UCRL 2667

UNCLASSIFIED

UNIVERSITY OF CALIFORNIA

Radiation Laboratory

TWO-WEEK LOAN COPY

This is a Library Circulating Copy which may be borrowed for two weeks. For a personal retention copy, call Tech. Info. Division, Ext. 5545

BERKELEY, CALIFORNIA

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

UCRL-2667
Unclassified
Chemistry

UNIVERSITY OF CALIFORNIA

Radiation Laboratory

Contract No. W-7405- eng - 48

THE RADIATIONS OF ^{90}Mo AND ^{90}Nb AND THE NEW ISOMER ^{90m}Nb

Hirdaya B. Mathur and Earl K. Hyde

August 5, 1954

Berkeley, California

The Radiations of Mo^{90} and Nb^{90} and the New Isomer Nb^{90m}†

Hirdaya B. Mathur* and Earl K. Hyde
Radiation Laboratory and Department of Chemistry
University of California, Berkeley, California

August 5, 1954

ABSTRACT

Mo^{90} produced by $Nb^{93}(p,4n)$ reaction in the 184-inch cyclotron was found to decay by emission of positrons of maximum energy 1.15 ± 0.1 Mev. The gamma spectrum shows two prominent gamma rays of 120 and 250 kev in energy. The K/L conversion ratios of the two gamma rays are 3.6 ± 0.2 and 5.2 ± 0.2, respectively. Gamma-gamma coincidence studies indicate that both the gamma rays in Mo^{90} are delayed. The 120 kev transition is found to have a half-life of 24 ± 3 seconds, indicating thereby the presence of a new isomer, Nb^{90m}. The delay in 250 kev state is somewhere between 5×10^{-6} to 0.1 second.

The 14.6-hour Nb^{90} formed in the decay of Mo^{90} emits positrons of maximum energy 1.7 ± 0.1 Mev. There are three gamma rays of 140 kev, 1.14 and 2.2 Mev in the gamma spectrum of Nb^{90}. Coincidence studies show that the 140 kev and 1.14 Mev gamma rays are in coincidence with one another and with the annihilation radiation while the 2.2 Mev gamma ray is delayed.

---

†This research was performed under the auspices of the United States Atomic Energy Commission.

*On leave of absence, Department of Chemistry, University of Delhi, Delhi, India.

The Radiations of Mo^{90} and Nb^{90} and the New Isomer Nb^{90m}†

Hirdaya B. Mathur* and Earl K. Hyde
Radiation Laboratory and Department of Chemistry
University of California, Berkeley, California

August 5, 1954

I. INTRODUCTION

This paper deals with a study of the radiations of Mo^{90} and of the niobium isomers Nb^{90} and Nb^{90m} formed in its decay. Mo^{90} has been studied previously by Diamond[1] who prepared it by proton bombardment of niobium in the Harvard cyclotron. Diamond reported Mo^{90} to be a positron emitter with a half-life of 5.7 ± 0.2 hours. The mass assignment was made by identification of 14.6-hour Nb^{90} formed in its decay. He reported positrons of maximum energy 1.4 Mev and gamma rays with energies of 1.0, 0.24-0.26, and 0.1-0.13 Mev.

At Diamond's suggestion we extended the study of Mo^{90} and also carried out a detailed study of the gamma rays of 14.6-hour Nb^{90} previously reported by Boyd.[2] During the course of our work, we found positive evidence for a previously unreported nuclear isomer and incomplete evidence for two others.

---

†This research was performed under the auspices of the United States Atomic Energy Commission.

*On leave of absence, Department of Chemistry, University of Delhi, Delhi, India.

II. MOLYBDENUM-90

In our experiments with Mo^{90} produced by the bombardment of Nb^{93} with 80 Mev protons in the 184-inch cyclotron, we found Mo^{90} to have positrons of maximum energy 1.15 ± 0.1 Mev. Figure 1 shows the positron endpoint as determined by an anthracene crystal spectrometer.

Figure 2 shows the gamma spectrum of Mo^{90} as determined by a sodium iodide crystal-photomultiplier assembly coupled to a 50-channel differential pulse analyzer. There are two gamma rays of 120 and 250 kev energy in addition to the annihilation radiation. The small peak at 65 kev is due to the platinum x-rays produced by the platinum backing on which the sample was mounted. Using the values given by Kahn and Lyon[3] for the counting efficiency as a function of energy of a sodium iodide crystal 1.5 inches in diameter and 1-inch thick we assumed a counting efficiency of 100 percent for the 120 kev gamma rays and 60 percent for 250 kev gamma rays, and found the two gamma rays to be in almost equal abundance. We were not able to detect the presence of 1 Mev gamma rays in a freshly prepared sample of Mo^{90}, though a gamma ray of 1.14 Mev did appear later as Mo^{90} decayed to Nb^{90}.

Conversion electrons of the 120 and 250 kev gamma rays were also measured by a magnetic double-focusing spectrometer. Figure 3 shows the spectrum thus obtained. The K/L conversion ratios of 120 and 250 kev gamma rays were determined to be 3.6 ± 0.2 and 5.2 ± 0.2, respectively. We are indebted to Dr. T. O. Passell for help in running the beta ray spectrometer.

With the help of Dr. F. Asaro and Mr. F. S. Stephens we carried out gamma-gamma coincidence studies on Mo^{90} and obtained the following results. Putting 510 kev annihilation radiation at the gate, we did not observe any coincidences either with 120 or 250 kev gamma rays. Similarly, by using 120 kev gamma rays, no coincidences were observed with either 250 kev gamma rays or the annihilation radiation. Likewise we got no coincidences with 120 kev gamma rays or the annihilation radiation when 250 kev gamma rays were put at the gate. The nonexistence of coincidences between 510 kev annihilation radiation and the two gamma rays of 120 and 250 kev, coupled with the fact that there are very few x-rays in Mo^{90}, indicates that both the gamma rays are delayed.

