygen to Tc_2O_7. At 300°, TcO_2 reacts with chlorine to form products that hydrolyze readily and can be separated by distillation.

When the hydrate $TcO_2 \cdot 2H_2O$ dissolves in a concentrated solution of sodium or potassium hydroxide, the ion $Tc(OH)_6^{2-}$ is formed. The orange solution containing hydroxotechnetate(IV) ions absorbs light with a maximum at 410 mμ and is readily oxidized by hydrogen peroxide, bromine water, or ions of tetravalent cerium to form the pertechnetate (*103*).

C. Technetic Acid and Its Salts

As was mentioned, when technetium heptoxide dissolves in water, technetic acid $HTcO_4$ is formed, which on slow evaporation of the solution over concentrated H_2SO_4 separates in the form of dark red hygroscopic crystals. The composition of these crystals corresponds to the formula $HTcO_4$. The character of the curves obtained by potentiometric titration indicates that technetic acid is a relatively strong monobasic acid and can be titrated with indicators used in acidimetry (*79, 96*).

The vapor pressure of technetic acid and its aqueous solutions can be calculated from the following equations:

$$\text{For solid } HTcO_4,\ \log p = 8.207 - \frac{2395}{T} \pm 1\%$$

$$\text{For a saturated solution, } \log p = 8.201 - \frac{2375}{T} \pm 2\% \qquad (99)$$

Some salts of technetic acid, the pertechnetates, have been isolated in the pure form. Thus, NH_4TcO_4, $KTcO_4$, $NaTcO_4$, $RbTcO_4$, $CsTcO_4$, $LiTcO_4$, $AgTcO_4$, $TlTcO_4$, $(C_6H_5)_4AsTcO_4$, and nitron pertechnetate have been obtained thus far. The latter two salts are practically insoluble and can be used as weighing forms in quantitative analysis.

Pure ammonium pertechnetate is a crystalline, nonhygroscopic substance showing no sign of decomposition after being heated for several hours at 100°. In a vacuum at 550°, NH_4TcO_4 decomposes to form TcO_2. However, very pure NH_4TcO_4 sublimes without appreciable decomposition.

The density of NH_4TcO_4 is 2.73 g/cm³. Potassium pertechnetate $KTcO_4$ melts at 540° and sublimes without decomposing at about 1000°.

Fragments of NH_4TcO_4 produced by electron bombardment at 80°–160° have been studied by mass spectrometry (*104*). The following ions arranged in order of decreasing quantities were thus detected: $Tc_2O_7^+$, TcO_4^+, TcO_3^+, TcO_2^+, TcO^+, $Tc_2O_5^+$, $Tc_2O_6^+$, and $Tc_2O_4^+$.

Table XI shows the lattice parameters of salts of technetic acid obtained by X-ray diffraction, and their solubility in water. All the salts of technetic acid are isomorphous with the corresponding salts of rhenic acid. The solubility of salts of technetic acid is somewhat higher than that of the corresponding perrhenates. Thus, the solubility of $KTcO_4$ is

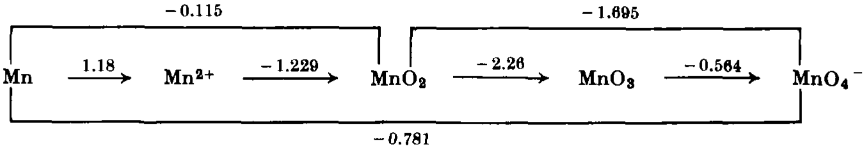
21.3 g/1000 g of water, and that of $KReO_4$ is 14.7 g/1000 g of water (*105*). In aqueous solutions, the TcO_4^- ion is the most stable one. The ionic radius of Tc^{7+} is 0.56 Å (*111*). This value is close to the ionic radius of Re^{7+} (0.56 Å), but greater than that of Mn^{7+} (0.46 Å).

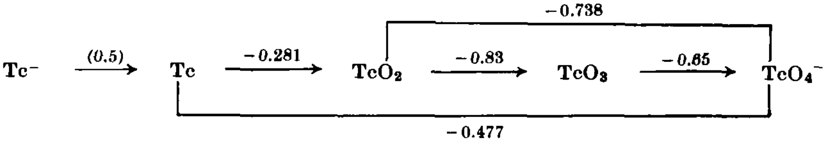
The calculated ionization potential of Tc^{7+} is 95 eV; this value is intermediate between those of Mn^{7+} (122 eV) and Re^{7+} (79 eV). The length of the Tc—O bond in the tetrahedral ion TcO_4^- is 1.75 Å, and

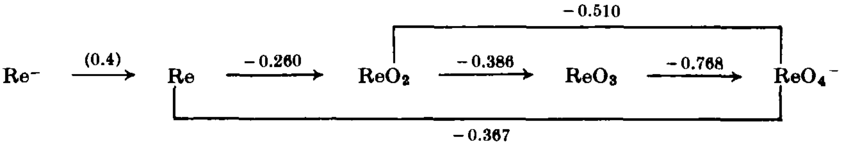
TABLE XI

CRYSTAL LATTICE PARAMETERS AND SOLUBILITY OF SALTS OF TECHNETIC ACID

Compound	Lattice type	Lattice parameters (Å) a_0	b_0	c_0	Density (g/cm³)	Solubility in water at 20°C (g/100 g)	Reference
NH_4TcO_4	$CaWO_4$	5.790	—	13.310	2.73	—	(*106, 107*)
$NaTcO_4$	$CaWO_4$	5.339	—	11.869	3.4	—	(*108, 109*)
$KTcO_4$	$CaWO_4$	5.654	—	13.030	—	2.13	(*106, 107*)
$RbTcO_4$	$CaWO_4$	5.758	—	13.54	—	1.167	(*107, 110*)
$AgTcO_4$	$CaWO_4$	5.319	—	11.875	5.1	0.563	(*107, 110*)
$CsTcO_4$	Ortho-rhombic	5.718	5.918	14.304	—	0.412	(*106, 110*)
$TlTcO_4$	Ortho-rhombic	5.501	5.747	13.45	—	0.072	(*110*)







the length of the Re—O bond in ReO_4^- is 1.97 Å (*112*). It is not surprising therefore that the pertechnetate ion has a stability intermediate between those of the ReO_4^- and MnO_4^- ions. This is also confirmed by the oxidation-reduction diagram on page 23 (*91*).

It is apparent that the oxidation potential of the TcO_2/TcO_4^- couple in an acid aqueous solution occupies an intermediate position between the corresponding potentials for Mn and Re. The pertechnetate ion (TcO_4^-) is therefore a weaker oxidant than MnO_4^-, but a stronger one than ReO_4^-.

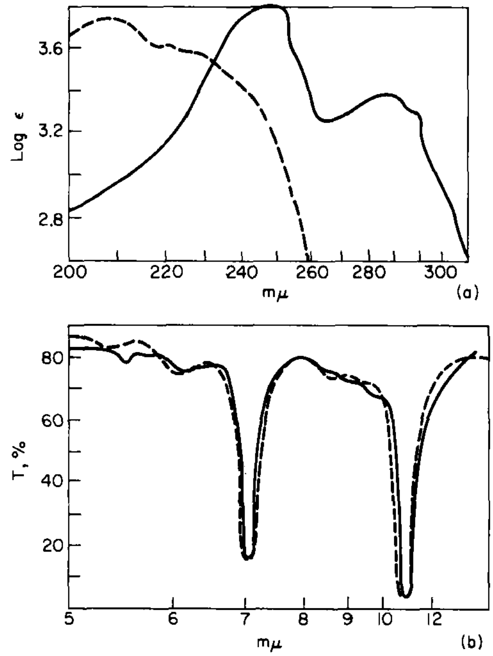


FIG. 4. Absorption spectra of $KTcO_4$ and $KReO_4$: (a) in the ultraviolet, (b) in the infrared; ——, $KTcO_4$; - - -, $KReO_4$.

Aqueous solutions of pertechnetates display strong light absorption in the ultraviolet and infrared; this can be utilized for the quantitative determination of technetium. Figure 4 illustrates the infrared and ultraviolet regions of the absorption spectrum of $KTcO_4$ and $KReO_4$.

Certain physicochemical properties of $NaTcO_4$ and $KTcO_4$ and dissociation constants of $KTcO_4$ and $CsTcO_4$ at 18° were determined by continuous electrophoresis on a porous filler (*113*). These data are shown in Table XII.

The radius of the solvated ion, calculated from the Stokes equation, was found to be 5×10^{-8} cm, which is in good agreement with the literature data. The decrease in transference numbers and degree of dissociation for $KTcO_4$ with changing concentration indicates the incompleteness of its dissociation. From the equation

$$K_d = \frac{[C] \cdot U_0}{U_{an} - U_0} f_c \cdot f_{an}$$

were calculated the dissociation constants of $KTcO_4$ and $CsTcO_4$, which at 18° are, respectively, 0.122 and 0.231. In this equation, K_d is the dissociation constant; $[C]$ is the cation concentration; U_0 is the mobility of the TcO_4^- anion, determined experimentally; U_{an} is the mobility of the TcO_4^- anion at full dissociation; and f_c and f_{an} are the activity

TABLE XII

PHYSICOCHEMICAL PROPERTIES OF $NaTcO_4$ AND $KTcO_4$ AT 18°C

Compound	Electrolyte concentration, g-eq/l	Mobility U, $\times 10^5$ $cm^2/sec\ V$	Ionic equivalent conductance, $ohm^{-1}\ cm^2$	Equivalent conductance, $ohm^{-1}\ cm^2$	Transference number of anion	Radius of solvated anion, Å	Degree of dissociation, α
$NaTcO_4$	0.0	53.0[a]	51.1	94.6	0.540	4.6	1.00
	0.0005	52.1	50.3	93.1	0.540	—	1.00
	0.005	48.5	46.8	88.1	0.531	—	0.98
	0.01	49.0	47.3	87.8	0.538	—	1.00
	0.02	47.3	45.6	85.1	0.536	—	1.00
					av. 0.537		
$KTcO_4$	0.0	53.0[a]	51.1	115.7	0.442	4.6	1.00
	0.0005	51.3	49.5	113.2	0.437	—	0.98
	0.02	42.2	40.7	100.2	0.406	—	0.94

[a] The limiting solubility of TcO_4 anions at 18° was obtained by extrapolation to zero concentration.

coefficients of the cation and anion for a monovalent-monovalent compound. We should note the good agreement between the dissociation constant of $KTcO_4$, equal to 0.122 and obtained by the electromigration method, and the value calculated from the thermodynamic data, $K_d = 0.129$ at 25° (*99*).

D. TECHNETIUM SULFIDES

Technetium forms two sulfides, Tc_2S_7 and TcS_2. When hydrogen sulfide is passed through acid solutions of pertechnetates, an insoluble sulfide of heptavalent technetium Tc_2S_7 is obtained. A detailed study of the dependence of the precipitation of technetium on time and the hydrochloric acid concentration showed that in 6 *N* HCl solution a reduction starts of the pertechnetate ions to lower oxidation states that are not precipitated by hydrogen sulfide. In 9 *N* HCl solution, this reduction goes to completion. The TcO_4^- ion differs appreciably in this respect from the ReO_4^- ion, which does not change its valence state up to 11 *N* HCl solution (Fig. 5) (*62*, *114*, *115*).

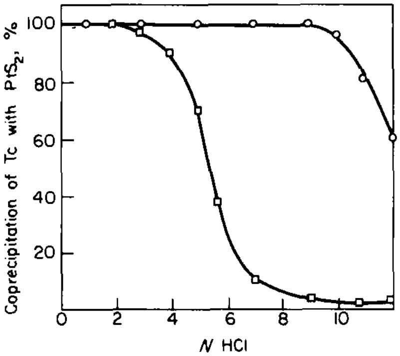


FIG. 5. Copreciptiation of Tc_2S_7 and Re_2S_7 with platinum sulfide at various HCl concentrations: □, Tc_2S_7; ○, Re_2S_7.

The dark brown Tc_2S_7 is best precipitated from 2–4 *N* HCl or H_2SO_4 solutions at the temperature of a boiling water bath by passing gaseous H_2S through the solution (*116*). In a sulfuric acid medium, Tc_2S_7 can also be precipitated with thiosulfate or thioacetamide (*60*, *117*).

The technetium heptasulfide precipitate is usually contaminated with elemental sulfur, which can be removed by thoroughly washing the precipitate with carbon disulfide. Technetium sulfide is insoluble in ammonium polysulfide, but dissolves readily in a mixture of ammonia and hydrogen peroxide. It is analogous in this respect to Re_2S_7. Technetium heptasulfide is fairly volatile and sublimes at 100° in a stream of chlorine (*118*). At higher temperature, it decomposes to form the amorphous disulfide TcS_2 (*91*).

Crystalline TcS_2 can be obtained by heating Tc_2S_7 with elemental sulfur in an autoclave for 24 hours at 1000°. The formation of TcS_2 from the elements is also probable (*91*). Technetium disulfide is isomorphous with rhenium disulfide and has an MoS_2-type structure. When heated to 1000° in a hydrogen or hydrogen sulfide atmosphere, TcS_2 is reduced to the metal.

It should be noted that technetium heptasulfide is widely employed in various processes for isolation and purification of technetium. The concentration process is usually concluded by separating Tc_2S_7.

E. HALOGEN COMPOUNDS OF TECHNETIUM

The known halogen and oxyhalogen compounds of technetium are shown in Table XIII.

TABLE XIII

KNOWN HALOGEN AND OXYHALOGEN COMPOUNDS OF TECHNETIUM

Degree of oxidation	Fluorine	Chlorine	Bromine
Tc^{7+}	TcO_3F	TcO_3Cl	—
Tc^{6+}	TcF_6 $TcOF_4$	$TcCl_6$	—
Tc^{5+}	TcF_5	$TcOCl_3$	$TcOBr_3$
Tc^{4+}	—	$TcCl_4$	—

When technetium metal was reacted with excess of fluorine in a closed nickel vessel for 2 hours at 400°, a volatile yellow product was formed (*119*). It was purified by sublimation. According to the results of chemical analysis, this compound can be expressed by the simplest formula TcF_6. Technetium hexafluoride is a golden yellow substance, stable during storage in a closed nickel or dry Pyrex vessel. It melts into a yellow liquid at 33.4°, and boils at 55.3°. It is colorless and monomeric in the vapor phase. Table XIV shows the results of measurement of the vapor pressure of TcF_6 at various temperatures.

X-ray diffraction showed that at –5.3° TcF_6 changes its cubic structure to an orthorhombic one, which is isomorphous with the corresponding crystal structures of the known transition metal hexafluorides. The infrared spectrum in the region 600–2000 cm^{-1} is similar in character to the spectra of other hexafluorides. The absorption maximum is at 745 cm^{-1}. At 300°K the magnetic moment $\mu = 0.45$ Bohr magneton. When dissolved in alkaline solutions, technetium hexafluoride hydrolyzes to form a black precipitate of technetium dioxide and pertechnetates. This behavior of TcF_6 is analogous to that of ReF_6, which also disproportionates to the insoluble ReO_2 and soluble ReO_4^-.

TABLE XIV

VAPOR PRESSURE OF TcF_6

Pressure (mm Hg):	59	78	100	115	140	760
Temperature (°C):	0	4.9	9.3	12.0	15.7	55.3

When technetium metal is fluorinated directly, the yellow technetium pentafluoride TcF_5 is formed as a by-product (*120*). It crystallizes in an orthorhombic system with unit cell parameters $a_0 = 7.6$ Å, $b_0 = 5.8$ Å, $c = 16.6$ Å, and is isostructural with CrF_5. Its melting point is 50°. TcF_5 is more stable than ReF_5, but in glass begins to decompose at 60°. In 1962 Colton (*121*) reported obtaining the chloride of hexavalent technetium. When gaseous chlorine is passed over technetium metal at 200° a reaction begins, which at 400° takes place rapidly with the formation of two volatile products. One is a dark-green solid substance that melts readily to form a green liquid. Chemical analysis showed that the ratio of chlorine to technetium is approximately 6, i.e., this compound has the empirical formula $TcCl_6$. When $TcCl_6$ dissolves in an alkaline solution, hydrolysis takes place with the formation of technetium dioxide and pertechnetate ions in the ratio 1 : 2, which also confirms the hexavalent state of technetium in this compound. The green technetium hexachloride is very unstable; it decomposes even at room temperature to $TcCl_4$.

The chloride of tetravalent technetium is obtained together with $TcCl_6$ when gaseous chlorine reacts with metallic technetium at 400° (*121*). In addition, it can be obtained by reacting technetium heptoxide with carbon tetrachloride in an autoclave at 400° (*122*). Technetium tetrachloride consists of fine blood-red crystals, which sublime in a stream of chlorine. Measurement of the magnetic susceptibility over a wide temperature range showed $TcCl_4$ to be paramagnetic ($\mu = 3.14$ Bohr magnetons at 25° and $\theta = -57°$) (*123*).

Technetium tetrachloride reacting with oxygen forms the oxychloride of heptavalent technetium. On dissolving in concentrated HCl, it yields the complex ion $TcCl_6^{2-}$ (*94*).

In a mass-spectrometric study of the products resulting from the reaction between Tc_2O_7 and UF_4, the existence of the oxyfluoride of heptavalent technetium was suggested (*104*). This compound was recently isolated and its properties were studied (*124*).

Technetium oxyfluoride is formed by passing fluorine over technetium dioxide at 150°; it condenses in a trap cooled with Dry Ice. Pure TcO_3F consists of yellow crystals, which melt at 18.3° to form a liquid of the same color. The vapor pressure of the solid and liquid oxyfluoride may be obtained from the equations:

$$\text{For solid } TcO_3F\ [t = (-8.78) - (+18.28^\circ)],\ \log p = 12.448 - \frac{3239.4}{T}$$

$$\text{For liquid } TcO_3F\ [t = (+18.28) - (+51.82^\circ)],\ \log p = 8.417 - \frac{2064.6}{T}$$

According to the determinations of Selig and Malm (*124*), the boiling point of TcO_3F is approximately 100°, the heat of sublimation 14.832 kcal/mole, the heat of melting 5.377 kcal/mole, and the heat of vaporization 9.453 kcal/mole. Technetium oxyfluoride is stable at room temperature in nickel or monel vessels. It hydrolyzes in water to form $HTcO_4$ and HF. In its properties, TcO_3F occupies an intermediate position between MnO_3F and ReO_3F (Table XV).

TABLE XV

PROPERTIES OF MANGANESE, TECHNETIUM, AND RHENIUM OXYFLUORIDES

Compound	Melting point (°C)	Boiling point (°C)	Color
MnO_3F	−38	~ 60	Green
TcO_3F	+18.3	~ 100	Yellow
ReO_3F	+147	~ 164	Yellow

When reacting with excess of fluorine at 400° and 4 atm, TcO_3F is quantitatively converted to TcF_6.

The oxychloride of heptavalent technetium was obtained by reacting $KTcO_4$ dissolved in 18 *M* H_2SO_4 with 12 *N* HCl. This compound is extracted with chloroform, carbon tetrachloride, and hexane (*107*). It is also suggested that technetium oxychloride is formed by the reaction of technetium chloride with oxygen (*94*). However, technetium oxychloride has not been isolated in pure form and data on its properties are therefore lacking.

