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A robust, field-deployable method for the electrodeposition of actinides

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Several methods for the electrodeposition of actinides for alpha-spectrometry analysis have been developed over the past few decades, but none have been specifically designed to facilitate rapid analysis in a field situation. This paper describes the development of an electrodeposition procedure that is specifically adapted for use in a mobile lab. Using these techniques one would be able to obtain preliminary results in the event of a radiological incident. Quantitative yields with associated uncertainties have been determined for the procedure. It has also been shown that short deposition times can provide quantitative results.

Introduction

Isotope actinide analysis by electrodeposition is a well-developed field in the science of radiochemistry. Chemical procedures for the preparation and electroplating of actinides in solution have existed since the 1940s, with established procedures developed during the 1970s still widely in use today.[1–5] Indeed, the success of such vetted procedures has been so great that there have been relatively few attempts to advance these procedures over the last 30 years. Nevertheless, several notable papers have reported optimized parameters for certain techniques and for achieving the highest recoveries of specific actinides.[6–8] However, all of these papers assume a standard laboratory setting for their methods and none have tried specifically to address adapting their methods for work in the field with a mobile radiochemistry lab.

For use in a mobile radiochemistry lab these techniques have to be optimized for a different set of goals: mobility, automation, and speed. To achieve mobility the reagents must be shelf-stable and minimally hazardous; in addition, the equipment should be rugged and the procedure should not evolve any toxic gases. Since the potential for automation is a highly desirable feature for any field application, the procedure must be free steps that would be difficult to automate such as fuming with a base and using a color-changing indicator. Steps that require subjective, judgment calls, such as a critical evaporation, should be avoided. Finally, in order to obtain rapid results, the procedure must be free of tedious steps such as a pH adjustment. Also, a minimal deposition time to achieve quantitative results should be investigated and established.

The method that seemed to best suit our needs was that first described by KRESSIN,[1] using the sodium bisulfate-sodium sulfate electrolyte. This method has since been explored in other papers where it was described as “very robust.”[7] The electrolyte can be prepared so that it is pre-adjusted to an optimal pH, so that no further adjustment is needed. The electrolyte and its decomposition product are both excellent solvents for ignited oxides.[7] The result is that the evaporation step is less critical and require much less human judgment.

This work reports the yields of uranium, neptunium, plutonium, americium, and curium using the method adapted from BAJO.[7] The current density employed in all trials was 0.606 A/cm^2, which was significantly higher than used by BAJO. The results show that quantitative results can be obtained with as little as 25 minutes of deposition time.

Experimental

The first part of the experiment consisted of determining the yields of uranium, neptunium, and plutonium, americium, and curium in 10 trials. The large number of experiments allowed for excellent characterization of the recoveries for each element as well as well as the inherent variance in the results. The second part of the experiment consisted of single experiments to determine the electrodeposition time dependency of each actinide. Deposition times of 5, 10, 15, 20, 25, 30, 40, 50, and 60 minutes were evaluated.

Solutions of natural uranium, ^{237}Np, ^{239}Pu, ^{241}Am, and ^{244}Cm were prepared from National Institute of Standards and Technology (NIST) traceable standards obtained from Analytics Inc. Stock solutions were prepared by diluting a known volume of these standards. There were three working standards: one of natural uranium (approximately 1.02 Bq/ml), one of ^{237}Np and ^{239}Pu (0.617 Bq/ml and 0.432 Bq/ml, respectively), and one of ^{241}Am and ^{244}Cm (0.523 Bq/ml and 0.351 Bq/ml, respectively). The solutions were combined in this manor and co-deposited to form three samples in order to increase the speed of the method, while ensuring that there were no interfering spectral lines.

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All other reagents used in the trials (1.00M $NaHSO_4$, 1.00M Na_2SO_4, 1.5M NH_4OH) were reagent grade materials, which were diluted with distilled, de-ionized water.