III. THE 24-SECOND ISOMER, Nb^{90m}

The gamma-gamma coincidence studies suggested the existence of an isomeric state of Nb^{90}. The ground state of Nb^{90} is the 14.6-hour activity previously studied by Boyd,[2,4] Kundu and Pool,[5] and Jacobson and Overstreet.[6] We were successful in isolating a 24 ± 3-second activity formed in the decay of Mo^{90}. A carrier-free sample of Mo^{90} of high specific activity was placed on shelf one of our scintillation counter for a 1-minute growth period. The crystal was not grounded and carried a potential of 500 volts negative with respect to the sample. The sample was then quickly withdrawn and the recoil daughter atoms of Nb^{90m} and Nb^{90} collected from the molybdenum source during the growth period were counted. The gamma spectrum was determined by a 50-channel differential pulse analyzer. Figure 4 shows the gamma spectrum of the

recoil activity immediately after the growth period. The gamma spectrum of Mo^{90} is also shown in the same figure for comparison. The readings of the register at the peak of the 120 kev gamma ray were taken every 0.2 minute for a 2-minute period without disturbing the count switch, and from the analysis of the data a half-life of 24 ± 3 seconds was obtained for the recoil activity (see Fig. 5).

The fact that this 24-second activity is the product of the decay of Mo^{90} was further confirmed by plotting the yield of the recoil activity in a 1-minute growth period as a function of time at which the milking was done. A half-life of 5 hours was obtained for the molybdenum parent as shown in Fig. 6, confirming thereby the genetic relationship.

The 24-second isomer was proved to be a niobium activity in the following manner. From the work of Huffman, et al.,[7] Kraus and Moore[8] and Hicks, Stevenson and Gilbert[9] it was known that niobium and molybdenum form complexes in strong hydrochloric acid which are strongly adsorbed on anion exchange resins. On reinvestigation we found that a mixture of molybdenum and niobium in 6 M HCl is adsorbed by Dowex-1, a strong base quaternary amine polymer. Niobium can be eluted with 5 M HCl but molybdenum is strongly held at this hydrochloric acid concentration. Mo^{90} activity in 6 M HCl solution was run through a 4 cm x 0.5 cm column of Dowex-1 previously equilibrated with 12 M HCl. The molybdenum on the column was washed free of niobium activity with 5 M HCl and after a growth period of 1 minute, niobium formed by decay during this period was quickly stripped from the column by 5 M HCl,

collected in a 2 ml lusteroid cone and studied in a scintillation counter for the determination of the gamma spectrum. The spectrum showed the presence of 120 kev gamma rays decaying with a half-life of 24 ± 3 seconds, thereby further establishing that the 24-second activity was a niobium activity.

From the lifetime-energy relationships of Goldhaber and Sunyar[10] this 24-second activity must be either E3 or M3.

IV. SEARCH FOR 250-KEV ISOMERIC STATE

From our gamma-gamma coincidence studies, it was concluded that both 120 and 250 kev gamma rays were delayed. Since the 250 kev gamma ray did not occur in the gamma spectrum of the 24-second isomer, it was evident that it did not follow the 120 kev gamma transition.

It may be that the main positron decay of Mo^{90} goes to a level in Nb^{90} which deactivates by a 250-120 kev cascade. The abundance ratios suggest this since after correction for crystal counting efficiency the number of 250 and 120 kev photons is nearly equal and their sum is equal to the total number of annihilation photons.

Chemical separation of niobium from Mo^{90} showed only the presence of 120 kev gamma rays of 24-second half-life and therefore the half-life of the 250 kev state is not more than 24 seconds. By performing the chemical separation rapidly and from the recoil studies, we estimated the half-life of the 250 kev transition to be less than a few seconds. Since we were not able to observe any coincidences of 250 kev gamma rays

with either 120 kev gamma rays or the annihilation radiation, the half-life of the 250 kev gamma rays should be greater than 5 microseconds, the resolving time of our coincidence circuit. Estimates of the half-life of the 250 kev transition from the experimental lifetime-energy relationships of Goldhaber and Sunyar,[10] excluded the possibility of its being an M4 or E4 transition because the estimated lifetime of ~30 hours is contradicted by our experimental results. The estimated lifetime for an E3 or M3 transition is approximately 2 seconds.

Having established the delay in 250 kev transition to be somewhere between 5 microseconds and 1 second, we made use of a novel device to narrow down the limit to be less than 0.1 second. A carrier-free sample of Mo^{90} mounted on a platinum plate was supported on a stand with its face at a distance of about 0.5 cm from a moving tape of aluminum or paper. A potential difference of 900 volts was applied between the tape and the sample, the negative terminal of the battery being connected to the tape. Those few recoiling atoms of niobium formed in the decay of Mo^{90} which escaped from the source were collected on this tape and were transported through a scintillation counter. The gamma spectrum was studied by means of the 50-channel differential pulse analyzer. The time taken to transport the recoil atoms of niobium on the tape to the scintillation counter could be varied by changing the speed of the driving motor. With the slowest speed it took nearly 5 seconds for the recoils to reach the scintillation counter which was at a distance of 1 foot from the sample, while at the fastest speed of the motor, the time taken was about 0.1 second. When the tape was moved at the slowest speed for

1 minute, we obtained a peak at 120 kev in the gamma spectrum but there was no indication of any gamma ray of 250 kev energy. By increasing the speed the number of total counts under the 120 kev peak was reduced. It is therefore possible to discriminate in favor of a shorter half-life. We got no indication of 250 kev radiation even by increasing the speed to the maximum and it was concluded that the delay in the 250 kev transition should be less than 0.1 second and more than 5 microseconds.

