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THE PURIFICATION OF 10 CURIES OF Cm^{242}

by

E. P. Horwitz, C. A. A. Bloomquist,
H. W. Harvey, D. Cohen,
and L. J. Basile

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INTRODUCTION

This report describes the purification of 10 Ci of Cm^{242} , produced by neutron irradiation of $\text{Am}^{241}\text{O}_2$, encapsulated in high-purity aluminum. The purified curium will be used as an alpha source in an instrument designed to obtain chemical analysis by alpha-particle scattering. The purity requirements for curium employed in such an instrument are the following:

1. High decontamination from capsule material.
2. High decontamination from fission products.
3. High decontamination from chemical reagents used in processing, with the exception of NH_4^+ , Cl^- , or NO_3^- .
4. Less than 25% americium in curium by mass.

Because of the high level of alpha-gamma activity of irradiated Am^{241} , special equipment was required to process the capsule. The dissolution of the capsule and the separation from fission products were performed by remote control in a high-level cave. A containment box within the cave housed the equipment and apparatus used for processing. After removal of fission products, the gamma activity was reduced sufficiently to allow further processing in a glovebox. The containment box and the apparatus therein are shown in Fig. 1.

EQUIPMENT

The equipment used for processing the capsule by remote control in a high-level cave was designed with simplicity, reliability, and safety as the prime criteria. These criteria were realized by the use of standard-size laboratory glassware and equipment housed in a specially designed containment box.⁽¹⁾ A high degree of reliability was provided by manual operation through master-slave manipulators. Figures 1, 2, 3, and 4 show the general layout and apparatus employed. Special equipment and materials used are listed in the appendix.

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Fig. 1. Inside View of Containment Box Showing Apparatus for Dissolving Capsule and Separating Fission Products

120-9095

Fig. 2. Back of Containment Box Showing Transfer Port, Extended-reach Manipulator, and Filter System

120-9097

Fig. 3. Overall View of Containment Box Showing Hydraulic-lift Table and Manipulator Booting

Fig. 4. View of Outside of Cave Showing Controls for Remotely Operated Equipment

Additional processing of the curium sample in a glovebox employed standard radiochemical techniques and equipment.

CHEMICAL PROCESSING

The sample initially contained 45 mg of $\text{Am}^{241}\text{O}_2$ encapsulated in high-purity aluminum. The capsule was irradiated with neutrons in the MTR reactor for 3 weeks. The nvt was 2.13×10^{20} . After 41 days of cooling, the capsule, which read approximately 45 R/hr on contact, was removed from a lead storage pot and transferred (by remote control) into the containment box.

The chemical processing is divided into the following four steps:

1. Dissolution of the capsule.
2. Solvent extraction of fission products.
3. Ion-exchange separation of lanthanide fission products from americium and curium.
4. Separation of americium and curium.

Each step will be individually described below. Flowsheets showing the entire process are presented in Figs. 5 and 6.

Fig. 5

Flowsheet for the Recovery of Cm^{242} from Irradiated $\text{Am}^{241}\text{O}_2$ in an Aluminum Capsule

Fig. 6. Flowsheet for Separating Americium and Curium

alcohol, aided considerably in reducing the dislodging of the solid phase. The supernatant liquid contained most of the aluminum and fission product cesium.

2. Solvent Extraction

The hydroxide precipitate was dissolved in 40 ml of 8M HCl and contacted in a separatory funnel with an equal volume of 30 v/o Alamine-336 in diisopropylbenzene, which had been pre-equilibrated with 8M HCl. The two phases were equilibrated by shaking the separatory funnel with the manipulators. The organic phase was scrubbed once with 8M HCl, and the combined scrub and feed solution was washed with toluene several times to remove any residual amine solution. The resultant aqueous phase was evaporated to dryness. The organic phase removed essentially all of the Fe, Zr⁹⁵, and Pu^{238,242} from the aqueous phase.

3. Ion-exchange Separation

The residue from evaporation contained americium and curium chlorides, lanthanide chloride fission products, and LiCl from the LiOH

1. Dissolution of Capsule

The dissolver solution contained 30 g of NaOH and 60 g of NaNO₃ in 180 ml of solution. The temperature of the dissolver pot was raised to 70°C to facilitate the reaction of NaOH and aluminum. Once the reaction started, no additional heat was required. Fifty milligrams of Fe(III) as the chloride was added to the dissolver pot to give a larger volume and lower specific activity of the precipitate. Dissolution of the capsule was complete in 4 hr.

