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THE PRESENT STATE OF THE ANALYTICAL CHEMISTRY OF TECHNETIUM

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I. INTRODUCTION

Interesting properties of technetium have been discovered in recent years. Unlike its nearest analogue, the perrhenate ion, the pertechnate ion exhibits exceptional anti-corrosion properties[1], greatly superior to those of CrO_4^{2-} ions. For example, iron which has been immersed in ammonium pertechnate solution with a technetium concentration of only 5 $\mu g\ ml^{-1}$ undergoes no rusting over a period of several years. This reveals promising possible applications of technetium compounds as effective inhibitors of the corrosion of iron and steel. These compounds may prove particularly useful for preventing the corrosion of homogeneous boiling reactors[2], certain submarine parts, etc.

Metallic technetium and its alloys (for example an alloy containing 50% Tc and 50% Mo) are superconductors at low temperature[3,4] and can be used to replace super-purity niobium in inertial control systems in rocket technology[2], as memory elements in electronic machines[5,6], and in thermonuclear-synthesis assemblies for the production of magnetic fields of high intensity[6]. Many fundamental properties of this element have not been studied, since large quantities are not available. When larger quantities are produced, new properties of technetium and extensive possibilities for its use in industry may be revealed.

Thus the problems of preparing large (kilogramme) quantities of technetium and separating it from the neighbouring elements rhenium, molybdenum, and ruthenium are now of pressing importance. It is therefore of interest to examine the latest achievements in the analytical chemistry of technetium, since recent reviews on the chemistry of technetium[6-12] devote little space to this topic, and there are no special reviews on the subject.

II. METHODS OF ISOLATING AND CONCENTRATING TECHNETIUM

A large number of technetium isotopes with mass numbers from 92 to 107 and half-lives from several seconds to 2×10^6 years are now known. The most important isotopes of technetium, their radioactive characteristics, and methods of preparation are given in Table 1.[13]

Four of the isotopes given in Table 1: ^{95m}Tc, ^{96}Tc, ^{97m}Tc, and ^{99m}Tc, are used as tracer atoms in the study of the chemical properties of technetium. The most readily available for this purpose is the nuclear isomer ^{99m}Tc, which is formed with high specific activity from molybdenum irradiated with neutrons. The other three isotopes: ^{97}Tc, ^{98}Tc, and ^{99}Tc are long-lived, with half-lives $>10^5$ years, and can be used for the study of the chemistry of technetium in ponderable quantities. The last of these isotopes is the most readily available, since it is formed by the fission of uranium and plutonium nuclei or by the prolonged irradiation of molybdenum in a reactor.

TABLE 1. Most important isotopes of technetium.

Isotope	Half-life	Decay type	Energy of radiation, MeV		Method of preparation
^{95m}Tc	60 days	e.c. ~96% i.t. ~3% β^+ ~0.4%	β^+ γ	0.4 0.201	$^{95}Mo(p,n)^{95m}Tc$
^{96}Tc	4.2 days	e.c	γ	0.77–0.84	$^{96}Mo(p,n)^{96}Tc$
^{97m}Tc	91 days	i.t.	γ	0.096	$^{97}Mo(p,n)^{97m}Tc$
^{97}Tc	2.6×10^6 years	e.c.	γ		$^{97}Mo(d,2n)^{97}Tc$ $^{97m}Tc \rightarrow {}^{97}Tc$
^{98}Tc	1.5×10^6 years	β^-	β^- γ	0.30 0.66; 0.75	$^{98}Mo(p,n)^{98}Tc$
^{99m}Tc	6.04 h	i.t.	γ	0.14	$^{98}Mo(n,\gamma)^{99}Mo \xrightarrow{\beta} {}^{99m}Tc$
^{99}Tc	2.12×10^5 years	β^-, no γ	β^-	0.296	fission products from uranium and plutonium; daughter ^{99m}Tc

1. Isolation of Technetium from Irradiated Molybdenum

The best method for obtaining relatively large quantities of technetium is by isolating it from the mixture of uranium fission products or from the waste products of the atomic [energy] industry. Because of the high level of radiation, however, all operations involved in the isolation of technetium from these materials must be carried out in special radiochemical laboratories using apparatus with remote control. When small (milligramme) quantities are required, technetium can also be obtained by the prolonged neutron irradiation of very pure molybdenum in a nuclear reactor, according to the reaction

$$^{98}Mo(n,\gamma)^{99}Mo \xrightarrow[67\ h]{\beta^-} {}^{99m}Tc \xrightarrow[6.1\ h]{i.t.} {}^{99}Tc \text{ (long-lived, } 2.12\times10^5 \text{ years)}.$$

When the ^{99}Mo has decayed, the technetium can be isolated in ordinary radiochemical laboratories.

The first ponderable quantities of technetium were obtained by irradiating 5.7 kg of pure metallic molybdenum powder in a nuclear reactor for 130 h with a neutron beam at 5×10^{11} neutrons $cm^{-2}\ s^{-1}$.[14,15] In this case, according to calculations, 2.8 mg of technetium, i.e. only 5×10^{-5}%, was formed.

A variety of methods have been described for extracting small quantities of technetium from molybdenum irradiated with neutrons, protons, or deuterons. After dissolution, the main bulk of the molybdenum was removed by precipitating silver molybdate[16] or lead molybdate[17] or by precipitation with 8-hydroxyquinoline from ammonium acetate solution[18]. Technetium can be extracted from an ammoniacal solution of molybdenum by coprecipitating the pertechnate ion with sparingly-soluble crystalline $MgNH_4PO_4$ and $MgHPO_4$ [19] After dissolution of the precipitate in 6 M HCl, the technetium was reduced to a lower valency by passing H_2S, after which $MgNH_4PO_4$ or $MgHPO_4$ was again precipitated from ammoniacal solution. Under these conditions, technetium remained in solution. Further concentration and purification was achieved by coprecipitation with certain sulphides (Re_2S_7, PtS_2, CuS, etc.[15]) or by ion-exchange[15,20] or electrochemical[15,16,21,22] methods. A chromatographic method for the isolation of technetium using strongly-basic anion-exchange resins (Dowex I-X8, IRA-400, etc.)[23] has also been developed. The metallic molybdenum which had been irradiated with neutrons was dissolved in a 10% NaOH + 30% H_2O_2 mixture, the solution was boiled to remove H_2O_2, and passed through a chromatographic column containing the resin. Molybdenum was weakly absorbed by the resin and eluted with 3 M NaOH solution, after which the technetium was eluted with 1 M $HClO_4$ or NH_4ClO_4 solution. When technetium is being isolated from kilogramme quantities of molybdenum, however, precipitation methods are unsuitable, because of the large volumes of solution and precipitate involved. Ion-exchange chromatography is also inapplicable, so that methods have been developed for isolating technetium by extraction and distillation.

Extraction methods are based on the extraction of pertechnate ions from alkaline media by means of chloroform in the presence of tetraphenylarsonium chloride[24,25] or with pyridine or methyl derivatives of pyridine[26-28]. Another effective method involves the extraction of technetium by ketones from 3–5 *N* solutions of alkalis or alkali metal carbonates[28-32]. The last method is used fairly frequently to isolate the nuclear isomer ^{99m}Tc for analytical purposes from molybdenum trioxide irradiated with neutrons. The molybdenum trioxide MoO_3 is dissolved with heating in 3–4 *N* KOH or NaOH solution in the presence of small quantities of hydrogen peroxide, after which the technetium is extracted from the solution by ethyl methyl ketone, by treatment for 5–10 min. The organic phase is washed 2–3 times with small volumes of 3–4 M K_2CO_3 solution to remove traces of molybdenum and radioactive impurities. The technetium is then re-extracted into the aqueous phase using chloroform or other non-polar solvents.

