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LineCHROMATOGRAPHIC CATION EXCHANGE SEPARATION OF DECIGRAM
QUANTITIES OF CALIFORNIUM AND OTHER
TRANSPLUTONIUM ELEMENTS*D. E. Benker, F. R. Chattin, E. D. Collins, J. B. Knauer
P. B. Orr, R. G. Ross, and J. T. WigginsStart First _____ 35
Page Here.Oak Ridge National Laboratory
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Oak Ridge, TN 37830**MASTER**

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CHROMATOGRAPHIC CATION EXCHANGE SEPARATION OF DECIGRAM
QUANTITIES OF CALIFORNIUM AND OTHER
TRANSPLUTONIUM ELEMENTS

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D. E. Benker, F. R. Chattin, E. D. Collins, J. B. Knauer
P. B. Orr, R. G. Ross, and J. T. Wiggins

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High pressure cation exchange is used routinely at the Transuranium Processing Facility (TRU) to separate decigram quantities of transplutonium elements that have been produced in the High Flux Isotope Reactor. The process is based on chromatographic elution from Dowex 50W-X8 resin using ammonium alpha-hydroxyisobutyrate (AHIB) as the eluent (1). Since 1967, a total of 4.6 g of ^{252}Cf , 0.5 g of ^{249}Bk , 19 mg of ^{253}Es , and 10 pg of ^{257}Fm (estimated) have been separated at TRU using this procedure. Original development of this process at ORNL was done by Campbell and Buxton (2,3), and was later adapted for processing at high activity levels at TRU by Baybarz, et al (4). The use of high pressure with very small resin has helped mitigate two problems associated with processing highly-radioactive solutions of transplutonium elements. First, radiation damage is reduced since higher flow rates and quicker separations are possible; and second, radiolytic gassing is suppressed.

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This paper will discuss the equipment and process steps used in the initial separation of transplutonium elements and list some typical results.

Equipment

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The ion exchange equipment is located on a metal rack (1.8 m x 0.9 m x 0.4 m) in one of the TRU hot cells, and is maintained and operated with two master-slave manipulators that penetrate the 1.4-meter-thick shielding wall. A flow diagram is shown in Fig. 1.

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A positive-displacement pump (Beckman Accuflo No. 312880), powered by an in-cell electric motor, is used to transfer eluent through the chromatographic column. The column is 13.4 mm in diameter by 1.2 m high, filled with 145 mL of resin, and is jacketed for heating to about 70°C with hot water. Usually, hot water for equipment in the hot-cells is recirculated; however, in this case, the operating pressure of the column (up to 5 MPa) is higher than the water pressure in the jacket (0.4 MPa) and if a leak were to develop in the column wall, radioactive process solution would be forced into the jacket. In order to protect personnel from a potentially serious radiation hazard, the water from the jacket is discharged to a tank used for collecting radioactive waste solutions, even though under normal operating conditions the water is not contaminated.

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A separate column, 14 mm in diameter and 0.2 m high, is used for the initial loading of the feed solution, which is

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50 transferred from a vacuum-pressure pot (about 1 liter in volume). This column contains 35 mL of resin and is not jacketed.

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Both ion exchange columns, the vacuum-pressure pot, and the piping and valves used to interconnect the pump, vacuum-pressure pot and the columns are all made of stainless steel. The resin bed in each column is held by a stainless steel frit (5 μ m) in the bottom fitting on each column.

Start First _____
Page Here.35 A flow-through alpha-detector in the column effluent line is used to monitor the progress of an elution, and a movable neutron probe is used to determine the location of the ^{252}Cf band. (Other transplutonium isotopes in TRU solutions generate neutrons, but the quantity is trivial when compared to the neutrons from mg quantities of ^{252}Cf .) Both detectors are silicon surface-barrier diodes (supplied by Harshaw or ORTEC) (5), and are wired to separate count rate meters and recorders outside of the hot cell. The diode for the neutron probe is covered with a thin piece of polyethylene and measures protons from a n,p reaction.

