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The Radiochemical Engineering Development Center (REDC) at the Oak Ridge National Laboratory is the production, storage, and distribution center for the heavy-element research program of the U.S. Department of Energy. The REDC and the neighboring High Flux Isotope Reactor (HFIR) were built to produce quantities of transuranium elements for use in national and international research programs and since 1966 has been the main center of production for transcurium elements in the United States. In 2009, REDC successfully completed Campaign 74, its latest Bk-249/Cf-252 production campaign. The Transuranium Analytical Laboratory (TAL), located within REDC, provides the needed chemical and radiochemical analyses on a wide variety of nuclear matrixes in support of these production campaigns of transcurium isotopes. Titrations, dissolutions, separations, and dilutions of high activity samples are completed in hot-cells and glove-boxes in preparation for analytical radiochemistry determinations completed at the TAL in support of the REDC's mission. Within Campaign 74, the Transuranium Analytical Laboratory implemented a quick and reliable radiochemical method for the determination of Bk-249 that was used throughout the purification process at key hold points to ensure the delivery of a final purified product.

Keywords Berkelium; Bk-249; Californium; Cf-252; extraction chromotography; formic/thiocynate; TEVA; TTA

INTRODUCTION

The Radiochemical Engineering Development Center (REDC) at the Oak Ridge National Laboratory (ORNL) has been operating since the mid-1960s in support of the Transuranium Element Program (TEP) for the U.S. Department of Energy. The TEP consists of target rods, containing primarily curium oxide, remotely fabricated at REDC, irradiated in the High Flux Isotope Reactor (HFIR), and then processed at the REDC for the separation and purification of heavy actinide elements, including plutonium through fermium. The americium and curium are then fabricated back into targets for a new irradiation cycle while the berkelium, californium, einsteinium, and fermium are distributed to researchers around the globe. Part of the californium product is also used in the Californium Sales/Loan program. Detailed descriptions of the production and processing of transplutonium elements at the REDC/HFIR complex can be found in a number of previously published reports (1–3).

Since its construction, the REDC/HFIR complex (see Fig. 1) has established itself as the center for the production, storage, and distribution for the transuranium isotopes, including ^{248}Cm, ^{249}Bk, ^{249}Cf, ^{252}Cf, ^{253}Es, ^{254}Es, ^{255}Fm, and ^{257}Fm. In addition, another 30 rare research isotopes, such as ^{242}Cm, ^{245}Cm, and ^{250}Cf, have been produced in small quantities for special research interests (4). Over 1000 shipments of these transuranium elements have been made to more than 30 different laboratories in the United States and several foreign countries.

CAMPAIGN 74

Overview

Campaign 74 consisted of 7 targets containing 35 curium oxide pellets with a maximum of 10 g of actinides present in each. These targets (see Fig. 2) were irradiated for approximately 10 HFIR cycles, and then transferred to the REDC for processing and purification runs. A typical HFIR cycle consists of full-power operation for 21 to 23 days followed by a refueling outage. Figure 3 shows the principle nuclear reactions for the production of transplutonium elements in HFIR.

The HFIR produces transplutonium elements through the transmutation of the curium targets. The transmutation involves the combination of two processes. These are neutron absorption, which increases the nuclear mass by 1, and beta decay which increases the atomic number by 1. For example, Cm-244 absorbs neutrons, thus becoming Cm-245, and then Cm-246, and so on up to Cm-249. The half-life of Cm-249 is short enough that most will beta decay to Bk-249 which then captures a neutron thus becoming Bk-250. The beta decay of

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FIG. 1. HFIR/REDC (2008).

Bk-250 leads to the formation of Cf-250 and so on. This isotope production process finally stops at Fm-257 (5).

Figure 4 shows the outline of the hot cell processing steps employed by REDC staff during the purification of Cf-252 and Bk-249 in Campaign 74. REDC combines ion-exchange and solvent extraction techniques to separate the transplutonium elements from the lanthanide fission products and the many other elements present in the target rods.

The goal of Campaign 74 was twofold. First, separate and purify Cf-252 to be used in the REDC Cf-252 Sales/Loan Program where the californium goes through further purification processes and then is fabricated into neutron sources. These sources are produced for many applications, both in industry and research, because of Cf-252's intense neutron emission.