To isolate the short-lived isomer ^{99m}Tc, use is made not only of the above extraction methods but also of chromatographic methods with synthetic anion-exchange resins[33] or inorganic sorbents such as alumina[34,35] and zirconium hydroxide[36]. As the ^{99m}Tc from the molybdenum, adsorbed on the inorganic sorbents, accumulates on the column, the technetium is eluted at intervals with 0.1 M HNO_3 or H_2SO_4 in the case of alumina or 2 M HNO_3 in the case of zirconium hydroxide. Methods based on the electrochemical separation of ^{99m}Tc from non-aqueous media[37,38] and on the irradiation of certain carbonyl compounds of molybdenum[39-41] have also been proposed. These methods have not been widely used in analytical chemistry, however, because of the time required for the electrochemical separation and the complexity of preparation and low stability to irradiation shown by the carbonyl compounds of molybdenum.

The most effective methods for separating technetium from very large quantities of molybdenum are the distillation methods. A method based on the codistillation of technetium and perchloric acid has been described[22]. To prevent the distillation of molybdenum dissolved in the $HClO_4$, phosphoric acid was added to form the non-volatile molybdophosphate complex.

Boyd and coworkers[15] showed that the distillation of technetium with concentrated sulphuric acid provides a fairly effective method for separating technetium from molybdenum. Thus when 6 ml of acid were taken per gramme of metallic molybdenum, 75% of the technetium passed into the distillate, and this figure increased to 90% when the quantity of acid was doubled. After two distillations, more than 98% of the technetium is extracted. This method was used to isolate milligramme quantities of technetium from 5.7 kg of molybdenum. As an example, we can describe a method developed[15] for the isolation and concentration of technetium from molybdenum. The molybdenum, irradiated with neutrons, was left for 6 weeks until the ^{99}Mo had decayed, after which it was dissolved in concentrated H_2SO_4. The sulphuric acid was then distilled from solutions containing approximately 190 g of the metal. The resulting distillate was diluted to a concentration of 4 M with respect to sulphuric acid, heated to boiling, and treated with bromine water. Platinum was then added to the solution (1 mg per 200 ml) and platinum sulphides were precipitated. The precipitate was filtered off, dissolved in an $NH_4OH + H_2O_2$ mixture, the solution was evaporated to dryness, the residue was treated with concentrated H_2SO_4 or $HClO_4$, and the technetium was distilled into a flask cooled with ice. After 4-fold dilution, the sulphides were precipitated from the solution. Spectroscopic analysis of the resulting concentrate showed the presence of technetium, together with fairly large quantities of molybdenum. The methods used to purify technetium from molybdenum and also from rhenium, which is present in traces in molybdenum and is concentrated with the technetium, will be described below.

The milligramme quantities of technetium isolated from molybdenum irradiated with neutrons have played an important part in the study of the chemical and physical properties of this element. The further development of research and the practical application of technetium require large quantities (tenths of a kilogramme) of the element, however, and these cannot be obtained from molybdenum. At the present time, therefore, increasing attention is being paid to the isolation of technetium from uranium fission products.

2. Isolation of Technetium from Uranium Fission Products

The nuclear reactor gives, in addition to other fission products, one of the most long-lived isotopes of technetium — ^{99}Tc. The yield of this isotope in the fission of ^{235}U with thermal neutrons amounts to ~6.2%. When the reactor has operated for a prolonged period, however, considerable quantities of ^{239}Pu and ^{241}Pu accumulate, and the fission of these isotopes provides an additional source of technetium. According to calculations[42], considerable quantities of ^{99}Tc accumulate in the fuel elements of the first atomic power-station. Thus the consumption of 50% of the ^{235}U gives 600 mg of ^{99}Tc per kg of ^{235}U. According to other data[43], the production of 10 kg of Pu in the nuclear reactor leads to the accumulation of 150 g of ^{99}Tc. Thus the development of atomic power provides an opportunity for the production of technetium in large quantities. Particularly suitable materials for this purpose are the waste solutions from atomic plants. Treatment of these solutions makes it possible, for example, to obtain 400 g of technetium per month[3].

Ponderable (milligramme) quantities of technetium were first isolated from uranium fission products by Parker *et al.*[44] A rod of metallic uranium which had been irradiated in a nuclear reactor was dissolved in 37% HCl and the UCl_4 formed on dissolution was oxidised with H_2O_2 and bromine water to UO_2Cl_2. The technetium was then coprecipitated with PtS_2 using hydrogen sulphide, the precipitate was dissolved in a mixture of H_2O_2 and NH_4OH, and the solution was evaporated to dryness. The subsequent purification of the technetium was carried out by distilling Tc_2O_7 from 18 *N* H_2SO_4.

The first gramme of technetium was obtained in 1952 from the waste products from plutonium production[45]. Because of the high concentration of nitrate ion in the solution used, it was impossible to concentrate the technetium in the form of sulphides. Use was therefore made of the organic base tetraphenylarsonium chloride, which forms sparingly soluble precipitates with perchlorate ions added to the waste solutions and coprecipitates the structurally-similar pertechnate ion. The precipitate was dissolved in concentrated H_2SO_4 and the technetium was deposited electrolytically on platinum electrodes. The resulting black deposit of TcO_2 was dissolved in 18 M H_2SO_4, the technetium was distilled off, and technetium sulphide was precipitated from the distillate. The use of electrolysis in this procedure makes it impossible to regenerate the expensive tetraphenylarsonium chloride. A method was therefore developed[46] to avoid the decomposition of this reagent. The mixture of tetraphenylarsonium perchlorate and pertechnate was dissolved in alcohol and the solution was passed through a column of anion-exchange resin in the Cl^- form. The perchlorate and pertechnate were absorbed on the resin and the tetraphenylarsonium cation passed through the column. The technetium was then eluted with 2 *N* NaOH solution.

Technetium has also been concentrated and isolated by precipitation and coprecipitation methods from the waste products from the processing of atomic fuel[47,48]. Technetium and ruthenium were coprecipitated on iron hydroxide in the presence of hydrazine hydrate at a controlled pH of 2–3, the precipitate was dissolved in HNO_3, and tetraphenylarsonium pertechnate was precipitated and reprecipitated several times. Tc_2S_7 was then precipitated from 2 *N* HCl. The precipitate was dissolved in an NH_4OH + + H_2O_2 mixture and pure $KTcO_4$ was isolated. Technetium can also be isolated from alkaline solutions of uranium fission products by coprecipitating Tc^{IV} with Fe_3O_4.[49]

The chromatographic and extraction methods for isolating and concentrating technetium from fission products appear to be the most effective. One of the earliest extraction experiments was carried out by Tribalat and Beydon[24,50], who extracted technetium with a solution of tetraphenylarsonium chloride in chloroform. The equilibrium constant for the extraction reaction

$$(C_6H_5)_4As^+(aq.) + TcO_4^- \rightleftarrows (C_6H_5)_4AsTcO_4(org.),$$

is $\sim 3 \times 10^6$. The isolation was carried out as follows. Irradiated uranium trioxide UO_3 was dissolved in H_2SO_4 and the solution was treated with ammonium persulphate to oxidise I^- ions to elementary iodine, which was extracted with toluene. The aqueous solution was boiled to remove traces of iodine, neutralised with $(NH_4)_2CO_3$, and treated again with ammonium persulphate. TcO_4^- was then extracted with a solution of tetraphenylarsonium chloride in chloroform.

