

OPTIMIZATION OF SOURCE PREPARATION METHODS
FOR ALPHA SPECTROSCOPY
IN EMERGENCY RESPONSE SITUATIONS

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2. EXECUTIVE SUMMARY

The nation's current focus on emergency response and preparedness in the event of a radiological incident has given impetus to develop novel rapid analysis methods for radionuclide identification and quantification. The goal of this research project was to examine and optimize three methods of sample preparation for alpha spectroscopy to enable the faster and more efficient analysis of actinide elements. The three techniques investigated in this project were evaporation, electrodeposition and microprecipitation. Each method was scrutinized to optimize method performance while keeping the time required for sample preparation in mind.

Evaporation was found to be the method that required the least amount of sample manipulation before deposition onto the counting media. An evaporation temperature of approximately 140 °C was determined as the most effective. No dependency on evaporation or temperature was seen for energy resolution or yield results. For the best yield results, it was established that the sample should be added to the planchet at the same time in the center of the planchet. Evaporation was the fastest method examined, but the samples produced were inferior in regards to yield and resolution compared to the other methods investigated.

For electrodeposition it was found that the general method as published by Kressin using planchets that had been both washed and electropolished showed the best yield results. Energy resolution was however best for planchets that had been washed but not electropolished. A study on the amount of solution deposited over time showed the fraction of activity in solution to decrease steadily up to about 100 minutes. Variation of the deposition current led to the recommendation of keeping the current set between 0.8 A and 1.2 A for the best results in yield. The best energy resolution results were seen when the current was set at 1.0 A. Overall, samples prepared by electrodeposition showed superior energy resolution and acceptable yields; however the method was discovered to be lacking in reproducibility. Use of a multiposition electrodeposition unit allowed for the preparation of up to 12 samples in approximately 4 hours.

The microprecipitation method was studied using the cerium fluoride method. Parameters varied included the amount of cerium carrier and hydrofluoric acid, the precipitation temperature and the time that the precipitate was allowed to settle. A study of the influence of the carrier and acid concentrations on energy resolution and yield revealed that the best results were obtained if the amount of hydrofluoric acid is kept at 1 mL. The best energy resolution was achieved by addition of 0.01225 mg of Ce, while the best yield was obtained by addition of 0.0050 mg of Ce. When the precipitation time was varied, the best energy resolution was seen for samples with a precipitation time between 30 and 50 minutes. The highest yield was however achieved if the sample is allowed to settle for 30 minutes. Overall the reproducibility of the microprecipitation method was found to be far superior compared to the other methods. The use of a multiposition sampling manifold combined with a precipitation time of 30 minutes allowed for the preparation of 12 samples in less than one hour. Based on these results microprecipitation was singled out as the most promising method for source preparation for alpha spectroscopy in emergency response situations.

3. INTRODUCTION

3.1 Background

The nation's current focus on emergency response and preparedness in the event of a radiological incident has given impetus to develop novel rapid analysis methods for radionuclide identification and quantification. A fast quantification of the amount of radioactivity released is necessary to estimate the exposure risk to the public and to allow for swift and informed decision making in the immediate aftermath of the incident. The rapid identification of the radionuclides released is necessary for this purpose as well, but it is even more essential to permit attribution of the released radionuclides to a potential source. Information about the source of the radioactive material involved in the incident needs to be made available to intelligence agencies as quickly as possible. The task in particular requires detailed information on the isotopic composition of the material released.

Analytical response following a radiological incident will vary significantly from routine surveillance monitoring plans. Such an incident will pose specific challenges in addition to the ones usually associated with environmental monitoring. These challenges will include handling non-standard environmental and anthropogenic matrices with a wide range of activity from background to hot particle levels, and rapid turn-around-time with a high confidence level for reporting information needed for remediation/recovery efforts. In developing effective emergency response protocols, each of these challenges must be addressed. This leads to an inherent paradigm shift in the assessment criteria that are used to determine the suitability of a method. The goal of the proposed research is to develop optimized methods for source preparation for the determination of alpha emitting radionuclides.

