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Optimization of Uranium Molecular Deposition for Alpha-Counting Sources

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Optimization of Uranium Molecular Deposition for Alpha Counting Sources

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Abstract

Method development for molecular deposition of uranium onto aluminum 1100 plates was conducted with custom plating cells at Lawrence Livermore National Laboratory. The method development focused primarily on variation of electrode type, which was expected to directly influence plated sample homogeneity. Solid disc platinum and mesh platinum anodes were compared and data revealed that solid disc platinum anodes produced more homogenous uranium oxide films. However, the activity distribution also depended on the orientation of the platinum electrode relative to the aluminum cathode, starting current, and material composition of the plating cell. Experiments demonstrated these variables were difficult to control under the conditions available. Variation of plating parameters among a series of ten deposited plates yielded variations up to 30% in deposition efficiency. Teflon particles were observed on samples plated in Teflon cells, which poses a problem for alpha activity measurements of the plates. Preliminary electropolishing and chemical polishing studies were also conducted on the aluminum 1100 cathode plates.

Introduction

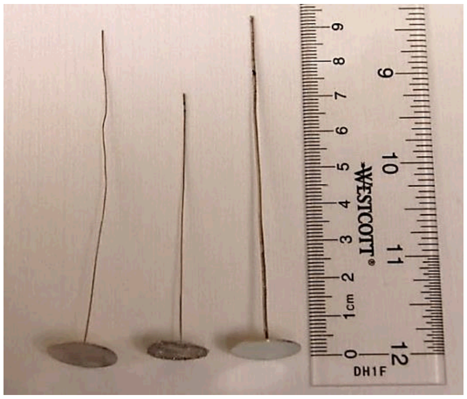
The ^{234}U, ^{235}U, and ^{238}U decay constants (λ) are widely used for radioisotopic dating of materials. Uranium chronometry is regularly applied by the fields of nuclear forensic analysis and geochronology. Both ^{234}U and ^{235}U are common chronometers used in nuclear forensic analysis and the understanding of geologic time is largely based on accurate knowledge of $\lambda_{U\text{-}235}$ and $\lambda_{U\text{-}238}$.[1,2] The most commonly accepted values for $\lambda_{U\text{-}235}$ and $\lambda_{U\text{-}238}$ were determined by Jaffey et al. (1971) and have very small 1σ uncertainties of 0.068% (^{235}U) and 0.054% (^{238}U).[3] However, measurements of comparable accuracy have never been conducted to verify the Jaffey et al. results.[4] Recent work has called for new measurements of $\lambda_{U\text{-}235}$ and $\lambda_{U\text{-}238}$ given the importance of these decay constants and their uncertainties for understanding Earth's history, and the apparent discordance often observed in high-precision U/Pb ages.[4] Additional direct measurements of $\lambda_{U\text{-}234}$ are also warranted to confirm recent work to re-measure $\lambda_{U\text{-}234}$, which relied on ^{234}U/^{238}U isotope ratio measurements of natural materials assumed to be closed systems.[5]

Lawrence Livermore National Laboratory (LLNL) is leading an effort to re-determine $\lambda_{U\text{-}234}$, $\lambda_{U\text{-}235}$, and $\lambda_{U\text{-}238}$. The values $\lambda_{U\text{-}234}$ and $\lambda_{U\text{-}235}$ will be measured via direct alpha counting experiments using a low geometry alpha counter and α-γ coincidence counting. These experiments require homogenous sources with well-constrained geometries and atomic concentrations. The high-precision measurements of Jaffey et al. relied on molecular plated sources subsequently analyzed by direct alpha-counting experiments in an intermediate-geometry 2π alpha spectrometer.[3] Historically, molecular deposition has been used to plate thin films of material onto metallic discs to enable quantitative counting experiments.[6] Ingelbrecht et al. have noted many different cell types and methods for plating, suggesting each unique experimental set-up requires its parameters to be individually optimized.[7] The goal of this work was to characterize and optimize source production methods to produce uranium sources suitable for direct alpha-counting experiments. Multiple variables were investigated, most notably the type of platinum anode. Additionally, Teflon cells were tested because they should resist uranium sorption and increase plating yield. Cathode polishing was also targeted for optimization because it has been shown to improve source homogeneity.[6]

Methods

Depleted uranium sources were prepared by electrodeposition using methods reported by Parker et. al,[6] then characterized by alpha spectrometry, autoradiography, and scanning electron microscopy (SEM). Three platinum electrodes, pictured in Figure 1, were tested with either a glass (Figure 2) or Teflon (Figure 3) molecular deposition cell. Of the three platinum electrodes used, two had solid platinum discs and one had a platinum mesh surface. The thickness of the wire stems attached to each electrode varied between 0.4 and 1.0 mm diameter. The diameter of the platinum mesh electrode surface was 1.5 cm. The diameter of both solid platinum disc electrodes was 1.7 cm. The exposed cathode surface in both cell types was 1.65 cm in diameter, yielding a plating area of 2.14 cm^2. The inside wall of the Teflon cell was machined with a 30^o reverse bevel at the bottom, similar to that described by Jaffey et. al.[3] This indents the wall 0.25 mm to prevent removal of the source edges when the cell is disassembled.

