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## Californium Electrodepositions at Oak Ridge National Laboratory\*

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### Abstract

Electrodepositions of californium isotopes were successfully performed at Oak Ridge National Laboratory (ORNL) during the past year involving two different types of deposition solutions, ammonium acetate ( $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$ ) and isobutanol ( $(\text{CH}_3)_2\text{CHCH}_2\text{OH}$ ). A californium product that was decay enriched in  $^{251}\text{Cf}$  was recovered for use in super-heavy element (SHE) research. This neutron-rich isotope,  $^{251}\text{Cf}$ , provides target material for SHE research for the potential discovery of heavier isotopes of  $Z=118$ . The californium material was recovered from aged  $^{252}\text{Cf}$  neutron sources in storage at ORNL. These sources have decayed for over 30 years, thus providing material with a very high  $^{251}\text{Cf}$ -to- $^{252}\text{Cf}$  ratio. After the source capsules were opened, the californium was purified and then electrodeposited using the isobutanol method onto thin titanium foils for use in an accelerator at the Joint Institute for Nuclear Research in Dubna, Russia. Another deposition method, ammonium acetate, was used to produce a deposition containing  $1.7\pm 0.1$  Ci of  $^{252}\text{Cf}$  onto a stainless steel substrate. This was the largest single electrodeposition of  $^{252}\text{Cf}$  ever prepared. The  $^{252}\text{Cf}$  material was initially purified using traditional ion exchange media, such as AG50-AHIB and AG50-HCl, and further purified using a TEVA- $\text{NH}_4\text{SCN}$  system to remove any lanthanides, resulting in the recovery of  $3.6\pm 0.1$  mg of purified  $^{252}\text{Cf}$ . The ammonium acetate deposition was run with a current of 1.0 amp, resulting in a 91.5% deposition yield. Purification and handling of the highly radioactive californium material created additional challenges in the production of these sources.

**Keywords:** californium, electrodeposition, ammonium acetate, isobutanol, super heavy element

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## Introduction

Electrodeposition is a technique that has been used in radiochemistry as a means to prepare thin solid films with applications ranging from source preparation for  $\alpha$ -spectrometry to target fabrication for accelerator bombardments. Historically, electrochemical depositions have been performed from both aqueous and organic matrices. With lanthanides and actinides, these techniques are often referred to as "molecular plating" because a molecular form of the element, rather than the metallic, is deposited. Isopropanol and isobutanol deposition methods have been used extensively. [1–3] Aqueous solutions, ammonium acetate and ammonium sulfate, though not used as extensively as organics, have been discussed in the literature for several years. [4–6]

## Purification of the Californium Material

Electrodeposition, both organic and aqueous, requires meticulous purification of the analyte fractions before electrodeposition, as trace amounts of organic or metal contaminants can limit the yield. Ion exchange chromatography was used to achieve the necessary purity of the materials for these depositions. Standard separation and purification techniques including an alpha-hydroxyisobutyric acid (AHIB) column, a cation cleanup column, and anion hydrochloric acid (HCl) column were utilized. In addition to the standard methods, a TEVA-ammonium thiocyanate separation was also added. [7]

The AHIB acid column was used to separate the californium (Cf) from curium (Cm) daughters. This separation uses a cation exchange resin (AG50X4) with an AHIB reagent. [8, 9] The Cf-Cm mixture is loaded onto the resin in dilute acid. Then the column is eluted with AHIB over a pH range from 4.2 to 4.8, to allow for the gradual separation of cations based on the complexation ability of the AHIB reagent for the particular cation. The cation cleanup column is used primarily to separate the Cf from the residual AHIB reagent. Acid is added to the Cf fraction from the AHIB column until the final solution is about 0.3 *M* nitric (HNO<sub>3</sub>); this solution is then loaded onto an AG50X4 cation resin column. The loaded resin is washed with about 10 bed volumes of 0.1 *M* acid (HNO<sub>3</sub> or HCl). The Cf can be stripped off the resin at this point with 8 *M* HNO<sub>3</sub> or 6 *M* HCl. Another option is to continue to wash the column with about 3 bed volumes of 2 *M* HCl prior to stripping with the higher molarity solutions. The washing with 2 *M* HCl appears to remove common metal contaminants (i.e., Fe, Ca, Na) from the Cf material. The anion HCl column was utilized when additional purification from iron (Fe) contamination was needed. A column

was made of MP1 anion exchange resin. The Cf material was dissolved in 8–10 *M* HCl and passed through the MP1 resin. Iron will form chloride complexes and attach to the anion resin while the Cf passes through in the loaded eluate.

