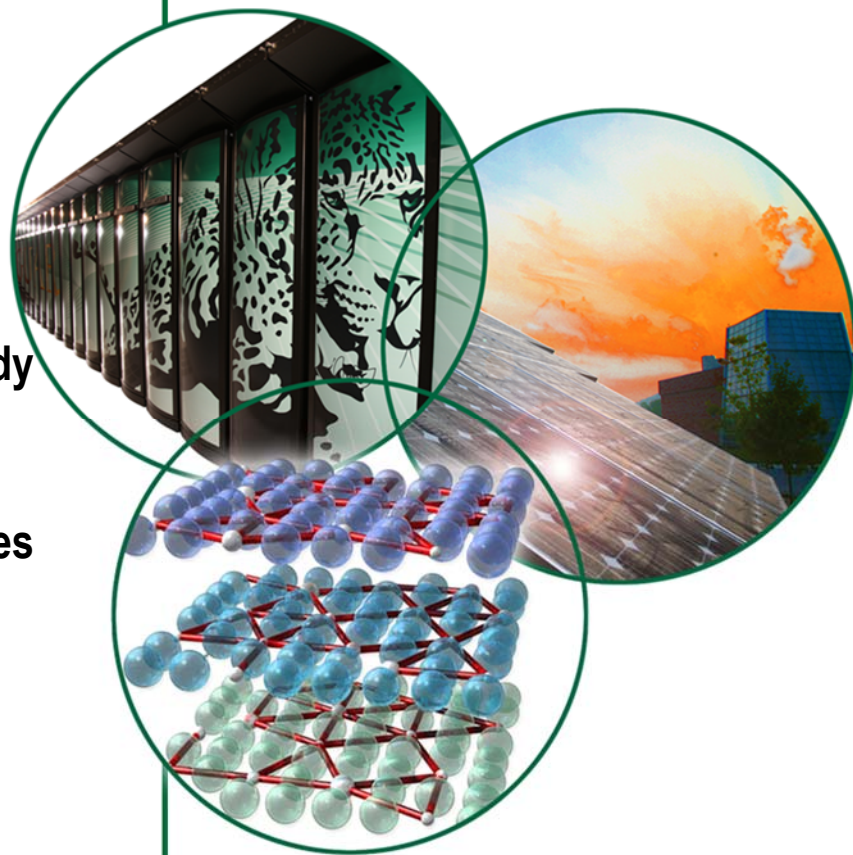


Rapid Bk-249 Analytical Protocol for Cf-252/Bk-249 Processing Campaigns

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Rapid Analytical Protocol for Bk-249

Presentation provides:

- **Overview of the Nuclear Analytical Chemistry and Isotopics Laboratories Group's support of Campaign 74 & 75**
- **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.**
- **Builds upon the established technique of liquid-liquid extraction of oxidized berkelium (IV) with 0.5M 2-thenyltrifluoroacetone (TTA) in xylene from actinides and trivalent lanthanide fission products**
- **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**
- **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.**

Introduction

- **The Radiochemical Engineering Development Center (REDC) and the High Flux Isotope Reactor (HFIR)**

- 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, a Bk-249/Cf-252 production campaign. In 2011/2012, REDC completed Campaign 75.**

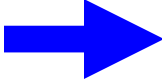
- **The Nuclear Analytical Chemistry and Isotopics Laboratories Group's high level laboratory, the Transuranium Analytical Laboratory (TAL)**

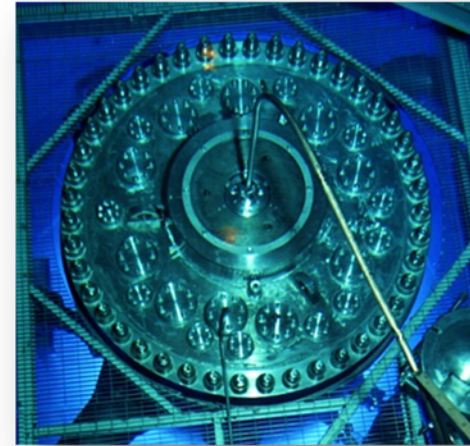
- provides the needed chemical and radiochemical analyses on a wide variety of nuclear matrixes in support of these production campaigns of transcurium isotopes. Titrations, dissolutions, separations, and dilutions of high activity samples are completed in hot-cells and glove-boxes in preparation for analytical radiochemistry determinations completed at the TAL in support of the REDC's mission.



