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The Radiochemistry of Technetium

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The Radiochemistry of Technetium

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November 1960

Subcommittee on Radiochemistry
National Academy of Sciences—National Research Council

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FOREWORD

The Subcommittee on Radiochemistry is one of a number of subcommittees working under the Committee on Nuclear Science within the National Academy of Sciences - National Research Council. Its members represent government, industrial, and university laboratories in the areas of nuclear chemistry and analytical chemistry

The Subcommittee has concerned itself with those areas of nuclear science which involve the chemist, such as the collection and distribution of radiochemical procedures, the establishment of specifications for radiochemically pure reagents, availability of cyclotron time for service irradiations, the place of radiochemistry in the undergraduate college program, etc.

This series of monographs has grown out of the need for up-to-date compilations of radiochemical information and procedures. The Subcommittee has endeavored to present a series which will be of maximum use to the working scientist and which contains the latest available information. Each monograph collects in one volume the pertinent information required for radiochemical work with an individual element or a group of closely related elements.

An expert in the radiochemistry of the particular element has written the monograph, following a standard format developed by the Subcommittee. The Atomic Energy Commission has sponsored the printing of the series.

The Subcommittee is confident these publications will be useful not only to the radiochemist but also to the research worker in other fields such as physics, biochemistry or medicine who wishes to use radiochemical techniques to solve a specific problem.

W. Wayne Meinke, Chairman
Subcommittee on Radiochemistry

INTRODUCTION

This volume which deals with the radiochemistry of technetium is one of a series of monographs on radiochemistry of the elements. There is included a review of the nuclear and chemical features of particular interest to the radiochemist, a discussion of problems of dissolution of a sample and counting techniques, and finally, a collection of radiochemical procedures for the element as found in the literature.

The series of monographs will cover all elements for which radiochemical procedures are pertinent. Plans include revision of the monograph periodically as new techniques and procedures warrant. The reader is therefore encouraged to call to the attention of the author any published or unpublished material on the radiochemistry of technetium which might be included in a revised version of the monograph.

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II. Table of Isotopes of Technetium

Isotope	Half-life	Type of decay	Method of preparation
Tc^{92}	4.3m	β^+, EC	$Mo^{92}(p,n)$
Tc^{93m}	43.5m	IT $\sim$80%, EC $\sim$20%	$Mo^{92}(d,n)$
Tc^{93}	2.75h	EC 88%, β^+ 12%	$Mo^{92}(d,n)$
Tc^{94}	53m	β^+ $\sim$75%, EC $\sim$25%	$Mo^{94}(p,n)$
Tc^{95m}	60d	EC 96+%, IT $\sim$3%, β^+ $\sim$0.4%	$Mo^{95}(p,n)$
Tc^{95}	20.0h	EC	$Mo^{95}(p,n)$
Tc^{96m}	51.5m	IT	$Mo^{96}(p,n)$
Tc^{96}	4.20d	EC	$Mo^{96}(p,n)$
Tc^{97m}	91d	IT	$Mo^{97}(p,n)$
Tc^{97}	2.6×10^{6}y	EC	daughter Ru^{97}
Tc^{98}	1.5×10^{6}y	β^-	$Mo^{98}(p,n)$
Tc^{99m}	6.04h	IT	daughter Mo^{99}
Tc^{99}	2.12×10^{5}y	β^-, no γ	daughter Tc^{99m};fission
Tc^{100}	15.8s	β^-	$Mo^{100}(p,n)$
Tc^{101}	14.0m	β^-	$Mo^{100}(d,n)$
Tc^{102}	5s	β^-	fission
Tc^{102}	4.5m	β^-	fission
Tc^{103}	1.2m	β^-	fission
Tc^{104}	18m	β^-	fission
Tc^{105}	10m	β^-	fission
Tc^{107}	$<$1.5m	β^-	fission

See "Table of Isotopes" by D. Strominger, J. Hollander, and G. Seaborg, Reviews of Modern Physics 30, 585-904 (1958), for more complete information and for references to the original literature.

III. REVIEW OF THOSE FEATURES OF TECHNETIUM CHEMISTRY OF CHIEF INTEREST TO RADIOCHEMISTS

1. General Remarks

In many respects, the analytical behavior of Tc is similar to that of Re. Both form stable XO_4^- anions that give insoluble salts with large cations; both form volatile heptoxides; and both form acid-insoluble heptasulfides. However, there are subtle differences between the two elements that can cause them to behave very differently under certain conditions. The vapor pressure of Tc_2O_7 [1] is much higher than that of Re_2O_7 at low temperatures (e.g. 10^{-1}mm at 100° C, compared to $\sim 3 \times 10^{-5}$mm for Re_2O_7). In contrast to rhenium, technetium (VII) is therefore easily lost upon evaporation of acid solutions unless a reducing agent is present or the evaporation is conducted at a low temperature. Ignorance of these factors has led to a multitude of conflicting statements concerning the volatility of technetium.

Another important property of Tc(VII) is its relatively greater ease of reduction, and the slowness of some of the intermediate steps in the reduction process. Pertechnetate ion is reduced to a lower oxidation state by hydrochloric acid, thiocyanate ion[2], organic impurities present in tetraphenylarsonium chloride[3], anion exchange resin[4], and some organic solvents. Yet the complete reduction to Tc(IV) is slow, and by analogy with rhenium[5], a multiplicity of reaction products may be expected. Unless precautions are taken to maintain technetium in the appropriate oxidation state, erratic results will be obtained.

2. Metallic technetium

Technetium metal can be prepared by reduction of the sulfide with hydrogen at 1100° C [6,7]. A purer product is obtained by hydrogen reduction of ammonium pertechnetate at 500-600° C [8], or by electrodeposition from 2N H_2SO_4 in the presence of traces of fluoride[9]. The metal has a density of 11.49 and melts at 2140 ± 20° C under atmospheric pressure[10].

Technetium metal dissolves in nitric acid, aqua regia, and hot, concentrated sulfuric acid. It is insoluble in hydrochloric acid and, in contrast to rhenium, in neutral or alkaline hydrogen peroxide[7,8]. It tarnishes slowly in moist air.

3. Solution chemistry of technetium

By analogy with rhenium, all oxidation states between -1 and +7 may be expected for technetium. Of these, the +7 is the most important, though the +4, +5 and +6 states may also be of interest in some analytical applications.

a. Oxidation State +7

Ammonium pertechnetate. The most common compound of Tc(VII) is ammonium pertechnetate, NH_4TcO_4 , a white, water soluble salt. It is usually obtained by dissolving technetium heptasulfide in ammonia and hydrogen peroxide. When prepared in this manner, it is often heavily contaminated with $(NH_4)_2SO_4$ and NH_4NO_2, and decomposes to TcO_2 on heating[6,11], but a somewhat purer product has apparently been sublimed in vacuo without decomposition[12].

Technetium heptoxide and pertechnetic acid. The yellow, crystalline oxide has been prepared by burning the metal in oxygen at 400-600° C [13]. It melts at 119.5° C and boils at 311° C. Technetium heptoxide dissolves in water to give a colorless solution of $HTcO_4$. The vapor pressures of both the acid and the heptoxide are rather high even at low temperatures[1], and while this is a handicap in some respects, it also makes possible a number of chemical separations.

The coprecipitation behavior of pertechnetate ion has been investigated in some detail. It forms slightly soluble salts with large cations, e.g., Tl^+, Ag^+, Cs^+, nitron, and $(C_6H_5)_4As^+$. At 0° C, precipitation with the last-mentioned reagent is feasible at concentrations as low as 5 mg Tc/l [14]. At lower concentrations, any of the XY_4^- anions may be used as carriers: e.g., ReO_4^-, ClO_4^-, IO_4^-, and BF_4^- [15,16,17]. In acid solutions, molybdenum also precipitates, but in basic solutions, it does not interfere. Decontamination from other fission products is excellent: a single-step β decontamination factor of 10^5 has been reported. The principal remaining contaminants are Zr, Nb, and Ru [17]. Coprecipitation with $(C_6H_5)_4AsReO_4$ is probably the fastest known separation method for Tc; when milking 5 sec. Tc^{102} from 11.5 min. Mo^{102}, Flegenheimer et al[18] were able to precipitate and filter the sample in 5-6 seconds.

Removal of the technetium from the organic precipitate may be accomplished by wet combustion, by electrolysis in concentrated H_2SO_4, or by passing an alcohol solution of the precipitate through a strong-base anion exchanger in the chloride form. The organic cation passes through the exchanger, while the pertechnetate is adsorbed and may be subsequently eluted by $HClO_4$ [8,19].

Pertechnetate does not coprecipitate with manganese and ruthenium dioxides, zirconium hydroxide, tantalic and niobic acids, the 8-hydroxyquinolate and benzidinate of molybdenum (VI)[20,21], silver molybdate[22], lead molybdate, ferric hydroxide, and α-benzoin oxime molybdate[23].

Technetium heptasulfide. This compound can be prepared by precipitation from solutions 2 to 4 N in HCl or H_2SO_4 by means of hydrogen sulfide[7,11]. As little as 3 mg/l of technetium may be precipitated by H_2S from 4 M H_2SO_4 [11,23]. The precipitation is sluggish and incomplete under some conditions, particularly if the technetium is not all in the +7 state[7,15]. Many of the precautions required in the precipitation of rhenium[24,25,26] are equally applicable to technetium.

