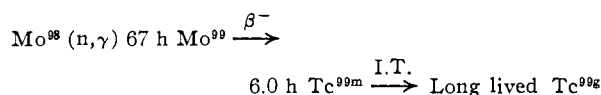


Molybdenum was next considered as a target material for the nuclear synthesis of technetium. The outlook for producing weighable amounts of the element seemed encouraging as measurements⁴ of the decay of Tc^{99m} had suggested that Tc^{99g} might possess a half-life exceeding 40 years and other investigations⁵ carried out during 1944 had indicated a reasonable value for the thermal neutron cross-section of Mo^{98} . The isolation of Tc^{99g} was achieved and a brief announcement has appeared.⁶

Details on the methods employed for the preparation and isolation of milligram amounts of technetium produced in pure molybdenum metal will be presented in this paper. Although gram quantities of long-lived technetium may be isolated from uranium fission-product mixtures,⁷ on occasion it may be advantageous to use pure molybdenum as a source material. After a time sufficient for the decay of 67 h Mo^{99} also formed, chemical operations for the separation of technetium may be conducted with a minimum of γ -ray shielding. Chemical studies performed with 6.0 h Tc^{99m} and with cyclotron-produced technetium tracers will be reported also. These latter investigations using sub-microgram amounts were essential to the development of the isolation procedure to be described and to our search for technetium on the surface of the Earth and in meteorites.⁸

Production Method.—Neutron capture by the isotope of mass 98, present with an abundance of 24.00% in the naturally occurring molybdenum, gives 67 h Mo^{99} which decays emitting beta particles to form the six-hour isomer, Tc^{99m} . The latter isotope undergoes an isomeric transition (I.T.) to form a long-lived Tc^{99g} which in turn decays to stable ruthenium



The rate of formation of Tc^{99g} may be computed from the equation

$$dN_{\text{Tc}^{99g}}/dt = \bar{n}\bar{v} \sigma_{ac} N_{\text{Mo}^{98}} - \lambda N_{\text{Tc}^{99g}} \quad (1)$$

where $\bar{n}\bar{v}$ is the flux of thermal neutrons (n/cm.²/sec.); σ_{ac} , the isotopic activation cross-section (cm.²/atom Mo^{98}); $N_{\text{Mo}^{98}}$, the number of Mo^{98} atoms; λ , the radioactive transformation constant, equal to $0.693/T_{1/2}$, where $T_{1/2}$ is the half-life of Tc^{99g} , and t , the bombardment time in seconds. The number of Tc^{99g} atoms formed after an irradiation time t is

$$N_{\text{Tc}^{99g}} = \bar{n}\bar{v} \sigma_{ac} N_{\text{Mo}^{98}} t \quad (2)$$

as the second term on the right-hand side of eq. 1 is negligible relative to the first (*i.e.*, the rate of decay of the Tc^{99g} is negligible relative to its rate of formation).

(4) G. T. Seaborg and E. Segré, *Phys. Rev.*, **55**, 808 (1939).

(5) L. Seren, H. N. Friedlander and S. H. Turkel, *ibid.*, **72**, 888 (1947). More recent work (D. J. Hughes, R. C. Garth and J. S. Levin, *ibid.*, **91**, 1423 (1953)) has given 0.13 ± 0.05 b. for the neutron absorption cross-section.

(6) E. E. Motta, G. E. Boyd and Q. V. Larson, *ibid.*, **72**, 1270 (1947).

(7) G. W. Parker, J. Reed and J. W. Ruch, U. S. Atomic Energy Commission Declassified Document, AEC-D-2043, January 9, 1948.

(8) G. E. Boyd and Q. V. Larson, *J. Phys. Chem.*, **60**, 707 (1956).

To produce quantities of technetium sufficient for chemical studies, 5700 g. of the purest molybdenum metal powder commercially obtainable⁹ was irradiated for one year in an average thermal neutron flux of 5×10^{11} n/cm.²/sec. Using $\sigma_{ac} = 0.13 \pm 0.05 \times 10^{-24}$, which is the accepted value,⁵ and substituting into eq. 2, a value of 1.7×10^{19} atoms is obtained for $N_{\text{Tc}^{99g}}$. This corresponds to 2.8₃ mg. of Tc^{99g} formed in 5.7 kg. of molybdenum. The problem of the isolation was that of separating 0.5 p.p.m. of technetium from molybdenum metal.

Experimental

Analytical Procedures.—To monitor the extraction of technetium from its molybdenum matrix, it was necessary to develop a rapid, convenient radiochemical analytical procedure which would allow a determination of the efficiency of each operation. The long-lived technetium produced in molybdenum was known to be a pure, low energy (*ca.* 0.3 Mev.) β -ray emitter, so that a mica end-window Geiger counter could be used as a detector. The co-separation of technetium with a variety of substances formed in acid, neutral and basic solutions was investigated.¹⁰ The co-precipitation of technetium by CuS , CdS , As_2S_3 , PtS_2 and Re_2S_7 formed in 3 *M* HCl solutions has been reported²; however, it seemed desirable to check the efficiency of some of these "carriers" in sulfuric acid solutions, as the initial step in the isolation procedure to be described involved a co-distillation of technetium with concentrated sulfuric acid. Quantitative coprecipitation (95 to 100%) of technetium with rhenium heptasulfide was found for H_2SO_4 concentrations between 3 and 12 *M*, and with platinum sulfide between 0.25 and 12 *M*. As little as one mg. of rhenium or platinum precipitated from 100 ml. acid gave a quantitative collection of the technetium.