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Reagents

The cation exchange resin is Dowex 50W-X8 which has been hydraulically classified. The chromatographic column is filled with resin in the size ranges of 28-35, 35-42, or 42-56 μ m, while the loading column is filled with 56-70 μ m resin.

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1 The eluent solutions are prepared by dissolving a weighed amount of alpha-hydroxyisobutyric acid (manufactured by Eastern

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50 Chemical Corp.) in demineralized water, adjusting the pH with ammonium hydroxide, and then diluting with demineralized water to the final volume. Eluent solutions are prepared a couple of days before a series of runs and have been stored for as long as four weeks in the hot-cell before being used.

Processing Steps

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35 Feed Preparation. Feed solutions are adjusted to less than 2 liters of 0.3 M HNO_3 before processing. Since the feed is usually from a LiCl-anion exchange run (6), the solution contains LiCl (about 3 M) and HCl (about 1 M). The lithium and chloride ions are removed and the solution is converted to the nitrate form by precipitating the metal hydroxide with 1 M LiOH, filtering through a glass frit, washing with water, and finally re-dissolving with strong and then dilute HNO_3 . In order to improve the actinide recovery during the filtration step, up to 200 mg of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ is added as a carrier before the precipitation. Also, a waiting period of 90 minutes between the precipitation and the filtration steps has been found to significantly improve the filtration--increasing the filtration rate, and reducing the amount of actinides in the filtrate and left undissolved on the filter.

Feed Loading. The adjusted feed solution is transferred by vacuum to the vacuum-pressure pot. The pot is pressurized to 0.3 MPa with N_2 , and the feed solution is forced through the

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loading column at 2.7 mm/s (16 ml/cm²·min). The elution column is by-passed. The actinides form a tight band at the top of the column. This can be verified by locating the ²⁵²Cf with the neutron probe. The resin is then washed with water and 310 ml of 0.3 M NH₄NO₃ to displace H⁺ ions that would interfere with the actinide separation during the elution. Very little movement of the actinide band takes place during the washing step.

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The use of the loading column is desirable for two reasons. First, the pressure resistance in the smaller column is considerably less, so it is not necessary to use the high-pressure pump to transfer the highly radioactive solutions. This facilitates pump repairs in the glove box facility that is used. Second, the use of the loading column eliminates the need to wash H⁺ ions from the major portion of the resin which is in the elution column. This lessens the radiation damage to the resin and allows larger batches of ²⁵²Cf (39 watt/g) per run. (For a typical batch of feed, ²⁵²Cf is the primary contributor to radiation exposure, and also the major mass, since most of the americium-curium will have been removed in the previous processing step, LiCl-anion exchange.)

Feed batches containing up to 200 mg of ²⁵²Cf have been handled successfully. The largest run that has been made contained 380 mg of ²⁵²Cf. During that run, about 10% of the actinides did not elute from the loading column because of

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severe radiation damage to the resin, and the actinides had to be recovered with a strong acid leach of the resin. Several runs have been made with 240 to 320 mg of ^{252}Cf in the feed; but even though all the californium did elute, the widths of the elution bands were increased to the point that the intermediate fractions between the einsteinium and californium peaks contained from 10 to 50% of the einsteinium and californium in the feed and had to be recycled.