At trace levels, the sulfides of Pt, Re, Cu, Mn, and many other elements may be used as carriers. Detailed studies on the optimum conditions for coprecipitation have been made[20,21,23,27]. Cu^{++} is a very effective carrier at acid concentrations of 0.2-3N, and offers the advantage of being easily separable from TcO_4^-. The sulfide is dissolved in ammoniacal hydrogen peroxide, the peroxide destroyed by boiling, and the copper removed by passing the solution through a cation exchanger (e.g. Dowex 50) in the ammonium form[33]. The resulting pertechnetate solution is still contaminated with ammonium sulfate and nitrite. If material of low solids content is required, the technetium may be electrodeposited as the dioxide on a platinum cathode, and redissolved in a minimum amount of ammoniacal hydrogen peroxide[23] Thioacetamide[28] or sodium thiosulfate[15,26] may be used to advantage instead of hydrogen sulfide (Fig. 1).

Many other elements in this region of the periodic table precipitate under the same conditions, so that the method is more useful for purposes of concentration than separation. However, the lower oxidation states of Tc do not precipitate with H_2S in strongly acid solutions, and one may therefore separate Tc from Re by conducting the precipi-

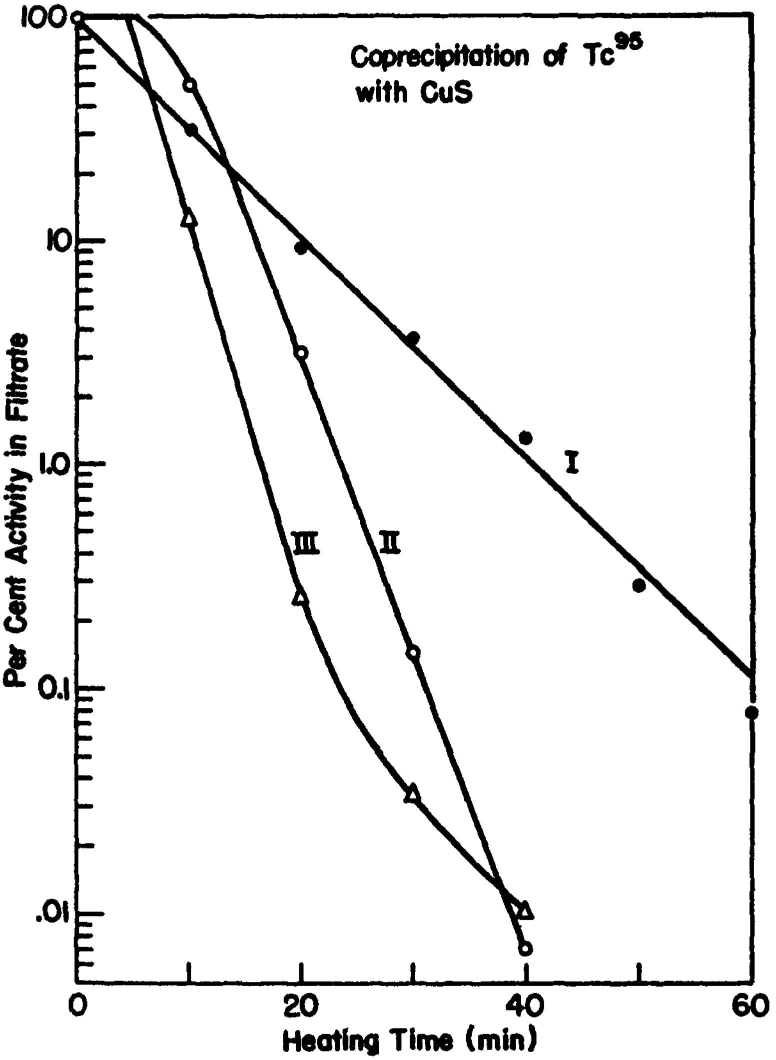

Fig. 1.

Coprecipitation of TcO_4^- with copper sulfide.

Curve I 2 mg Cu^{++}/40 ml 0.2M $HClO_4$, precipitated with H_2S.
Curve II 2 mg Cu^{++}/40 ml 0.2M $HClO_4$, pptd. w. thioacetamide (0.5%).
Curve III 1 mg Cu^{++}/20 ml 0.5M H_2SO_4, pptd. w. thioacetamide (0.5%).
Solutions initially at room temp.; heated to 90-100°C within 5-7 min.

tation in a medium that reduces Tc(VII), e.g. 9-10N HCl [15,23,29]. The separation is not sharp, however, since several percent of technetium coprecipitate with the rhenium, and measurable amounts of rhenium remain in solution.

b. Oxidation State +4

Technetium (VII) is reduced to lower oxidation states by many reducing agents. In dilute sulfuric acid medium, hydrazine, hydroxylamine, ascorbic acid, and stannous chloride produce a state that readily yields the hydrated dioxide, judging from its coprecipitation with the analogous rhenium compound[15]. It is not clear whether this state is responsible for the yellow thiocyanate complex of Tc(IV) observed by Crouthamel[2]. The dioxide can also be made by electrolytic reduction of pertechnetate solutions[30], by hydrolysis of $TcCl_6^{=}$, and by reduction of TcO_4^- by zinc in dilute hydrochloric acid solutions[31].

This state of Tc(IV) is oxidized to Tc(VII) by nitric acid, hydrogen peroxide, and atmospheric oxygen. It is carried by ferric hydroxide, and one may take advantage of this fact to separate technetium from rhenium[15].

Reduction of TcO_4^- to a cationic form of Tc(IV) has been reported by de Carvalho[32], using hydrazine at pH 8 to 9 or hydriodic acid as reductants. The assignment of a cationic character to this species was based on its immobility in paper electrophoresis. However, this behavior is equally consistent with that of an insoluble substance, such as TcO_2.

Strong hydrochloric acid reduces TcO_4^- to $TcCl_6^{=}$ [15,33], though the reaction is slow and proceeds through several intermediate oxidation states. At room temperature, 1 hr. is required for complete reduction[15]. The reduction has also been carried out with iodide ion[6,31]. The $TcCl_6^{=}$ ion undergoes slow hydrolysis even in 3F HCl, judging from changes in its absorption spectrum[19]. Reduction of TcO_4^- by $SnCl_2$ in 1-2M HCl gives a new Tc(IV) species with a UV-absorption band at 3220 A[34]. In 0.75-0.5 M HCl, a second oxygenated species, with an absorption band at 3500 A was obtained in addition. Hexachlorotechnetate (IV) ion coprecipitates with thallium and α- α' dipyridyl hexachlororhenates (IV), but is not carried by cupferrates, phosphates and phenylarsonates of tetravalent cations[15]. In basic solution, it hydrolyzes promptly to the dioxide, which is carried by ferric hydroxide[15]. A separation from rhenium may be based on this fact. Pertechnetate is reduced to $TcCl_6^=$ by conc. HCl, the technetium is coprecipitated with $Fe(OH)_3$, and oxidized to the +7 state by dissolving the precipitate in conc. HNO_3. The iron is then removed by an ammonia precipitation[15].

Thomason[35] has observed a pink species of Tc(IV) during electrolytic reduction of a pertechnetate solution in the presence of phosphate ion. Nothing is known about the analytical behavior of this species.

The $TcCl_6^=$ ion is oxidized to Tc(VII) by HNO_3, H_2O_2, Cl_2, Ce(IV) and MnO_4^- [15,28], but seems to be more resistant to air oxidation than the oxygenated species of Tc(IV).

c. Oxidation States +6 and +5

These states are somewhat harder to prepare than the +4 state, and have not been too well characterized.

Gerlit[15] obtained Tc(VI) by hydrazine reduction of cold, alkaline pertechnetate solutions. Since his experiments were carried out with 6 hr. Tc^{99m}, the compound could not be isolated but had to be characterized by radiochemical techniques. It is neither extracted by ketones or pyridine, nor precipitated by ferric hydroxide, but is carried quantitatively by molybdenum 8-hydroxyquinolate, and silver and lead molybdate. In the presence of dioximes, it can be extracted into inert solvents such as chloroform. At an OH^- concentration of 0.02 to 0.05 N the compound slowly disproportionates to Tc(VII) and Tc(IV) in the ratio of $\sim 2:1$. The above facts are consistent with its identification as $TcO_4^=$.

Another oxidation state of technetium has been observed in the reduction of TcO_4^- to $TcCl_6^=$ by 6-8 M HCl. At 100° C, the reaction is complete in ~ 12 hours. During the first two hours, an intermediate oxidation state forms that extracts into hexone with a partition coefficient of > 30 (compared to ~ 11 for TcO_4^-), absorbs light strongly at 2350 Å (molar absorbancy, $\varepsilon \approx 3 \times 10^4$), and forms a red complex with thiocyanate[33]. Crouthamel[2] was able to show that this complex ($\varepsilon = 52{,}200$ at 5130 Å) is due to Tc(V). It can be produced directly from Tc(VII), since thiocyanate itself will reduce Tc(VII) to Tc(V). Unfortunately, both Mo and Re interfere by partial reduction to colored, extractable thiocyanate complexes, and by causing side reactions that prevent complete conversion of Tc(VII) to Tc(V). Interestingly enough, stronger reducing agents such as $SnCl_2$ also interfere, by carrying the reduction below the +5 state. This explains the observations of Perrier and Segrè[20] that technetium does not extract into ether in the presence of thiocyanate and stannous chloride.

Crouthamel also obtained evidence for the formation of Tc(VI), (V), and (IV) in the potentiometric titration of TcO_4^- by Ti(III) in 12 M H_2SO_4. In this medium, Tc(VI) disproportionates within 3-4 minutes to Tc(V) and Tc(VII), whereas Tc(V) disproportionates to Tc(VII) and Tc(IV) within an hour. In 2 M H_2SO_4 or HCl, saturated with $(NH_4)_2SO_4$ and

NH_4Cl, respectively, a red color (absorption maximum ~ 5000 Å) was observed at the stoichiometric endpoint of Tc(V). No such color was observed in 10 to 12 M acid.