3.2 Source Preparation and Analysis

Source preparation and analysis are key factors in emergency response situations. While turn-around time will be of utmost importance, the quality of the source produced will have to be adequate enough to differentiate between alpha energies to allow for identification of individual alpha-emitting radioisotopes.

For distinguishing mixed alpha emitters, typical instrumentation includes the alpha spectrometer containing a solid state detector - usually the passivated implanted planar silicon (PIPS) detector, and various types of mass spectrometers (MS).

Mass spectrometers are very sensitive, detecting trace and ultra trace levels of radionuclides with detection limits on the order of fractions of a picogram per gram of environmental samples of uranium, plutonium, and americium. MS is ideal for long-lived radionuclides because the spectral data does not depend on the decay kinetics of the isotope, providing an analysis time advantage over alpha spectroscopy systems. Mass spectrometers can produce results in minutes versus hours, especially at low radionuclide concentrations. Potential molecular, isobaric and non-spectral interferences from multi-elemental matrix constituents require however some degree of sample pre-concentration or separation to provide conclusive results.

Nonetheless alpha spectroscopy systems based on PIPS detectors have several advantages over MS systems for emergency response purposes. Such systems have smaller footprints, are easier portable, and do not require special electrical, exhaust and plumbing for installation. In addition, with the advent of a new fabrication process combining oxide passivation, photolithography and ion-implantation, the silicon detectors are particularly robust and are therefore ideal for use in mobile radioanalytical laboratories. Some of the advantages of these detectors include a better energy resolution, which is of particular importance for identification of actinide isotopes and the easy clean-up of potentially contaminated detectors. The latter is particularly important when dealing with higher levels of radioactivity, as can be expected following a radiological incident.

The biggest limitation of alpha spectrometry is source preparation. Aqueous samples cannot be introduced directly into the chamber for counting. This requires preparation of a suitable solid deposit that can be placed under the detector. Due to the nature of alpha radiation, many factors must be taken into consideration that would not normally be of concern with the detection of other types of radiation. High-resolution alpha spectroscopy requires a very thin, as close to monatomic as possible, uniform source. Additionally, no foreign matter should be in the source due to the fact alpha particles are easily attenuated. Alpha particles are relatively massive and have a charge of +2, therefore they expend their energy over a short distance and typically show limited penetration into materials with typical path lengths on the order of a few centimeters or less in air. Some parameters important for acceptable results are limiting self absorption, limiting absorption in the air and the detector window, minimizing coincidence losses and minimizing backscatter. Because of these sample requirements, preparation time for the samples can be more time consuming than sample preparation methods for other types of counting. There are several different methods available for preparing source standards for alpha spectroscopy, such as evaporation, micro-precipitation and electrodeposition. Each of these source preparation methods has its advantages and disadvantages. A brief overview of the three most common methods for alpha source preparation is given below.

3.3 Methods for Source Preparation

3.3.1 Evaporation

Evaporation is one of the oldest and simplest procedures for the preparation of samples for alpha spectroscopy. It does not require nearly as much time or effort as the other methods described here. Due to the limitations of this method, it is therefore most commonly used when samples need to be processed quickly and a high degree of sample uniformity is not required.

After a planchet is cleaned with water or dilute hydrochloric acid, an aliquot of the sample is pipetted onto a planchet and then heated on a hot plate until the sample is dry. The performance of the method is mainly governed by the temperature of the hot plate, time required for drying, the method of sample addition and the planchet geometry. In particular a hot plate temperature that is too high can cause sputtering of the sample resulting in unwanted sample loss. Other common problems affecting this method are the possibility of non-uniform sample spreading on the planchet and self-attenuation caused by a sample that is too thick. The latter is mainly due to the lack of selectivity inherent to the procedure. Any matter as well as contaminants present in solution will be deposited

on the planchet in addition to the radionuclides of interest. The resulting residual mass left on the planchet after evaporation can cause unwanted self-attenuation that gives rise to peak tailing and broadening.

