Neutron Activation Cross Section of Technetium-98†

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The cross section for the reaction $Tc^{98}(n,\gamma)Tc^{99m}$ was determined by thermal neutron irradiation of a cyclotron-produced sample containing Tc^{95}, Tc^{97m}, Tc^{97g}, Tc^{98}, and Tc^{99}. The degree of selectivity and background reduction required to permit an accurate measurement of the Tc^{98} content, 2.68±0.54 disintegrations per minute, was attained by means of β-(740-kev γ) coincidence counting. At a thermal flux of 2.1×10^{12} neutrons cm^{-2} sec^{-1}, a saturation activity of 375±85 dis/min Tc^{99m} per dis/min of Tc^{98} was obtained. Using the latest value of the half-life of Tc^{98}, $(1.5\pm0.7)\times10^6$ years, one finds a cross section of 2.6±1.3 barns. Relative cross sections are also given for the production of several technetium isotopes by bombardment of molybdenum with 10.2-Mev deuterons.

INTRODUCTION

IN recent years, numerous attempts have been made to detect long-lived ($>1.5\times10^8$ yr) Tc^{98} in terrestrial materials by neutron activation analysis.[1–3] While the likelihood of occurrence of such an isotope has been greatly reduced by the discovery of 1.5×10^6-yr Tc^{98} by Katcoff[4] and Boyd *et al.*,[5] the possible existence of a second, still longer-lived, isomer of Tc^{98} is not excluded, as pointed out by Segrè[6] and Mayer.[7] It would be of interest to obtain (n,γ) cross sections for the formation of both Tc^{99m} and Tc^{99g} from 1.5×10^6-yr Tc^{98}, and from the longer-lived isomer as well, if it exists. As a first step in this direction, the cross section for the reaction

$$\underset{1.5\times10^6\text{-yr }\beta^-}{Tc^{98}(n,\gamma)Tc^{99m}}\qquad\underset{\text{6-hr I.T.}}{}$$

has been determined.

As can be seen from any nuclide chart, production of Tc^{98} in pure form is not feasible. Regardless of the choice of bombarding particle and target material (except for separated isotopes of far greater purity than presently obtainable), any Tc^{98} formed will always be accompanied by greater or lesser amounts of 60-day Tc^{95m}, 90-day Tc^{97m}, 10^5-yr Tc^{97g}, and 2.1×10^5-yr Tc^{99g}. In our case, the only available materials were two sources, *A* and *B*, prepared by bombardment of natural molybdenum with 10.2-Mev deuterons in the Washington University cyclotron. Source *B* was prepared a year later than source *A*.

In order to determine the activation cross section, the number of Tc^{98} atoms in the source had to be known. From the known Tc^{95} and Tc^{97m} content of source *A*, and an estimated formation cross section of Tc^{98}, it appeared that source *A* should contain several times 10^{12} atoms of Tc^{98}, corresponding to a few times 10^{-10} grams. This amount was hardly sufficient for mass spectrometric analysis; moreover, the sample would be destroyed in the determination. For this reason, direct counting appeared to be the only feasible method. Here, the principal difficulty consisted in identifying and accurately measuring a few disintegrations per minute of Tc^{98} in the presence of about 184 dis/min of Tc^{95m} and 12 400 dis/min of Tc^{97m}, as well as smaller amounts of Tc^{97g} and Tc^{99g}. Clearly, some selective counting technique was required.

Katcoff[4] states that Tc^{98} decays by emission of a 0.3-Mev β^- particle, coincident with 2 gamma rays of 0.74- and 0.65-Mev energy, respectively. It should then be possible to detect Tc^{98} by counting the 0.74-Mev γ ray, in which case the 0.81- and 1.02-Mev γ rays of Tc^{95} would interfere, or by counting the 0.3-Mev β^- in coincidence with the 0.74-Mev γ ray. Here again, interference by Tc^{95} could be expected, mostly due to γ-γ and x-γ coincidences from its complex spectrum. However, the exact amount of interference could be determined from source *B*, which had been prepared 12 months later, and therefore contained a greater relative amount of Tc^{95}. The disintegration rate of Tc^{95} in source *B*, about 23 000 dis/min, was high enough so that all corrections for Tc^{95} could be determined to a high degree of accuracy, once the relative Tc^{95} content of sources *A* and *B* had been found.

