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# PURIFICATION OF $^{244}$Cm AND $^{250}$Cf-$^{252}$Cf FOR RADIATION PROPERTY MEASUREMENTS

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# PURIFICATION OF $^{244}$Cm AND $^{250}$Cf-$^{252}$Cf FOR RADIATION PROPERTY MEASUREMENTS

by

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# ABSTRACT

Curium-244 was purified by cation exchange chromatography with ammonium α-hydroxyisobutyrate as the elutriant. The ~8 mg of purified $^{244}$Cm contained only 0.2 wt % $^{243}$Am and 1 x $10^{-7}$ wt % $^{250}$Cf-$^{252}$Cf. An additional cycle of cation exchange chromatography with 0.2 mg of the purified $^{244}$Cm decreased the $^{243}$Am concentration to 9 x $10^{-4}$ wt % and the $^{250}$Cf-$^{252}$Cf to <1 x $10^{-9}$ wt %. Alpha and gamma spectral analyses showed the $^{244}$Cm to be radiochemically pure. Only low concentrations of nonradioactive impurities were found by emission spectrographic analyses.

About 2.4 nanograms of $^{250}$Cf-$^{252}$Cf was purified by cation exchange chromatography, anion exchange, and solvent extraction. The purified $^{250}$Cf-$^{252}$Cf was radiochemically free of plutonium, americium, and curium. An undetermined amount of $^{249}$Bk was probably present, but it contributed insignificant alpha, gamma, and neutron radiations. No gamma-emitting impurities were detected by gamma spectral analysis.

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# PURIFICATION OF $^{244}$Cm AND $^{250}$Cf-$^{252}$Cf FOR RADIATION PROPERTY MEASUREMENTS

## CURIUM PURIFICATION

### Principle

Curium-244 for measurements of its radiation properties(1) was purified by the cation exchange chromatographic technique of Smith and Hoffman(2) because this technique will separate adjacent actinide elements. With this technique the actinides were sorbed on a few microliters of cation exchange resin that were then transferred to a column of the same resin ("Dowex" 50-X4, 200-400 mesh, $NH_4^+$ form).* The actinides were eluted in order of decreasing atomic number with ammonium α-hydroxyisobutyrate (AAHIB) except that plutonium(IV) eluted with californium. Figure 1 shows the elution profile. Transcurium elements and plutonium were eluted before curium, but americium started to elute at the curium peak.

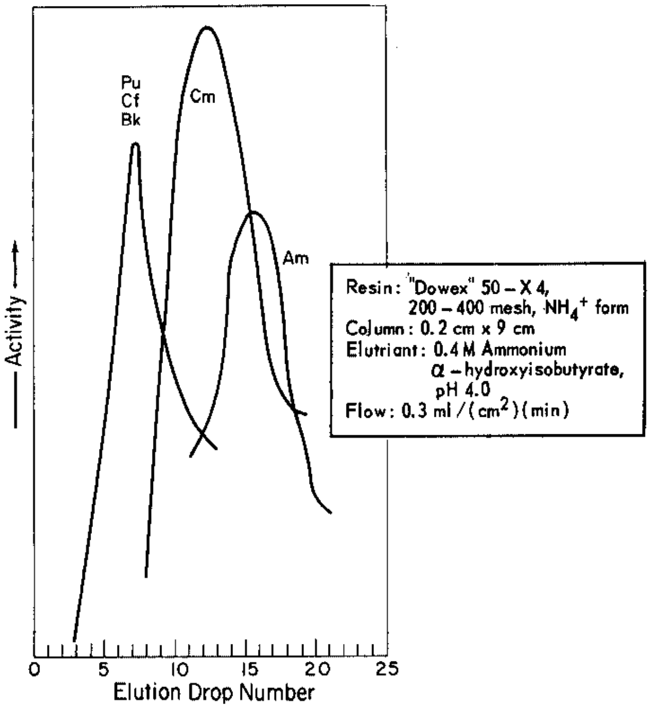

FIG. 1 ACTINIDE ELUTION PROFILE

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* "Dowex" is a trademark of Dow Chemical Co., Midland, Mich.

Curium was purified with two chromatographic cycles. The first cycle removed most of the transcurium elements and about 80% of the americium. A second cycle removed 99.5% of the americium remaining in a portion of the first cycle product.

Each resin column was loaded to one mg of curium or less, because larger loadings caused gassing that adversely affected the column performance. Also, the separation of curium from americium was poorer with larger loadings. About 30 to 50% of the curium loaded was recovered in the curium fraction; the remainder was rejected because of the americium content.