The oxyfluoride of hexavalent technetium is formed as a by-product of the direct fluorination of metallic technetium (*120*). Technetium oxyfluoride is a blue crystalline substance melting at 134°C. In its properties it resembles the corresponding rhenium analog. The magnetic susceptibility $\mu_{\text{eff}} = 1.76$ Bohr magnetons at 25° and $\theta = 9°$.

When bromine vapors act on technetium dioxide at 350°, a brown product is formed that apparently is the oxybromide of pentavalent technetium $TcOBr_3$ (*94*). This compound sublimes in a stream of bromine at 400°. In aqueous solutions, it hydrolyzes according to the general equation

$$3Tc^{5+} \rightarrow 2Tc^{4+} + Tc^{7+}$$

characteristic of compounds of pentavalent technetium and rhenium.

When gaseous chlorine reacts with technetium dioxide, a light brown product is obtained that sublimes at 900° and is paramagnetic (*79, 94*). However, no chemical analysis of this compound has been made, since it decomposes rapidly in aqueous solutions, via the reaction characteristic of pentavalent technetium. All this permits the assumption that the compound obtained has the composition $TcOCl_3$.

F. COMPLEX HALOGEN COMPOUNDS OF TECHNETIUM

In the pentavalent and tetravalent states, technetium displays a tendency to form complex compounds of the type $MeTcX_6$ and Me_2TcX_6.

When alkali metal chlorides react with a solution of technetium hexafluoride in iodine pentafluoride, complex halogen salts of pentavalent technetium are formed. In this manner, $NaTcF_6$ and $KTcF_6$ were obtained and isolated in pure form (*120*). They are yellow crystalline compounds, isomorphous with the corresponding salts of ruthenium but differing from the rhenium salts (Table XVI).

For $NaTcF_6$, the magnetic susceptibility $\mu_{\text{eff}} = 2.25$ Bohr magnetons at 25°C and $\theta = 130°$.

A common method for preparing complexes of this type, with the exception of TcF_6^{2-}, is the reduction of pertechnetates by the corresponding concentrated hydrohalic acids or the dissolution of hydrated technetium dioxide in these acids. All the halogen complexes of technetium are isomorphous with the corresponding rhenium compounds.

Potassium hexachlorotechnetate can be obtained by reducing potassium pertechnetate with concentrated HCl (*117*). However, in HCl the reduction is relatively slow and can be accelerated by reductants, for example H_3PO_2 or I^- (*79, 91*). In the latter case, the intermediate

TABLE XVI

CRYSTAL STRUCTURE OF Tc, Re, AND Ru COMPLEX FLUORIDE SALTS

Compound	Crystal structure	Crystal lattice parameters
$NaReF_6$	Cubic system	$a_0 = 8.18$ Å,
$NaTcF_6$	Rhombic system	$a_0 = 5.77$ Å, $\alpha = 55.8°$
$NaRuF_6$	Rhombic system	$a_0 = 5.80$ Å, $\alpha = 54.5°$
$KReF_6$	Tetragonal system	$a_0 = 10.01$ Å, $c_0 = 5.13$ Å
$KTcF_6$	Rhombic system	$a_0 = 4.97$ Å, $\alpha = 97.0°$
$KRuF_6$	Rhombic system	$a_0 = 4.96$ Å, $\alpha = 97.5°$

compound formed is a red binuclear complex of the composition $K_4(Tc_2OCl_{10})$ (*91*), which by reacting further with HCl forms K_2TcCl_6.

The golden-yellow octahedral crystals of potassium hexachlorotechnetate have a strong paramagnetism, which obeys the Curie-Weiss equation, and are isomorphous with the corresponding rhenates and platinates. Its unit cell dimension $a_0 = 9.82$ Å. The effective magnetic moment is equal to 4.05 Bohr magnetons, which is in good agreement with the theoretical calculations (3.88 Bohr magnetons) for three unpaired electrons.

K_2TcCl_6 is extracted from acid solutions by various solvents, for example alcohols and a solution of trioctylamine hydrochloride in cyclohexane.

The $(TcCl_6)^{2-}$ ion, in contrast to the $(ReCl_6)^{2-}$ ion, hydrolyzes readily to form the hydrated dioxide $TcO_2 \cdot xH_2O$, and is therefore stable only in concentrated HCl solutions. By analogy with rhenium, we can expect the formation of several mixed chlorohydroxo complexes of tetravalent technetium. Indeed, Boyd (*91*) observed a gradual change in the absorption spectrum, which has peaks at 240 and 338 mμ, even in 3 *N* HCl. In neutral solutions, the hydrolysis of $(TcCl_6)^{2-}$ to the dioxide takes place rapidly and completely. Hexachlorotechnetates are oxidized to pertechnetates by hydrogen peroxide, nitric acid, chlorine, and the Ce^{4+} and MnO_4^- ions (*60, 117, 122*), but are more resistant to the action of atmospheric oxygen than the oxygen compounds of tetravalent technetium.

On heating in a vacuum to 1100°, K_2TcCl_6 decomposes to technetium metal and chlorine, as confirmed by X-ray powder photography (*79*).

Potassium hexabromotechnetate K_2TcBr_6 is obtained from the hexachlorotechnetate by successive evaporation with hydrobromic acid (*125*). This compound forms dark red or even black crystals that crystallize in a face-centered cubic structure ($a_0 = 10.37$ Å). Its magnetic moment was measured only in solution and is 3.94 Bohr magnetons.

Potassium hexaiodotechnetate K_2TcI_6 can be obtained from the corresponding chloro- or bromotechnetate by evaporation with hydriodic acid (*125*). It consists of black crystals whose structure has not been finally determined.

The rose-colored potassium hexafluotechnetate K_2TcF_6 can be obtained by the reaction between K_2TcCl_6 or K_2TcBr_6 and molten KHF_2 (*94*, *126*). Its structure is analogous to the structure of K_2ReF_6 (K_2GeF_6 type). Potassium hexafluotechnetate is stable in aqueous solutions and is decomposed only by hot concentrated alkali, in contrast to the other halogen complexes, which readily hydrolyze even in acid solutions. Like the other hexafluotechnetates, the free acid H_2TcF_6 can be obtained from the potassium salt by means of ion exchangers. The sodium and ammonium salts are soluble in water. The barium salt becomes less soluble on aging. The solubility of K_2TcF_6 at room temperature is 1.5 g/100 g of water.

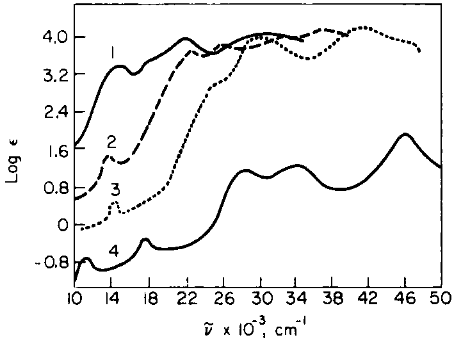


FIG. 6. Absorption spectra of halide complexes of Tc^{4+}; (1) K_2TcI_6, (2) K_2TcBr_6, (3) K_2TcCl_6, (4) K_2TcF_6.

The ion $(TcF_6)^{2-}$ absorbs light with a maximum at 574 cm^{-1}. The absorption spectra of the various halogen complexes of technetium (Tc^{4+}) are illustrated in Fig. 6.

G. COMPLEX COMPOUNDS OF TECHNETIUM

In the lower oxidation states, technetium has a strong tendency to form complexes with various ligands. The oxidation state of technetium becomes considerably stabilized in this manner. Thus, the first compound of pentavalent technetium to be isolated and adequately described was the brown complex with diarsine (D) (*o*-phenylenebisdimethylarsine) of the composition $[Tc^{5+}D_2Cl_4]^+$ Cl (*127*). It is obtained by oxidizing the orange complex $[Tc^{3+}D_2Cl_2]\cdot Cl$ with gaseous chlorine in accordance with the reaction:

$$[Tc^{3+}D_2Cl_2]\cdot Cl \underset{TiCl_3}{\overset{Cl_2}{\rightleftarrows}} [Tc^{5+}D_2Cl_4]Cl$$

(*orange*) $\mu_{eff} = 2.7$ Bohr magnetons (*brown*) $\mu_{eff} = 0.9$ Bohr magnetons

The conductivity of the complex of pentavalent technetium with diarsine in nitrobenzene and the magnetic moment agree with the formula for this compound cited earlier. Oxidation from the trivalent to the pentavalent state for technetium is somewhat more difficult than for rhenium. Thus, the Ce^{4+} ion oxidizes rhenium, but not technetium. The oxidation state of 5 for technetium has been confirmed by potentiometric titration with a standard $TiCl_3$ solution. The complex of pentavalent technetium is reduced to a complex of trivalent technetium, two equivalents of $TiCl_3$ being consumed. The corresponding compounds of technetium and rhenium are very similar in properties and are apparently isomorphous.

Complexes of technetium have also been obtained with thiocyanate (*128*), α-picolinic and sulfosalicylic acids (*129*), α-furyldioxime (*130*), *p*-thiocreosol (*131*), thioglycolic acid (132), thiourea, dimethylglyoxime, potassium xanthate (*133*), etc. They are colored for the most part, are of interest in colorimetric determinations, and will therefore be examined in detail in Section V on analytical chemistry.

When potassium pertechnetate is reduced polarographically in 0.1 *N* potassium cyanide solution, only one wave corresponding to a 3-electron reduction is obtained, indicating the possible formation of a stable complex cyanide of tetravalent technetium (*103*). Indeed, by dissolving hydrated technetium dioxide or K_2TcCl_6 in an alkaline solution of potassium cyanide, one can obtain a yellow complex ion, which has been separated in the form of a dark-brown thallium salt of the composition $Tl_3[TcO(OH)(CN)_4]$ or $Tl_3[Tc(OH)_3(CN)_4]$. Under similar conditions, rhenium forms the complex ion $[ReO_2(CN)_4]^{3-}$, in which rhenium is pentavalent. The ion $[Tc(OH)_3(CN)_4]^{3-}$ strongly absorbs light at 380 mμ with a molar extinction coefficient of 4.44×10^4 (mole cm)$^{-1}$. On the basis of deviations from the Lambert-Beer law, the instability constant of the complex was determined to be $K = (1.3 \pm 0.6)10^8$ mole^{-1}. The complex is readily decomposed by acids and in the presence of oxidants oxidizes to TcO_4^- (*134*).

In 1959 Fergusson and Nyholm (*135*) first isolated and characterized complex compounds of trivalent and divalent technetium of the composition $(Tc^{3+}D_2X_2)\cdot X$ and $(Tc^{2+}D_2X_2)$, where X = Cl, Br, I, and D = *o*-phenylenebisdimethylarsine.

The overall scheme for the preparation of these compounds from K_2TcCl_6 is as follows:

$$K_2TcCl_6 \xrightarrow[\text{water–alcohol solution of HCl}]{\text{boiling with excess arsine in}} (Tc^{3+}D_2Cl_2)Cl \xrightarrow{\text{boiling with LiBr in alcohol}}$$

$$(Tc^{3+}D_2Br_2)Br \xrightarrow{\text{boiling with LiI in alcohol}} (Tc^{3+}D_2I_2)I \xrightarrow{\text{excess } I_2} (Tc^{3+}D_2I_2)I^3$$

$$(Tc^{3+}D_2I_2)I \underset{\text{oxidation with iodine}}{\overset{\text{treatment with } SO_2 \text{ or boiling with alcohol}}{\rightleftarrows}} (Tc^{2+}D_2I_2)$$

Complex compounds of divalent technetium are obtained from the corresponding compounds of trivalent technetium when treated with SO_2 or when boiled with alcohol. The properties of these compounds are shown in Table XVII.

When $KTcO_4$ is reduced with potassium amalgam in the presence of excess KCN or $K_3[Tc(OH)_3(CN)_4]$, an olive-green solution containing complex ions of univalent technetium $[Tc(CN)_6]^{5-}$ is formed. The complex $K_5Tc(CN)_6$ has an absorption maximum at 810 cm^{-1} with a molar

TABLE XVII

PROPERTIES OF COMPLEX COMPOUNDS OF DI- AND TRIVALENT TECHNETIUM

Oxidation state	Compound	Color	μ_{eff} (20°) (Bohr magnetons)	Absorption spectrum λ_{max} (mμ)	Absorption spectrum $E \times 10^{-3}$	Molar conductance in nitromethane at 25° (ohm^{-1}) ($c = 1 \times 10^{-3}$ M[a])
Tc^{3+}	$(TcD_2Cl_2)Cl$	Orange	2.7	441	3.92	75
	$(TcD_2Br_2)Br$	Red	3.2	472	5.56	77
				302	3.08	
	$(TcD_2I_2)I_3$	Dark red to black	3.4	574	4.00	86
				359	6.69	
				294	11.23	
Tc^{2+}	(TcD_2I_2)	Yellow	3.0	514	2.79	Slightly soluble, does not conduct current
				474	1.00	

[a] For a monovalent-monovalent electrolyte in nitromethane at a concentration of 10^{-3} M, 70–90 ohm^{-1}.

extinction coefficient of 1.2×10^2. The salt is isomorphous with analogous rhenium and magnesium compounds and has a cubic unit cell with $a_0 = 12.106$ Å. $K_5Tc(CN)_6$ does not contain water of crystallization, and its density is 1.8 g/cm^3. Thallium (Tl^+) precipitates a brick-red precipitate of the composition $Tl_5[Tc(CN)_6]$, soluble in ammoniacal hydrogen peroxide and dilute acids. All the compounds of Tc^+ are stable in the solid state in dry air, but are very sensitive to oxidation in solution. The oxidation product is the ion $[Tc(OH)_3(CN)_4]^{3-}$ (*134*, *136*).

Carbonyl compounds of univalent and neutral technetium also have been obtained and isolated. At a pressure of 400 atm and temperature of 220°–275°, carbon monoxide reacts with Tc_2O_7 or TcO_2 to form technetium carbonyl (*137*, *138*). Measurement of the molecular weight has shown that this compound is dimeric, i.e., has the formula $Tc_2(CO)_{10}$ (*138*).

Technetium carbonyl is a colorless diamagnetic compound, which sublimes at a moderate temperature in a vacuum and decomposes slowly in air. Its unit cell has the dimensions $a_0 = 14.73$ Å, $b_0 = 7.22$ Å, $c = 14.90$ Å, $\beta = 104.6°$, and contains four molecules (*139*). In carbon tetrachloride, technetium carbonyl slowly reacts with halogens to form penta- and tetracarbonyls in accordance with the general reaction:

$$Tc_2(CO)_{10} + X_2 \rightarrow 2Tc(CO)_5X \rightarrow [Tc(CO)_4X]_2 + 2CO \qquad \text{(where } X = \text{Cl, Br, I)}$$

Table XVIII shows the relative rates of formation of carbonyl chlorides of technetium, manganese, and rhenium.

TABLE XVIII

RATE OF FORMATION OF Tc, Mn, AND Re CARBONYL CHLORIDES

	Time necessary for formation		
Element	$Me(CO)_5Cl$	$[Me(CO)_4Cl]$	Insoluble precipitate
Mn	5 min	2 days	1 week
Tc	6 days	2 weeks	2 months
Re	3 months	4 months	4 months

The chemical properties of technetium carbonyl halides are intermediate between those of the analogous compounds of manganese and rhenium. When the pentacarbonyl halide compounds are heated in air at 100°, they are converted to dimeric tetracarbonyl halides. The reverse reaction takes place in an autoclave in the course of 40 hours at

100° and a carbon monoxide pressure of 1000 atm. The iodine derivatives are the most soluble. Nitric acid oxidizes the technetium carbonyl halides to the TcO_4^- ion. Infrared spectra of the carbonyl halide compounds of technetium and their possible structures are discussed in references (*140*, *141*). Technetium carbonyl hydride has also been obtained in unweighable quantities (*140*).

H. ORGANOMETALLIC COMPOUNDS OF TECHNETIUM

Organometallic technetium compounds have recently been isolated. Thus, Baumgartner *et al.* (*142*) report on the preparation, as a result of the β decay of $Mo^{99}(C_6H_6)_2$, of the complex technetium dibenzene cation $[(C_6H_6)_2Tc]^+$, which coprecipitates in the form of hexafluophosphate with $Re(C_6H_6)_2PF_6$.

The reaction of $TcCl_4$ with a solution of sodium cyclopentadienyl in tetrahydrofuran forms bisdicyclopentadienyltechnetium $[(C_5H_5)_2Tc]_2$. It consists of golden yellow crystals unstable in air and melting at 155° (*143*). Bisdicyclopentadienyltechnetium is diamagnetic, is not decomposed by water at room temperature, and dissolves in 10% aqueous tetrahydrofuran. It is interesting to note that under similar conditions rhenium forms a compound of the composition $(C_5H_5)_2ReH$ (*144*, *145*). Determination of the molecular weight and infrared spectra indicates the absence of the Tc—H bond in bisdicyclopentadienyltechnetium. However, the nature of the bond between the ring and the metal is similar to that in $(C_5H_5)_2ReH$ and differs from this bond in the paramagnetic $(C_5H_5)_2Mn$ (*146*). It is possible that, as in the case of technetium carbonyl, a Me—Me bond exists in $[(C_5H_5)_2Tc]_2$.

During the β decay of Mo^{99} in molybdenum biscyclopentadienyltricarbonyl, $[C_5H_5Mo^{99}(CO)_3]_2$, cyclopentadienyltricarbonyltechnetium, $C_5H_5Tc(CO)_3$, is formed. This compound is a diamagnetic colorless substance with a melting point of 87.5°. Its absorption spectrum has a maximum at 36.5×10^3 cm^{-1} ($\log \epsilon_{max} = 3.69$) (*147–149*).

In 1963 Gobbild and Ihrman patented a method for preparing trichloromethylcyclopentadienetechnetium, isopropylbenzene and other cyclopentadiene derivatives (*150*).

I. TECHNETIUM HYDRIDE

The reduction of potassium perrhenate, labeled with the Tc^{99} isotope, by a solution of potassium in ethylenediamine forms a complex rhenium hydride assigned the composition $KReH_4 \cdot 2H_2O$ (*151*). The rhenium hydride precipitate contained 90% of the radioactivity of Tc^{99} introduced into the initial potassium perrhenate. When the product was further purified by removing the unreacted $KReO_4$ and KOH by extraction with ethanol and ether, the radioactivity of Tc^{99} was preserved in the hydride. The authors of reference (*151*) concluded that TcO_4^- is also reduced to the hydride $KTcH_4 \cdot 2H_2O$, isomorphous with $KReH_4 \cdot 2H_2O$. However, later X-ray structural studies by Knox and Ginsberg (*152*) showed that rhenium hydride has the formula K_2ReH_8, and the lattice parameters are $a_0 = 9.61$ Å and $c_0 = 5.51$ Å. The X-ray powder pattern of technetium hydride was found to be similar to that of rhenium hydride, showing the analogous structure of these two compounds. Since no other studies of technetium hydride were made in this work, it is now difficult to evaluate reliably its composition and properties.

