The Isolation of Technetium by Coprecipitation or Anion Exchange

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1. Coprecipitation of Technetium with Molybdate. — Technetium-99 having a long half-life is usually separated from fission products of uranium-235 after a long irradiation and cooling time. But technetium-99m is easily prepared as a decay product of molybdenum-99 from neutron irradiated molybdenum. Articles[1-3] on the coprecipitation of technetium mainly refer to that with sulfide, perrhenate and perchlorate. In this paper, the coprecipitation behavior in connection with the separation of technetium from molybdenum is reported.

Experimental. — Technetium-99m is not a β emitter but a γ emitter, whereas molybdenum-99 is a β and γ emitter. Accordingly the γ-ray spectrum peak of technetium-99m (0.140 MeV.) is measured with 256 channel pulse height analyzer, whereas molybdenum-99 is simply determined by measurement of β-ray activity with G-M counter.

Fifty milligrams of ammonium molybdate is irradiated in a J. R. R.-1 Reactor for 2 hr. at a flux of 10^{11} neutrons/cm^2/sec. Since the half-life of molybdenum-99 is 67 hr. and that of technetium-99m is 6.04 hr., radioactive equilibrium is reached after 23.08 hr. The irradiated sample is dissolved in 10 ml. of water after a day.

Two milliliters each of various precipitants is added to 1 ml. portion of this sample solution. A 5% solution of lead nitrate, calcium chloride, barium chloride, silver nitrate or uranyl nitrate is used as the precipitant. When calcium chloride is used, 1 ml. of 3 M aqueous ammonia is required for the complete precipitation of calcium molybdate. The precipitate formed is separated

TABLE I-1. COPRECIPITATION RATIO OF TECHNETIUM-99 m WITH SOME MOLYBDATES

Form of precipitate	Precipitation ratio of Mo-99 %	Precipitation ratio of Tc-99m %
$PbMoO_4$	99.2	99.6
	96.0	99.6
	86.4	87.5
$CaMoO_4$	94.4	23.1
	93.3	12.3
	96.5	20.1
	97.7	33.7
$BaMoO_4$	96.3	10.9
	94.7	41.4
	75.1	39.6
Ag_2MoO_4	85.5	51.6
	95.9	67.8
	96.7	41.8
UO_2MoO_4	85.0	35.2

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[1] J. B. Gerlit; "International Conference on the Peaceful Uses of Atomic Energy", Vol. 7, United Nations Publication, New York (1955), p. 145.

[2] G. W. Parker, J. Reed and J. W. Ruch, AECD-2043.

[3] N. Matsuura, M. Kojima and A. Iguchi, *Japan Analyst (Bunseki Kagaku)*, 7, 792 (1958).

from the supernatant solution by the aid of a centrifuge, a filter tube or an usual filtering funnel. The β and γ-ray activities of precipitates and supernatant solutions are measured by comparing them with the activities of the sample solution to which no precipitant was added. The separation ratio is calculated from those data and is shown in Table I-1.

Results. — A 99.6% portion of technetium-99m is coprecipitated with lead molybdate. About 70% of technetium-99m remains in the solution after calcium molybdate is precipitated, but a few per cent of molybdenum also remains by single precipitation. Seventy per cent of technetium-99m is not precipitated with barium molybdate or uranyl molybdate. J. A. Swartout[4] used silver molybdate in order to isolate technetium from molybdenum, but in the present study 50~60% of technetium is coprecipitated with silver molybdate.

The results mentioned above, are applied in two ways. One is an easy preparation of technetium-99m solution from irradiated calcium molybdate, and the other is an isolation of technetium-99m and molybdenum-99 from fission products by coprecipitation with lead molybdate.

(1) Fifty milligrams of calcium molybdate irradiated in J. R. R.-1 Reactor for 2 hr. is washed on a Toyo 5B filter paper with 10 ml. of water or 1% ammonium hydroxide and the β and γ activities of washings are measured. The results are shown in Table I-2.