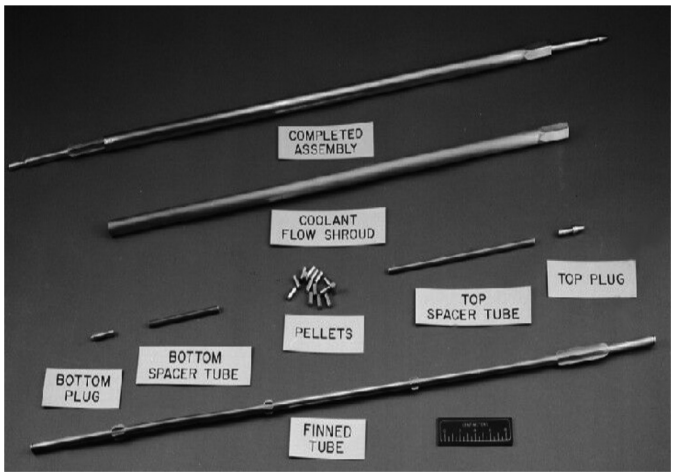

FIG. 2. HFIR target rods.

The second goal of Campaign 74 was to separate and purify >20 mg of Bk-249 which was immediately shipped to the Joint Institute for Nuclear Research in Dubna, Moscow. The Bk-249 was then used in experiments, attempting to synthesize a new chemical element. This work was completed by fabricating the Bk-249 into a target and placing it into a beam of ^{48}Ca in hopes of creating the super-heavy element (SHE) 117. Recently, this successful synthesis of element 117 was confirmed with the publication of a scientific paper by Yuri Oganessian and his team in the journal, *Physical Review Letters* (6).

Since Bk-249 has a half-life of only 320 days, the purification process was completed as quickly as possible by the REDC staff. It was imperative to prepare a Bk-249 product of high quality, but it also had to be of sufficient quantity to be of use to the scientists in Russia.

In the end, the final products achieved within Campaign 74 were as follows:

~240 mg Cf-252
~24 mg Bk-249.

Analytical Support

Approximately 400 samples, including over 1300 analyses and 6000 determinations, were completed at the Transuranium Analytical Laboratory (TAL) in support of the separation and purification of Cf-252 and Bk-249 during Campaign 74. The vast majority of these samples received routine characterization for gross alpha, alpha spectrometry (PHA), gross neutron, gamma spectrometry, and free acid determinations. The gross alpha and PHA were used for actinide determinations, gross neutron for additional confirmation of Cf-252 content, and gamma spec for fission products. As stated above, a primary concern of Campaign 74 was maintaining as much Bk-249 as possible throughout the separation processes, and considering its short half-life, Bk-249 determination hold points were established. Approximately fifty Bk-249 determinations were completed throughout the campaign.

Bk-249 DETERMINATIONS

A simple rapid method for the radiochemical separation and determination of Bk-249 in highly radioactive HFIR-irradiated target dissolver solutions was tested and implemented during Campaign 74. This method builds upon the well established technique of liquid-liquid extraction of oxidized berkelium(IV) with 0.5 M 2-thenoyltrifluoroacetone (TTA) in xylene (7) from actinides and trivalent lanthanide fission products, but couples it with the further decontamination of all fission products, including tetravalent cerium and zirconium, through the use of TEVA® resin extraction chromatography. Subsequent beta counting is completed by liquid scintillation for the determination of Bk-249. This method provides an excellent separation and determination of berkelium in 2.5 hours.

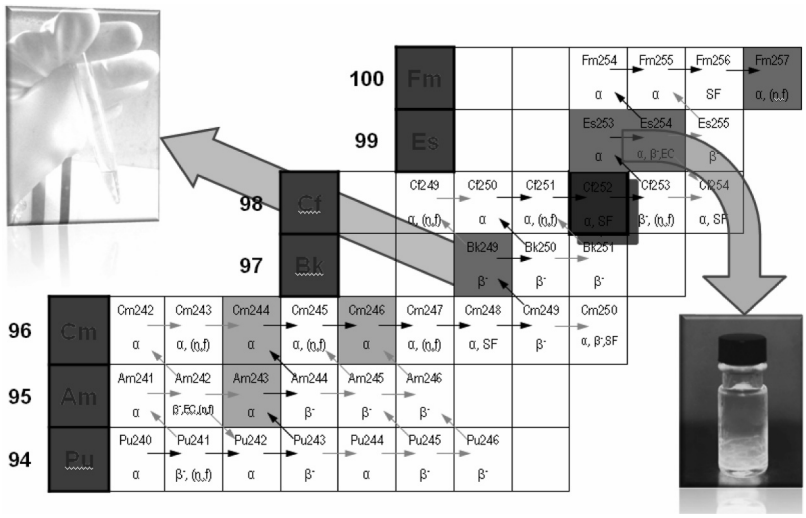

FIG. 3. Principle nuclear reactions for the production of transplutonium elements in HFIR.