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Elution. After the actinides have been loaded, column effluent is routed through the separation column, and the high pressure pump is then used to generate pressures from 2 to 5 MPa to transfer eluent at a superficial velocity of 2.0 mm/s (12 ml/cm²·min) through the elution column. The eluent solutions are: 240 ml of 0.25 M AHIB--pH 3.9 to elute the actinides from the loading column onto the separation column; enough 0.25 M AHIB--pH 4.2 (usually 1.5 liters) to elute all the fermium, einsteinium, and californium, 750 ml of 0.25 M AHIB--pH 4.6 to elute berkelium, 500 ml of 0.25 M AHIB--pH 4.8 to strip americium, curium, and cerium; and finally, 500 ml of water to flush reagents from the equipment. The effluent is divided into about 15 fractions that are each collected in a small (250 ml) polyethylene bottle. Changing of the effluent bottle during the einsteium and californium elution to collect einsteinium, intermediate (or mixed einsteinium-californium),

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and californium product fractions, is determined by closely watching the response from the flow-through alpha-detector (Fig. 2). Typically, 1 or 2 einsteinium fractions, 1 or 2 intermediate fractions (containing less than 5% of einsteinium and californium in the feed), and 2 or 3 californium fractions are collected. The intermediate fractions are taken when the valley between the einsteinium and californium peaks occurs on the alpha trace. Usually the first bottle is started at about 10^5 cts on the downside of the einsteinium alpha peak to the minimum, and the second bottle is collected from the minimum point to about 10^5 cts on the upside of the californium peak. The first intermediate fraction may sometimes be treated as a good einsteinium product, but the second intermediate fraction will usually have to be recycled. Sometimes the alpha trace will show a small fermium peak just ahead of the einsteinium. This peak will be from ^{255}Fm (20 h half-life) which is still present in the feed solution from the beta decay of its parent, ^{255}Es (40 d half-life), a very minor einsteinium isotope.

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In runs where the fermium alpha peak cannot be seen because of a high background count on the alpha detector, the fermium is assumed to be in one or both of the two fractions taken just prior to the einsteinium. The berkelium is primarily a beta emitter and is not detected by either the alpha or neutron detector, but will be in one (or split between two) of the three fractions that are taken after the californium alpha peak. If there is a significant amount of ^{244}Cm in the feed

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(mg quantities), the alpha-trace will show a third major peak when americium and curium are eluted at the end of the run.

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Observation of the ^{252}Cf band movement with the neutron probe (Fig. 3), provides advance information on when to expect einsteinium in the eluate, and can be used as a backup indicator for changing effluent collection bottles during the einsteinium-californium elution should the alpha-detector fail. Also, it can detect problems as the run progresses; such as, insufficient resin in the columns, or incomplete elution from the loading column.

Results

The distribution of einsteinium, californium, berkelium, and curium for a typical batch of feed is shown in Table I. The einsteinium and berkelium product fractions are usually decontaminated from ^{252}Cf by factors of 10^3 - 10^4 and 10^2 - 10^3 , respectively; and the californium product fractions are usually decontaminated from ^{253}Es by a factor of 10^2 . The maximum concentrations of ^{252}Cf , ^{249}Bk , and ^{253}Es in the product fractions are typically about 0.4 mg/ml, about 50 ug/ml, and about 3 ug/ml, respectively.

Resin Damage and Disposal

Radiation damage to the resin is more severe in the loading column where the actinides load in a concentrated band. If the

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Table I. Actinide Distribution for Typical Run

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	^{253}Es	^{252}Cf	^{249}Bk	^{244}Cm
Feed, mg	0.6	150	15	25
% in Es product	96.3	0.05	--	--
% in Cf product	1.5	98.2	0.3	--
% in Bk product	0.1	0.3	99.5	--
% in Rework	2.1	1.5	0.2	100

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actinides load up to the resin capacity (about 2 meq/ml), the radiation dose for a typical run would be about 20 MGy. Because of this high radiation dose, the resin in the loading column is discarded after each run by removing the bottom fitting from the column and slurring the resin out the bottom of the column with water. The appearance of the used resin is unchanged from fresh resin except that the top 10% of the resin bed is black. Disposal of the resin in the elution column is done in the same manner, and is usually done after processing a total of 300-400 mg of ^{252}Cf (2-3 runs) for a total radiation dose to the resin of up to 0.8 MGy. However, during the most recent processing campaign, a total of 830 mg of ^{252}Cf and 3.3 mg of ^{253}Es was satisfactorily processed in five runs with one batch of resin for an estimated dose of 2 MGy. The

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appearance of the resin from the elution column is usually uniform in color and is only slightly darker than that of fresh resin.

