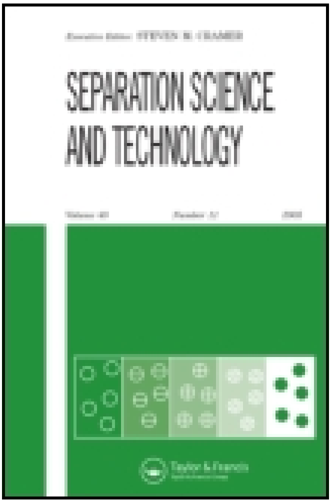

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Fermium Purification Using Teva™ Resin Extraction Chromatography

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FERMIUM PURIFICATION USING TEVA™ RESIN EXTRACTION CHROMATOGRAPHY

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ABSTRACT

The Radiochemical Engineering Development Center at Oak Ridge National Laboratory processes irradiated targets to recover the transplutonium actinides for research and industrial users. In a typical processing campaign, dekagram quantities of curium are recovered for recycle into targets for subsequent irradiation and processing; decigram quantities of californium are recovered for fabrication into neutron sources; and milligram quantities of einsteinium and berkelium as well as picogram quantities of fermium are recovered for distribution to the research community. The transcurium actinides are separated in a series of chromatographic elutions using a cation-exchange resin and ammonium α-hydroxyisobutyrate as the eluant. The fermium fraction from these final purification runs still contains significant amounts of rare earth fission products, such as yttrium, dysprosium, and holmium. In the most recent campaign, a process using a TEVA™ resin extraction chromatography column was developed and tested to determine its effectiveness in providing a fermium product free of rare earth fission products. Gamma spectroscopy indicated that dysprosium and holmium were reduced to levels less than minimum detectable limits and that only 0.07 pg of ^{91}Y remained in the final fermium product, which contained 0.5 pg of ^{257}Fm. An overall decontamination factor of ~ 10^3 was achieved for fission product removal.

INTRODUCTION

The Radiochemical Engineering Development Center (REDC) at the Oak Ridge National Laboratory (ORNL) has been operated since the mid-1960s to support the Transuranium

Element Production Program for the U.S. Department of Energy. The REDC fabricates curium targets for irradiation at the High Flux Isotope Reactor to produce macroscopic quantities of the man-made transcurium actinide elements and subsequently processes the irradiated targets to recover and purify the elements for distribution to the industrial and research communities. In a typical processing campaign, dekagram quantities of curium are recovered for recycle into targets for subsequent irradiation and processing; decigram quantities of californium are recovered for fabrication into neutron sources; and milligram quantities of einsteinium and berkelium as well as picogram quantities of fermium are recovered.

The processing of the irradiated targets is accomplished using accepted aqueous processes employed in typical REDC operations for the dissolution of the targets, separation of the impurities from the transplutonium actinides and fission products, separation of the transplutonium actinides from the fission products, and finally separation of the transplutonium actinides into individual product fractions. All of these processing activities are done in the heavily shielded hot cell facilities. The overall processing, as well as individual process descriptions, is found in a number of previously published reports (1-4).

After the individual product fractions are separated, several processing steps follow that are necessary for final product purification (5). These include ion-exchange chromatographic separation using ammonium α-hydroxyisobutyrate (AHIB) eluant and cation exchange for impurity removal and product concentration. These processes work well for most of the actinide product fractions; however, because of the small quantity of fermium present, any impurity contributes significantly to the mass of the product and the total radioactivity. This extraneous mass and radioactivity are typically the result of fission product impurities that are carried through the various separation steps. At the request of the researcher who received the product fraction from a previous campaign, an investigation into removing these impurities from the fermium fraction was initiated.