3.3.2 Electrodeposition

Electrodeposition is one of the most prevalent methods of sample preparation for alpha spectroscopy. The process of electrodeposition involves adding a mixture of the sample solution and an electrolyte solution to an electrochemical cell and applying voltage to the cell for a certain set current and a certain set amount of time. The planchet on the radionuclides are to be deposited serves as the cathode of the cell and a wire inserted into the solution serves as the anode. The electrochemical reaction taking place in the cell allows radionuclides present as ions in solution to be deposited onto the cathode. The deposition can occur either by a spontaneous process or by a nonspontaneous process. During a spontaneous process, radionuclides are deposited due to a favorable electrode potential existing between the ion and electrode. For nonspontaneous process to occur, an external voltage must be applied. In the framework of this project only nonspontaneously occurring electrodeposition processes were investigated.

The deposition of actinides can be difficult to control due to the decomposition of water and reactions of anions and cations at electrodes [1]. For this reason, each individual step of the electrodeposition process and the composition of the sample solution must be examined to determine optimum conditions. Overall, the effectiveness of electrodeposition of trace components of actinides depends on the electrode potential, the resulting current, the electrode surface area and material, the properties of the electrolyte solution, the duration of electrodeposition and the temperature [2]. The two most commonly used methods are the Kressin method [3] and the Talvitie method [4]. The Kressin method uses a self-buffered solution of sodium sulfate-sodium bisulfate as an electrolyte solution. In contrast the Talvitie method uses a solution of ammonium sulfate adjusted to a pH of 2 as electrolyte. This research used the Kressin method as the general method for sample preparation by electrodeposition because it does not require extensive and time intensive pH adjustments.

3.3.3 Microprecipitation

Microprecipitation is another widely used sample preparation method for alpha spectroscopy that rivals electrodeposition in sample yields. It is newer than the electrodeposition methods and proponents of this method state that the spectral resolution of microprecipitated samples is almost as good as that of electrodeposited samples and that the precipitation procedures are much faster, more reliable, and generally show chemical yields greater than 98 % [5].

The microprecipitation method that will be evaluated in this project is based on the coprecipitation of actinide elements using cerium as a carrier. A carrier is defined as a substance that is added in an appreciable amount, which, when associated with a radionuclide, will carry this nuclide through the chemical and physical process. In many solutions, especially those of environmental samples, the concentration of the radionuclide of interest is too low to cause precipitation even in the presence of high concentrations of its counter-ion, because the product of the concentrations does not exceed the solubility product. If a radionuclide is present in solution at sub-micro

concentrations, the radionuclide will not form an insoluble compound upon addition of a counter-ion. In these cases, the radionuclide can often be brought out of solution by co-precipitation, associating it with an insoluble substance that precipitates from solution. The cerium carrier acts as the insoluble substance that upon addition of hydrofluoric acid will co-precipitate with the radionuclide.

An aqueous solution of cerium nitrate is added to a centrifuge tube containing the sample solution. Concentrated hydrofluoric acid is added and the solution is swirled to mix. The solution is then filtered using a vacuum filtration system is applied to speed the filtration process. The precipitate formed is retained on the filter, which is then dried under an infrared lamp and mounted onto a planchet to be analyzed by alpha spectroscopy. The precipitation process and therefore the performance of the method is controlled by factors such as the type of carrier, the total amount of carrier used, the ratio of carrier to hydrofluoric acid, precipitation time and temperature.

3.4 Research Objective

The objective of this research was to optimize the three methods for source preparation described above and to evaluate their suitability in emergency response situations. A comparison of an electrodeposition and a microprecipitation method has previously been reported in the literature [6], but the study did not investigate the optimization of either procedure and was not focused on the specific needs of emergency response analytics. Several different parameters need to be evaluated to determine the usefulness of each source preparation method for emergency response analysis. The prepared source should have the best spectral resolution possible. This is important because many alpha emitting isotopes emit alpha particles with very similar energies; some differ by only 10-20 keV. Most detectors cannot obtain spectral resolutions better than 12 keV. Therefore source preparation must be as clean as possible to eliminate attenuation in the sample itself. The method should also achieve the highest yield possible. For the sake of counting statistics, a high yield must be obtained in order to shorten the length of time the source will need to be measured. If approximately 10,000 counts are obtained under a peak, the counting error will be an acceptable 1 %. The reduction of source preparation time was the major goal of the proposed research. If any of the steps in the sample preparation are rushed, however, the yield and energy resolution of the sample can become compromised. Certain areas of the source preparation can be optimized to a certain extent, however, without compromising the sample thinness or cleanliness.

