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ION EXCHANGE PURIFICATION OF
PROMETHIUM-147 AND ITS
SEPARATION FROM AMERICIUM-241,
WITH DIETHYLENTRIAMINEPENTAACETIC
ACID AS THE ELUANT

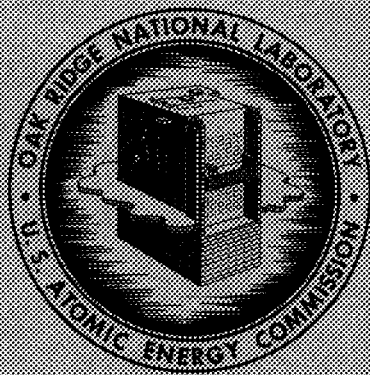
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ION EXCHANGE PURIFICATION OF PROMETHIUM-147 AND ITS SEPARATION
FROM AMERICIUM-241, WITH DIETHYLENETRIAMINEPENTAACETIC
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ABSTRACT

Based on a half-life of 2.64 ± 0.02 years, a calculated weight of 2.032 g of $\text{Pm}_{2}^{147}\text{O}_3$ in 9 g of fission-produced rare-earth and americium oxides was separated in two runs by cation exchange (Dowex 50W-X4 resin, 80 mesh), with diethylenetriaminepentaacetic acid solution as the eluant.

Promethium, computed as the element, was present to the extent of about 23.5 wt % in the starting mixture and was increased to 98 wt % in the first run and to 99 wt % in the second, with yields of 58.2 wt % and 61.8 wt % respectively. A decontamination factor of 2.7×10^9 was realized in the removal of americium from the product. This is the highest decontamination factor yet achieved for this separation, which will be used at ORNL.

Procedures, a modified elution curve, methods of analysis, losses, material balances, and a description of the equipment are given. In addition, a possible colorimetric analysis scheme (qualitative) is given for determining the proportions of neodymium and promethium in a solution.

INTRODUCTION

In 1959 the Isotopes Division of ORNL used an ion exchange procedure to produce about 20 kilocuries of $\text{Pm}_{2}^{147}\text{O}_3$, approximately 65% pure; 0.2 M citric acid at pH 3 was the eluant.¹ The impurities remaining were Sm_2O_3 and Nd_2O_3 , about 30%; $\text{Am}_{2}^{241}\text{O}_3$, about 5 to 6%; and about 40 mc of $\text{Eu}^{152-154}$ gamma activity.

With interest stimulated in the use of $\text{Pm}_{2}^{147}\text{O}_3$ in x-ray sources, work was started at ORNL toward developing new and more efficient ion exchange processes for the purification of promethium. Experiments were done with stable rare earths, using as feed approximately equal mixtures of 14 rare earths and yttrium. The concentration of each rare earth was about 7 wt %. This work led to the pilot-plant process described in this report.

¹R. S. Pressly et al., Purification of Kilocurie Quantities of Pm^{147} by Ion Exchange, ORNL-2928 (July 5, 1960).

LABORATORY EXPERIMENTS WITH STABLE ELEMENTS

The systems described below had the following conditions in common:

1. The resin volume of the column was 1800 ml.
2. The flow rate was about 1 liter/hr.
3. The rare-earth loading was one-third of the resin volume.

A brief description of the eluants and the resins follows; all columns were operated at 75°C. Important observations are also included:

1. One-half percent diethylenetriaminepentaacetic acid (DTPA) solution at pH 7.5; 1.2% cross-linked hydrogen-form Dowex 50W resin, 60 mesh.
2. One-half percent DTPA solution at pH 7.5; 4% cross-linked, hydrogen-form Dowex 50W. A better separation was obtained with the change in resin, apparently due to less resin diffusion.²
3. One-half percent DTPA solution at pH 5.5; 4% cross-linked, hydrogen-form Dowex 50W, 60 mesh.
4. One-half percent ethylenediaminetetraacetic acid (EDTA) solution at pH 7.5; 4% cross-linked Dowex 50W resin, 60 mesh, copper form.
5. Citric acid solution, 0.2 M, pH 2.9; 4% cross-linked, hydrogen-form Dowex 50W resin, 60 mesh.
6. One-half percent citric acid solution at pH 4.5; 4% cross-linked, hydrogen-form Dowex 50W resin, 60 mesh.