## Containment Facility

Two connected gloved boxes(3) formed the containment facility for the purifications (Figure 2). One box was for the first cycle of curium purification. This box was equipped with a high level drain for liquid waste and a feed line for introducing liquids into the box. The other box, which was kept at a lower contamination level, was for the second cycle of curium purification and the one cycle of californium purification. Both boxes were equipped with centrifuges and electrical, air, and vacuum services.

## Apparatus and Reagents

Ion Exchange Columns. The columns were similar to the one shown in Figure 3.

Cation Exchange Resin. 'Baker Analyzed' reagent-grade "Dowex" 50-X4, 200-400 mesh resin in the hydrogen form was washed successively with concentrated hydrochloric acid, distilled water, concentrated ammonium hydroxide, and distilled water. This cycle was repeated, and the resin was then washed with water until the wash was neutral. The resin was stored under distilled water.

Ammonium α-Hydroxyisobutyrate (AAHIB), 0.4M, pH 4.0. 20.82 g of α-hydroxyisobutyric acid (Eastman Organic Chemical #3025, 2-methyllactic acid) was dissolved in 450 ml of distilled water. The pH of the solution was adjusted to 4.0 by adding concentrated ammonium hydroxide. The solution was diluted to 500 ml with distilled water and was passed through a column of "Dowex" 50-X8, 200-400 mesh, $NH_4^+$ form cation exchange resin to remove cationic impurities. Finally, the pH of the solution was measured and readjusted if necessary.

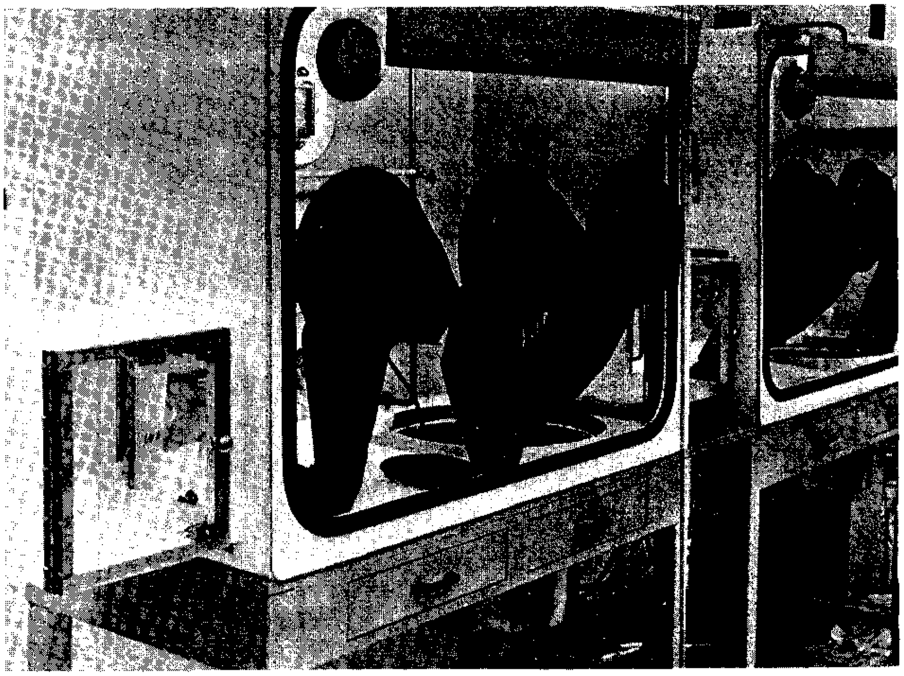

FIG. 2 CONTAINMENT FACILITY

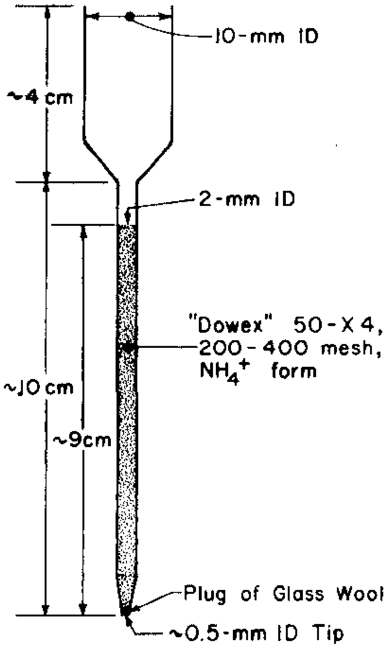

FIG. 3 COLUMN FOR CATION EXCHANGE CHROMATOGRAPHY

*Curium Stock Solution.* The curium stock solution contained about 40 mg of curium in 2 ml of 1-2M $HNO_3$. This curium, a product of the Transuranium Program,(4) had been treated (1) to remove plutonium by anion exchange, (2) to lower the fission product content by precipitating double sulfates, and (3) to remove lanthanides by the Tramex process.(5) Americium in the curium had been reduced to 1 wt % by double carbonate precipitation of Am(V); the $^{250}Cf$-$^{252}Cf$ content was $1 \times 10^{-4}$ wt %.

