

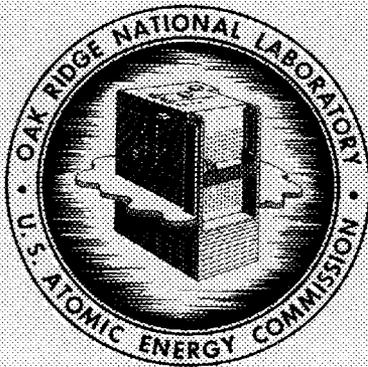


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EVIDENCE OF THE ABSENCE OF LONG-LIVED  
ISOTOPES OF PROMETHIUM FROM FISSION OF  
URANIUM, AND THE PURIFICATION OF  
PROMETHIUM FOR THE ESTABLISHMENT OF  
A PRIMARY SPECTROGRAPHIC STANDARD

P. B. Orr  
R. S. Pressly  
E. J. Spitzer



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## TABLE OF CONTENTS

Abstract . . . . .	1
Introduction . . . . .	1
Equipment and Procedure . . . . .	2
Column Loading . . . . .	4
Elution and Analysis . . . . .	4
Analyses to Detect Promethium and Accompanying Elements . . . . .	8
Emission Spectrography . . . . .	8
Mass Spectrography . . . . .	10
Radioactivity Analyses . . . . .	13
Activation Analyses. . . . .	17
References . . . . .	18



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ABSTRACT

A sample of high-purity promethium, produced by uranium fission, was separated by ion exchange on Dowex 50 W-X4 hydrogen-form resin, with diethylenetriaminepentaacetic acid and citric acid as eluants. Within the limits of detection, no isotope of promethium with a half-life of greater than 2.6 yrs was found in the product which had decayed through two half-lives of  $^{147}\text{Pm}$ . The promethium contained only traces of yttrium, samarium, and neodymium and was of sufficient purity to establish spectra for a promethium standard for use at ORNL.

INTRODUCTION

Much work over many years has been done searching for element 61 in nature. In 1939 Hopkins<sup>1</sup> reported the concentration by fractional crystallization of the double nitrate salt of magnesium and material thought to be element 61, which occurred in the rare earth fraction between samarium and neodymium. He also reported the concentration of element 61 (which he called illinium) between terbium and gadolinium when they were crystallized as the bromates. However, these observations were never substantiated. Since the discovery of 2.67-year  $^{147}\text{Pm}$  (promethium, element 61) by Marinsky and Glendenin in 1947<sup>2</sup> as a fission product of uranium, there has been speculation as to the possible occurrence of a long-lived or even a stable isotope of promethium in fission.

The purposes of this work were (1) to develop an ion exchange method to purify promethium and to determine within the limits of detection of present-day analytical methods if such an isotope does exist and (2) to produce promethium of sufficient purity to provide a spectrographic standard.

The purification problems, some of which had already been partially solved<sup>3</sup>,

were related to the ion-exchange treatment of the crude promethium starting solutions in which any long-lived isotopes would be expected to occur. The mass and emission spectrography problems existed because good standards had not yet been established for promethium.

#### Acknowledgement

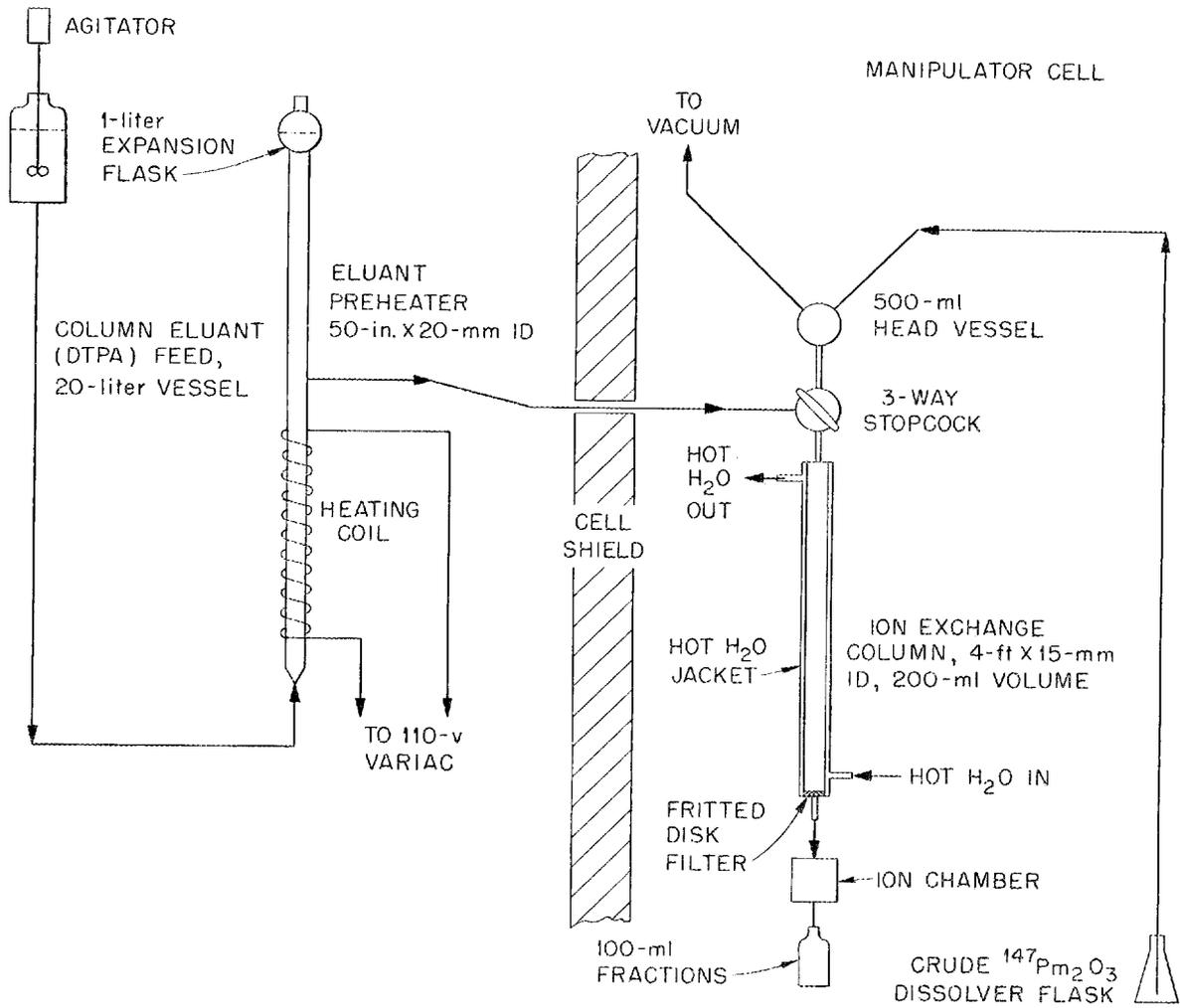
The authors are indebted to H. A. Parker, R. R. Rickard, and M. E. Pruitt for the radiochemical analyses and to J. A. Norris for the emission spectrographic work.