Each of the methods was optimized based on the yield and energy resolution that can be achieved as well as the time required for source preparation. The optimized procedures were then compared with each other. This comparison can then be used as the basis for selection of the best method for a given analysis scenario, whether it be emergency response or routine sample analysis.

4. EXPERIMENTAL DETAILS

4.1 Materials and Detection Methods

4.1.1 Materials and Tracers

A solution of ^{241}Am in 1.0 M hydrochloric acid was used as radioactive tracer in all experiments. The solution had a specific activity of $100 \text{ Bq}\cdot\text{mL}^{-1}$ and was prepared by diluting a concentrated stock solution obtained from Isotope Products. The stock solution has a purity of greater than 99%, contributions from other alpha emitting radioisotopes can therefore be neglected. All chemicals used were analytical grade and obtained either from Fisher Scientific, J.T. Baker or Sigma-Aldrich. A list of all the chemicals and materials used can be found in Appendix I and II respectively.

4.1.2 Alpha Spectroscopy

A Canberra Alpha Analyst model with 16 detector chambers was used for measurement of the sources prepared for alpha spectroscopy. The chambers were equipped with Canberra Passivated Implanted Planar Silicon (PIPS) detectors. The detectors had an active area of 450 mm^2 and their minimum resolution was listed by the manufacturer as 10.2 keV. The GENIE 2000 alpha analyst software from Canberra was used to operate the data acquisition system and to analyze the spectra obtained. Samples were loaded in suitable planchet holders and placed in the chamber at a specified shelf level. There are 10 shelf levels in each chamber that are spaced approximately 2.5 mm apart. Shelf level four, which is approximately 15 mm from the detector, was used to count all samples prepared. Count times were set to allow for at least 10,000 counts to be accumulated under the ^{241}Am peak for each sample, resulting in a counting error of 1 % or less. Electrodeposited standard sources were used to perform an energy and efficiency calibration for each detector. The data recorded for each sample measurement included energy resolution (FWHM) in keV, live time, and number of counts recorded under the ^{241}Am peak with error.

4.1.3 Liquid Scintillation Counting

A Perkin Elmer model 3100TR liquid scintillation counter was used to assay the activity of the stock solutions used and to determine the amount of radioactivity remaining in solution after electrodeposition. The counting protocol used had a count time set for 60.0 minutes per sample with the count mode set to normal and the pre-count delay set to 0. The 2 sigma % terminator was enabled. Background subtraction was performed manually using the count rate obtained from a sample blank measured with each set of samples.

4.2 Evaporation

4.2.1 General Method

Sources for alpha spectroscopy were prepared by evaporation using the liquid drop method from an aqueous solution [7]. A planchet was placed onto a hot plate at a given

temperature and an aliquot of the tracer solution was pipetted directly onto the planchet. The aliquot was evaporated to complete dryness and the sample was then assayed by alpha spectroscopy. The setup for this procedure is shown in Figure 4.1 below. Lipped planchets were used for evaporation to prevent any sample loss from the sides of the planchets.