The electrodeposition apparatus was obtained commercially from Phoenix Scientific Sales, but was modified significantly before use. The constant voltage power supply was replaced with a constant current power supply by Protek, capable of delivering up to 3 A to each cell with a floating voltage of 0–30 V. All materials that contact the electrodeposition solution are disposable, except for the platinum wires. Each cell (Fig. 1) is made up of a 20-ml LSC vial by Wheaton with the bottom cut off. The caps are black phenolic open caps, also by Wheaton. The planchets are polished on one side and covered with plastic, which is removed prior to use, and have a diameter of 1.905 cm and a thickness of 0.889 cm. The area available for deposition is 1.98 cm^2.

The samples were prepared by adding 0.250 ml of each of the three stock solutions to an appropriately labeled beaker. Then 0.625 ml of a 1.00M $NaHSO_4$ solution was added to each beaker and swirled to ensure adequate mixing. The beakers were then placed on a hotplate and taken to dryness. The hotplate should be hot enough to ensure rapid evaporation, but should not be hot enough that it causes splattering of the solution onto the walls of the beakers. Once dry, the beakers were allowed to bake for 15 additional minutes. The beakers were then removed and allowed to cool. Then 5 ml of the electrolyte solution (0.52M Na_2SO_4 and 0.06M $NaHSO_4$) were added to beakers, dissolving the residue. At the stated concentrations the electrolyte solution is buffered at a pH of 2.0. Each solution was then transferred to individual deposition cells, shown in Fig. 1. Then another 5 ml of the electrolyte solution was added to the beakers and transferred to the deposition cells. The platinum wire electrodes were then lowered into the solution to a final height of 5 mm above the planchets. The cells were then covered by a splatter guard and samples were electrodeposited at 1.2 A for a specified time. For the repeated trials to characterize the recoveries of each element the deposition time was 60 minutes. After the deposition time had elapsed, the remaining volume of the cells was filled with 1.5M NH_4OH and the current was allowed to run for an additional minute before being shut off. The cells were then removed from the deposition unit and the remaining solution was discarded. The planchets were then removed from the cells and rinsed liberally with distilled de-ionized water. The planchets were then allowed to dry before being counted.

Once dry, the planchets were counted using a Canberra Alpha Analyst and Alpha Acquisition and Analysis software. The unit was energy and efficiency calibrated using a custom electrodeposited alpha-source prepared and certified by Analytics Inc., containing ^{238}U, ^{234}U, ^{239}Pu, ^{241}Am. The absolute efficiency was approximately 29% for each detector with a source distance of about 0.5 cm. Uncertainties of individual counts were determined by using one sigma as calculated from the counting statistics.

A first order exponential curve was used to fit a plot of each actinide's recovery versus deposition time in order to determine the deposition rate and the electrodeposition half-time. The equation which was fit to the experimental data was of the form:

$$y = a(1-e^{-bx})$$

where a is the maximum recovery and b is the deposition rate constant. The 10 trials characterizing the recovery of each actinide with a deposition time of 60 minutes was analyzed for standard deviation of the set.