In the isolation of technetium from industrial solutions, extensive use has recently been made of extracting agents such as amines and ketones, which give high distribution constants for TcO_4^-.[28,51-55] For example, the extraction of technetium with pyridine from alkaline media makes possible selective and almost quantitative separation of technetium from nitrate and other solutions. This can be seen from Tables 2 and 3,[28] which give the distribution constants for technetium and certain other elements obtained by the fission of uranium, for extraction with pyridine from alkaline $NaNO_3$ and Na_2CO_3 solutions.

High distribution constants for technetium are given by methyl derivatives of pyridine. For example, the distribution constants for technetium in extraction from 2 M $(NH_4)_2CO_3$ solution using pyridine and 2-methylpyridine are 7.5 and 242 respectively. 3-Methyl- and 4-methyl-pyridines give even higher values of *E* than 2-methylpyridine. 2,4-Dimethylpyridine has proved particularly effective for the isolation of technetium from solutions with high nitrate ion concentration (for extraction from 4 *N* $NaNO_3$–0.5 *N* NaOH, $E = 50$). The technetium is usually recovered by distillation of the pyridine and its methyl derivatives, which can be used again. Another convenient method involves the re-extraction of technetium with non-polar solvents: chloroform, hexane, kerosene, and petrol, which also purify the technetium solution from organic impurities.

Amines have recently been used[3] to isolate kilogramme quantities of technetium from industrial wastes remaining after the fluorination of uranium irradiated in reactors. The technetium was recovered by repeated extraction with 2,4-dimethylpyridine, followed by purification by extraction with trioctylamine in petrol and repeated crystallisation as ammonium pertechnate from NH_4NO_3 solution.

TABLE 2. Distribution constants (E) for technetium in extraction with pyridine from alkaline $NaNO_3$ solutions of different concentration.

$NaNO_3$, M	E	
	2 N NaOH	0.25 N NaOH–2.0 M Na_2CO_3
0	54	740
0.25	—	110
0.50	19	89
0.75	—	71
1.0	16	58
1.5	12	52
2.0	—	42

TABLE 3. Distribution constants (E) for various uranium fission products in extraction with pyridine from 0.25 N NaOH–2.0 M Na_2CO_3 solution.

Fission product	E
^{99}Tc	740
^{137}Cs	$2.87 \cdot 10^{-3}$
^{106}Ru	$1.27 \cdot 10^{-1}$
^{95}Zr, ^{95}Nb	$6 \cdot 10^{-4}$
$^{152-155}Eu$	$6 \cdot 10^{-3}$
^{90}Sr	$3.48 \cdot 10^{-3}$

Another effective method[52,54] for the isolation of technetium in this case is by extraction with a 0.3 M solution of trilaurylamine in an organic solvent. After the removal of uranium with 0.5 N HNO_3 and of neptunium with 0.1 N H_2SO_4, the technetium was re-extracted with 1 N NH_4OH or 4 N NaOH.

An extraction method using tributyl phosphate in kerosene has been developed for isolating technetium from sulphuric acid solutions[56]. Tributyl phosphate has not found wide application, however, because of the poor extraction of technetium from nitrate solutions by this solvent (the distribution constants for extraction from 0.5 M and 4 M HNO_3 are 1.36 and 0.04 respectively).

Chromatographic methods are based on the extensive sorption of pertechnate ion from weakly acidic, neutral, and alkaline media by strongly basic anion-exchange resins; most other fission elements (^{137}Cs, ^{90}Sr, $^{152-155}Eu$, etc.) are not absorbed by anion-exchange resins. Appreciable sorption of TcO_4^- takes place even from solutions with high concentrations of nitrate ion, which is usually present in the waste solutions from the atomic industry. Table 4 [28] gives the distribution constants for technetium between Dowex-1 resin and $NaNO_3$ solutions of different concentration.

According to data obtained by other workers[57], who carried out experiments under factory conditions and in plant assemblies, TcO_4^- is readily absorbed by strongly basic anion-exchange resins from solutions with nitrate ion concentrations up to 7.5 N. This has made it possible to develop an effective and economic chromatographic method for isolating technetium from neutral industrial solutions ("Purex wastes")[57]. The solution was passed through a chromatographic column containing 5 litres of anion-exchange resin, and after desorption the technetium was separated from traces of ruthenium by oxidising the latter to RuO_4 and sorption on a cation-exchange resin. The technetium was then precipitated as the sulphides.

TABLE 4. Distribution constants (E) for technetium between Dowex-1 anion exchange resin and alkaline (0.25 N NaOH) $NaNO_3$ solutions of different concentration.

$NaNO_3$, M	E
0	4500
0.5	575
1.0	340
2.0	190
3.0	142
4.0	125
5.0	121
6.0	122

The method makes it possible to obtain in one stage a high yield (> 80%) of technetium with a chemical and radiochemical purity >99%.

In one of the latest improved chromatographic methods[58] acidic nitrate solutions of uranium fission products were treated with NaOH and the alkaline solutions were passed through a column of strongly basic anion-exchange resin. The technetium was then eluted with HNO_3, alkali was added to the solution, and the technetium was extracted with ethyl methyl ketone.

A new method for the production of technetium was recently developed in the USA[2,59]. In the processing of atomic fuel from gas-diffusion plants, technetium is separated from uranium hexafluoride by passing their heated mixture through a column packed with magnesium fluoride, in which the technetium is retained. The mechanism of the absorption of the technetium has not been studied in detail, but data which have been obtained suggest that the phenomenon is based on physical adsorption.

3. Methods of Isolating Technetium from Minerals in the Search for the Element in Nature

The detailed study of the chemical and physicochemical properties of technetium and its production in ponderable quantities have made it possible to undertake intensive searches for technetium in nature, and these have led to the detection of technetium in the sun's atmosphere and in young stars[60]. The question of the possible discovery of technetium in terrestrial materials is important in the geochemistry of this element[61-66]. Boyd and coworkers' searches[62] for technetium in various minerals showed that some of the minerals contained extremely small traces of the element.

Recently, Kenna and Kuroda[64-66] isolated appreciable quantities of technetium (10^{-9} g) from pitchblende obtained in the Congo. Like Boyd, Kenna and Kuroda considered that the presence of technetium in the minerals results from the spontaneous fission of uranium or the activation of molybdenum, ruthenium, and niobium by powerful cosmic radiation.

A variety of methods, depending on the mineral studied, are available for the isolation and determination of technetium in natural materials. Chromatography, distillation, and coprecipitation have been used[62] in the analysis of minerals such as MoS_2 and yttrotantalite. The mineral was fused with five times its weight of Na_2O_2 in a zirconium or iron crucible. To control the chemical process, radioactive technetium (usually $^{96}Tc + {}^{95m}Tc$) was added

