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FINAL PURIFICATION OF THE HEAVY ACTINIDES FROM THE FIRST FOUR CAMPAIGNS OF THE TRU PROGRAM

R. D. Baybarz and P. B. Orr

ABSTRACT

Special glassware equipment was fabricated to isolate the transplutonium elements from the first four campaigns of the TRU program. The processing included LiCl-anion exchange for inner actinide group separation, chromatographic elution from a cation-exchange column for Cf isolation, and solvent extraction for berkelium purification. A total of 76 grams of ^{244}Cm was processed to recover 2.3 mg of ^{252}Cf and 0.2 mg of ^{249}Bk .

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INTRODUCTION

Because of the pressing need for the transcurium elements, two equipment racks containing temporary glassware were constructed and installed in Cubicle 5 of the TRU Facility to make possible the isolation of these elements at the earliest possible date. This equipment included ion-exchange columns, a precipitation vessel, a bowl-type centrifuge, an evaporator, and a vacuum system for transferring liquids and filtration.

Prior to the final purification steps, as described in this report, the target material was initially processed by the TRU Operations Group in the following manner:

1. The Al-actinide targets were dissolved in NaOH- NaNO_3 and the Na_3AlO_3 was filtered off.
2. The actinide oxides were dissolved in either HNO_3 -HF or HCl.
3. The Pu was removed by ion exchange or solvent extraction.
4. The fission products were removed by solvent extraction⁽¹⁾ (Tramex Process).

This processing is reported in references 2 and 3.

From September 1966 to May 1967 four groups of targets were processed in four campaigns:

1. Four HFIR prototype targets, which originally contained 9.57 g ^{242}Pu each, were irradiated at Savannah River Laboratory and discharged from the reactor in February and March of 1966.
2. Three SRL type slugs (P-2, P-5, and P-8), which originally contained 33.82 g ^{242}Pu each, were discharged in October of 1966.
3. Three SRL type slugs (P-1, P-6, and P-7), which originally contained 33.82 g ^{242}Pu each, were discharged in February and March, 1967.
4. Five HFIR targets (56-A, 6-A, 10-A, 34-A, and 35-A), which originally contained 9.57 g ^{242}Pu each, were irradiated both at SRL and in the HFIR. These were discharged from the HFIR in March of 1967 because of rupture of the target element.

The targets processed in each succeeding campaign contained increasingly larger amounts of the transcurium elements per gram of starting ^{242}Pu .

DESCRIPTION OF EQUIPMENT

Two metal racks, 69" x 34" x 16.5", containing the glassware used for final processing of the heavy actinides were installed in Cubicle 5. Fig. 1 is a photograph of the rack placed in the right-hand side of the cubicle and containing 12 four-liter pyrex vessels 5" I.D. x 13", and 4 two-liter pyrex pots 5" I.D. x 7". A bowl-type centrifuge and a small vacuum pump are also mounted in this rack. The metal strips shown in front of each row of glass pots are the mounting brackets for the dip leg valves for each of the pots as well as 1 or 2 special vent line valves.

The equipment was fabricated to do a multitude of operations by using the glass pots as feed, receiving, and storage vessels. Each pot was equipped with a dip leg and a vent line, and by proper connection with jumper lines it was possible to precipitate, centrifuge, filter, evaporate, condense, and solvent extract. Several of the vessels were modified for particular operations.

The precipitation vessel was equipped with a bottom drain and valve and had a spray ring mounted in the top to facilitate washing the sides of the vessel.

The evaporator had an internal flat quartz coil mounted in the bottom of the vessel, enclosing a 600 watt coil of Nichrome wire submerged in transformer oil, which was used to heat the solutions. A water cooled condenser was used to condense the distilled vapors.

The centrifuge was a variable speed, bowl-type centrifuge into which solids from the precipitation vessel were discharged.

A small laboratory diaphragm type vacuum pump was used for liquid transfer and filtration. A soda-lime trap was used ahead of the pump to prevent vapors from corroding the pump mechanism.

The left-hand rack is shown in Fig. 2. This rack contains 8 collection vessels, one anion-exchange column, and two longer cation-exchange columns. A circulating hot water bath and finger pump are

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Fig. 1. TRU Feed Adjustment Rack.