The advantage of the coincidence counting method was not only increased selectivity, but also appreciable background reduction. The coincidence counting rate of Tc^{98} was about 6 times lower than the gamma singles counting rate; at the same time, interference from Tc^{95m} dropped by a factor of 1.40 and the background, by a factor of 60, from 193±0.04, counts/min to 0.0307 ±0.0033 counts/min.

Once the Tc^{98} content of the source had been ascertained, it should be a relatively simple matter to determine the activation cross section by irradiating the sample in a known neutron flux, and measuring the

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[1] E. Alperovitch, Ph.D. dissertation, Columbia University, January, 1954 (unpublished); U. S. Atomic Energy Commission Report NYO-6139 (unpublished). E. Alperovitch and J. M. Miller, Nature **176**, 299 (1955). Anders, Sen Sarma, and Kato, J. Chem. Phys. **24**, 622 (1956).
[2] W. Herr, Z. Naturforsch. **9a**, 907 (1954).
[3] G. E. Boyd and Q. V. Larson, J. Phys. Chem. **60**, 707 (1956).
[4] S. Katcoff, Phys. Rev. **99**, 1618 (1955).
[5] Boyd, Sites, Larson, and Baldock, Phys. Rev. **99**, 1030 (1955).
[6] E. Segrè (private communication, January, 1956).
[7] M. G. Mayer (private communication, January-February, 1956).

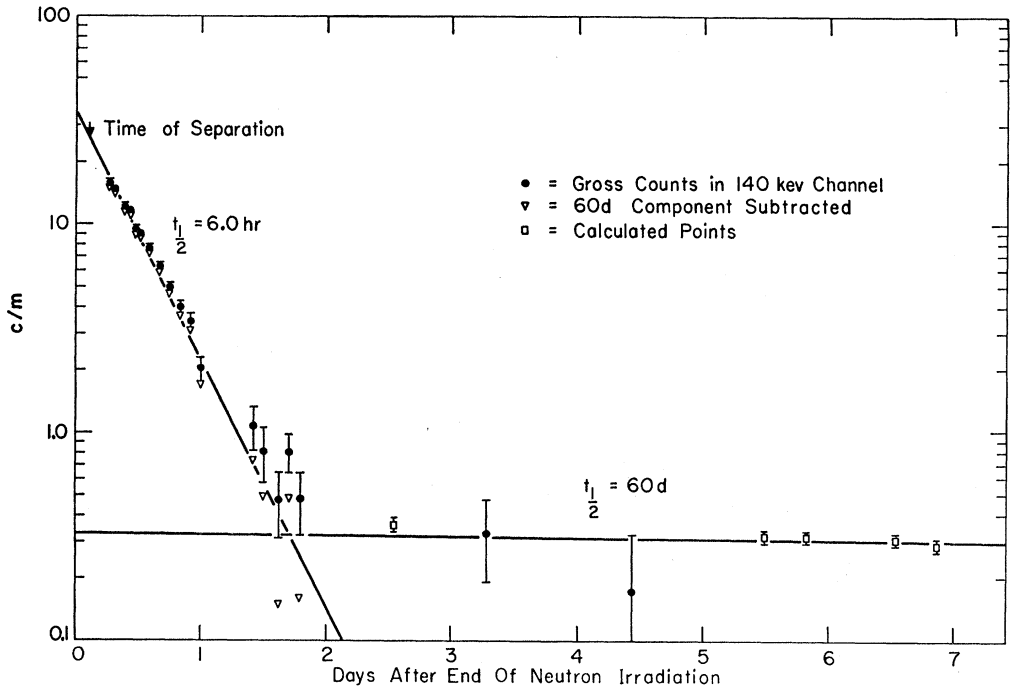

FIG. 1. Sample *A*. Decay curve of technetium fraction after neutron irradiation. After the decay of 6-hr Tc^{99m}, several calculated points at 140 kev were obtained by multiplying the 201-kev counting rate of the sample by the ratio of the 140-kev/201-kev counting rates of a strong Tc^{95} source.

amount of 6-hr Tc^{99m} formed. It must be remembered, however, that Tc^{99m} is also produced by 4 interfering reactions:

$$Mo^{98}(n,\gamma)Mo^{99} \xrightarrow[66\text{ hr}]{\beta^-} Tc^{99m}, \quad (1)$$

$$U^{235}(n,f)Mo^{99} \xrightarrow[66\text{ hr}]{\beta^-} Tc^{99m}, \quad (2)$$

$$Tc^{99}(n,n')Tc^{99m}, \quad (3)$$

$$Ru^{99}(n,p)Tc^{99m}. \quad (4)$$

For this reason, precautions had to be taken to preclude interference from these sources.