The overall efficiency for collection of recoils by this method is quite small (<0.01 percent) but by using very intense carrier-free sources we had no difficulty in collecting a few hundred counts per minute of the 24-second isomer and hence should have had no trouble in collecting enough of the 250 kev state for identification if its half-life were greater than 0.1 second.*

V. THE RADIATIONS OF 14.6-HOUR Nb^{90}

Boyd[2] reported Nb^{90} to be a positron emitter with a maximum energy of approximately 1.7 Mev while Diamond,[1] and Kundu and Pool[5] have reported the positrons to have a maximum energy of 1.2 Mev. Boyd and Ketelle[4] reported three gamma rays of energies 140 kev, and 1.14 and 2.23 Mev in Nb^{90}.

In our determination of the positron endpoint of Nb^{90} by means of an anthracene crystal spectrometer coupled to a 50-channel differential pulse analyzer, we obtained a value of 1.7 ± 0.1 Mev for the positron endpoint as shown in Fig. 7. The gamma spectrum of Nb^{90} is shown in

---

*Some more recent work by Mathur, Larsh, and Hyde indicate that the half-life is about 20 milliseconds.

Fig. 8. There are three gamma rays of energies 140 kev, 1.14 and 2.20 Mev in addition to the annihilation radiation. Taking into account the counting efficiency of the sodium iodide crystal for the three energies, the ratios of their abundances are 1/2.8/1.7.

Coincidence measurements made on the gamma rays of Nb^{90} showed that the 140 kev and 1.14 Mev gamma rays are in coincidence with each other and with the annihilation radiation. From the quantitative data the indication is that the 140 kev transition lies above the 1.14 Mev gamma ray. This is in keeping with the expectations from the systematics of the first excited state of even-even nuclei since in Zr^{90} one would expect the first excited state to be greater than 1 Mev.[11] The 2.20 Mev gamma ray showed no coincidences with 140 kev or 1.14 Mev gamma rays or the annihilation radiation. Since Nb^{90} has very few x-rays, this result suggested the possibility of a delayed transition involving the 2.20 Mev level in Zr^{90}. From a Nb^{90} sample zirconium was precipitated as barium fluozirconate and did not show any gamma ray of 2.20 Mev in its gamma spectrum. By performing this separation rapidly and counting the resulting barium fluozirconate precipitate in a scintillation counter, we can fix the delay to be less than 1 minute.

We hope by further study to establish conclusively whether the 2.20 Mev gamma ray is delayed since there are but a very few well-established examples of delayed transitions in even-even nuclei. Almost the only cases are Hf^{180m}, Pb^{202m}, Pb^{204m}, and Pb^{206m}.

VI. EXPERIMENTAL PART

Cyclotron Bombardments.--During the course of this work, Mo^{90} was produced by $Nb^{93}(p,4n)Mo^{90}$ reaction by bombarding Nb^{93} (100 percent abundance) in the form of 5-mil foil. Protons of 80 Mev energy from the 184-inch cyclotron were used for bombardment.

In addition to the reaction mentioned previously, Mo^{90} was also prepared in a novel way by the bombardment of bromine with accelerated nitrogen ions. This was done in the 60-inch cyclotron using a beam of hextuplicately charged nitrogen ions.[12] The nitrogen ions have a continuous spread of energy with a maximum of 140 Mev. Sodium bromide wrapped in a thin tantalum foil was bombarded to carry out the following reactions:

$$_{7}N^{14} + {}_{35}Br^{81} \longrightarrow {}_{42}Mo^{91} + 4\,{}_{0}n^{1}$$

$$_{7}N^{14} + {}_{35}Br^{81} \longrightarrow {}_{42}Mo^{90} + 5\,{}_{0}n^{1} .$$

At the end of the bombardment the activity in the molybdenum fraction was about 9/10 Mo^{91} and 1/10 Mo^{90}.

In some cases Nb^{90} was produced by the bombardment of 5 mil zirconium foils with 20 Mev protons in the Berkeley linear accelerator. In addition, Nb^{90} was also produced by bombarding silver foils with 340 Mev protons in the 184-inch cyclotron.

Radiochemical Procedures.--For the isolation of molybdenum, the niobium foils were dissolved in a mixture of concentrated HNO_3 + HF and

the solution was evaporated to dryness. The residue was then taken up in 6 M HCl, centrifuged to remove Nb_2O_5 and molybdenum was extracted from the supernatant with an equal volume of diethyl ether. The extraction was repeated thrice. Ether from the three extractions was evaporated over 5 ml of distilled water which was then saturated with hydrogen chloride gas and the resulting solution was run through a 4 cm x 0.5 cm column of Dowex-1 anion exchange resin previously equilibrated with concentrated hydrochloric acid. The resin column was then washed free of niobium with 5 M HCl following which the molybdenum activity was eluted from the column with 1 M HCl.

In the nitrogen ion bombardment, sodium bromide was dissolved in 6 M HCl and molybdenum was extracted with diethyl ether. Thereafter, the chemical procedure was the same as that described in the preceding paragraph.

For the extraction of niobium from zirconium targets, the foils were dissolved in hydrofluoric acid and all the zirconium was precipitated from the solution as barium fluozirconate by adding Ba^{++}. The resulting solution was saturated with hydrochloric acid and niobium was extracted into di-isopropyl ketone.

The silver targets were dissolved in 10 M HNO_3 and niobium coprecipitated on MnO_2 by adding a few drops of a dilute solution of potassium permanganate and heating the solution in a water bath. The precipitate of MnO_2 was dissolved in concentrated hydrochloric acid and niobium was extracted into di-isopropyl ketone. Part of the manganese was extracted by the ketone.