Busey[34] has recently studied the reduction of TcO_4^- by HCl, confirming some of the observations of Crouthamel[2] and Alperovitch[33]. Reduction with HCl alone, or H_3PO_2 in 8 M HCl, gives what appears to be a singly oxygenated species of Tc(V), such as $TcOCl_4^-$. It is stable in 3 M HCl, but disproportionates in 1 M HCl. A different species of Tc(V), possibly $TcCl_6^-$, is formed when a solution of $TcCl_6^=$ in 12 M HCl is irradiated in sunlight.

d. Oxidation state +3 and unidentified lower states

Thomason has prepared a green solution containing Tc(III) by controlled cathode potential electrolysis of TcO_4^- in a phosphate buffer at pH 7 [35]. It is easily oxidized by air to Tc(IV). Gerlit[15] reports that an oxidation state lower than (IV) is obtained in the reduction of TcO_4^- by Zn in concentrated HCl. This state does not coprecipitate with thallium hexachlororhenate (IV) from hydrochloric acid solutions, with rare earth or alkaline earth oxalates from weakly acid or neutral solutions, or with copper and zinc sulfides from weakly acid solutions. It is carried quantitatively by iron and zirconium hydroxides, and the sulphide, hydroxide, and 8-hydroxyquinolate of manganese. It is readily oxidized by oxygen, hydrogen peroxide and nitric acid. Although Gerlit interprets this oxidation state as Tc(II), the above evidence definitely does not rule out its assignment to Tc(III). For comparison, one should note that in dilute(1N)HCl, technetium is quantitatively deposited on amalgamated zinc powder[23].

It is not known whether these species are cationic, nor have any other cationic states of Tc been identified with any certainty. Flagg and Bleidner[22] report that solutions of electrodeposited Tc (TcO_2?) in dilute acids, and pertechnetate solutions treated with HCl or $SnCl_2$ were adsorbed on basic alumina columns, suggesting reduction to a cation. Boyd et al[36] conducted electromigration experiments on TcO_4^- solutions in 4 M H_2SO_4. Their results indicated the presence of both cationic and anionic species, but since pure ReO_4^- solutions gave the same results, the evidence is not conclusive. Some adsorption on cation exchange resin was observed for TcO_4^- solutions in 1-2 N H_2SO_4 and 0.25-0.75 N HNO_3 [27,35], but the exchange was irreversible and may have been due to precipitation of TcO_2 on the resin.

A technetium-phthalocyanin complex of unspecified valence has been used to separate Tc and Re, using the copper-phthalocyanin complex as a carrier[37]. Rhenium does not form such a complex.

4. Volatilization Methods

Owing to the volatility of Tc_2O_7, technetium in the +7 oxidation state may be co-distilled with acids. An illustrative graph has been given by Boyd et al[23].

Perchloric acid. This acid gives good yields and even a partial separation from rhenium[16,38], but since it oxidizes ruthenium to the volatile RuO_4, a Tc-Ru separation in the distillate is required. Glendenin[16] reduced RuO_4 to insoluble RuO_2 by boiling the distillate (collected in excess 6 N NaOH) with alcohol for 1-2 minutes. The Tc and about 1% of the Ru remained in the solution. Unfortunately, further separations by solvent extraction of TcO_4^- are not feasible in this medium, since perchlorate interferes.

Molybdenum is also carried to a significant extent, unless complexed by phosphoric acid[39,40].

Sulfuric acid. In this medium, a clean separation from Ru may be obtained[16], with separation factors of 10^5 or better, but the yields of Tc are occasionally very poor due to its reduction by trace impurities in the acid[23,28]. Much more reproducible results are obtained in the presence of oxidizing agents [e.g., Ce(IV), CrO_3, etc.], but since RuO_4 distills under these conditions, it has to be removed in a separate step such as precipitation of RuO_2 with alcohol or formaldehyde[16,20]. Some effort should be made to find an oxidizing agent that is non-volatile, stable in boiling sulfuric acid, strong enough to keep Tc in the +7 state, yet not so strong as to oxidize lower states of Ru to RuO_4. If Ru contamination is not a problem, Ce(IV) may be used to advantage. It is stable, non-volatile, and changes color on reduction.

In the distillation of sulfuric acid-water mixtures, a substantial fraction of the Tc distills with the low-boiling aqueous fraction, possibly as $HTcO_4$. Once the water has been removed, the distillation appears to follow a first-order rate law (Fig. 2), the rate constant depending on the still design and reflux ratio. To avoid contamination by spray, a Kjeldahl head should be used. For optimum reproducibility, it is advisable to heat the flask electrically, by means of a heating mantle with quartz fabric insulation.

Sulfuric acid-hydrochloric acid. When 6 N HCl is distilled into 80% H_2SO_4 at 180-200° C, Re volatilizes while most of the Tc is reduced to the non-volatile +4 state and stays behind[20]. Separation factors of up to 50 have been obtained by this procedure[27].

Other systems. Because of the great differences in vapor pressures of the acids and heptoxides at low temperatures, Tc

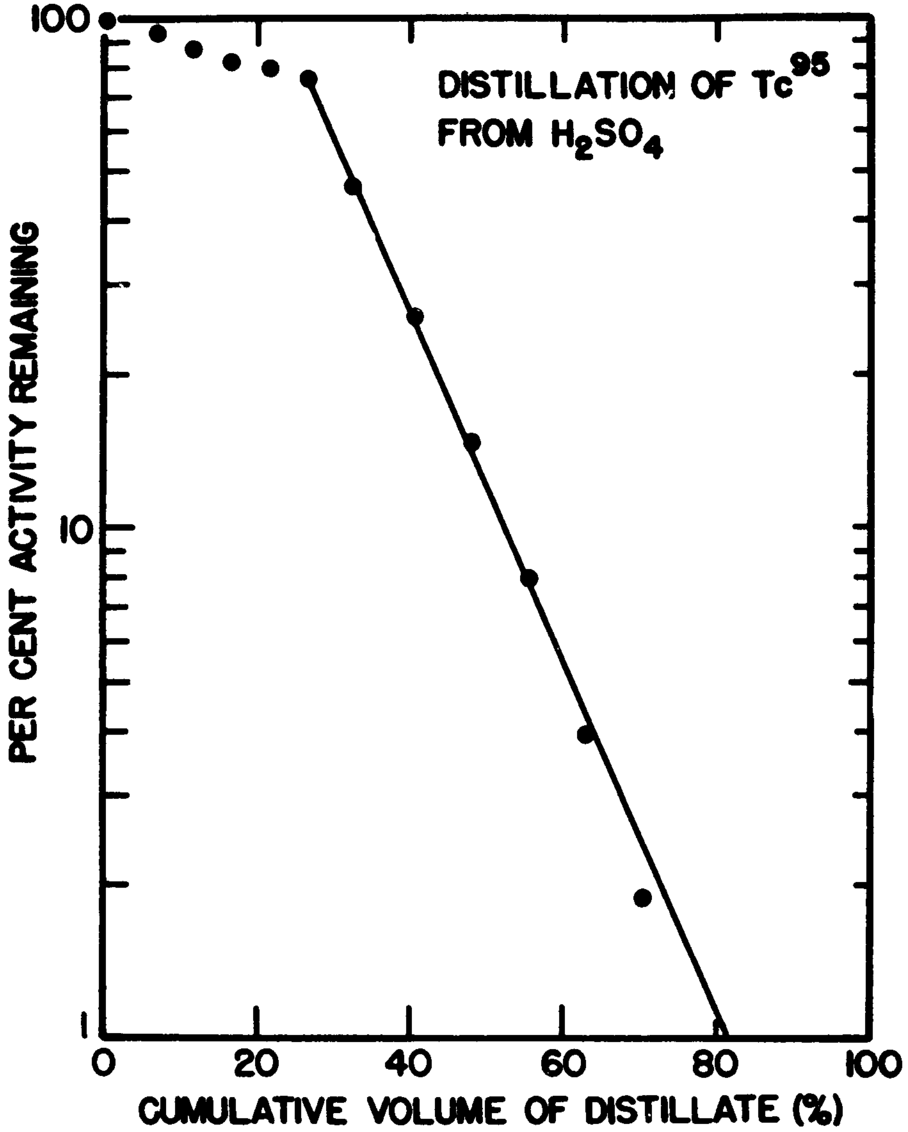

Fig. 2.

Distillation of TcO_4^- from mixture of H_2SO_4 (10 ml) and H_2O (3.5 ml) in the presence of 0.5 millimoles CrO_3. Distillation rate: 0.5 ml/min.

may be separated from Re by repeated alternating evaporation with HNO_3 and HCl [41]. The technetium in the distillate may be coprecipitated with tetraphenylarsonium perchlorate.

Technetium heptoxide may be separated from molybdenum trioxide by fractional sublimation at ⩾ 300° C [6,20]. Ruthenium and technetium can be separated from basic solution by distilling RuO_4 in a chlorine stream[42]. Rhenium and technetium volatilize if the sulfides are heated to 100° C in a chlorine stream[20], but this reaction has not been used for chemical separations.

5. Extraction of technetium into organic solvents

Pyridine. Goishi and Libby[43] found that pyridine extracts TcO_4^- from 4 N NaOH solution with a partition coefficient of 778. Gerlit[15] found a partition coefficient of only 39 in 5 N NaOH, and claims that Mo(VI) and Ru(IV) are extracted to a substantial degree. Perrhenate and permanganate are also extracted under these conditions.