The separation of lanthanides from the Cf was of special concern. The separation, using  $^{145}\text{Sm}$ ,  $^{153}\text{Gd}$ , and  $^{249}\text{Cf}$  as tracers, was investigated using BioRad AG 50X8 in AHIB, Eichrom LN resin in both  $\text{HNO}_3$  and HCl, and Eichrom TEVA resin in  $\text{NH}_4\text{SCN}$  [7]. The TEVA  $\text{NH}_4\text{SCN}$  system was found to completely separate  $^{145}\text{Sm}$  and  $^{153}\text{Gd}$  from  $^{249}\text{Cf}$  and was adopted into the process used in purifying the  $^{252}\text{Cf}$ .

### **Use of Surrogate and Tracers for Research and Development**

Experimental parameters (run time, current density, voltage, electrolyte concentration, and initial analyte mass) were studied and modified to optimize the uniformity and adherence of the deposition while maximizing yield.

The procedure utilized samarium (Sm) as the plating material, both with and without a  $^{153}\text{Sm}$  and  $^{140}\text{La}$  radioactive tracers.

### **Reagents and Evaluation Techniques**

Surface characterization studies were performed by scanning electron microscopy, electron microprobe analysis, radiographic imaging, and x-ray diffraction. High-purity reagents were also used throughout the electrodeposition process: ammonium acetate ( $\text{NH}_4\text{CH}_3\text{COO}$ ) certified ACS reagent grade from Fischer Chemical,  $\text{Sm}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  from Fischer Chemical, ultra-pure HCl and  $\text{HNO}_3$  from EMD Chemicals, and  $\text{NH}_4\text{OH}$  certified ACS reagent from Sigma-Aldrich.

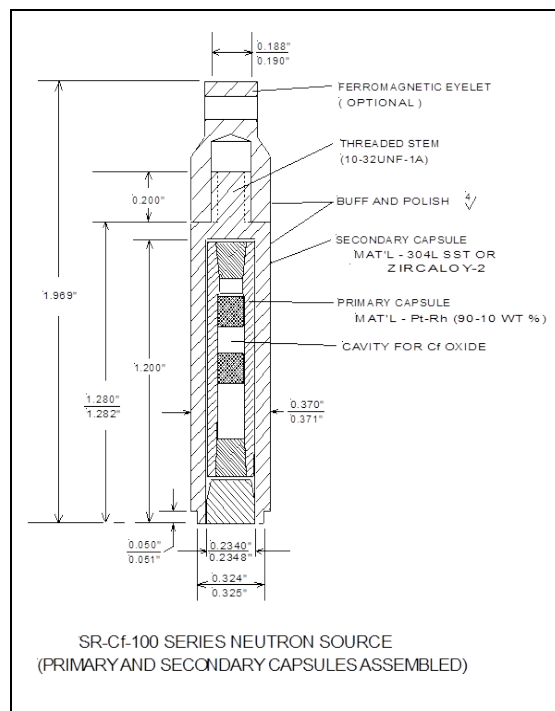
The  $^{153}\text{Sm}$  tracer ( $t_{1/2} = 1.95$  d) was obtained from irradiation of 99.2 wt %  $^{152}\text{Sm}_2\text{O}_3$  in the ORNL's High Flux Isotope Reactor (HFIR) at an unperturbed thermal neutron flux of  $4.05 \times 10^{14}$  neutrons/cm<sup>2</sup>/s. The  $^{140}\text{La}$  tracer ( $t_{1/2} = 1.68$  d) was obtained from the decay of  $^{140}\text{Ba}$  ( $t_{1/2} = 12.7$  d). Separation of daughter La(III) from parent Ba(II) was achieved using cation exchange chromatography (BioRad AG-50X4 resin). Each electrodeposition experiment used ~5  $\mu\text{Ci}$  of radioactive tracer.