According to results obtained from the use of systems 1-3, it was determined that DTPA changes the ordinary order of elution of the rare earths. By use of citric acid, they are eluted in the reverse order of atomic number, lutetium coming off first and yttrium having an apparent atomic number of 65.5, eluting between terbium and dysprosium. The following is a list of the elution order for a DTPA system:

- | | | |
|---------------|---------------|-------------------|
| 1. Dysprosium | 6. Lutetium | 11. Yttrium |
| 2. Holmium | 7. Terbium | 12. Neodymium |
| 3. Erbium | 8. Europium | 13. Praeseodymium |
| 4. Thulium | 9. Gadolinium | 14. Cerium |
| 5. Ytterbium | 10. Samarium | 15. Lanthanum |

For system 5, extremely good results were obtained at the light end, with complete breaks between Sm and Nd, Pr and Ce, Ce and La.

²R. D. Hansen and Stanley Chaberek, Ion Exchange Separation of Yttrium from Rare Earths with Diethylenetriaminepentaacetic Acid, Dow Chemical Co.

RESULTS OF THE LABORATORY WORK

The results of the work with stable rare earths indicated the following:

1. Promethium of high purity could possibly be obtained from low-concentration feed (less than 1% promethium) in two passes, by the following procedure:

- (a) One-half percent DTPA solution at pH 5.5; 4% cross-linked, hydrogen-form Dowex 50W resin; column temperature, 75 to 80°C. By this process, yttrium will be eluted between troublesome europium and promethium. This additional element should permit all the europium and most of the samarium to be eluted before the promethium starts to elute. A sharp separation of promethium and neodymium should also be made.
- (b) A second pass through the column (after reconverting to the hydrogen form), with 0.2 M citric acid at pH 2.9 to 3.0 and 4% cross-linked Dowex 50W resin at 75 to 80°C, should remove the yttrium and most of the remaining samarium and neodymium.

2. From the remainder of the 20 kilocuries of promethium produced in 1959, promethium of high purity should be obtained in one pass through an ion exchange resin, with the DTPA solution at pH 5.5 and a temperature of 70 to 80°C.

Since the order of elution of yttrium and the other rare earths was changed in the DTPA system, it is hoped that the elution order of Am^{241} in the promethium feed solution will be changed also.

DESCRIPTION OF WORK WITH FISSION PRODUCTS

Description of Equipment. - With the exception of the preheaters and the container for the eluant solution, all the equipment was inside a shielded manipulator cell.

Eluant Container. - A 20-liter polyethylene bottle with bottom drain line was used.

Preheater for Eluant. - A glass tube (50 in. long, with an inside diameter of 20 mm) was used with a draw-off line 26 in. from the bottom. A 1-liter expansion flask was located at the top, and an inlet line was located at the bottom. The bottom half of the tube was filled with Raschig rings and had an electrical heating element wound on the outside.

Vessel for Providing the Column Head. -- A 500-ml round flask with three outlets was used: one to a vacuum line, a second to the crude Pm_2O_3 dissolver flask, and a third to the ion exchange column. This flask was used as a vessel for the feed solution and as a vacuum transfer vessel from the dissolver flask.

Ion Exchange Column. -- A jacketed column 4 ft long with an inside diameter of 15 mm was used. A coarse, sintered-filter disk at the bottom supported the resin bed. The column has a capacity of 200 ml of hydrogen-form Dowex 50W-X4 resin, which was dry-classified on an 80-mesh screen.

Flow rate of the eluant was set at about 200 ml/hr by use of a stop-cock on the column discharge. The temperature was held to about 75°C by means of hot water.

Dissolver Flask for the Crude Pm_2O_3 . -- A 500-ml Erlenmeyer flask was used to dissolve the crude oxide in aqueous HCl.

PROCEDURE

A flow diagram for the process is shown in Fig. 1.