Tetraphenylarsonium chloride. Pertechnetate also extracts into chloroform in the presence of tetraphenylarsonium ion[3]. The equilibrium constant for the reaction:

$$[(C_6H_5)_4As^+]_{aq} + TcO_4^- \rightleftharpoons [(C_6H_5)_4AsTcO_4]_{org}$$

is ~ 3 x 10^6. The corresponding constant for chloride is 200 [3]. At chloride concentrations of 1 M or less, distribution coefficients as large as 100 can easily be realized at reagent concentrations of 7 x 10^{-3} M. In neutral or basic sulfate solutions the distribution coefficients are even more favorable. Perrhenate and perchlorate follow technetium in this extraction, but molybdenum does not interfere in basic solution, and the decontamination from other fission products should be at least as good as in the precipitation reaction[17], if care is taken to remove iodine before extraction. Trivalent gold as chloro- or bromoaurate is also extracted and must be removed by reduction with H_2O_2, or by distillation.

It is advisable to have small amounts of an oxidizing agent, such as hydrogen peroxide, present during the extraction, so that TcO_4^- will not be reduced by impurities in the reagent. Any wash solutions used should contain a sufficient concentration of tetraphenylarsonium ion (about 5×10^{-5} M) to prevent premature back-extraction of TcO_4^- into the aqueous layer.

The technetium may be recovered from the organic phase by back-extraction into 0.2 N $HClO_4$ or 12 N H_2SO_4. In the latter case, three back-extractions are required.

Other organic solvents. Extraction of TcO_4^- into hexone, butex, and other solvents has also been investigated[27,32,44] None of these extractions will separate Tc from Re, but they may serve to separate it from molybdenum and many other elements. Of particular interest are the recent extensive studies of Gerlit[15] and Boyd & Larson[45,46]. Gerlit investigated the extraction of Tc(VII), Re(VII), Mo(VI) and Ru(IV) into 21 organic solvents, from acid, alkaline, and neutral solutions. In acid solution, alcohols, ketones, and tributyl phosphate are the best extractants for ReO_4^- and TcO_4^-; in basic solution, ketones and cyclic amines. Many possible separations of Tc from Ru and Mo may be inferred from his data. For example, in 5 N NaOH, hexone extracts Tc(VII), Re(VII), Mo(VI) and Ru(IV) with partition coefficients of 17, 8.2, < 0.001 and < 0.001. Boyd & Larson conducted an exceedingly thorough study of the extraction behavior of TcO_4^- in 34 solvents, and found that tertiary amines as well as quaternary ammonium salts gave the largest partition coefficients. Strongly basic solvents (e.g. amines) extract TcO_4^- as an "-onium" salt, whereas solvents of lower basicity extract either free pertechnetic acid or an inorganic pertechnetate[15,45,46]. In the former case, the partition coefficient decreases with increasing salt concentration, whereas the reverse is true in the latter case[15].

Back-extraction of the technetium into the aqueous phase may be accomplished in several ways. In some cases, a pH change will suffice; in others, displacement by another anion such as perchlorate, nitrate, or bisulfate is most effective. A third possibility was pointed out by Gerlit: the partition coefficient in a given oxygen-containing solvent may be decreased sufficiently by addition of a non-polar solvent to permit quantitative back-extraction into the aqueous phase.

Extraction of lower oxidation states. It seems that many new separations could be developed, based on selective reduction of Tc(VII) to lower oxidation states. The red thiocyanate complex of Tc(V) extracts well into alcohols, ethers, and ketones[2,15,33], and into a solution of trioctylphosphine oxide or trioctylamine hydrochloride in cyclohexane or 1,2-dichloroethane[19]. The extractability of Tc(VI) has already been mentioned. The $TcCl_6^{=}$ ion will extract into chloroform in the presence of fairly high concentrations of tetraphenylarsonium ion[33], but nothing else seems to be known regarding the solvent extraction behavior of the lower oxidation states of technetium.

The principal disadvantage of all extraction methods is the inevitable introduction of organic matter which may reduce TcO_4^- and cause difficulties in subsequent steps.

6. Chromatographic Behavior of Technetium

Pertechnetate ion is very strongly adsorbed by strong-base anion exchangers[27,36,47,48], and can be eluted only by ions with very high affinity for the resin, such as perchlorate and salicylate. Perrhenate is almost as strongly held (the ratio of distribution coefficients is ~ 1.6 to 2, i.e. comparable to adjacent rare earths). These two elements may therefore be separated by ion-exchange chromatography, but good separations require some care, and tend to be slow ($\geq$ 3 hours). Even in less delicate separations, such as Tc-Mo, not much time can be gained, since the elution of the strongly adsorbed Tc is bound to be time-consuming. However, cation-exchange resins adsorb technetium only to a negligible extent, so that technetium can be rapidly separated from cationic elements.

Thiocyanate. Atteberry and Boyd[49] separated TcO_4^- and ReO_4^- on Dowex-2 resin (sulfate form), using an ammonium sulfate-thiocyanate solution at pH 8.3-8.5. The two peaks were partially resolved, but the cross-contamination was rather high. Hall and Johns[50] separated technetium from molybdenum, using Amberlite IRA-400 resin and 0.5 M ammonium thiocyanate.

Perchlorate. Much better results are obtained if perchlorate ion is used as the elutriant[4,33,51,52]. Because of some peculiarities of commercial resins, the highest practically attainable separation factors of TcO_4^- and ReO_4^- are 10^4-10^5. On Dowex-1 (8% crosslinkage), the peak elution volumes of ReO_4^- and TcO_4^- in 0.2 M $HClO_4$ are 23.6 ± 0.4 and 43.7 ± 0.7 free column volumes, respectively[4] (Fig. 3). They are virtually the same in ammoniacal ammonium perchlorate solutions, and are very nearly inversely proportional to the first power of the perchlorate concentration.

In past work, where speed was not essential, flow rates

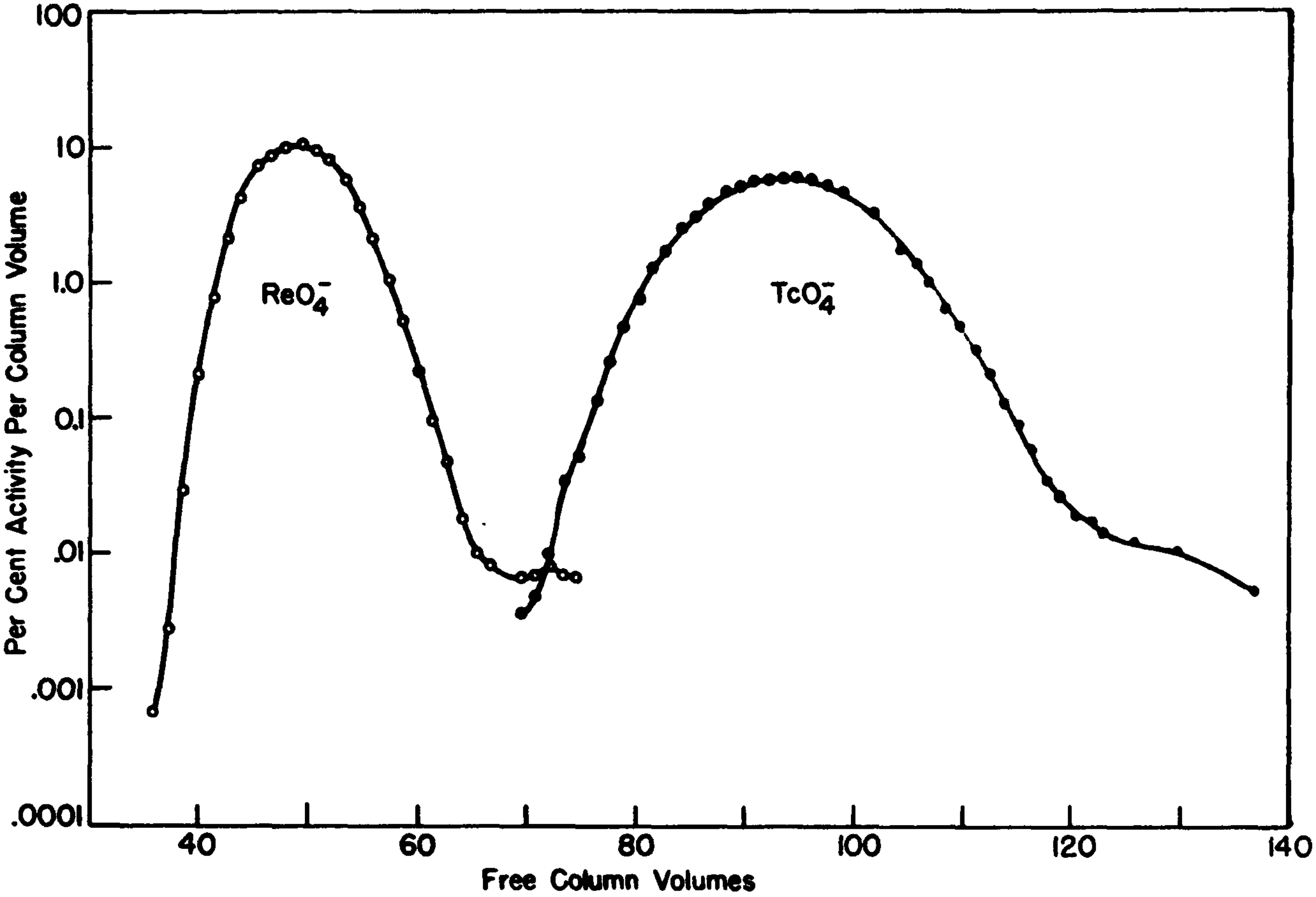

Fig. 3. Anion-exchange separation of perrhenate and pertechnetate.[4] Dowex 1-X4, ClO_4^- form, 200-400 mesh; 3.5 meq/dry gram. Column: 23.0 cm x 0.204 cm^2. Eluted with 0.1M NH_4ClO_4; flow rate 0.75 cm/min. A somewhat better separation could be obtained by using resin of higher cross-linkage (8-10%) and slower flow rates (0.2-0.5 cm/min.).

of 0.2-0.4 cm/min have generally been used, at perchlorate concentrations of 0.1 to 0.25 M. For columns of 10-20 cm length, times on the order of a day are required for a separation. It should be possible to reduce this time substantially by choosing the optimum elution conditions from Glueckauf's graphs[53]. Molybdenum is also adsorbed by anion exchange resins, and may be eluted by hydroxide[52,54], oxalate[50], or hydrochloric acid[55], though in the last two cases, there is some danger of reducing Tc(VII). Separation factors of $> 10^3$ should be readily attainable.