J. METHODS OF PREPARING ELEMENTAL TECHNETIUM

The methods for preparation of elemental technetium are in most cases similar to those used in the preparation of metallic rhenium. They differ only in the details of the microquantitative operations. These methods are based on the reduction of various technetium compounds with electric current or hydrogen. Such compounds can be technetium sulfide or ammonium pertechnetate. Obviously, the preparation of elemental technetium should be preceded by operations for its isolation, purification, and preparation of the corresponding compounds.

In initial studies with visible technetium samples, the chief method for isolation and purification of technetium was the precipitation of its heptasulfide. Technetium sulfide was therefore used to obtain weighable quantities of technetium metal (*153*). Technetium sulfide was placed in a quartz capillary connected to a system that made it possible alternately to pump out the volatile reduction products of technetium sulfide and to create a hydrogen atmosphere in the system. Such consecutive operations made it possible to obtain 100 μg of technetium metal by reduction with hydrogen at 1100°C.

Mooney (*68*, *154*) established the elemental state of technetium by X-ray structural analysis at about the same time. The purity of technetium obtained by this method is not high, since the samples contain sulfur whose quantity depends on the temperature and time of the reduction.

When Tc_2S_7 is dissolved in a mixture of ammonia and hydrogen peroxide, ammonium pertechnetate, which is more convenient for the preparation of technetium metal, is formed in a mixture with ammonium sulfate. This mixture can be readily reduced at relatively low temperature first to the lower technetium oxides, and then to technetium metal (*92*).

Ammonium pertechnetate sublimates readily, and for this reason a loss of technetium can occur if the reaction mixture is heated rapidly. Therefore the reduction is carried out in two stages. In the first stage, heptavalent technetium is reduced with hydrogen to the relatively involatile TcO_2 by slowly raising the temperature to 200°–225°C for about 1 hour. In the second stage the temperature is raised to 600°–800°C, and TcO_2 is reduced to the metal in the course of 1 hour. Simultaneously, ammonium sulfate is removed by sublimation. Thus, 0.6 g of spectroscopically pure technetium was obtained (*92*). Similarly, 10 g of technetium metal with a negligible amount (less than 10^{-5} %) of Na, Mo, Mg, and Si impurities was obtained from pure ammonium pertechnetate (over 99 %) (*93*). The largest amount of technetium metal obtained by chemists to date has been about 100 g, according to published data.

Another good but still insufficiently proven method is the preparation of technetium by pyrolytic decomposition of $(NH_4)_2TcCl_6$ (*94*). In a nitrogen atmosphere at the temperature of red heat, this salt decomposes without melting, forming a fine silver-gray powder of technetium metal. The electrolysis of a technetium solution was used for the preliminary separation of technetium and for the purpose of obtaining it in the elemental state.

Electrolytic methods of obtaining technetium metal have not yet been sufficiently developed and do not give results as satisfactory as the method of reduction with hydrogen. Attempts to obtain technetium metal by electrolytic reduction at a platinum cathode were made by its discoverers in a study of the chemical properties of technetium (*11, 118*). However, instead of elemental technetium, products of its incomplete reduction were apparently obtained.

Studies of the electrodeposition of technetium have been made in recent years by Flagg and Bledner (*155*) and Boyd, Larson, and Motta (*115*). The latter showed that, in a 2 N solution of H_2SO_4 at 3–6 V, technetium deposits on a platinum cathode, and still better on a polished copper or nickel cathode. To exclude hydrogen overvoltage, fluoride ions were added to the solution. In this study, technetium formed an invisible microfilm on the surface of the electrodes. The yield did not exceed 60–70 %. It is necessary to keep the pH constant during the electrolysis, since in the absence of a buffer a brownish black precipitate or a colloid suspension of TcO_2 is formed.

Contamination with the dioxide appears to be a drawback in the electrolytic preparation of technetium that is difficult to eliminate. For this reason, after depositing technetium, Bainbridge *et al.* (*156*) reduced it further with hydrogen at 1000°C. Eakins and Humphries (*157*) deposited metallic technetium from its solution in 2 N H_2SO_4 on a copper and platinum cathode during the electrolysis of a 0.2 % solution of ammonium pertechnetate. The current density was 25–30 mA/cm^2. Only 25 % technetium was thus deposited as a film 5 mg/cm^2 thick. The remainder of the technetium was reduced to TcO_2 and remained in the electrolyte. A complete separation of technetium can be achieved by continually adding peroxide to the electrolyte in order to oxidize the technetium.

The authors found that the presence of fluoride ions does not improve the electrolysis.

Technetium is also quantitatively deposited on a mercury cathode, forming the corresponding amalgam. As was stated, metallic technetium can be obtained by reduction with metallic amalgamated zinc (*115*), but Schwochau and Herr (*134*) showed that a mixture of technetium metal and dioxide is apparently formed in the deposit at the same time. When the pertechnetate is reduced in an acid medium with a coarse-grained zinc powder, the content of the metal amounts to only 20 %. The oxygen content in technetium metal usually is not controlled, and therefore many samples of technetium obtained by reduction with hydrogen and particularly by electrolysis contain a certain amount of dioxide or oxygen dissolved in the metal. This is confirmed by the fact that, when technetium powders are fused in an inert gas atmosphere, 10–20 % of the original weight is lost (*158*). This loss is apparently accompanied by the sublimation of technetium dioxide. The presence of oxygen in technetium can appreciably distort its chemical and physical properties, as was shown, for example, by studies of the superconductivity of technetium (*77*). When technetium is used as a standard source of β-radiation, it is usually electrodeposited on metallic substrates. The presence of the dioxide may lead to a loss of technetium as a result of the oxidation of TcO_2 to Tc_2O_7 by atmospheric oxygen. Technetium deposited by electrolysis should therefore be reduced further with hydrogen.

K. TECHNETIUM ALLOYS

A considerable number of binary and ternary systems of technetium with various elements of the periodic system have now been investigated. Even before the experimental preparation and identification of the structure of technetium alloys, Ageev *et al.* (*159*) established the nature of the alloys formed by elements of the manganese subgroup with transition metals. Their hypothesis that the behavior of technetium in such alloys is similar to that of rhenium was partially confirmed by Compton (*160*), who identified the α-Mn phase in Zr–Tc and Nb–Tc alloys, similar to the α-Mn phase in the Zr–Re and Nb–Re systems. Compounds of the composition $ZrTc_6$ and $NbTc_3$ were identified at the same time.

TABLE XIX

BINARY TECHNETIUM ALLOYS

System	Phase	Composition of alloy (at.% Tc)	Compounds of technetium with second component	Lattice parameters (Å)
Sc–Tc	α-Mn	88.5	—	$a_0 = 9.509$
Ti–Tc	$MnZn_2$	66.7	—	$a_0 = 5.223$; $c_0 = 8.571$
Ti–Tc	α-Mn	87.5	—	$a_0 = 9.579$
	α-Mn	85.7	—	—
	CsCl	66.7	—	—
	CsCl	50	—	$a_0 = 3.110$
Zr–Tc	α-Mn	85.7	$ZrTc_6$	$a_0 = 9.637$
	$MgZn_2$	66.7	—	$a_0 = 5.219$; $c_0 = 8.655$
Hf–Tc	α-Mn	87.5	—	$a_0 = 9.603$
	α-Mn	85.7	—	—
	$MgZn_2$	66.7	—	—
	CsCl	50.0	—	$a_0 = 3.270$
V–Tc	*bbc*	10	—	—
	bbc	25	TcV_3	$a_0 = 3.026$
	bbc	30	—	—
	bbc	40	—	$a_0 = 3.024$
	CsCl	50	TcV	$a_0 = 3.023$
	bbc	60	—	$a_0 = 3.034$
	bbc + *hcp*	75	—	—
	hcp	95	—	—
Nb–Tc	*bcc*	5	—	—
	bcc	10	—	$a_0 = 3.276$
	bcc	20	—	$a_0 = 3.244$
	bcc	30	—	$a_0 = 3.217$
	bcc	40	—	$a_0 = 3.192$
	bcc	50	—	$a_0 = 3.170$
	bcc + α-Mn	60	—	—
	α-Mn	75	$NbTc_3$	$a_0 = 9.547$
	α-Mn	85	—	—
	hcp	97	—	—
	hcp	(100)	—	$a_0 = 2.743$; $c_0 = 4.400$
Ta–Tc	α-Mn	83.4	—	$a_0 = 9.565$
	α-Mn	80.0	—	—
	CsCl	50.0	—	$a_0 = 3.172$
Cr–Tc	σ	75	—	$a_0 = 9.290$; $c_0 = 4.846$
	σ	60	—	$a_0 = 9.217$; $c_0 = 4.803$
Mo–Tc	σ-βTc	75	—	—
	σ	70	—	$a_0 = 9.509$; $c_0 = 4.945$
	Cr_3O	60	—	$a_0 = 4.934$

TABLE XIX—*cont.*

BINARY TECHNETIUM ALLOYS

System	Phase	Composition of alloy (at. % Tc)	Compounds of technetium with second component	Lattice parameters (Å)
	Cr_3O	56	—	$a_0 = 4.931$
	Cr_3O	53	—	$a_0 = 4.942$
W–Tc	σ	75	—	$a_0 = 9.479$; $b_0 = 5.166$
Mn–Tc	σ	60	—	$a_0 = 9.15$; $c_0 = 4.80$
Fe–Tc	σ	60	—	$a_0 = 9.130$; $c_0 = 4.788$
	σ	50	—	$a_0 = 9.077$; $c_0 = 4.756$
	σ	40	—	$a_0 = 9.010$; $c_0 = 4.713$
Al–Tc	Ni_2Al_3	—	Tc_2Al_3	$a_0 = 4.16$; $c_0 = 5.13$
	Monoclinic	—	$TcAl_4$	$a_0 = 5.1$; $b_0 = 17.0$ $c_0 = 5.1$; $\beta_0 = 100°$
	$MnAl_6$	—	$TcAl_6$	$a_0 = 5.58$; $b_0 = 7.63$; $c_0 = 9.00$
	WAl_{12}	—	$TcAl_{12}$	$a_0 = 7.527$
Zn–Tc	—	—	Zn_2Tc_{11}	—
P.3–Tc	$MgZn_2$	—	$GdTc_2$	$a_0 = 5.397$; $c_0 = 8.883$
	$MgZn_2$	—	$TbTc_2$	$a_0 = 5.375$; $c_0 = 8.843$
	$MgZn_2$	—	$DyTc_2$	$a_0 = 5.365$; $c_0 = 8.830$
	$MgZn_2$	—	$HoTc_2$	$a_0 = 5.353$; $c_0 = 8.813$
	$MgZn_2$	—	$ErTc_2$	$a_0 = 5.340$; $c_0 = 8.792$
	$MgZn_2$	—	$TuTc_2$	$a_0 = 5.334$; $c_0 = 8.775$
	$MgZn_2$	—	$LuTc_2$	$a_0 = 5.309$; $c_0 = 8.847$
	$MgZn_2$	—	YTc_2	$a_0 = 5.373$; $c_0 = 8.847$

Compounds of this type together with technetium-molybdenum alloys (*78*, *161*) are superconductive at relatively high critical temperatures (9.7°K for $ZrTc_6$ and 10.5°K for $NbTc_3$). These critical temperatures of technetium alloys are considerably higher than those of analogous rhenium alloys. Particularly high is the critical temperature of a technetium-molybdenum alloy (40 % Tc), which is 15°K according to Compton (*160*) and 13.4 ± 0.3°K according to Darby and Zegler (*78*). Van Ostenberg *et al.* (*162*) and Morin and Maita (*163*) measured the nuclear magnetic resonance, magnetic susceptibility, and specific heat of the transition to the superconductive state of alloys of technetium with molybdenum and niobium. In the alloys with niobium, they found phases corresponding to crystal structures of *bcc* and α-Mn type. A similar study of several binary systems including technetium and transition metals was made by Darby *et al.* (*158*). Technetium and other components of high purity were used to prepare the alloys. The small amounts of technetium at the disposal of the researchers did not permit an accurate determination of the limits of existence of the intermediate phases, but they were able to evaluate the structural types, lattice parameters, and approximate regions of existence of the phases (Table XIX). This study established that the Tc–Re, Tc–Ru, and Tc–Os alloys are characterized by a continuous series of solid solutions. In alloys with Sc, Ti, Zr, Hf, Nb, and Ta, an x phase isostructural with the α-Mn phase was found. In these alloys, this phase is stabilized by the second component only if the atomic radius of the latter is greater than the radius of the technetium atom, and the concentration of the stabilizing element depends on its position in the periodic system relative to technetium.

In contrast to the data of Mattias (*161*), who proposed the formation of solid solutions in the Mo–Tc system, the formation of intermediate phases is more probable (see Table XIX). The presence of the Cr_3O phase at a molybdenum content of about 46 at.% is the only exception of its kind to the stoichiometry of A_3B type usual in such cases. The presence of a CsCl-type phase in certain alloys distinguishes technetium from rhenium, where such structures are unknown for binary systems. The behavior of technetium during the formation of the σ phase also distinguishes it from rhenium and manganese.

Manganese and rhenium form σ phases in alloys with elements of the vanadium and chromium group, while technetium forms them only with elements of the chromium group. In this respect, technetium resembles ruthenium. On the contrary, when the average concentrations of technetium and rhenium in the σ phases are compared, similarities in behavior are observed. The Tc–Fe system was studied by Buckley and Hume-Rothery (*164*) up to a 15 at.% technetium content of the alloy. According to the data of radioautographic studies, technetium is evenly distributed, i.e., a true fusion takes place. The addition of technetium to iron causes a very slight rise of the melting point of the alloy and a lowering of the transition temperature. The slight slopes of the δ-liquidus curves in the Tc–Fe system characterize technetium as a very weak stabilizer. In the technetium-aluminum system (*165, 166*) a large number of phases are observed, whose composition and lattice parameters are given in Table XIX.

Van Ostenberg *et al.* (*167*) studied the magnetic susceptibility of alloys of technetium with vanadium. In another study (*168*), they determined the nuclear magnetic resonance of technetium-vanadium alloys and measured the Knight shift. The TcV and TcV_3 phases were observed in Tc–V alloys, and their crystal structure was thoroughly studied. In the Tc–V system, stable solid solutions of *bbc* type exist in the range of technetium concentrations up to 60 at.%, and approximately 10 at.% vanadium dissolves in technetium. In the concentration interval between 60 and 90 at.% technetium, two solid solutions exist. The CsCl structure is observed at equivalent quantities of the two elements.

The solubility of technetium in zinc at 750°C was studied (*169*), and the Zn_2Tc_{11} phase was found in technetium-zinc alloys (*170*). Alloys of technetium with rare earth elements having an $MgZn_2$ structure were obtained (*171*). The solubility of technetium in nickel (*156*) and mercury with the formation of the corresponding amalgams (*157*) is well known. By analogy with rhenium, alloys of technetium with Co, Pd, Pt, W, and other elements should also be expected. In addition to binary systems, certain ternary systems containing technetium are known. For example, the thermodynamic properties of the U–C–Tc system (*172*) were determined, and the Knight shift was measured for the V–Al–Tc system (*167*) in the *bbc* region. To explain the effect of technetium on the structure of alloys of uranium and fission products, alloys containing 10 wt.% of elements entering into the composition of the fission products (Zr, Nb, Mo, Tc, Ru, Rh, Pd) were studied (*173*). Technetium has a pronounced effect on the stabilization of the γ region. However, a comparison of the curves representing the change in hardness with the time and temperature of annealing showed that the effect of technetium on the properties of the alloy can be neglected. Some technetium alloys may be of major importance in nuclear power engineering, catalytic processes, high-temperature electrophysical investigations, and as anticorrosion coatings.

L. THERMODYNAMIC CONSTANTS OF TECHNETIUM AND ITS COMPOUNDS

The thermodynamic properties of technetium and its compounds have been studied very inadequately. The main reason for this is the difficulty of obtaining them in pure form and the instability of many of them in aqueous solutions.

Tables XX–XXII list the data that we have collected on the heat of formation, entropy, and heat of transition of certain technetium compounds.

A brief survey of the chemical properties of technetium shows that its chemistry has been insufficiently studied. For example, only two technetium oxides, Tc_2O_7 and TcO_2, are known. The existence of the remaining ones is indicated only by indirect data obtained from mass-spectrometric study of fragments arising from the electron bombardment of NH_4TcO_4. Incomplete and sometimes contradictory data are also encountered in connection with the description of halogen, oxy-

TABLE XX

HEAT OF FORMATION OF TECHNETIUM AND SOME OF ITS COMPOUNDS AT 298.16°K (*91*)

Compound	State	Heat of formation H° (kcal/mole)
Tc	Crystalline	0.0
TcO_2	Crystalline	103.7 ± 2.0
TcO_3	Crystalline	129.0 ± 5.0
Tc_2O_7	Crystalline	266.1 ± 2.6
$HTcO_4$	Crystalline	167.4 ± 1.3
TcO_4^-—aq	In solution	173.0 ± 1.3
$KTcO_4$	Crystalline	242.5 ± 1.5

TABLE XXI

ENTROPY AT 298.16°K (*91*)

Compound	State	Entropy S° (cal/deg mole)
Tc	Crystalline	7.4 ± 0.2
	Gaseous	43.26 ± 0.01
TcO_2	Crystalline	14.9 ± 0.5
TcO_3	Crystalline	17.3 ± 0.6
Tc_2O_7	Crystalline	45.8 ± 2.0
$HTcO_4$	Crystalline	33.3 ± 2.0
TcO_4^-—aq	In solution	46.0 ± 0.1
$KTcO_4$	Crystalline	39.7 ± 0.1
K_2TcCl_6	Crystalline	79.5 ± 1.0

TABLE XXII

HEATS OF TRANSITION (*98, 99, 124*)

Compound	Nature of transition	Heat of transition (kcal/mole)
Tc_2O_7	Solution	11.6 ± 0.08
	Fusion	16.6 ± 0.5
	Vaporization	16.3 ± 0.2
	Sublimation	32.95
TcO_3F	Fusion	5.377
	Vaporization	9.453
	Sublimation	14.832

halogen, complex, organometallic, and other compounds of technetium. This situation has apparently developed not only because the study of technetium in the lower oxidation states is difficult owing to their instability, but also because many investigators worked with trace quantities of technetium.

It may be assumed that the development of nuclear technology will make available weighable quantities of technetium to many researchers, resulting in a more complete study of the chemical properties of this interesting element. Table XXIII lists the best known compounds of technetium.