For several years the method used for the separation of the actinides from trace fission products was the elution of the actinide elements from cation resin with alcoholic-HCl solution (6). This method has proved to be successful in the past, but the preparation of reagents, stability of the reagents, and unpredictability of the results have been the cause of some concern. To accomplish this separation, researchers at Argonne National Laboratory have developed an extraction chromatographic resin (the quaternary amine, Aliquat™•336, impregnated into Amberchrom™ CG-71ms support resin), which is marketed by Eichrom

Industries, Inc., under the TEVA trade name (7,8). The process was developed for the separation of americium from a mixture of trivalent lanthanides (9). The potential use of this method for the separation of fermium from trace fission products was attractive for several reasons: (a) reagent makeups were simple and for the most part nonhazardous, (b) the separation could be accomplished with small-volume samples, (c) the separation could be made quickly, and (d) the loading/elution sequence was simple. Additionally, the TEVA™ resin has proven to be very effective in the separation of actinide and fission product fractions in analytical samples at the REDC. It was this successful use that led to its potential application to the fermium purification.

EXPERIMENTAL

The TEVA™ resin used in these experiments was obtained from Eichrom Industries as prepacked columns containing 2 mL of 80- to 160-µm particle size resin with a free column volume of 1.3 mL. Dowex 50W-X4 cation-exchange resin, <38-µm particle size, was obtained from Dow Chemical Company and was sequentially washed with 0.1, 2.0, 6.0, 2.0, and 0.1 *M* HCl and finally rinsed with water prior to its use in these experiments. Hydrochloric acid solutions were prepared from Ultrex™ reagents obtained from J. T. Baker Chemical Company. All water was obtained from a Cole-Parmer Ion-X water deionization system. The ammonium thiocyanate and formic acid solutions were prepared from reagent-grade chemicals obtained from J. T. Baker Chemical Company. The mixed europium (^{152}Eu, ^{154}Eu, and ^{155}Eu) and the ^{248}Cm used in the development experiment came from previously processed materials at the REDC.

The procedure for separating the lanthanide and actinide fractions using TEVA™ resin extraction chromatography was given in the product technical reference sheet and other published reports (9). Partitioning experiments using an analog curium-europium (Cm-Eu) mixture were performed to test the method and develop a procedure for use in the subsequent purification of the fermium fractions generated in the transuranium element processing campaign.

Cm-Eu Partitioning

The feed for the analog Cm-Eu partitioning experiment was prepared by mixing an aliquot from a europium fraction from previous separation experiments with an aliquot from a ^{248}Cm product fraction separated from ^{252}Cf. The combined fractions were taken to dryness using an infrared heat lamp and argon gas purge. The solids were dissolved in concentrated nitric acid, heated to reflux and digested, and taken to dryness again. A small aliquot of feed reagent (2.0 *M* NH_4SCN–0.1 *M* CH_2O_2) was added to dissolve the solids; however, only a small portion of the solids was dissolved with the initial addition. This solution was decanted to the feed bottle, and subsequent additions of the feed reagent were added and decanted until all the solids were dissolved and no measurable radioactivity was detected in the drying cone with beta-gamma instrumentation. The final volume of the feed solution was 8 mL. A 1-mL sample was taken for analytical determinations, and the remaining 7 mL was used for the partitioning experiment.

A prepacked TEVA™ resin column was pretreated with 10 mL of 2.0 *M* NH_4SCN–0.1 *M* CH_2O_2 solution by gravity flow. The feed solution was then added to the reservoir of the column and allowed to gravity flow through the column. The loading of the feed solution was monitored by using beta-gamma instrumentation. After all the feed solution had passed through the column, a visible band was noted at the top of the column. Scanning the column with the beta-gamma detector showed a narrow loading band at the top of the resin bed. The column was then rinsed with 12 free column volumes of 1.0 *M* NH_4SCN–0.1 *M* CH_2O_2 to elute the europium fraction. To strip the curium product from the column, approximately 3.5 free column volumes of 0.25 *M* HCl was passed though the column and collected into a separate bottle. The raffinate and product bottles were sampled for analysis, and a final scan showed no detectable radioactivity remaining on the column.