The co-precipitation of technetium present in neutral and alkaline solutions was measured using two insoluble rhenium compounds: tetraphenylarsonium perchrenate and nitron perchrenate (diphenyl-endo-anilo-hydro-triazole). The former precipitant worked best ($95 \pm 5\%$ co-precipitation) at a pH of 7 with one mg. of rhenium per 10 ml. at 25°, or with one mg. per 200 ml. at 0°. The use of nitron perchrenate as a carrier was limited because its complete precipitation was possible only from neutral or weakly acid solutions and because of the formation of other insoluble salts with certain anions such as sulfate, for example.

The analytical procedure applied in monitoring the isolation operations was as follows: The technetium containing aliquot was brought to 30 ml. volume in 4 *M* H_2SO_4 , heated to 90° and treated with bromine water to remove reducing substances present (usually SO_2) and to convert the technetium to a sulfide-insoluble oxidation state. One ml. of chloroplatinic acid (2 mg. Pt/ml.) was added and platinum sulfide was precipitated. After digestion for 30 minutes at 90°, centrifuging, decanting, washing and recentrifuging, the precipitate was collected on a circular disc of low porosity filter paper (Whatman No. 50) which was mounted, covered with one mil aluminum foil and beta counted at 30% geometry.

The final technetium solutions were assayed by electro-deposition. Perrier and Segré² have mentioned that technetium could be deposited on platinum cathodes by a process used by Hoelmann¹¹ for electroplating rhenium, but no quantitative data were given. We were unable to obtain more than a 50% electrodeposition in 150 minutes of 6.0 h Tc^{99m} tracer on bright platinum cathodes from 0.1 *N* sulfuric acid solutions, although rhenium was plated quantitatively. A larger deposition (60–70%) could be realized, however, when polished copper or nickel cathodes were used. Electrolyses were conducted at a potential (3–

(9) North American Phillips Co., 120 mesh Mo metal powder. Chemical assay showed $99.2 \pm 0.1\%$ Mo with approximately 0.04% iron impurity. Qualitative spectrochemical analysis revealed traces of Al and Cu and approximately 0.01% Ca. Polarographic analysis further showed *ca.* 3 p.p.m. of rhenium.

(10) For details, see: "Studies on the Tracer Chemistry of Elemental 43," G. E. Boyd, E. E. Motta and Q. V. Larson, Oak Ridge National Laboratory Report MonC-99, April 1, 1947, Declassified December 23, 1954.

(11) H. Hoelmann, *Z. anorg. Chem.*, **211**, 195 (1933).

6 volts) sufficient to evolve hydrogen gas to determine the importance of pH and whether fluoride ion would facilitate a quantitative deposition. Approximately 15 ml. of solution was employed in a glass cell equipped with a rotating platinum anode which served as a stirrer. After 30 to 180 minutes electrolysis the cathode discs containing the electrodeposit were washed, dried and counted. The cell solution plus electrode washings and an aliquot from the original technetium solution were analyzed by the platinum sulfide precipitation technique. The fraction electroplated was computed from analyses of the initial and final solutions (Table I).

TABLE I
ELECTRODEPOSITION OF TECHNETIUM ONTO POLISHED COPPER CATHODES AT ROOM TEMPERATURES
(Co-deposition with 1 mg. Re; C.D. = 11.8 ma./cm.²; time = 120 min.)

pH	NH ₄ HF ₂ (M)	Fraction electrodeposited (%)	Comments
1.2	0	30.6	Bright Re deposit
1.2	0	45.9 ^a	Bright Re deposit
1.2	2 × 10 ⁻³	76.6	Bright Re deposit
5.5	0	84.7	Black Re deposit
5.5	2 × 10 ⁻³	91.3	Black Re deposit
10.5	0	3.1	Black Re deposit
10.5	2 × 10 ⁻³	21.1	Black Re deposit

^a 150 minutes deposition.

Small amounts of fluoride ion, presumably by raising the hydrogen overvoltage, improved the electrodeposition of technetium over a wide range in acidity. The optimum deposition, however, was at approximate neutrality. Repeated measurements of the plating of technetium at room temperature onto polished copper cathodes from aqueous solutions of pH 5.5 containing 10⁻³ M ammonium bifluoride showed that 89.0 ± 1.5% could be deposited in 2 hr. using a current density (C.D.) of 100 ma./cm.². Quantitative measurements of the electrodeposition of technetium and rhenium from 0.1 N sulfuric acid containing fluoride ion onto smooth nickel cathodes for a C.D. = 100 showed that the amount of each element remaining in solution decreased exponentially with time; the times for 50% deposition were 42 minutes for rhenium and 93 minutes for technetium, respectively. Weight losses on reduction of heavier electrodeposits with hydrogen gas at 300° have indicated them to be technetium dioxide dihydrate.

Separation of Technetium from Molybdenum.—The separation of tracer technetium from molybdenum described by Perrier and Segré² was based on the precipitation of the latter element using 8-hydroxyquinoline, followed by concentrating the technetium with rhenium heptasulfide, or with nitron perrhenate precipitated from the supernatant liquid. For the processing of kilogram amounts of molybdenum metal, however, this procedure seemed inappropriate because of the large volumes of precipitate and liquid necessarily involved. A direct separation of technetium away from molybdenum was preferred. Our early studies¹ and those of others¹² on the separation of technetium from ruthenium suggested that a removal from molybdenum could be effected by co-distilling the technetium with concentrated sulfuric acid. Measurements in which the ratio of acid to molybdenum metal was varied showed that with 6 ml. acid/g. metal 75% of the technetium appeared in the distillate, while with a ratio of twelve to one, 90% was recovered on distilling to a dry molybdic oxide residue, and over 98% after two distillations. Approximately 15% of the sulfuric acid was consumed in dissolving the irradiated metal.