HFIR/REDC (2008)

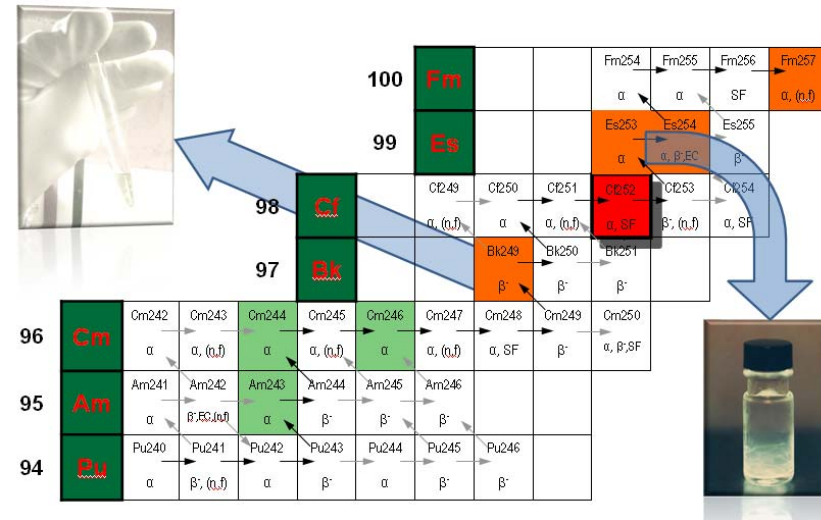
Transuranium Element Program

- Target rods, containing primarily curium oxide are remotely fabricated at the Radiochemical Engineering Development Center (REDC)
- Irradiated in the High Flux Isotope Reactor (HFIR) 
- Processed at the REDC for the separation and purification of heavy actinide elements, including plutonium through fermium.



HFIR Reactor Vessel

- REDC/HFIR Complex
 - ^{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
- Over 1000 shipments of these transuranium elements have been made to more than 30 different laboratories in the United States and several foreign countries.