Fermium Product Purification

The fermium feed for final purification was a collection of fermium fractions from four first-cycle hot cell cation-exchange chromatography runs, using ammonium α-hydroxyisobutyrate (AHIB) as the eluant, to separate the fermium, einsteinium, californium, and berkelium products, and three second-cycle shielded-cave AHIB cation-exchange chromatography runs to separate the fermium and einsteinium fractions to produce purified einsteinium products. This composite fermium feed contains a mixture of ^{255}Fm and the desired ^{257}Fm isotopes. Because of its short half-life (20 h) and characteristic alpha energy (7.02 MeV), ^{255}Fm is used as a tracer during the separation runs to determine the position of the ^{257}Fm (100-d half-life) product during elutions and its concentration in the various fractions.

An overview of the flowsheet used for processing the fermium fractions is given in Figure 1. The product fractions from the various chromatographic runs were combined, and a preliminary AHIB cation-exchange chromatography run was made to separate the fermium from any residual einsteinium and to concentrate the fermium product. The fermium product fraction was acidified to 0.3 *M* H^+ with 6.0 *M* HCl, to break the butyrate complex, and pressured (18 psig Argon) through a column containing 1.5 mL of Dowex 50W-X4 cation-exchange resin (free column volume of 0.75mL) to load the fermium and other trivalent elements. The column was then washed with 20 free column volumes of 0.1 *M* HCl and 4 free column volumes of 2.0 *M* HCl to remove monovalent and divalent cationic impurities. The elution was monitored with an alpha drop detector to determine the presence of alpha activity in the eluate. At the initial detection of alpha activity in the eluate drops, the eluant was switched to 6.0 *M* HCl and the fermium product was collected in 3.5 free column volumes followed by a final strip of 6 free column volumes of 6.0 *M* HCl to remove any residual radioactivity.

The fermium product from the initial cation-exchange run was evaporated to dryness with an infrared heat lamp and argon gas purge. The initial radiation reading on the dried product was 10 mR/h at contact. Less than 0.1 mL of 0.1 *M* formic acid was added to the dried fermium product, and the material readily dissolved when slightly heated. The dissolved product was adjusted to a final volume of 6 mL with 2.0 *M* NH_4SCN–0.1 *M* CH_2O_2 solution. A prepacked TEVA™ column was preconditioned with 10 mL of 2.0 *M* NH_4SCN–0.1 *M* CH_2O_2, and the fermium feed solution was then added and allowed to gravity flow through the column to load the fermium and trivalent fission products. The column was then rinsed with 8 free column volumes of 1.0 *M* NH_4SCN–0.1 *M* CH_2O_2 (2 × 4 free column volumes) to elute the trivalent fission products. The fermium product was then eluted from the column in approximately 2.5 free column volumes of 0.25 *M* HCl. The column was then stripped with 0.25 *M* HCl to remove any residual radioactivity. Again, the elution of the fission products and fermium was monitored using an alpha drop detector, and radiation readings of the collected fractions were made for comparative purposes.

A final cation-exchange run was made on the fermium product fraction to remove any residual ammonium thiocyanate from the product solution. This run was essentially identical to the initial cation-exchange run except that the fermium product was eluted from the column in 2.0 *M* HCl with monitoring of the eluate with the alpha drop detector. The fermium product from this final cation-exchange run was transferred to a leached quartz shipping cone, dried under an infrared heat lamp with an argon gas purge, and packaged for shipment.