Hydrochloric acid. In this medium, the volume distribution coefficients for TcO_4^- on Dowex-1 range from 10^2 to 10^3, according to Kraus et al[47]. Somewhat higher values have been given by Huffman et al[48]. At higher concentration, it is reduced to $TcCl_6^=$, which is held even more strongly[33].

Nitric acid. Technetium can be eluted from Dowex-1 with 4 N HNO_3 at reasonable rates[48]. At this concentration, the volume distribution coefficient is about 20. Huffman et al[48] have developed a separation of Mo and Tc, involving elution of Mo(VI) by 1 M HCl, and Tc(VII) by 4 M HNO_3. The only drawback of this separation is the need to recover Tc from an HNO_3 solution. If the acid is evaporated with great care, losses may be kept quite low, but this step is far from foolproof.

Paper chromatography. Technetium can also be separated from molybdenum by paper chromatography[56] and electrophoresis[32]. The separation from rhenium is incomplete under most conditions except when Tc is selectively reduced by HCl [57], HI, or hydrazine[32].

7. Electrochemical Behavior

Technetium can be electrodeposited as the dioxide from

2 M NaOH [30]. A partial separation from Mo and Re may be obtained at a controlled cathode potential of -1.1V vs. the saturated calomel electrode, but the deposition only takes place at technetium concentrations of 10^{-4} M or greater. Flagg and Bleidner[22] electrolyzed carrier-free Tc^{95+96} on a platinum cathode in dilute H_2SO_4 (pH = 2.36) and obtained a 99.5% yield after 65 minutes at -0.8V vs. the saturated calomel electrode.

Boyd et al[23] have electroplated technetium under a variety of conditions. Optimum results were obtained at pH 5.5 in the presence of about 10^{-3} M fluoride ion. Yields were higher when copper cathodes were used instead of platinum. At a current density of 100 ma/cm^2, 89.5 ± 1.5% was deposited in 2 hours. However, yields of 98-99% were obtained at similar current densities even for Pt cathodes, at pH 2 to 5, and fluoride concentrations of 5×10^{-3} M, when plating times of up to 20 hrs. were used[28].

In 2 N H_2SO_4 containing traces of fluoride, the electrodeposit consists of metallic technetium[9], which is insoluble in ammoniacal hydrogen peroxide. The dioxide plated at lower acid concentrations will, however, dissolve in ammonia and hydrogen peroxide, sodium hypochlorite, and nitric acid.

IV. DISSOLUTION OF SAMPLES CONTAINING COMPOUNDS OF TECHNETIUM

When dissolving technetium-containing samples, two precautions should always be observed. First, it is essential that acid solutions be heated only under reflux conditions, to prevent volatilization losses. Second, the dissolution should be done under strongly oxidizing conditions, to ensure conversion of all lower states to Tc(VII). Complications due to slow exchange with carrier, etc., are less likely to arise for this state than for any other.

Molybdenum targets can be dissolved in nitric acid or aqua regia, but in both cases the excess acid interferes with many subsequent operations. These complications are avoided in the procedure of Boyd et al[23], who dissolve molybdenum metal in concentrated sulfuric acid, and oxidize the solution with H_2O_2 after neutralization.

Other materials can often be brought into solution by fusion with Na_2O_2 - NaOH fluxes.

V. COUNTING TECHNIQUES FOR USE WITH ISOTOPES OF TECHNETIUM

1. Counting

The β-emitting isotopes, Tc^{92}, Tc^{94}, and Tc^{99g}-Tc^{105}, can be counted in G-M or β-proportional counters in conventional manner. Most of the remaining light isotopes decay largely by electron capture or isomeric transition, with the emission of γ-rays or x-rays, and can therefore be measured by γ-scintillation or x-ray proportional counters. The former method is particularly useful for Tc^{95} (201 kev γ), Tc^{99m} (141 kev γ) and Tc^{96} (several γ's in the range 0.771-0.842 Mev).

The isotope Tc^{97g} emits only Mo x-rays in its decay, and must therefore be counted on an x-ray proportional counter. This is also true of Tc^{97m}, since its 97 kev γ-ray is highly internally converted, and the conversion electrons are too soft to be counted conveniently.

The 1.5×10^6y Tc^{98} presents somewhat of a problem, since it cannot be produced free of 60d Tc^{95}, 90d Tc^{97m}, 2.6×10^6y Tc^{97g}, and 2.1×10^5y Tc^{99g}. Fortunately, it emits two γ-rays of 0.769 and 0.669 Mev in coincidence with a 0.3 Mev β^-, and can therefore be counted selectively in the presence of much larger amounts of the other isotopes.

2. Chemical Yield Determination

Technetium does not have a stable isotope that can be used as a carrier, and although there are many excellent non-isotopic carriers available (e.g., insoluble perrhenates and perchlorates, and the sulfides of copper, platinum, and rhenium) the inevitable fractionation between these carriers and technetium makes it impossible to obtain accurate chemical yields.

Fortunately, the radiations and half-lives of technetium isotopes are sufficiently diverse to permit their use in yield determinations. For example, the 60d Tc^{95} has been used as a yield monitor for Tc^{99m} since its principal radiation, a 201 kev γ ray interfered but slightly with the counting of the 140 kev γ ray of the latter[58]. Moreover, the degree of interference could be easily determined and corrected for. Other isotopes that may be useful for yield determinations are 6h Tc^{99m}, which emits only the previously-mentioned 140 kev γ ray, and soft conversion electrons; 2.12×10^5 year Tc^{99g}, a pure β^--emitter with $E_{max} = 0.29$ Mev, and 91d Tc^{97m}, which emits only Tc x-rays and a highly internally converted γ ray of 96 kev energy.

In each case, the chemical yield of the "yield monitor" may be determined by selective counting, before or after the decay of the principal activity. In the case of Tc^{99}, chemical analysis by colorimetric[2] or other methods is possible, but even for this long-lived isotope, the specific activity is so high (3.78×10^4 d min^{-1} μg^{-1}), that the amounts likely to be used for yield monitoring can be measured more accurately by β-counting than by chemical methods.

VI. Collection of Detailed Radiochemical Procedures for Technetium

Procedure 1

Source - G. E. Boyd, Q. V. Larson and
E. E. Motta, JACS 82, 809 (1960)

Isolation of Tc^{95m} + Tc^{96} from Molybdenum

1. Introduction

This is probably the best, though not the fastest, procedure for separating Tc from a molybdenum target. It involves separation of molybdenum by anion exchange chromatography. If a separation from rhenium is required, either Proced. 4 or 14 may be used subsequently.

2. Procedure

The molybdenum target was dissolved in concentrated H_2SO_4 under reflux, the acid was neutralized with NaOH and the solution was treated with H_2O_2 to oxidize technetium to Tc(VII). This alkaline solution was passed through a small column of anion exchanger (Dowex-1, 21 x 50 mm.) which absorbed the pertechnetate ion completely. Residual absorbed molybdate was removed by elution with 1 M $K_2C_2O_4$ solution, and, after a water rinse, the technetium was eluted with 1.0 N $HClO_4$. A concentration of the technetium activity was effected by precipitating CuS from the acid. Subsequently, the sulfide was dissolved in alkaline hydrogen peroxide, and the copper was removed by passing the resulting solution through a micro-column of cation exchanger (Dowex-50). The technetium contained in the effluent was electrodeposited onto a platinum cathode, dissolved in ammoniacal hydrogen peroxide, evaporated to dryness in a platinum dish and the resulting ultra-micro quantities of NH_4TcO_4 were made to 5 ml. volume in a volumetric flask.

Procedure 2

Source - S. Tribalat, J. Beydon, Anal. Chim. Acta 8, 22 (1953)

Separation of Technetium from Molybdenum

1. Introduction

This procedure is based on the extraction of pertechnetate into chloroform in the presence of tetraphenylarsonium ion. It is fast and gives good separations. In order to keep the reagent concentration in the final solution as low as possible, the extraction is carried out at R = 5×10^{-5} M.

2. Procedure

Ten grams MoO_3 are dissolved in 20 ml H_2O, containing 0.1 g $Na_2S_2O_8$ and the minimum amount of 10 N NaOH. (Note 1). The pH is adjusted to 10-11 by addition of $NaHCO_3$, if necessary, the solution is made 5×10^{-5} M in tetraphenylarsonium ion, and is shaken with 50 ml freshly purified $CHCl_3$ for 5 min. The distribution coefficient is about 15.

The organic layer is filtered through filter paper moistened with chloroform, dried with Na_2SO_4, refiltered, and washed with 30 ml very dilute NaOH (pH 10-11). The solution is refiltered, and the technetium is recovered from the organic phase by prolonged shaking with water. In general, no more than 15% of the Tc should remain in the chloroform and the first wash.

Procedure 3

Source - J. Flegenheimer and W. Seelmann-Eggebert,
Proc. Intern. Conf. Peaceful Uses of Atomic
Energy, Geneva, 1955, 7, 152 (1956)

Separation of Tc^{102} and Mo^{102}

1. Introduction

This is the fastest known procedure for the separation of Tc and Mo. It is based on precipitation with tetraphenylarsonium ion. The yield is not quantitative, and the separation is not complete, but the sample can be counted within 5-6 seconds after the separation.