TABLE XXIII

COMPOUNDS OF TECHNETIUM

Oxidation state	Compounds
Tc^{7+}	Tc_2O_7, $HTcO_4$, Tc_2S_7, TcO_3F, TcO_3Cl, $MeTcO_4$, where $Me = K^+$, NH_4^+, Cs^+, Na^+, Rb^+, Li^+, Ag^+, Tl^+, $(C_6H_5)_4As^+$, etc.
Tc^{6+}	TcF_6, $TcCl_6$, $TcOF_4$
Tc^{5+}	TcF_5, $TcOCl_3$, $TcOBr_3$, $NaTcF_6$, $KTcF_6$, $[Tc(\text{diarsine})_2Cl_4]Cl$
Tc^{4+}	TcO_2, TcS_2, $TcCl_4$, Me_2TcX_6 ($Me = Na^-$, K^-, and $X = Cl^-$, Br^-, I^-, F^-), $[Tc(OH)_3(CN)_4]Tl_3$
Tc^{3+}	$[Tc(\text{diarsine})_2X_2]X$, where $X = Cl^-$, Br^-, I^-
Tc^{2+}	$[Tc(\text{diarsine})_2X_2]$, where $X = Cl^-$, Br^-, I^-
Tc^+	$K_5Tc(CN)_6$, $Tc(CO)_5X$, $[Tc(CO)_4X]_2$, where $X = Cl^-$, Br^-, I^-
Tc	$Tc_2(CO)_{10}$

IV. Methods of Isolating Technetium

A. DISSOLUTION OF SAMPLES CONTAINING TECHNETIUM

Technetium is obtained at the present time, either from nuclear fuel-processing waste or from molybdenum targets irradiated with neutrons in a reactor and with deuterons or protons in a cyclotron. Depending upon the composition of the raw material containing technetium, various methods for its processing are used. To concentrate technetium and separate it from the accompanying elements, use is made of distillation, precipitation, extraction, chromatography, etc.

In dissolving samples containing technetium, two precautions should be taken. First, acid solutions can be heated only with a reflux condenser to prevent the loss of technetium in the form of volatile compounds. Second, the dissolution should take place only in a strongly oxidizing medium in order to convert all the technetium compounds of lower valences to the TcO_4^- ion.

The molybdenum targets used for preparing technetium by reactions of the type (n,γ), (d,n), (p,γ) can be dissolved in nitric acid or aqua regia, but in both cases the excess acid hinders the subsequent operations. For this reason, the dissolution is best carried out in concentrated sulfuric acid followed by neutralization of technetium with hydrogen peroxide and oxidation. Samples of natural minerals (molybdenite, yttrotantalite, etc.) are dissolved by first fusing them with a mixture of sodium hydroxide and sodium peroxide.

B. DISTILLATION

Because of the high vapor pressure of Tc_2O_7, technetium can be distilled with acids. This process has been discussed in great detail by Boyd *et al.* (*115*). Figure 7 shows the results of their investigation. All the acids can be subdivided into three groups: acids with which technetium does not distill (HCl, HBr, HI), acids with which the distillation of technetium is incomplete and becomes appreciable only after over half the acid has been distilled off (HNO_3, aqua regia, H_2SO_4), and acid with which technetium distills off completely, 75 % thereof being distilled off with the first 20 % of the distillate ($HClO_4$). Perchloric acid makes it possible not only to distill technetium in a good yield, but also to separate it partially from rhenium (*114*, *174*, *175*). In the presence of ruthenium, $HClO_4$ also oxidizes the latter to the volatile RuO_4, so that a further

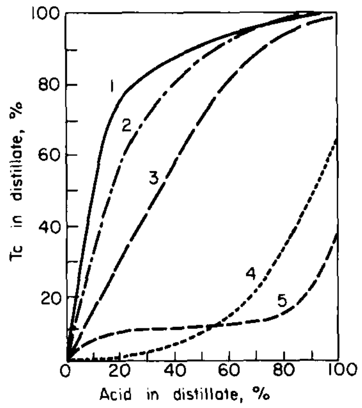


FIG. 7. Distillation of technetium with various acids: (1) $HClO_4$, (2) $H_2SO_4 + K_2Cr_2O_7$, (3) $H_2SO_4 + Na_2S_2O_8$, (4) H_2SO_4, (5) HNO_3.

separation of technetium from ruthenium is required. Molybdenum is likewise partially distilled if it is not bound in a complex with phosphoric acid (*156*, *176*).

Distillation from sulfuric acid can produce a good separation of technetium from ruthenium (degree of purification about 10^5), but the distillation of technetium is incomplete, probably because it is partly reduced by its impurities (*115*). The addition of oxidants (Ce^{4+}, $Cr_2O_7^{2-}$, $Na_2S_2O_8$, KIO_4, $KBrO_3$) increases the amount of distillable technetium, but under these conditions the distillation of RuO_4 also takes place.

The sublimation methods of isolating technetium are also based on the volatility of Tc_2O_7. Thus, technetium can be isolated from irradiated MoO_3 by fractional sublimation at 300°C (*11*). Quite recently a brief report was published concerning a new, very promising method of isolating technetium from spent nuclear fuel (*177*). In the course of its regeneration by the fluorination method, technetium hexafluoride TcF_6 is apparently formed (m.p. 33.4°, b.p. 55.3°) and is trapped by a magnesium fluoride packing.

C. PRECIPITATION

The most common method is the isolation of technetium in the form of the insoluble sulfide Tc_2S_7. This method can be used to precipitate technetium with hydrogen sulfide from 4 *M* H_2SO_4 or HCl when it is present in concentrations of no less than 3 mg/liter (*116*, *178*). At a lower concentration, it is necessary to use carriers; Pt, Re, Cu, Mn, and certain other elements can be employed. A detailed study of the process of coprecipitation has been made by several authors (*11*, *62*, *117*, *178*, *179*). Instead of hydrogen sulfide, thioacetamide (*100*) or sodium thiosulfate (*117*) can be successfully used to precipitate technetium. Many elements of the periodic system are precipitated under the same conditions, so that this method is more suitable for concentrating technetium than for purifying it. Technetium in the lower valence states is not precipitated by H_2S in the presence of concentrated hydrochloric acid; this can be utilized to separate Tc from Re.

In addition to the sulfide, technetium can be precipitated in the form of the pertechnetate ion, which forms poorly soluble salts with the cations Tl^+, Ag^+, Cs^+, $(C_6H_5)_4As^+$, and nitron. Anions of the type YX_4^-, (ReO_4^-, ClO_4^-, IO_4^-, BF_4^-) can be used as carriers (*117*, *174*, *180*).

The coprecipitation with $[(C_6H_5)_4As]ReO_4$ is probably the fastest method of isolating technetium, for example, in extracting Tc^{102} (half-life 5 seconds) from Mo^{102} (half-life 11.5 minutes). Flegenheimer (*61*) precipitated and filtered a sample in 5–6 seconds. From the organic precipitate, technetium can be isolated by wet combustion, electrolysis in concentrated sulfuric acid, or passage of an alcohol solution through an ion-exchange resin in the chloride form. The TcO_4^- ion is adsorbed by the resin and can be eluted off with an $HClO_4$ solution (*91*, *92*).

D. CHROMATOGRAPHY

The pertechnetate ion is very strongly adsorbed by most anion-exchange resins (*178–182*) and can be eluted off only by ions having a high affinity for the resin, such as the perchlorate or salicylate ion. The perrhenate ion is firmly held by the resins, almost to the same degree as the pertechnetate ion. The ratio of the distribution coefficients of TcO_4^- and ReO_4^- ranges from 1.6 to 2, i.e., is almost the same as that of rare earth elements. Hence, their separation requires long columns and much time.

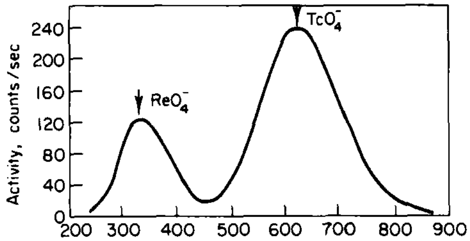


FIG. 8. Chromatographic separation of TcO_4^- and ReO_4^- on Dowex-2 anion exchanger. Volume of eluting solution (cm^3) plotted along abscissa.

Atterby and Boyd (*183*) separated technetium from rhenium on a Dowex-2 resin in the sulfate form by using a solution of ammonium sulfate and thiocyanate at pH 8.3–8.5 as the eluent. The separation was not sufficiently distinct, since the peaks of TcO_4^- and ReO_4^- partially overlapped. There is evidence that better results are obtained by using the perchlorate ion as the eluent (*19*, *21*, *28*, *184*). Owing to certain characteristics of industrial resins, the separation factor that can be obtained practically is not more than 10^4–10^5. Figure 8 shows the result of a chromatographic separation of TcO_4^- from ReO_4^- on a Dowex-2 resin. A 0.1 M NH_4ClO_4 solution was used as the eluent.

MoO_4^{2-} ions are also adsorbed by ion-exchange resins, but can be washed off with a solution of sodium hydroxide (*21*, *185*), oxalate (*186*), or hydrochloric acid (*187*). In the latter two cases, there is danger of reducing the heptavalent technetium.

A 4 N HNO_3 solution can also be used for the elution (*182*, *188*, *189*). However, the drawback of this method is that the subsequent isolation of technetium is hindered, since the evaporation can cause its loss.

Nelson *et al.* (*190*) studied the adsorption of technetium and rhenium from concentrated 9 *M* solutions of HCl and $HClO_4$ on a Dowex-50-X4 resin. The adsorption of technetium is very slight under these conditions if an oxidant is present in the solution. In a 9 *M* $HClO_4$ solution, in the absence of an oxidant, technetium was apparently adsorbed in the form of its reduced species (*190*).

Nikitin (*191*) studied the possibility of a group separation of elements in solutions of hydrofluoric acid on an AB-17 anion exchanger. After the adsorption of the elements from a 1 *M* HF solution, followed by washing the column with hydrofluoric acid of increasing concentration, technetium was washed out with 20 *M* HF in the fraction containing Ti, Zr, Pd, Sn, Hf, W, Ir, and Re.

An original method of chromatographic separation of molybdenum from technetium was worked out by Ryabchikov and Borisova (*192*). On a column with an EDE-10 anion exchanger (100–150 mesh) in the phosphate form was placed 0.1–0.2 cm^3 of a sodium molybdate solution containing daughter Tc^{99m}. Five to ten minutes after the Tc^{99m} was charged, elution was carried out with a 2 *M* solution of phosphoric acid. According to the authors' report, all the technetium was washed out with the first portions of the eluent (30 cm^3). The column was then washed with water to a neutral reaction. Molybdenum was removed from the column with a 10% sodium hydroxide solution. The adsorption of technetium from a phosphoric acid solution on the resin was 4% (probably because of a partial reduction of heptavalent technetium), and that of molybdenum was 73%. This is explained by the fact that phosphoric acid displaces the TcO_4^- ions from the resin, and with MoO_4^{2-} ions forms the heteropoly acid $H_7[P(Mo_2O_7)_6]$, which is firmly held by the anion exchanger. When an alkali is passed through this acid is decomposed, and molybdenum is quantitatively washed out. To remove cation impurities from the technetium concentrate, use was made of the KU-2 resin (*65*, *193*).

Trace amounts of technetium can be removed from molybdenum and ruthenium by paper chromatography (*194–196*) and by paper electrophoresis (*197–199*). The separation of TcO_4^- and ReO_4^- ions was not observed in all the systems of solvents investigated, with the exception of some cases of selective reduction of heptavalent technetium to the lower oxidation states by hydrochloric acid (*196*), hydrazine, hydrobromic and hydriodic acids (*197*), or thiourea (*200*).

E. ELECTROCHEMICAL METHODS

Technetium can be recovered from solution electrochemically. According to Rogers (*101*), at a cathodic potential of −1.1 V relative to the saturated calomel electrode in 2 *N* NaOH, black technetium dioxide separates. If the technetium concentration in the solution is less than 10^{-4} mole/liter, it deposits as a thin film on the cathode. Under these conditions of electrolysis, molybdenum and rhenium are partially removed from the technetium.

Flagg and Bledner (*155*) deposited technetium from a dilute solution of sulfuric acid (pH 2.36) on a platinum cathode at a potential of 0.8 V (relative to the saturated calomel electrode). During the electrolysis, they obtained a 99.5% yield of deposited technetium in 65 minutes.

Boyd *et al.* (*115*) studied the process of electrochemical deposition of technetium in more detail. They found that the optimum results are obtained at pH 5.5 in the presence of about 10^{-3} mole of F^- ions and by replacing platinum cathodes with copper ones. At a current density of 100 mA/cm^2 during the first two hours, $84.5 \pm 1.5\%$ technetium was deposited. In 2 *N* H_2SO_4, technetium deposits as the metal (*91*, *157*), and, at lower concentrations of the acid, as the dioxide.

To deposit Tc^{99m} from irradiated molybdenum, methods have been proposed that are based on electrochemical deposition in nonaqueous solutions, particularly from ether solutions of $MoCl_2$ or molybdenum hydroxyquinolate (*201*, *202*).

F. EXTRACTIVE METHODS OF ISOLATING TECHNETIUM

In view of the general advantages of extraction over other methods of isolating technetium, this method is particularly widely used for this purpose. This is also due to the fact that certain solvents (acetone, methylethyl ketone, pyridine) are practically selective toward technetium. The extractive behavior of technetium has been treated in many studies, the most important of which are those of Gerlit (*117*) and Boyd and Larson (*203*).

Technetium is extracted with an organic solvent in the form of pertechnetates or in lower oxidation states in the form of complex compounds. The TcO_4^- ion can be bound to various large organic cations or bases, for example tetraphenylarsonium $(C_6H_5)_4As^+$, triphenylguanidine, methylcapryl chloride, quinoline (*204*), trilaurylamine, nitron, and apparently cupferron (*205–209*), although the composition of technetium cupferronate has not been established. The pertechnetate of the corresponding cation formed has a high affinity for organic solvents and is readily extracted by them from aqueous solutions.

The isolation of technetium in the form of tetraphenylarsonium pertechnetate has met with the most widespread acceptance. The equilibrium constant of the reaction

$$[(C_6H_5)_4As]^+ + TcO_4^- \rightleftarrows [(C_6H_5)_4AsTcO_4]_{org} \qquad \approx 3 \times 10^6$$

The analogous constant for the Cl^- ion is approximately 200. Tetraphenylarsonium pertechnetate is extracted with benzene, chloroform, or nitrobenzene. The latter produces a somewhat greater extraction (*39*). During the extraction, no separation from perrhenates and perchlorates occurs, but the removal of molybdenum, tungsten, and ruthenium in alkaline media is fairly extensive.

During the extraction, technetium is also associated with iodine and trivalent gold, which should be separated first. Reextraction of technetium into an aqueous phase is accomplished with a 0.2 N $HClO_4$ solution or a 12 N H_2SO_4 solution (*60*), or by reducing technetium to the lower oxidation states with an HCl solution of divalent chromium (*39*).

In addition to salts with organic cations, heptavalent technetium can be extracted in the form of technetic acid or its salts with inorganic cations. In this case, the extraction is based on the affinity of the TcO_4^- ion for the organic solvent, although the nature of the cation also plays an important part.

The general conclusions reached by Boyd, who studied the extraction of technetium with 75 solvents from acid, alkaline, and neutral media are as follows:

(a) The extraction of TcO_4^- ion by aliphatic, aromatic, and chlorohydrocarbon compounds is insignificant. Indeed, the slight extraction of technetium with chloroform (0.6–1.9%) observed (*209*) can be explained by the presence of water in the latter. An appreciable extraction requires the presence of a donor atom (oxygen, nitrogen).

(b) An increase in the dielectric constant favors the extraction.

(c) In homologous series, the extraction decreases with increasing hydrocarbon chains of molecules of the extracting agent.

(d) The extraction depends on the structure of the extracting agent. For instance, the distribution ratio of technetium increases from primary to tertiary alcohols, ketones, and amines. Quaternary amines and their salts have the highest distribution coefficient not only in acid but also in neutral and alkaline media. The presence of a ring in the alcohol or ketone molecule also increases the extraction.

Boyd suggests that strongly basic solvents such as amines extract technetium in the form of "onium" salts, whereas less basic solvents extract free $HTcO_4$ or pertechnetates. In acid media, the best extracting agents were found to be alcohols, ketones, and tributyl phosphate; in alkaline solutions, ketones and cyclic amines. An appreciable extraction of technetium from HNO_3, HBr, HCl, and H_2SO_4 solutions can also be achieved with ether (*79*, *209*, *210*). The distribution ratio of technetium in 1 M HNO_3 is 1.267. However, the best results are obtained by

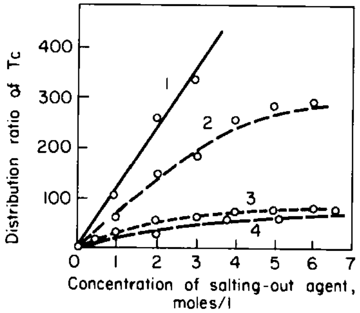


FIG. 9. Extraction of Tc^{99m} with methyl ethyl ketone with various salting-out agents: (1) Li_2SO_4, (2) K_2CO_3, (3) KOH, (4) $(NH_4)_2CO_3$.

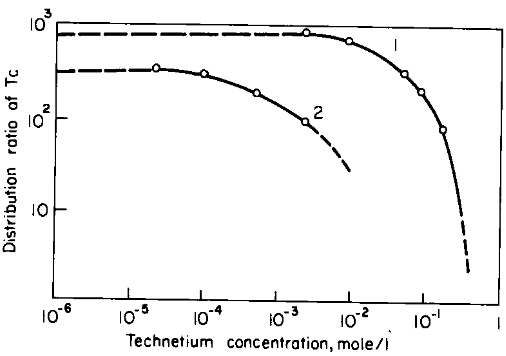


FIG. 10. Effect of technetium concentration on its extraction with acetone and pyridine from a 2 M solution of Na_2CO_3: (1) extraction with pyridine, (2) extraction with acetone.

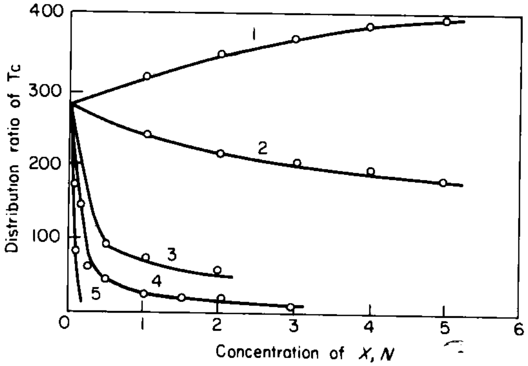


FIG. 11. Effect of extraneous anions on the extraction of Tc^{99m} with methyl ethyl ketone: (1) 2 M K_2CO_3 + x K_2MoO_4, (2) 2 M K_2CO_3 + x KOH, (3) 2 M K_2CO_3 + x KCl, (4) 2 M K_2CO_3 + x $NaNO_3$, (5) 2 M K_2CO_3 + x $KReO_4$.

extracting from alkaline media with acetone (*211*), methyl ethyl ketone (*66*, *117*), and pyridine (*93*, *212*) (Figs. 9–10).

As salting-out agents that raise the distribution ratio of technetium and prevent the phases from mixing, one can use strong solutions of alkalies or carbonates, and, for methyl ethyl ketone, the neutral salts Li_2SO_4, Na_2SO_4, Na_2MoO_4, etc. The distribution ratio increases in the series of cations $Li^+ > K^+ > Na^+ > NH_4^+$, linked to the hydroxyl group or the CO_3^{2-} or SO_4^{2-} group. An appreciable effect on the extraction of technetium is exerted by its concentration (see Fig. 10), which becomes important beginning at approximately 10^{-3} *M*.