Side View.



End View.

Figure 1. Three platinum electrodes used as anodes in electrodeposition. From left: solid disc electrode with thin wire stem, mesh electrode with thin wire stem, and solid disc electrode with thick wire stem.

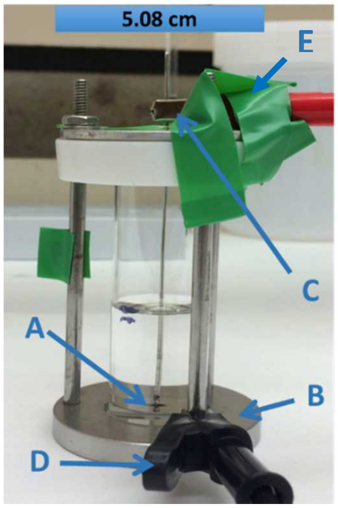


Figure 2. Glass chimney molecular deposition cell. A: Platinum disc electrode suspended a few mm above an aluminum 1100 plate. B: Stainless steel cell base with inset for aluminum disc. A thin Teflon washer (not visible) sits between the disk and the bottom of the glass chimney. C: Anode (red alligator clip). D: Cathode (black alligator clip). E: Green electrical tape to stabilize platinum anode position.

Figure 3. Teflon chimney molecular deposition cell. A: Stem of platinum electrode inserted into cell. B: Stainless steel cell base with inset (not visible) for aluminum disc. C: Teflon chimney.

Chemicals. Isopropyl Alcohol (IPA) (99.9 % HPLC grade, SigmaAldrich Chromosolv), concentrated perchloric acid (65-71%, SeaStar), concentrated acetic anhydride (99+%, Alpha Aesar), concentrated phosphoric acid (86.9%, SeaStar), and concentrated acetic acid (99.9985% glacial, Alpha Aesar) were used as received. Concentrated nitric acid (67-70%, SeaStar) was used as received or diluted by volume with milli-Q water. Solutions of 5% HNO_3, 0.05M HF were prepared by weight using milli-Q water, Seastar concentrated nitric acid, and concentrated HF (47-51%, Seastar). Milli-Q 18.2 megaohm ionic purity water was obtained through a Millipore filtration system. Depleted uranium (DU) was obtained as UO_2, around 1960 ± 10 years, from the Cerac company, with the following isotopic composition (atom % ± 2σ): 99.790 ± 0.174 % ^{238}U, 0.20662 ± 0.00025 % ^{235}U, and 0.0007771 ± 0.0000083 % ^{234}U. The Cerac DU was dissolved in nitric acid, and Th removed by LaF_3 co-precipitation approximately 2 months prior to the beginning of plating experiments.

Plating Cell Components. Aluminum 1100 discs of 2.54 cm (1 in) diameter, 0.813 mm thick, and mechanically polished to a mirror finish were obtained from Anthony Gallien Inc. and rinsed with IPA and milli-Q water before use. The mechanically polished discs were used in plating experiments as received, without further electropolish or chemical treatment. The disposable 2.54 cm (1 in) outer diameter PTFE Teflon washers for the glass cells were obtained from D.K. Milovik Company Inc. The borosilicate glass chimneys were purchased from Research & Development Glass Products & Equipment, Inc. in Berkeley, CA, and rinsed with 5% HNO_3/0.05% HF, Milli-Q water, and IPA before use. Teflon chimneys composed of polytetrafluoroethylene (PTFE) or perfluoroalkoxy alkane (PFA) were custom designed at LLNL and manufactured by D.K. Milovik Company Inc. in Livermore, CA. All Teflon components were washed with cleaning solution (5% HNO_3, 0.05M HF), Milli-Q water, and IPA before use.