Fig. 2. TRU Ion Exchange Rack.

located at the bottom. The vertical metal strip at the right side of the rack is the mounting for the plastic dip leg valves for all the collection vessels.

Anion-Exchange Column. This was a hot water jacketed vessel 1 1/2" I.D. x ~2' long. The actual resin bed was 1 1/2" x 16", supported at the bottom by a sintered glass frit. Since this column was normally used in a high-molarity LiCl system, it was necessary to have a restraining barrier at the top to prevent the resin from floating, as well as to prevent the movement of the resin by radiolytic gas bubbles while large quantities of actinides were being processed. This restraint was accomplished by first loading the column with the desired resin in the proper amount (~450 ml volume). A thin mat of glass wool was then placed on the resin, followed by an 80 mesh Pt screen disk. The glass wool prevented the resin from seeping past the screen. On top of the screen, 2 to 3 in. of ~1/8" glass beads served as a restraining weight. Fig. 3 is a photograph of a typical column with resin restraint. In addition to the above reasons for restraining the resin, the screen served to keep the resin bed flat which is a necessity for good band formation. The top of the column had a solution inlet and a vent for the release of pressure.

Cation-Exchange Column. Although two of these columns are shown in the photograph, only one was ordinarily used. The column was 1" I.D. with a resin bed about 20" long (~250 ml volume) and had a hot water jacket. Although the resin used in this column did not float in the eluant or loading solution, it is a good practice to use a restraining barrier on top, particularly if very large quantities of actinides are to be loaded. The restraint prevented movement of the resin by radiolytic gasses and also maintained a flat resin bed. The top of the column had an inlet line and vent.

Concentration Column. This column is not shown in the photograph. It was a column ~1" I.D. with a bed length of ~6 in. It did not have a water jacket nor a restraining barrier since chromatographic separation was not accomplished here.

Collection Vessels. These were 8 two-liter pyrex pots, each with a vent and dip leg. Column fractions were stored in these.

Fig. 3. Typical Column with Resin Restraint.

Circulating Hot Water Bath. This was a thermostatically controlled bath with a capacity of ~2 liters. It was used to maintain the temperature of the ion-exchange columns at 80°C.

Finger Pump. This was a controlled flow device used primarily to transfer liquids to the columns. The pumping action was obtained by the action of metal fingers pressing on a plastic tube. The flow could be varied by varying tube size and also motor speed. This pump was reliable and built up a positive pressure of 10-15 psi.

Alpha Flow-Through Detector. This device is shown in Fig. 4 which is a photograph of the detector with the flow-through chamber removed. The assembled alpha detector is shown in Fig. 5. The column effluent passed through the detector which activated a count rate meter and recorder outside the cell. As the alpha-active material was eluted from the column and passed through the detector, the count rate meter indicated its presence. The various column fractions were determined in this manner. Although there was considerable attenuation of alpha activity by the mylar window of the detector, energies above ~5 Mev were easily detected.

Neutron Probe. The neutron probe was a silicon diode detector with a polyethylene face, and it was possible to detect the presence of neutrons by an α , p reaction. This device with a count rate meter was used to follow the ^{252}Cf band progress on the column and to detect Cf in solutions.

FLWSHEET

The flow diagram for each step in the cubicle 5 processing is shown in Fig. 6. This overall flowsheet is broken down into four individual processing flowsheets as follows:

1. Fig. 7 - The transplutonium element partitioning by LiCl-anion exchange.
2. Fig. 8 - The Cf isolation by chromatographic elution with α -hydroxyisobutyrate on a cation column.
3. Fig. 9 - The Bk isolation by selective extraction of tetra-valent Bk.

PHOTO 88408

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Fig. 4. Alpha Flow-Through Detector Disassembled.

Fig. 5. Alpha Flow-Through Detector.

Fig. 6. Flow Diagram of Transplutonium Element Isolation.

Fig. 7. Transplutonium Element Partition by LiCl Anion Exchange.

Fig. 8. Californium Isolation by Elution with α -hydroxyisobutyrate on a Cation Resin Column.

Fig. 9. Berkelium Isolation by Selective Extraction of Bk⁴⁺.