The neutron irradiated molybdenum was processed¹³ in ca. 190-g. aliquots to give two approximately two-liter volumes of sulfuric acid distillate containing about 0.10 mg. of element 43. The distillate was diluted to 4 M, heated to boiling and treated with bromine water, and platinum sulfide (1 mg. Pt per 200 ml.) was precipitated to "carry

(12) L. E. Glendenin, "National Nuclear Energy Series," Vol. IV, 9, Paper 329, McGraw-Hill Book Co., New York, N. Y., 1951.

(13) Six weeks after removal from the Oak Ridge pile to allow for the complete decay of the 67 h Mo.

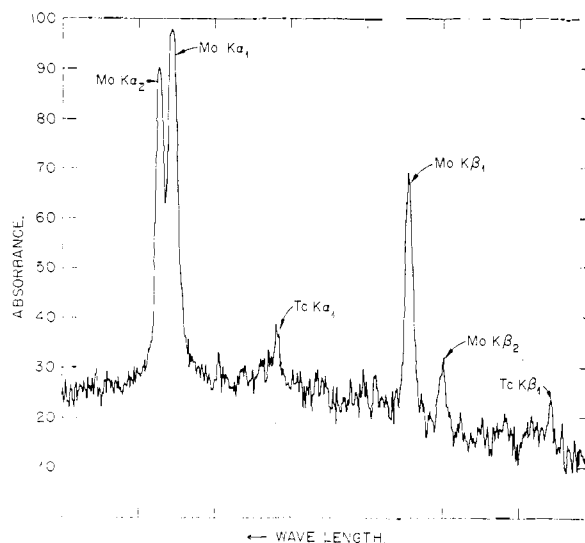


Fig. 1.—Densitometer tracing of an X-ray emission spectrogram taken on a sulfide concentrate isolated from neutron irradiated molybdenum.

down" the technetium. After filtration, this precipitate dissolved readily in 50 ml. of a mixture of re-distilled ammonia plus 30% hydrogen peroxide. The ammoniacal technetium-containing solution was evaporated to dryness taking care that it remained alkaline. The residue was taken up in 25 ml. of concentrated H₂SO₄ or HClO₄, and the technetium was distilled away from the platinum and ammonium sulfate and collected in an ice-cooled receiver. An impure technetium sulfide was precipitated from this distillate after a fourfold dilution. An X-ray emission spectrum taken on a typical sulfide concentrate (Fig. 1) showed the presence of technetium together with somewhat larger quantities of molybdenum.¹⁴

Separation of Technetium from Rhenium.—The rhenium impurity originally present at about 3 p.p.m. in the molybdenum was concentrated together with technetium throughout the foregoing steps. To obtain pure technetium it was therefore necessary to separate the rhenium. This was the most difficult task in the isolation procedure. Perrier and Segré² have reported a separation using moist hydrochloric acid gas when both rhenium and technetium were contained in concentrated sulfuric acid at 180°. This result was sufficiently attractive that the experiment was repeated using radiotracers. When such a distillation was conducted at 200° about 93% of the rhenium was swept out of the sulfuric acid solution together with less than 5% of the technetium, suggesting indeed that the latter element, in contrast with rhenium, does not form a compound volatile under these conditions. An explanation of this difference in behavior apparently is to be found in the fact that hot hydrochloric acid will reduce technetium but not rhenium to a valence state which is non-volatile.

Separation of technetium and rhenium by fractional precipitation from hydrochloric acid solutions also was investigated (Fig. 2). Above a concentration of 9 N virtually no technetium was coprecipitated at 90° by platinum sulfide, whereas rhenium was removed quantitatively even up to 10 N. It seems probable that the reduction of heptavalent technetium by high chloride ion concentrations must be involved, because complete coprecipitation from sulfuric acid solutions up to 24 N was observed.

The possibility that a fractional crystallization of pertechnetate and perrhenate salts might be utilized to effect a rhenium-technetium separation was investigated with the results shown in Fig. 3. Evidently a Nernst distribution holds for the partition of microgram quantities of pertechnetate ion between saturated potassium perrhenate solution and crystalline salt. This method appeared feasible only when relatively large quantities of rhenium were to be separated from technetium.

(14) This molybdenum contamination was reduced greatly by a subsequent redistillation of the technetium from a perchloric-phosphoric acid mixture.

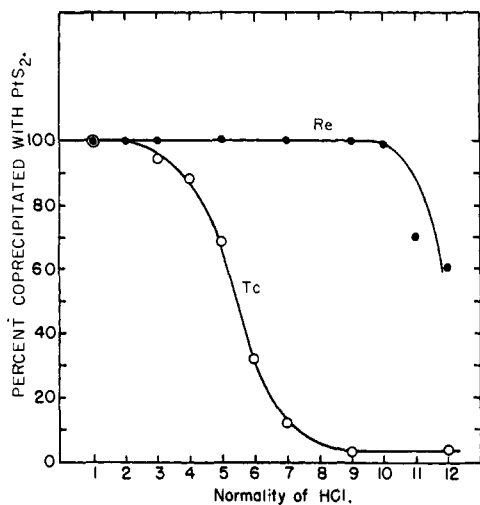


Fig. 2.—Co-precipitation of technetium and rhenium with platinum sulfide in hydrochloric acid solutions of varying normalities at 90°.