Molecular Deposition. Mass aliquots of DU stock solution containing approximately 10 μg DU in 2.5 M HNO_3 were dried down in a PFA vial at 130°C and fumed with nitric acid (16 M, 50 μL) twice to destroy organics before being dissolved in 50 μL Milli-Q water. Room temperature IPA (500 μL) was added to the DU solution and the entire sample volume was transferred to an assembled cell. Five additional IPA aliquots totaling 11,500 μL were successively added to the original sample vial and transferred to the cell to ensure quantitative transfer of the DU. A platinum anode was suspended in the 12 mL solution volume 2-3 mm above the aluminum cathode plate. A potential of 600 V was applied for 90 minutes at room temperature or until current stopped flowing per the power supply readout. Power supplies used were a Matsusada Precision TB360W or Fisher Scientific FB1000-1 Electrophoresis power supply. The plated samples were baked on a hot plate at 500°C for 120 minutes inside of an aluminum foil tent to convert the plated uranium nitrate into a uranium oxide layer. Between samples the Pt electrodes and Teflon cells were cleaned twice by boiling in 2.5 M HNO_3, or 8 M HNO_3, respectively, for at least 45 minutes, and then rinsing with Milli-Q water. Glass chimneys and Teflon washers were used only once.

Aluminum Polishing. Aluminum 1100 plates were electropolished using a polishing solution containing 4.14 mL perchloric acid and 7.86 mL acetic anhydride at ~113 mA and 6 V using a Fisher Scientific FB1000-1 Electrophoresis power supply according to established procedure.[6] Alternatively, aluminum 1100 plates were chemically polished by submersion in a solution of 5.200 mL milli-Q water, 1.244 mL 16 M nitric acid, 31.090 mL perchloric acid, and 2.488 mL acetic acid.

Autoradiography. Activity distribution in the uranium oxide deposits was imaged by autoradiography using a GE Typhoon FLA 7000 scanner and SR-type phosphor screen image plates scanned at 626 V after a 22-hour exposure with the image plate in direct contact with samples. Images were processed with ImageJ software.

Electron Microscopy. SEM and back-scatter electron (BSE) images were acquired using an FEI Inspect F SEM equipped with an Everhart-Thornley secondary-electron detector. Energy dispursive X-ray spectra (EDS) corresponding to BSE images were obtained and analyzed with Bruker Esprit 2.0 software.

Alpha-Spectrometry. The alpha activity of plated samples was characterized with an Ortec alpha-duo counting system, with an Ortec Ultra-AS ion-implanted Si detector.

Results and Discussion

Thirteen quantities were identified as variable parameters of the molecular deposition process (Table 1). Of the thirteen parameters, ten were held constant and three (sample homogeneity, starting current, and cell type) varied among plating experiments. It was hypothesized that electrode type would influence the sample homogeneity. Thus, the sample homogeneity parameter was studied by changing electrode types. Because of the size relationship between electrode type and cell type, it was not possible to systematically control the cell type parameter among a series of plated samples. Electrode type and cell type were not studied in isolation because the solid disc electrodes were too large for the Teflon cell diameter and could only be used with a glass cell. Likewise, the smaller diameter mesh electrode was used exclusively with the Teflon cells.

A consistent starting current among plated samples was not achieved and the parameter(s) that control starting current are presently unknown. However, starting current likely depends on multiple factors including differences in electrode type, cell type, electrode position, and most notably electrode height above the aluminum plate. Electrode height and position were not well-controlled because the experimental design used an alligator clip and electrical tape to suspend the electrode above the aluminum at an approximately centered location. Neither the electrode position nor height could be precisely controlled by clipping the electrode to an alligator clip.

Table 1. Experimental parameters and their corresponding controlling factors. Parameters are separated into constant and variable categories.

	Parameter	**Controlling Factor**
Constant Parameters	Source (cathode) area (cm^2)	Fixed at 2.14 cm^2
	Cathode material	Aluminum 1100
	Plating voltage (V)	600
	Deposition time (min)	90 (or until current reached zero)
	Total solution volume (mL)	12
	Organic solvent	Isopropyl alcohol
	Baking time (min)	120
	Baking temperature (°C)	500
	Aluminum cathode polishing	none
	Mass DU	Approximately 10 µg
Variable Parameters	Sample homogeneity	Type of platinum electrode
	Cell type	Glass or Teflon
	Starting current	unknown

1. Molecular Deposition Plates

A series of 10 μg DU plates were produced according to the constant and variable parameters outlined in Table 1. Different electrode types, cell types, and starting currents were used to produce plates A-J (Supplemental Table 1). Figure 4 displays a plot of count rate vs. starting current for plates A-J. Given the wide variation among plating parameters, a large variation in relative yield taken from the count rate was expected among the ten plates. For example, the starting current varied between <1 and 7 mA among plates A through J (Supplemental Table 1). Despite this, the variation in relative yield taken from the count rate was at most 30%.
Given the lack of direct correlation among the starting current and count rate variables, a variation in relative yield higher than 30% was expected. The relative yield variation of only 30 % indicates the plating procedure is relatively robust in terms of the amount of activity deposited despite observed variations within the range of starting currents, electrode types, and cell types used.