The absorption curve of β-ray shows that calcium-45 coexists in the washings. This solution is passed through a cation-exchange column and almost all of the β contaminations are removed by this treatment.

TABLE I-2. SEPARATION OF TECHNETIUM-99m FROM IRRADIATED $CaMoO_4$

Washing	γ Activity of Tc-99m cpm/ml.	β Activity of impurities cpm/ml.	β Activity after resin treatment cpm/ml.
H_2O	129000	6240	691
1% NH_4OH	74565	12250	—

(2) Twenty milligrams of uranyl nitrate is irradiated in J. R. R.-1 for 2 hr. Neptunium-239 is separated by nitrate form anion exchanger[5]. Then the solution containing uranium and fission products is neutralized with ammonium hydroxide and ammonium biuranate formed is removed by filtering. A few milligrams of ammonium molybdate and lead nitrate are added to this solution. Lead moybdate is separated and washed with water. This precipitate shows a γ-ray spectrum of technetium-99m free from other fission products. (Fig. 1-1)

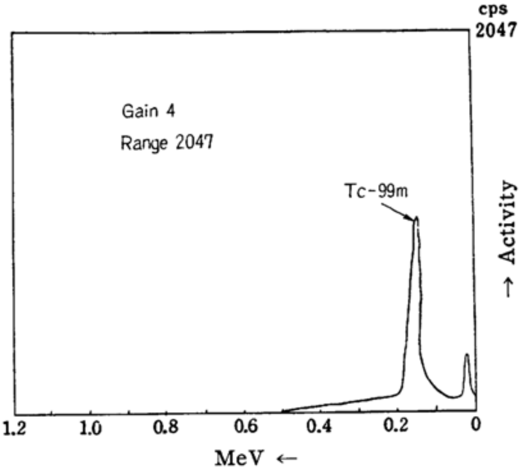

Fig. 1. γ-Ray spectrum of $PbMoO_4$ precipitation.

2. Isolation of Technetium from Fission Products by Anion Exchanger. — Several methods[1,2,6,7] were reported on the separation of technetium-99m from irradiated uranium. These were mainly based on the coprecipitation with sulfide or the solvent extraction. Hall and Johns[8] reported an anion-exchange separation of molybdenum and technetium. According to their results, molybdenum is eluted from a perchlorate form anion exchanger with 10% sodium hydroxide solution, and the technetium is then washed out with 2.0 M ammonium thiocyanate solution. This is a good separation method but thiocyanate solution is unfavorable for further treatment. In another report[9], the dependence of distribution coefficient of technetium on the nitric acid and hydrochloric acid concentrations was measured, and it is known that technetium forms a chloride complex anion within the 0.1~12 N hydrochloric acid concentration range and that it is strongly absorbed at lower nitric acid concentrations, but eluted easily with nitric acid of higher acidity. In the

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[4] J. A. Swartout, Nat. Nucl. Energy Series, "The Fission Products", Book 2, McGraw-Hill Book Co., Inc., London (1951), Paper 97.

[5] F. Ichikawa, This Bulletin, **31**, 778 (1958).

[6] D. C. Lincoln and W. H. Sullivan, Nat. Nucl. Energy Series, "The Fission Products", Book 2, McGraw-Hill Book Co., Inc., London (1951), Paper 99.

[7] R. P. Schuman, ibid., Paper 100.

[8] N. F. Hall and D. H. Johns, *J. Am. Chem. Soc.*, **75**, 5787 (1953).

[9] E. H. Huffman, R. L. Oswalt and L. A. Williams, *J. Inorg. Nucl. Chem.*, **3**, 49 (1956).

present paper, the separation of technetium from irradiated uranium by anion exchangers is studied, following the papers mentioned above.