EXPERIMENTAL

A. Counters

The β-γ coincidence spectrometer consisted of an Anton Type 1001T Geiger-Mueller tube with a 2-mg/cm² mica window; a 3.8×5.1 cm thallium activated sodium iodide crystal mounted on a Dumont 6292 photomultiplier tube; cathode followers for both tubes; an RIDL Model 115B single-channel pulse height analyzer with self-contained linear amplifier and coincidence circuit; and the usual complement of scalers, high voltage supplies, and recorders. In order to ensure optimum geometry, the counters were mounted only 1.5 mm apart. They were surrounded by a 10-cm thick Pb shield, lined with a graded x-ray absorber consisting of 2 mm of Sn and 0.25 mm of Cu.

The coincidence resolving time of the entire circuit, 11.46±0.061 μsec, was measured by counting accidental coincidences between Tc^{99g}, a pure β-emitter, and Be^7, a pure γ emitter. The counting efficiency[8] of the Geiger counter for the 0.3-Mev β-particles of Tc^{98} and Tc^{99} was determined by means of a calibrated Co^{60} source, since the β particles of Co^{60} are of nearly the same energy. The same isotope was used to evaluate self-absorption and self-scattering corrections, whenever needed.

The counting efficiency of the sodium iodide crystal was determined at several different energies, and values at 0.740 and 0.201 Mev obtained by interpolation. The resolution of the crystal for the Ba^{137} γ-ray was 7.7%.

After neutron irradiation, the sample was counted on a gamma-ray spectrometer of very similar design, but with a smaller crystal, 3.8×1.3 cm. The counting efficiency of the crystal for the 140-kev γ ray of Tc^{99m}, 0.244, was determined by means of a Mo^{99}+Tc^{99m} source, calibrated by 4π β counting.

B. Neutron Irradiation

The samples, aliquots of sources *A* and *B*, were sealed in quartz ampoules and irradiated in the isotope hole No. 1 and vertical thimble No. 24 of the CP-5 reactor at the Argonne National Laboratory. The irradiation times ranged from 14 to 17 hours. The procedure and experimental data quoted below refer specifically to source *A*, but apply with only minor changes to samples *B*-1 and *B*-2.

[8] In the present paper, this term denotes the quotient: number of particles (or γ rays) detected/number of particles (or γ rays) emitted. No attempt has been made to break it down into geometry factor, detector efficiency, back-scattering correction, etc. In the case of γ rays, only the photopeak was counted.

TABLE I. Beta 740-kev gamma coincidence counting data for source A.

Time (min)	Total counts	Counts/min	Background	Coincidences due to Tc^{95}	Accidental coincidences	Tc^{98} net coincidence counting rate
975	82	0.0842	0.0307	0.0164	0.0005	0.0366±0.0093
5321	348	0.0654	0.0307	0.0155	0.0005	0.0187±0.0035
3840	237	0.0617	0.0307	0.0144	0.0005	0.0161±0.0040
					Weighted mean:	0.0196±0.0041 counts/min=2.66±0.57 dis/min

TABLE II. 740-kev gamma singles counting data for source A.

Time (min)	Counts	Counts/min	Background	Correction for Tc^{95}	Net counting rate of Tc^{98}
152	643	4.23	1.93	2.28	0.02±0.17
342	1506	4.41	1.93	2.26	0.22±0.11
475	1925	4.05	1.93	2.01	0.11±0.09
				Weighted mean:	0.13±0.08 counts/min=2.8±1.7 dis/min

In order to preclude interference by Mo, U, and Tc^{99g}, the same precautions were taken as in our mineral experiments. The Tc^{99g} content was determined in the presence of the 90 kev e^- of Tc^{97m} by means of an aluminum absorption curve. The effective (n,n') cross section under the conditions of this irradiation was measured by irradiating 0.4 μg of Tc^{99} simultaneously with the Tc^{98} sample. The correction turned out to be quite negligible, 0.04%.