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The used resin from both columns may contain a small amount of actinides that failed to elute from the resin. The amount is estimated by counting fast neutrons from ^{252}Cf with the in-cell neutron probe. The resin usually contains <100 ug of ^{252}Cf which can be recovered with static leaches with strong HNO_3 . Several batches of resin have been calcined in an electric resistance furnace and the ashes leached with HNO_3 , but very little additional ^{252}Cf was recovered.

Additional Separations

The einsteinium-fermium and californium fractions collected during the initial separation described above, are processed by means of a second-cycle of high-pressure chromatographic cation exchange for additional partitioning of the actinide elements. The equipment and processing steps are similar to those described above.

The einsteinium-fermium fractions are taken to a shielded cave (a small hot-cell), where the second-cycle run is made to remove residual californium (10-200 ug of ^{252}Cf) from the einsteinium-fermium. The elution column in the cave is 8 mm in diameter and 1.2 m high and contains 21 mL of resin. Batch runs are usually limited to <500 ug of ^{253}Es and take 4 to 6 h. One run is usually sufficient to reduce the ^{252}Cf content in

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50 the einsteinium-fermium fraction to <1 ug. This represents, for the combined initial and second cycle run, an overall decontamination factor of californium from einsteinium of about 10^5 . With the ^{252}Cf content <1 ug, the einsteinium-fermium can then be taken to a glove box for further purification before packaging for shipment.

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35 The californium fractions are taken to another hot-cell at the TURF Californium Facility (7) where a second-cycle run is made to further decontaminate the californium from ^{244}Cm and recover a second batch of ^{253}Es . The ^{253}Es grows into the californium from the beta decay of ^{253}Cf (18 d half-life) and is recovered again at this point primarily to augment the einsteinium production, though some researchers prefer this material because of its high-isotopic purity. The growth of ^{253}Es will peak at 28 days after an einsteinium-californium separation, and if possible, the second-cycle run is scheduled to take place near that time. These runs are limited to <125 mg of ^{252}Cf and take up to 6 h. After this run the californium is stored for about 2 years and then reprocessed by means of another high-pressure ion exchange run to recover ^{248}Cm , the alpha-decay daughter of ^{252}Cf (2.6 y half-life). The ^{248}Cm is more desirable to some researchers, than the more readily available ^{244}Cm because of its very low specific activity (0.2 GBq/g for ^{248}Cm as compared to 2 TBq/g for ^{244}Cm). Since 1970 about 0.8 g of ^{248}Cm has been recovered.

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Summary

Decigram quantities of highly radioactive transplutonium elements are routinely partitioned at TRU by chromatographic elution from cation resin using AHIB eluent. By using two high-pressure ion exchange columns, a small one for the initial loading of the feed and a large one for the elution, batch runs containing up to 200 mg of ^{252}Cf can be made in about 5 hours (2 hours to load the feed and 3 hours for the elution). The number of effluent product fractions and the amount of actinides that must be collected in intermediate fractions are minimized by monitoring the response from a flow-through alpha-detector. This process has been reliable and relatively easy to operate, and will continue to be used for partitioning transplutonium elements at TRU.

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Acknowledgement

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Figure 1. Equipment diagram

Figure 2. Response from flow-through alpha-detector during
elution of run 52-CX-2

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Figure 3. Movement of ^{252}Cf peak as measured by neutron probe
during run 52-CX-2

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Fig. 1. Equipment diagram.

Fig. 2. Response from flow-through α -detector during elution of run 52-CX-2.

Fig. 3. Movement of ^{252}Cf peak as measured by neutron probe during run 52-CX-2.