Whereas the series of anions CO_3^{2-}, MoO_4^{2-}, SO_4^{2-} favors the extraction of technetium, the ions Cl^-, NO_3^-, CNS^-, CH_3COO^-, ReO_4^- (Fig. 11) sharply reduce the distribution coefficient of technetium, and do so at a relatively low content (for example, for ReO_4^-, about 10^{-3} *M*). The negative effect of nitrates is of great importance in the extractive recovery of technetium from fuel-processing wastes, where the content of nitrates is high. This effect can be avoided to some extent by replacing pyridine with its methyl derivatives (*93*, *213*). Apparently the compounds KNO_3, KCl, KOH, and NH_4OH, which have a slight solubility in these extracting agents that is comparable to the solubility of the pertechnetates, decrease their distribution ratio, whereas salts that are practically insoluble therein (K_2SO_4, K_2CO_3, K_2MoO_4) increase this ratio. The extraction from alkaline media is extremely selective, since most ions (OH^-, CO_3^{2-}, MoO_4^{2-}, SeO_3^{2-}, AsO_4^{2-}, WO_4^{2-}, Sb^{5+}, VO_3^-, etc.) have a distribution coefficient of less than 0.001. An exception is rhenium, whose extraction coefficient is very high. In extraction with acetone, methyl ethyl ketone, and pyridine, an effective removal of ruthenium also takes place (*66*, *93*, *117*, *214*).

A considerable number of studies have been devoted to the extractive recovery of technetium. Morgan and Sizeland (*179*) studied the extraction of TcO_4^- in hexane, butex, and other solvents; Tribalat used methyl isobutyl ketone and isoamyl alcohol (*213*, *215*); Kan used triisooctylamine and bis-2-ethylhexylorthophosphoric acid (*216*). Extraction with tributyl phosphate was studied in particular detail (*217*, *218*). Spitsyn *et al.* (*208*) established the formation of the compound $HTcO_4 \cdot 3TBP$. The extraction with tributyl phosphate together with the extraction with pyridine (*219*), methyl ethyl ketone (*66*, *220*), acetone (*211*), and trilaurylamine (*204*) is recommended for the technological recovery of technetium from fuel-processing wastes and irradiated molybdenum.

Reextraction of technetium into the aqueous phase was achieved by driving off the excess solvent, changing the pH or the oxidation state of technetium by displacement with other ions (nitrate, perchlorate), and diluting the extracting agent with a nonpolar solvent (*117*). In extracting heptavalent technetium, it is necessary to consider the possible reduction of technetium by the organic solvent or the impurities, and also the influence of extraneous radioactive radiation (*221*). Münze (*222*) explained the discrepancy in the data of various authors on the determination of the distribution coefficients of Tc^{99m} by the existence of lower valences that result from the β decay of the parent molybdenum.

In addition to technetic acid and its salts, use is made for analytical purposes of extraction of various complex compounds of technetium where the latter is selectively reduced to lower oxidation states (Table XXIV).

TABLE XXIV

EXTRACTABILITY OF COMPLEX COMPOUNDS OF TECHNETIUM

Complex-forming agent	Extracting agent	Reference
Thiocyanate	Alcohols, ethers, ketones; solution of trioctylphosphine oxide and trioctylamine chloride in cyclohexane with dichloroethane	(*91, 117, 128*)
p-Thiocresol	$CHCl_3$, CCl_4, ether, benzene, toluene	(*131*)
1,5-Diphenylcarbohydrazide	CCl_4	(*223*)
Potassium xanthate	$CHCl_3$, CCl_4	(*133*)
K_2TcCl_6	Solution of tetraphenylarsonium salt in chloroform, trioctylamine chloride in cyclohexane	(*60*)
α-Picolinic acid	Extracts partially with chloroform	(*129*)
Cupferron	Ether, $CHCl_3$	(*209*)
3-Toluene, 4-dithiol	CCl_4	(*224*)
Sulfosalicylic acid	Isoamyl alcohol, toluene, ether	(*129*)

G. SEPARATION OF TECHNETIUM FROM RHENIUM

Rhenium has been used as a nonisotopic carrier of its chemical analog technetium in the isolation and identification of the latter, and also in geochemical investigations. In the latter case, attempts to detect technetium in nature were undertaken in the case of minerals where the rhenium content was sufficiently high. The necessity of separating technetium from rhenium can also arise in the preparation of technetium from irradiated molybdenum (*225*). Despite the similarity in chemical properties of the two elements, several fairly effective methods for their separation have been elaborated. In most cases, these methods involve the separation of microquantities of technetium from macroquantities of rhenium.

1. *Distillation*

In the distillation from perchloric acid, a partial separation from rhenium takes place, and the first fractions of the distillate are rich in technetium (*114*, *174*, *175*). Owing to the great difference in vapor pressures of the higher oxides of technetium and rhenium, as in the first case, a certain separation of these elements can be achieved by a second alternate distillation with HNO_3 and HCl (*226*). However, neither method gives quantitative results, and almost no use is made of either in practice. When HCl is passed through concentrated sulfuric acid in which technetium and rhenium are dissolved, rhenium distills off as the chloride at 180°–200°C, while technetium is reduced and remains in the original solution (*118*). The separation factor reaches 50 (*179*). The distillation of technetium and rhenium in the form of chlorides in a stream of chlorine yields their mixture in the distillate. From the distillate, rhenium is driven off under vacuum at 300°C. Under these conditions, technetium chloride is reduced to the metal and is not distilled (*227*).

2. *Precipitation*

In contrast to rhenium, technetium is not precipitated by hydrogen sulfide at hydrochloric acid concentrations above 9 N. Multiple reprecipitation of rhenium sulfide that has occluded some technetium makes it possible to separate technetium from rhenium almost quantitatively (*225*). The difference in oxidizing capacity of technetium and rhenium is utilized for coprecipitating with ferric hydroxide technetium forms reduced with concentrated hydrochloric acid, while the rhenium remains in solution. The lower solubility of potassium perrhenate as compared to that of pertechnetate can be used for separating large amounts of the elements by fractional crystallization ($D = 0.1$) (*225*).

3. *Electrochemical Methods of Separation*

At a platinum cathode in a 2 M NaOH solution at a potential of −1.1 V, technetium is reduced to TcO_2 and separated from rhenium. The concentration of technetium should be no less than 10^{-4} N and much below the rhenium concentration (*101*). We have proposed (*228*) a method of separating technetium from rhenium by continuous electrophoresis on a porous filler. When a solution of TcO_4^- and ReO_4^- is treated with thiourea, a selective reduction of Tc^{7+} to Tc^{5+} takes place with the formation of a cationic complex of technetium with excess

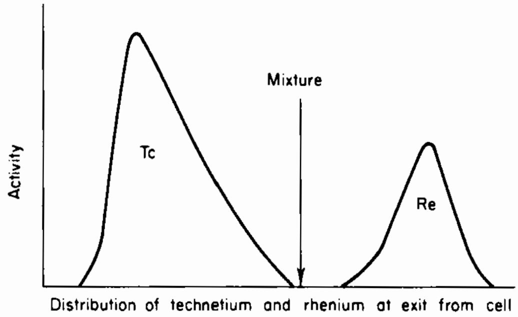


Fig. 12. Separation of technetium from rhenium by continuous electrophoresis.

reagent, while the rhenium remains in the form of the ReO_4^- anion. When the electric field is applied, a well-defined separation of technetium from rhenium occurs (Fig. 12).

4. *Separations Based on the Instability of Certain Compounds of Technetium and Rhenium*

Such methods include a separation based on the different stabilities of phthalocyanine complexes of technetium and rhenium (*18*), and a method based on the difference in hydrolyzing capacity of compounds of the type K_2TcCl_6 and K_2ReCl_6 (*91*).

5. *Extraction*

Although rhenium and technetium behave almost analogously during extraction, they are separated to some extent during extraction in the form of cupferronates (*209*). It is also possible to utilize the ability of technetium to form extractable complexes upon reduction with weak reductants.

6. *Chromatography*

These methods are the most efficient and ensure a separation factor of 10^4–10^5. Technetium and rhenium are precipitated in the form of pertechnetate and perrhenate on the anion exchanger Dowex-1 (*184*) or Dowex-2 (*183*); the elements are then successively eluted with ammonium sulfate in a mixture with thiocyanate (*183*) or perchlorate (*184*) ions.

H. Separation of Technetium from Ruthenium

When technetium is obtained from the fission fragments of uranium, in which the rhenium isotopes are practically absent, the separation of technetium from ruthenium involves major difficulties. This problem faced the researchers in the first studies of technetium, since some of its isotopes were obtained through the decay or irradiation of ruthenium.

In order to separate technetium and ruthenium, they were distilled from perchloric acid, ruthenium was reduced to the insoluble RuO_2 with alcohol (*174*), and this was followed by distillation from sulfuric acid. However, despite the relative complexity of the method, complete removal of ruthenium could not be achieved. Contamination of the technetium fraction with ruthenium ranged from 0.003% in the method of Hoffman and Lundell (*229*) to 3% in the method of Glendenin (*174*).

Subsequently, precipitation and extraction became the principal methods for separating technetium from ruthenium. The precipitants of technetium (with a rhenium carrier) used were nitron (*11, 117*) and tetraphenylarsonium chloride (*204*). The latter proved to be particularly effective, since it precipitated technetium but occluded practically no ruthenium. Analogous results are obtained in the extraction of tetraphenylarsonium pertechnetate with chloroform. In present-day schemes of isolating technetium from fission fragments, its separation from ruthenium is accomplished by a series of successive precipitations of rhenium on ferric hydroxide (*230*, *231*) and also by the extraction of technetium with pyridine, which does not extract ruthenium (*93, 214*). The complexity of the extractive separation of technetium from ruthenium is due to the presence of a large number of valence and ionic forms of ruthenium, many of which are capable of being extracted with technetium. However, in alkaline media, ruthenium is reduced by the organic solvent to lower valences and is not extracted.

The extraction of ruthenium can be accomplished only in the presence of an oxidant in the solution, for example, a hypochlorite (*61*, *214*). The extraction of technetium with methyl ethyl ketone (*66*, *117*), acetone (*211*), pyridine (*93*, *214*), and triphenylguanidine (*205*) makes it possible to obtain a ruthenium decontamination factor of 10^5 or higher. A poor separation was obtained by extraction with tributyl phosphate from fuel-processing wastes. Here the separation factor does not exceed a few hundred, and only in combination with ion exchange can it be raised to approximately 10^4 (*218*).

I. ISOLATION OF SHORT-LIVED TECHNETIUM ISOTOPES

Until recently, studies of the chemical properties of technetium involved the use of primarily its short-lived isotopes: Tc^{99m} ($T_{1/2} = 6.0$ hours), Tc^{95m} ($T_{1/2} = 60$ days), and Tc^{97m} ($T_{1/2} = 90$ days). Of these, Tc^{99m} is the most accessible and the most frequently employed. A large number of methods, which are partially listed in Anders' survey (*60*), have been developed for its isolation. Some that have found uses in the isolation of Tc^{99m} from Mo^{99} by the isotope generator technique are described below.

Successful operation of such a generator requires that the method of separation of technetium and molybdenum have a high separation factor, provide a high yield of technetium, and permit the repeated use of molybdenum with a minimum loss of the latter. Furthermore, the operations should be simple and rapid, the final solutions should be obtained in a form suitable for further use, and the processing of high-activity preparations should permit the automation of the processes and be safe. Extraction and chromatography are used for this purpose. Alkaline molybdate solutions are usually employed in the extraction, and the extracting agents can be acetone (*211*), methyl ethyl ketone (*66, 117*), and pyridine (*93, 212*).

Although of all these extracting agents pyridine yields the highest distribution ratio, acetone and methyl ethyl ketone are the most convenient in laboratory practice. This is due to the higher boiling point of pyridine and its unpleasant odor, whereas acetone and methyl ethyl ketone evaporate readily on moderate heating.

Irradiated molybdenum trioxide is dissolved in a calculated amount of alkali with a few drops of hydrogen peroxide. The excess alkali lowers the distribution ratio, but promotes a better layer separation. The salting-out agents, which sharply increase the distribution ratio of technetium during the extraction, are the molybdate itself and concentrated solutions of Na_2CO_3, K_2CO_3, and $(NH_4)_2CO_3$. The distribution ratio of technetium during extraction with methyl ethyl ketone from a 3 *M* solution of K_2CO_3 is about 300, whereas for molybdenum and practically all other radioactive impurities it is $2–5 \times 10^{-4}$. Sulfates, particularly lithium sulfate, are equally effective salting-out agents. The salting-out agent is added to the molybdate solution in a quantity such that its concentration in the final solution is of the order of 2–3 moles/liter. The volume of the solution is chosen in accordance with the apparatus employed.

The extraction is carried out in separatory funnels, and, in the case of high activities, in automatic laboratory-type extractors. A certain amount of mechanically occluded molybdenum and other impurities may be present in the organic phase. They are removed by washing the organic phase with small portions of K_2CO_3 or $(NH_3)_2CO_3$. Ammonium carbonate decreases the amount of mineral salts in the technetium solution, since it decomposes on subsequent distillation of methyl ethyl ketone. After the distillation of methyl ethyl ketone, a final solution of potassium or ammonium pertechnetate "without carrier" is obtained. The purity of Tc^{99m} is controlled by means of the half-life and reaches over 99.99 %. The yield is about 99.9 %. Practically no molybdenum is lost during the extraction, and its solution can be used many times. Only the water partially carried away with the organic solvent must be replaced. Similar results are obtained by extracting technetium with acetone, for which the distribution ratio reaches a relatively high value. However, its drawback is the extraction of a certain quantity of alkali and mixing with the solutions of neutral salting-out agents.

In addition to extraction, chromatographic methods have also been commonly adopted for the separation of technetium from molybdenum. As an example, let us discuss the isolation of Tc^{99m} by Tucker, Greene, and Murrenhoff (*232*). Uranium metal or uranium oxide containing the fission products is dissolved in nitric acid. The solution, diluted to a nitric acid concentration of 2–3 M, is passed through a chromatographic column containing alumina. Iodine, tellurium, and molybdenum are adsorbed from acid solutions, but the remaining fission products are not retained by the column. The column is washed with nitric acid, water, and a weak solution of ammonia to remove I^{131}. Molybdenum is isolated by passing a 1 M solution of ammonia through the column. The solution of ammonium pertechnetate obtained is acidified with nitric acid to pH 1–2, and Mo^{99} is readsorbed on alumina pretreated with nitric acid.

The column with Al_2O_3 is washed with a 0.1 M HNO_3 solution as Tc^{99m} accumulates, and the latter is washed out with small portions of 0.1 M HNO_3. The yield of technetium is about 80 %, and its radiochemical purity is approximately 99.99 %. This relatively simple and efficient method of obtaining technetium is applicable not only to fragment Mo^{99}, but also to irradiated samples of natural molybdenum. Instead of a simple glass column used with activities of the order of a few curies, use is made of a more complex apparatus with remote control and pneumatic supply to the solutions. A drawback of all chromatographic methods as compared to extractive ones is the considerable content, in the final solutions, of mineral substances that hinder the further use of Tc^{99m}. For medical purposes therefore, where a neutral solution of technetium with a minimum content of extraneous salts is required, Scheer and Maier-Borst (*233*) have slightly modified the technique of Tucker and Greene. From irradiated molybdenum adsorbed on alumina, they washed out Tc^{99m} with 0.2 N H_2SO_4 solution. Subsequently, the precipitation of the SO_4^{2-} ion and neutralization of the solution were carried out with barium hydroxide.

Still better results are obtained by washing out the technetium with acetone or pyridine. Potassium molybdate precipitated on activated alumina does not dissolve in acetone and remains on the column, whereas the soluble pertechnetate is quantitatively washed out with acetone.

After the acetone has been driven off, a neutral solution from which extraneous salts have been removed and containing Tc^{99m} is obtained. Obviously, alumina is not the only adsorbent for Mo^{99}. Thus, Nelson and Kraus (*234*) used zirconium hydroxide for this purpose and washed Tc^{99m} out with 2 *M* HNO_3. Ryabchikov and Borisova (*192*) used EDS-10P resin in the phosphate form. Technetium was washed out of the resin with 2 *M* H_3PO_4 solution. An original method of isolating Tc^{99m} was developed by Nefedov and Toropova (*235*). It is based on the fact that the β decay of Mo^{99} leads to the formation of daughter Tc^{99m}, which as a result of the rupture of chemical bonds is in a form substantially different from the parent substance. As a result, from a chloroform solution of irradiated molybdenum hexacarbonyl $Mo^{99}(CO)_6$, extraction with water can quantitatively separate radiochemically pure Tc^{99m}

Molybdenum hexacarbonyl (*54*) and molybdenum dicyclopentadienyltricarbonyl $[C_5H_5Mo^{99}(CO)_3]_2$ can also be used to isolate Tc^{99m} by distillation (*147*). A drawback of these methods is the complexity of preparation and the relatively low radiation stability of the carbonyl compounds of molybdenum. The other short-lived technetium isotopes used in practice, Tc^{95m} and Tc^{97m}, can be separated from irradiated molybdenum only once, since they are formed directly by nuclear reactions with molybdenum and have no radioactive precursors. The methods described above are completely suited for their isolation.

J. ISOLATION OF Tc^{99} FROM IRRADIATED MOLYBDENUM

There are two ways of isolating the main long-lived isotope, Tc^{99}: extraction from fission fragments of uranium or plutonium present in the waste waters of plants processing nuclear fuel, and irradiation of natural molybdenum with neutrons in a nuclear reactor. Since the cross section of the reaction $Mo^{98}(n,\gamma)Mo^{99}$ is small, the formation of appreciable amounts of technetium requires long periods of time and the irradiation of kilogram quantities of molybdenum.

The method of isolating technetium from irradiated molybdenum cannot compete with its separation from fission fragments, since the cost of the technetium thus obtained is considerably higher (by a factor of several thousand). However, at the time when the methods of isolating technetium from fission fragments had not been sufficiently developed, both methods were used to the same extent. Owing to the extremely simple technological processing of irradiated molybdenum, primarily molybdic trioxide, this method has not yet been completely abandoned (*236*). If the decay and burn-up of the technetium formed are neglected, its accumulation resulting from the irradiation of molybdenum by neutrons is described by the equation

$$N = 3.5 \times 10^{-18}\, P\Phi t \text{ mg Tc}^{99} \text{ for metallic Mo} \quad (3)$$

$$N = 1.85 \times 10^{-18}\, P\Phi t \text{ mg Tc}^{99} \text{ for MoO}_3 \quad (4)$$

where N is the amount of Tc^{99} at the end of the irradiation (mg), P is the weight of the irradiated molybdenum or MoO_3 (g), and Φt is the integrated neutron flux.

Thus, the irradiation of 1 kg of molybdic trioxide in a flux of 10^{13} n/(cm^2 sec) for 1 year forms about 7 mg of technetium. Usually, molybdic trioxide is irradiated; despite its lower content of molybdenum atoms (lower by a factor of 5) per unit volume it considerably simplifies the subsequent processing. Since the separation of technetium and rhenium is a relatively difficult problem, prior to the irradiation it is necessary to select a raw material free from rhenium or take special steps to purify it.