4. Fig. 10 - The Am-Cm separation by precipitation of Am-K double carbonate.

DESCRIPTION OF THE PROCESSING

LiCl Anion Exchange

A TrameX product, supplied as an evaporated solution from the strip column, was feed-adjusted and processed by LiCl-anion exchange⁴ using the flowsheet shown in Fig. 7. The predominant radioactive contaminants were ¹⁰³⁻¹⁰⁶Ru and ⁹⁵Zr with smaller amounts of rare earth activity. Ionic contaminants included Zr, Cr, Fe, Ni, and Sn. The principal ionic contaminant, zirconium, was evidenced as suspended white solids and appeared to be primarily colloidal zirconia. Filtration was required to remove this material from solution. The solids were primarily zirconia containing significant amounts of tin and nickel, but the solids did not contain an appreciable amount of radioactivity. The precipitate was difficult to filter and was not readily soluble in concentrated HCl but could be dissolved in HNO₃-HF.

The TrameX product, which contained 2-6 M LiCl, was concentrated to 12.5 M LiCl by evaporating to a temperature of 137°C. Following acid adjustment to 0.1 M HCl, it was necessary to refilter the adjusted feed since additional zirconia precipitated during concentration.

Feed containing 4 to 10 g of curium plus lesser amounts of Am, Bk, and Cf was passed through an anion-exchange column of Dowex 1-10X resin (200-300 mesh). The actinides and many of the contaminants loaded on the anion resin from 12.5 M LiCl. In order to obtain satisfactory separation the actinides had to be loaded in no more than the top 20% of the resin bed. The location of the actinides was determined by means of the in-cell neutron probe. Curium losses in the feed effluent were less than 0.01%. Most of the nickel and rare earths were eluted from the resin with 5 to 8 column displacement volumes of 10 M LiCl-0.1 M HCl-0.1 M NH₂OH·HCl-5 v/o CH₃OH. Hydroxylamine was used to maintain cerium in the trivalent state, and methanol was used to suppress radiolytic gas formation.⁵ Elution with this solution was continued until an

Fig. 10. Americium-Curium Separation by Precipitation of K-Am Double Carbonate.

increase in alpha activity was noted in the effluent. Curium losses to this wash were less than 1.0%.

The profile of alpha activity in the eluate as indicated by the in-line alpha monitor for a typical run is shown in Fig. 11. As soon as an increase in alpha activity was detected in the eluate, the eluting solution was changed to 9 M LiCl-0.1 M HCl. Elution was continued until about 90% of the curium was eluted (See Fig. 11). The eluting solution was then changed to 8 M LiCl-0.1 M HCl. At the beginning of this elution, the californium band was determined by neutron detection to be at the top of the column. Elution with 8 M LiCl was continued until the californium band approached the bottom of the column, at which point the eluting solution was changed to 8 M HCl, and the remaining actinides were stripped off the resin column. This elution sequence provided an americium-curium fraction nearly free of ionic and radioactive contaminants and with no detectable berkelium or californium. The americium-curium-berkelium fraction contained about 10% of the americium and curium and about 60% of the berkelium. The remaining berkelium was eluted with the californium fraction along with ~0.5% of the americium-curium. Although berkelium is not obtained in a single product fraction, this elution sequence gives product fractions that are amenable to final isolation of the elements in subsequent processing. In a typical feed, the curium to californium mass ratio was about 2×10^4 to 1. This was reduced to about 100 to 1 in the californium fraction providing a curium decontamination factor of about 200. Elution of californium with 8 M HCl afforded excellent decontamination from many contaminant ions which form chloride complexes. Contaminants such as Fe, Sn, Zr, and Pu^{+4} remain on the column but can be stripped with 0.5 M HCl.

The anion resin was not adversely affected by a single run, and 2 or 3 runs could be made before radiation induced discoloration was detectable. The resin was changed after three runs although it might have been possible to use it somewhat longer.

Californium Isolation

The flowsheet for californium isolation from the berkelium-californium product fraction is shown in Fig. 8. This product which

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Fig. 11. Profile of Alpha Activity in Eluate from LiCl Anion Exchange Column.

contains HCl and LiCl must be converted to a low-acid feed for the butyrate column. Lithium chloride was removed by precipitating metal hydroxides, washing, and redissolving in hydrochloric acid. In order to insure complete precipitation, about 50 mg of iron per liter of solution was added as carrier. The metal hydroxide was filtered, washed, and dissolved in a small volume (~25 ml) of 8 M HCl. Iron was removed by passing this solution through a small anion column which preferentially sorbs iron while the actinides pass through the column. The acid concentration of the column effluent was reduced by evaporating to a small volume, and adding sufficient HCl to produce a final solution of ~50 ml at an acidity of 0.05 to 0.1 M.