Feed material for the column was a portion of the Pm_2O_3 originally separated at ORNL in 1959 and was processed in two runs. Analysis of the feed material is shown below:

<u>Element</u>	<u>Approximate Activity</u>
Pm^{147}	3576 mc/ml
Am^{241}	2.78×10^9 counts $\text{min}^{-1} \text{ml}^{-1}$
$\text{Eu}^{152-154}$	About 6 mc

The relative rare-earth and americium contents for the two runs are shown below:

	<u>Run 1</u>		<u>Run 2</u>	
Pm_2O_3	22.6%	0.903 g	22.6%	1.128 g
Am_2O_3	5.9%	0.237 g	5.9%	0.300 g
$\text{Sm}_2\text{O}_3, \text{Nd}_2\text{O}_3$	71.5%	<u>2.860 g</u>	71.5%	<u>3.575 g</u>
		4.000 g		5.003 g

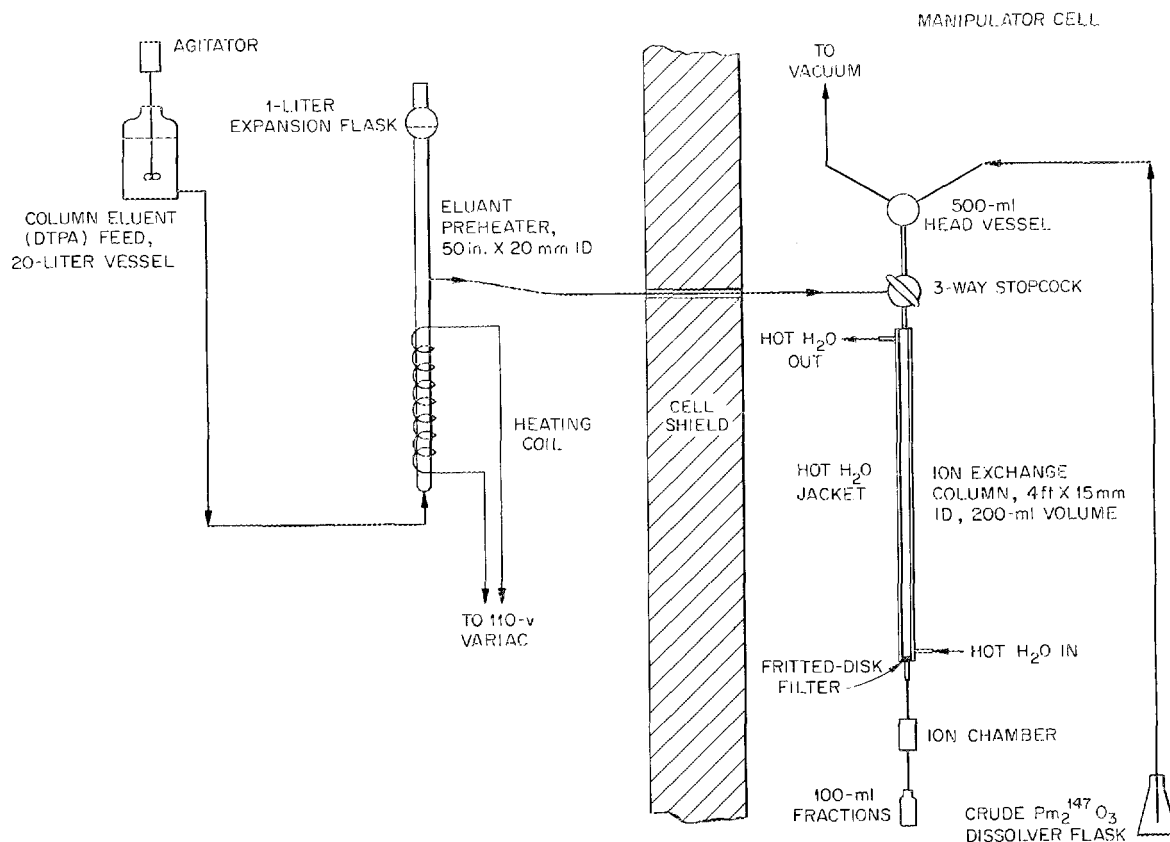


Fig. 1. Flowsheet for Pm¹⁴⁷ Purification from Am²⁴¹.