### **Isobutanol Electrodeposition Method Used for Target Production for Super Heavy Element Research**

Recently produced Cf material at ORNL HFIR contains ~80%  $^{252}\text{Cf}$  atom percent. This material is not suitable for SHE target material due to the huge amount of radiation released during decay and spontaneous fissioning.

Therefore decayed  $^{252}\text{Cf}$  sources were evaluated as potential SHE target material. At ORNL, several SR-Cf-100 series Cf sources were in storage, some fabricated in the early 1970's. (Figure 1)

Figure 1: SR-Cf-100 series neutron source capsule design. The primary capsule was stainless steel, while the secondary capsule was a zirconium alloy.

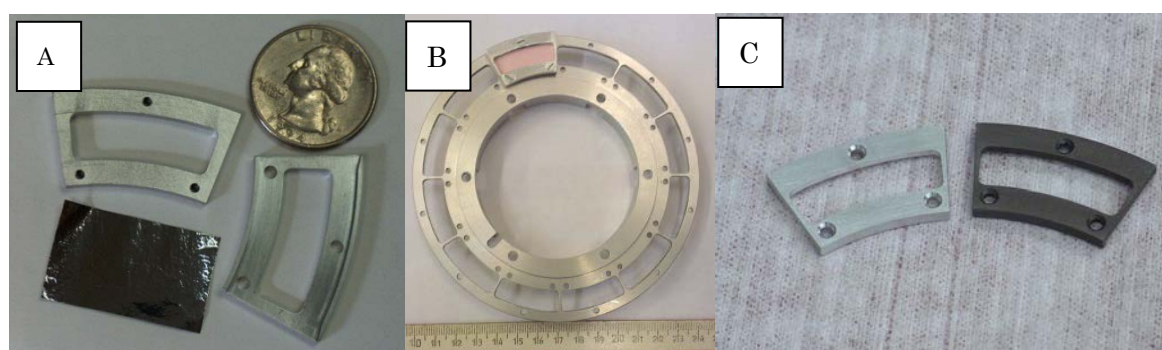


This decay-enriched Cf material contained about 50%  $^{249}\text{Cf}$ , 20%  $^{250}\text{Cf}$ , 30%  $^{251}\text{Cf}$ , and  $<0.05\%$   $^{252}\text{Cf}$ . Several candidate sources were reviewed, resulting in the selection of 17 sources for processing. The capsules were cut open in a hot cell and leached with  $\text{HNO}_3$ , resulting in the recovery of  $15.8 \pm 0.2$  mg of mixed Cf material. This material was then purified as previously described.

A 14 cm diameter rotating target wheel is used in the accelerator at the Joint Institute for Nuclear Research in Dubna, Russia. This wheel previously had been designed to hold three to six target segments of electrodeposited material on thin foils. Because of the higher radiation dose expected from the mixed Cf material, the target segments were reduced in size so that the target wheel would hold 12 individual segments. (Figure 2, B) Each segment consists of a curved frame (aluminum front and stainless steel back) containing a  $3 \text{ cm}^2$  deposition area. (Figure 2, A) The Cf material was deposited onto 1.5 micron thick titanium (Ti) foil which was mounted in the