2. Procedure

The lead molybdate sample is dissolved in a mixture of tartaric and hydrochloric acids in the presence of ReO_4 carrier. (Note 1). The solution is transfered to a Büchner funnel with detachable top, fitted with a membrane filter and mounted on a filter flask. The entire assembly is placed directly below a GM counter. Tetraphenylarsonium chloride solution is added, and the suction is turned on. As soon as the solution has drained, the sample may be counted.

Note 1. The tartaric acid complexes the molybdenum, thereby preventing its precipitation. It would seem that an even cleaner separation might be obtained from an ammoniacal ammonium tartrate solution.

Procedure 4

Source - R. N. Sen Sarma, Edward Anders, and
J. M. Miller, J. Phys. Chem. 63,
559 (1959)

Separation of Technetium and Rhenium by Anion Exchange

1. Introduction

Technetium and rhenium are separated by elution with perchlorate ion. Separation factors of up to 10^5 are possible, but the method is slow (2 hrs. - 2 days). Any strong-base anion exchanger may be used.

2. Procedure

The solution containing TcO_4^- and ReO_4^- is concentrated to as small a volume as possible, and is adsorbed on an anion exchange column in the perchlorate form. The column should be so large that it is saturated to no more than 5% of its capacity, and the length/diameter ratio should be at least 30. The resin particle size should be chosen so as to give flow rates of 0.2 - 0.5 cm/min. At lower flow rates, "tailing" increases, and at higher flow rates, the peaks broaden excessively.

After the sample solution, followed by two rinses of 3 column volumes of water, has flowed through the column, the top section of the column is rinsed very thoroughly, to prevent contamination of the elutriant with any rhenium that might have adhered to the walls. The elution is then performed with 0.1 $\underline{M}$ $HClO_4$ or NH_4ClO_4. For Dowex-1X8 resin, the peak elution volumes of ReO_4^- and TcO_4^- are about 43 and 82, respectively, so that a cut should be taken at about 60 free column volumes.

The technetium can be recovered from the perchlorate solution by electrolysis, by a sulfide precipitation, or by reduction to the +4 state and coprecipitation with $Fe(OH)_3$.

Procedure 5

Source - E. Anders

Separation of Tc^{99m} from Mixed Pile Activities

1. Introduction

This procedure combines solvent extraction by tetraphenylarsonium ion (Procedure 2) with a distillation step. It is fairly fast (3 hrs.), and gives decontamination factors greater than 10^4 for all pile-produced activities, except rhenium. Yields are 50-80%. It can be modified to give a separation from rhenium by adding an anion exchange step (Procedure 4), or a TcO_2 coprecipitation with $Fe(OH)_3$ (Procedure 14).

The samples used in this procedure were water-soluble concentrates that had been isolated from minerals suspected to contain a long-lived Tc^{98} isomer (cf. Procedure 7). A molybdenum fraction was always separated to determine the contribution, if any, of Tc^{99m} grown from Mo^{99} to the observed Tc^{99m} activity.

2. Procedure

(1) The sample is dissolved in 3 ml 2 $\underline{N}$ NH_3 containing the following holdback carriers: 2 mg Mo(VI), 1 mg W(VI), 0.5 mg of Sb(V), 1 μg each of Au(III), As(V), Zn(II), Cu(II), Ge(IV). (Note 1). Enough 30% H_2O_2 is added to convert all Mo to the red peroxymolybdate. The solution is heated on a water bath for 10 minutes, to ensure exchange with the carriers.

(2) The solution is cooled and transferred to a 30 ml Ultramax separatory funnel with teflon valve. Enough tetraphenylarsonium sulfate solution (Note 2) is added to give a final molarity of ϕ_4As^+ of $\sim 10^{-3}$ (about 10 drops of

a 5×10^{-2} $\underline{N}$ solution is required for a sample volume of 5-10 ml), 7 ml of $CHCl_3$ is added, and the technetium is extracted into the chloroform.

(3) The chloroform layer is transferred to a second funnel, and is washed with 5 ml 0.2 $\underline{N}$ NH_3 that is 10^{-4} $\underline{N}$ in $(\phi_4As)_2SO_4$. (Note 3).

(4) The chloroform layer from the preceding extraction is transferred to a third funnel, and is contacted with 5 ml 1 $\underline{N}$ H_2SO_4 that is 10^{-4} $\underline{N}$ in $(\phi_4As)_2SO_4$. The chloroform layer is transferred to a fourth funnel.

(5) (This step and the following one may be omitted if a slightly lower yield can be tolerated.) The aqueous layer from Step (2) is again made 10^{-3} $\underline{N}$ in $(\phi_4As)_2SO_4$, and extracted with 7 ml $CHCl_3$.

(6) The chloroform extract from Step (5) is successively contacted with the wash solutions from Steps (3) and (4), and is then combined with the chloroform layer from Step (4).

(7) The combined chloroform extracts are shaken with three 7 ml portions of 12 $\underline{N}$ H_2SO_4 (Note 4). For a more complete back-extraction of the technetium, 1 drop of 0.2 $\underline{N}$ $HClO_4$ may be added to each 7 ml portion of H_2SO_4.

(8) To remove any chloroform droplets, the combined aqueous layers are filtered through coarse, moist filter paper into a distilling flask with air inlet tube. About 1 gram of ceric sulfate is added to the solution, along with one drop each of 0.2 $\underline{M}$ KBr and 0.2 $\underline{M}$ $KBrO_3$.

(9) The solution is heated to about 80° C for 10 min. while bubbling a stream of nitrogen through it. This should volatilize any bromine activity.

(10) Glass beads are added to the flask, a condenser with a Kjeldahl trap is attached, and the solution is distilled to near dryness at a rate of 1-1.5 ml/min. (Note 5).

(11) The distillate is cooled in ice, 3 mg of Cu^{2+} carrier is added, and the acidity is adjusted to 1 N by slow addition of conc. NH_3.

(12) Thioacetamide in 5% solution is added to give a concentration of 0.5%, and the solution is heated to just below boiling for 40 min. (Note 6). A wetting agent (e.g. Schleicher & Schuell Anti-Creep) is added, and the solution is filtered through a coarse membrane filter. (Note 7).

Note (1). Antimony and tungsten holdbacks are added in larger amounts since these elements tend to contaminate the molybdenum fraction.

Note (2). Tetraphenylarsonium sulfate can be prepared from the chloride by passing a 0.05 N solution of the latter through a Dowex-1 column in the sulfate form. This conversion is desirable to prevent interference by chloride in the subsequent distillation.

Note (3). Some tetraphenylarsonium ion must be present in the wash solutions, to prevent back-extraction of the technetium.

Note (4). The principal remaining impurities at this point are Au (extracted as chloro- or bromoaurate) and Br. Both will carry on a sulfide precipitate even in the presence of holdbacks, and must therefore be removed by distillation. However, if they are known to be absent, the back-extraction can be done much more efficiently into 0.2 N $HClO_4$, in which case the technetium is isolated by a sulfide precipitation. The perchloric acid solution cannot be distilled safely, owing to its content of organic matter.

Note (5). To prevent bumping, nitrogen should be bubbled through the solution. An electric heating mantle with quartz-fabric insulation may be used to advantage.

Note (6). In 1 N H^+, technetium can normally be quantitatively coprecipitated with CuS in 20 minutes, but in the presence of large amounts of ammonium salts, the reaction is somewhat slower.

Note (7). Normally, the precipitate is readily filterable through ordinary filter paper, but membrane filters offer better retentivity and speed.

Procedure 6

Source - G. E. Boyd, Q. V. Larson, J. Phys. Chem. 60, 707 (1956)

Isolation of Long-lived Tc from Minerals

1. Introduction

This procedure was used in a search for long-lived Tc in nature. It should be adaptable to the isolation of technetium from various materials.

2. Procedure

The mineral (MoS_2 or yttrotantalite) was fused with the five-fold amount of Na_2O_2 in a zirconium or iron crucible. Fusions were conducted with 25 g. aliquots of ore in iron and with 1-10 g. aliquots in zirconium crubibles. In nearly all cases γ-emitting radioactive technetium (usually 4.2 d Tc^{96} + 60 d Tc^{95m}) was added to the ore to permit the monitoring of the chemical processing at every step.

The fusion mixture was dissolved in water, and the solution brought to boiling and digested to destroy residual peroxide. Upon cooling to room temperatures, ferric hydroxide from iron originally present in the ore and mainly from the corrosion of the iron crucible was then allowed to settle. Separate tests using radio-tracers showed no technetium was lost by coprecipitation with iron hydroxide. After filtering to remove the iron, volumes of solution ranging from 1 to 45 liters were passed through a 9.6 cm. by 22 cm. deep bed of strong-base anion exchanger (viz., Dowex-2 or Amberlite IRA 410) which extracted all of the technetium (as proved by tracers), the rhenium, and a small part of the molybdate, sulfate or ruthenate, etc., also formed by the oxidizing, alkaline fusion. Cationic constituents such as Na, Cu, Ni, etc., passed through the resin bed. Molybdate and other anions were eluted with 1 M $NaNO_3$ at pH 10 or with 2 N NaOH solution after rinsing the bed with distilled water.

