Analytical Chemistry of the Elements

TECHNETIUM
PROMETHIUM
ASTATINE
FRANCIUM

ANALYTICAL CHEMISTRY OF

TECHNETIUM, PROMETHIUM, ASTATINE and FRANCIUM

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Translated by R. KONDOR

ANALYTICAL CHEMISTRY OF TECHNETIUM, PROMETHIUM, ASTATINE AND FRANCIUM

Analytical Chemistry of the Elements

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FOREWORD

The Vernadskii Institute of Geochemistry and Analytical Chemistry of the USSR Academy of Sciences has begun the publication of a series of monographs on the analytical chemistry of individual elements. This series, *Analytical Chemistry of the Elements*, will include about fifty volumes, and it is planned to complete the publication during the coming five years. The necessity for such a project has been felt for a long time. We also have at our disposal the accumulated experience of numerous laboratories which now can (and should) be summarized. In this way the present series originated, the first of its kind. The analytical chemistry of any element with its different compounds is at present extremely varied; this is due to the complexity of the modern materials investigated and the wide range of concentrations determined, as well as to the variety of the methods employed.

With this in mind, a general plan has been worked out for the present series, both with respect to the contents and to the presentation of the material.

The monographs contain general information on the properties of the elements and their compounds, followed by a discussion of the chemical reactions which are the basis of the analytical work. The physical, physicochemical, and chemical methods for the quantitative determination of the element are given in the following order: first, the analysis of raw materials, next the analysis of the typical semi-manufactured products, and last, that of the finished products—metals or alloys, oxides, salts, and other compounds and materials. The underlying principles are always explained; whenever necessary, the exhaustive description of the entire analytical procedure is given. Due attention is paid to rapid analytical methods. A separate place is allotted to techniques for the determination of impurities in high purity materials.

Particular stress is placed on the accuracy and the sensitivity of the various methods, in view of the general tendency toward increased sensitivity of determination of traces of impurity elements.

The monographs contain an exhaustive and up-to-date bibliography. They are intended for a wide circle of chemists: in the first place, for the analysts of research institutes and industrial laboratories of various branches of the national economy, and also for teachers and students of chemistry in institutions of higher education.

Our most prominent experts participated in the preparation of the monographs, drawing upon their own extensive experience in the analytical chemistry of the element in question.

Each volume of the series will be published separately as soon as it has been made ready for publication. [A list of currently available volumes will be found facing the title page. Further titles are in preparation.]

We invite all our readers to send us their comments and criticisms on the monographs.

Editorial Board

PREFACE

This monograph describes the analytical chemistry of the four artificial elements technetium, promethium, astatine, and francium. These were all discovered in the late 1930's, but most of the information on their properties has been obtained during the last ten years. The rapid advance in the chemistry of these elements in recent years is due not only to improvements in methods of preparation, but also to the increasing scope of practical application.

All four elements have no stable isotopes, and exist in nature in insignificant amounts. Of all the artificial elements, only Tc, Pm, At and Fr do not belong to the actinide group.* Other common features include similar methods of nuclear synthesis (accelerators, nuclear reactors), the same code of practice for handling high-activity preparations, and related techniques of radiometric identification and determination. This explains why these elements are treated together in a single monograph, though their chemical properties differ widely.

Very few reviews or monographs deal with the analytical chemistry of technetium, promethium, astatine, and francium. A series of pamphlets appeared in the USA in 1960–1961, mainly on the radiochemical methods of separation of these elements (*Nuclear Science Series of the National Research Council*). We must also mention articles in the periodical *Uspekhi Khimii* by Lavrukhina (**27**, 1209. 1958) and Pozdnyakov (**34**, 300. 1965), and finally the book *Tekhnetsii* (*Technetium*) (1965) by Kotegov, Pavlov and Shvedov. However, the analytical chemistry of these elements has scarcely been treated in these sources.

In this book we attempt to correlate as far as possible all the experimental data on the analytical chemistry of these elements. The chapters on technetium and astatine were written by Pozdnyakov and those on promethium and francium by Lavrukhina. The bibliography at the end of each chapter includes papers published up to 1966. The authors hope that this book will be of use to scientists, engineers, and postgraduate students working in analytical or nuclear chemistry. The book

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* According to the hypothesis of Seaborg, elements with atomic numbers of 104 or higher should not exhibit actinide properties. However, up till now only a very short-lived isotope of element 104 has been identified, and its chemical properties have not been studied.

is not free of errors, and the authors would be indebted to readers for any critical comments.