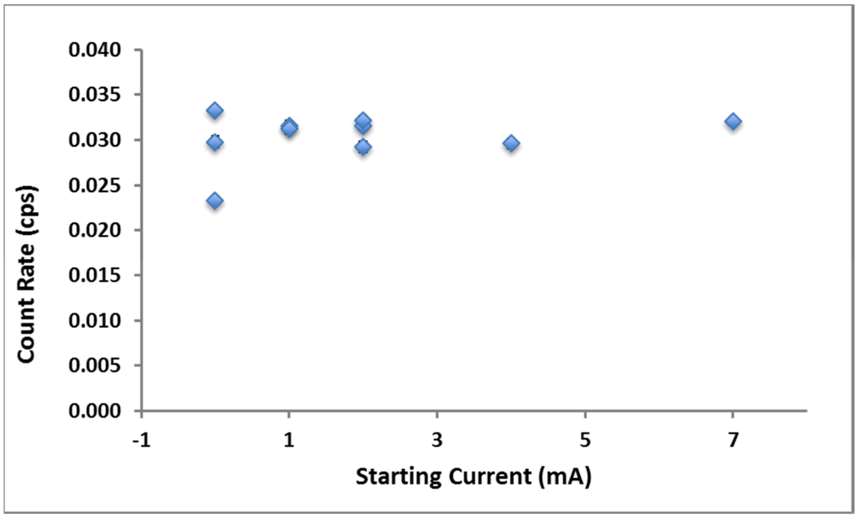


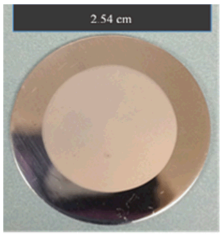
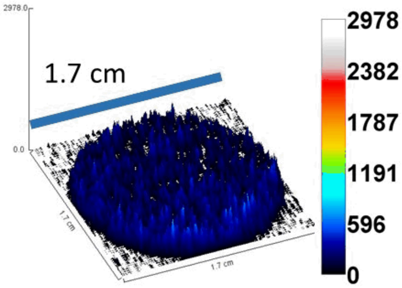
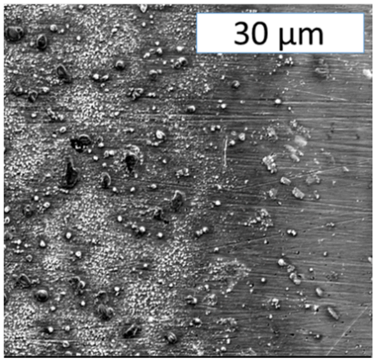
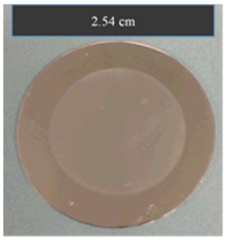
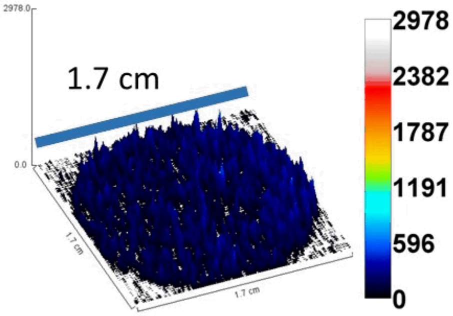
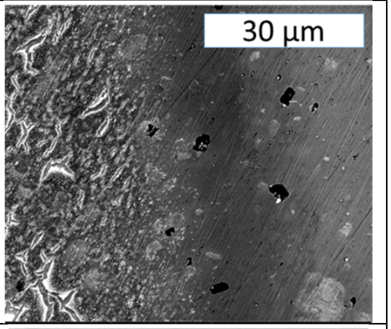
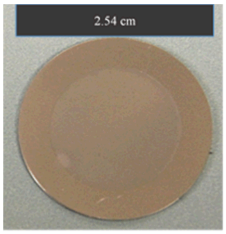
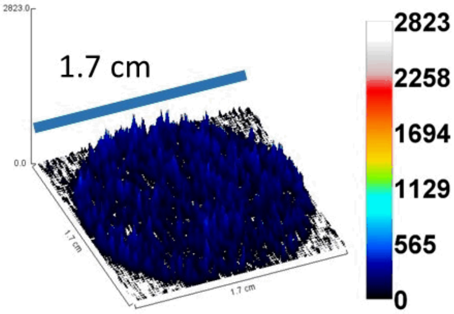
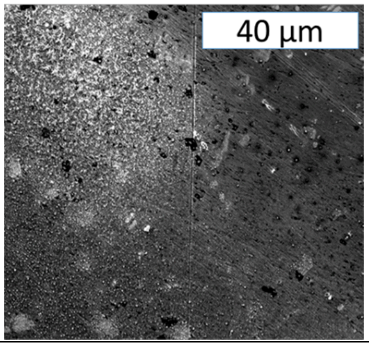
Figure 4. Variation of starting current with count rate among plates A through J.