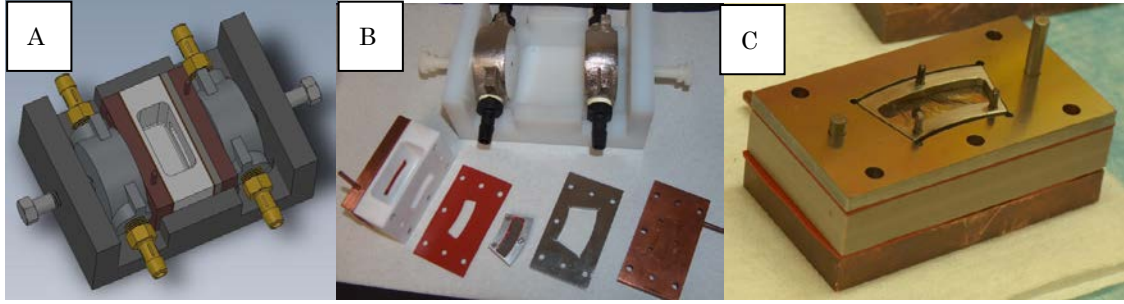
frame. There was a concern that some of the Cf material would deposit onto the front frame that was in contact with the electrodeposition solution. To prevent this occurring, the front aluminum (Al) frame was anodized and Teflon coated. (Figure 2, C)

Figure 2: (A) The components of the target segment relative to the size of a quarter. The back frame (top) is stainless steel, the front frame (right) is Al, and the foil is 1.5 micron thick Ti foil. (B) The target wheel with one segment attached. (C) Two front frames, left one is untreated Al, while the right one has been anodized and Teflon coated.



Since the thin Ti foil is very fragile, the decision was made to mount the Ti foil into the frame prior to electrodeposition. The electrodeposition unit was designed with the assembled segment fitting into the side of the deposition well. (Figure 3) Materials evaluated for the well of the unit were Teflon (polytetrafluoroethylene), acrylic (polymethyl methacrylate), and PEEK (polyether ether ketone). The anode and cathode blocks were copper with a stainless steel frame holding the segment in place. Silicon gaskets were placed on both sides of the well with the front edge of the segment up against the gasket to create a liquid-tight fit from the side. The unit was assembled using 10 screws, five from each side, passing through the copper plates and anchoring in the well material. The PEEK material maintained shape the best as the system was assembled and screws tightened.

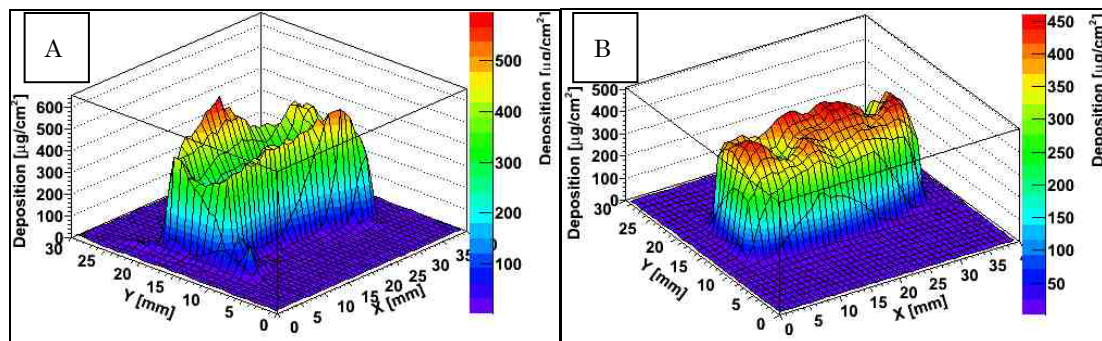
Figure 3: (A) Illustration of the assembled deposition unit. (B) Components of a deposition unit prior to assembly showing from right to left: copper cathode, stainless steel holder for segment, assembled Ti foil target segment, silicon gasket, Teflon well with copper anode attached. The pieces at the top of the picture are the blocks for chilled water to cool the electrodes. (C) Electrodeposition unit assembled with the target segment in place waiting for the copper cathode to be attached. The well is PEEK material. Two non-metal pegs, shown sticking out of the surface, are used for alignment and remain in the assembled unit.



Several test runs with the newly designed unit were performed using 1.2 mg of natural Sm with  $^{153}\text{Sm}$  tracer.