The crude oxide was dissolved in a 500-ml Erlenmeyer flask in sufficient HCl to bring the concentration of HCl in the final solution to less than 0.1 N. The acid concentration was kept low in order to minimize the spread of the rare-earth band during adsorption on the resin.

After dissolution, the crude promethium solution was transferred to the column-head vessel by vacuum and then adsorbed on the hydrogen-form Dowex 50W-X4 resin in the column at full column flow (about 250 ml/hr). The column was then washed with about 250 ml of water to remove excess acid from the system.

Elution was done with 0.5% DTPA, the pH having been adjusted to 5.0 with NH₄OH. Flow rate was set at 200 ml/hr. The discharge line of the column was a small-bore Tygon tube which penetrated an ion chamber, which, in turn, was connected into an electrometer-recorder system to indicate

and record any activities as they were eluted. Collection of 100-ml fractions was begun when the electrometer first indicated a rise in radioactivity. (This was due to $\text{Eu}^{152-154}$.)

Each 100-ml fraction was analyzed for Am^{241} , Pm^{147} , and $\text{Eu}^{152-154}$. When the Pm^{147} peak was reached, samples of the first and last fractions of the peak were analyzed spectrographically, by use of a containment technique developed at ORNL by the staff of the Analytical Chemistry Division.³ All fractions with promethium purity above 99% were combined as one product. Fractions of approximately 80% purity were combined as another product.

Each 100-ml fraction was acidified with 1.5 ml of concentrated HCl to break the DTPA complex and was then passed through dry-classified 60-mesh Dowex 50W-X4 resin in a column 10 in. long and 20 mm in inside diameter. When all fractions were thus adsorbed, the column was washed with 300 ml of distilled water to remove excess DTPA and HCl.

The promethium band was stripped from the resin with 1 liter of 6 N HCl; this was followed by a 200-ml water wash. The PmCl_3 solution was then evaporated to dryness on a hot plate and fumed with 50 ml of 70% HNO_3 and small amounts of H_2O_2 to destroy fines from the resin.

The residue, $\text{Pm}(\text{NO}_3)_3$, was fumed twice with 50 ml of concentrated HCl in order to reconvert it to PmCl_3 . Then it was diluted to 500 ml in approximately 1 N HCl, in which form the product was ready for sale. Analysis of the two products from run 2 is given below:

Percentage of Pm	Percentage of Sm	Percentage of Nd	Percentage of Starting Material	Am^{241} Content	$\text{Eu}^{152-154}$ Content
99	< 1	< 1	61.8	Nil	Nil
75	~12	~12	25.0	Nil	Nil

METHODS OF ANALYSIS

Promethium-147. -- This isotope was determined by liquid-scintillation beta counting and end-window flow-type proportional counting. Analysis

³J. A. Norris, The Analysis of Promethium-147, ORNL CF-61-4-81 (Apr. 26, 1961).

of the final product was done by spectrographic analysis, with graphite electrodes. The weighed sample was analyzed for samarium and neodymium, but not for promethium; the promethium was determined by difference.

Promethium-146. - This isotope was identified by using a multichannel spectrometer, with the 0.46-, 0.74-, and 1.02-Mev gamma rays being identified in order to detect it. The analysis was qualitative.

Europium-152-154. - The assay for $\text{Eu}^{152-154}$ was made by using a multichannel gamma spectrometer. The 970-kev and 1.277-Mev Eu^{154} gamma rays were identified.

Americium-241. - Determination of this isotope was made by means of alpha proportional counting and a multichannel gamma spectrometer. The 60-kev gamma radiation was identified.

DISCUSSION

The DTPA elution and the use of Dowex 50W-X4 resin (hydrogen form) exceeded expectations for the separation of americium from promethium. These experiments showed that high-purity promethium can be made and that little or no americium will remain as a contaminant.

The americium was separated from promethium by the change in the order of elution of americium. In a system using 0.2 M citric acid, the americium is eluted along with the promethium. In the DTPA system, americium is eluted along with the europium, which changes the order of elution so that the americium no longer elutes like element 61 but like element 63. A curve showing only the order of elution is given in Fig. 2. This graph shows only the activities present; stable neodymium and samarium are not shown.