The precipitate was separated by centrifugation and washed thoroughly, first with 0.1M NaOH, and finally with 1M LiOH. Gas formation in the precipitate frequently dislodged the collected solid as soon as the centrifuge stopped. Thus, the complete removal of supernatant liquids from the precipitate was very difficult. However, the addition of methanol to the supernatant liquid, amounting to 10 v/o of

wash. Small quantities of sodium and aluminum chlorides were also present. The solid residue was dissolved in 10 ml of 11.3M LiCl-0.01M HCl-1 v/o methanol and loaded on an ion-exchange column, 1 cm in diameter, containing Dowex 1-X10, 200-400 mesh, and thermostated at 75°C. The ion-exchange column was previously equilibrated with 11.3M LiCl-0.01M HCl-1 v/o methanol. (The presence of methanol in the LiCl solutions inhibits the loss of HCl by radiolysis.)⁽²⁾ The bed volume of the column was 10 ml; the free-column volume (which will be referred to hereafter as the column volume) was ~5 ml. The tube containing the feed solution was rinsed four times, giving a total feed volume of 15 ml, or ~3 column volumes. The concentration of LiCl in the feed solution was greater than 11.3M due to the presence of LiCl salt in the americium-curium chloride residue. Thus, the actinide fraction absorbed in a narrow band⁽³⁾ <1 ml in volume, the position of which was clearly visible due to the radiation damage of the ion-exchange resin. The activity level of the band was equivalent to >370 W/liter of resin bed.

The column was eluted with 10.0M LiCl-0.01M HCl-2 v/o methanol. Selected eluate fractions were assayed for alpha and beta activity. The primary lanthanide fission product by activity was Ce¹⁴¹. After 14 column volumes, the beta activity was reduced by >10⁴. The alpha activity in the combined 14 column volumes was negligible in comparison to the total alpha activity in the feed. The actinide fraction was stripped from the column with 2M HCl. Throughout the column run, the temperature was maintained at 75°C by means of a temperature bath outside the cave. The flow rate of the column was maintained at ~0.25 ml/cm²/min during the loading, elution, and stripping operations by means of regulated nitrogen pressure applied to the top of the column.

Radiometric assay of the actinide fraction showed the presence of 10 Ci (3.0 mg) of Cm²⁴² and ~35 mg of Am²⁴¹.

4. Americium-Curium Separation

With the fission products removed from the actinide fraction (Am²⁴¹-Cm²⁴²), the gamma activity was reduced to essentially that of ~35 mg of Am²⁴¹. The actinide fraction was accordingly transferred from the cave to the glovebox where the americium-curium separation could be performed more easily.

The americium-curium mixture was put through two hydroxide-precipitation cycles using NH₃ and HCl. The resultant gelatinous hydroxide was dissolved directly in 5 ml of 4.0M K₂CO₃ solution containing a few drops of 3.2M KHCO₃. The carbonate solution was heated to 85°C and made 0.1M in KOCl by the addition of 0.5 ml of a KOCl stock solution.*

*The KOCl stock solution was prepared by mixing commercial Ca(OCl)₂ with 3M K₂CO₃ solution in a 1:3 mole ratio for 30 min in an ice bath and filtering the resultant mixture. The filtrate solution was analyzed and found to be 1.2M KOCl and 2.4M K₂CO₃.

After 2.5 min, a noticeable precipitate of KAmO_2CO_3 formed. The solution was maintained at 85°C for 20 min, cooled to room temperature, and allowed to stand at room temperature for 1 hr before separating the precipitate of Am(V) .* The precipitate of KAmO_2CO_3 was separated by centrifugation and washed once with 1 ml of 4M K_2CO_3 .

The combined supernatant and wash liquid was very slowly neutralized with 8M HCl by: first, freezing the carbonate solution in a Kjeldahl flask placed in a dry-ice acetone bath; second, adding the 8M HCl ; and third, removing the flask from the bath and allowing the resultant solid mixture to warm to room temperature. The entire procedure took ~20 min and considerably reduced the effervescence of CO_2 . The slightly acid solution was diluted with water to dissolve excess KCl .