#### EQUIPMENT AND PROCEDURE

The arrangement of the equipment and a flow diagram for the process are shown in Fig. 1. A 20-liter polyethylene bottle with bottom drain line fed eluant through a preheater, half filled with Raschig rings and attached to a 1-liter expansion flask at the top. A 500-ml round-bottom flask served as a container for the feed solution and also provided vacuum transfer from a 500-ml Erlenmeyer flask in which the crude oxides of promethium were dissolved in HCl and diluted to suitable concentration. The ion-exchange purification was carried out in a 4 ft x 15 mm i.d. jacketed column, loaded with 200 ml of 70-mesh acid form Dowex 50 W-X4 resin and operated at about 75°C by means of circulating hot water. With the exception of the preheater and eluant solution, everything was handled inside a shielded manipulator cell.

Feed material consisted of fractions saved from ion-exchange experiments performed in 1959 and estimated to contain 2-3% Pm. The uranium fuel from which the fission-produced rare earth fractions originally came was discharged from a reactor about 1957. The promethium had decayed through about two half-lives, increasing the probability that it would contain enhanced concentrations of possible long-lived isotopes. This feed material was processed in four passes through the column. Analysis of the feed material was as follows:

Element	Activity	Total
<sup>147</sup> Pm	2,793 mc/ml	1,256 curies
<sup>241</sup> Am	0.767 mg/ml	345 mg
<sup>152</sup> Eu	Low	-
<sup>154</sup> Eu	0.0814 mc/ml	36.6 mc
<sup>155</sup> Eu	~0.43 mc/ml	193.5 mc

Fig. 1. Flowsheet for <sup>147</sup>Pm Purification.

Column Loading - The crude oxide was dissolved in 6 M HCl and then, in order to minimize the spread of the rare earth band during adsorption on the resin, was diluted with water to give a solution <0.1 M. After dissolution, the crude promethium solution was transferred to the head vessel of the column by vacuum and then adsorbed on the hydrogen-form Dowex 50 W-X4 resin in the column at full column flow, about 250 ml/hr.

Because of the small size of the manipulator cell in which the ion exchange work was done, and the relatively large amounts of fission-produced neodymium and samarium in the feed, it was necessary to make the first column loading in several batches in order to assure ultimate product of very pure promethium. The additional runs permitted the following experimental data to be obtained from changes in column loading lengths and elution flow rates:

Batch	Length of column loading	Elution flow rate, column volumes/hr	Comments
1	1/3	1	Normal for Pm separation
2	1/3	1	Normal for Pm separation
3	1/3	2	Flow two times normal
4	1/3	2	Flow two times normal
5	1/2	2	Loading length 50% > normal and flow two times normal.
6	1/2	2	Loading length 50% > normal and flow two times normal.

The results of these experiments show that the length of the column loading may be increased to as much as one-half the resin length, and the elution rate of the heated (75°C) column doubled, without adversely affecting the first-pass separation. Figures 2, 3, and 4 show the elution curves of a typical run from each set of conditions in the above data.

Elution and Analysis - In all cases the eluant was boiled in the preheater to remove the dissolved air in order to prevent gassing in the heated column. Elution of the first three passes was done at 75°C with 0.5% DTPA adjusted to pH 6.0 with NH<sub>4</sub>OH; the final elution was 75°C, using 0.2 M citric acid adjusted to pH 3.0 with NH<sub>4</sub>OH to remove the 0.5% yttrium impurity. The eluant discharge line of the column was a small-bore Tygon tube that penetrated an ion chamber which, in turn, was connected to an electrometer recorder system to indicate and record any radioactivity as the column was eluted. Collection of 100-ml fractions was begun when the electrometer first indicated a rise in radioactivity (due to <sup>155</sup>Eu and <sup>241</sup>Am on the first pass and to <sup>147</sup>Pm on the other three passes).