These runs were used to evaluate the optimized parameters for the deposition of the mixed Cf material. Rate of deposition appeared to be a significant parameter. The tests showed that the higher the voltage the more rapid the deposition of the material. For example, when the upper voltage limit was set to 400 volts, 99% of the material deposited in 2 hours, resulting in  $382 \mu\text{g}/\text{cm}^2$ . (Figure 4, A) However, when the upper voltage limit was set to 250 volts, 4 hours was required for 87% of the material to be deposited, resulting in  $349 \mu\text{g}/\text{cm}^2$ . (Figure 4, B) This makes it appear as if the higher voltage was better until one examined the radiographic images of the segments. The faster deposition resulted in most of the material being deposited around the edges of the foil, while the slower deposition presented a more uniform deposition. Thus, for uniformity, lower voltage and a slower deposition rate proved to be most advantageous. [1, 2]

Figure 4: Radiographic images of electrodeposited  $^{153}\text{Sm}$  target segments. (A) Upper voltage limit set to 400 volts. (B) Upper voltage limit set to 250 volts.



The mixed Cf deposition was conducted at  $0.3 \text{ mA/cm}^2$  with the voltage limited to 150 volts for 4 hours. The surfaces exposed to the electrolyte solution were anodized and coated with Teflon to ensure deposition only on the foils themselves. The electrolyte solution consisted of  $\sim 1 \text{ mg}$  of mixed Cf dissolved in  $100 \text{ }\mu\text{L}$   $0.1 \text{ M}$   $\text{HNO}_3$ ,  $300 \text{ }\mu\text{L}$  isopropanol, and  $8.4 \text{ mL}$  isobutanol. This was stirred with a magnetic stir-bar and kept at a constant temperature of  $15^\circ\text{C}$  with chilled-water blocks.

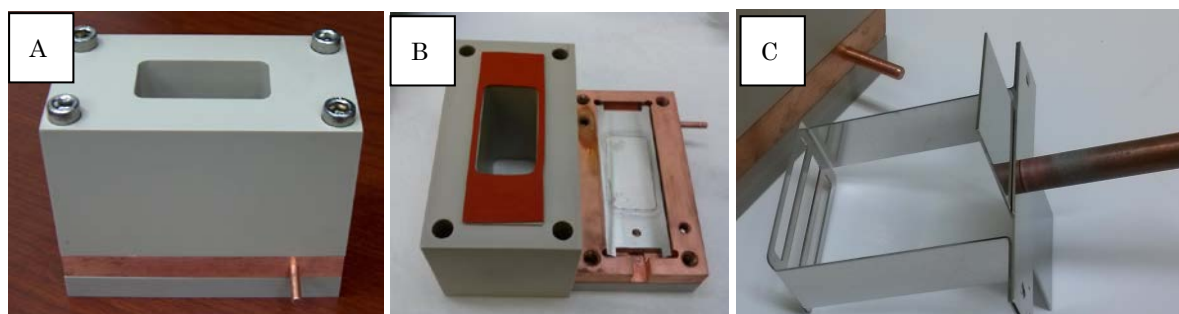
Seventeen deposition runs resulted in 12 successful segments for the target wheel. The average deposition efficiency of the 12 successful runs was 93.3 % (range of 82.5–98.6 %) with an average density of  $309 \text{ }\mu\text{g/cm}^2$  (range of  $239\text{--}382 \text{ }\mu\text{g/cm}^2$ ). The unsuccessful depositions were related to uneven distribution on the Ti foil, torn Ti foils, or the presence of contaminants in the Cf material that required additional cleanup.

### **Ammonium Acetate Electrodeposition Method Used to Produce the World's Largest $^{252}\text{Cf}$**

#### **Electrodeposition**

This project was designed to electrodeposit  $1 \text{ Ci}$  of  $^{252}\text{Cf}$  onto a stainless steel substrate. Due to the high radiation of this material, all steps were performed in a hot cell. The deposition area was rectangular in shape ( $0.75 \text{ inch} \times 1.5 \text{ inch}$ ), resulting in a deposition area of  $7.2 \text{ cm}^2$ . A chimney-type deposition unit was designed with a polished stainless steel plate (304L) inside a copper cathode on the bottom with a platinum anode inserted from the top. (Figure 5) The distance between the anode and the cathode was  $1.0 \text{ cm}$ .