Alternatively, to the solution of silver in 10 M HNO_3, a few drops of $La(NO_3)_2$ was added and the solution was saturated with ammonia gas. After centrifuging, the precipitate of $La(OH)_3$ was removed, washed with distilled water and then saturated with hydrogen chloride gas. The resulting solution was run through a column of the anion-exchange resin Dowex-1, the column was washed with concentrated hydrochloric acid a few times and finally niobium was desorbed from the column with 5 M HCl.

Beta-Ray Spectrometer.--The spectrometer used was a double-focusing type of 25-cm radium. It is after the design of Svartholm and Siegbahn,[13] and by Shull and Dennison.[14] A detailed description of this instrument has been given by O'Kelley.[15]

Scintillation Spectrometer.--The gamma ray scintillation spectrometer used in this work was assembled by A. Ghiorso and A. E. Larsh of this laboratory. The photomultiplier was a Dumont 6292 tube coupled to a sodium iodide (thallium activated) crystal, 1.5-inch in diameter and 1-inch thick. The output from the photomultiplier after being amplified in a preamplifier was fed into a linear amplifier. The final pulse was then analyzed by a 50-channel differential pulse height analyzer designed by Ghiorso and Larsh. Details of this equipment will be given in a forthcoming publication of Ghiorso and Larsh.

For gamma-gamma coincidence studies, a second sodium iodide-photomultiplier assembly in combination with a single-channel pulse analyzer was incorporated into the above instrument.

VII. ACKNOWLEDGMENTS

The authors wish to express their thanks to James T. Vale and Lloyd Houser and members of the 184-inch cyclotron crew for the numerous 184-inch cyclotron bombardments. Similarly, acknowledgment is made to G. B. Rossi, W. B. Jones, A. Ghiorso, and members of the 60-inch cyclotron crew for the nitrogen ion bombardments. The linear accelerator bombardments were carried out through the courtesy of W. W. Olson, R. D. Watt and the accelerator crew.

We also wish to acknowledge the indispensible assistance of Dr. T. O. Passell for beta-ray spectroscopy and to Dr. F. Asaro and Mr. F. S. Stephens for coincidence studies. The moving tape apparatus for the collection of recoil activity was designed and assembled by Mr. Herman P. Robinson and Mr. Donald G. Paxson.

VIII. REFERENCES

1. R. M. Diamond, Phys. Rev. 89, 1149 (1953).

2. G. E. Boyd, Oak Ridge National Laboratory Report ORNL-229, February 1949 (unpublished) as reported by Hollander, Perlman, and Seaborg, Table of Isotopes, Revs. Modern Phys. 25, 469 (1953).

3. B. Kahn and W. S. Lyon, Nucleonics 11, 61 (November 1953).

4. G. E. Boyd and B. H. Ketelle, unpublished data (1951) as reported by Hollander, Perlman, and Seaborg in Revs. Modern Phys. 25, 469 (1953).

5. D. N. Kundu and M. L. Pool, Phys. Rev. 76, 183 (1949).

6. L. Jacobson and R. Overstreet, Radiochemical Series: The Fission Products (McGraw Hill Book Company, Inc., New York, 1951), National Nuclear Energy Series, Plutonium Project Record, Volume 9, Div. IV., Paper No. 91.

7. Huffman, Iddings, and Lilly, J. Am. Chem. Soc. 73, 4474 (1951).

8. K. A. Kraus and G. E. Moore, J. Am. Chem. Soc. 73, 9 (1951).

9. Hicks, Stevenson, and Gilbert, private communication.

10. M. Goldhaber and A. W. Sunyar, Phys. Rev. 83, 906 (1951).

11. G. Scharff-Goldhaber, Phys. Rev. 90, 587 (1953).

12. Rossi, Jones, Hollander, and Hamilton, Phys. Rev. 93, 256 (1954).

13. N. Svartholm and K. Siegbahn, Arkiv. Mat. Astron. Fysik 33A, No. 21 (1946); see also Hedgran, Siegbahn and Svartholm, Proc. Phys. Soc. (London) 63A (1950).

14. F. Shull and D. Dennison, Phys. Rev. 71, 681 (1947); 72, 256 (1947).

15. G. D. O'Kelley, Ph.D. Thesis, University of California Radiation Laboratory Unpublished Report UCRL-1243 (March 15, 1951).