Transuranium Nuclide Production Paths

Campaign 74 : 2009

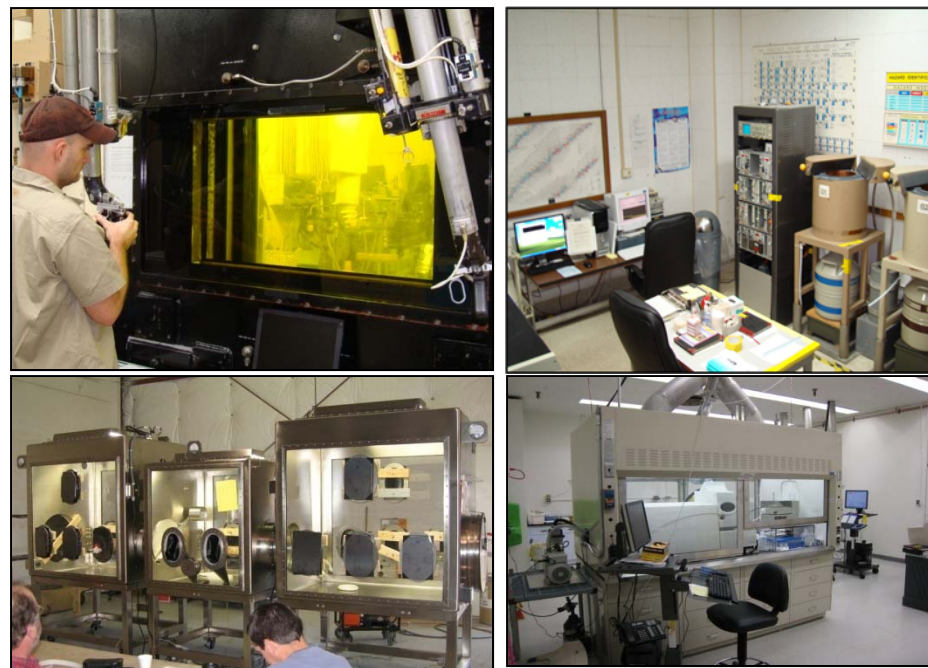
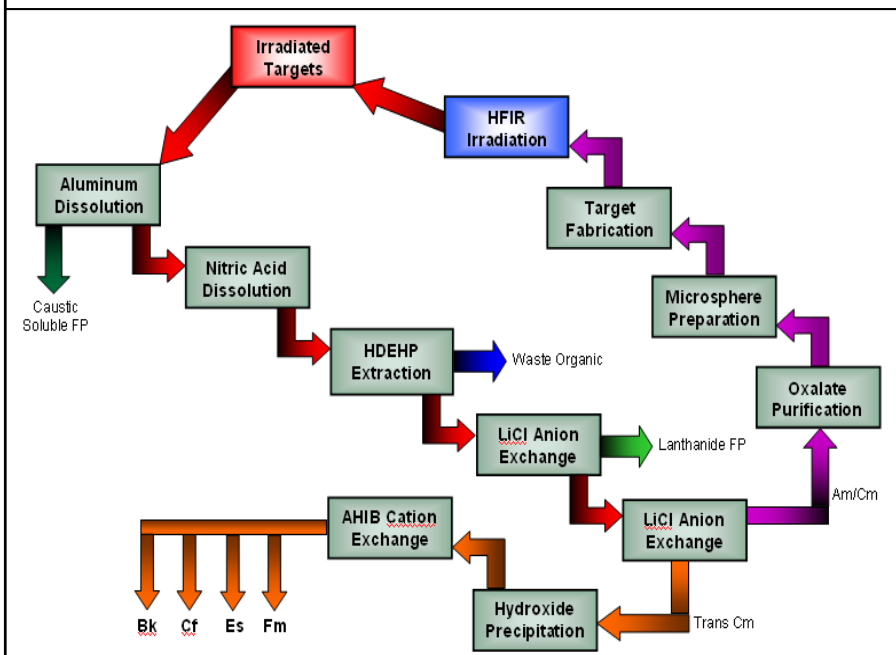
Overview

- **Seven targets processed**
 - 35 curium oxide pellets per target
 - Maximum 10 g actinides per target
- **Targets irradiated for ~10 HFIR cycles**
- **Final Products**
 - ~240mg Cf-252
 - ~24mg Bk-249
- **REDC Cf-252 Sales/Loan Program**
- **Bk-249 shipped to the Joint Institute for Nuclear Research in Dubna, Moscow where it was fabricated into a target and placed into a beam of ^{48}Ca creating for the first time super-heavy element (SHE) 117**

Analytical Support

- **Approximately 400 samples, 1300 analyses, and 6000 determinations**
 - Gross Alpha and Gross Beta determination
 - Alpha Spectrometry
 - Gamma Spectrometry
 - Total Rad Sr by Extraction Chromatography
 - Total Pu by 2-Thenoyltrifluoroacetone (TTA) Extraction
 - Total U by Spectrophotometric Ammonium Thiocyanate Method
 - Bk-249 Separation and Determination
 - ICPMS for actinides, fission products, impurities
- **Bk-249 Analysis- Approximately 50 hold points throughout the purification process where quick turn around analysis was performed.**

Campaign 75 : 2011/2012



Mainline Processing Scheme for HFIR Targets

Analytical Hotcell, Gloveboxes, Counting Room, ICPMS

Objective

Test and Implement a simple rapid method for the radiochemical separation and determination of Bk-249 in highly radioactive HFIR irradiated target dissolver solutions during Campaign 74.