This feed was passed through the 30 inch cation column which was packed with about 250 ml Dowex 50-12X resin (sized to about 200 mesh) in the ammonium form. The actinides loaded in a tight band at the top of the column. Separation was obtained by chromatographic elution from the resin at 80°C with α -hydroxyisobutyrate solutions.⁶ The progress of the elution was followed by means of the neutron detector to locate californium on the resin column and by means of the in-line alpha detector to properly select the product fractions. Initial elution with 0.4 M α -hydroxyisobutyrate at pH 4.2 was continued until the neutron activity reached the bottom of the column and alpha activity started to appear in the eluate. This required about 800 ml of solution. The elution was then continued with 0.4 M α -hydroxyisobutyrate at pH 4.8 until all the berkelium, americium, and curium were eluted. This required about 500 ml of solution.

The product fractions in butyrate solutions were converted to acid solutions by cation exchange. The butyrate solutions were acidified to pH 1.0 and passed through small columns of Dowex 50-4X resin to load the actinides. The resin columns were washed with 0.2 M acid to remove residual butyrate, and the actinides were stripped into 6 to 8 M acid. Californium stripped into HCl represents a purified product fraction. The berkelium-curium-americium fraction was stripped in 8 M HNO₃ which is convenient for subsequent berkelium isolation.

Berkelium Isolation

The process outlined in Fig. 9 was used to isolate pure berkelium from the americium-curium-berkelium fractions from both the LiCl anion exchange columns and from the californium isolation column. Berkelium from the LiCl column was precipitated as the hydroxide to remove residual LiCl. The curium content in this fraction provided sufficient carrier to insure complete berkelium precipitation. The precipitate was washed and dissolved in 8 M HNO_3 , which is a suitable medium for oxidation and extraction of berkelium.

Berkelium was oxidized to the tetravalent state by the addition of 0.5 M NaBrO_3 . The feed solution was allowed to stand 15 minutes to insure complete oxidation, and the berkelium was then selectively extracted into 1 M di(2-ethylhexyl)phosphoric acid (HDEHP) in decane.⁷ The organic solvent was pretreated with 8 M HNO_3 -0.5 M NaBrO_3 to remove all reducing impurities. The feed solution was contacted twice with equal volumes of solvent. The organic phases were combined and scrubbed twice with equal volumes of 8 M HNO_3 -0.5 M NaBrO_3 . Berkelium was stripped from the solvent by two consecutive half-volume contacts with 8 M HNO_3 -0.1 M H_2O_2 , which reduced berkelium to Bk^{+3} . Two solvent extraction cycles are required to produce a pure berkelium product. A curium decontamination factor of about 10^5 was accomplished in each extraction cycle, and the final product was free of detectable alpha contamination.

Americium-Curium Separation

Ordinarily in TRU processing the americium and curium are used as a mixture for recycling to the HFIR. The process shown in Fig. 10 was used to separate some of the americium and curium for use in research. The mixed americium-curium was precipitated as hydroxide to remove lithium chloride. Ammonium hydroxide was used in order to obtain additional decontamination from nickel. The hydroxides were washed and then dissolved in a small volume of 0.5 M HNO_3 . This solution, containing up to 10 g of americium plus curium, was added with vigorous agitation to one liter of 5 M K_2CO_3 . The trivalent actinides formed soluble carbonate complexes. By adjustment of the solution to 0.1 M $\text{K}_2\text{S}_2\text{O}_8$ and digestion

for 3 hours at 80°C, the americium was quantitatively oxidized to the pentavalent state, which forms an insoluble double carbonate, $K_5AmO_2(CO_3)_3$.⁸ The precipitate was filtered, washed with 0.5 M K_2CO_3 , and dissolved in 0.5 M HNO_3 . This product contained 98% of the americium and about 2% of the curium, and a second precipitation cycle was used if additional americium purification was required. Americium oxide was prepared by precipitating the oxalate with oxalic acid and calcining at 800°C. Americium separated from curium by two successive precipitation cycles and converted to the oxide contained as little as 0.005 wt% curium and ~1 wt% calcium.