### Procedure

*Preparation of Resin Column.* The column was packed with washed resin. Before use, the resin column was washed with two 3-ml portions of 0.4M AAHIB. After washing, the flow was 2.5 to 3 minutes per drop. The drop volume was about 25 µl. Flow was stopped with a clamped piece of "Tygon"* tubing on the tip.

*First Purification Cycle.* Twenty-four aliquots of the stock solution were purified by the following procedure:

> From the stock solution, an aliquot containing about 1 mg of $^{244}Cm$ was added to 2 ml of water in a 15-ml centrifuge cone. To the cone was added about 50 µl of "Dowex" 50-X4, 200-400 mesh, $NH_4^+$ form cation exchange resin and 1 ml of water to wash the resin down the side of the cone. The cone was centrifuged, and the resin and solution were mixed several times to equilibrate the ions with the resin. The cone was centrifuged again, the supernate was removed, and about 1 ml of water was added to the resin.
>
> All AAHIB over the resin in the prepared column was removed, and the water-resin mixture in the cone was transferred to the column with a pipet. The cone and pipet were washed with 0.5-1 ml of water, and this wash was added to the column. The column was vibrated with a "Vibro-Graver"** to dislodge resin beads on the side of the column, and the liquid over the resin was removed. Following these operations, the column was filled with 0.4M AAHIB, and the elution was begun. Three fractions were collected: Pu-Cf-Bk fraction (Drops 1 through 9); Cm fraction (Drops 10 through 16); Am fraction (Drops 17 through 20).

One resin column was used for six aliquots. After each aliquot was eluted, the column was flushed with 1 ml of AAHIB, agitated with a wire to remove bubbles, and flushed again with 1 ml of AAHIB. About 50 µl of resin was removed to make room for the resin containing the next aliquot.

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* Trademark of U. S. Stoneware Co., Akron, Ohio.

**Product of Burgess Vibrocrafters, Inc., Grayslake, Ill.

The 24 curium fractions were combined, evaporated to incipient dryness, and evaporated three times with concentrated nitric acid to destroy the AAHIB. The residual solution was diluted to 4 ml with 1M $HNO_3$. This product solution of the first purification cycle was found by alpha analysis to contain 7.8 mg of $^{244}$Cm.

Second Purification Cycle. From the 7.8 mg of $^{244}$Cm, 0.2 mg was further purified by a second cycle of cation exchange chromatography with a single elution. Each drop of the curium fraction (Drops 12 through 19) was collected in a separate 15-ml centrifuge cone and was diluted to 1 ml with 1M $HNO_3$. After a $10^5$ dilution, the $^{244}$Cm content of each drop was determined by alpha counting. Some of the 1-ml dilutions were used in further analyses; others were reserved for measurements of the radiation properties of curium.(1)

## CALIFORNIUM PURIFICATION AND ANALYSIS

The 24 Pu-Cf-Bk fractions from the first purification cycle were combined, evaporated to about 0.5 ml, and then evaporated three times with concentrated nitric acid. Curium in these combined fractions was removed with one cycle of cation exchange chromatography with AAHIB as the elutriant. After curium removal, the elutriant was adjusted to 8M $HNO_3$, and plutonium was absorbed on "Dowex" 1 anion resin. Alpha spectral analysis of the californium solution did not detect other actinide alpha emitters. However, gamma spectral analysis revealed the presence of $^{152}$Eu, $^{154}$Eu, and $^{95}$Zr, which then were separated from the californium by a laboratory-scale Tramex solvent extraction.(5)

At this point, the solution contained $1.79 \times 10^6$ dis/min of $^{252}$Cf and $3.60 \times 10^5$ dis/min of $^{250}$Cf (1.2 ng of each californium isotope). Analysis showed the $^{250}$Cf-$^{252}$Cf to be free of other alpha- and gamma-emitting nuclides.

## ANALYSIS OF PURIFIED CURIUM

Table I (page 12) lists the amounts of $^{244}$Cm in the fractions collected.