After a second water rinse, both perrhenate and pertechnetate were displaced quantitatively with 2 N $NaClO_4$ or 2 N $HClO_4$. The eluent solution usually contained approximately 5-10 mg. of rhenium, and microgram or smaller quantities of technetium, although sometimes as much as one gram of rhenium was present. After acidification (if necessary), the eluate was heated, treated with bromine water to oxidize any reduced technetium, and then treated with H_2S gas to precipitate rhenium and technetium sulfides. Quantitative coprecipitation of technetium was insured by digestion at 90°, then the rhenium sulfide was separated by filtering, dissolved with ammonia and hydrogen peroxide and the solution evaporated to near-dryness on a steam-bath. This residue was taken up in 10 N HCl, the solution heated for one hour, and rhenium sulfide again precipitated with hydrogen sulfide. Technetium is not coprecipitated under these conditions, and remains in the supernatant acid solution. After filtration, this supernatant was diluted to a concentration of 1 N, heated, treated with bromine water, and then with hydrogen sulfide to precipitate residual fractional milligram quantities of rhenium together with technetium which is again coprecipitated. One or more of these cycles served to give a considerable reduction in the amount of rhenium.

Further reduction of the rhenium content of the technetium fraction was accomplished by use of ion-exchange chromatography using a 0.78 cm. by 30 cm. deep bed of 120-200 mesh strong-base anion exchanger, Dowex-2. The final rhenium sulfide precipitate mentioned above was dissolved in ammoniacal hydrogen peroxide, and the pertechnetate and perrhenate ions in this solution were absorbed on the top of the bed. The chromatographic separation was performed using perchlorate solutions as eluents at flow rates averaging less than 0.5 ml/min. Fractions containing the technetium were combined, made 1 N in HCl, heated and treated with bromine, and then one mg. of copper was precipitated as copper sulfide. This "technetium concentrate" was processed as required by the various assay methods: (1) For spectrochemical analysis, it was dissolved in ammonia and hydrogen peroxide and the technetium electroplated on to the ends of 1/4-inch diameter cylindrical copper electrodes after adjusting the solution to approximate neutrality and adding fluoride ion to assist the electrodeposition. (2) For spectrophotometric analysis using a Beckman Model DU spectrophotometer, the copper sulfide was dissolved in ammoniacal peroxide, then copper was removed by passage through a small cation-exchange column (Dowex-50) and finally the solution was evaporated to a volume of one ml. (3) For polarographic analysis the treatment was the same as for (2), except for the omission of the evaporation step. (4) For activation analysis the CuS was carefully wrapped in pure polystyrene foil and irradiated for six hours with neutrons after which it was dissolved in ammoniacal peroxide, treated with a cation exchanger to remove copper and other activated cationic impurities, chromatographed on a small anion-exchange column (Dowex-1) to obtain a pure technetium fraction, and then examined with scintillation spectrometer for the presence of the characteristic 141 Kev. γ-ray of an induced 6.0 h Tc^{99m} activity. (5) For mass spectrometric analysis the CuS was dissolved and copper was removed as before, then the technetium was electroplated onto iridium and finally reduced to its metal in hydrogen gas at about 400°. In all cases above just preceding the assay step the amount of initially added technetium radio-tracer was determined to permit an estimate for the "over-all" chemical yield, or recovery for the separation from the starting material.

Procedure 7

Source - E. Anders

Isolation of Long-lived Tc from Minerals

1. Introduction

This procedure was used in a search by neutron activation analysis for long-lived Tc^{98} in nature. It was primarily designed for chromite, columbite, and other non-silicate oxide minerals, but can be adapted to a variety of materials.

2. Procedure

Fifty grams of the finely powdered (-100 mesh) mineral was fused with 100 grams of NaOH and 40 grams of Na_2O_2 for 20-30 min. in a covered nickel crucible. More Na_2O_2 was added, if necessary, to ensure the oxidation of Mn to $MnO_4^{=}$. The melt was poured on a steel plate, cooled, transferred to a beaker, and dissolved with mechanical stirring by addition of 250 g of ice. Care was taken to have an excess of $MnO_4^{=}$ present at all times to ensure oxidation of any TcO_2 to TcO_4^-. If required, $KMnO_4$ was added.

The solution was centrifuged, the residue washed twice with 50 ml portions of H_2O, and the combined solutions recentrifuged. The centrifugate was adjusted to about 1$\underline{F}$ NaOH by addition of 12 $\underline{N}$ H_2SO_4, and Na_2O_2 was added to reduce $MnO_4^{=}$ to MnO_2. The solution was heated to coagulate the precipitate, and filtered. The filtrate was neutralized with 12 $\underline{N}$ H_2SO_4, and refiltered to remove small amounts of Zr, Pb, Sn, Nb, Ta, Ti, Si, W, and other elements precipitated under these conditions. The acidity was adjusted to 1$\underline{F}$ H^+, 20 mg of Cu^{2+} per liter of solution was added, and copper sulfide was precipitated by bubbling H_2S through the hot solution. After a digestion time of 2 hrs., the solution was filtered through a coarse membrane filter, the precipitate transferred to a 125 ml distilling flask, and dissolved in 1-2 ml conc. HNO_3. Twenty ml of conc. H_2SO_4, 10 ml 85% H_3PO_4, and 2 g $Ce(SO_4)_2$ were added, and the flask connected to a distilling apparatus equipped for steam distillation. The heat was adjusted so as to give a distillation rate of 0.5 to 0.8 ml/min, and the temperature of the solution measured at frequent intervals. The fraction distilling below 210° C, containing nearly all of the excess HNO_3, was discarded. Steam was passed through the solution as soon as the temperature had reached 230°, and the distillation continued between 240 and 260° until 75 to 90 ml had distilled over. An aliquot of the distillate was titrated against NaOH, and the acidity adjusted to 1-1.5 N H^+ by addition of H_2SO_4. Two mg of Cu^{2+} carrier[*] was added, the distillate heated to about 80° on the steam bath, and the sulfide precipitated as before. The precipitate was filtered through a fritted glass funnel and dissolved in a 5:1 mixture of concentrated NH_4OH and H_2O_2. Because of the rapid catalytic decomposition of H_2O_2 by Cu^{2+}, the solvent was added in 0.05 to 0.1 ml portions, and the solution removed by suction before adding fresh solvent[**].

The solution (2-3 ml) was heated on the steam bath until most of the NH_3 had evaporated[***], cooled, and acidified with 6 N H_2SO_4, to give a final acidity of 0.1 N H^+. This solution

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[*] Specially purified.

[**] In the presence of large amounts of rhenium, some unreacted sulfide usually ran through the filter during the dissolution. In this case, the solution was heated to coagulate the sulfide, and refiltered.

[***] The heating ensured the conversion of sulfo-salts to TcO_4^-. Tracer experiments indicated that if this step is omitted, losses of $\geqslant$ 30% can occur due to differences in the chemical behavior of the two species.

was heated on the steam bath for 10 minutes*, cooled, and transferred to a Dowex 1-X8 (200-400 mesh) anion exchange column of about 18 cm length, previously converted to the ClO_4^--form. The separation was performed according to Procedure 4. The effluent was acidified with H_2SO_4 to give a final acidity of 1 N H^+, 0.5 to 1 mg Cu^{2+} was added, and CuS precipitated as in the previous step. Another complete anion exchange cycle followed at this point. The sulfide from this cycle was dissolved in NH_3 and H_2O_2 as before, and separated from Cu^{2+} by passing the solution through a quartz ion exchange column (0.2 cm^2 x 8 cm) filled with Dowex 50W-X8, 200-400 mesh, ammonium form. The column was rinsed with 2 ml 2 N NH_3, the combined effluent was reduced in volume, transferred to a quartz vial and evaporated to dryness under vacuum. The vials were then sealed and irradiated. After irradiation, the samples were processed as in Procedure 5.

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* This step was needed in order to remove CO_2 and NO (from NO_2^- formed by oxidation of NH_3 by H_2O_2). Otherwise, the gases were liberated in the anion exchange column, causing channeling and consequently poor separation.

Procedure 8

Source - E. Jacobi, Helv. Chim. Acta
31, 2118 (1948)

Separation of Technetium and Molybdenum

1. Introduction

This procedure, which is adapted from the 1939 paper of Perrier and Segrè, gives only moderate separation factors, but it is fairly rapid (40 min.) and gives good yields (70%). Molybdenum is precipitated with 8-hydroxyquinoline, and the technetium in the filtrate is coprecipitated with copper sulfide.

2. Procedure

Precipitate molybdenum with 8-hydroxyquinoline from neutral solution, filter, and make the solution 0.6 M in HCl (total volume 50 ml). Add 0.3-2 mg Cu^{++} carrier, heat, pass H_2S into the solution for 15 min., filter, and wash the precipitate with H_2S water.

Procedure 9

Source - K. T. Bainbridge, M. Goldhaber,
E. Wilson, Phys. Rev. 90,
430 (1953)

Separation of Tc^{99m} from Mo^{99}

1. Introduction

This procedure involves co-distillation of technetium with perchloric acid. Ruthenium and rhenium will also distill under these conditions, but molybdenum will not, if sufficient phosphoric acid is present.

2. Procedure

Molybdenum metal is dissolved in a mixture of $HClO_4$ and H_3PO_4. (The phosphoric acid complexes Mo and prevents its distillation.) Technetium is distilled in an air stream at 120-200° C, and the distillate is collected in water or dilute H_2SO_4. The fraction distilling below 120° C may be discarded. The distillate is redistilled in the presence of Mo holdback carrier, and the 120-200° C fraction is again collected. The technetium can be recovered from the distillate by electrolysis at pH 5.5 or by sulfide precipitation.

Procedure 10

Source - J. B. Gerlit, Proc. Internat. Conf.
Peaceful Uses of Atomic Energy, Geneva,
1955, 7, 145 (1956)

Separation of Technetium from Ruthenium, Rhenium and Molybdenum

1. Introduction

This procedure has been reconstructed by the author from a brief statement in Gerlit's paper. It makes use of the fact that neither TcO_4^- nor ReO_4^- extract into mixtures of halogenated and oxygenated solvents, even though they do extract into pure oxygenated solvents.