Curium in the carbonate filtrate was recovered by precipitation with 1 M NaOH. It was found that NH_4OH would not precipitate curium hydroxide quantitatively from K_2CO_3 solution. Curium losses in the filtrate following precipitation with excess NaOH were less than 0.1%. The curium hydroxide was filtered, dissolved in 0.5 M HNO_3 and reprecipitated with oxalic acid. The curium oxalate was calcined at 800°C to yield curium oxide. The resultant oxide contained ~2 wt% ^{243}Am and ~1 wt% Ca.

Run Summaries

The normal flowsheet for the isolation of the transplutonium elements is shown in Fig. 6; however, the feed material for this processing was not always uniform (particularly during the 1st campaign) and variations were made in this flowsheet.

The four HFIR prototype targets were processed by TRU Operations in three runs.

1. Run 2-TR3 involved one rod containing an initial 9.6 g ^{242}Pu . The solution received in Cubicle 5 contained some organic extractant and relatively large quantities of Fe, Cr, Ni, and Zr corrosion products. Prior to the anion exchange step, the actinides were precipitated as the hydroxides, with NH_4OH , to reduce volume and the bulk of the Li and Ni. The hydroxides were dissolved in HNO_3 , and the solution was adjusted to 8 M in $LiNO_3$ and loaded on the Dowex 1 X-10 column, which had been preconditioned with 8 M $LiNO_3$ and heated to 80°C. The bulk of the Cr was removed in the loading raffinate and a 8 M $LiNO_3$ wash. The actinides were eluted together with 4 M HNO_3 . A

feed adjustment converting the nitrates to chlorides was made prior to the normal LiCl anion exchange separation. Subsequent operation of the nitrate column proved this method to be potentially hazardous as is discussed in the section on radiation effects.

2. Run 2-TR⁴ solution was a dissolving of 3 HFIR targets and was received as a HNO₃ solution containing some LiNO₃. A feed adjustment step was necessary to convert this material to the chloride form, prior to the LiCl anion exchange step.
3. Run 2-TR5 was a cleanup run; the solution had been put through an experimental berkelium extraction step by TRU Operations, and was HNO₃ solution as received in Cubicle 5. A nitrate-to-chloride feed adjustment was made prior to the LiCl-anion exchange separation.
4. Run 3-TRL solution was a dissolving of the first three SRP slugs. Because of equipment difficulties in the Pu removal cycle, the bulk of the actinides were received in Cubicle 5 as 3-TR2. However, two batches of 3-TRL were received, the first of which was purified through the normal flowsheet. The second batch contained some organic extractant from Tramex. This organic phase was removed and the aqueous solution was put through the normal processing. In the 0.5 M HCl strip of the LiCl-column, about 0.6 g of ²⁴²Pu was recovered.
5. Run 3-TR2 solution was received in two batches, both of which were purified by the normal flowsheet.
6. Run 3-TR3 solution was received in three batches. This was done to limit the loading on the LiCl-column to no more than 10 g of ²⁴⁴Cm per batch, because of column size and resin volume limitations. The first two batches were processed using the normal flowsheet. The third batch, because of difficulties encountered in the Tramex cycle, contained an abnormal quantity of corrosion Zr and some organic extractant. It was necessary to return this material to TRU Operations for removal of organic phase and filtration. This was done and the solution was returned to Cubicle 5. During the evaporation (feed adjustment) step prior

to loading on the LiCl-column, extreme foaming was observed, which prevented a complete volume reduction. The separations obtained on this LiCl anion column were very poor, making recycle of the actinides necessary. The causes of the separations failure were thought to be: (a) Too large a feed loading volume, resulting in a lengthy loading time, (b) Abnormal quantity of Zr which diluted and lengthened the loading band, and (c) Instrument failure in the flow-through alpha detector. The actinides were recycled with no further difficulty.

7. Run 3-TR⁴ solution was the fourth portion from the second three SRP slugs. Because of the large quantity of Zr in 3-TR³, a special Zr removal solvent extraction step had been made on this material by TRU operations after it had been through the Tramex cycle. This resulted in a much superior feed for Cubicle 5 processing. Only one filtration was required prior to loading on the anion column.
8. Run 4-TR¹ involved the five ruptured HFIR targets. This material had a Zr removal step before it was transferred to Cubicle 5. Normal flowsheet procedure was used.