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CHAPTER I

Technetium

GENERAL INFORMATION

Discovery and natural occurrence

Technetium (from the Greek word *technetos*—artificial) is the first artificially pro-
duced chemical element. Its existence was predicted as early as 1869 by Mendeleev
[25], who called it ekamanganese. All attempts undertaken in the following 70 years
to find an element with atomic number 43 in nature were unsuccessful. The discoveries
of the elements ilmenium [158, 169], devium [208, 209], lucium [70], nipponium
[268], and masurium [12, 78, 171, 266, 267, 287], which were initially considered
to fill the place of ekamanganese, proved to be false.

The failure of the attempts of scientists to find technetium in the earth's crust
can be explained by the absence of this element in nature because only radioactive
isotopes of technetium exist with a half-life much shorter than the age of the earth.
With the advance of nuclear physics conditions were created for the detection and
preparation of technetium. This was first synthesized in 1937 according to the reaction
$_{42}Mo^4(d, n)_{43}Tc^{4+1}$ when molybdenum was bombarded by deuterons in the cy-
clotrone of the University of California. The Italian scientists Segre and Perrier
separated an unweighable amount $(10^{-10}g)$ from the irradiated molybdenum.
Its chemical properties were similar to those of rhenium [279, 280] and it was named
technetium [281]. Later, other nuclear reactions were proposed which lead to the
formation of various isotopes of this element. At present technetium is obtained

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in nuclear reactors in kilogram amounts [260]. In the thermal neutron fission of U^{235} one of the most long-lived technetium isotopes Tc^{99} is formed in the reactor in a yield of 6.2% together with other fission products.

After some properties of technetium had been investigated and its emission spectrum obtained attempts were again made to find naturally occurring technetium. The discovery of technetium in nature in the 1950's became a very topical problem in the geochemistry of this element [53, 54, 58, 86, 170, 196]. In 1951 Moore [255] found lines of ionized technetium in the spectrum of the solar atmosphere. In the following year Merrill [239, 249] found several lines of technetium in the spectra of some S and M stars. The presence of technetium in stars was also confirmed by other scientists [152] and its abundance differed little from that of the neighboring elements. From this information together with the fact that the most long-lived technetium isotope has a half-life of only $2.6 \cdot 10^6$ years [85, 198] it was concluded that technetium in stars is formed by nuclear reactions.

Table 1

TECHNETIUM CONTENT IN SOME NATURAL SUBSTANCES [86]

Sample	Method of determination	Technetium content, g/kg
MoS_2 (Climax, Colorado)	Spectroscopic	$<4 \cdot 10^{-10}$
MoS_2 (Nevada)	Spectroscopic	$<1.5 \cdot 10^{-9}$
$KReO_4$ (pure)	Spectroscopic	$<8 \cdot 10^{-9}$
MoS_2 (Miami, Arizona)	Spectroscopic	$<1.8 \cdot 10^{-7}$
	Activation	$<1 \cdot 10^{-9}$
	Spectroscopic	$<1.7 \cdot 10^{-9}$
	Activation	$8.3 \cdot 10^{-11}$
MoS_2 (Nevada)	Activation	$1.3 \cdot 10^{-10}$
Osmium–iridium concentrate	Spectroscopic	$<1.6 \cdot 10^{-8}$
Yttrotantalite (West Africa)	Mass-spectrometric	$<6 \cdot 10^{-11}$
Iron–nickel meteorite	Spectroscopic	$<4.5 \cdot 10^{-10}$

Papers [53, 54, 58, 86, 170, 172, 204–207, 222, 223, 272, 273] discuss the problem of finding long-lived technetium isotopes in the earth's crust. It was found that in some minerals technetium occurs in very small amounts. Table 1 gives the results of the determination of technetium in some natural substances (various determination methods have been used). According to Boyd et al. [86] this technetium is of secondary origin, formed by the action of hard cosmic rays on molybdenum, ruthenium, or niobium. Technetium in an amount of about 10^{-9}g was isolated from pitchblende [204–207]. In this case the technetium was a product of the spontaneous fission of U^{238}. As shown in [60, 172, 204, 222, 223] 1 kg of pitchblende (50% U) contains $2.5 \cdot 10^{-10}$g of Tc^{99} (10.5 disintegrations per minute).