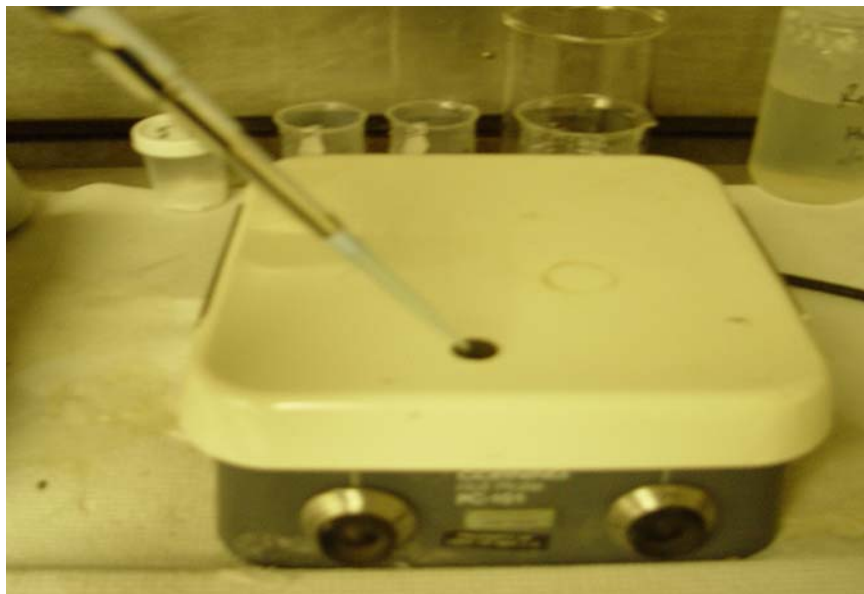


Figure 4.1 Experimental setup for evaporation

A standard hot plate was used for this method. The temperature of the hot plate was monitored using an Extech model number 42510 infrared thermometer. The infrared thermometer used had an accuracy of $\pm 2\%$ of readout or $\pm 2\text{ }^{\circ}\text{C}$, whichever is greater. The temperature measured at different locations on the hot plate varied greatly for any fixed heat level of the hot plate.

4.2.2 Investigation of Temperature and Evaporation Time Relationships

The goal of this study was to determine the ideal temperature at which the sample will dry in the shortest amount of time without any sample loss due to sputtering from local overheating. The evaporation was performed with the hot plate set to different heat levels. The temperature of the plate was recorded as well as the time necessary for complete sample evaporation.

4.2.3 Investigation of the Method of Sample Addition

The quality of samples prepared by evaporation can also depend on the method by which the aliquot is added to the planchet. The aliquot can either be added completely at the same time, full volume addition, or in smaller increments at different locations, drop-by-drop addition. To study the effect of full volume addition, the total $350\text{ }\mu\text{L}$ aliquot was pipetted onto the center of the planchet at the same time. Alternatively, the $350\text{ }\mu\text{L}$ aliquot was added in drops at different locations spread across the planchet.

4.3 Electrodeposition

4.3.1 Apparatus

The experimental setup used for the electroplating process consisted of a 12 volt electrodeposition unit with a current range from 0 to 2.0 amps and an electrodeposition cell. The electroplater provided a current to the cell in order to deposit the sample onto a planchet placed at the bottom of the cell. The electroplater used had the capacity to operate 12 electrodeposition cells in parallel. The cells were all feed by a central power supply. The station for each cell included a control dial to adjust the current, a current meter and a platinum electrode. In addition it was equipped with toggle switch to reverse the current on each of the twelve stations individually. Reversal of the current is necessary to electropolish the planchets used for deposition. A picture of the deposition unit is shown in Figure 4.2.