2. Electrode Type and Homogeneity

Electrode type was hypothesized to influence the activity distribution homogeneity of the plated sources. Table 2 shows a comparison among the optical images, 3-D autoradiographs, and SEM images for plates A, C, and J which correspond to three different electrodes. Among the three electrodes, two had solid platinum discs and one had a mesh surface. 3-D autoradiographs show the spatial distribution and signal intensity of the DU activity plated onto each aluminum disc. The activity distribution on each plate observed with autoradiography provided qualitative sample homogeneity information. The autoradiography results show the solid disc electrode with a thin wire stem (plate C) and the solid disc electrode with a thick wire stem (plate J) produced more even distributions of activity compared to the mesh electrode with a thin wire stem (plate A). Both plates C and J have areas of moderate (dark blue) signal intensity on both halves of their circular plated areas. In contrast, plate A has an area of high signal intensity (light blue) on one edge of the plated surface and an area of low signal intensity (black) on the opposite edge. Overall, the mesh electrode concentrated the activity on one half of plate A.

Secondary electron images display the plated and non-plated interface with plated uranium oxide in the lower left corner and bare aluminum 1100 in the upper right corner. Secondary electron images show differences in surface morphology features and illustrate inhomogeneity on a micrometer scale. The images of the three plates display cracks and irregularly spaced particles of uranium oxide.

Table 2. Plates A, C, and J. Optical, 3-D autoradiograph, and SEM images. Optical images of plated sources have white areas covered with uranium oxide. Lighter colors in the autoradiograph and 3-D autoradiograph images have areas of higher signal intensity which correspond to areas of higher activity. SEM images show surface morphology.

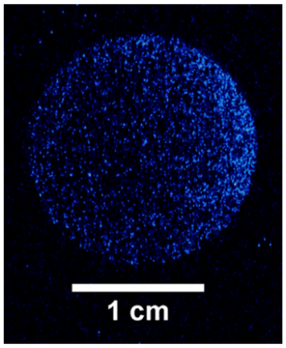
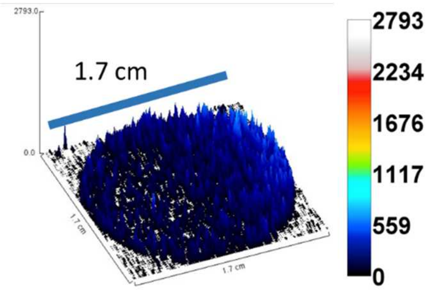
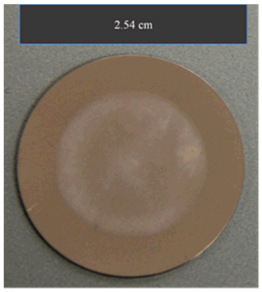
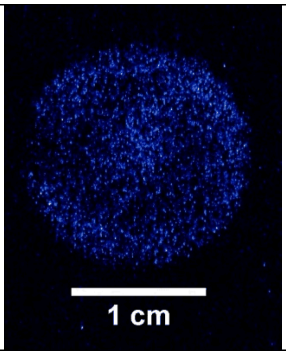
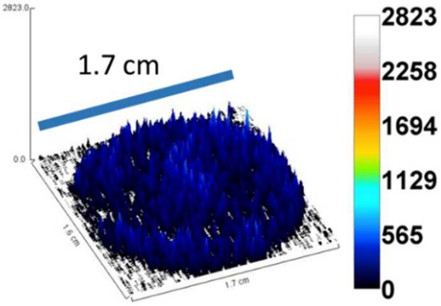
Plate Name and Electrode Type	Optical Images of Plates	3-D Autoradiographs	SEM Images
Plate A: Mesh electrode with thin wire stem			
Plate C: Solid disc electrode with thin wire stem			
Plate J: Solid disc electrode with thick wire stem			