It is hoped that the cost of separation and purification can be reduced as a result of these experiments, so that large quantities may be made available for research on the chemistry of promethium as well as for the production of large-scale x-ray sources. Furthermore, it is hoped that adequate amounts of high-purity Pm^{147} may thus become available for research on the metal.

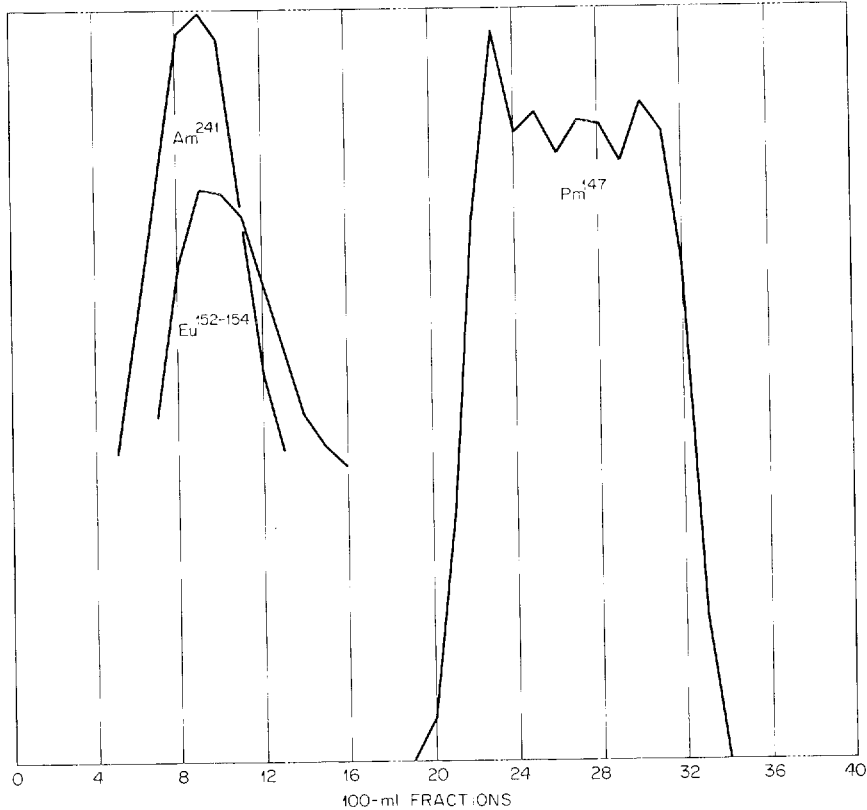
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Fig. 2. Curve Showing Only the Order of Elution of $\text{Eu}^{152-154}$, Am^{241} , and Pm^{147} .

The following table shows the material balance for run 2.

	<u>Curies</u>	<u>Percentage</u>
Pm^{147} starting material	894.1	100.00
Product, 99% pure	552.6	61.81
Product, 75% pure	223.65	25.01
Pm^{147} in Sm fractions	46.00	5.14
Pm^{147} in Nd fractions	24.47	2.74
Losses	47.38	5.30

No difficulty was encountered with radiation-induced decomposition of the DTPA during processing. However, some high-activity Pm^{147} fractions were held for about two weeks before conversion to the chloride,

and at the end of this period a pink precipitate was found. It was very soluble in small amounts of HCl, indicating that it was not a DTPA precipitate. Although it was not investigated, the precipitate may have been a basic salt of promethium.

CONCLUSIONS AND RECOMMENDATIONS

The procedure for separating Pm^{147} from Am^{241} by use of DTPA eluant and Dowex 50W-X4 resin (hydrogen form) resulted in the preparation of 99% pure Pm^{147} . This process gave the best separation to date.

During the work it was noticed that in daylight the purified neodymium and promethium solutions were lavender-pink. However, in the light from a mercury-vapor lamp, the neodymium solution was dark blue, while the promethium solution retained its lavender-pink color. This information may be useful to those who need to qualitatively analyze solutions that contain these elements.

No work was done to determine the radiation stability of the ion exchange resin.

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