Isotopes of technetium

At present 16 isotopes and 6 isomers of technetium are known, with mass numbers of 92 to 107 and half-lives of a few seconds to $2.6 \cdot 10^6$ years (Table 2) [6, 16, 26, 322]. The decay schemes of the radioactive nuclei and the classification of β-decay are given in [7, 9, 138, 215]. Almost all the isotopes can be obtained by irradiating molybdenum, niobium, or ruthenium by neutrons, protons, or α-particles. The isotopes with mass numbers of 99–107 are also formed in the fission of uranium, thorium, or plutonium nuclei. Four of the isotopes shown in Table 2, Tc^{95m}, Tc^{96}, Tc^{97m}, and Tc^{99m}, are used as tracers for studying the chemical properties of technetium. The most accessible atom for this purpose is the nuclear isomer Tc^{99m} formed when molybdenum is irradiated by neutrons. Three other isotopes with half-lives of 4 to 90 days are obtained when molybdenum is irradiated by deuterons or protons [155, 110, 251, 340]. The isotopes Tc^{97}, Tc^{98}, and Tc^{99} are long-lived (with a half-life of more than 10^5 years), and so can be used in weighable amounts to study the chemistry of technetium. The last isotope is the most accessible since it is formed by the fission of U or Pu nuclei, or by long-term irradiation of Mo in reactors.

Tc^{99m} (6.04 hr)

$\gamma (2.0 \pm 0.1 \text{ kev})$

$\gamma (140 \text{ kev})$
98.6%

$\gamma (142 \text{ kev})$
1.4%
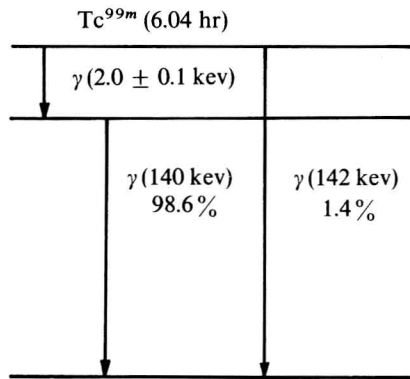
Figure 1

Decay scheme of the isotope Tc^{99m}

A few papers describe the nuclear properties of technetium isotopes [6, 211, 311, 323, 348]. Tc^{99} was investigated most, its nuclear spin is 9/2, magnetic moment $+5.657$ nuclear magnetons, and electric quadrupole moment $Q = 0.3 \cdot 10^{-24} \text{ cm}^2$. If the isomeric transitions in the Tc^{93}, Tc^{95}, Tc^{97}, and Tc^{99} isotopes are compared, it can be concluded that in all these nuclei the ground state corresponds to the proton levels $1g_{1/2}$, and the excited state to $2p_{1/2}$. It follows from the decay scheme of Tc^{99m} shown on Figure 1 [243] that in the majority (98.6%) of cases the decay proceeds in two stages: first a γ-quantum with an energy of 2 kev is emitted and then a γ-

Table 2

ISOTOPES OF TECHNETIUM [6, 9, 16, 322]