Irradiated molybdic trioxide or metallic molybdenum is left standing for 1 month to allow the transmutation of all Mo^{99} into technetium and the decay of short-lived impurities. Even pure molybdic trioxide is fairly radioactive as a result of activation of the impurities, and for this reason its processing requires special protective measures. The radioactive impurities may include Co^{60}, Fe^{59}, Zn^{65}, W^{187}, Sb^{124}, Zr^{95}, etc. (*237*). Subsequent treatment of irradiated molybdenum is carried out by various methods.

Boyd *et al.* (*225*) irradiated 5.7 kg of metallic molybdenum in a reactor in the course of 1 year. The irradiated molybdenum was dissolved in sulfuric acid with simultaneous distillation of technetium. The sulfuric acid solution of technetium obtained was diluted to 4 M H_2SO_4 and treated with bromine water. A platinum salt was added to the solution as the carrier, and platinum sulfide, which occludes technetium, was precipitated with hydrogen sulfide. The sulfide precipitate was dissolved in ammoniacal hydrogen peroxide. The solution obtained was evaporated off, and technetium was separated from the platinum and ammonium sulfate by distillation from $HClO_4$ or H_2SO_4. Since the initial molybdenum contained a certain amount (3×10^{-5} mole) of rhenium, which was concentrated together with technetium, the two metals were separated by distillation and chromatography. The total yield was 30–60% of the initial technetium.

The processing of molybdic trioxide begins with its dissolution in alkali with the addition of a small amount of hydrogen peroxide. The dissolution is sometimes preceded by treatment of the MoO_3 with nitric acid to oxidize the technetium, but the presence of nitrates may subsequently decrease the extraction, which together with precipitation is used for the isolation of technetium.

Spitsyn and Kuzina (*65*, *238*) coprecipitated technetium on magnesium hydrogen phosphate or magnesium ammonium phosphate. To this end, a solution of molybdate at pH 7.5–8 was mixed with magnesium hydrogen phosphate for 3 hours. After three to four adsorption operations, most of the technetium was successfully removed with the precipitate from the solution. The precipitates obtained were dissolved in 6–12 M HCl, and hydrogen sulfide was passed through the solution to reduce the technetium. Since the hydrogen phosphate precipitate occludes only Tc^{7+}, during the subsequent precipitation of magnesium ammonium phosphate with ammonia the bulk of the technetium remained in solution. The solution containing technetium was filtered off, evaporated, and the residue dissolved in nitric acid. The nitric acid solution at pH 2 was passed through a KU-2 cation-exchange resin to separate the impurities. The filtrate was evaporated off and heated to decompose ammonium nitrate. The residue was treated with a mixture of hydrogen peroxide and ammonia and dried. The ammonium pertechnetate obtained was acidified with hydrochloric acid, and technetium sulfide was precipitated from the solution. Use of this method produced about 0.5 mg of technetium from 200 g of MoO_3.

The best methods of isolating technetium from irradiated molybdenum are the extractive ones. Faddeeva *et al.* (*66*) quantitatively isolated about 1 mg of technetium by using methyl ethyl ketone.

The extraction of technetium with acetone from alkaline media, proposed by Kuzina *et al.* (*211*), has proven to be the most efficient method of separating technetium from irradiated molybdenum. In the presence of Na_2MoO_4 and NaOH as the salting-out agents, acetone extracts technetium almost quantitatively. Using this method, the authors processed several kilograms of molybdic trioxide and isolated several tens of milligrams of technetium (*236*).

Molybdic trioxide was dissolved in alkali, and alkalies or alkali metal carbonates were added as the salting-out agents to the solution so that their concentration was 2–3 M. Practically all the stable and radioactive impurities remained in the aqueous phase. Even a single extraction permitted the separation of 60–90 % technetium with a decontamination factor of about 10^6 relative to molybdenum and radioactive impurities. In the final purification, the extracting agent was washed with small portions of alkaline solutions. Acetone or methyl ethyl ketone was distilled off, and technetium remained as a weakly alkaline solution of the salt of the corresponding cation.

K. ISOLATION OF Tc^{99} FROM FISSION FRAGMENTS

Technetium has one of the highest yields among fragments formed during the fission of nuclear fuel. In addition to Eq. (2) to determine the accumulation of technetium in the fission products one can use a simplified formula, relating the power of the reactor to the quantity of the technetium formed,

$$N_{\mathrm{Tc}} = 28Pt \text{ mg} \tag{5}$$

where P is the reactor power (Mw), and t is the time of operation of the reactor (days). According to this formula, in a reactor with a power of 285,000 kw, about 8 g of technetium is formed daily, or approximately 3 kg per year.

The power of modern nuclear plants at the present time is approximately 6×10^6 kw, and therefore the total amount of technetium formed in them is appreciable and attains tens of kilograms per year. With the development of atomic power engineering in the near future, the yearly production of technetium in nuclear reactors will increase steadily. Tentative data on the increase in the production of technetium as a fission fragment, summarized by taking the planned development of nuclear power engineering in most countries of the world during 1963–1980, are shown in Table XXV.

TABLE XXV

Year:	1963	1965	1970	1980
Amount of Tc formed in nuclear power plants (kg):	60	200	500	4000

The total amount of technetium accumulated in the world by 1980 will apparently exceed 10,000 kg. However, the step of isolating technetium usually does not enter into most schemes of processing nuclear fuel. Technetium is mainly obtained only at pilot plants processing waste solutions that remain after the separation of uranium and plutonium. In such plants, only a small part of the total amount of waste solution is used for the preparation of various radioactive isotopes. Their technetium capacity amounts to several kilograms per year. The technetium content in solutions to be processed is low and amounts to 5–100 mg/liter.

Table XXVI gives some examples of compositions of waste solutions to be processed after the refining of nuclear fuel in redox processes (extraction processes involving the use of hexone as the solvent and aluminum nitrate as the salting-out agent) and in the purex processes (extracting agent—tributyl phosphate, salting-out agent—nitric acid).

In order to obtain fragment technetium, in addition to fuel-processing wastes, earlier studies (*174*, *205*) made use of uranium preparations specially irradiated with neutrons. A typical method of this type is that proposed by Tribalat (*205*).

Irradiated uranium oxide was dissolved in sulfuric acid, iodide ion being added as carrier of radioactive I^{131}. Iodine was then oxidized with ammonium persulfate and extracted with toluene. Traces of elemental iodine were eliminated by boiling, and the solution was neutralized with Na_2CO_3 and again boiled with $(NH_4)_2S_2O_8$ to oxidize technetium. Iodine had to be eliminated, since it is subsequently extracted together with technetium. Tetraphenylarsonium chloride, $[(C_6H_5)_4As]Cl$, was added to the solution, and technetium was extracted with chloroform as tetraphenylarsonium pertechnetate. Technetium was separated from the organic phase by evaporation or reextraction in $HClO_4$ or H_2SO_4, followed by precipitation or distillation.

TABLE XXVI

COMPOSITION OF WASTE SOLUTIONS CONTAINING TECHNETIUM (*91*)

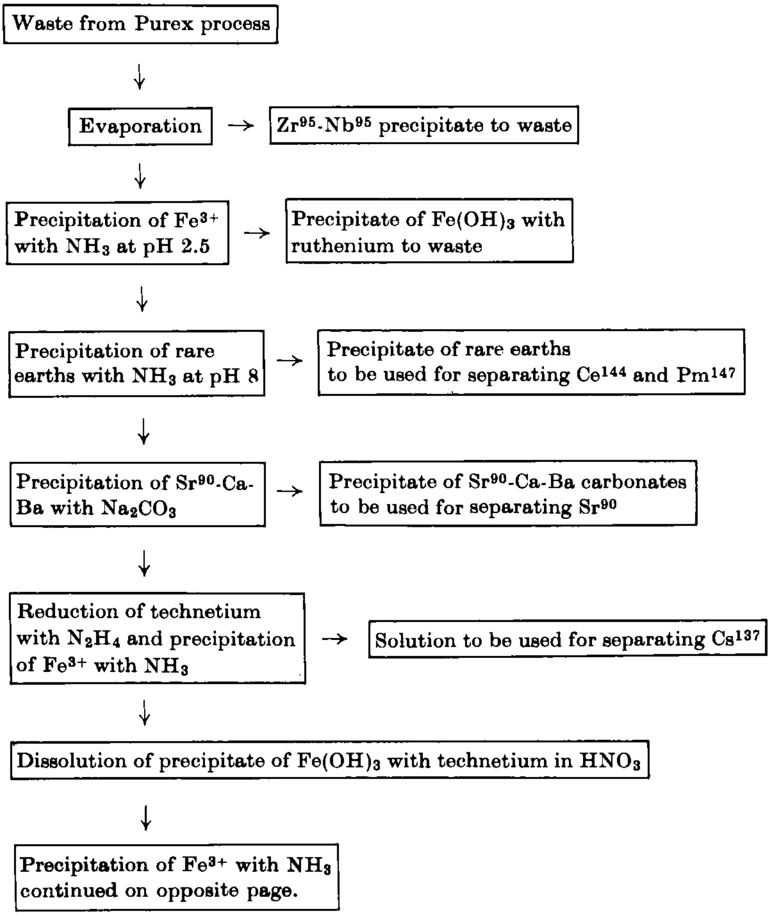
Solution components	Concentration in the process	
	Redox	Purex
$Al(NO_3)_3$	1.4 *M*	—
NH_4NO_3	1.9 *M*	—
$Hg(NO_3)_2$	0.0125 *M*	—
HNO_3	—	3.9 *M*
Cs^{137}	8.87 curies/liter	4.4 curies/liter
Sr^{90}	0.94 curies/liter	4.6 curies/liter
Ru^{106}	0.10 curies/liter	9.0 curies/liter
Ce^{144}	0.87 curies/liter	88.7 curies/liter
Pm^{147}	1.06 curies/liter	17.0 curies/liter
Tc^{99}	6.5 mg/liter	41 mg/liter
Corrosion products Fe, Ni, Co	1–2 g/liter	—

Technetium was first separated from fuel-processing wastes by Parker and Martin (*71*, *108*). In their method, perchloric acid was added to the solution containing technetium fragments, and tetraphenylarsonium chloride was used to precipitate the isomorphous mixture $[(C_6H_5)_4As]ClO_4 \cdot [(C_6H_5)_4As]TcO_4$ on heating. The cooled solution was filtered, the filtrate containing almost all the radioactive impurities was discarded, and the residue was decomposed by electrolysis in concentrated sulfuric acid. The crude technetium deposited on platinum electrodes was purified by distillation from $HClO_4$ and deposition as the sulfide. Later, use was made of methods based primarily on the precipitation of reduced forms of technetium on ferric hydroxide.

The report of Rapp at the First International Conference on Peaceful Uses of Atomic Energy (*230*) cites one of the first industrial processes of this type. Waste solutions containing fission products are evaporated, and the precipitation of ferric hydroxide by means of carbamide hydrolysis or with ammonia is carried out at pH 2.5 in the presence of hydrazine. The ferric hydroxide precipitate thus occludes over 90% ruthenium and technetium. The filtered deposit is dissolved in nitric acid, which reoxidizes technetium to TcO_4^- ion, and tetraphenylarsonium pertechnetate is precipitated from the solution obtained. Technetium is subsequently purified by being reprecipitated as the pertechnetate and then the sulfide. Technetium sulfide is dissolved in a mixture of hydrogen peroxide and ammonia, and the ammonium pertechnetate obtained is crystallized out of the solution.

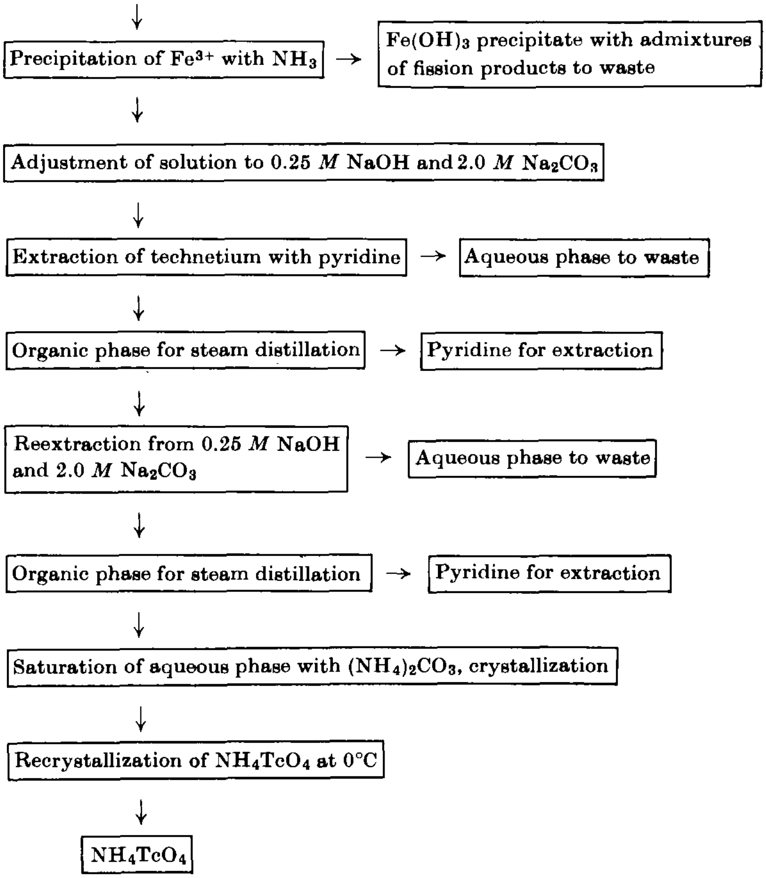
A disadvantage of all methods using the tetraphenylarsonium ion is the high cost of the reagent and the necessity of consuming large amounts of organic material. Of major interest in this respect is Boyd's suggestion concerning utilization of the tetraphenylarsonium ion. The tetraphenylarsonium pertechnetate precipitate is dissolved in alcohol and passed through an anion-exchange resin in the chloride form. The TcO_4^- ion is thus adsorbed and later eluted off with 2 *M* $HClO_4$. The tetraphenylarsonium chloride that has passed through the column is reused. Subsequently, the precipitation of technetium with tetraphenylarsonium ion was successfully eliminated. Such an improved scheme of processing waste solutions into isotopes was proposed by Lamb *et al.* (*231*) for the purex and redox processes. In this scheme, in order to remove ruthenium from technetium, the removal of ruthenium being particularly difficult, the latter was precipitated on ferric hydroxide under conditions where technetium remained in the solution, and technetium was precipitated as the sulfide.

After Rimshaw and Malling (*93*) determined that pertechnetates could be extracted with pyridine and its methyl derivatives from media containing nitrates, this scheme was modified in the part involving the final purification of technetium, ruthenium and other impurities being still satisfactorily removed. Instead of precipitating technetium as the sulfide, it was subjected to a double extractive purification. The part of the scheme of processing waste solutions, involving the recovery of technetium from the wastes resulting from the extraction with tributyl phosphate (purex process), is approximately as shown in the diagram



on this page. This scheme was carried out at an experimental plant of the Oak Ridge National Laboratory.

After the solution is evaporated and the cake precipitated from the filtrate at pH 2.5 is removed, ferric hydroxide, which occludes almost all the ruthenium, is precipitated with ammonia. Rare earths and alkaline earth elements (see scheme) are then separated. After technetium is reduced with 0.1 *M* hydrazine hydrate solution, Fe^{3+} ions are added to the solution. Ferric hydroxide, which is then precipitated with ammonia at pH 3, occludes the reduced technetium and the remaining ruthenium. The precipitate is dissolved in nitric acid, and a second precipitation of ferric hydroxide is performed. Technetium is oxidized with nitric acid, and, once in the heptavalent state, is not occluded by $Fe(OH)_3$. Only ruthenium reaches the precipitate. The technetium solution is neutral-



ized, and its concentration is made 0.25 *M* in NaOH and 2 *M* in Na_2CO_3. A certain excess alkalinity promotes the phase separation.

When technetium is extracted with pyridine from such a solution, the distribution coefficient of technetium is 740, whereas most impurities are practically not extracted with pyridine. The presence of nitrate ions decreases the distribution coefficient of technetium somewhat, but it nevertheless remains sufficiently high. After the extraction, pyridine is steam-distilled, a 0.25 *M* NaOH and 2 *M* Na_2CO_3 concentration is reestablished in the aqueous solution, and a second extraction of technetium is performed. Pyridine is distilled off, and the aqueous solution containing technetium is saturated with $(NH_4)_2CO_3$ or NH_4NO_3, and cooled to 0° in order to crystallize NH_4TcO_4. After three crystallizations, the pertechnetate has a radiochemical purity of over

99.998 % and a chemical purity of over 99.99 %. This scheme apparently may be regarded as the most successful at the present time, although several other methods of isolating technetium from fuel-processing wastes have been proposed as well. Thus, a patent has been granted for a process of isolating technetium from waste solutions by precipitation on the anion-exchange resin "D-Acidite FF" in OH form followed by elution of technetium with 10 *M* HNO_3 and extraction with methyl ethyl ketone (*220*).

Coleman *et al.* (*204*) developed a method for isolating technetium from residues of fluorination of spent fuel by extraction with trilaurylamine. Campbell (*218*) studied the separation of technetium by extraction with tributyl phosphate from a mixture of fission products "cooled" for 200 days. However, these methods apparently have not yet found practical application.

Brief communications (*177*) have recently appeared concerning a new method of obtaining technetium in the course of the processing of spent nuclear fuel in gaseous diffusion plants. Technetium hexafluoride is formed along with UF_6 during fluorination of uranium and usually escapes together with this compound. By adsorbing technetium on magnesium fluoride, one can concentrate technetium and separate it from uranium. Extraction of the concentrate with 2,4-dimethylpyridine removes fission product impurities, fluorine, sodium, etc., from the technetium, and the latter crystallizes out in the form of high-purity NH_4TcO_4. The use of this method has sharply reduced the cost of technetium and increased its production. However, further improvement in methods of isolating technetium from fission products and an increased scale of production are necessary in order to make technetium more accessible for scientific and practical purposes.

L. Isolation of Technetium from Ores

The problem of isolating technetium from natural materials faced researchers when they attempted to find it in the earth's crust. In addition to the primary origin, a certain amount of technetium could have also formed as a result of the interaction of molybdenum and ruthenium with cosmic radiation and as a result of the spontaneous fission of uranium. The difficulty of isolating technetium from natural materials consisted in the need for an extensive concentration of microquantities of technetium and separation from macroquantities of a large number of impurities. Since the geochemical behavior of technetium should be analogous to that of rhenium because of the similarity in their chemical and physical properties, the prospecting for technetium was carried out in minerals containing rhenium, i.e., mainly molybdenum minerals. Physicochemical analytical methods made it possible to detect 10^{-8}–10^{-10} g of technetium, but in most cases their application involved the elimination of certain interfering elements, mainly molybdenum and rhenium. The separation of technetium from rhenium was the most difficult problem, since, because of the similarity in properties, the permissible content of rhenium in the samples analyzed should be extremely low.