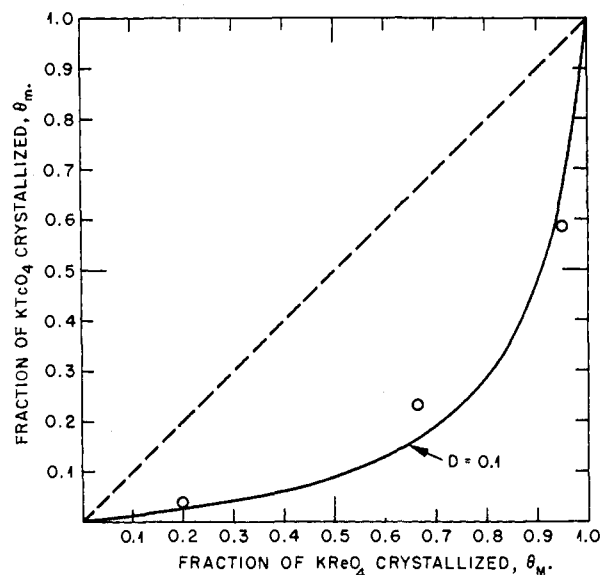


Fig. 3.—Separation of KTCO_4 from KReO_4 by fractional crystallization. (Solid curve was computed from $\theta_m = D\theta_M/1 + (D - 1)\theta_M$.)

The most satisfactory rhenium-technetium separation was obtained by ion-exchange chromatography using strong-base anion exchangers. One of our procedures based on differential elution with alkaline thiocyanate solution has been reported.¹⁵ Subsequently, an even more efficient perhenate-pertechnetate anion-exchange separation using sodium perchlorate or perchloric acid¹⁶ solutions as eluting agents has been found. Equilibrium distribution measurements showed that the differences in ion-exchange affinity were almost as small as those observed in rare earth separations, so that multi-stage fractionation (*i.e.*, anion-exchange columns) was required.

Pure technetium was precipitated either as a sulfide or was electroplated on a platinum anode after purification from rhenium either by differential volatility, fractional precipitation and/or by ion-exchange chromatography. Finally, ammonium pertechnetate was formed by oxidizing Tc_2S_7 or TcO_2 with ammoniacal hydrogen peroxide. Over-

(15) R. W. Atteberry and G. E. Boyd, *THIS JOURNAL*, **72**, 4805 (1950).

(16) R. N. Sen Sarma, E. Anders and J. M. Miller, *J. Phys. Chem.*, **63**, 559 (1959).

all yields ranged from 30% initially up to 65% in the later separations. The dark brown technetium sulfide formed in acid solutions was quite insoluble; less than 3 mg. of technetium per liter could be precipitated from 4 *M* sulfuric acid. Freshly prepared ammonium pertechnetate was white; on standing a light pink and occasionally a brown coloration developed.

Characterization of Technetium Isolated from Molybdenum

The purified technetium product isolated from neutron irradiated molybdenum was characterized by its optical spark spectrum which showed prominent lines at 4031.6, 4088.6, 4095.7 and 4262.1 Å. free of interferences either from rhenium or from molybdenum.¹⁷ As little as 0.1 µg. of technetium may be detected using the strong line at 4031.63 Å.

The attenuation of the beta radiations emitted by the technetium was measured using aluminum absorbers, and the absence of γ -rays associated with the decay was established (Fig. 4). The maximum β -ray energy derived from the range in aluminum was 0.29 ± 0.01 Mev. in satisfactory agreement with accurate magnetic β -ray spectrometer determinations which have given 0.290 Mev.¹⁸

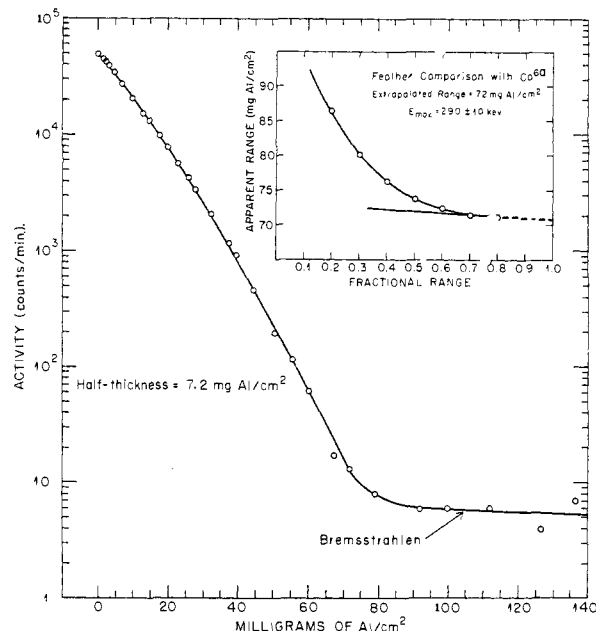


Fig. 4.—Absorption of β -rays emitted by Tc^{99m} isolated from neutron irradiated molybdenum. (Feather comparison conducted with electroplated Co^{60} and Tc^{99m} sources.)