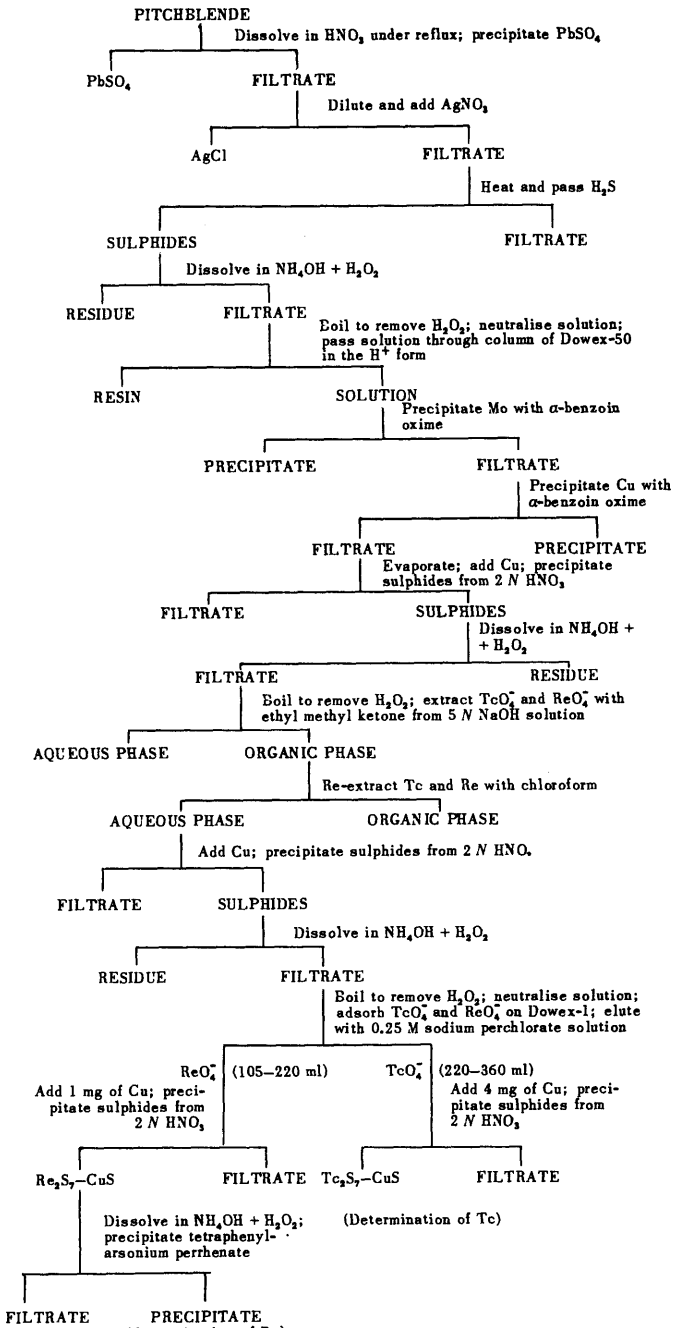


Fig. 1. Scheme for separating technetium from pitchblende.

at each stage to the material being studied. The melt was dissolved in water, the solution was boiled and cooled, and iron was precipitated as the hydroxide, 1–45 litres of the filtrate was passed through a 22 cm×9.6 cm column of strongly basic anion-exchange resin (Dowex-2 or Amberlite IRA-410). The anion-exchange resin absorbed all the technetium, rhenium, and a small proportion of molybdenum, ruthenium, sulphate, etc. Sodium, copper, nickel, etc. cations passed through the column. Molybdates and other anions were then eluted with 1 M $NaNO_3$ at pH 10 or with 2 N NaOH, after the column had been washed with distilled water. Technetium and rhenium were eluted with 2 N $HClO_4$ or $NaClO_4$. The solution was acidified, heated, and treated with bromine water, after which rhenium and technetium sulphides were precipitated. The precipitate was dissolved in an $NH_4OH + H_2O_2$ mixture, the solution was evaporated to dryness, and the residue was dissolved in 10 M HCl. The main bulk of the rhenium was separated from technetium by precipitating rhenium sulphide with hydrogen sulphide in this medium. Further separation of technetium from rhenium was achieved by the methods of ion-exchange chromatography described below. Finally, technetium was coprecipitated with copper sulphide (1–1.5 mg Cu) and this "technetium concentrate" was treated by one of a number of methods for quantitative determination of technetium.

In addition to the above methods, methods involving the extraction of technetium have been used in the analysis of pitchblende[66]. A scheme illustrating the analytical operations involved in the isolation and purification of technetium from this mineral is shown in Fig. 1.

III. METHODS OF SEPARATING TECHNETIUM FROM RHENIUM, MOLYBDENUM, AND RUTHENIUM

The most difficult task in the isolation of technetium from irradiated products is its separation from the neighbouring elements rhenium, ruthenium, and molybdenum. In the isolation of technetium from irradiated molybdenum it is necessary to separate it quantitatively not only from molybdenum, but also from rhenium, which is usually present in traces in the molybdenum and is concentrated with the technetium. In the extraction of technetium from fission products it is necessary to separate it from ruthenium isotopes, which, although formed in approximately the same yield as ^{99}Tc, exhibit a very much higher specific activity.

Technetium is separated from these elements by methods involving distillation, extraction, precipitation and crystallisation, anion-exchange chromatography, etc.

1. Distillation Methods

Since the oxide Tc_2O_7 is volatile, heptavalent technetium can be codistilled with certain strong acids. Acids can be divided into three groups according to the extent to which codistillation of technetium with the acid takes place (Fig. 2 [15]): (1) with acids such as $HClO_4$ codistillation is quantitative, up to 75% of the technetium codistilling with the first 20% of distillate; (2) with HNO_3, aqua regia, H_2SO_4, and fuming H_2SO_4, codistillation is incomplete, appreciable quantities of technetium beginning to codistil only when more than half of the acid has been transferred to the distillate; (3) with acids such as HCl, HBr, and HI, technetium is not codistilled, since these acids reduce technetium to non-volatile compounds.

The degree of codistillation of technetium is influenced chiefly by the oxidising power of the acid, temperature, and the stability of the volatile oxide. The addition of oxidising agents to acids such as H_2SO_4 and H_3PO_4 increases appreciably the degree of codistillation of technetium, as can be seen from the curves in Fig. 2. The lower extent of the codistillation of this element with H_2SO_4 is due to the possible presence of reducing impurities.

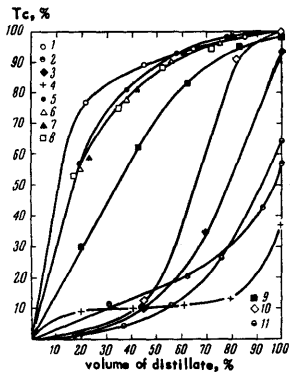


Fig.2. Codistillation of technetium with various acids.
1) $HClO_4$; 2) H_2SO_4; 3) fuming H_2SO_4; 4) HNO_3; 5) $H_2SO_4 + KIO_4$; 6) $H_2SO_4 + K_2Cr_2O_7$; 7) $H_2SO_4 + Na_2S_2O_8 + AgNO_3$; 8) $H_2SO_4 + KBrO_3$; 9) $H_2SO_4 + Na_2S_2O_8$; 10) $H_3PO_4 + KMnO_4$; 11) aqua regia.

The ability of technetium to undergo ready reduction in hydrochloric acid solutions has been used to develop a distillation method for separating technetium from rhenium[9,15,67]. The distillation is carried out at 180–200° from a mixture of sulphuric and hydrochloric acids. In this case an appreciable proportion of the rhenium (~95%) enters the distillate, whereas almost all the technetium is reduced to the tetravalent state by the hydrochloric acid and remains in the solution. The separation factor is equal to 50. This process was recently made the basis of another method[68] involving the reduction of pertechnate ion with hydroxylamine (the perrhenate ion is not reduced in the process). The rhenium is distilled from sulphuric acid containing hydroxylamine. The method can be used to separate 10 mg of rhenium from microquantities of technetium.

A method has been described for separating technetium and rhenium by distillation of the elements as the chlorides[69]. The distillation is carried out from a mixture of metallic technetium and rhenium or their sulphides, in a current of chlorine. Rhenium is then distilled from the distillate at 300° *in vacuo*; the technetium chloride decomposes, leaving metallic technetium.

Partial separation of these two elements can be achieved by codistillation with perchloric acid[9], but in this case ruthenium distils with the technetium.