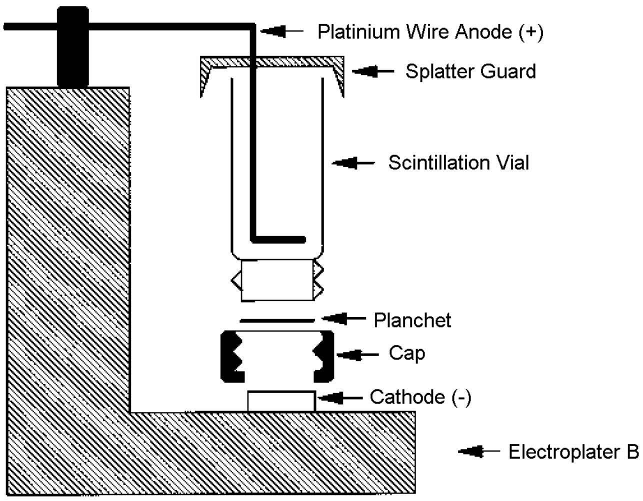

Fig. 1. Diagram of the electrodeposition cell used in all experiments

Results and discussion

The results of the repeated trials of each actinide are presented in columns 2 and 3 of Table 1. The best recoveries were realized for the uranium, plutonium, and americium isotopes. For these isotopes recoveries of 100% are achieved with the associated standard deviations of the sets. The recoveries for neptunium and curium are high but are not optimal. The cause for the procedure's various levels of success likely lies in the one-size-fits-all approach to controlling the pH of the electrolyte solution. For the sake of the level of simplicity sought for this field method, we constructed the electrolyte so that it would buffer the cell at a pH of 2.0. It has been demonstrated that a pH of about 2.0 is sufficient to yield optimal recoveries for uranium, plutonium, and americium.[6] While a higher pH of about 2.5 is optimal for the recovery of neptunium and curium.[8] Because the oxidation states of many actinides can vary considerably with pH it is not possible to deposit all actinides optimally using only one electrolyte pH value. Nevertheless, the recoveries of all actinides studied are sufficiently high and well characterized to justify using this procedure in the field to obtain preliminary results.

The rest of Table 1 is dedicated to presenting the results of the electrodeposition time trials of each actinide. A graphical representation of the time trial results for each element is given in Figs 2a–2e. These curves are similar to those that have been previously published,[6,8] but the rise of each curve is somewhat steeper as can be shown quantitatively by their associated rate constants in Table 1. The recoveries of all actinides are virtually complete with only 25 minutes of electrodeposition time. The increased rate of deposition seen in the results is likely a result of the high current density (0.606 A/cm^2) employed in the all trials.

This high current density does have the potential to ruin the results if too much of the electrolyte evaporates. If the degree of evaporation is high, the buffering capacity of the cell will break down as the solution becomes more concentrated. During evaluation of this method at the University of Texas at Austin a few milliliters of solution was observed to be lost during a 60 minute deposition. However, during evaluation of this method at the Los Alamos National Laboratory the evaporation of the electrolyte was sufficient to halt the experiment after only 15 minutes of deposition time. The difference in elevation and climate between the two locations is the likely cause of the dramatically different results. Local climatic conditions in Los Alamos (elevation 2225 m and generally very low humidity) promote evaporation to a much larger degree than climatic conditions in Austin (elevation 152 m and generally very high humidity).

In order to adapt this procedure for use in Los Alamos some alterations were made. First a taller cell was used to promote reflux action within the cell volume so that some of the evaporated electrolyte could be recaptured. Second the current applied to the cell was decreased to 0.77 A, thus reducing the amount of heat the electrolyte absorbs. Finally the area of the planchet available for deposition was reduced using a cell with a narrower mouth. With the diameter of the active area reduced to 1.27 cm the same current density level of 0.606 A/cm^2 can be achieved with only 0.77 A, thus reducing the heat load on the electrolyte. Experiments using the modified cells produced virtually identical uranium recoveries to the previously described cell. Trials of other actinides were not attempted.

Table 1. Experimental results showing the average recoveries and uncertainties (standard deviation of the sets) of the repeated trials at 60-minute of electrodeposition time and the results of the first order exponential rise to a constant fit of the time-trial plots

Element	Average recovery, %	Uncertainty, %	Max. recovery, %	Rate, min^{-1}	Half-time, min	R^2
Uranium	98.19	2.84	98.82	0.0922	7.52	0.9356
Neptunium	87.91	4.22	92.18	0.0650	10.66	0.9046
Plutonium	98.71	5.90	106.80	0.0783	8.85	0.9273
Americium	95.54	5.35	99.23	0.0892	7.77	0.9458
Curium	78.37	7.96	79.91	0.0961	7.21	0.9490

R^2 is the square of the correlation coefficient, which is a measure of the reliability of the regression to model the relationship between the deposition rate constant and the recovery.