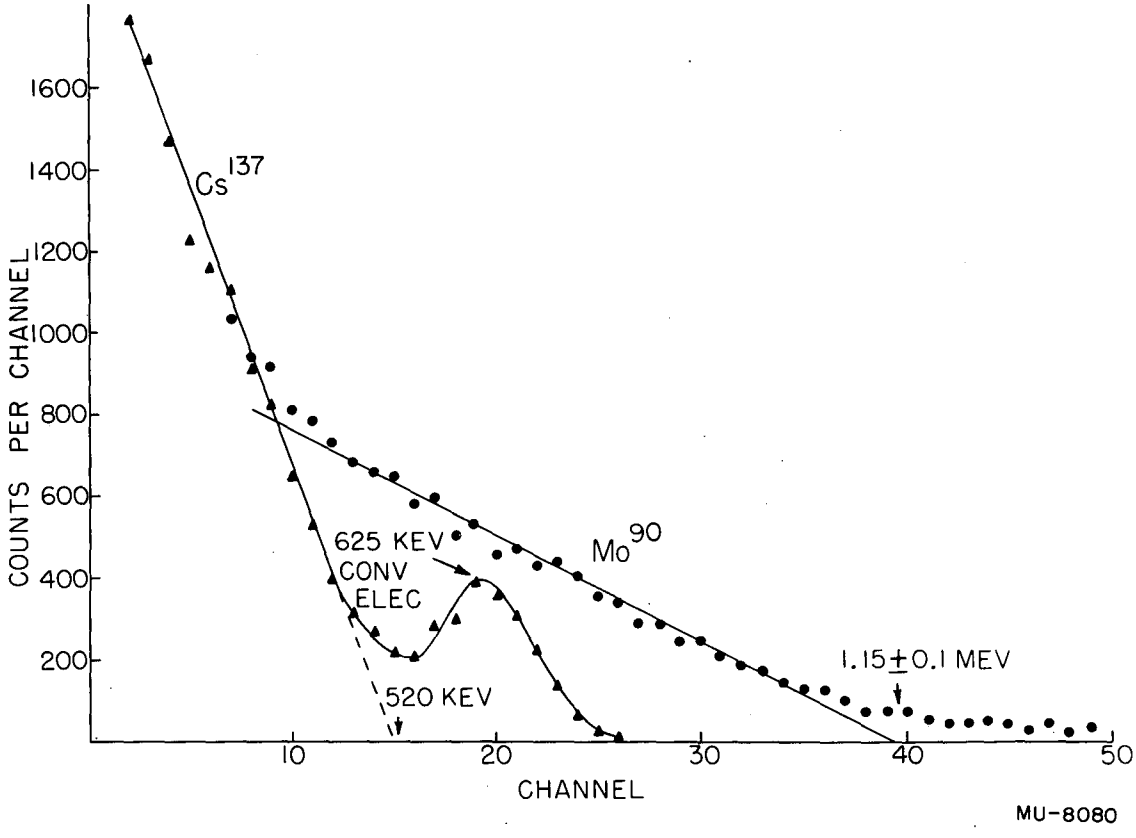

Fig. 1 Positron endpoint of Mo^{90} as determined on an anthracene crystal spectrometer. Cs^{137} was used as a standard. Data taken on a 50-channel pulse height analyzer.

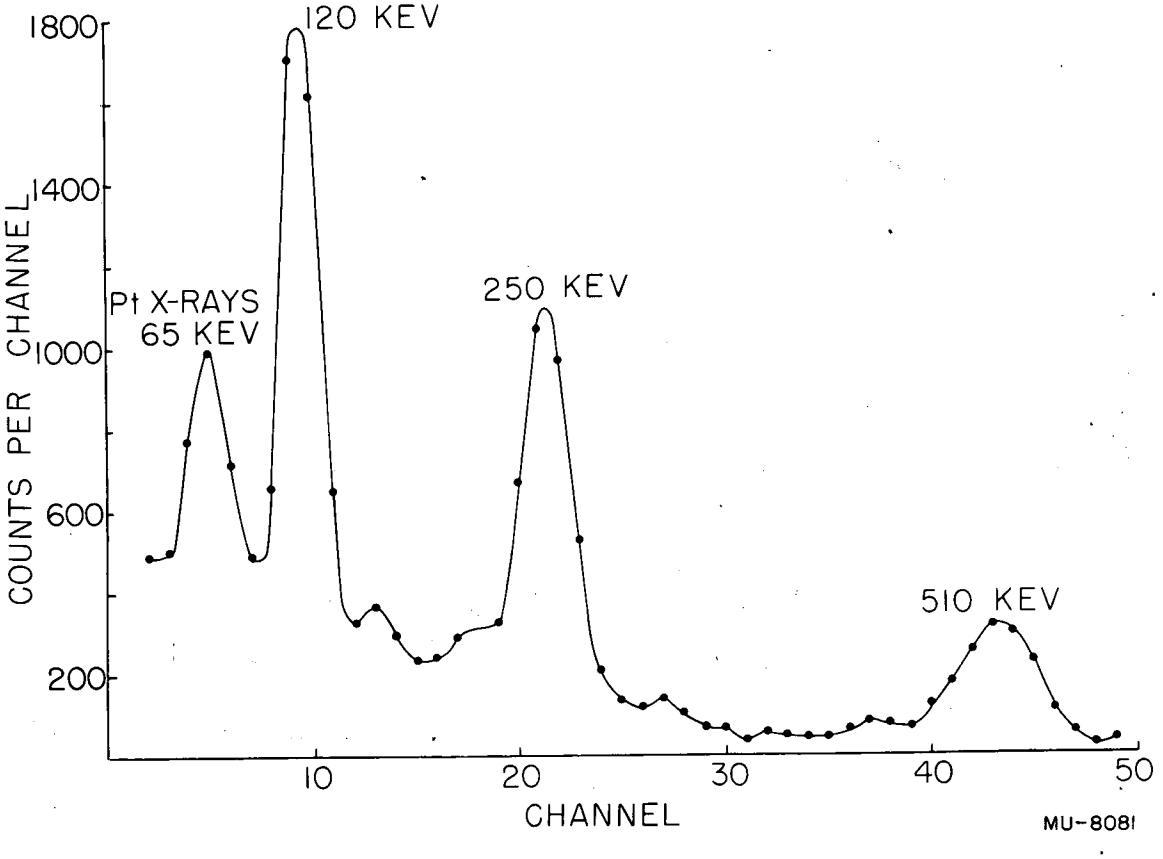

Fig. 2 Gamma spectrum of Mo^{90} as determined with a sodium iodide crystal-photomultiplier combination coupled to a 50-channel pulse height analyzer.