Codistillation of technetium with sulphuric acid has been used to separate technetium and ruthenium[9]. In this case separation factors of the order of 10^5 and above are obtained. In the absence of oxidising agents, however, the degree of codistillation of technetium is often very low, because of its reduction by impurities present in the acid[9,15]. (A detailed study[70] of the distillation of technetium with H_2SO_4 showed that technetium can be distilled quantitatively with H_2SO_4 if highly pure acid and scrupulously clean distillation apparatus are used.) In practice, therefore, complete distillation of technetium is best achieved by adding oxidising agents, which should moreover be non-volatile, stable in boiling sulphuric acid, sufficiently powerful to retain technetium in the heptavalent state, but incapable of oxidising lower valency states of ruthenium to the volatile RuO_4. It is very difficult to select oxidising agents satisfying these requirements, and Ce^{IV} and CrO_3 are usually employed. In the distillation of technetium in the presence of oxidising agents some ruthenium distils as RuO_4, so that for the quantitative separation of technetium from ruthenium, the RuO_4 is reduced to insoluble RuO_2 by boiling the distillate with alcohol for 1–2 min.

Technetium and ruthenium can be separated from alkaline solutions by distillation of the RuO_4 in a current of chlorine[71].

2. Methods of Separation Based on Precipitation and Crystallisation

A convenient method for separating large quantities of rhenium from technetium involves the fractional precipitation of rhenium sulphide from concentrated hydrochloric acid solutions. Under these conditions technetium is not precipitated and remains in solution. Curves illustrating the dependence of the coprecipitation of microquantities of technetium and rhenium with platinum sulphide on the hydrochloric acid concentration at 90° are shown in Fig. 3.[15] Almost no technetium is coprecipitated at an HCl concentration 9 M and above, whereas rhenium is coprecipitated up to 10 M HCl. This difference in coprecipitation is due to the reduction of the pertechnate ions by hydrochloric acid to a lower valency state in which technetium is not coprecipitated with metal sulphides. An interesting feature is that complete coprecipitation of technetium with sulphides is observed from other acidic media (for example 24 *N* H_2SO_4) exhibiting no reducing properties. The separation by the above method is not quantitative, however (some Re remains in the solution), and the complete purification of Tc from Re requires the use of more refined methods (for example chromatography).

Satisfactory separation of Tc from Re can be achieved by reducing Tc^{VII} with HCl and coprecipitating Tc^{IV} with $Fe(OH)_3$.[29,72] The technetium can then be oxidised to the heptavalent state by oxidising the precipitate in concentrated HNO_3 or dilute H_2SO_4 in the presence of H_2O_2, and precipitating the iron from solution with ammonia.

The separation of ponderable quantities of Tc and Re can be achieved by fractional crystallisation of potassium pertechnate and perrhenate (Fig. 4)[15], and small quantities of ruthenium can be separated by recrystallising $KTcO_4$.[8]

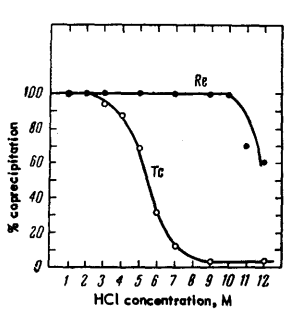


Fig.3. Coprecipitation of technetium and rhenium with PtS_2 at different HCl concentrations (90°).

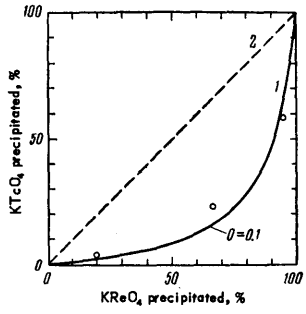


Fig. 4. Separation of $KTcO_4$ from $KReO_4$ by fractional crystallisation:
1) experimental data; 2) calculated data.

Precipitation methods for separating technetium and molybdenum have been described above. These involve the precipitation of molybdenum with 8-hydroxyquinoline or α-benzoin oxime or as silver or lead molybdate. On the other hand, the pertechnate ion can be separated from an alkaline solution containing molybdenum or ruthenium, by coprecipitation with tetraphenylarsonium perrhenate or perchlorate. The latter is more convenient, since the technetium is subsequently more readily separated.

3. Extraction Methods

Extraction methods are very effective for the recovery of technetium from various materials and its separation from most elements of the Periodic System, but they generally do not give quantitative separation of this element from its analogue rhenium. Some extraction methods are fairly effective for the separation of technetium from molybdenum and ruthenium, however. As noted above, appreciable separation of technetium from molybdenum and ruthenium can be achieved by extraction with pyridine [26-28] from alkaline media and by ketones [28-32] from 3–5 N solutions of alkalis or alkali metal carbonates. In this case the technetium can be re-extracted in the aqueous phase with chloroform or other non-polar solvents. Another effective method for the separation of technetium and molybdenum is that based on the extraction of tetraphenylarsonium pertechnate with chloroform [24,25,50]. Before extraction it is best to add small quantities of oxidising agent such as H_2O_2 to prevent the reduction of TcO_4^- by impurities in the organic reagents. During washing, the solution should contain a sufficient concentration of tetraphenylarsonium ion ($\sim 5 \times 10^{-5}$ M) to prevent the premature re-extraction of TcO_4^- into the aqueous phase. The technetium is re-extracted with 0.2 N $HClO_4$ or 12 N H_2SO_4. Finally, technetium and molybdenum can be separated by extracting the molybdenum with ether from hydrochloric acid solutions [8,67,73]. In this case the best results are obtained [73] by extracting the molybdenum with ethyl ether from 1 M HCl–1 M NH_4NCS solution. Radiochemically pure technetium is left in the aqueous phase in ~80% yield.

An effective extraction method for the separation of technetium and ruthenium was developed in the Geochemical Institute of the USSR Academy of Sciences [74]. It is based on the extraction of technetium as triphenylguanidinium pertechnate from sulphuric acid by means of chlorex (β-chloroethyl ether). The technetium can be re-extracted with 3 N NH_4OH solution.

TABLE 5. Extraction of technetium compounds by various organic solvents.

Technetium compound	Extracting agent	Applications	References
Salts with organic cations or bases: tetraphenylarsonium triphenylguanidinium methyltricapryl-ammonium quinolinium trilaurylammonium nitron	benzene, chloroform, nitrobenzene, chlorex (β-chloroethyl ether)	separation of Tc from fission products and irradiated molybdenum separation from Ru, Mo, and other elements	24,25,45 74 77 78 52 29
Technetic* acid and its salts			
$HTcO_4$	isopentanol, isobutyl methyl ketone, tributyl phosphate in kerosene	separation of Tc for its determination in fission products	6,56,78
Pertechnate ion: from acidic media	alcohols, ketones, trioctylamine in chloroform, hexane, or ether	isolation from waste solutions from the atomic industry and irradiated Mo. Separation from isotopes of Mo, Ru, Cs, Sr, Nb, and other elements	7,26–32, 51–56, 75,80, 81
from alkaline media	ketones, cyclic amines		
Complexes of technetium reduced to a lower valency state: thiocyanato-complexes	alcohols, ethers, ketones, solution of trioctylphosphine oxide and trioctylamine hydrochloride in cyclohexane and dichloroethane	extraction–spectrophotometric determination, separation from Mo and other elements	8,29,73, 82,83
p-Thiocresolate	chloroform, ether, benzene, CCl_4, toluene	ditto	84
1,5-Diphenylcarbohydrazide	CCl_4	»	85
Hexachlorotechnate	trioctylamine in cyclohexane and tetraphenylarsonium [chloride] in chloroform	»	7,11
Xanthate	chloroform, CCl_4	»	86
Toluene-3,4-dithiol	CCl_4	»	87
Compounds with α-picolinic and sulphosalicylic acids	chloroform	»	89
Cupferronate	ether, chloroform	partial separation from Re	76

* Presumably pertechnic acid is meant here (Ed. of Translation).