3. Electrode Effects on Activity Distribution

A tilted electrode was observed to change the spatial distribution of the plated activity on the aluminum plate. The weight of the red alligator clip (Figure 2) frequently caused the platinum electrode to tilt sideways during plating. The non-parallel orientation of the platinum anode disc relative to the aluminum cathode that resulted from this tilting influenced the spatial distribution of the plated DU observed in the optical image, autoradiography image, and 3-D autoradiograph of plate E. 3-D autoradiographs reveal the spatial distribution and signal intensity. The high signal intensity present predominantly on one side of plate E suggests one side of the electrode disc was closest to the aluminum surface. The greater mass of DU observed on the portions of plate E closest to the platinum anode was likely the result of increased current density in this area.

The spatial distribution of the platinum in the mesh electrode also influenced the spatial distribution of plated DU. An optical image, autoradiography image, and 3-D autoradiograph of plate I are shown in Table 3. The 3-D autoradiograph of plate I has a circular ring pattern of high signal intensity along with one line of high intensity radiating out from an approximately central point. This circular pattern with a radial line corresponds to the structure of the platinum wire used to support the platinum mesh electrode. The DU plated most heavily on areas directly below the thick wire frame of the Pt mesh electrode and less on the areas covered by the thin mesh. This behavior was likely also caused by higher current density below areas of higher platinum density.

Table 3. Plates E and J. Optical, autoradiograph, and 3-D autoradiograph images. Optical images of plated sources have white areas covered with uranium oxide. Lighter colors in the autoradiograph and 3-D autoradiograph images have areas of higher signal intensity which correspond to areas of higher activity.

Plate Name and Electrode Type	**Optical Images of Plates**	**Autoradiograph Images**	**3-D Autoradiographs**
Plate E: Solid disc electrode with thick wire stem			
Plate I: Mesh electrode with thin wire stem			

4. Teflon Particles

Unknown particles of material were noted on plated samples through visual inspection immediately after removal from the both the glass and Teflon plating cells. Energy dispersive X-ray spectroscopy (EDS) of an unknown particle spot on plate H displayed a high fluorine content. The presence of fluorine strongly suggests the particles were pieces of Teflon. A washer in the glass plating cell is composed of Teflon and the chimneys of the Teflon cells are composed of PFA and PTFA Teflon. The presence of Teflon poses a problem because it could interfere with alpha-particle emissions from the plated surface and artificially reduce the measured activity of the plate.

It was hypothesized that the Teflon flakes observed on plated samples were caused by loose particles on the machined surfaces of the Teflon chimneys. To try to remove the Teflon flakes, Teflon chimneys were exposed to a standardized gross ultrasonic detergent cleaning process followed by a standardized chemical cleaning process for the treatment of stainless steel components.[8] These cleaning processes were unsuccessful and Teflon flakes continued to appear on plated samples. The Teflon chimneys were then exposed to a second cleaning process. The inner milled surface of each chimney was scrubbed for approximately 10 minutes with a toothbrush and toothpaste. Toothpaste was used because it contains an abrasive grit. After removal of loose toothpaste, chimneys were submerged in milli-Q water and sonicated for 40 minutes. The toothpaste cleaning and sonication cycle was repeated twice for each chimney. Finally, each chimney was boiled in a 2.5 % HNO_3 solution for 70 minutes. This second cleaning process also produced no marked decrease in the amount of Teflon flakes observed.