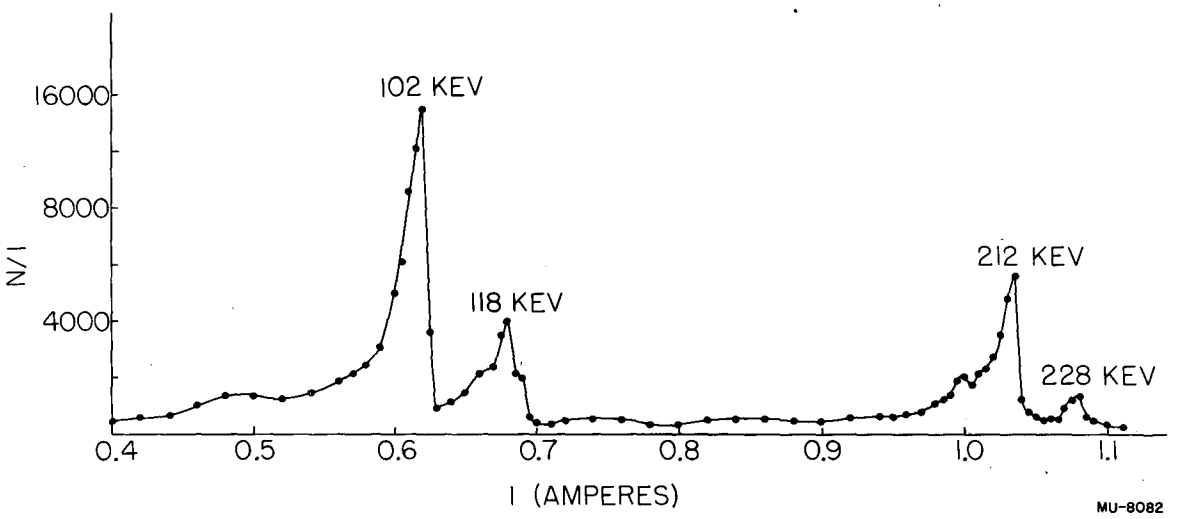

Fig. 3 Conversion electrons of the 120 and 250 kev gamma rays of Mo^{90}.

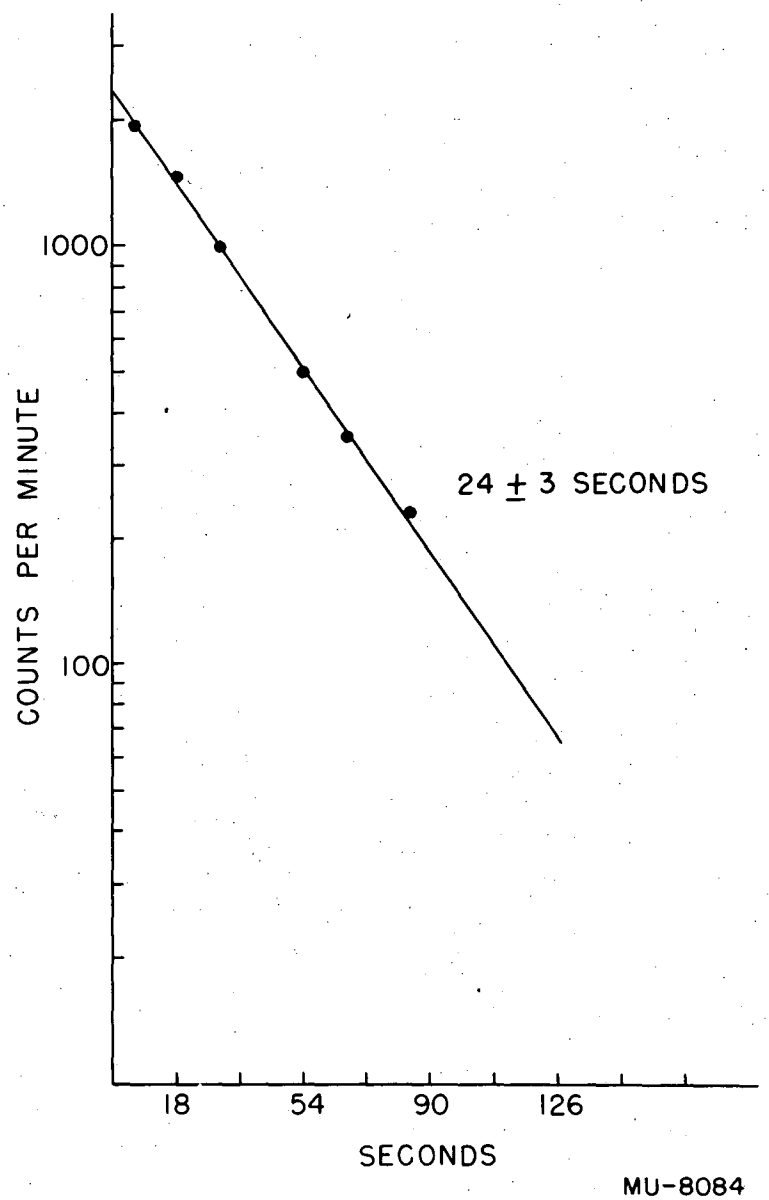

Fig. 4 Gamma spectrum of 24-second Nb^{90m} as determined with a sodium iodide crystal-photomultiplier combination coupled to a 50-channel pulse height analyzer. The gamma spectrum of Mo^{90} is shown for comparison.