The molybdenum contamination was measured by adding 2 mg of inactive molybdenum to the sample *after* irradiation, under conditions where the exchange between active and carrier molybdenum was known to be complete, and separating it into a technetium and molybdenum fraction (Figs. 1 and 2). The 140-kev γ ray of Tc^{99m} was counted in both samples, and, after correcting for chemical yields, the amount of Tc^{99m} grown from Mo^{99} up to the time of separation calculated from Rubinson's modification of Bateman's equations.[9] The yield of Mo was determined spectrophotometrically, and the yield of Tc, by counting the 201 kev γ ray of Tc^{95}. The correction for Tc^{99m} grown from Mo^{99} amounted to 3.8%.

The radiochemical purity of the samples was proven by the absence of extraneous activities in both the β- and γ-decay curves.

No attempt was made to check for ruthenium contamination, since its chemical behavior made its presence most unlikely.

The neutron fluxes and cadmium ratios were measured by the reactor staff by irradiating gold foils in the reactor and comparing the resulting activity with that produced by a calibrated neutron source. The fluxes quoted are believed to be accurate within 5%.

RESULTS AND DISCUSSION

A. Technetium-98 Content of Source *A*

The coincidence counting results are summarized in Table I.

[9] W. Rubinson, J. Chem. Phys. **17**, 542 (1949).

It is seen that a small but definite net counting rate attributable to Tc^{98} remains after correcting the gross β-(740-kev γ) coincidence counting rate for background, x-γ and γ-γ coincidences due to Tc^{95}, and accidental coincidences between the conversion electrons of Tc^{97m} and γ rays of Tc^{95} and Tc^{98}. From the mean net coincidence rate $N_{\beta\gamma}$ of 0.0196±0.0041 counts/min, one can calculate the absolute disintegration rate R, if c_β and c_γ, the β- and γ-counting efficiencies, are known. For a sample with a mass thickness equal to that of source A, $c_\beta=0.159\pm0.004$, while c_γ for a 740-kev γ ray is 0.0463

TABLE III. Relative cross sections for the production of technetium isotopes by bombardment of natural molybdenum with 10.2-Mev deuterons.

Isotope	Tc^{95m}	Tc^{95g}	Tc^{96m+g}	Tc^{97m}	Tc^{98}
Relative cross section	1.00	13.3	3.3	2.4	12

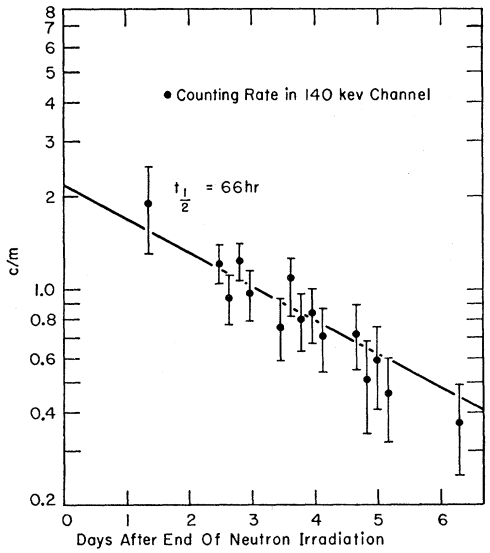

FIG. 2. Sample A. Decay curve of molybdenum fraction after neutron irradiation.

TABLE IV. Neutron activation cross sections of Tc^{98}, Tc^{99}, and Mo^{98}.

Sample	Location in reactor	Thermal flux	Tc^{98} (n,γ) barns[a]	Tc^{99} (n,n') millibarns	Au-Cd ratio	Mo^{98} (n,γ) barns
A	Isotope hole No. 1	2.1×10^{12}	2.6 ± 1.3	0.0091 ± 0.0018	620	0.21 ± 0.03
B-1	Vertical thimble 24*D*	2.5×10^{13}	3.2 ± 1.6	$2.74\ \pm0.14$	6.6	0.36 ± 0.05
B-2	Vertical thimble 24*E*	2.6×10^{13}	3.4 ± 1.7	$3.07\ \pm0.15$	7.2	0.35 ± 0.05

[a] The specific activity, in dis/min of Tc^{99m} per dis/min of Tc^{95}, was known to better than 10%. Again, the over-all error was chiefly due to the uncertainty in both the half-life of Tc^{98} and the Tc^{98} content of the sources.