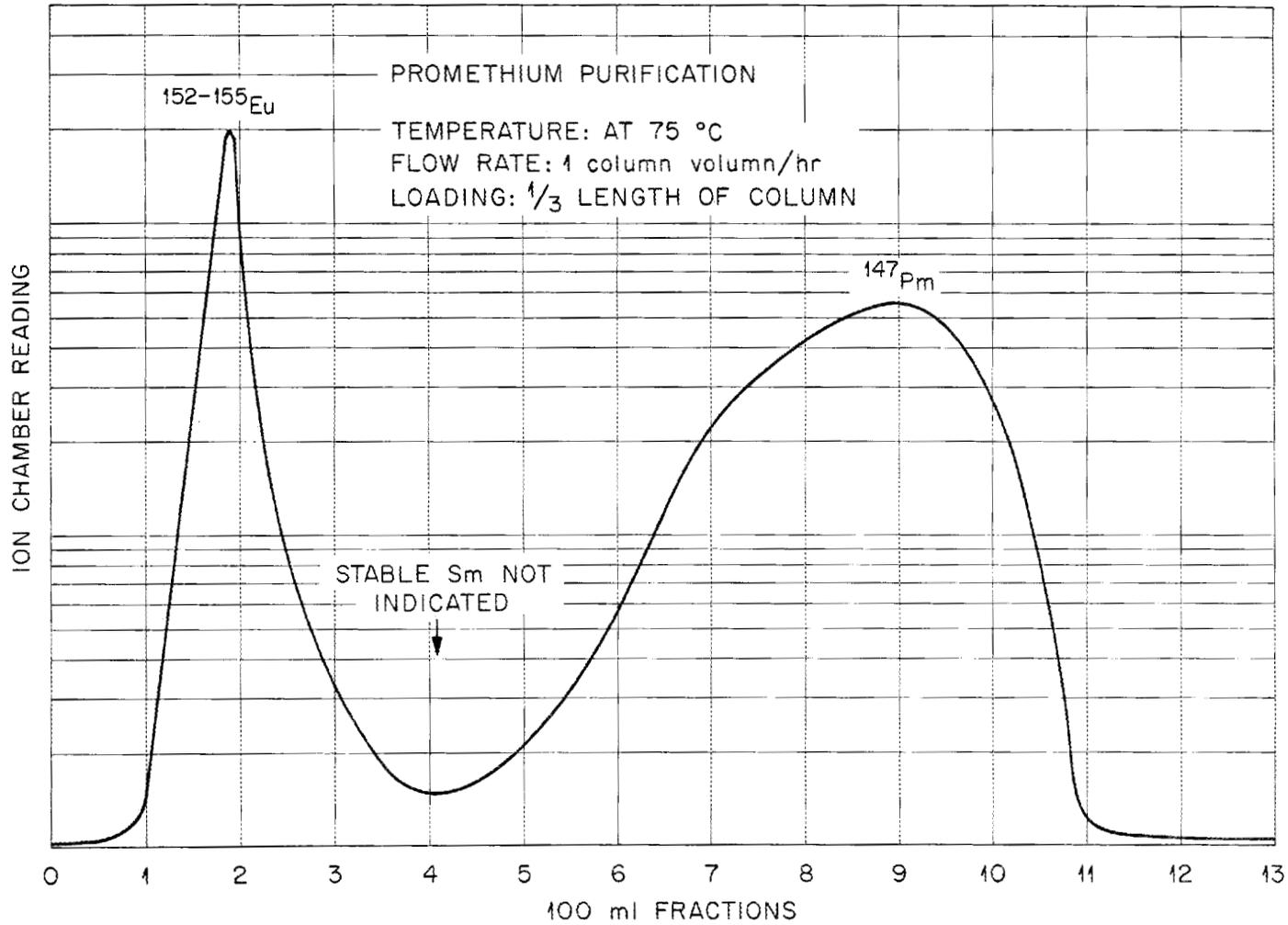


Fig. 2. Promethium Purification Elution Curve.