Goals during the development of the New Method:

- **Much simpler method that requires substantially less time**
 - Quick turn around, high through-put analysis
 - ALARA considerations when working on high level radioactive samples
- **Achieve superior separation of Bk-249 from high levels of other actinides, lanthanides, and fission products, in particular cerium and zirconium**
- **Utilize less hazardous chemicals and generate less waste**

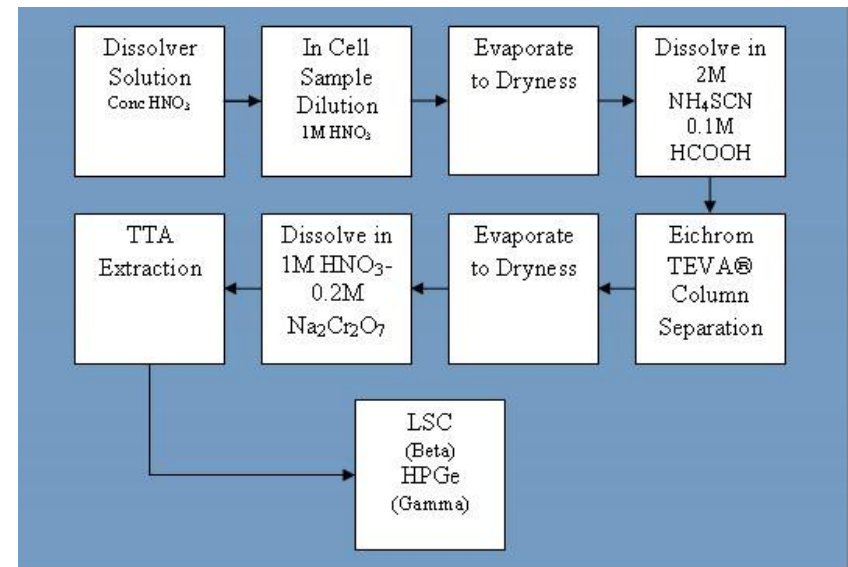
Past method of analysis for Bk-249 analysis:

- **High Pressure Chromatograph utilizing ammonium α -hydroxyisobutyrate (AHIB)**
- **Coupled with liquid-liquid extraction of berkelium (IV) with TTA-xylene**
 - Tedious and time consuming (8 hrs)
 - Poor separation of zirconium from berkelium

Methods and Materials

TEVA® Resin Chromatography / TTA Extraction Method

- This method builds upon the established technique of :
 - liquid-liquid extraction of oxidized berkelium (IV) with 0.5M 2-thenyltrifluoroacetone (TTA) in xylene from actinides and trivalent lanthanide fission products.
- Coupling it with the further decontamination of all fission products, including tetravalent cerium and zirconium, through the use of:
 - TEVA® resin extraction chromatography utilizing ammonium thiocyanate in formic acid.
- Subsequent beta counting is completed by liquid scintillation for the determination of Bk-249.