Past methods used at the TAL to achieve the separation and determination of berkelium employed the use of a small high-pressure chromatography system, utilizing a column of cation-exchange resin with the eluent of ammonium α-hydroxyisobutyrate (8). Further purification of the berkelium was then achieved by TTA extraction and determination by beta counting on a gas-flow proportional counter. While this process was successful, it was long and tedious. Further, while the butyrate column managed to separate the berkelium from the cerium, zirconium was still a significant contaminant. Multiple decontamination back extractions were required in the TTA procedure to obtain a clean separation which further lengthened the overall procedure. The total time required for the completion of this method was greater than 8 hours.

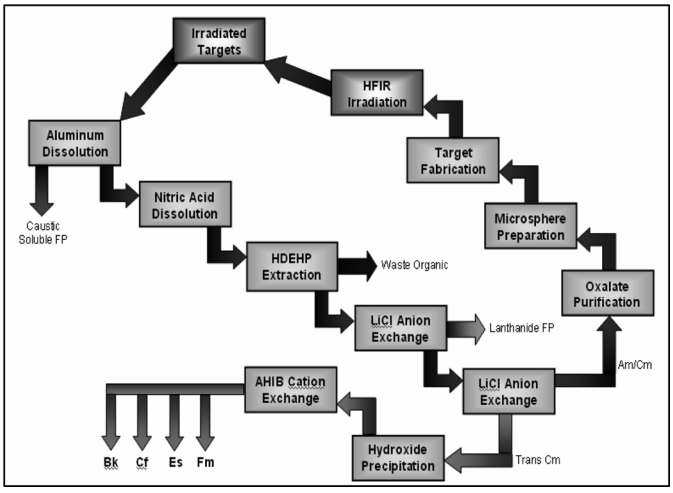

FIG. 4. Mainline processing scheme for HFIR targets.

EXPERIMENTAL

Instruments

Packard Model 2500TR Liquid Scintillation Counter using Ultima Gold LSC cocktail. High Purity Germanium (N-type coaxial) detector for gamma counting.

Chemicals and Reagents

1 N HNO_3, Eichrom TEVA® column, 100–150 µm, conditioned with 15 mL of 2 M NH_4SCN-0.1 M HCOOH, 1 M and 2 M NH_4SCN-0.1 M HCOOH, 1 N HNO_3 – 0.2 M $Na_2Cr_2O_7$, 0.25 N HCl, 5 M H_2SO_4, 0.5 M 2-thenyltrifluoroacetone (TTA) in xylene.

Procedure

Target dissolver solution samples were obtained in Cubicle 8, our analytical chemistry hot cell, where subsequent dilutions in 1 N HNO_3 were completed to reduce activity to acceptable limits, and the samples were transported to an open port glove box for processing. Figure 5 is a flowsheet of this procedure for the separation and determination of berkelium.

Prior to its use, the TEVA® column was conditioned by passing 15 mL of 2 M NH_4SCN-0.1 M HCOOH through it. To prepare the sample for addition to the TEVA® column, an aliquot estimated to contain 1 ng of Bk-249 was pipetted into a 15 ml glass beaker, slowly evaporated to dryness on a hotplate, and the remaining solids dissolved in 5 ml of 2 M NH_4SCN-0.1 M HCOOH. This sample feed solution was then passed through the column, retaining the actinides, including trivalent berkelium, but allowing the lanthanides to pass through. the column was rinsed with 15 mL of 1 M NH_4SCN-0.1 M HCOOH to remove any lanthanides sorbed onto the column. The column was rinsed with

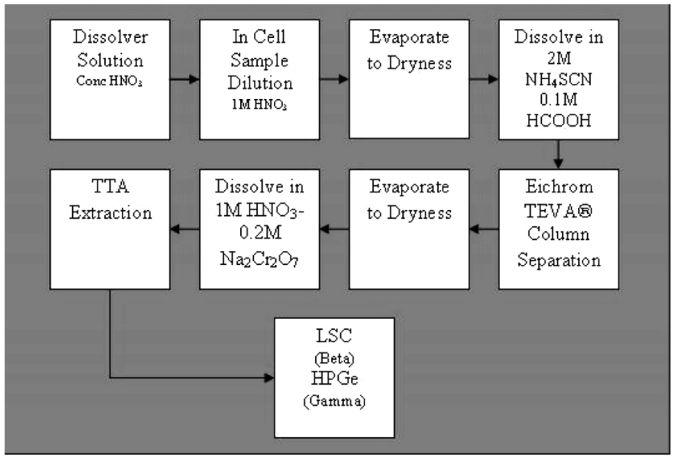

FIG. 5. Bk-249 separation and determination flowsheet.