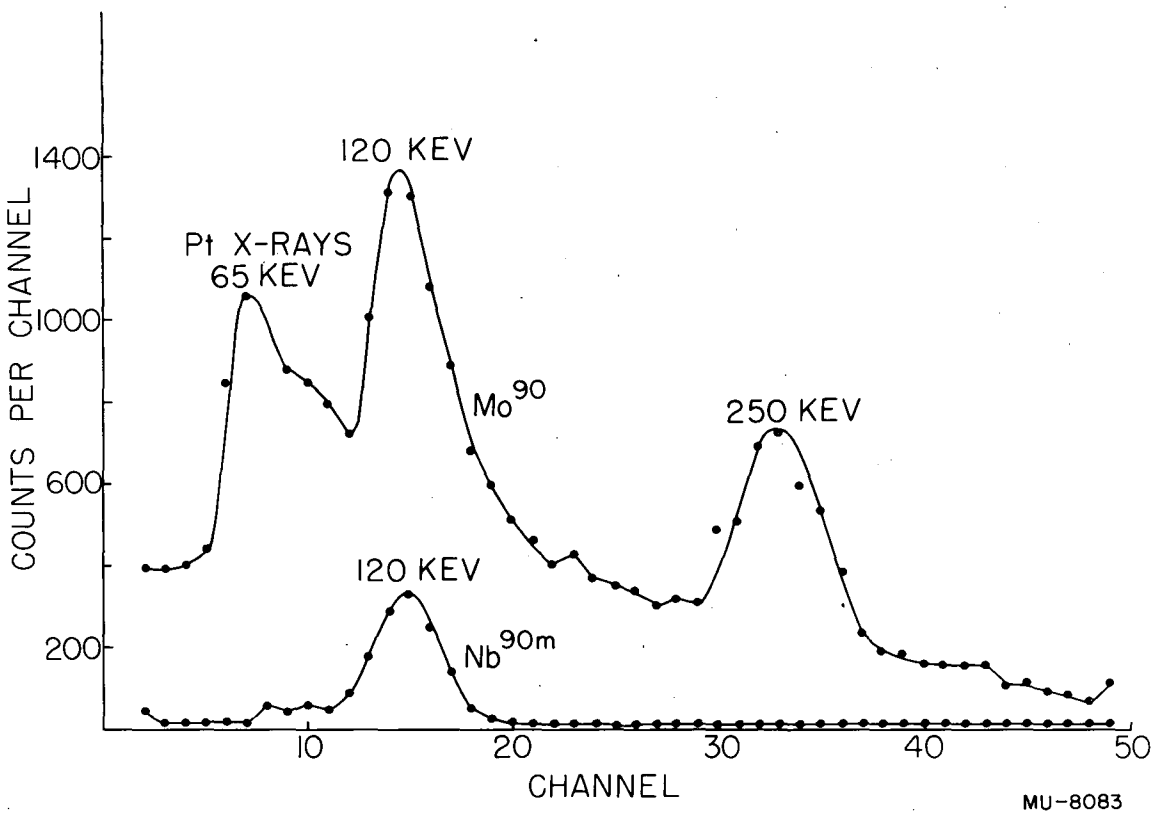

Fig. 5 Decay of gamma ray of 120 kev in Nb^{90m}.

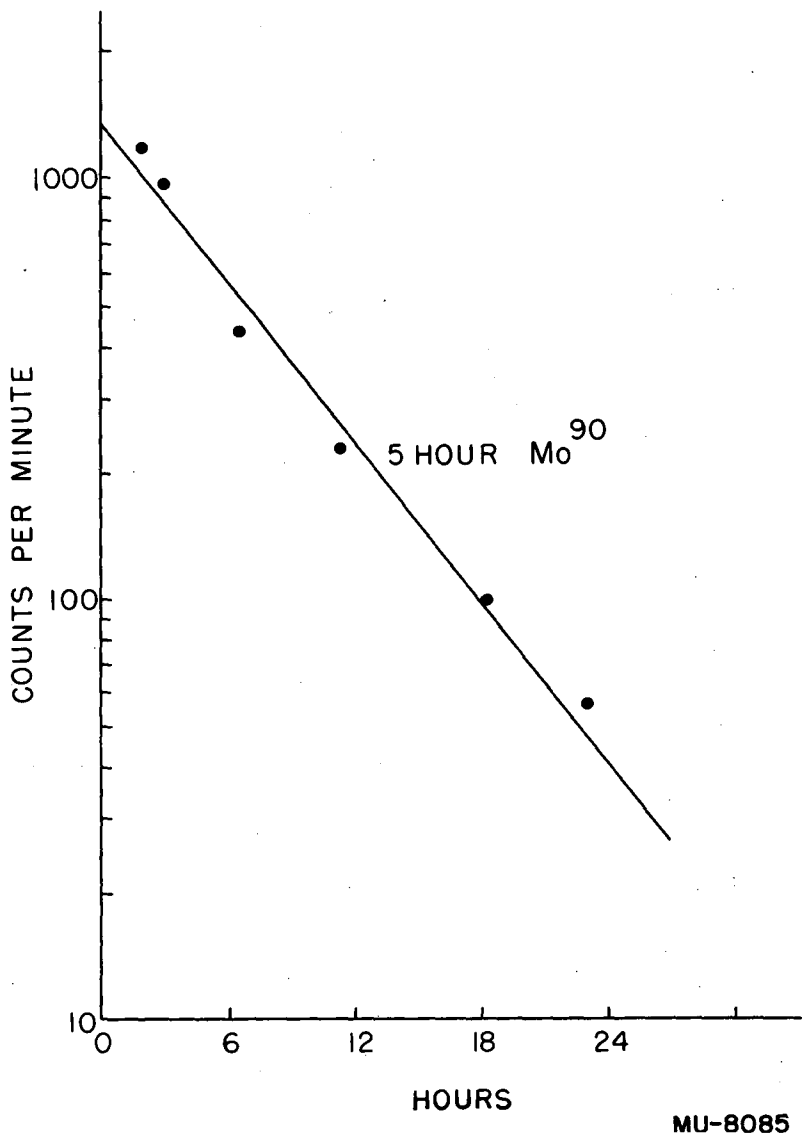

Fig. 6. Yield of 24-second Nb^{90m} from timed milkings of Mo^{90} parent sample.