To precipitate Cm^{242} from the highly salted solution, 10 mg of high-purity Fe(III) ** in 1M HCl was added to serve as a carrier and to reduce the specific activity of the solid phase. The iron-curium mixture was carried through two hydroxide-precipitation cycles, using NH_3 and HCl solutions. Gas formation in the precipitate was extensive and occasionally dislodged the precipitate after centrifugation.

The hydroxide precipitate was dissolved in 8M HCl , and the Fe(III) was removed by liquid-liquid extraction using 14 v/o Alamine-336 in xylene. A vortex stirrer was used to equilibrate the aqueous and organic phases in a 12-ml centrifuge tube. Four separate extractions and three toluene washes of the aqueous phase reduced the Fe(III) and amine concentrations to a negligible level. The aqueous phase was evaporated to dryness, and the residue was dissolved in 2M HNO_3 .

The nitrate solution was analyzed spectrophotometrically for americium and curium using a Cary Model 14 spectrophotometer. The results showed 2.5 mg of curium and 0.45 mg of americium in the nitrate solution. Radiometric assay of the KAmO_2CO_3 fraction showed the presence of 0.2 mg of Cm^{242} . Thus, the yield of curium in the americium-curium separation was 93%. The final curium product contained 15% americium and 85% curium by mass, which corresponds to an alpha-activity ratio of $5.8 \times 10^3:1$ ($\text{Cm}^{242}:\text{Am}^{241}$). The flowsheets (Figs. 5 and 6) show a loss of 0.3 mg of Cm^{242} between the ion-exchange step and the americium-curium separation. This loss can be accounted for by the decay of Cm^{242} during the 35-day period between the ion-exchange column run and the completion of the americium-curium separation.

*Preliminary studies on the solubility of KAmO_2CO_3 in 3, 4, and 5M K_2CO_3 - 0.1M KOC l solutions showed that the concentration of americium in solution decreases rapidly during the first 3 hr after oxidation.

**The Fe(III) in 1M HCl was purified by anion-exchange absorption in 8M HCl .

APPENDIX

Special Equipment and MaterialsI. Containment Box

A. Construction

1. Size: 4 ft. deep, 6 ft wide, and 6 ft high
2. Materials
 - a. Aluminum floor plate and panels, painted with two coats of Amercoat No. 33
 - b. Lucite wall sheeting
 - c. PVC corner and joining materials
 - d. Unistrut reinforcing
 - e. Plywood pallet, painted with fire-resistant paint
 - f. RTV silicone caulking
 - g. Urethane gaskets on transfer port and front panel
3. Boots for Manipulators
 - a. Upper boots: PVC, 0.006 in. thick
 - b. Lower boots: Hyperlon-coated urethane
4. Double-door transfer porch: 12 x 12 x 9-in. transfer area
5. Gloves on sides and back of box for decontamination

B. Ventilation

1. Inlet filters: 12 x 12 x 6 in.; absolute filters (99.95% efficient); one filter used as spare
2. Exhaust filters: 8-in. diameter x 6 in. thick; absolute filters (99.95% efficient)
3. Negative pressure as per manometer = 0.250 in.

II. Apparatus in Containment Box

- A. Motorized laboratory jack, rod runner, rotating ringstand
- B. Steam dissolver pot
- C. Heating jacket for ion-exchange column; column remotely changeable
- D. Fraction collector, manually operated
- E. Separatory funnels, manually operated

- F. Beta-counting probe
- G. Alpha-counting probe
- H. Magnet for handling counting plates
- I. Counting-plate evaporator station
- J. Oil-filled micropipetting attachment
- K. Berkeley pipetting equipment
- L. Centrifuge
- M. Vortex stirrer
- N. Evaporator and condenser train

III. External Equipment

A. Manipulation

1. Model 8 master-slave manipulators
2. Extended-reach master-slave manipulator, used for transfers
3. One-ton-capacity crane

B. Transport

1. Radio-controlled "mule" for transport of sample and containment box⁽⁴⁾
2. Lift table for movement of containment box

C. Utilities

1. Quick-connect bulkhead and regular fittings with double-end shut-off
 - a. 1/4-in. ID for gas
 - b. 3/8-in. ID for liquids
2. Self-storing coil hose for all liquids and gases
3. CO₂ fire-extinguisher system
4. AC-DC electricity

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