It has been suggested [75] that in the separation of a mixture of technetium and ruthenium in uranium fission products the extraction be first carried out with pyridine from 4 N NaOH in the absence of oxidising agent. In this case only technetium, which is present in solution as TcO_4^-, is extracted. NaOCl is then added to the aqueous phase, the Ru is oxidised to RuO_4^{2-}, and extracted with pyridine.

Partial separation of technetium from rhenium can be achieved by extraction of the cupferron complex of technetium after reducing the latter to a lower valency state [76]. In this connection, mention may be made of the need for study of the extraction separation of technetium and rhenium using ethyl methyl ketone, from alkaline solutions containing reducing agents, such as hydrazine or hydroxylamine.

Extraction methods are widely used in the analytical chemistry of technetium for separation, isolation, and determination. Table 5 gives data on the extraction of technetium compounds with different organic solvents and the fields in which they are used.

4. Chromatographic Methods of Separation

The most effective method for the quantitative separation of technetium from rhenium and molybdenum is ion-exchange chromatography. In the isolation of technetium this method is generally used in the last stage of the purification of technetium from these elements, when the main bulk of the impurities have been removed by other methods, such as distillation, extraction, precipitation, etc. As already noted, the chromatographic method is based on the extremely strong sorption of the pertechnate ion by strongly basic anion-exchange resins, from which it can be eluted only by ions with a high affinity for the resin. The nature of the eluent thus plays an extremely important part in methods for the chromatographic separation of technetium, rhenium, and molybdenum. The eluents used in analytical practice are solutions containing the anions SCN^-,[90,91] NO_3^-,[91] and ClO_4^-.[62,92]

Atteberry and Boyd[90] separated TcO_4^- and ReO_4^- on Dowex-2 resin in the SO_4^{2-} form, using as eluent a mixture of ammonium sulphate and thiocyanate, with pH 8.3–8.5. Rhenium was first eluted with a 0.1 M solution of these salts, after which technetium was extracted by increasing the concentration of the salts in the eluent to 1 M. Technetium and rhenium were also separated by successive elution from a column of Amberlite IRA-400 resin in the Cl^- form using NH_4CNS and HNO_3 solution[91]. Rhenium was eluted with 5% NH_4CNS solution and technetium with 4 M HNO_3.

A more effective separation of TcO_4^- and ReO_4^- was achieved by using perchloric acid or ammonium perchlorate as eluent[62,92]. The separation was carried out[92] on a 23 cm × 0.204 cm column filled with Dowex-1-X4 anion-exchange resin in the ClO_4^- form (200–400 mesh); 0.2 M $HClO_4$ was used as eluent. The elution of rhenium required 23.6 free column volumes and the elution of technetium 47.7 free column volumes (Fig. 5). The same quantities of eluents are used when ammonium perchlorate solution is taken for this purpose. The volumes of eluents used to extract rhenium and technetium are inversely proportional to the perchlorate ion concentration.

In the development of a method for the chromatographic separation of TcO_4^- and ReO_4^-, it was found[92] that the efficiency of separation of the anions is influenced considerably by effects such as the possible partial reduction of technetium by the anion-exchange resin or the formation of radio-colloids; this often leads to indistinct peaks and less effective separation. To eliminate these effects, it would be useful to study the anion-exchange separation of technetium and rhenium by means of concentrated solutions of hydrochloric acid, which selectively reduces Tc^{VII} to Tc^{IV} with the formation of the complex anions $TcCl_6^{2-}$. Some anion-exchange resins, particularly the AV-17 resin produced in the Soviet Union, have a high absorbing power for complex anions from acidic media[93]. This can apparently be used for the effective separation of technetium and rhenium.

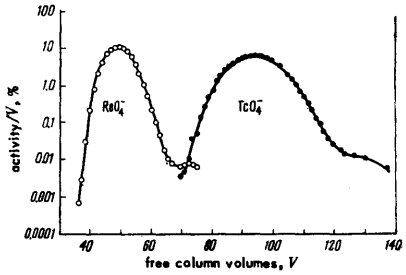


Fig. 5. Chromatographic separation of technetium and rhenium on Dowex-1-X4 anion-exchange resin. Rate 0.75 cm min^{-1}.

Chromatographic methods for the separation of Tc and Mo have been based on the successive elution of MoO_4^{2-} with 1 M HCl [94] or 3 M NaOH [23] and TcO_4^- with 4 M HNO_3 or 1 M $HClO_4$ respectively.

Lederer and coworkers[95-97] developed a method for separating technetium and molybdenum by paper chromatography, and Garvalho[98] developed a method using electrophoresis. The separation of Tc and Re by these methods was not efficient, but more effective separation was achieved by the selective reduction of TcO_4^- with HCl,[99] HI, or NH_2NH_2.[98]

5. Electrochemical and Other Methods

Electrochemical methods are based on the selective electrolytic reduction of Tc to TcO_2 under definite conditions and its deposition on electrodes, while Re and Mo remain in solution. Rogers[21] developed a method for the electrolytic deposition of Tc on a Pt cathode from 2 M NaOH solution at a controlled cathode potential of 1.1 V.

Boyd *et al.*[15] studied the electrodeposition of technetium under different conditions and showed that the optimum deposition is achieved from neutral media containing 10^{-3} M F^- ion. The small quantity of F^- ions apparently increases the hydrogen overvoltage and improves the electrodeposition of Tc. The deposition is also improved by replacing the Pt cathode with polished Ni or Cu electrodes.

A method based on complex formation by technetium with phthalocyanine has also been developed for separating small quantities of technetium and rhenium[61]. Rhenium does not form these complexes. In the separation it is best to use copper phthalocyanine as carrier.

IV. METHODS OF DETERMINING TECHNETIUM

1. Gravimetric Methods

Large quantities of technetium are readily and conveniently determined by gravimetric methods. Two methods for the determination of technetium are known: (1) precipitation of technetium(VII) sulphide and weighing as Tc_2S_7;[15,100] (2) precipitation and weighing as tetraphenylarsonium or nitron pertechnates[46].

Technetium sulphide is often the final product in general schemes for the purification of technetium. The concentration process is usually completed by the precipitation of Tc_2S_7. The precipitation is carried out from 2–4 M HCl or H_2SO_4 using hydrogen sulphide. The precipitate is washed carefully several times with carbon disulphide to remove the sulphur formed. A necessary condition for maximum precipitation of technetium is that the element be in the heptavalent state. This method can be used to determine technetium concentrations down to 3 μg ml^{-1}.

In the precipitation of tetraphenylarsonium pertechnate, the sensitivity of the determination is reduced to 5 $\mu g\ ml^{-1}$. The precipitation is usually carried out from hot alkaline solution at pH 8–9 by adding 0.05 M $(C_6H_5)_4AsCl$ solution. The resulting precipitate is washed several times with cold distilled water, dried at 110°, and weighed as tetraphenylarsonium pertechnate $(C_6H_5)_4AsTcO_4$. Permanganate, perrhenate, perchlorate, iodide, and bromide ions interfere.

2. Spectrophotometric Methods

Aqueous solutions of the pertechnate ion absorb strongly in the ultraviolet range (Fig. 6). Careful measurement of the absorption spectra reveals characteristic peaks with maxima at 247 mμm and 285 mμm.[8,101-104]. It was also found that for these wavelengths Beer's law is obeyed to a pertechnate ion concentration 10^{-3} M. This makes it possible to determine 1 μg of technetium spectrophotometrically[62,108]. This method is particularly convenient for the simultaneous determination of technetium and rhenium (Fig. 6).