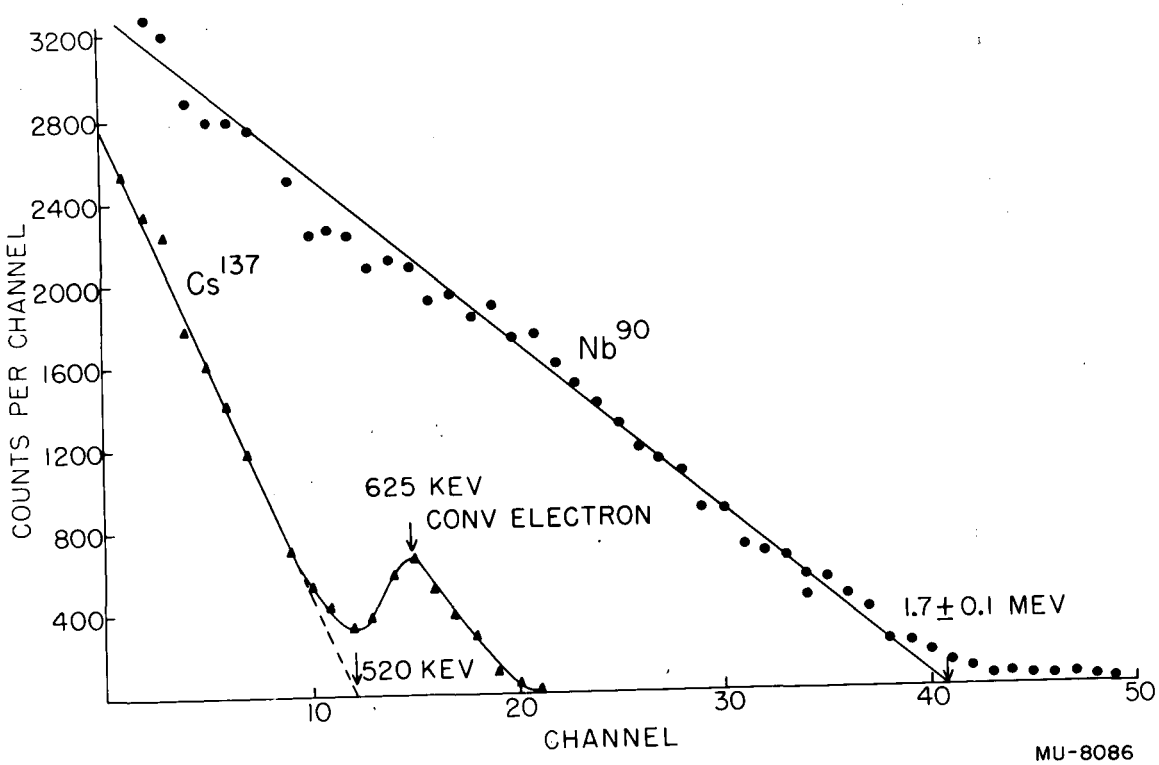

Fig. 7 Positron endpoint of Nb^{90} as determined on an anthracene crystal spectrometer. Cs^{137} was used as a standard. Data taken on a 50-channel pulse height analyzer.

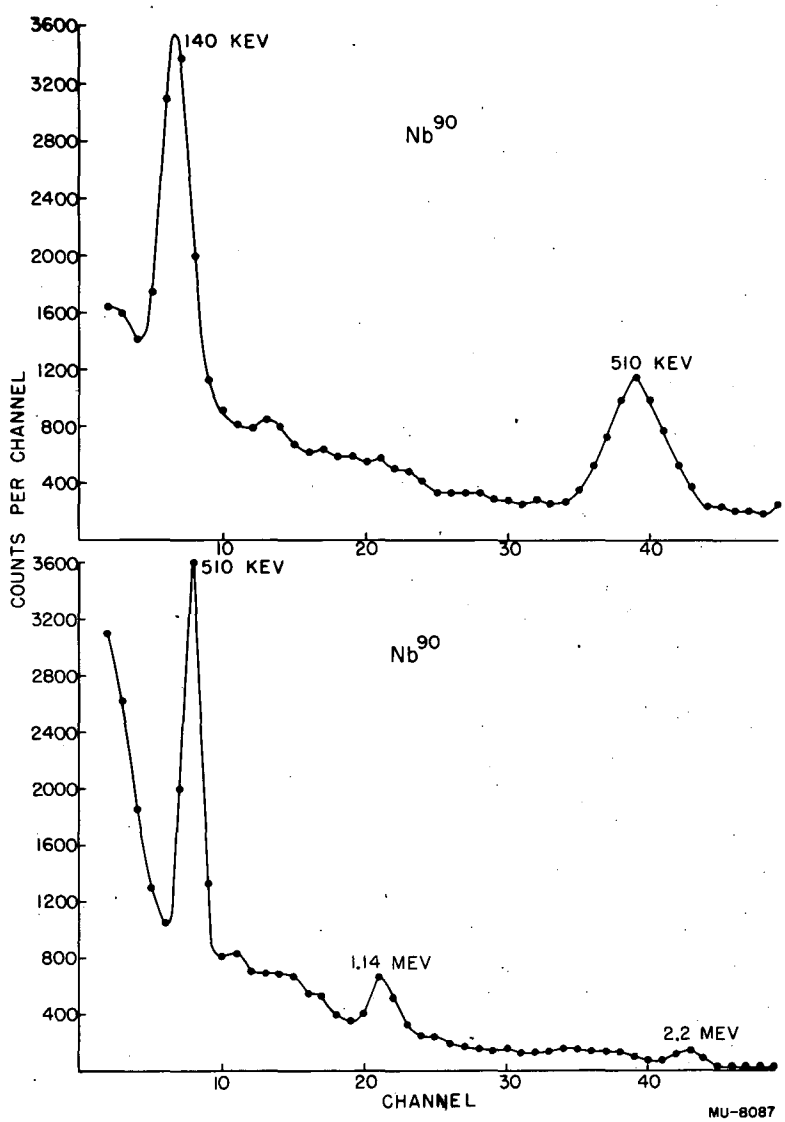

Fig. 8 Gamma spectrum of 14.6-hour Nb^{90} as determined with a sodium iodide crystal-photomultiplier combination coupled to a 50-channel pulse height analyzer.