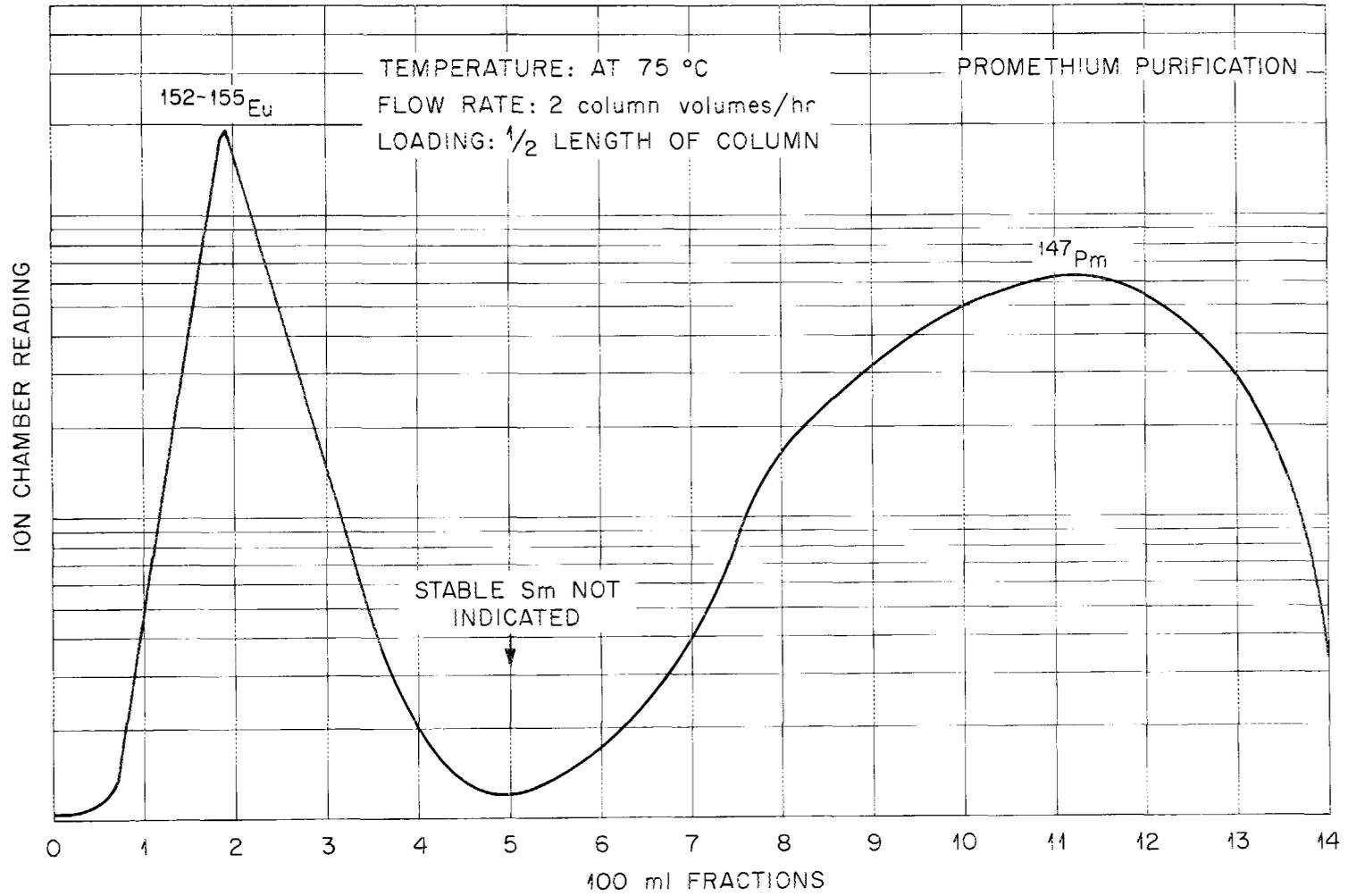


Fig. 3. Promethium Purification Elution Curve.

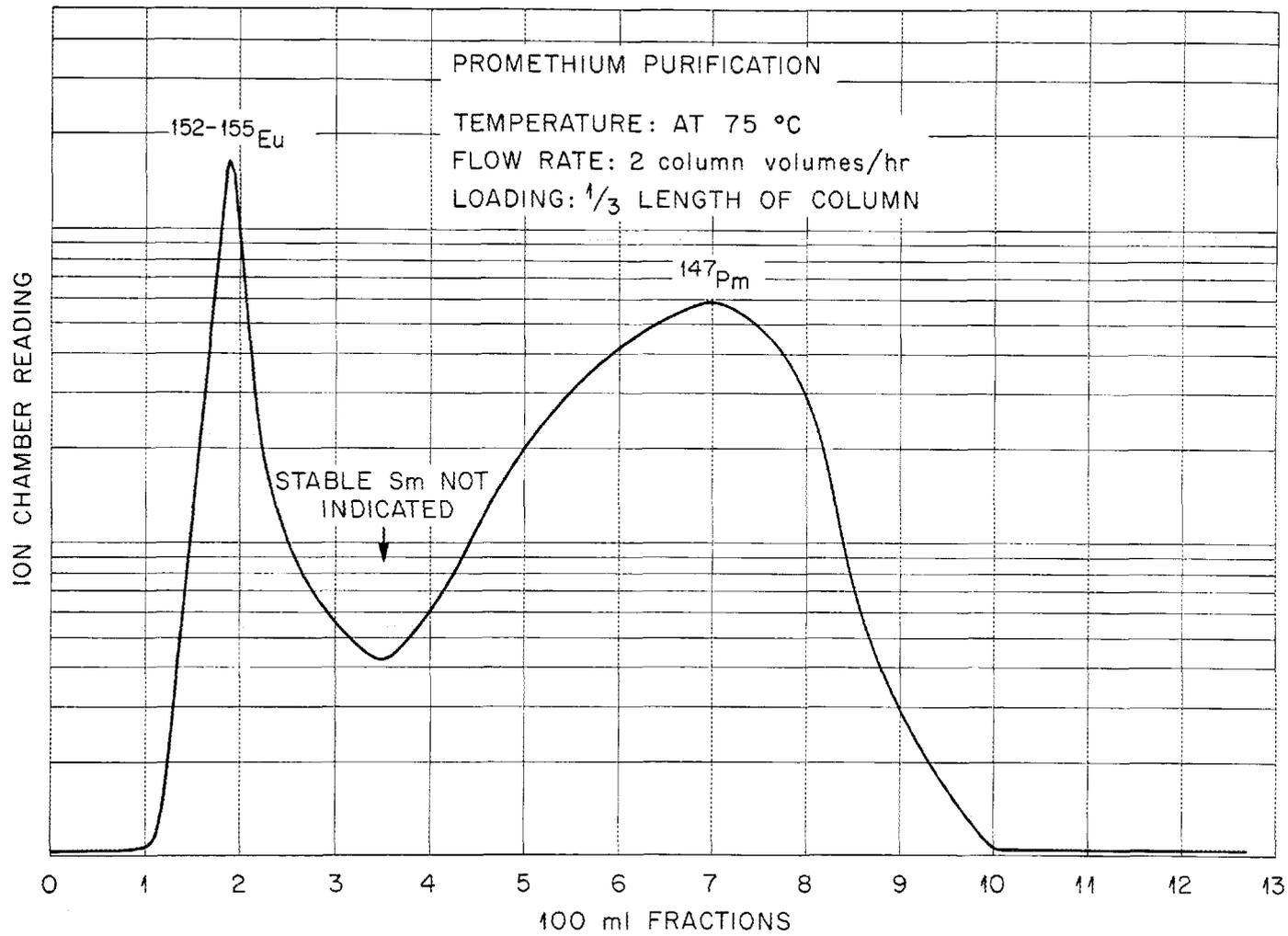


Fig. 4. Promethium Purification Elution Curve.

Each 100-ml fraction from the first pass was analyzed radiochemically for  $^{241}\text{Am}$ ,  $^{147}\text{Pm}$ , and  $^{154}\text{Eu}$ . Only those fractions containing little or no  $^{241}\text{Am}$  and  $^{154}\text{Eu}$  were used to load the column for the second pass. Figure 5 is a photograph of the column in operation during the second pass. The dark portion of the column at the bottom clamp is a mixture of neodymium and promethium. Extending about 2 in. above the dark portion is the lighter neodymium band in the process of being resolved. The 2-in. light section below the mixture is the promethium band being formed.