The half-life of 9.4×10^5 y for technetium isolated from neutron irradiated molybdenum given in our preliminary report⁹ has differed considerably from a later value of 2.12×10^5 y determined by painstaking measurements on technetium isolated from the uranium fission products.¹⁹ Inasmuch as no other specific activity measurements have been published and since technetium isolated from the fission products is now known not to be isotopically pure, it was considered worth while to undertake a remeasurement using different radioassay procedures and methods for estimating the weight of technetium. The 4π beta counting technique²⁰ was used to measure the activity contained in a deposit of either KTCO_4 or NH_4TcO_4 evaporated from aqueous solutions on to thin polyvinyl chloride films (VYNS, 10µ/

(17) Private Communication: C. Feldman and M. M. Murray, Analytical Chemistry Division, Oak Ridge National Laboratory. See also: D. Timma, *J. Optical Soc.*, **39**, 898 (1949); W. F. Meggers, *Spectrochim. Acta*, **4**, 317 (1951). The triplet in the rhenium spectrum at 3640 Å. may be used to detect as little as 0.1 µg. of this element.

(18) L. Feldman and C. S. Wu, *Phys. Rev.*, **87**, 1091 (1952).

(19) S. Fried, A. H. Jaffey, N. F. Hall and L. E. Glendenin, *ibid.*, **81**, 741 (1951).

(20) H. H. Seliger and A. Schwehel, *Nucleonics*, **12**, No. 7, 54 (1954).

cm.²) mounted over 1.25 cm. diameter circular holes in thin aluminum sheets and made conducting by sputtering with gold. The radioactive solutions containing accurately known amounts of technetium were pipetted directly onto the film using calibrated 9.94 or 24.98 microliter pipets, and, when dried, gave deposits of ca. 2 $\mu\text{g.}/\text{cm.}^2$ surface density. The solution containing fission-product technetium was made by weighing out 17.676 ± 0.002 mg. of specially purified KTcO_4 and dissolving it in water to 10 ml. volume in a volumetric flask. Aliquots of this solution were diluted with potassium acid phosphate buffer (0.1 M) to a pH of 7.0, and the magnitude of the half-wave observed in the reduction of Tc(VII) to Tc(IV) was measured polarographically using the ORNL High Sensitivity Polarograph. Detailed studies²¹ have shown that the diffusion current for this reduction is linearly proportional to the concentration of Tc(VII) in solution. Accordingly, the concentration of the pertechnetate solution prepared from technetium isolated from neutron irradiated molybdenum was estimated by comparing its diffusion current with that for the standard solution. The concentrations of the fission-product and molybdenum-derived pertechnetate solutions were determined also from the optical densities they gave when measured at 2445 Å. in a Cary Model 14 recording photoelectric spectrophotometer. Agreement to within 2% of the polarographic values was found. Specific activities for technetium from both origins were computed from the known weights of the element counted and from the disintegration rates found after correcting the 4π beta count rates for the combined effects of film and self-absorption. Variable self-absorption in the evaporated deposits appeared to be the principal source of uncertainty because of the low energy of the β -rays emitted in the decay of $\text{Tc}^{99\text{m}}$. The slightest contamination of the deposits with dust or with silica was found to invalidate the counting results completely. The accuracy of the 4π beta counting method therefore depended on using the highest reproducible disintegration rate, and, hence, the shortest reproducible half-life, obtained after many trials. These measurements are summarized in Table II.

TABLE II
SPECIFIC ACTIVITY OF LONG-LIVED TECHNETIUM ISOLATED FROM THE URANIUM FISSION PRODUCTS AND FROM NEUTRON IRRADIATED MOLYBDENUM

Source ^a	Wt. of Tc ($\mu\text{g.}$)	Fraction of β -rays counted, f_β	Av. specific activity (d./min./ $\mu\text{g.} \times 10^{-4}$)	Stand. dev.
U-Tc (13)	0.2123	0.930	3.63	0.10
U-Tc (6)	.2694 ^b	.926	3.78	.08
Mo-Tc (19)	.1998	.922	3.74	.11

^a Value in parentheses is number of independent sources prepared and measured. ^b New KTcO_4 solution also analyzed polarographically.

Several features of the data in Table II may be noted: (a) The average values 0.930, 0.926 and 0.922 for the correction for film and self-absorption agree well with the value of 0.92 found in recent precision measurements of f_β for 300 Kev. beta particles using coincidence counting techniques.²² (b) The ratio of the difference in the average specific activity values obtained in the two series of measurements with technetium from the uranium fission products to the standard deviation of this difference (the "t" test) indicated that these averages were comparable and that all nineteen values may be pooled to give an average of 3.68×10^4 d./min./ $\mu\text{g.}$ (c) Application of the "t" test to the comparison of the average specific activity of technetium isolated from neutron irradiated molybdenum with the average for Tc from uranium suggested that it was probable (*i.e.*, 99% confidence level) that no significant difference existed. This result is consistent with a long half-life

(21) H. H. Miller, M. T. Kelley and P. F. Thomason, "Polarographic Studies of the Reduction of Pertechnetate Ion in Aqueous Solutions," International Congress of Polarography, Cambridge, England, Aug. 24-29, 1959. The authors are indebted to P. F. Thomason for the polarographic standardizations.

(22) (a) R. Gunnick, L. J. Colby, Jr., and J. W. Cobble, *Anal. Chem.*, **31**, 796 (1959); (b) J. S. Merritt, J. G. V. Taylor and P. J. Campion, *Can. J. Chem.*, **37**, 1109 (1959).

and/or a low abundance for Tc^{98} in fission-product technetium and with the non-occurrence therein of a long-lived Tc^{100} . The grand average for all the specific activity determinations conducted on technetium was 3.71×10^4 d./min./ $\mu\text{g.}$ with a standard deviation of 0.10×10^4 . The average half-life value for $\text{Tc}^{99\text{m}}$ corresponding to this specific activity was $2.16 \pm 0.06 \times 10^5$ years which appears to be slightly higher than the value of 2.12×10^5 years reported by Fried and co-workers.¹⁹ Considering the accuracy of each value, however, it seems probable that they do not disagree.