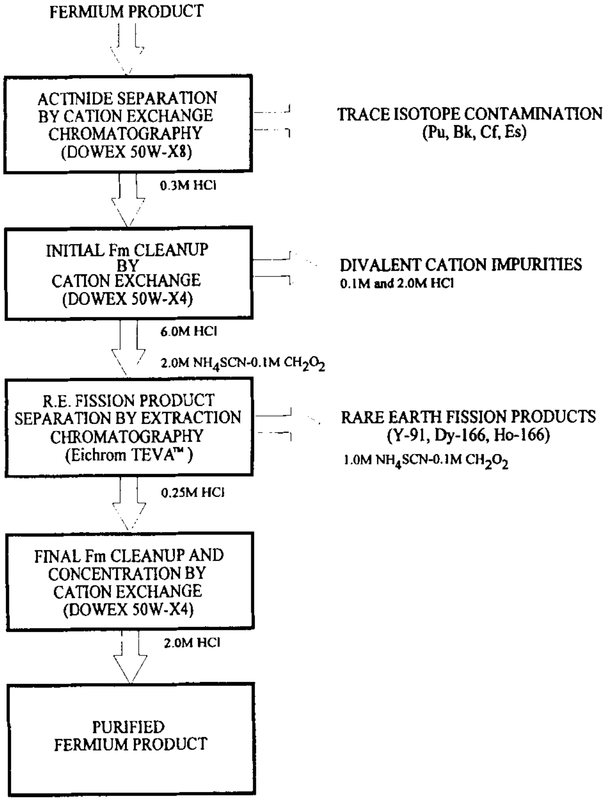

FIGURE 1. Schematic of fermium product purification.

RESULTS AND DISCUSSION

Cm-Eu Partitioning

The 7 mL of feed for the Cm-Eu partitioning experiment contained 155 µg ^{248}Cm and 12.3, 4.7, and 0.47 µCi of ^{152}Eu, ^{154}Eu, and ^{155}Eu, respectively. The analysis of the raffinate/rinse solution showed 33 µg ^{248}Cm (21.3 % of feed) and 12.7, 5.1, and 0.46 µCi of ^{152}Eu, ^{154}Eu, and ^{155}Eu, respectively. The analysis of the stripped curium product solution showed 137 µg ^{248}Cm (88.4% of feed) and <1.7, <0.68, and <0.007 µCi of ^{152}Eu, ^{154}Eu, and ^{155}Eu, respectively. The material balance for the ^{248}Cm showed a 10% excess and was attributed to a dilution error or an error in analytical preparation or counting. Since this was an experiment to determine the feasibility of the method, the resolution of the material balance discrepency was not pursued. These results show a decontamination factor (DF) of >6 for europium in the curium product and a DF of ~5 for curium in the europium rinse fraction. Table 1 summarizes the results of the Cm-Eu partitioning experiment.

These results were somewhat disappointing because of the loss of curium to the rinse/raffinate and the low DFs for the product solutions. This loss and the low DFs were attributed to the presence of butyrate in the feed solution, which interfered with the load and rinse sequence. The europium solution, from which the feed solution was prepared, was a product from an AHIB separation of lanthanide products and contained degraded AHIB. This degraded butyrate could also account for the difficulty experienced with the dissolution of the dried feed stock in the ammonium thiocyanate–formic acid solution. These butyrate interferences were confirmed by the analytical group, which routinely uses the TEVA™ columns in the preparation of sample solutions.

Fermium Product Purification

The fermium fractions from the preliminary AHIB cation- exchange chromatography runs provided the feed solution for the initial cation exchange. Since the butyrate appeared to interfere with the loading/elution of the TEVA™ resin in the Cm-Eu analog run, this cation-exchange run was performed to obtain a feed that was free of butyrate and any divalent cation impurities. The fermium feed loaded well on the cation-exchange resin, with no activity detected in the eluant using an alpha drop detector. The low-acid column rinse was also completed with no increase in alpha activity in the eluant. During the 2.0 *M* HCl elution of the column, a very distinct yellow band (divalent impurities) washed off the column ahead of the actinide band. When the alpha activity started to increase on the alpha drop detector, the product fraction was collected, and this collection continued until the alpha trace returned to background levels. The actinide product fraction contained 256 pg ^{255}Fm (with 1 ng ^{252}Cf, 3 ng ^{253}Es, and 136 ng ^{238}Pu as actinide impurities) and 115 pg ^{91}Y, 0.85 pg ^{166}Dy, and 0.18 pg ^{166}Ho (as fission product impurities). This product analysis was used as the basis for the calculation of the DFs for the TEVA™ resin extraction chromatography run. No significant activity was noted in any of the other fractions from the initial cation-exchange run.