Feed for the third pass consisted of the fractions comprising the promethium peak from the second pass as shown by the electrometer recorder chart.

The final purification pass removed the 0.5% yttrium impurity which was found by emission spectrography in the peak of the promethium fraction of the third pass.

Each of the four 100-ml fractions collected from the peak of the final purification was acidified with 1.5 ml of concentrated HCl to break the promethium-citric acid complex and was then passed through its own 4 in. x 10 mm i.d. 60-mesh Dowex 50 W-X4 resin column. When all fractions had been adsorbed, each column was washed with 100 ml of distilled water to remove excess HCl and citric acid.

Each promethium band was stripped from the resin with 200 ml of 3 M  $\text{HNO}_3$ , the column washed with 200 ml of water, and the eluant evaporated to dryness and fumed twice with 100 ml of 70%  $\text{HNO}_3$  plus small amounts of  $\text{H}_2\text{O}_2$  to destroy fine resins. The  $\text{Pm}(\text{NO}_3)_3$  residues, designated Pm-3, Pm-4, Pm-5, and Pm-6, were fumed twice with concentrated HCl to convert them to  $\text{PmCl}_3$ , and then were diluted with water to 1 M HCl and analyzed.

## ANALYSES TO DETECT PROMETHIUM AND ACCOMPANYING ELEMENTS

### Emission Spectrography

The four promethium samples were analyzed spectrographically by a containment technique developed at ORNL by the staff of the Analytical Chemistry Division.<sup>4</sup> The purity of the promethium was determined by the use of samarium, yttrium, and neodymium standards, and by taking into consideration the amount of promethium on the electrodes. Yttrium, samarium, and neodymium impurities less than 0.1% could not be detected by this method. The following table shows the amount of promethium on each electrode:



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Fig. 5. Promethium Column in Operation During Second Pass Using DTAP as Eluant.

Sample from fraction	Pm activity on electrode, mc	Pm weight on electrode, mg
Pm-3	966	1.03
Pm-4	816	0.78
Pm-5	937	1.0
Pm-6	1020	1.1

The promethium spectrum obtained from this analysis (Fig. 6) will be used by ORNL as a future standard for promethium analysis. Results of the spectrographic analysis are listed below:

Sample from fraction	Total Pm content, curies
Pm-3	32.2
Pm-4	27.2
Pm-5	31.25
Pm-6	<u>34.2</u>
	124.85

The percentage of promethium in all samples was 99.8%; yttrium, <<0.1%; samarium, <0.2%; neodymium, <<0.1%.

### Mass Spectrography

The ionization characteristics and technique for mass analysis of promethium were identical to those for other rare earth elements.<sup>5</sup> The ionization chamber of the mass spectrometer was constructed to accept expendable bases of the sample-supporting ribbon filaments and to contain most of the radioactive material. Simple hand-drawn pipets were used for loading the solution onto these bases. Figure 7 shows a photograph of the filament (0.001-in. x 0.030-in. x 0.500-in. tantalum) and the tip of a pipet.

One microgram of promethium nitrate in solution was evaporated in the center of the tantalum ribbon. When the solution had been taken to dryness, the filament temperature was increased to about 750°C (dull red) to convert the nitrate to oxide. Ion currents of  $3 \times 10^{-10}$  amp were obtained for periods of 15 to 30 min. One-nanogram sample produced currents of  $3 \times 10^{-12}$  amp for 5 to 10 min over a temperature range of 1400° to 1700°C.

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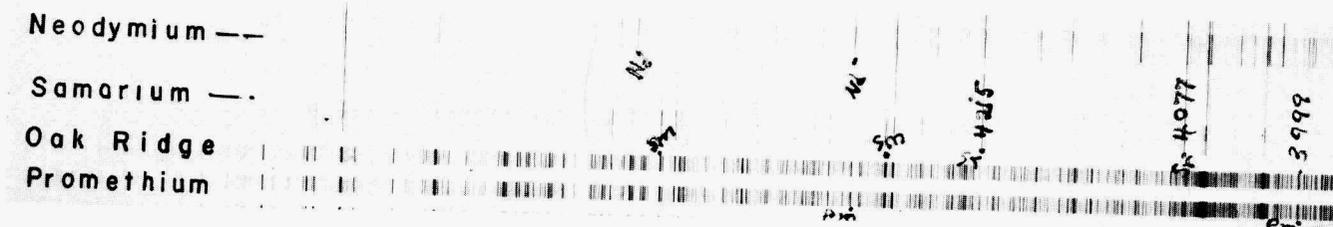


Fig. 6. Promethium Spectra, with Lines of Neodymium and Samarium Standards.