Chemical Behavior of Technetium when Present in Low Concentrations

Wet Volatility.—That volatile compounds play an important part in technetium chemistry became evident during the isolation of the element described above. Accordingly, its co-distillation with a number of strong acids was investigated using cyclotron produced γ -ray emitting technetium tracer (4.2 d Tc^{96} + 60 d $\text{Tc}^{96\text{m}}$) separated from proton irradiated molybdenum metal by an ion-exchange method: the metal 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 21×50 mm.) which absorbed the pertechnetate ion completely. Residual absorbed molybdate was removed by elution with $1 M \text{K}_2\text{C}_2\text{O}_4$ solution, and, after a water rinse, the technetium was eluted with $1.0 N \text{HClO}_4$. 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. One-tenth ml. aliquots of the tracer solution were added to 50 ml. volumes of reagent-grade strong acids which were distilled and collected in consecutive fractions. The radioactivities of these distillates and that in the residue from the distilling flask were measured and compared with the activity shown by a second 100λ aliquot of the tracer solution measured at the same time.

A plot (Fig. 5) of the per cent. total activity distilled against per cent. of total volume collected showed that the acids may be classified into three groups: (a) those, such as HCl , HBr and HI with which technetium did not co-distill; (b) HNO_3 , aqua regia, H_2SO_4 and fuming H_2SO_4 where co-distillation was incomplete, and occurred to an appreciable extent only after more than half of the acid had distilled; (c) acids like HClO_4 where the co-distillation was quantitative, and as much as 75% of the technetium co-distilled with the first 20% of overhead condensed.²³

The addition of an oxidant to either H_2SO_4 or to H_3PO_4 appeared to be essential to effect a complete technetium recovery. However, the addition of $\text{Na}_2\text{S}_2\text{O}_8$ to H_2SO_4 without Ag^+ ion gave a less complete volatilization in the early fractions than when the silver catalyst was present. The addition of dichromate, peroxydisulfate plus silver, periodate or bromate to concentrated sulfuric acid gave almost identical volatility curves suggesting that once technetium was completely oxidized its co-distillation was governed by the temperature.

Temperature also appeared to be important in the co-distillation of tracer quantities of manganese and of rhenium. In contrast with technetium, no volatilization of radio-manganese (6.5 d Mn^{52} + 310 d Mn^{54}) could be achieved from boiling 72% perchloric acid (b.p. 203°), although it has been reported that as much as 90% may be distilled from sulfuric acid containing KIO_4 when the temperature is maintained below 150° by the addition of nitric acid.^{24,25} Co-distillation of rhenium tracer with perchloric acid showed that only about two-thirds of the total could be volatilized

(23) Small volatilization losses of technetium from 72% HClO_4 at room temperatures have been observed. Collection of the acid condensate in an ice-cooled vessel is recommended.

(24) J. D. H. Strickland and G. Spicer, *Anal. Chim. Acta*, **3**, 543 (1949).

(25) J. T. Byrne, *J. Chem. Phys.*, **19**, 504 (1951).

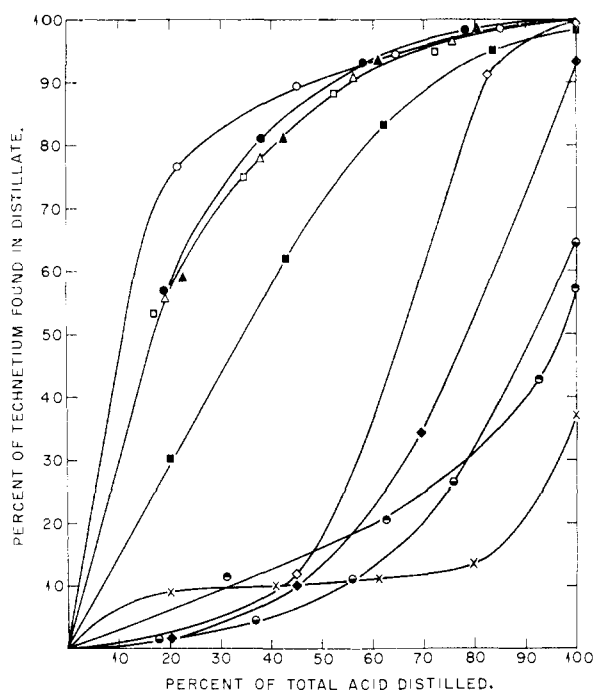


Fig. 5.—Co-distillation of technetium with various acids: O, HClO₄; ●, H₂SO₄ + KIO₄; △, H₂SO₄ + K₂Cr₂O₇; ▲, H₂SO₄ + Na₂S₂O₃ + AgNO₃; □, H₂SO₄ + KBrO₃; ■, H₂SO₄ + Na₂S₂O₈; ◇, H₃PO₄ + KMnO₄; ◆, fuming H₂SO₄; ○, H₂SO₄; ⊙, aqua regia; X, HNO₃.

and that this occurred mainly in the last stages of the distillation. In concentrated sulfuric acid, rhenium tracer was observed to co-distil before technetium, but, if K₂Cr₂O₇ was added to the acid, then the technetium appeared first in the distillate.