±0.0020. We thus find

$$R=N_{\beta\gamma}/c_\beta c_\gamma=2.66\pm0.57 \text{ dis/min}.$$

Because of the type of circuitry used, the gamma singles counting rate in the 740-kev channel, N_γ, had to be determined independently, rather than concurrently with the coincidence counting rate, $N_{\beta\gamma}$. We may, therefore, calculate a second value for R, 2.8 ± 1.7 dis/min, from the mean value of N_γ given in Table II, and c_γ. In view of the large probable errors, the close agreement is somewhat fortuitous.

From the weighted mean of the above disintegration rates, 2.68 ± 0.54 dis/min, and the half-life of Tc^{98}, 1.5×10^6 yr$\pm0.7\times10^6$ yr,[10] one finds $(3.0\pm1.5)\times10^{12}$ for the number of Tc^{98} atoms in source *A*.

From this number, we can calculate a relative cross section for the production of Tc^{98} from molybdenum, and compare it with the cross sections for several other technetium isotopes. It has been assumed that each technetium nuclide of mass *A* is produced by a (d,n) reaction on a molybdenum nuclide of mass *A*-1. The results are summarized in Table III.

B. Irradiation Results

An aliquot of source *A* was irradiated for 14 hours in the isotope hole No. 1 of the CP-5 reactor, at a flux of $2.1\times10^{12}n$ cm^{-2} sec^{-1}. After irradiation, the sample was separated into a technetium and a molybdenum fraction, as described above. After applying all necessary corrections, a saturation activity of Tc^{99m} of 174 dis/min of 140-kev gamma rays was obtained for a sample containing 19.2% of source *A*. Correcting this disintegration rate for an e/γ ratio of 0.11 of the 140-kev γ ray of Tc^{99m}, and using previously quoted figures for the flux and the Tc^{98} content of source *A*, we obtain a cross section of 2.6 ± 1.3 barns for the reaction:

$$Tc^{98}(n,\gamma)Tc^{99m}.$$

Since the large probable error arises mainly from the uncertainty in half-life, $\pm0.7\times10^6$ yr,[10] the saturation specific activity of 375 ± 85 dis/min Tc^{99m} per dis/min of Tc^{98} at a neutron flux of 2.1×10^{12} is also given, in order to permit a recalculation of the cross section when a more accurate value for the half-life becomes available.

In two additional experiments, aliquots of source *B* were irradiated at higher neutron fluxes in vertical thimble No. 24, and the cross section was calculated as above. Here it was necessary to infer the Tc^{98} content from the Tc^{95} counting rate, under the assumption that the formation cross sections of the two nuclides were the same in both cyclotron irradiations. Subject to the validity of this assumption, we can compare the results of the three experiments in Table IV.

The agreement is fairly satisfactory. However, another point is worth noting. It had been suggested by the author,[11] in order to explain irreproducible results in the activation analysis of minerals for Tc^{98}, that the cross section of Tc^{98} might have a resonance in the epithermal region. In this case, the effective cross section would depend rather sensitively on the neutron spectrum.

An approximate measure of the epithermal flux is given by the gold-cadmium ratios in column 6. In addition, the effective inelastic scattering cross section of Tc^{99g} (column 5) serves as an indicator of the fast component of the spectrum, the threshold of the reaction $Tc^{99g}(n,n')Tc^{99m}$ being $\gtrsim0.14$ Mev. Both of these indicators show a large difference between the neutron spectrum in the isotope hole and the vertical thimbles. This difference causes a noticeable change in the activation cross section of Mo^{98} (column 7), presumably due to the existence of an epithermal resonance. However, the change in the cross section of Tc^{98} (column 4) is certainly too small to explain the observed discrepancies, so that the previous suggestion must now be withdrawn.

It must be pointed out in conclusion that our cross section was computed on the assumption that there exists no long-lived state of Tc^{98} other than 1.5×10^6-yr Tc^{98}. Should there be a second isomer, it certainly was present in our source and contributed to the neutron-induced Tc^{99m} activity.

[10] G. D. O'Kelley and Q. V. Larson, Southwide Chemistry Conference, December, 1956 (unpublished).

[11] E. Anders, Progress Report for the U. S. Atomic Energy Commission, Contract AT(11-1)-382, November 30 1956.