Mass number	Half-life	Type of decay	β energy, Mev	γ energy, Mev	Production reactions
92	4.3 min	β^+, e.c.*	4.1	1.3	Mo (p, n) Mo $(d, 2n)$
93	43.5 min	e.c. (18%) i.t.** (82%)		0.39 (82%); 2.66 (18%)	Mo (d, n) [346]
93	2.7 hrs	e.c. ($\sim$85%) β^+ ($\sim$15%)	0.82 ($\sim$13%) 1.67 ($\sim$2%)	0.86 (2.6%); 1.35 (60%); 1.49 (30%) 2.03 (0.35%); 2.44 (0.3%); 0.874 (73%)	Mo (d, n) [346] Mo (p, γ) Mo $(d, 2n)$
94	52.5 min	e.c. (21%) i.t. (24%) β^+ (55%)	0.56 (1%) 2.41 (54%)	1.85 (11%); 2.73 (1%) 3.27 ($\sim$1%)	Nb $(\alpha, 3n)$ [215, 236, 346]
94	4.9 hrs	e.c. (93%) β^+ (7%)	0.9 (2%) 2.41 (5%)	0.705 (100%) 0.846 (72%) 0.874 (100%)	Mo (p, n) Mo $(d, 2n)$ [252] Nb $(\alpha, 3n)$ [236] Ru^{94} $\xrightarrow{\beta^+}$
95m	60 days	i.t. ($\sim$4%) e.c. β^+?	0.477 (<1%) 0.68 (<1%)	0.039 (i.t.) 0.204 (71%) 0.256 ($\sim$1%) 0.584 (40%) 0.617 (2%) 0.788 (13%) 0.822 (8%) 0.837 (29%) 1.042 (4%)	Mo $(d, 2n)$ [110, 340]
95	20 hrs	e.c.		0.205 (1%) 0.680 (2%) 0.765 (82%) 0.84 (10.5%) 0.93 (1.7%) 1.06 (4%)	Mo $(d, 2n)$ [340, 346]
96m	52 min	i.t.		0.034	Mo (p, n) Mo $(d, 2n)$
96	4.3 days	e.c.		0.310 (4%) 0.770 (100%) 0.800 (86%) 0.840 (100%) 1.115 (15%)	Nb (α, n) Mo $(d, 2n)$ [251] Mo (d, n) [251] Mo (p, n) Ru (n, p)
97	90.5	e.c.		0.090; 0.099	Mo $(d, 2n)$ [340] Mo (p, n) Ru $\xrightarrow{\text{e.c.}}$ Mo (d, n) [340]

Table 2 (continued)

Mass number	Half-life	Type of decay	β energy, Mev	γ energy, Mev	Production reactions
97	$2.6 \cdot 10^6$ yrs	e.c.			Mo $(d, 2n)$ Tc^{97m} $\xrightarrow{\text{i.t.}}$ [199]
98	$1.5 \cdot 10^5$ yrs	β^-, γ	0.30	0.74; 0.65	Ru (n, p) [199] Mo (p, n) [84] Mo (d, n)
99m	6.04 hrs	i.t.		0.002 (1.4%) 0.140 (1.4%) 0.142 (98.6%)	Mo^{99} $\xrightarrow{\beta^-}$ Ru (n, p) [310] Th (fission) U (fission) Mo^{99} $\xrightarrow{\beta^-}$
99	$2.12 \cdot 10^5$ yrs	β^-	0.292		Tc^{99m} $\xrightarrow{\text{i.t.}}$ U (fission) [155, 190]
100	15.8 sec	β^-, γ	2.20, 2.88, 3.38	0.542; 0.60; 0.71; 0.81; 0.89; 1.01 1.14; 1.31; 1.49; 1.80	Tc^{99} (n, γ) Mo^{100} $(d, 2n)$ Rh^{103} (n, α) [86, 125]
101	14.3 min	β^-, γ	1.4	0.307	Mo (d, n) Ru (γ, p) Ru (n, np) [148] U (fission) [149]
102	4.5 min (5 sec)	β^-, γ β^-	~ 2 4.2	0.473 > 0.662	Ru (n, p) U (fission) [148]
103	50 sec	β^-, γ	2.0; 2.2	0.135; 0.215 0.350	Ru (n, np) [148] U (fission) [214, 215]
104	18 min 7.8 min	β^-, γ	1.8; 2.4 3.3	0.36; 0.89 2.5; 3.5 4.05	Mo (d, xn) Ru (d, xn) [213, 215] Ru (n, p) [148] U (fission) Mo^{104} $\xrightarrow{\beta^-}$ Pu (fission) [63a]
105	7.7 min (10 min)	β^-, γ	3.4	0.110	U (fission) [213] U (fission) Mo $\xrightarrow{\beta^-}$ [215]
106	37 ± 4 sec				Pu (fission) [63a]
107	29 ± 3 sec				U (fission) [147] Pu (fission) [63a]

* e.c.—electron capture   ** i.t.—isomeric transition

quantum with an energy of 140 kev. The 2 kev γ-quanta emitted in the process are converted to a great extent. Because of the low energy of the isomeric transition, the conversion takes place on the weakly bound electrons of the outer shells. Therefore, changes in the structure of the electron cloud affect the coefficient of internal conversion of the γ-rays, and also the half-life of the isomer. The half-life of Tc^{99m} (metal) is 6.04 ± 0.03 hr, which is 1 sec longer than $T_{1/2}$ in $KTcO_4$ and 8.6 sec shorter than $T_{1/2}$ in Tc_2S_7.