An example of the method of isolating technetium from molybdenum-containing minerals is the study of Boyd and Larson (*21*). Molybdenite MoS_2 was fused with sodium peroxide. The radioactive tracer added to the melt was the Tc^{95m} isotope, the radioactivity of which indicated the chemical yield of technetium at all stages of the process. The melt was leached out with water and boiled in order to decompose the peroxide. The separated precipitate of ferric hydroxide was filtered off, and the filtrate was passed through a column with strongly basic resin (Dowex-2, Amberlite IRA-410), which adsorbed a certain amount of molybdates and ruthenates. The latter were eluted off the column with a 1 *M* solution of $NaNO_3$ or a 2 *M* solution of NaOH. The TcO_4^- and ReO_4^- ions were then eluted off with a 2 *N* solution of $HClO_4$ or $NaClO_4$. The mixture of technetium and rhenium sulfides was then precipitated with hydrogen sulfide from the solution after an additional oxidation of technetium with bromine water. Sulfides were dissolved in a mixture of hydrogen peroxide and ammonia, and the solution obtained was evaporated almost to dryness. The residue was dissolved in 10 *N* HCl, the solution for reducing technetium was heated for 1 hour, and Re_2S_7 was precipitated with hydrogen sulfide. Technetium did not precipitate and remained in the solution. The HCl solution, diluted to 1 *N*, was treated with bromine water, and Tc_2S_7 was precipitated with hydrogen sulfide.

To lower the rhenium content, one or several similar cycles were carried out. The final separation of technetium from rhenium was performed on the Dowex-2 anion exchanger. To this end, technetium and rhenium sulfides were dissolved in a mixture of H_2O_2 and NH_4OH, and the pertechnetate and perrhenate ions formed were deposited on the column. When a solution of perchlorate was passed through the latter at a rate of 0.5 ml/min, only rhenium was at first eluted, followed by technetium. The solution containing technetium was diluted, oxidized with bromine water, and, after addition of 1 mg of Cu^{2+} as the carrier, sulfides were precipitated. Copper sulfide together with the coprecipitated technetium constituted the technetium concentrate. From the latter, after dissolving the sulfide in a mixture of hydrogen peroxide and ammonia, technetium can be isolated by electrolysis for subsequent spectrographic determinations, or, after removal of copper, for spectrophotometric, polarographic, and mass-spectral analyses. The concentrate can also be used directly for activation analysis. This method was used to show that the technetium content in molybdenite does not exceed 10^{-9}–10^{-10} g/kg.

To confirm the calculated content of technetium formed by the spontaneous fission of uranium, Kenna and Kuroda (*28*) isolated technetium from the uranium ore, pitchblende, containing 47 % uranium. The pitchblende was dissolved in nitric acid, and lead was precipitated from the solution as a sulfate. After separation of lead, the filtrate was neutralized with ammonia, and hydrogen sulfide was bubbled through for several hours. The sulfide precipitate was filtered off and dissolved in a mixture of H_2O_2 and NH_4OH. Excess of peroxide was removed by boiling and, in order to prevent loss of technetium, the solution was kept alkaline by means of ammonia. To separate the cations, the solution was then passed through a column with a Dowex resin in the H form. The bulk of the molybdenum was removed from the solution that had passed through the column by precipitation with α-benzoin oxime. The precipitate was filtered off, the filtrate was brought up to 2 *N* in acid, and several milligrams of Cu^{2+} were added. Hydrogen sulfide was used to precipitate copper sulfide, with which technetium heptasulfide coprecipitated. The sulfide precipitate was dissolved in a mixture of H_2O_2 and NH_4OH, and several milligrams of rhenium were added as the carrier to the solution formed. The uranium solution was made alkaline to 5 *N* NaOH, and technetium and rhenium were extracted with methyl ethyl ketone. Traces of molybdenum and ruthenium were thus removed from technetium. The latter was reextracted into the aqueous phase, to which 2 mg of Cu^{2+} was added, and the sulfides were precipitated. The sulfides were dissolved as described, the solution was evaporated down to 5 ml, the pH was brought to about 7, and technetium and rhenium were adsorbed on a Dowex anion exchanger in the nitrate form. To separate technetium from rhenium, they were successively eluted with 0.25 *M* $NaClO_4$. To the technetium fraction obtained was added 4 mg of Cu^{2+}, the solution was acidified with hydrochloric acid, and technetium and copper sulfides were precipitated.

The sulfide precipitate was filtered off, washed, and dried. The technetium content was determined from measurements of the activity of the samples. The chemical yield of technetium in all the above isolation operations was 50 ± 10 %. The isolated amount of technetium (about 1×10^{-9} g) showed good agreement with the experimental data (approximately 4×10^{-10} g Tc/kg) and calculated data (5×10^{-10} g Tc/kg) on the technetium content of uranium ores.

V. Analytical Chemistry of Technetium

A. DETERMINATION OF TECHNETIUM FROM RADIOACTIVITY

Many publications devoted to the analytical chemistry of this element have appeared in recent years. All the existing methods for analysis of technetium consist of the following steps: dissolution of weighed amounts of the material being studied, isolation and concentration of technetium, separation of technetium from associated impurities, and determination of technetium.

Because of the extremely small amounts of technetium usually present in the initial raw material, it is difficult to draw a line between the analytical and technological methods for its isolation and purification. This problem has been discussed at some length in Section IV, and therefore we shall consider here only the methods for determination of technetium.

The first methods for determination of technetium were based on its radioactivity (*11*). The specific activity of the most widely distributed isotope Tc^{99} is 16.8 μC/mg, which corresponds to 37,800 disintegrations/min/μg. However, difficulties due to the low energy of its β particles ($E_{\max} = 0.29$ MeV) arise during measurement of the radioactivity of Tc^{99}. To allow for the errors caused by self-absorption, reflection from the substrate, counting geometry, etc., the sample should be thoroughly prepared for counting. In practice, an ordinary end-window counter with a mica window can determine about 10^{-7} g of technetium (*91*). Use of special low-background apparatus enables one to raise the sensitivity by another two to three orders of magnitude.

For the short-lived isotopes Tc^{99m}, Tc^{95m}, and Tc^{97m}, which have found practical application, the sensitivity of the radiometric method reaches approximately 10^{-16} g.

B. GRAVIMETRIC METHODS OF DETERMINING TECHNETIUM

Among the gravimetric methods, the most popular is the weighing of the precipitate in the form of tetraphenylarsonium pertechnetate (*204*, *239*). Its precipitation is carried out from neutral solutions with an excess of tetraphenylarsonium chloride $(C_6H_5)_4AsCl$ (*174*). The use of a special microtechnique has permitted the precipitation and weighing of 1.95 μg of technetium with a relative error of $\pm 4\%$ (*240*). Perrhenates, fluorides, iodides, bromides, oxidants, thiocyanates, mercury, bismuth, lead, silver, tin, and vanadyl ion as well as high nitrate ion concentrations (above 0.5 *M*) interfere with the determination.

Technetium can also be precipitated and weighed in the form of nitron pertechnetate ($C_{20}H_{17}N_4TcO_4$) (*118*). Nitron pertechnetate is precipitated from weak sulfuric acid or acetic acid solution with excess 5% nitron solution in 3% acetic acid at 80°C. ReO_4^-, NO_3^-, ClO_4^-, MeO_4^{2-}, and oxidants interfere with the determination.

In certain cases, a precipitate of technetium heptasulfide is used for determining technetium (*116*). The precipitation is carried out from 2–4 *N* hydrochloric or sulfuric acid solutions by passing through hydrogen sulfide. To achieve a better coagulation of the precipitate, the solution is heated to the temperature of a boiling water bath. The heptasulfide precipitate is usually contaminated with elemental sulfur, which should be removed before weighing by multiple washings of the precipitate with carbon disulfide. Many elements that form sulfides insoluble in acids interfere with the determination. The lower limit of the concentration of technetium at which it can be precipitated without introducing carriers is 3 mg/liter. This method is seldom used for the gravimetric determination of technetium, but is widely employed in the preparation of samples for radiometric measurement and neutron activation analysis (*21*).

C. COLORIMETRIC AND SPECTROPHOTOMETRIC METHODS OF DETERMINING TECHNETIUM

As has been indicated, pertechnetate ions strongly absorb ultraviolet light (see Fig. 4). Therefore the simplest spectrophotometric method of determining technetium is measurement of the optical density of TcO_4^- solutions at the absorption maxima (289 and 247 mμ). The molar extinction coefficients are, respectively, 2340 and 6200. Beer's law is preserved up to a concentration of about 10^{-3} mole/liter (*96*). This method permits the simultaneous determination of the concentrations of technetium and rhenium, and in the determination of technetium the sensitivity is approximately 10^{-6} g (*21*).

In its lower oxidation states, technetium forms with various reagents colored complexes that are used for its quantitative determination. Most frequent use is made of the thiocyanate method, in which the red compound of technetium with the thiocyanate ion is subjected to photometric analysis (*128*) (Fig. 13). The final composition of this compound has not yet been elucidated, but it is assumed to contain pentavalent technetium. In 4 *N* H_2SO_4, the thiocyanate ion reduces pertechnetate ions to pentavalent technetium, which forms a colored complex with an excess of the reagent. The reaction occurs slowly, and the full color develops only after 3 hours. The absorption maximum is at 510 mμ, and the molar extinction coefficient is approximately 47,500, which permits the detection of technetium at a concentration of 10^{-7} g/cm^3. According to the data of Crouthamel (*128*), the accuracy of the determination is ±2 %.

This technique has subsequently been improved by Howard and Weber (*241*). Their improvement consists essentially in reducing heptavalent technetium to the pentavalent state with ascorbic acid in the presence of Fe^{3+} ions, which protect the pentavalent technetium from further reduction. The thiocyanate ions interact with pentavalent technetium to form a red complex, which is extracted with butyl acetate and subjected to colorimetric analysis. The thiocyanate complex of molybdenum absorbs light appreciably at a wavelength of 510 mμ, which corresponds to the absorption maximum of the technetium complex (the molar extinction coefficient is 50,000). Therefore the measurements are performed at 585 mμ, at which the molar extinction coefficient of the technetium thiocyanate complex is fairly high (16,500) whereas the absorption of the molybdenum complex is insignificant (100 μg of molybdenum is determined as 0.4 μg of technetium). The solution obeys the Lambert-Beer law in the range 0.1–30 μg/cm^3. The relative error is ±2 %, and duration of the determination is 45 minutes. Chromium, copper, iron, manganese, nickel, ruthenium, vanadium, and tungsten do not interfere with the determination if the content of each does not exceed 1000 μg. Nitric acid present in amounts above 6 % lowers the results, since it partially oxidizes technetium to the heptavalent state.

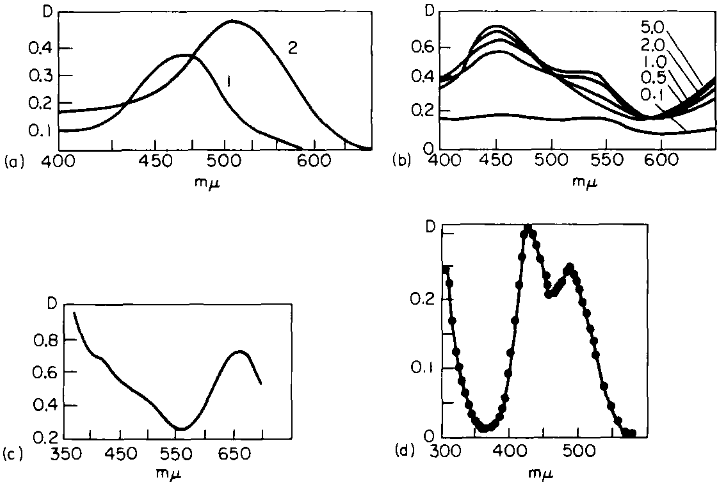


FIG. 13. Absorption spectra of complex thio compounds of technetium: (a) with thiocyanate, (1) Tc^{5+}, (2) Mo^{5+}; (b) with toluene-3,4-dithiol ($\lambda_{max} = 450$ mμ, $\epsilon = 15{,}000$), (c) with thioglycolic acid ($\lambda_{max} = 655$ mμ, $\epsilon = 1800$), (d) with thiourea.

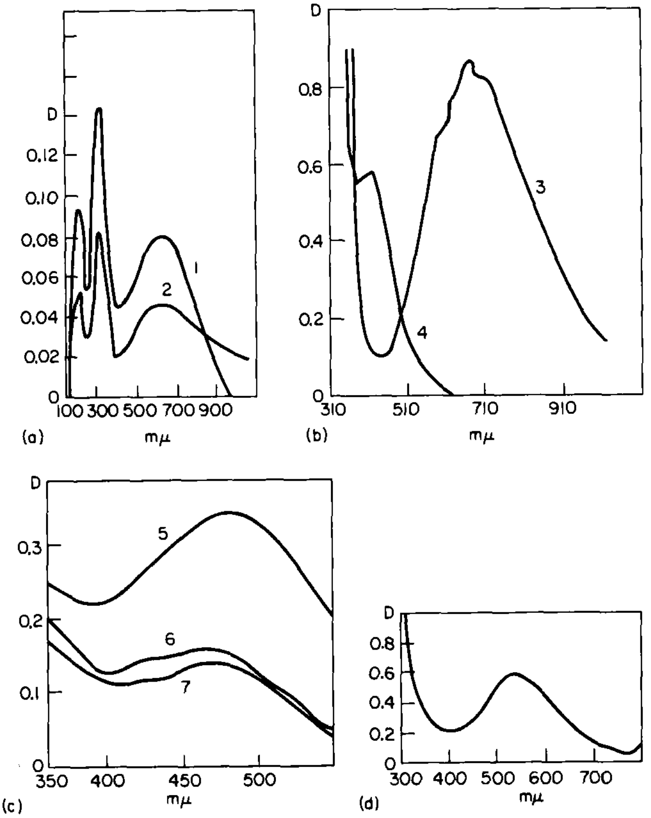


FIG. 14. Absorption spectra of technetium complexes: (a) with α-furyldioxime ($\lambda_{max} = 520$ mμ, $\epsilon = 13{,}180$); (b) with potassium ferricyanide ($\lambda_{max} = 680$ mμ, $\epsilon = 10{,}800$); (c) with α-picolinic acid ($\lambda_{max} = 4800$ mμ, $\epsilon = 4400$); (d) with 1,5-diphenylcarbohydrazide: (1) 1 *N* HCl, (2) 3 *N* HCl, (3) $Tc[Fe(CH)_6]$, (4) $Re[Fe(CN)_6]$, (5) after 20 minutes, 4.3 γ Tc, (6) after 20 hours, 2.4 γ Tc, (7) after 20 hours, 5.7 γ Tc.

Thio compounds are also characteristic reagents for Tc. Thus, Tc can be determined by using toluene-3,4-dithiol (*224*), thioglycolic acid (*132*), and thiourea (*133*). The method for colorimetric determination of technetium with *p*-thiocresol in concentrated acetic acid has been thoroughly studied (*133*). The yellowish brown complex formed is extracted with one of the following extracting agents: chloroform, carbon tetrachloride, ether, benzene, toluene.

In the chloroform solution, the absorption curve has two maxima: at 320–325 and at 410 mμ; at this wavelength, the molar extinction coefficient of technetium is 7350. The solution obeys the Lambert-Beer law up to a concentration of 5 μg/cm^3 (the region being studied). Ions of

Sn, Cd, Bi, Cu, Ag, Pb, Hg, Mo, W, and Re do not interfere with the determination.

Of interest are the recently proposed methods using α-furyldioxime (*130*), potassium ferricyanide, sulfosalicylic acid, and α-picolinic acid (*129*) (Fig. 14).

The method of determining Tc in the form of a complex with 1,5-diphenylcarbohydrazide is very sensitive (*223*). This compound is extracted with CCl_4. The absorption maximum is at 520 mμ and has a molar extinction coefficient of 48,600. The solutions obey the Lambert-Beer law up to 1.5 μg/ml. The accuracy of the method is ±2 rel. %. Fe^{3+}, CrO_4^{2-}, and Ce^{4+} ions have an adverse effect on the determination.

D. POLAROGRAPHIC METHOD OF DETERMINING TECHNETIUM

The existence of various oxidation states of technetium indicates the possibility of using the polarographic method for its quantitative determination. Thus Magee, Scott, and Wilson (*242*) showed that use can be made of waves at $E_{1/2} = -0.65$ V in a medium of 2 *N* KCl or 2 *N* KOH with potassium tartrate, and also at $E_{1/2} = -0.85$ V in a medium of 2 *N* KOH. In all cases, technetium is reduced to the tetravalent state:

$$Tc^{7+} + 3e \rightarrow Tc^{4+}$$

Colton *et al.* (*103*) confirmed the basic results of the preceding authors, but hold that in an alkaline medium the wave at $E_{1/2} = -0.85$ V does not correspond to a three-electron reduction, but only to a two-electron reduction of Tc^{7+} to Tc^{5+}. In addition, they showed that technetium can also be determined by using the wave at $E_{1/2} = -0.81$ V in a medium of 0.1 *M* KCN, which corresponds to the three-electron reduction:

$$Tc^{7+} + 3e \rightarrow Tc^{4+}$$

Love and Greendale (*243*) worked out a rapid polarographic method for determining Tc^{99} in a mixture of fission fragments. Their method consists in a selective reduction of technetium at a dropping mercury electrode at $E_{1/2} = -1.55$ V (relative to the saturated calomel electrode) in a medium of 1 *M* sodium citrate and 0.1 *M* NaOH. Under these conditions, technetium is reduced to oxidation states that are soluble in mercury; the amalgam formed is removed from the solution of fission fragments by settling in CCl_4. The amount of Tc^{99} is determined from the β activity of the amalgam. The decontamination factor for other fission fragments is about 10^5. A single determination requires only 3 minutes, and the accuracy is ±1 %.

Kuzina, Zhdanov, and Spitsyn (*244*) used a polarographic method to determine technetium in a neutral solution with 1 *M* $NaClO_4$ as the background electrolyte. In this solution, a well-defined diffusion wave of TcO_4^- with a half-wave potential $E_{1/2} = -0.8$ V is observed, which corresponds to a three-electron reduction (Fig. 15). The magnitude of the limiting current is directly proportional to the technetium concentration, at least in the interval studied, between 0.5×10^{-5} and 8×10^{-5} mole/liter.

As reported by Boyd (*91*), when the highly sensitive ORNL polarograph is employed, 5×10^{-8} g of technetium can be determined.

References (*90*, *244–247*) also discuss the possibility of a polarographic determination of technetium in neutral and alkaline media.

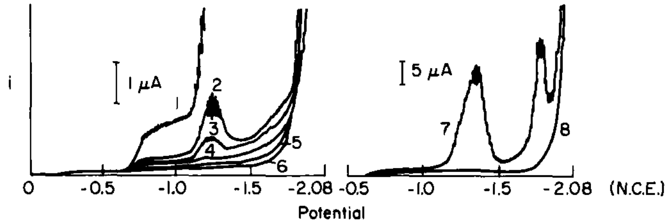


FIG. 15. Polarogram of TcO_4^- in neutral solutions and their composition. Concentration of NH_4TcO_4: (1) 8×10^{-5} *M*, (2) 2.2×10^{-5} *M*, (3) 1.64×10^{-5} *M*, (4) 1.11×10^{-5} *M*, (5) 0.52×10^{-5} *M*, (6) 1 *N* $NaClO_4$ (background), (7) 1 *N* $NaClO_4 + 8.05 \times 10^{-5}$ NH_4TcO_4, (8) 1 *N* $NaClO_4$ (background).