TABLE 1. RESULTS OF THE Cm-Eu PARTITIONING EXPERIMENT

Stream	^{248}Cm (μg)	^{152}Eu (μCi)	^{154}Eu (μCi)	^{155}Eu (μCi)	DF
Feed	155	12.3	4.7	0.47	
Raffinate/Rinse	33	12.7	5.1	0.46	5
Product	137	<1.7	<0.68	<0.007	>6

The product fraction from the initial cation-exchange run was dried and readily dissolved in 2.0 *M* NH_4SCN–0.1 *M* CH_2O_2 and loaded on a preconditioned TEVA™ column. Because of the uncertainty of the response of the alpha drop detector to detect the leading edge of the fermium elution peak, the product collection was started when the eluant was changed to 0.25 *M* HCl. When the alpha trace returned to the background level, the column was given the final strip with 0.25 *M* HCl. The contact radiation readings of the raffinate, two rinses, product, and strip were 3.5 mR/h, 6.0 mR/h, 1.4 mR/h, 1.7 mR/h, and background, respectively. These results suggested that the impurities had been successfully separated from the fermium product. The results of the analysis of the various fractions are given in Table 2, along with the calculated DFs for the fission product impurities. In the fermium product fraction, most of the gamma-emitting fission products were reduced to less than the minimum detectable limits. These lower-limit values are listed for the purpose of calculating the DFs and evaluating the effectiveness of the TEVA™ resin for these types of separations.

The results show that good separation and good material balances were obtained for the fermium product using the TEVA™ resin. The ^{255}Fm content in the product solution was a factor of 2.3 lower than the feed content due to the 24-h difference in the analysis of the two samples (^{255}Fm $t_{1/2}$ = 20.1 h). The ^{91}Y DF of 1600 for the product fraction was extremely good for a single-cycle separation. Because the ^{166}Dy and ^{166}Ho were at the minimum detectable limits, a greater-than value was calculated for the DFs. These values were in agreement with the ^{91}Y value and showed good separation for the single-cycle run. Good material balances were obtained for both the fermium and the fission products during the run. The gamma scan was used to analyze for a number of other gamma-emitting fission product impurities, but all

TABLE 2. RESULTS OF THE FERMIUM/FISSION PRODUCT PARTITIONING

Stream	^{255}Fm (pg)	^{91}Y (pg)	^{166}Dy (pg)	^{166}Ho (pg)
Feed	256	115	0.85	0.18
Raffinate		64.1	0.077	0.0037
Rinse 1		58.5	0.729	0.220
Rinse 2		0.80	0.004	
Product	111(decay)	0.07	<0.001	<0.0004
Strip	0.20			
Product DFs		1600	>850	>450

were at the minimum detectable limits, showing little fission product contamination in the fermium product.

The final cation- exchange run made on the fermium product from the TEVA™ resin run was made with no significant changes in the product fraction purity. The intent of the final cation exchange was to remove any residual ammonium thiocyanate and to prepare the product for shipment. The final product was stripped from the column, using the alpha drop detector to monitor the elution of the fermium product. The final product was prepared and shipped to the designated researcher.

CONCLUSIONS

The separation of fermium from associated fission product impurities was successfully demonstrated using TEVA™ resin extraction chromatography. This method was shown to be superior to the previously used cation-exchange/alcoholic-HCl elution method. The reagent makeups are much simpler and less hazardous. The procedure is simplified and requires less time to perform. This is very important when dealing with short half-life radioisotopes and because of ALARA considerations. The elutions can be easily monitored with standard radiation instrumentation; however, if radiation instrumentation is not available, good separations can be obtained based on the rinse volumes and eluant changes. A superior product was obtained using this method with little or no loss of the small quantity of the rare fermium radioisotopes.

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