Bk-249 Separation and Determination Flowsheet

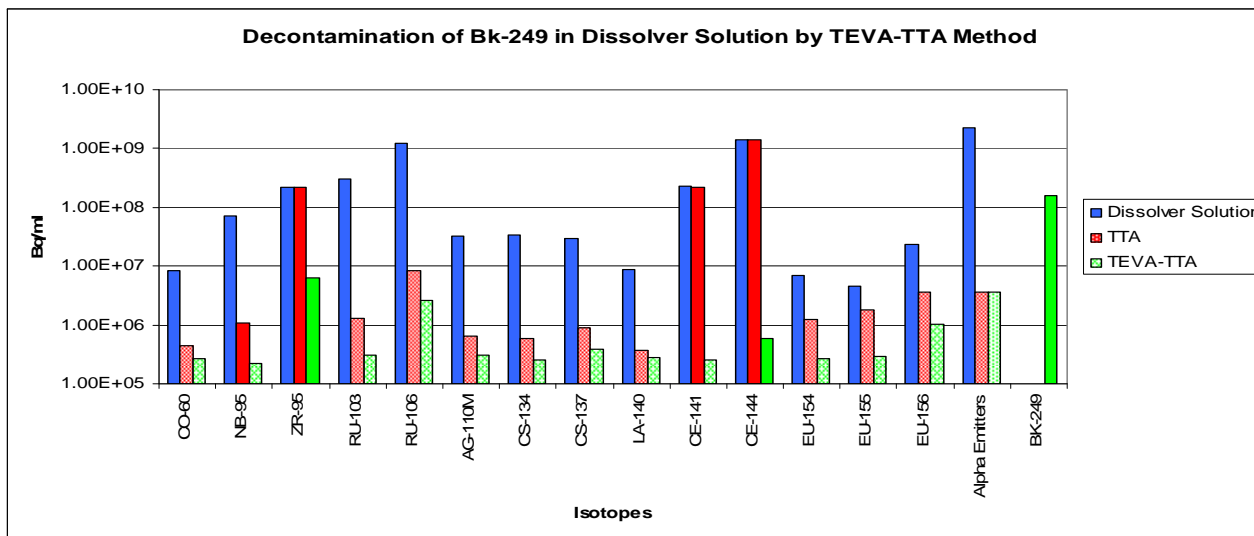
Results

- Excellent separation of berkelium from extremely high levels of other actinides, lanthanides, and fission products.
- Decontamination factors achieved through the use of this process 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.

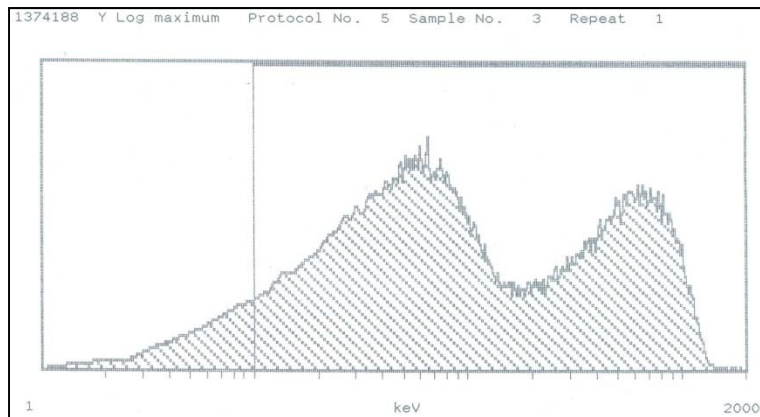
Decontamination of Bk-249 in Dissolver Solution by TEVA-TTA Method

Isotope	Dissolver Solution	TTA Alone		TEVA/TTA	
	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	

Percent reduction in fission products,
lanthanides, and actinides

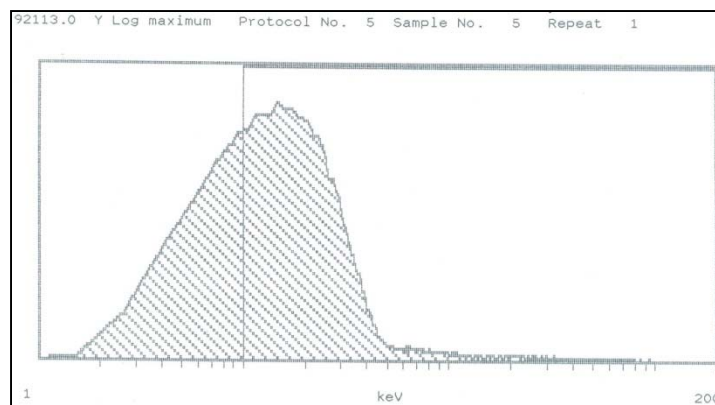


Decontamination achieved by TEVA/TTA Method



Beta Scintillation Spectrum (TTA Extraction only)

- High levels of Cerium, Zirconium
- Bk Spectrum buried under Ce, Zr



Beta Scintillation Spectrum (TEVA/TTA Method)

- Pure Bk spectrum

Discussion

- **Originally, researchers at Argonne National Laboratory developed the extraction chromatographic resin (the quaternary amine, Aliquat™-336, impregnated into Amberchrom™ CG-71ms support resin), which is now marketed by Eichrom Industries as TEVA® (2, 3).**
- **Studies have been conducted that successfully demonstrate separations of americium from trivalent lanthanides (europium) to which ammonium thiocyanate has been added (1). 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 (1, 4).**
- **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 (5).**
- **These successful uses led to this application of TEVA™ column separations in the determination of Bk-249.**

Summary

- **The separation and determination of Bk-249 was completed on HFIR-irradiated target dissolver solutions containing high levels of 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.**
- **Achieves superior separation of Bk-249 from high levels of other actinides, lanthanides, and fission products.**
- **The procedure is much simpler and the method requires substantially less time which is very important because of ALARA considerations.**
- **The reagents used are less hazardous and significantly less waste is generated during this process.**

Acknowledgements

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