### Curium from First Purification Cycle

Californium Content. The amounts of $^{252}$Cf and $^{250}$Cf in the californium fraction from the second curium-purification cycle were determined by alpha pulse height analysis. Since these measured amounts of californium were associated with about 0.2 mg of curium in the first

TABLE I

Purified Curium Fractions

| Fraction | Drop No. | Total $^{244}$Cm, dis/min | Total $^{244}$Cm, μg |
|---|---|---|---|
| First cycle (24 fractions combined) | - | $1.45 \times 10^{12}$ | 7800 |
| Second cycle | 12 | $6.38 \times 10^{8}$ | 3.4 |
| | 13 | $3.66 \times 10^{9}$ | 19.7 |
| | 14 | $4.22 \times 10^{9}$ | 22.7 |
| | 15 | $6.08 \times 10^{9}$ | 32.7 |
| | 16 | $8.68 \times 10^{9}$ | 46.7 |
| | 17 | $9.83 \times 10^{9}$ | 52.8 |
| | 18 | $6.30 \times 10^{9}$ | 33.9 |
| | 19 | $6.47 \times 10^{8}$ | 3.5 |

cycle product, the following ratios were calculated:

$$\mu g\ ^{252}Cf/\mu g\ ^{244}Cm = 5 \times 10^{-10} \text{ and } \mu g\ ^{250}Cf/\mu g\ ^{244}Cm = 5 \times 10^{-10}$$

Therefore, the californium content of the first cycle product was $1 \times 10^{-7}$ wt %.

Americium-243 Content. An aliquot of the solution containing the 7.8 mg of $^{244}$Cm from the first purification cycle was analyzed for $^{243}$Am by the calcium fluoride method(8) with the yield corrections based on $^{241}$Am. This analysis showed the $^{243}$Am content to be 0.2 wt %.

Alpha Pulse Height Analysis. Alpha spectral analyses showed only the following:

| | % of Total Alpha Disintegrations |
|---|---|
| $^{244}$Cm | 94.5 |
| $^{242}$Cm | 5.5 |

Emission Spectrographic Analysis. Table II lists average results of duplicate determinations on 200-μg samples.

### TABLE II

Spectrographic Analysis of Curium from First Purification Cycle

| Element | Concentration, ppm |
|---|---|
| Ca | 60 |
| Zn | 50 |
| Ce | <50 |
| La, P, Zr | <25 each |
| Al, Na | 10 each |
| Ba, Sn | <10 each |
| Mg | 5 |
| Cs, Cr, Fe, Mo, Nb, Ni, Pb, Sb | <5 each |
| Si | 3 |
| Bi, Ti | <3 each |
| Li, Mn | <1 each |
| Ag, B | <0.5 each |
| Be | <0.01 |

### Curium from Second Purification Cycle

Americium-243 in Drops 13 and 14 Combined. Drops 13 and 14 were combined to give 42.4 μg of $^{244}$Cm. Part of this material was submitted for mass spectrometric analysis; the remainder was analyzed for $^{243}$Am(6) and was found to contain 9 x $10^{-4}$ wt % $^{243}$Am.

Americium in Drop 15. The curium (32.7 μg) in Drop 15 contained 5 x $10^{-3}$ wt % $^{243}$Am.

Gamma Pulse Height Analysis. Drop 12 was analyzed in a 5" x 5" NaI(Tl) well crystal with a multichannel analyzer. Only the curium gamma activities were detected.

Alpha Pulse Height Analysis. An electrodeposited mount containing 3.30 x $10^4$ alpha dis/min from Drop 12 was analyzed with a silicon surface-barrier alpha counter and a multichannel analyzer. Of the total alpha disintegrations, 94.8% were from $^{244}$Cm and 5.2% were from $^{242}$Cm.

Mass Spectrometric Analysis. Three aliquots of Drops 13 and 14 combined were analyzed with twelve scans of each aliquot. Table III gives the average results at the two sigma limit.

TABLE III

Mass Spectrometric Analyses of Curium

| Mass | Abundance, wt % |
|---|---|
| 242 | 0.12 ±0.006 |
| 243 | 0.03 ±0.002 |
| 244 | 95.5 |
| 245 | 1.6 ±0.05 |
| 246 | 2.7 ±0.01 |
| 247 | 0.04 ±0.01 |
| 248 | 0.04 ±0.01 |

Californium. Although $^{250}$Cf-$^{252}$Cf was not determined, the total californium was estimated to be <1 x $10^{-9}$ wt % based on the separation achieved in the first purification cycle.

## ACKNOWLEDGMENT

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