Spectrophotometric methods based on the measurement of the absorption of technetium complexes are more sensitive. In Crouthamel's method[82], the absorption of the red complex formed by technetium(V) with thiocyanate ions was measured at 510 mμm. The method is very sensitive but certain elements such as uranium and iron interfere. Moreover, the complete development of the colour, which is produced by the slow reduction of Tc^{VII} to Tc^{V} by thiocyanate, requires a considerable time (~3 h), and this is a disadvantage.

In Howard and Weber's work[83] on the development of a rapid method for determining technetium in uranium materials, particular attention was paid to increasing the rate of the reduction process. The use of ascorbic acid for the reduction of Tc^{VII} to Tc^{V} was recommended for rapid development of the colour. Iron(III) was added to the solution to prevent further reduction to Tc^{IV}. The red thiocyanato-complex of technetium(V) was extracted from 3 *N* HCl with butyl acetate, and the extract was washed twice with 30% NaH_2PO_4 solution to remove iron. The spectrophotometry was then carried out at 585 mμm (ϵ = 16500) in the presence of molybdenum or at 510 mμm (ϵ = 50000) when molybdenum was absent. This method can be used to determine 0.3 μg of technetium in 5 g of uranium. The accuracy of the method is ±0.07 μg in the determination of 0.5 μg and ±0.2 μg in the determination of 30 μg of technetium. The determination requires 15 min.

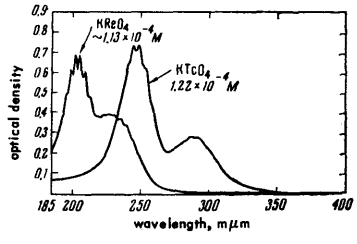


Fig. 6. Absorption spectra of aqueous $KTcO_4$ and $KReO_4$ solutions.

Miller and Thomason[105] developed a method for the spectrophotometric determination of technetium using thioglycollic acid as the complex-forming reagent. The absorption of the coloured solution was measured at 655 mμm. The method is rapid, but insufficiently sensitive. Moreover, many elements such as uranium, iron, etc. interfere in the determination. Later, the same authors developed another method[87], in which the complex formed by technetium with toluene-3,4-dithiol was extracted with carbon tetrachloride and the absorption was measured at 450 mμm. This method is more sensitive than that in which thioglycollic acid is used, but many elements again interfere in the determination and the extraction equilibrium is established only slowly.

Miller and Zittel[85] recently proposed a new method for the spectrophotometric determination of microgramme quantities of technetium using diphenylcarbazide (1,5-diphenylcarbohydrazide). The determination was carried out in 1.5 M H_2SO_4, in which diphenylcarbazide reduces Tc^{VII} to Tc^{IV} and forms a stable complex with the latter. The molar extinction coefficient of solutions of this compound is 48600. Complete development of the colour requires 35–40 min, after which the absorption of the solution is measured at 520 mμm. VO_3^-, MoO_4^{2-}, ReO_4^-, and Hg^{2+} cause little interference in the determination, but Fe^{3+}, Ce^{4+}, and CrO_4^{2-} should be removed from the solution. Thus in the determination of technetium in the presence of Cr^{VI}, technetium diphenylcarbazide was extracted with chloroform (the corresponding Cr^{VI} compound is not extracted) and the optical absorption of the extract was measured.

A convenient method for the determination of microgramme quantities of technetium in the presence of rhenium using *p*-thiocresol has been described[84]. *p*-Thiocresol does not react with Tc^{VII} and and Re^{VII}, but reacts with these elements in lower valency states to form coloured complexes which are readily soluble in CCl_4, benzene, and ether. In acetic acid solutions, *p*-thiocresol reduces technetium to the tetravalent state with the formation of a complex with absorption maxima at 320–325 mμm and 410 mμm. The maximum at 410 mμm is used for the determination of technetium. The molar extinction coefficient of the solutions of the compound at this wavelength is 7350. Re^{VII} is not reduced under these conditions and does not interfere in the determination. WO_4^{2-}, Sn^{2+}, Cd^{2+}, Bi^{3+}, Pb^{2+}, Ni^{2+}, Cr^{3+}, VO_3^-, UO_2^{2+}, S^{2-}, and MoO_4^{2-} do not interfere but ions of elements of the platinum group react with the reagent to form coloured complexes which are readily extracted by chloroform.

The ability of technetium to undergo comparatively ready reduction by concentrated HCl with heating, and to form the anionic complexes $TcCl_6^{2-}$, was used by the author of the present review to develop a new method for the spectrophotometric determination of technetium in the presence of microgramme quantities of molybdenum and rhenium[106]. The molar extinction coefficient of solutions of the chloro-complex of technetium(IV) is 32000. The method is simple, has a high sensitivity (0.2 μg), and low experimental error (~2%).

α-Furyl dioxime can also be used for the spectrophotometric determination of technetium[88,107]. The determination is carried out in the presence of $SnCl_2$ in 1 M HCl. The light absorption is measured at 520 mμm (ϵ = 13181). The presence of a 10-fold excess of molybdenum (10^{-4} M) relative to technetium (10^{-5} M) does not interfere in the determination. The sensitivity of the determination is not high, however (~1 μg), and the time required is fairly long (~2 h).

Methods have also been proposed for the determination of technetium with thiourea and dimethylglyoxime[86], potassium hexacyanoferrate(II), and sulphosalicylic and α-picolinic acids[89].

3. Radiometric Method

The simplest and earliest method for determining ^{99}Tc is the radiometric method, based on the measurement of the β-activity of this isotope on a proportional β-counter[108]. The specific activity of technetium is fairly high (37 800 counts min^{-1} μg^{-1}), so that this method can be used to estimate 0.1 μg of technetium. The low energy of the β-particles from ^{99}Tc (~0.3 MeV) introduces a number of difficulties into the measurement, associated with self-absorption in the specimen, back β-scattering, etc. Despite these disadvantages, the radiometric method in some cases makes possible more accurate determination of the technetium content than chemical methods.

Geiger–Muller counters are often used for the identification and determination of the activity of the nuclear isomer emitting soft γ-quanta (~0.3 MeV), but it is better to carry out the measurements on a γ-scintillation counter or spectrometer[9,109].

4. Spectroscopic Method

The spectrochemical method provides a sensitive method for the determination of technetium. It is based on the use of the resonance lines in technetium at 4297.06, 4262.26, and 4238.19 Å and Tc-1 at 4031.63 Å. The method can be used to determine 0.1 μg of technetium[62].

Milligramme quantities of technetium and rhenium can be determined by infrared spectroscopy[110]. Tetraphenylarsonium pertechnate is pressed with sodium bromide into a disc and the infrared absorption is measured at 11.09 mμm. MoO_4^{2-}, WO_4^{2-}, SO_4^{2-}, PO_4^{3-}, Br^-, NO_3^-, NCS^-, IO_3^-, UO_2^{2+} ions and the ions of organic acids do not interfere, but ReO_4^- and MnO_4^- ions absorb infrared radiation in an adjacent region and should be removed before the determination of technetium.

5. Polarographic Method

Traces of technetium can also be determined polarographically[111-113] from the waves produced in the polarographic reduction of Tc^{VII} at at dropping mercury electrode (Fig. 7)[113]. The first wave at pH 2, corresponding to the four-electron reduction of technetium, together with the first and second waves at pH 13, due to the three- and one-electron reductions respectively, can be used for the determination of technetium in the presence of rhenium. Measurement of the third catalytic wave gives maximum sensitivity and has been used[113] for the determination of very small quantities of technetium.

In neutral solutions with 1 M $NaClO_4$ as the supporting electrolyte a distinct diffusion wave with a half-wave potential $E_{1/2}$ = -0.8 V is observed[114], corresponding to the three-electron reduction. This has made it possible to determine technetium fairly accurately. In the range 5×10^{-3}–8×10^{-2} M, the technetium concentration is directly proportional to the magnitude of the limiting current.