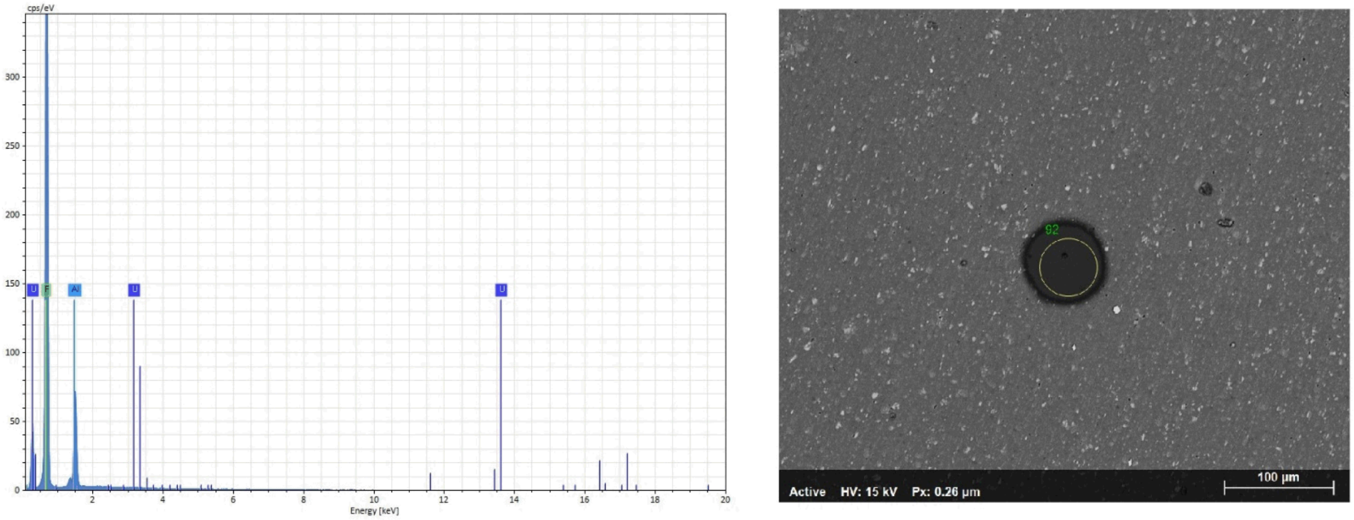


Figure 5. Left: EDS energy spectrum obtained with Bruker Esprit 2.0 software. Right: BSE image of the unknown spot.

5. Polishing Approaches

The results of preliminary electropolish and chemical polish studies of the aluminum 1100 plates were characterized with SEM. Secondary electron images of an electropolished plate (Figure 6) and a plate submerged in chemical polish for 1 minute (Figure 7) reveal signs of etching and pitting. A plate chemically polished for 30 seconds at 23°C shows the effects of aluminum flaking (Figure 7). Etching, pitting, and flaking are non-ideal for homogeneous molecular deposition of uranium because they produce a nonuniform plating surface.

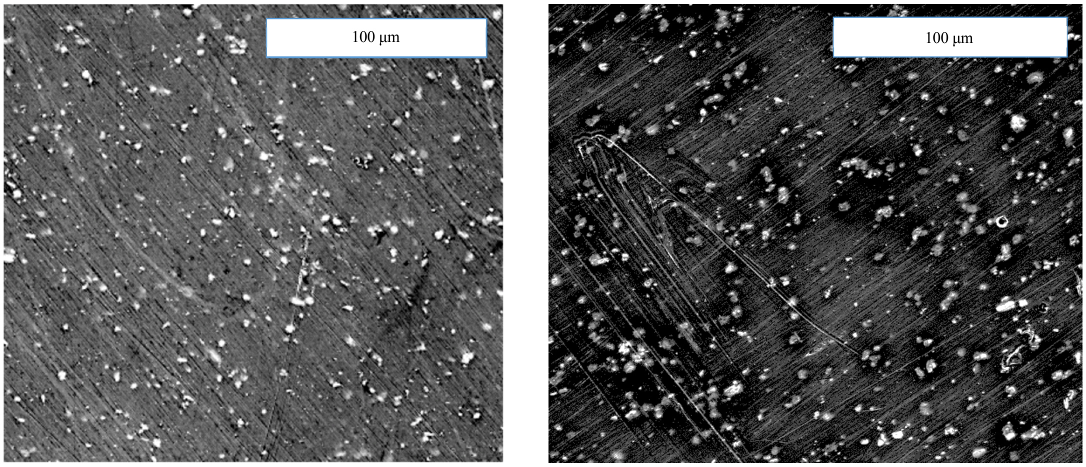


Figure 6. Left: unpolished aluminum 1100 plate. Right: electropolished aluminum.