It is suggested that three factors may be important in determining the "wet volatility" of technetium and its congeners: (a) the oxidizing power of the acid, (b) temperature and (c) the stability of the volatile oxide. Hot, concentrated HCl, HBr and HI reduce heptavalent technetium, so that it is perhaps not surprising that no co-distillation was found with these acids. The behavior in concentrated sulfuric acid without added oxidant may be attributed to the probable presence in it of reducing impurities such as SO₂. At the temperatures at which it distills both Tc₂O₇ and Re₂O₇ show appreciable vapor pressures.²⁶ The necessity for an oxidizing condition may be inferred also from the result with concentrated nitric acid (Fig. 5) where almost 40% of the technetium co-distills even though the boiling point of the acid is only 86°. The failure of Mn₂O₇ to co-distil from boiling perchloric acid (b.p. 203°) may be connected with its thermal decomposition at this temperature, while the incomplete volatilization of Re₂O₇ may have resulted because the temperature was not sufficiently high.

Solvent Extraction.—Preliminary investigations of the solvent extraction of technetium were conducted with the view to finding another feasible separations method for this element. Extractions were attempted first using di-isobutylcarbinol containing small amounts of dissolved diphenylthiourea. If technetium had behaved analogously to Ru(III), a good extraction from 1 M H₂SO₄ solution into the ketone should have been observed. Actually, only 15% of the technetium was extracted, regardless of whether or not the diphenylthiourea was present. Rhenium gave a slightly better transfer into the organic phase: approximately 40% passed into the pure alcohol.

It has been known for some time that rhenium, after reduction by Sn(II), may be extracted into diethyl ether from 3 N HCl solutions containing KSCN. A series of experiments (Table III) using Hg(I) and Sn(II) as reductants

(26) Thermodynamic considerations show that Tc₂O₇, but not Re₂O₇, is reduced by sulfur dioxide; cf., W. T. Smith, Jr., J. W. Cobble and G. E. Boyd, THIS JOURNAL, **75**, 5773 (1953).

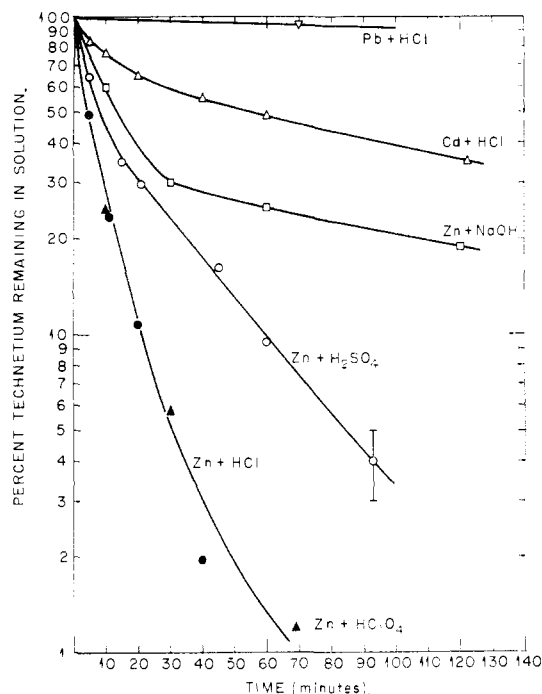


Fig. 6.—Rate of deposition of technetium on metals in acid and in alkaline aqueous solutions.

indicated that an analogous ether-extractable valence state of technetium also existed and that it was more readily formed than was that of rhenium. Interestingly, with technetium a yellow-brown coloration similar to that shown by rhenium was observed. Efficient re-extraction of the technetium from the organic phase could be accomplished by washing the ether with aqueous ammoniacal hydrogen peroxide solution.

TABLE III

EXTRACTION OF RHENIUM AND TECHNETIUM FROM 3 N HYDROCHLORIC ACID SOLUTIONS CONTAINING KSCN INTO DIETHYL ETHER (1:1 volume ratio)

Element	Fraction in ether phase, %		
	No reducing agent	Reduction with Hg(I)	Reduction with Sn(II)
Tc	5	61	97
Re	5	10	99

Reduction by Metals in Acid and Alkaline Solutions.—The apparent reduction of technetium by metallic zinc in acid solution and by stannous chloride and bismuth in alkaline solutions was mentioned by Perrier and Segré,² but no quantitative results were given. Detailed measurements, therefore, were made of the rate of deposition of microamounts of technetium on zinc, cadmium and lead in various acid solutions and in 2 N sodium hydroxide on these same metals, including iron.

One-gram quantities of amalgamated metal powder, or turnings, were shaken for varying periods with 50 ml. of aqueous normal acid solution containing a known quantity of radio-tracer. The supernatant liquid was decanted, and the metal was collected on a sintered glass funnel and washed with acetone and ether. Radioactivity assays were performed on the metal and solution phases, from which the fraction remaining in the latter was computed. Zinc alone appeared to effect a complete deposition (Fig. 6); only about 40 minutes being required in either hydrochloric or perchloric acid solutions.

Zinc metal acted to remove technetium tracer from 2 N sodium hydroxide solution also. The rate of reduction, however, was far slower than with acid solutions; even after 2 hr. nearly 20% of the technetium remained in solution.