0.25 N HCL to strip actinides, including berkelium(III), off of the column.

The strip solution was then transferred into a glass beaker, and slowly evaporated to dryness on a hotplate. The remaining solids were dissolved in 4.5 mL of 1 M HNO_3-0.2 M $Na_2Cr_2O_7$ which oxidizes the berkelium(III) to berkelium(IV), transferred into a 25 ml glass extraction tube, and heated in a block heater at 90°C for 15 minutes. After heating, 0.5 ml of 5 M H_2SO_4 was added to the solution that was then allowed to cool to room temperature. Next, 5 mL of 0.5 M 2-thenoyltrifluoroacetone (TTA) in xylene was added to the solution, and the vial vigorously shaken on a vortex mixer for 10 minutes. The sample vial was then centrifuged for 5 minutes, and an aliquot of the TTA/xylene phase transferred into a scintillation vial containing Ultima Gold LSC cocktail. This solution was then counted on a Packard Model 2500TR Liquid Scintillation Counter for beta activity. An additional aliquot of the TTA was transferred into a scintillation vial containing xylene and counted for gamma emitters on a High Purity Germanium (N-type coaxial) detector. This count was used for the determination of the fission product and the lanthanide contamination.

RESULTS

As outlined above, the aim of this work was to develop a simple rapid method for the radiochemical separation and determination of Bk-249 in highly radioactive HFIR-irradiated target dissolver solutions. The combination of these methods, extraction chromatography using TEVA® column followed by liquid-liquid extraction using TTA in xylene, employed on these target dissolver solutions resulted in an excellent separation of berkelium from extremely high levels of other actinides and fission products. Figures 6 and 7 display the composition of the target dissolver solution and decontamination factors for individual elements achieved through the use of this process. In particular, they display the marked difference the addition of the TEVA® column separation achieves over the TTA extraction method alone. While the selective liquid-liquid extraction of tetravalent berkelium with TTA-xylene achieves adequate separation from other actinides and trivalent fission products and lanthanides, the tetravalent cerium and zirconium are significant contaminants. In the TEVA/TTA method employed at the TAL, zirconium and cerium are reduced by 97% and 99.9% respectively. A test portion of REDC's pure Bk-249 product, which was quantified by direct beta counting, was also used to determine the recovery for the procedure. This test determined that we had achieved a recovery of 90% for the TEVA/TTA method.

Decontamination of Bk-249 in Dissolver Solution by TEVA-TTA Method

	Dissolver Solution	TTA Alone		TEVA/TTA	
Isotope	Bq/ml	Bq/ml	% Reduction	Bq/ml	% Reduction
CO-60	8.50E+06	4.47E+05	94.74%	2.72E+05	**96.80%**
NB-95	7.30E+07	1.09E+06	98.50%	2.19E+05	**99.70%**
ZR-95	2.20E+08	2.20E+08	**0.00%**	6.44E+06	**97.07%**
RU-103	3.00E+08	1.31E+06	99.56%	3.07E+05	**99.90%**
RU-106	1.20E+09	8.52E+06	99.29%	2.64E+06	**99.78%**
AG-110M	3.30E+07	6.56E+05	98.01%	3.12E+05	**99.05%**
CS-134	3.40E+07	5.83E+05	98.29%	2.52E+05	**99.26%**
CS-137	3.00E+07	8.90E+05	97.03%	3.85E+05	**98.72%**
LA-140	8.60E+06	3.62E+05	95.79%	2.74E+05	**96.81%**
CE-141	2.30E+08	2.20E+08	**4.26%**	2.55E+05	**99.89%**
CE-144	1.40E+09	1.40E+09	**0.00%**	5.88E+05	**99.96%**
EU-154	7.00E+06	1.24E+06	82.29%	2.63E+05	**96.24%**
EU-155	4.60E+06	1.80E+06	60.87%	2.96E+05	**93.57%**
EU-156	2.30E+07	3.59E+06	84.39%	1.05E+06	**95.43%**
Alpha Emitters	2.20E+09	3.70E+06	99.83%	3.70E+06	**99.83%**
BK-249				1.60E+08	

FIG. 6. Percent reduction in fission products, lanthanides, actinides by TEVA/TTA Method.

DISCUSSION

The active component of the TEVA resin is an aliphatic quaternary amine which has properties similar to those of typical strong anion exchange resins. However, because the functional groups are in liquid form, rather than fixed to a polymer backbone, these groups have greater mobility to coordinate around target ions. This means that the uptake of these ions is generally higher at much lower acid concentrations (9). TEVA resin therefore provides a simple effective method for the separation of tetravalent actinides in aqueous solutions.