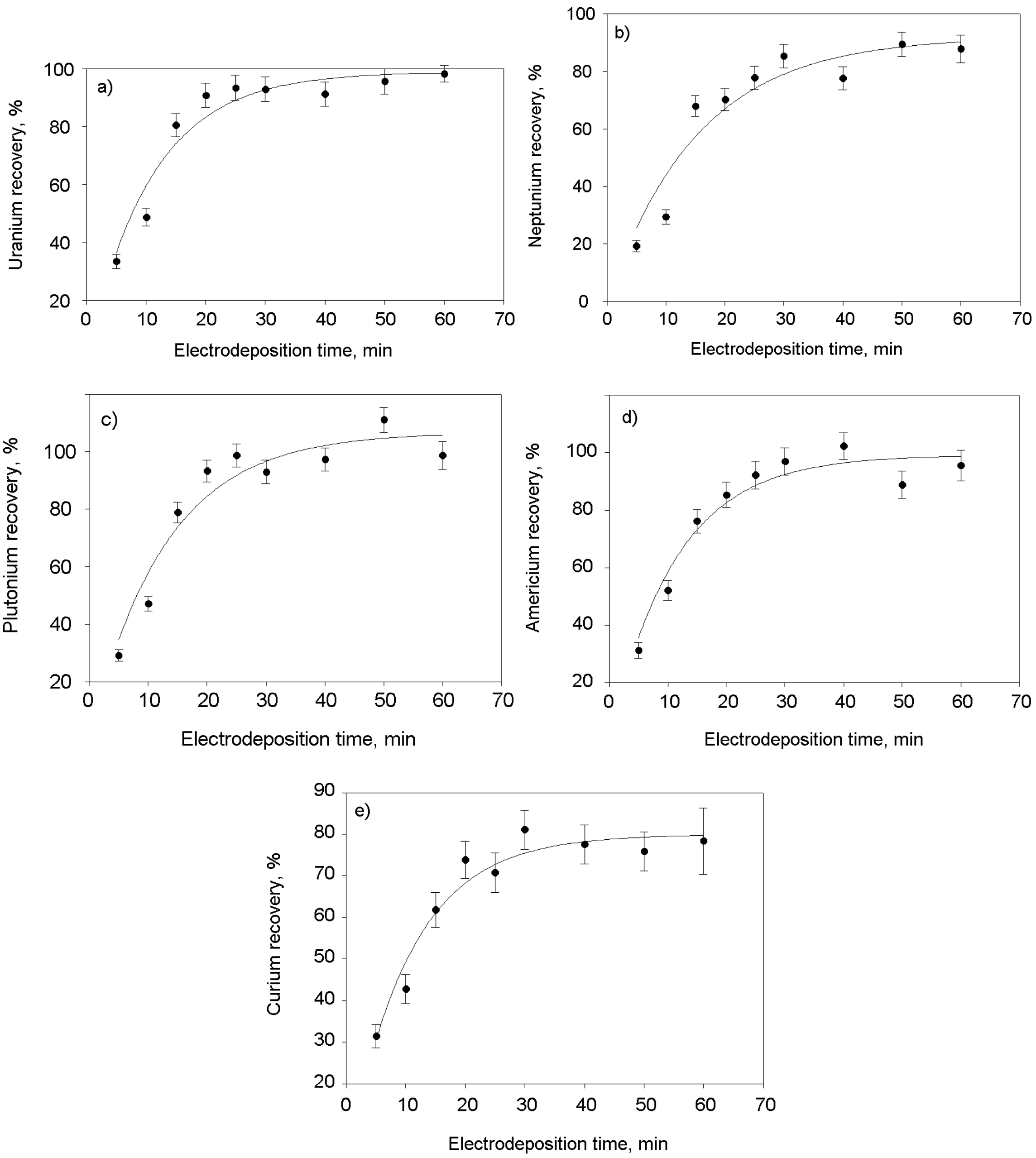

Fig. 2. Recoveries of (a) uranium, (b) neptunium, (c) plutonium, (d) americium, and (e) curium as a function of electrodeposition time. Current at 1.20 A and pH at 2.0. Uncertainties are derived from the propagation of error resulting from counting statistics, and uncertainties in the detector efficiency calculation

Conclusions

The electrodeposition method described in this paper is effective and expedient for preparing actinide samples in a field deployable mobile laboratory for alpha-spectrometry counting. Recoveries after 60 minutes of deposition time of uranium, plutonium, and americium were virtually 100%, while lesser, but still high, recoveries of neptunium and curium were realized. In all cases the variance in the recoveries are well characterized. All recoveries were virtually complete after only 25 minutes of deposition time.

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