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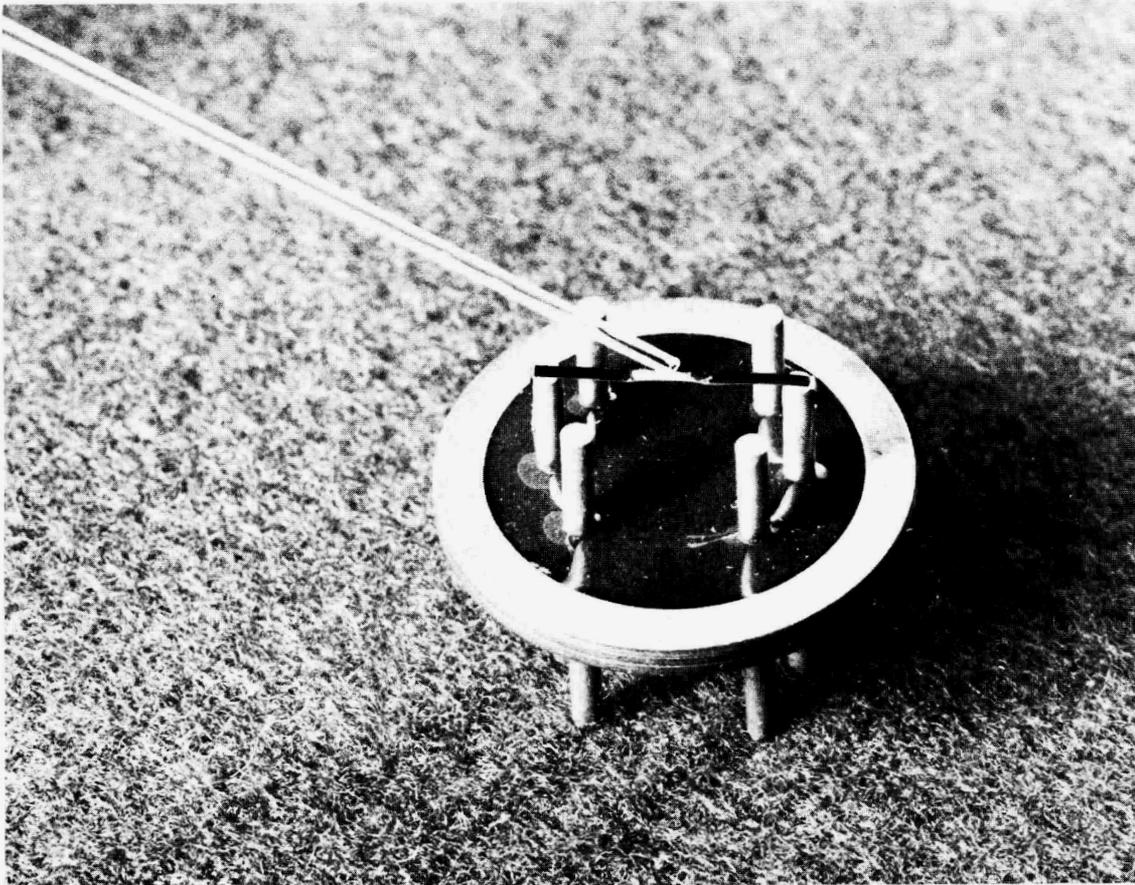


Fig. 7. Mass Spectrograph Filament Being Loaded with Promethium from a Hand Drawn Pipet.

A number of runs were made on the four purified promethium samples. The intensities of  $\text{Pm}^+$  and  $\text{PmO}^+$  at masses 147 and 163, respectively, were such that an upper limit of less than 0.005% was determined for each of the isotopes, other than  $^{147}\text{Pm}$ , from mass 138 to mass 156, inclusive. It was also found that  $\text{PmO}^+$  had about 10 times the intensity of  $\text{Pm}^+$ . (Hayden<sup>6</sup> had reported a  $\text{PmO}^+/\text{Pm}^+$  ratio of about 20/1 from a tungsten filament.) No attempt was made to ionize promethium with double or triple filaments to alter the  $\text{Pm}^+/\text{PmO}^+$  ratio as has been done with other rare earths.<sup>7</sup>

### Radioactivity Analyses

Promethium-147 was determined by a gas-flow method using thin-window beta-proportional counting, and  $^{241}\text{Am}$  was analyzed by gas-flow alpha counting. The instruments used in this work were calibrated by counting aliquots of standardized  $^{147}\text{Pm}$  and  $^{241}\text{Am}$  solutions. The beta spectrum (Fig. 8) was analyzed to determine the purity of  $^{147}\text{Pm}$  by its end-point energy and also to determine the presence of beta particles other than the 0.223 Mev beta of  $^{147}\text{Pm}$ .

The  $^{147}\text{Pm}$  used in this study was analyzed by gamma spectrometry (Fig. 9) using an RIDL model 34-8, 200-channel gamma spectrometer with a 3- x 3-in. sodium iodide detector and a 1.237-g/cm<sup>2</sup> beryllium absorber. The 1.42-Mev, 1.28-Mev, and 0.87-Mev photons were used to estimate the  $^{152}\text{Eu}$ ,  $^{154}\text{Eu}$ , and  $^{155}\text{Eu}$  respectively. The decay schemes of Funk, Mihelich, and Schwerdtfeger and those of Eldridge and Lyon<sup>9</sup> were used in analyzing for  $^{146}\text{Pm}$  and  $^{148}\text{Pm}$ . The low-energy (0.124-Mev) photon associated with  $^{147}\text{Pm}$  decay could be detected when a mount containing more than 5 mc of  $^{147}\text{Pm}$  was used with absorbers to stop the beta radioactivity (Fig. 10). A typical analysis of one of the fractions (Pm-3) is as follows:

$^{147}\text{Pm}$	0.664 curie/ml
$^{241}\text{Am}$	None detected in 5.0 mc $^{147}\text{Pm}$
$^{152}\text{Eu}$	None detected
$^{154}\text{Eu}$	None detected
$^{155}\text{Eu}$	None detected
$^{146}\text{Pm}$	$<3.0 \times 10^{-7}$ curie/curie $^{147}\text{Pm}$
$^{148}\text{Pm}$	$<1.0 \times 10^{-7}$ curie/curie $^{147}\text{Pm}$