RADIATION EFFECTS

At least one of the radiation effects observed during the four campaigns was an aid in the LiCl-anion-exchange separation of the Cm. The characteristic orange-red glow of the Cm on the resin (observed when cell lights were extinguished) was followed frequently during elution. Using this information and the peaks shown on the alpha flow-through detector, better fraction determinations were made. It was noted that when the anion column was first loaded, this glow could not be seen. After one or two column volumes of 10 M LiCl were put through and the Ni impurity was eluted ahead of the Cm, the glow appeared, indicating that the dark green Ni color masked the Cm glow. During elution of the Cm peak from the anion column and with the cell lights

cut off, the plastic tubing lines and the Cm collection vessels glowed very brightly. The lines had the appearance of Neon tubing.

Because of darkening of the resin in the anion-exchange column, the resin was not used for more than three runs. This resin discoloration was damage caused by the intimate Cm alpha radiation (up to ~30 g in three runs), and by the gamma activity from the residual Ru and Zr not completely removed in the Tramex process. The accumulative dosage to the resin would be on the order of 300 watt-hrs. Although no tests were made to determine crosslinkage damage, increases in elution volumes were noted for each successive run, particularly if the amount of actinides per run was close to 10 g. The alpha damage occurred primarily during the loading period while the actinides were static on the resin. The gamma damage was a continuing effect, since much of the Ru was fixed irreversibly in the resin.

During a nitrate anion exchange resin purification of about 8 grams of ^{244}Cm , an exothermic reaction occurred resulting in a shattering of the glass ion exchange resin column. The resulting reaction was more of an explosive nature rather than a gradual buildup of pressure and breakage of the column. It is believed that the heat from the decay of ^{244}Cm along with the nitrate solution caused a nitration of the resin. The localized heating from the ^{244}Cm caused a rapid exothermic reaction which resulted in a detonation.

Cation-exchange resin deterioration was not as significant a problem as that of the anion-exchange resin, because of the relatively small amounts of Cm loaded. The anion-exchange column separation reduced the Cm mass by a factor of 100 or more.

Cm in LiCl or HCl solutions was self-precipitated unless the solutions were periodically acidified.⁵

RESULTS

The overall ^{244}Cm material balance through Cubicle 5 for the four campaigns was 100.57% (Table 1). It will be noted that under the column labeled "Received from TRU Operations," only Cm is listed. The difficulties of analyses for the other elements, particularly in the presence of large quantities of ^{244}Cm , makes it impractical to obtain these.

Table 1. Transplutonium Element Isolation

Element	Received from TRU Operations	Recycle to TRU Operations	Known Losses	Isolated	Material Balance
Einsteinium-253				4.2 μ g	
Californium-252				2,345 μ g	
Berkelium-249				200 μ g	
Curium-244	78.53g	2.23g	0.57g	76.18g	100.57%
Americium-243 separated from 244Cm.				3.6g	

Table 2 shows the purity of a typical product.

Table 2. Typical Product Purity

Element	Material Form	Radioactivity	Ionic Contaminants
^{243}Am	AmO_2	^{239}Np daughter activity. No fission products detected. One gram measures ~ 50 r/hr gamma unshielded. With $3/8$ " lead shielding the γ activity is < 50 mr/hr.	$\sim 0.005\%$ ^{244}Cm $\sim 1-2\%$ Ca $< 1\%$ K
^{244}Cm	CmO_2	^{243}Cm gamma, spontaneous fission gamma. No fission product activity detected. One gram measures ~ 1 r/hr of fast neutrons, and ~ 200 mr/hr of gamma activity.	$\sim 2\%$ ^{243}Am $\sim 1\%$ Ca $\sim 1\%$ K
^{249}Bk	$\text{Bk}(\text{NO}_3)_3$ solution	^{249}Cf α and γ . No other transuranium element α activity. No fission product γ activity detectable.	None detectable.
^{252}Cf	CfCl_3 solution	Spontaneous fission gamma and neutron activity. One μ gram ^{252}Cf measures ~ 500 mr/hr fast neutrons, ~ 300 mr/hr γ activity.	None detectable.

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