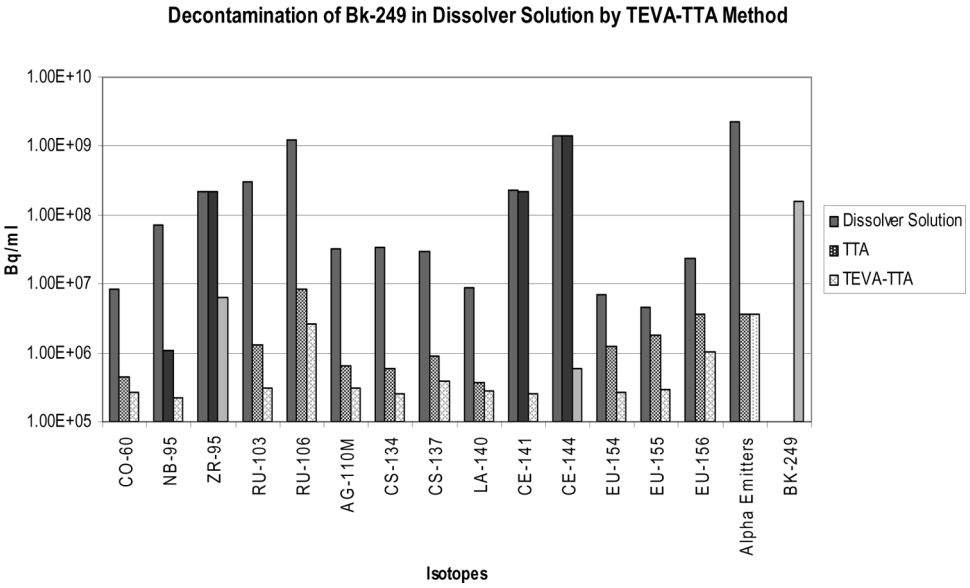

FIG. 7. Graph of decontamination achieved by TEVA/TTA method.

More importantly to the development of our method, TEVA resin has also been used to separate trivalent actinides from trivalent lanthanides in formic/thiocyanate solutions (9). Originally, researchers at Argonne National Laboratory developed the extraction chromatographic resin (the quaternary amine, Aliquat^{TM} · 336, impregnated into Amberchrom^{TM} CG-71ms support resin), which is now marketed by Eichrom Industries as TEVA® (10,11). As mentioned above, studies have been conducted that successfully demonstrate separations of americium from trivalent lanthanides (europium) to which ammonium thiocyanate has been added (9). These showed that americium was extracted much more readily than the europium. The reason for the higher separation factors achievable in thiocyanate solutions appears to be related to the tendency of the thiocyanate ligand to form inner sphere complexes more readily with actinides than with lanthanides (9,12).

An additional study was completed at the REDC during Campaign 72 in 1996 where researchers successfully completed the purification of fermium from trace fission products using TEVA® resin in formic/ammonium thiocyanate solutions (13).

These successful uses led to this application of TEVA^{TM} column separations in the determination of Bk-249.

CONCLUSION

The separation and determination of Bk-249 was completed on HFIR-irradiated target dissolver solutions containing high level actinides and fission products. This was completed through the use of TEVA® resin extraction chromatography followed by the selective liquid-liquid extraction of berkelium using 2-thenoyltrifluoroacetone-xylene. This method has proven to be superior to the previously used high-pressure chromatography (ammonium α-hydroxyisobutyrate) method followed by TTA extraction. The reagents used in the new system are less hazardous, and significantly less waste is generated in the process. The procedure is much simpler and the method requires substantially less time which is very important because of ALARA considerations.

ACKNOWLEDGEMENTS

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NOTE

This manuscript provides a quick overview of the Transuranium Analytical Laboratory's support of Campaign 74 with emphasis on the implementation of a quick and reliable radiochemical method for the determination of Bk-249 that was used throughout the purification process at key hold points to ensure the delivery of a final purified product.

This method builds upon the established technique of liquid-liquid extraction of oxidized berkelium (IV) with 0.5 M 2-thenoyltrifluoroacetone (TTA) in xylene from actinides and trivalent lanthanide fission products, but couples it with the further decontamination of all fission products, including tetravalent cerium and zirconium, through the use of TEVA® resin extraction chromatography.

Studies have been conducted that successfully demonstrate separations of americium from trivalent lanthanides (europium) to which TEVA® resin with ammonium thiocyanate has been utilized, but this appears to be the first analytical method where it is utilized for the separation and determination of Bk-249 in samples containing very high levels of fission products.