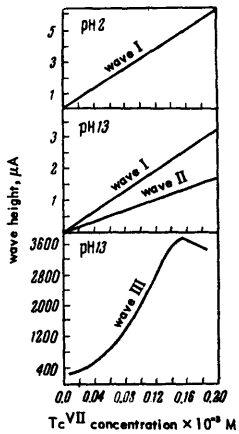


Fig. 7. Dependence of the height of the polarographic wave on the Tc^{VII} concentration.

Miller *et al.*[111] developed methods for determining technetium in buffer solution at pH 7, and White and Thomason[115] determined milligramme quantities of this element by potentiometric titration with chromium sulphate.

A recent paper[112] described a simple rapid method for determining technetium by coulometric titration at controlled potential (-0.70 V) in an acetate-buffer tripolyphosphate solution. The relative error in the determination of 0.5–5 mg of technetium is ±1%. Many ions, for example ReO_4^-, MnO_4^-, CrO_4^{2-}, Ce^{4+}, Cu^{2+}, Zn^{2+}, Cl^-, ClO_4^-, and SO_4^{2-}, do not interfere, but ions such as Fe^{3+}, MoO_4^{2-}, Ru^{4+}, UO_2^{2+}, VO^{2+}, F^-, and NO_3^- cause interference. Technetium can be separated from interfering elements by codistillation with sulphuric acid.

For the rapid determination of ^{99m}Tc in a mixture of uranium fission products, Love and Greendale[116] used the method of amalgam polarography. Technetium was concentrated in the mercury drop, after which its activity was measured. The coefficient of purification was 10^5 and the accuracy of the determination was ~1%.

6. Mass-Spectrometric Method

The mass-spectrometric method has been used for the identification of technetium in the isolation of the latter from the fuel elements of the reactor in the first atomic power-station[117] and, in conjunction with isotopic dilution methods, for quantitative determination[62].

The determinations were made on mass-spectrometers with a 60° magnetic field and chamber radius 15–20 cm. Technetium was deposited on the iridium emitter in the form of aqueous ammonium pertechnate solution from a micropipette[117], or electrolytically[62]. After the emitter had been heated at 400° in an atmosphere of hydrogen to reduce the technetium to the metal, the ion source of the specimen was placed in the mass-spectrometer, in which Tc^+ ions were produced at 1600–1800°.

In the quantitative determination of ^{97}Tc and ^{98}Tc in minerals[69] by this method a known quantity of ^{99}Tc was

TABLE 6. Sensitivity of methods for determining microgramme quantities of technetium.

Method	Sensitivity, g
Gravimetric	$(3—5)\cdot10^{-6}$
Spectrophotometric	$3\cdot10^{-7}—10^{-6}$
Radiometric	10^{-7}
Spectroscopic	10^{-7}
Polarographic	$5\cdot10^{-6}$
Mass-spectrometric (using isotopic dilution method)	$5\cdot10^{-9}$
Neutron-activation	$2\cdot10^{-11}$

introduced into the solutions containing the technetium to be determined, before deposition on the emitter; the ^{99}Tc served as isotopic diluent. The quantitative determination was made by the isotopic dilution method from the change in the isotopic composition on mixing ^{118}. The sensitivity of the determination is 5×10^{-9} g, which is much higher than the methods previously described.

7. Neutron-Activation Method

The most sensitive method for the determination of traces of technetium is neutron-activation analysis, which has been used successfully by Boyd and Larson [62] in the search for technetium in natural materials. The determination of the ^{99}Tc content by the neutron-activation method is based on irradiation of the specimen with slow neutrons and the formation, as a result of an (n,γ)-reaction, of the radioactive ^{100}Tc, with a half-life of 15.8 s. ^{99}Tc has a fairly high thermal-neutron capture cross-section (20 barn), and this makes it possible to determine down to 10^{-11} g of technetium by this method. Because of the fairly short half-life of ^{100}Tc, however, this method has not been widely applied.

The sensitivities of all the above methods of determination are compared in Table 6.

V. FUTURE DEVELOPMENTS

One of the main tasks in the analytical chemistry of technetium is the development of new, effective, and economic methods for concentrating technetium from its extremely dilute solutions containing high concentrations of various salts. A promising method in this connection is ion-exchange chromatography with strongly basic anion-exchange resins, which make it possible, for example, to extract and purify technetium from concentrated nitrate solutions. Study of the sorption capacity and selectivity of a variety of synthetic anion-exchange resins and inorganic sorbents for technetium ions in various media is therefore of interest.

The development of extraction methods for concentrating technetium from various materials is desirable. Of particular promise are extraction methods for isolating and purifying technetium from fairly concentrated technetium solutions, and also for the preliminary concentration of the element for subsequent spectrophotometric, spectroscopic, or polarographic determination.

Studies of the lower valency states (less than seven) of technetium with a view to their utilisation in analytical chemistry are necessary. In these valency states, technetium forms a variety of complexes which may be used for the selective concentration, separation, and determination of technetium in extraction, chromatographic, spectrophotometric, and other methods of analysis. The study of the varied analytical properties of this element, which exhibits both metallic and non-metallic character, and also the investigation of new possible applications in science and technology, are of interest.

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STRUCTURE AND PROPERTIES OF MOLTEN SALTS

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1. INTRODUCTION

Molten salts form a large class of the liquids which exhibit electrolytic conductivity. The principal structural units in molten salts are ions, they are therefore also terms ionic liquids.

The practical importance of molten salts has increased considerably in recent years in connection with the development of new branches of metallurgy and energetics. Molten salts are widely used for the electrolytic production of various light and rare metals[1,2], used in nuclear technology as heat transfer media or reactor fuels[2,3], employed as electrolytes in fuel cells[4], etc. Recently there has been a sharp increase in the number of publications — both research papers and review articles. Reviews and monographs on various aspects of the physics and chemistry of molten salts have been published by Belyaev *et al.*[5], Voskresenskaya[6], Delimarskii and Markov[7], Morachevskii[8-10], and many other authors[2,3,11-20]. The earlier investigations have been critically discussed and reviewed[1,21].

Electrolytic conductivity and other properties of molten salts are explained if the salts are considered to be composed of charged structural units — ions. In characterising the properties of molten salts and comparing them with the properties of ionic crystals, reference is sometimes made to dissociation on melting. However, here the term "dissociation" has only conventional significance, since during fusion there is no decomposition of neutral molecules into ions. The fusion of a salt is essentially the destruction of the crystal lattice, usually accompanied by an increase in volume. The extra volume produced ensures freer movement of ions, so that it is more logical to speak of the disordering or disintegration of the crystal lattices than of dissociation. The condensation of salt vapours, which consist of neutral molecules, is accompanied by self-dissociation, as a result of which ions, earlier bound in pairs, are socialised, are collectivised, to form an ionic liquid. In this respect there is a definite analogy between salts and metals, since in the condensation of metal vapours there is the collectivisation of the electrons[22].

It is natural for properties of molten salts such as electrical conductivity, viscosity, diffusion, surface tension, heats of phase transformations, and so forth to depend on the characteristics of the ions forming the melt — their dimensions, masses, polarisability, and charge. However, in considering this dependence it is necessary to take into account that the ions in the melt form a single collective, exhibiting a definite structure. Just as the properties of ionic crystals are determined not only by the properties of the individual ions, but also by the properties of their set, that is, the crystal lattice, the properties of molten salts can be understood only by studying their structure. In turn, a study of the properties of salt melts permits assessment of their structure and makes possible their quantitative characterisation.

The development of the theory of the liquid state as applied to molten salts shows that their principal properties are due to the structural peculiarities more than to