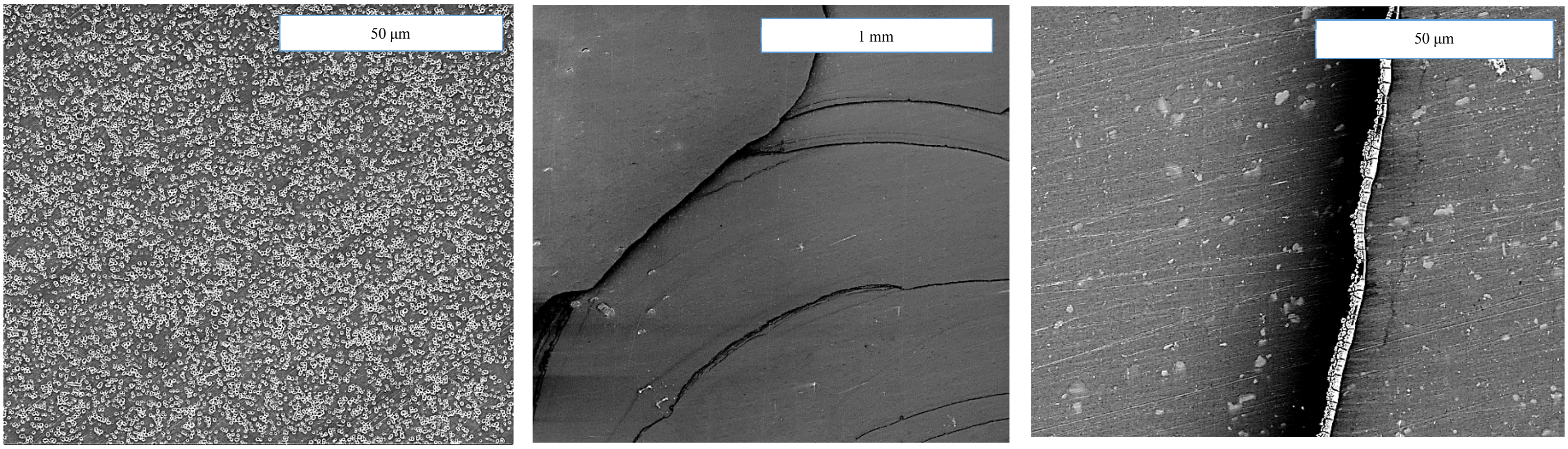


Figure 7. Left: aluminum 1100 surface after a 1 min chemical dip at 100°C, Center: flaking edges on the aluminum 1100 surface after a 30 second chemical dip at 23°C. Right: close up image of flaked edge.

Conclusions

A series of ten plates each containing approximately 10 µg DU were produced through molecular deposition methods. Ten plating parameters were held constant and three varied among the set of ten plates. Despite marked differences among the entire set of ten plates, the amount of DU deposited fluctuated by at most 30 %. Of the different platinum electrodes tested, the two solid disc electrodes produced the most homogeneous activity distribution. In addition, differences in plated source activity distribution were noted in 3-D autoradiograph images of plates E and I. A tilted solid disc platinum electrode caused most of the activity on plate E to be located on one half of the plate. Similarly, areas of plate I directly below thicker sections of the platinum mesh electrode corresponded to areas of higher uranium deposition. Given the effects of platinum distribution on plate I, it is likely the more uniform platinum material distribution of the solid discs compared to the wire mesh electrode contributed to the higher homogeneity of plates C and J compared to A.

An improved cell design with precision control of electrode height and orientation is needed. These improvements are required for future investigations to pinpoint the parameters that determine starting current and control yield. Further work should also include plating five copies of a 10 μg DU plate with a platinum disc electrode to verify the reproducibility of results. Current results indicating the solid disc electrodes produce the most homogeneous sources could be influenced by tilt effects. Parker et al. suggests constant agitation of the plating solution improves source homogeneity.[6] A stirring method to produce constant agitation of the plating solution should be developed in future work. Future work is also needed to develop a computer program to enable quantitative comparison among the activity distributions shown in autoradiograph images.

Teflon particles were observed on plated samples and electropolishing and chemical polishing results were poor. Backscatter electron microscopy maps are need to determine the spatial distribution and frequency of Teflon spots on plates in order to quantify how much the presence of small Teflon particles could interfere with alpha-activity measurements. Optimization of aluminum polishing techniques is also required.

Acknowledgments

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Supplemental Table 1: Molecular deposition plating parameters for plates A through J.

Plate	**A**	**B**	**C**	**D**	**E**	**F**	**G**	**H**	**I**	**J**
Type of Cell	PFA Teflon	PFA Teflon	Glass	Glass	Glass	Glass	Glass	PTFA Teflon	PTFA Teflon	Glass
Platinum Anode	Mesh	Mesh	Thin wire solid disc	Thick wire solid disc, Weld #1	Thick wire solid disc, Weld #1	Thick wire solid disc, Weld #1	Thin wire solid disc	Mesh	Mesh	Thick wire solid disc, Weld #2
Agitation of Solution	None	None	None	None	None	None	None	Some	None	None
Starting Electrode Height Above Aluminum (mm)	~3	~3	~3	2.4	5.5	5.7	4.9	~3	~3	~5
Was electrode height varied?	No	No	No	Yes	No	Yes	No	No	No	No
Starting Current (mA)	4	2	< 1	7	1	< 1	1	< 1	2	2
Ending Current (mA)	3	2	< 1	5	< 1	1	1	< 1	1	1
Plating Time (minutes)	90	90	86	90	90	90	90	90	90	90