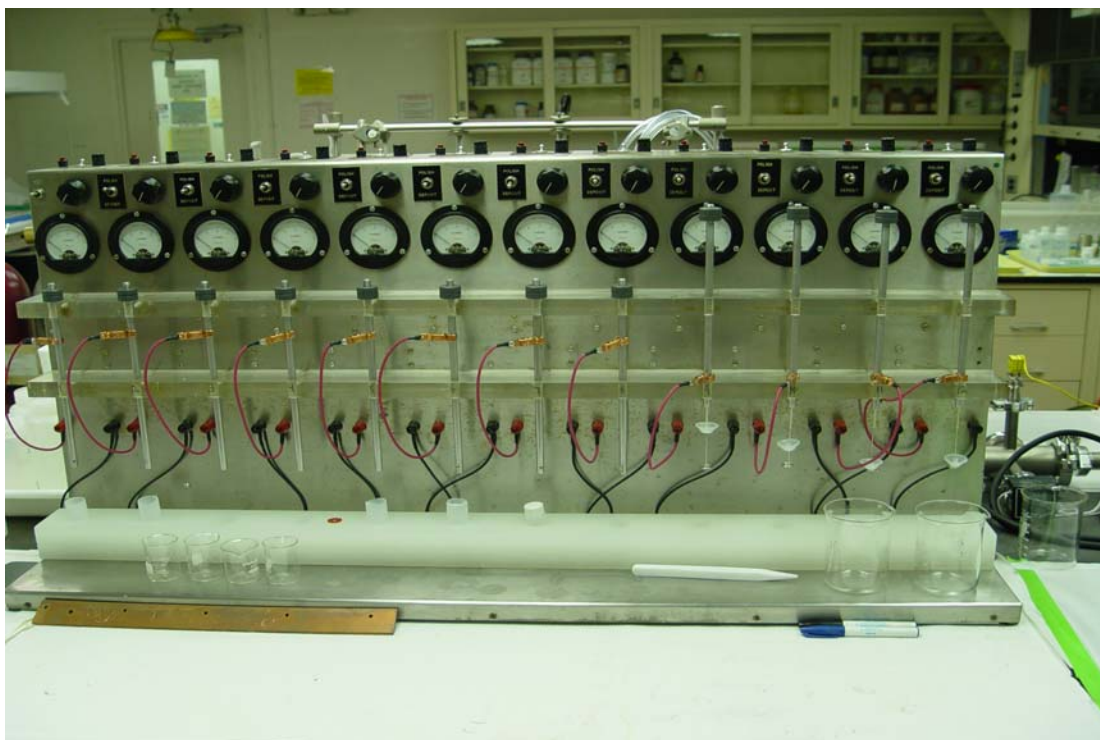


Figure 4.2 Electrodeposition Apparatus

The electrodeposition cell itself consisted of a plastic scintillation vial with the bottom cut out, the vial cap, a rubber seal and a copper anode on which a stainless steel planchet is placed. Figure 4.3 shows a schematic diagram of the cell and its components. Once the cell is assembled, it is placed onto a station on the electrodeposition unit and the platinum electrode is lowered into the cell.