Similar changes also occur when the pressure is increased [65, 286]. Thus, at a pressure of $1 \cdot 10^5$ atm the decay of Tc^{99m} is accelerated by 0.025% [65]. The influence of the physical factors and the chemical state of technetium on Tc^{99m} decay is treated in detail in [8, 95, 132, 317].

The isotope Tc^{99} with a long half-life is obtained in weighable amounts by separating it from a mixture of fission products of uranium or from natural molybdenum irradiated by neutrons. The first of these sources is more efficient and cheaper, since high yields of technetium isotopes are obtained by the fission of nuclear fuel. Below we give data [200] showing the yield of individual technetium isotopes by fission of uranium in the reactor.

	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 long-lived Tc^{99} is formed in particularly high yields. High yields of Tc^{99} are also obtained when other materials undergo fission (Table 3).

In long-term operation of the nuclear reactor technetium accumulates not only by the fission of U^{235}, but also by the fission of large amounts of Pu^{239} and Pu^{241}

Table 3

YIELD OF Tc^{99} IN THE FISSION OF U, Pu
AND Th NUCLEI BY NEUTRONS WITH
DIFFERENT ENERGIES [100]

Fissionable isotope	Neutrons	Yield, %
U^{233}	Thermal	4.8
U^{235}	Thermal	6.06
	14 Mev	5.17
U^{238}	Fast	6.3
Pu^{239}	Fast	5.9
	Thermal	5.9
Th^{232}	Fast	2.7
	8 Mev	3.1

formed in the reactor. The total amount of technetium can be determined [15] form the equation

$$N = \frac{99 \cdot 10^3 N_0 \sigma_f (1 + \beta) \delta \{1 - \exp[-(\sigma_c - \sigma_\gamma)\psi t]\} \exp(-\sigma_\gamma \psi t)}{6.02 \cdot 10^{23} \cdot 100 (\sigma_c - \sigma_\gamma)},$$

where N is the amount of technetium formed, mg/kg U^{235}; N_0 is the number of U^{235} nuclei in 1 kg of uranium; σ_c and σ_f are the cross sections of capture and fission of U^{235}, respectively, averaged according to the neutron spectrum of the reactor; σ_γ is the cross section of Tc^{99} capture; β is the ratio of the number of fissions of Pu^{239} and Pu^{241} to the number of fissions of U^{235}; δ is the yield of technetium in the fission of U^{235}, %, and ψt is the integrated neutron flux.
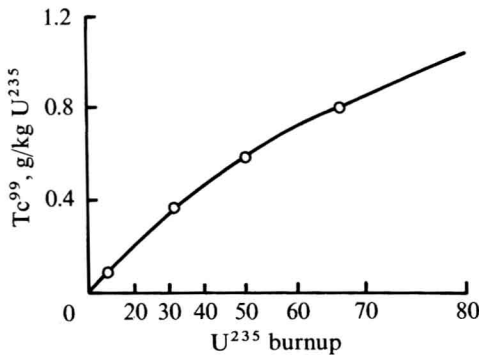

Figure 2

Amount of Tc^{99} formed in a nuclear reactor as a function of the U^{235} burnup [15]

According to calculations which agree with the result of the analysis of the spent fuel elements of the First Soviet Nuclear Power Plant, considerable amounts of Tc^{99} are formed. It can be seen from Figure 2 that even with a 50% burnup of U^{235}, about 600 mg of Tc^{99} are formed per kg of U^{235}. According to other data [163, 164] obtained in a nuclear reactor, 10 kg of Pu yield about 150 g of Tc; during the operation of a reactor with an output of 10^5 kw, approximately 100 g of Pu and 2.5 g of Tc are formed. To determine the accumulation of technetium in the fission products as a function of the output of the reactor, the following simplified equation can be used [16]

$$N = 28P \cdot t, \tag{1}$$

where N is the amount of Tc formed, mg; P is the output of the reactor, Mw; and t is the time of operation of the reactor, days.

According to (1), about 8 g of Tc are formed per day, or 3 kg per annum, in a nuclear reactor with an output of $2.85 \cdot 10^5$ kw. According to [16], tens of kilograms