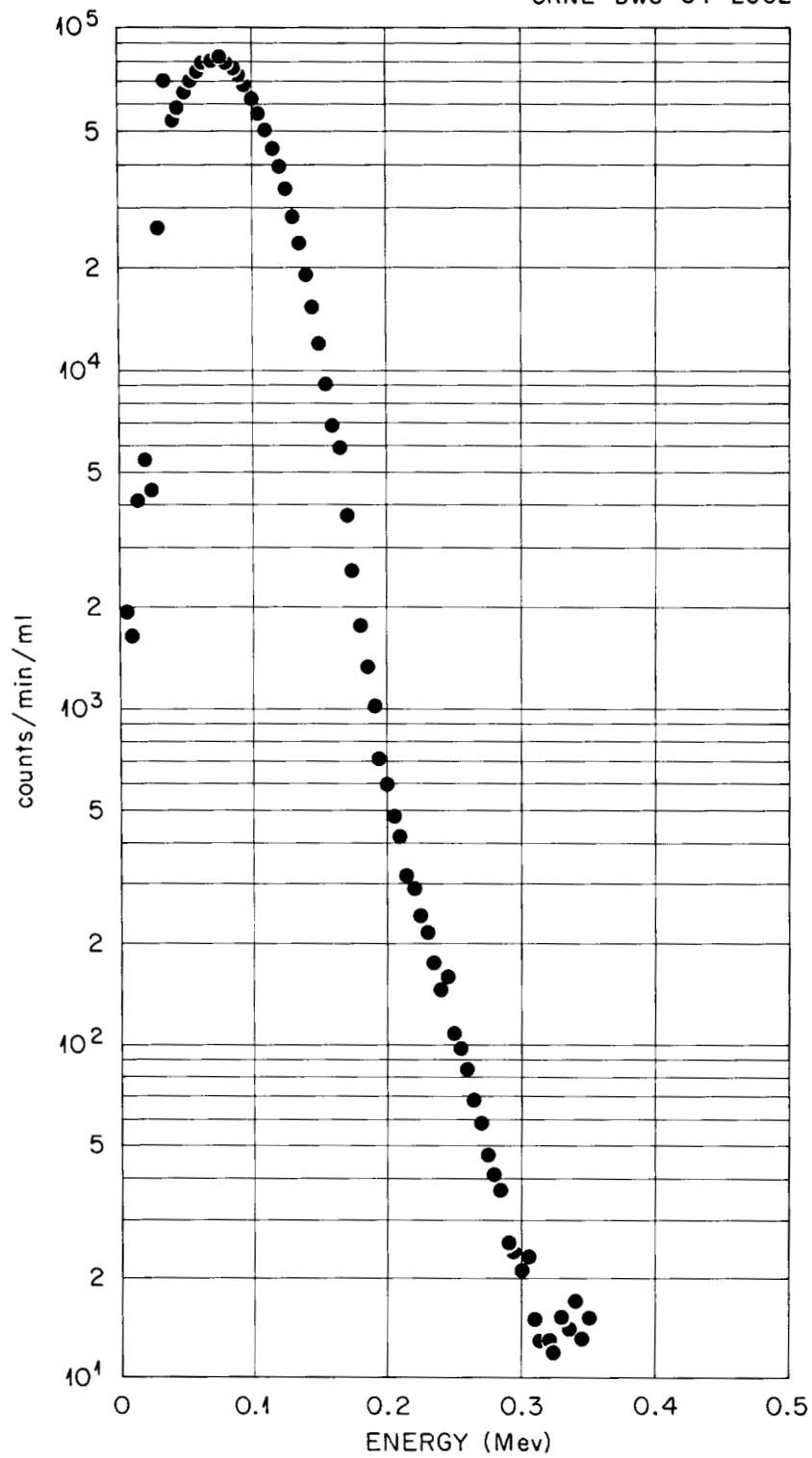
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Fig. 8. Beta Spectrum of Promethium-147 (Batch Pm-6).

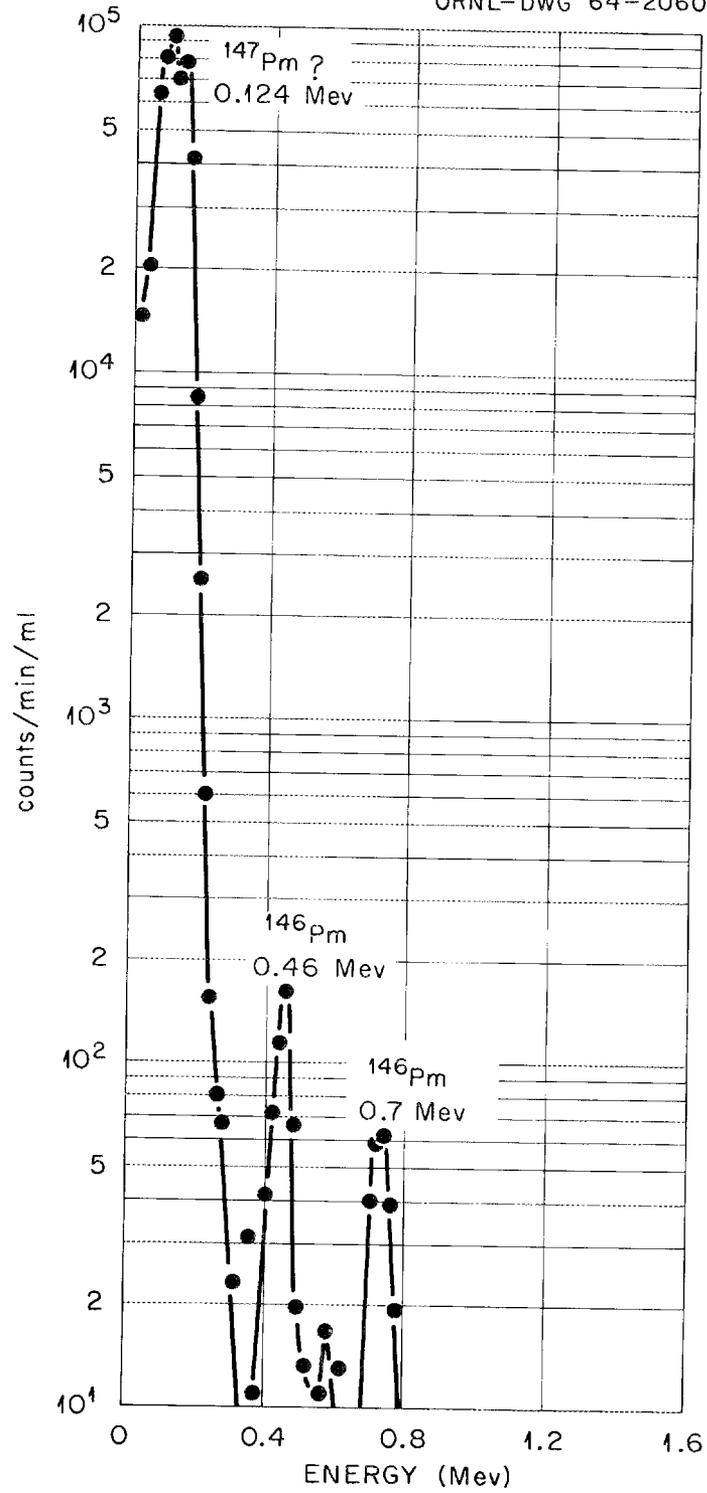
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Fig. 9. Gamma Spectrum of Promethium Showing No Europium Radioactivities.