Experimental.—Fifty milligrams of ammonium molybdate is irradiated as mentioned in section 1. The sample is dissolved into 1 or 2 ml. of water and poured on the top of hydroxide form anion exchanger Dowex 1 column (100~200 mesh, 1 cm.×5 cm.). The column is washed with 100 ml. of 10% sodium hydroxide and then technetium is eluted with nitric, hydrochloric or sulfuric acid of various concentrations. Results are shown in Fig. 2-1. From these data, it is shown that technetium is not eluted with 10% sodium hydroxide or 0.7 N nitric acid, but easily eluted with 7 N nitric acid. Then these behaviors are applied to the following experiment.

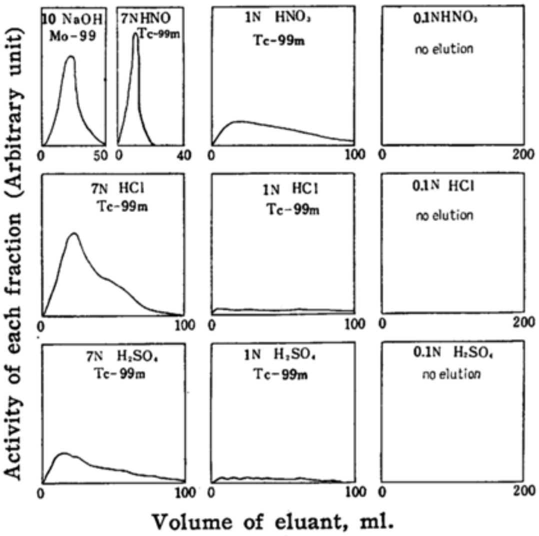

Fig. 2-1. Elution curves of Tc-99m with HNO_3, HCl and H_2SO_4 after elution of Mo-99.

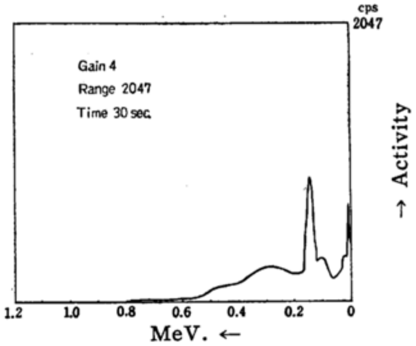

Fig. 2-2. γ-Ray spectrum of total fission products after removal of Np-239.

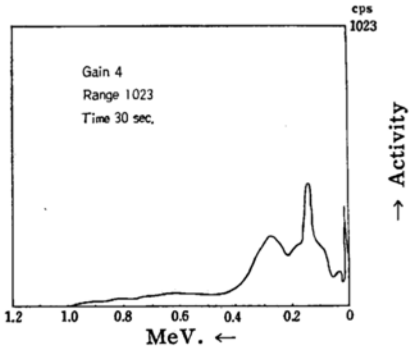

Fig. 2-3. γ-Ray spectrum of 10% NaOH fraction.

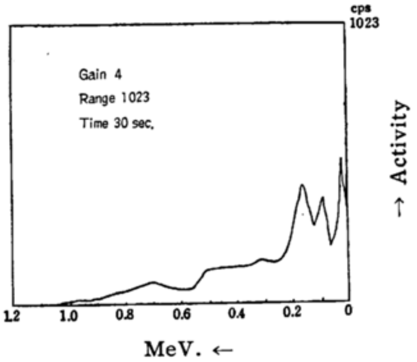

Fig. 2-4. γ-Ray spectrum of 0.7 N HNO_3

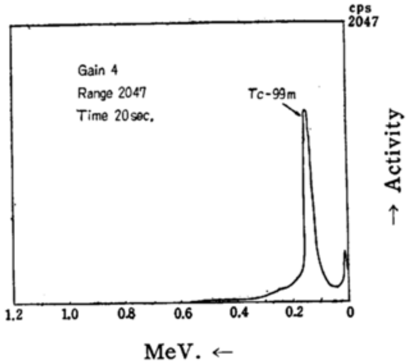

Fig. 2-5. γ-Ray spectrum of 7.5 N HNO_3 fraction.