Co-precipitation Studies.—The co-precipitation of technetium with a number of acid insoluble sulfides was first in-

vestigated by Perrier and Segré.² More recently, Jacobi²⁷ has reported that manganese sulfide formed by treating $Mn(NO_3)_2$ with an ammoniacal hydrogen sulfide solution also "carries down" this element. Quantitative measurements of the co-precipitation of technetium with CuS , PdS and Re_2S_7 formed in hydrochloric acid solutions at 95° and digested for 30 minutes (Table IV) were performed. Copper sulfide was of limited value because of its solubility in concentrated hydrochloric acid. The co-precipitation of technetium by palladium sulfide occurred through the entire range of acidity. However, adsorption effects may be important, for when palladium was precipitated at room temperature from 12 *N* hydrochloric acid little or no technetium was removed from solution. In some instances the failure of trace quantities of technetium to co-precipitate may be of practical value, as for example in the separation of technetium from fission products in the radiochemical analysis for technetium in such mixtures. It has been reported^{2,27} that neither zirconium hydroxide precipitated by ammonia nor the hydrous oxides of tantalum and niobium formed by the treatment of alkali tantalates or niobates with sulfuric

(27) E. Jacobi, *Helv. Chim. Acta*, **31**, 2118 (1948).

TABLE IV
CO-PRECIPITATION OF TECHNETIUM WITH VARIOUS ACID-INSOLUBLE SULFIDES AT 95°

HCl, <i>N</i>	Fraction of technetium co-precipitated (%) CuS	PdS	Re ₂ S ₇	PtS ₂ ^a
1	100	85	96	100
3	100	83	98	95
6	16	22	58	31
9	..	22	6.5	2
12	..	16; 1 ^b	1	2

^a Data taken from Fig. 3; ^b precipitation at room temperature, no digestion.

acid, nor the 8-hydroxyquinolate of molybdenum co-precipitates pertechnetate ion. We have observed additionally that Tc(VII) is not carried from aqueous solutions by these precipitates: ferric hydroxide, silver or lead molybdate and α -benzoin oxime molybdate.

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[CONTRIBUTION FROM THE ISTITUTO DI CHIMICA GENERALE DELL'UNIVERSITA' DI PALERMO]

Studies in Coördination Chemistry. VI. The Dielectric Polarization of Some Metal Chelates of *N*-Alkylsalicylaldimines¹

BY L. SACCONI, M. CIAMPOLINI, F. MAGGIO AND G. DEL RE

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Measurements have been made of the dielectric polarization at 25° of benzene and dioxane solutions of ten four-coördinated chelates of palladium(II), copper(II) and cobalt(II) with *N*-alkylsalicylaldimines. The small positive difference between the total polarization and the electronic polarization ($P_{2\infty} - P_E$) for palladium(II) chelates was attributed to atom polarization; these complexes, therefore, must have a *trans*-planar configuration. In the case of copper(II) chelates, the higher $P_{2\infty} - P_E$ values (50–100 cc.) can be considered as due, at least in part, to the existence of unsymmetrical (*cis* or more probably pyramidal) forms. The chelate of cobalt(II) with *N*-cyclohexylsalicylaldimine, whose magnetic moment (4.4 B.M.) agrees with a tetrahedral structure, shows a $P_{2\infty} - P_E$ value of about 500 cc. This fact corroborates our previous conclusion against a tetrahedral structure for the magnetically anomalous nickel(II) complexes with *N*-alkylsalicylaldimines.

Introduction

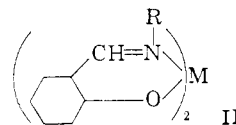
Comparatively few measurements of the dipole moments of metal complexes have been reported. One reason for this is the difficulty of explaining the large difference between the total and electronic polarizations observed for these compounds.^{2–4}

In the case of symmetrical complexes, such as the metal acetylacetonates, this difference $P_{2\infty} - P_E$ has been attributed⁵ entirely to atom polarization, even though it appears to be very large in comparison with the usual P_A values of organic compounds. In fact $P_{2\infty} - P_E$ values up to 68 cc. have been reported by MacQueen and Smith⁶ for eight-coördinated complexes which are believed to be symmetrical or found to be symmetrical as solids.

The atom polarization of a molecule is defined as that part of the total polarization which arises from changes in the geometrical structure of a molecule induced by an external field. It is obvious that its magnitude depends strictly on the various vibrational degrees of freedom of the molecule. Coop and Sutton⁵ showed that in the metal acetyl-

acetones the bending vibrations of the chelate groups, considered as rigid units, were sufficient to account for the P_A values of such complexes.

In a previous paper⁷ the dielectric polarization of bis-(*N*-alkylsalicylaldimine)-nickel(II) complexes was studied in an attempt to elucidate the behavior of these complexes, which, while diamagnetic in the solid state, become paramagnetic in solutions⁸ and melts.⁹ Furthermore, these nickel complexes have high $P_{2\infty} - P_E$ values. We felt that a similar study of analogous complexes containing other metals was needed to check our interpretation of the results and to determine the effect of the metal on the dielectric polarization. In this work, therefore, the dielectric behavior of bis-(*N*-alkylsalicylaldimine) complexes of palladium(II), copper(II) and cobalt(II), with the general formula



where R = Me, Et, *n*-Pr, *n*-Bu or *n*-Am, was investigated.

Experimental

Preparation of the Metal Complexes. Palladium(II).—A cold solution containing 1.1 g. (0.006 mole) of palladium

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(5) J. W. Smith and W. R. Angus, *Proc. Roy. Soc. (London)*, **A131**, 372 (1932); A. Finn, G. Hamps and L. E. Sutton, *J. Chem. Soc.*, 1254 (1938); I. E. Coop and L. E. Sutton, *ibid.*, 1269 (1938).

(6) J. MacQueen and J. W. Smith, *ibid.*, 1821 (1956).