E. SPECTRAL METHODS OF DETERMINING TECHNETIUM

The method of optical spectroscopy has a comparatively high sensitivity, which permits the determination of microgram quantities of technetium. Its spectrum is very rich in lines; the detection is possible by using an arc and a spark source (*81*). The following lines of technetium are used for its quantitative determination: 4297.06, 4262.26, 4238.19, and 4031.63 Å. This method can be used to detect about 1×10^{-7} g of technetium.

In 1962 (*248*) an infrared spectroscopic method of determining technetium was developed that permits the detection of technetium in amounts of the order of 5×10^{-6} g. MoO_4^{2-}, WO_4^{2-}, Br^-, NO_3^-, CNS^-, SO_4^{2-}, PO_4^{3-}, IO_3^-, UO_2^{2+} ions and organic acids do not interfere with the determination. MnO_4^- and ReO_4^- ions absorb infrared light in a neighboring region and should therefore be removed prior to the determination.

F. OTHER METHODS OF DETERMINING TECHNETIUM

Boyd *et al.* (*84*) developed a mass-spectrometric method of determining technetium. Chromatographically pure technetium was deposited electrolytically on an iridium wire and roasted at 400° in a stream of hydrogen. This wire served as the source of technetium ions in the mass-spectrometric analysis. In a technetium sample separated from a molybdenum target irradiated with 22-MeV protons, the isotopes Te^{95} (0.5%), Tc^{97} (56.0%), Tc^{98} (17.3%), and Tc^{99} (26.7%) were found. Approximately 5×10^{-9} g of technetium can be detected by this method. Similar results were obtained by Kukavadze *et al.* (*249*).

TABLE XXVII

SENSITIVITY OF QUANTITATIVE METHODS FOR DETERMINING TECHNETIUM

Method	Sensitivity (g)	Isotopes being determined
Gravimetric	2×10^{-6}	All isotopes
Spectrophotometric	1×10^{-7}	All isotopes
Spectrochemical	1×10^{-7}	All isotopes
Polarographic	5×10^{-8}	All isotopes
Mass-spectrometric	5×10^{-9}	Tc^{99}, Tc^{97}, and Tc^{98}
Neutron activation	3×10^{-10}	Tc^{98}
Radiometric	10^{-7}–10^{-10}	Tc^{99}
	$\sim 10^{-16}$	Tc^{99m}

Neutron activation is the most sensitive method for detecting technetium (*19*). For the reaction $Tc^{98}(n,\gamma)Tc^{99m}$, the thermal neutron capture cross section is 2.6 ± 1.3 barns (*37*), which permits the determination of 3×10^{-10} g of Tc^{98}. However, nuclear reactions forming Tc^{99m} can also take place on impurities contaminating the original technetium, namely:

$$Mo^{98}(n,\gamma)Mo^{99} \xrightarrow{\beta} Tc^{99m},\ Tc^{99}(n,n'),\ Tc^{99m},\ Ru^{99}(n,p)Tc^{99m}$$

For this reason, prior to the analysis it is necessary to purify the sample to be analyzed, and the degree of purification should be about 4×10^{10} for Mo, about 10^{10} for Re, and about 10^{6} for Ru. For the reaction $Tc^{99}(n,\gamma)Tc^{100}$, the neutron capture cross section is 20 barns (*21*), which permits the determination of 2×10^{-11} g of Tc^{99}.

It is apparent from this brief survey of the analytical chemistry of technetium that methods have now been developed, which make it possible to identify and quantitatively determine technetium when its content is very low. However, it should be noted that in most methods rhenium interferes with the determination. It is therefore necessary to develop new ways of isolating and purifying technetium and specifically determining it. In conclusion, the sensitivities of the various methods are given in Table XXVII.

VI. Uses of Technetium

A. INTRODUCTION

Despite its youth and the relatively small quantities available to researchers, technetium is beginning to find practical application. Obviously, it is hardly to be expected that the scale of its production and consumption will reach a magnitude commensurate with the consumption of any other natural element, since the complexity of nuclear fuel processing makes the cost of technetium exceedingly high. However, with the development of technetium chemistry and improvement in methods for its recovery, its cost is showing a constantly decreasing trend. Whereas the first samples of technetium were sold at a price approximately 30,000 times that of gold (*250*), at the present time it costs only $90 per gram (*251*). Nevertheless, its high price and the small quantities obtained make it impossible for a large group of researchers to work with weighable quantities of this element. This hinders detailed investigation of its physical and chemical properties. Nevertheless, even minute, sometimes imponderable, quantities of technetium have made it possible to determine some of its interesting properties that have found practical application.

B. USE OF TECHNETIUM AS A CORROSION INHIBITOR

The high corrosion resistance of technetium to various corrosive media and the comparatively small neutron cross section make technetium coatings fairly promising in nuclear power engineering (*252*). In his numerous studies, Cartledge (*253–259*) established that ammonium pertechnetate is a good corrosion inhibitor. Even in negligibly small concentrations (about 5×10^{-5} *M*), technetium prevents the corrosion of steel in aerated water at temperatures up to 250°C for very long periods of time. This is highly important for applications in water-cooled or water-moderated reactors.

The exact mechanism of inhibition has not yet been elucidated, but obviously differs from the mechanism proposed to account for the inhibiting properties of the ions of weak acids, CrO_4^{2-}, WO_4^{2-}, and PO_4^{3-}. It was shown that this inhibiting effect is not due to the radioactivity of technetium, since radioactive perrhenates are not inhibitors. The quantity of technetium adsorbed on the surface of iron is also much smaller than would be required to form even a monolayer.

Since the inhibiting properties of technetium disappear upon addition of any electrolytes, it may be assumed that the inhibition mechanism is due to the adsorption of the TcO_4^- ion on various defects of the surface and to the oxidation-reduction properties of the system TcO_4^-–TcO_2. However, Spitsyn and Kuzina (*236*) note a complete lack of corrosion of armco iron for 10 days at a technetium concentration of 6 mg $KTcO_4$ per liter and in solutions containing SO_4^{2-} and Cl^- ions. The inhibiting properties of technetium have already been utilized in preventing corrosion in a boiling nuclear reactor (*177*).

C. TECHNETIUM AS A SUPERCONDUCTOR

Study of the superconducting properties of technetium has shown that its critical temperature (the highest temperature at which the electrical resistance of a substance becomes zero) is 11.2°K according to the data of Daunt and Cobble (*76*), and 8.8°K according to the data of Darby and Zegler (*78*). The value of 11.2°K is the highest of all the elements. However, the studies of Darby and Zegler with massive technetium of high purity did not confirm this value. They attributed the difference in results to the presence of oxygen in the technetium. The superconductivity of technetium, particularly of its alloys with molybdenum, makes them promising materials for superconducting magnets. In this respect, technetium has advantages over an alloy of rhenium and molybdenum. An alloy consisting of 50 at.% molybdenum and 50 at.% technetium at a critical temperature of 12.6°K has an H_0 value (critical field at 0°K) of 75,000 gauss, whereas an analogous alloy of rhenium and molybdenum under the same conditions has an H_0 value of only 27,000 gauss (*160*). Mattias (*161*) cites a critical temperature of 15°K for an alloy of molybdenum with 60 at.% technetium, and 16°K for a 75% alloy. Darby and Zegler (*78*) determined the critical temperature for an alloy of molybdenum containing 60 at.% technetium to be 13.4 ± 0.3°K. There is reason to believe that this value can be raised to 18°K by sufficiently purifying the materials.

D. SOURCES OF β-RADIATION BASED ON Tc^{99}

The technetium isotope Tc^{99} makes it possible to prepare standard sources of β-radiation with an energy of 0.292 MeV (*156*, *260*). The lack of γ-radiation makes such sources safe and convenient to handle, and because of the long half-life of technetium (2.12×10^5 years) their activity remains practically constant with time.

An isotope whose properties may be close to Tc^{99} is Pm^{147}, which is also a pure β-emitter (0.227 MeV), but has a relatively short half-life (2.6 years), which makes sources based upon it unstable with time, and the separation of Pm^{147} from other rare earths presents a fairly complex problem. The specific activity of technetium, despite its long half-life, is sufficiently high and amounts to 3.78×10^7 counts/min/mg, which is sufficient for the preparation of relatively strong sources.

Technetium can be obtained with a very high degree of chemical and radiochemical purity (over 99.99%). This, combined with the capacity for electrolytic deposition of technetium on metal substrates and its high corrosion resistance, makes sources of β-radiation based on technetium reliable in performance and simple to prepare. Usually, technetium is electrodeposited on a metal substrate or a part thereof and is additionally reduced with hydrogen. The active spot is extremely strong mechanically and stable to the action of the atmosphere, so that there is no need of special protective coatings, which would substantially decrease the activity by absorbing the β-radiation.

In addition, the solubility of pertechnetates in organic solvents, particularly acetone, can be utilized in the preparation of film sources containing technetium. To an acetone solution of pertechnetate of a given concentration is added a film-forming substance, which after drying or polymerization forms a film with a uniform distribution of technetium throughout its volume.

E. USE OF TECHNETIUM IN PHYSICAL INVESTIGATIONS

In the form of the Tc^{99m} isomer, technetium has proven very convenient for studying the effect of the chemical and physical state of the isotope on the radioactive decay constant. Such changes in the half-life had been determined earlier for the electron capture of the Be^7 isotope as a function of its chemical state.

It is known that the half-life of an isotope remains constant and is independent of such external factors as pressure, temperature, and chemical composition of the compound in which the element is contained. However, during radioactive transformations, such as the capture of an orbital electron and isomeric transition, the half-life depends to some extent on the configuration of the electron shells. The latter in turn is related to the chemical state in which the element exists and to certain other factors, for example, pressure. This applies primarily to the outer electron shells, which undergo the greatest changes under the influence of chemical or physical effects. Changes in electronic structure of the atom bring about a change in the coefficient of internal conversion of γ-rays as well as a change in the half-life of the isomer. The decay scheme of the Tc^{99m} isomer (*261*) (Fig. 16) is characterized, in the overwhelming majority of cases (98.6%), by the presence of a two-step transition to the ground state. The γ quanta with an energy of 2.0 ± 0.1 keV that are then emitted are converted to a considerable extent.

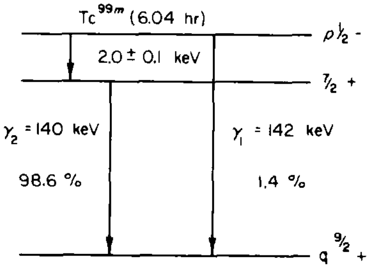


FIG. 16. Decay scheme of Tc^{99m}

The insignificant energy of the isomeric transition leads to the assumption that the conversion may take place only on weakly bound electrons of the outermost shells, i.e., changes in physical or chemical state should affect the decay constant.

Bainbridge *et al.* (*156*, *262*), using a differential chamber, compared the decay constants of Tc^{99m} in metallic technetium and its compounds—sulfide and potassium pertechnetate. The changes of the decay constant in these compounds had the following values:

$$\lambda_{KTcO_4} - \lambda_{Tc_2S_7} = 27 \pm 1 \cdot 10^{-4}\ \lambda_{Tc_2S_7}\ \mathrm{sec}^{-1}$$

$$\lambda_{Tc} - \lambda_{Tc_2S_7} = 3.1 \pm 1.2 \cdot 10^{-4}\ \lambda_{Tc_2S_7}\ \mathrm{sec}^{-1}$$

Thus, it was established that the half-life of Tc^{99m} (6.04 ± 0.03 hours) in $KTcO_4$ decreases by 1 second, and in Tc_2S_7 increases by 8.6 seconds as compared to elemental technetium; this is in good agreement with the theoretically predicted values (*263*).

Similar changes should also take place when the pressure increases. Indeed, at a pressure of 100,000 atm, the decay of Tc^{99m} is accelerated by 0.025% as compared to the metal under standard pressure (*264*). The value ($\Delta\lambda = 2.3 \pm 0.5 \times 10^{-4}\ \mathrm{sec}^{-1}$) agrees well with the calculated one ($\Delta\lambda = 2\text{–}4 \times 10^{-4}$), determined by Porter and McMillan (*265*). Changes in the radioactive decay constants of the Tc^{99m} isomer in the metal form at low temperatures were studied by Byers and Stamp (*266*). They established that the main factor affecting the decay rate is not the temperature (or the volume contraction that it causes), but the transition of technetium at low temperatures to the superconducting state and the associated redistribution of electrons. This is confirmed by the fact that at 77°K no appreciable changes in half-life were observed, whereas at 4.2°K (the critical temperature of metallic technetium is 8.8°K) these changes were noticeable. They decreased sharply if the superconducting state of technetium was removed by a strong magnetic field:

$$\lambda_{4.2^\circ K\ \mathrm{supercond}} - \lambda_{293^\circ K} = 6.4 \pm 0.4 \times 10^{-4}\ \lambda_{293^\circ K}\ \mathrm{sec}^{-1}$$

$$\lambda_{4.2^\circ K\ \mathrm{norm}} - \lambda_{293^\circ K} = 1.3 \pm 0.04 \times 10^{-4}\ \lambda_{293^\circ K}\ \mathrm{sec}^{-1}$$

Data on the influence of the chemical state and physical factors on the decay of the Tc^{99m} isomer have subsequently been frequently examined and discussed theoretically, as in references (*263, 265, 267, 268*).

F. USE OF TECHNETIUM IN MEDICINE

Among other isotopes of technetium, the one that has found most extensive application is its short-lived isomer Tc^{99m}. The low cost and ease of isolation of the Tc^{99m} isomer from molybdenum irradiated in a reactor permit its use in solving certain applied problems. In addition to its use in studies of the chemistry of technetium and investigations in nuclear physics, this technetium isomer has found particularly broad application in medicine.

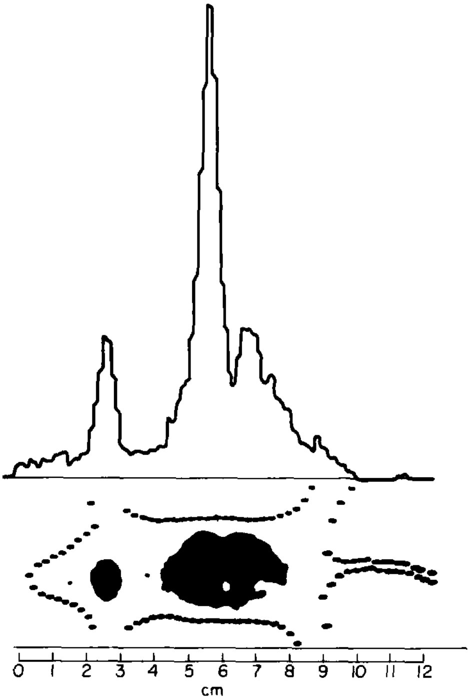


FIG. 17. Distribution of Tc^{99m} in the body of a mouse.

As shown in the studies of Scheer and Maier-Borst (*233*) and Harper *et al.* (*269*), Tc^{99m} has advantages over other isotopes for radiation diagnostics. In addition to the already mentioned availability of Tc^{99m}, the energy of its γ-radiation (140 keV) is satisfactorily collimated by diagnostic apparatus, which makes it possible to localize exactly damaged areas in the body (Fig. 17).

Technetium diffuses extremely fast through the intracellular space and is selectively retained by the thyroid gland, salivary glands, and stomach. It does not affect the blood, even when present in relatively large quantities, and can therefore be used for rapid diagnosis of diseases of the thyroid gland in amounts up to 10 mC and more. The short half-life of Tc^{99m} ($T_{1/2} = 6$ hours) markedly lowers the irradiation dose to the organs even when technetium is retained in the body. For instance, in the diagnosis of diseases of the thyroid gland, the irradiation dose from Tc^{99m} is 1000 times smaller than when I^{131} is used. Technetium as the sulfide can be coprecipitated with sulfur, forming stable colloids capable of depositing in the liver. Introduced as the thiocyanate into fat emulsions, Tc^{99m} accumulates in the liver parenchyma and can thus be used for diagnosing primary hepatoma, giving quite clear-cut results.

Pentavalent technetium Tc^{99m} in the form of various organic complexes can also be used for various types of diagnosis. For instance, the glycine complex of Tc^{99m} can be used for diagnosing urological diseases.

G. OTHER METHODS OF UTILIZING Tc^{99} AND OTHER TECHNETIUM ISOTOPES

In addition to the problems enumerated above of a scientific and applied nature that have been or can be solved by using technetium, there are many others in which its various isotopes can be of substantial use. These include, for example, prospecting for technetium in nature for the purpose of elucidating such cosmological problems as the origin and age of the earth, and the activity of the Sun and other stars (*17*, *270*). By analogy with rhenium, technetium can be regarded as a promising catalyst for certain chemical processes (*90*). It has been proposed that technetium be used for controlling the fuel burn-up in nuclear reactors (*271*). As in the case of rhenium, high-temperature thermocouples or resistance thermometers could apparently be prepared from technetium. In addition to Tc^{99}, short-lived technetium isotopes are also employed: Tc^{97m} (90 days), Tc^{95m} (60 days), and Tc^{99m} (6 hours). They are used as radioactive labels for the long-lived Tc^{99} in studies where the specific activity of Tc^{99} is insufficient or where its β-radiation is absorbed by the preparations. The Tc^{99m} isomer has been used to study most of the chemical and physical properties of technetium in ultralow concentrations. A brief survey of the methods of using technetium shows that during the 28 years since the date of its discovery, technetium has not only filled a vacant place in the Periodic Table, but has also become important in practical applications.

H. PHYSIOLOGICAL EFFECT OF TECHNETIUM AND SAFETY MEASURES INVOLVED IN ITS HANDLING

The physiological effect of technetium has been studied very little. Certain aspects are touched upon in the studies of Scheer and Maier-Borst (*233*), Bauman *et al.* (*272*), and Hamilton (*273*). According to Bauman's data, when injected, technetium penetrates into almost all the tissues of the body. Somewhat higher amounts of technetium, as compared to other organs, are found in the gastrointestinal tract, in the blood, and particularly in the thyroid gland (13–24% of the activity introduced). Although technetium can be eliminated relatively fast from the remaining organs (*273*), its concentration in the thyroid gland can lead to damage from the β-radiation.

Technetium has an appreciable specific activity (17 mC/g), but on the surface of dry technetium preparations the irradiation dose amounts to 0.1 r/hr/mg (*71*). The β-radiation of technetium ($E_{\max} = 0.292$ MeV) is absorbed by thin protective screens, layers of air, and apparatus walls. However, when technetium penetrates into the body, it may constitute a serious radiation hazard. In this connection, the volatility of many of its compounds, particularly technetium heptoxide, pertechnetic acid, chlorides, etc., should be remembered. Therefore all handling operations should be carried out in hermetically sealed apparatus where the gaseous by-products must be absorbed by alkaline solutions of oxidants. This is necessary to avoid not only the danger of radiation injury, but also losses of the costly technetium. No data are yet available on the chemical toxicity of technetium compounds.

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