2. Procedure

Make solution 5 N in NaOH and extract with equal volume of hexone (methyl-isobutyl ketone). The distribution coefficients are: $TcO_4^- = 17$; $ReO_4^- = 8.2$; $MoO_4^= < 0.001$; Ru(IV) < 0.001. Wash with 5 N NaOH as required.

Discard aqueous layer and add enough $CHCl_3$ to organic phase (amount not given) to permit quantitative back-extraction of ReO_4^- and TcO_4^- into water.

Make solution 2 N in H_2SO_4, reduce Tc with hydrazine to +4 state, and extract ReO_4^- into iso-amyl alcohol.

Procedure 11

Source - V. I. Spitsyn, A. F. Kuzina,
Doklady Akad. Nauk SSSR 124
846 (1959)

Isolation of Tc^{99} from Molybdenum

1. Introduction

This procedure is based on the fact that Tc(VII) will coprecipitate with $MgNH_4PO_4$, whereas its lower oxidation states will not. It is rather original in several respects, but should probably be tested more fully.

2. Procedure

The irradiated MoO_3 is dissolved in ammonia, and the technetium is coprecipitated with $MgNH_4PO_4$ and $MgHPO_4$. The precipitate is dissolved in 6 N HCl, and the technetium is reduced to the +4 and +2 (sic) states by passing H_2S into the solution for some time. The solution is then made basic with ammonia, and the resulting $MgNH_4PO_4$ precipitate is discarded. The filtrate is evaporated to dryness and the ammonium chloride is sublimed off. (Note 1).

The residue containing Tc is taken up in HNO_3, the pH is adjusted to 2, and the solution passed through a cation exchanger (KU-2). Technetium, being in an anionic state, passes through the column.

The solution is evaporated to dryness in a quartz boat, and the ammonium nitrate is volatilized at 180° C. The residue is dissolved in 2-3 drops of ammoniacal hydrogen peroxide, evaporated to dryness, and taken up in 4 ml 4 M HCl. Technetium heptasulfide is then precipitated from this solution.

(Note 1). This step presumably requires careful temperature control, to prevent losses of Tc.

Procedure 12

Source - E. H. Huffman, R. L. Oswalt, L. A. Williams, J. Inorg. Nucl. Chem. 3, 49 (1956)

Separation of Technetium and Molybdenum by Anion Exchange

1. Introduction

This procedure gives a fairly simple and rapid ion-exchange separation of technetium and molybdenum, using HCl and HNO_3 as elutriants. The method of recovery of technetium from the nitric acid solution is not foolproof, however, and may lead to losses.

2. Procedure

Molybdenum and technetium in 0.5 ml of 1.0 M hydrochloric acid were added to a column of resin (Dowex-1, 250-500 mesh, Cl^- form) 3 mm in diameter and 21 mm in length. When the levels of liquid had just reached the top of the resin, elution was continued with 8 ml of 1.0 M hydrochloric acid, at the rate of 1 ml in 15 minutes, to remove molybdenum. Technetium was then removed from the column with 8 ml of 4.0 M nitric acid at the same rate of elution. The total molybdenum recovered in the first 4.0 ml of hydrochloric acid was 100% of the amount used and the recovery of technetium in the first 4.4 ml of nitric acid was 98%. For some reason, 0.1% of the technetium activity appeared in the first milliliter of hydrochloric acid with the molybdenum, but no more appeared in the next 7 ml.

The samples were evaporated to dryness on platinum counting plates.

Procedure 13

Source - John Q. Adams and E. Anders (unpublished)
See also N. F. Hall & D. H. Johns,
JACS 75, 5787 (1953)

Separation of Technetium and Molybdenum by Anion Exchange

1. Introduction

In strongly basic solution, molybdenum is only weakly held by the resin, e.g., in 3 M NaOH, $D = 12$ (D = amt. per g of dry resin/amt. per ml of solution). For TcO_4^-, D is on the order of 10^3, so that a clean separation can easily be accomplished.

2. Procedure

The basic solution containing Tc and Mo in their highest oxidation states is adsorbed on the column (Dowex 1-x8, 200-400 mesh, OH^- form), and the molybdenum is eluted with 25-30 free column volumes of 3 M NaOH. The molybdenum peak should appear at about 15 free column volumes. The technetium is then stripped with about 15 column volumes of 1 M $HClO_4$ or NH_4ClO_4. The first 3-4 column volumes should not contain any Tc and may be discarded. If a separation from Re is desired, the elution may instead be carried out with 0.1 - 0.2 M ClO_4^- solutions (Procedure 4).

Procedure 14

Source - J. B. Gerlit, Proc. Internat. Conf.
Peaceful Uses of Atomic Energy, Geneva,
1955, 7, 145 (1956)

Separation of Technetium and Rhenium

1. Introduction

This appears to be one of the fastest procedures for the separation of Tc and Re. It is based on the reduction of Tc(VII) to Tc(IV) by strong HCl, and coprecipitation of Tc(IV) by $Fe(OH)_3$.

2. Procedure

Dissolve sample in a small volume of conc. HCl and heat to about 75° C for one half hour. Add ferric ion, dilute the solution somewhat, and precipitate $Fe(OH)_3$ with ammonia. Wash the technetium-containing precipitate thoroughly with a hydrazine sulfate solution, dissolve in a small amount of conc. HNO_3 [thereby oxidizing Tc(IV) to Tc(VII)] and remove the iron by another ammonia precipitation.

Procedure 15

Source - L. E. Glendenin, Natl. Nuclear Energy
Ser., Div. IV-9, Paper 259,
1545 (1951)

Separation of Technetium from Fission Products

1. Introduction

This procedure involves a sulfuric acid distillation and coprecipitation with tetraphenylarsonium perrhenate. It gives excellent decontamination from Ru and Mo, but several of the steps are tricky, and should be revised.

2. Procedure

Step 1. To 5 ml of an active uranyl nitrate sample, add 10 ml of conc. HBr and evaporate almost to dryness. Repeat the evaporation with HBr twice.

Step 2. Transfer the residue completely, with a minimum amount of wâter, to a distillation flask. Add carefully 10 ml of H_2SO_4. Heat gently to boiling and distill into a 50-ml centrifuge tube containing 20 ml of water until less than 2 ml of H_2SO_4 remains in the flask (Note 1).

Step 3. Add 10 mg of rhenium carrier to the distillate, heat nearly to boiling, and saturate with H_2S for 5 to 10 min with continued heating. Centrifuge, and discard the supernatant solution.

Step 4. Wash the Re_2S_7 with about 10 ml of H_2O and dissolve by heating with 1 ml of conc. HNO_3. Add 5 ml of conc. HBr and evaporate nearly to dryness. Repeat the evaporation first with 5 ml of HNO_3 and then with 5 ml of HCl (Note 2).

Step 5. Dilute the residue to 20 ml with H_2O, add about 2 mg of iron carrier, heat, and add NH_4OH until $Fe(OH)_3$ is just precipitated (Note 3).

Step 6. Centrifuge, and discard the $Fe(OH)_3$ precipitate. Repeat the scavenging by a second addition of about 2 mg of iron carrier. Centrifuge, and discard the precipitate.

Step 7. Heat, and add 1 ml of 0.05 M $(C_6H_5)_4AsCl$ to precipitate $(C_6H_5)_4AsReO_4$. Wash three times with 5 ml of H_2O, dry at 110° C for 10 min, weigh and mount.

(Note 1) If reducing substances are present in the H_2SO_4, yields will be low. Unfortunately, strong oxidizing agents cannot be added, since they will oxidize Ru to RuO_4, causing it to distill.

(Note 2) The evaporations with HNO_3 and HCl are likely to cause losses. It would be better to remove iodine by solvent extraction instead (Procedure 16).

(Note 3) It is imperative that Tc be in its highest oxidation state in this step, so that it will not carry on $Fe(OH)_3$.

Procedure 16

Source - S. Tribalat, J. Beydon, Anal. Chim.
Acta 8, 22 (1953)

Separation of Technetium from Fission Products

1. Introduction

This procedure involves extraction of pertechnetate into chloroform in the presence of tetraphenylarsonium ion.

Dissolve UO_3 in H_2SO_4 containing a few µg of I^- holdback. Add $S_2O_8^=$ and extract I_2 into toluene. Heat solution to boiling to remove traces of I_2, neutralize with $(NH_4)_2CO_3$, add more $S_2O_8^=$ and heat to boiling. Extract TcO_4^- into $CHCl_3$ at $R = 10^{-4}$ M. Other fission products do not seem to interfere.

The technetium can be recovered from the organic phase by back-extraction into $HClO_4$ or H_2SO_4 (Procedure 5) or by evaporation to dryness.

Procedure 17

Source - G. W Parker, U.S. Atomic Energy Comm.
Report ORNL-1116 (Jan. 29, 1952),
pp. 26-30

Isolation of Tc^{99} from Mixed Fission Products ("Redox" Waste)

1. Introduction

This process is designed for large-scale separation of Tc^{99} from mixed fission product wastes. It involves coprecipitation with tetraphenylarsonium perchlorate.

2. Procedure

To 100 gallons solution containing 1 g Tc(VII) is added 17 g $HClO_4$ carrier. The solution is heated, an excess of tetraphenylarsonium chloride is added, and the precipitate is filtered after cooling. The mixed perchlorate-pertechnetate precipitate is dissolved in ethyl alcohol, the solution is passed through a strong-base anion exchanger in the chloride form, and the adsorbed pertechnetate eluted with about 10 free column volumes of 2 N $HClO_4$.

Alternatively, the precipitate can be dissolved in conc. H_2SO_4. The technetium can either be co-distilled with the acid, and precipitated as the sulfide, or separated as the dioxide by electrolysis between bright platinum electrodes.

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