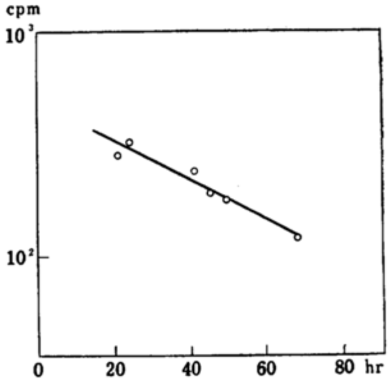

Fig. 2-6. β-Ray decay curve of 7.5 N HNO_3 fraction.

TABLE II. RECOVERY OF TECHNETIUM-99m FROM FISSION PRODUCTS

Exp. No.	Fraction	Total volume of fraction	Sample volume for γ spectrometry	Range of γ spectrometer	Time for measurement	Peak height of Tc-99m	Recovery ratio of Tc-99m
		ml.	ml.	cps	sec.		%
1*	Σ F. p.	50	2	1000	—	27.8	100
	7 N HNO_3	20	2	300	—	62.5	27
				Counts per channel			
2	Σ F. P.	50	2	2047	30	32.3	100
	10% NaOH	70	5	1023	30	26.1	**
	0.7 N HNO_3	50	5	1023	30	0	0
	7 N HNO_3	20	5	2047	20	59.8	46.3

* Data of Expt. No. 1 are measured by single channel pulse height analyzer.

** Tc-99m found in NaOH fraction may be a decay product of Mo-99.

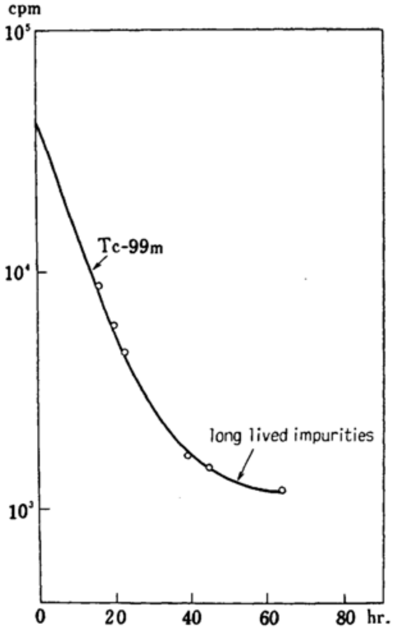

Fig. 2-7. γ-Ray decay curve of 7.5 N HNO_3 fraction.

Twenty milligrams of irradiated uranyl nitrate is used as a starting material. Neptunium-239 is removed by a nitrate form anion exchanger[5]. Thus, about 50 ml. of 7.5 N nitric acid solution of fission products is obtained. This solution is dried up and redissolved in 1 ml. of water and poured onto the hydroxide form anion exchanger. The column is washed with 150 ml. of 10% sodium hydroxide, with 200 ml. of 0.7 N nitric acid and finally with 20 ml. of 7.5 N nitric acid. γ-ray spectra of each fraction are measured by a 256 channel pulse height analyzer. They are shown in Figs. 2-2~5. As Fig. 2-5 shows, the pure spectrum of technetium-99m is found in 7.5 N nitric acid fraction. Decay of β and γ activities are shown in Figs. 2-6 and -7. After 3 days technetium 99m is disintegrated away almost completely, leaving impurities of long half-life.

Results.—Technetium is not eluted with 10% sodium hydroxide and eluted with 3~7 N nitric acid. But with other kinds of acid or dilute nitric acid, the elution of technetium is very slow or unpredictable. This is probably due to the complex formation. Some species of fission products may behave as an anion, and some others may form insoluble hydroxides in these chemical circumstances. These will be caught on a hydroxide form anion exchanger. Species which may form insoluble hydroxide will be eluted with 0.7 N nitric acid. Molybdenum-99 is washed out with sodium hydroxide and other anionic species will be removed with sodium hydroxide and 0.7 N nitric acid.

Recovery of technetium is calculated and shown in Table II. About 40~45% of technetium-99m is recovered in 7.5 N nitric acid solution. Purity in γ-ray activity is about 95% at the separation time.

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