Figure 5: The electrodeposition unit used in the ammonium acetate deposition of  $^{252}\text{Cf}$ : (A) assembled PEEK unit with copper cathode on bottom, (B) opened from bottom, showing silicon gasket on PEEK well and stainless steel deposition plate embedded in the copper cathode, and (C) platinum anode showing the slits to allow gas escape.





The ammonium acetate deposition method has been used at ORNL for the past several decades and was selected for this project because of concerns about high levels of intense radiation in an organic solvent. Ammonium acetate electrodeposition is performed at ~12 volts, which is lower than organic depositions, and at a higher amperage, ~138 mA/cm<sup>2</sup>. No temperature control is required for this method, but significant gas evolution is present. Several test runs were performed using 4.5 mg of Sm with a <sup>140</sup>La tracer. Parameters evaluated were pH, type of acid, current, voltage, deposition time, deposition unit materials (Teflon, acrylic, PEEK), and plate metal (stainless or platinum). Thickness measurements using scanning electron microscopy were performed on a Sm-containing sample and the measurements indicated a plate-to-peak average thickness of 5.3±0.1 μm. For a 1 Ci deposition, 1.86 mg of <sup>252</sup>Cf must be deposited. Previous experiences with a large deposition of this material resulted in ~60% deposition yields, so ~4 mg of <sup>252</sup>Cf was selected for use in this deposition. The Cf sample was purified using the methods described earlier in this paper. The purified <sup>252</sup>Cf material (3.6 mg <sup>252</sup>Cf, 62% of the total Cf) was dissolved in a small amount of HCl and then added to 12 mL of 0.35 M ammonium acetate with a pH of 3.0. A constant current was maintained at 138 mA/cm<sup>2</sup> for the duration of a 5 hour deposition run with a maximum of 12 volts reached during this time. The resulting deposition was very successful, with a 91.5% yield, which resulted in 1.7±0.1 Ci of <sup>252</sup>Cf being deposited on the plate. (Figure 6) The density of all Cf isotopes on the plate was 739 μg/cm<sup>2</sup>, of which 62% was <sup>252</sup>Cf.

Figure 6: Electrodeposited stainless steel plate containing 1.7 Ci of <sup>252</sup>Cf. Picture taken with camera located inside hot cell.



### **Discussion**

The use of ammonium acetate as an electrolyte provides an aqueous matrix that requires low voltage (10–20 V) to achieve quantitative depositions; however, significant bubbling can occur by electrolysis. The aqueous-based ammonium acetate method was selected for use with the extremely high levels of radioactivity from the  $^{252}\text{Cf}$  material. Organics can require voltages in excess of ~100 volts for successful deposition, requiring the use of simple safety shields to provide personnel protection and a water cooling system to maintain a lower operating temperature. Both methods have unique advantages and have provided successful and effective depositions at ORNL.

### **Conclusion**

Unique decay-enriched  $^{251}\text{Cf}$  material was recovered from aged sources stored at ORNL. This material was electrodeposited using the isobutyl alcohol method to produce 12 Ti foil target segments with an average deposition of  $309\ \mu\text{g}/\text{cm}^2$ . These segments will be assembled onto a target wheel and used for SHE discovery experiments at the Joint Institute for Nuclear Research in Dubna, Russia.

Another deposition method, using ammonium acetate, was used to produce a deposition containing 1.7 Ci of  $^{252}\text{Cf}$  onto a stainless steel substrate. A constant current was maintained at  $138\ \text{mA}/\text{cm}^2$  for the duration of a 5 hour

deposition run with a maximum of 12 volts reached during this time. This deposition was very successful, resulting in a 91.5% deposition yield and  $1.7 \pm 0.1$  Ci (3.3 mg) of  $^{252}\text{Cf}$  deposited on the plate. This was the largest single electrodeposition of  $^{252}\text{Cf}$  ever prepared.

The Cf material for both depositions was initially purified using traditional ion exchange media, AG50-AHIB and AG50-HCl columns, and further purified using a TEVA-NH<sub>4</sub>SCN system to remove lanthanides.

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