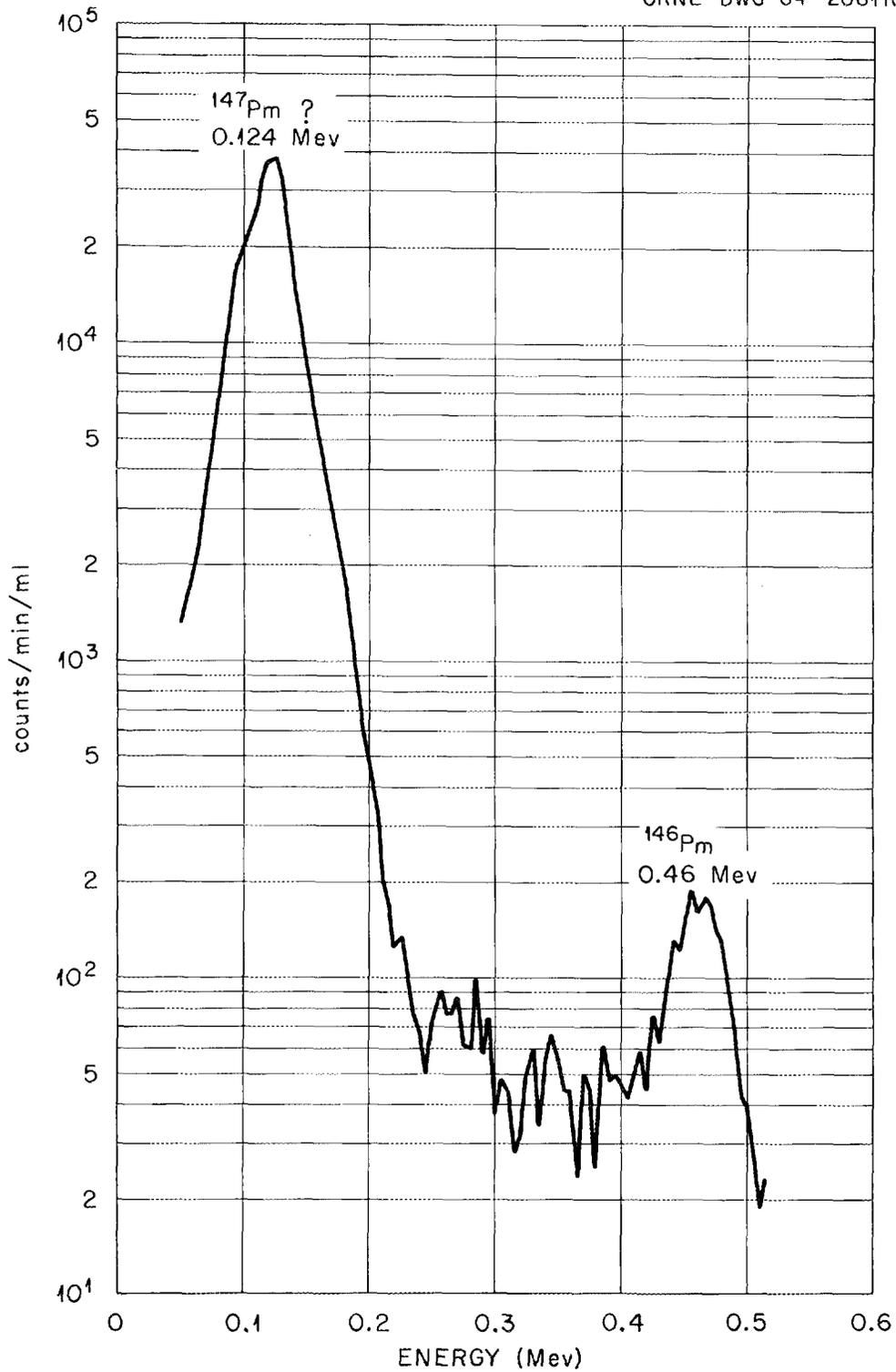
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Fig. 10. Gamma Spectrum of Promethium (Batch Pm-6).

## Activation Analyses

About 32  $\mu\text{g}$  of  $^{147}\text{Pm}$  from fraction Pm-3 was activated in the Low Intensity Test Reactor at ORNL for 2 hr in a thermal neutron flux of  $1.5 \times 10^{13} \text{ n/cm}^2$ . sec. The subsequent decay time of the irradiated promethium removed all activation products except those with half-lives longer than two days.

Prior to activation, the gamma spectrum of the  $^{147}\text{Pm}$  (using an RIDL, model 34-12, 400-channel gamma spectrometer with a 3- x 3-in. sodium iodide detector and a 1.237-g/cm<sup>2</sup> beryllium absorber) indicated the presence of  $^{146}\text{Pm}$  and the absence of 42-day  $^{148}\text{Pm}$  and any other photon-emitting impurities. The gamma spectrum after irradiation comprised photons from the decay of 5.4-day  $^{148}\text{Pm}$ , which prevented direct detection of extraneous photon emitters. Even after a chemical separation to separate the heavy rare earths from the promethium no activation products emitting photons greater than 0.2 Mev were detected.

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