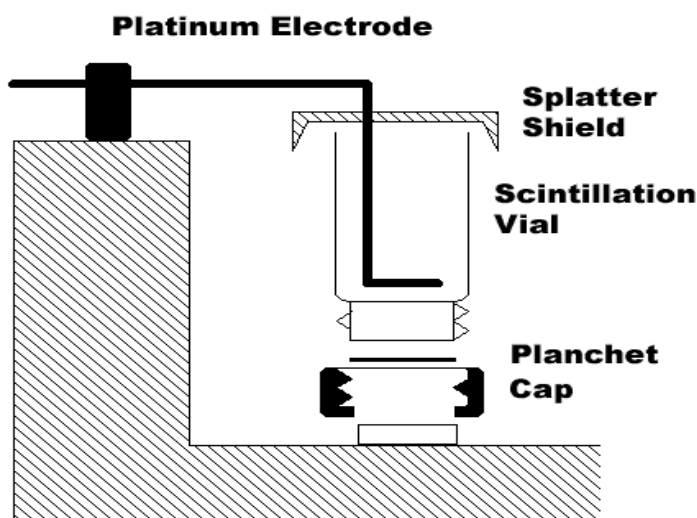


Figure 4.3 Electrodeposition Cell

4.3.2 General Method

The electrodepositions were carried out using the general procedure developed by Kressin [3]. 700 μL of the ^{241}Am stock solution was placed into a 50 mL beaker. Subsequently 2 mL of a 5% sodium bisulfate (NaHSO_4) solution as electrolyte and 0.5 mL of perchloric acid (HClO_4) were added to the beaker. The beaker was placed on a hot plate at temperatures between 180°C and 200°C to drive off the perchloric acid. Complete removal of perchloric acid was reached when the sample stopped developing white fumes. Addition of the perchloric acid was carried out to destroy any organic material present in solution that might interfere with the deposition process. After all perchloric had been driven off, the beaker was allowed to cool before rinsing it with de-ionized (DI) water, adding 1 mL of hydrochloric acid (HCl) and placing it back on the hot plate to dry. Addition of HCl and subsequent drying was repeated 2 to 3 times. Afterwards the sample was allowed to cool again to room temperature before adding 3 mL of DI water. The sample was left to dissolve for 10 minutes and then 4 mL of a 15% sodium sulfate sulfate (Na_2SO_4) is added. The sodium sulfate served as the second constituent of the electrolyte solution and simultaneously acted as a buffer to maintain a pH of approximately 2 in solution. The sample was transferred to the electrodepositing cell, the beaker was rinsed with DI water and the rinse was also added to the cell. After the solution had been transferred to the cell and the cell had been placed on the electrodeposition unit, the platinum wire was lowered into the cell until it was suspended about 3-4 mm above the planchet. The electroplater was subsequently switched to the deposition setting, turned on and the current was adjusted to 1.0 A. The current was monitored for approximately the first 15 minutes and again after 1 hour of plating time. Cells were also monitored for leakage throughout the process. After the sample was allowed to deposit for 2 hours, 2 mL of 4 M potassium hydroxide (KOH) were added and the deposition was continued for an additional 2 minutes. The addition of the KOH was carried out to increase the pH of the solution and to prevent the redissolution of deposited Am. The cell was disassembled at the end of the deposition and the planchet was washed

with 1 % ammonium hydroxide (NH_4OH). Afterwards the planchet was heated on a hot plate until dry and the sample was assayed by alpha spectroscopy.

4.3.3 Study of the Use of Washed Planchets

The Kressin method requires for the planchets to be washed prior to electrodepositing a sample onto them [3]. Planchets are typically shipped with a plastic coating to protect the surface that the sample will be electrodeposited onto. Removal of the plastic coating can leave organic residue behind that might interfere with the deposition. Once the plastic is removed, the planchet is therefore typically washed with acetone and nitric acid (HNO_3) to remove any residue left. Several samples were electrodeposited onto washed planchets and the same number of samples was electrodeposited onto unwashed planchets to determine if washing the planchets before plating had any influence on the energy resolution of the sample or the sample yield.

4.3.4 Investigation of the Use of Electropolished Planchets

The deposition method published by Kressin calls for the planchets to be electropolished before the sample is electrodeposited [3]. This is achieved by adding 10 mL of a mixture of 4.5 mL of 51% sulfuric acid (H_2SO_4), 3.5 mL of 86% phosphoric acid (H_3PO_4), and 2.0 mL of DI water to the cell. The toggle switch on the deposition unit is set to the polish setting for each cell containing a planchet to be electropolished and a current of 1.0 A is applied for 15 minutes. The goal of the electropolishing is to further clean the surface of the planchet and make it smoother for a more homogenous deposition. Once the polishing step is complete, the cells remain assembled with the planchet contained in the cell. The cell is however rinsed several times with DI water to remove all traces of the acidic. A separate study was conducted to determine if electropolishing of the planchets before deposition has a beneficial effect on the plating. Several samples were electrodeposited onto electropolished planchets and the same number of samples was electrodeposited onto planchets that had not been electropolished.

4.3.5 Study of the Influence of Deposition Current

The Kressin method requires that a current of 1 A is applied to the deposition cell [3]. A set of experiments as carried out to confirm this and to find the optimum current setting for the deposition unit used. The deposition was carried out using planchets that had both been washed and polished. In these experiments the same method as described for the general procedure was used, however the current applied to the cell was varied in increments of 0.2 A from 0.6 A to 1.4 A. The plating time was kept constant at 2 hours. Aliquots of 100 μL of sample solution were taken from the cell at the end of the deposition and assayed by liquid scintillation. The planchets were rinsed with 1 % ammonium hydroxide, heated on a hot plate to dry and counted by alpha spectroscopy. The results from the alpha spectroscopy performed on the planchets were compared to data obtained using the liquid scintillation.

4.3.6 Determination of a Deposition Time Profile

The deposition method as published by Kressin calls for a deposition time of 2 hours [3]. To reduce the time necessary for the procedure it is important to determine the exact time at which complete sample deposition is achieved. To answer this question, aliquots of

sample solution were taken at regular time intervals during the electrodeposition process. The deposition was carried out using planchets that had both been washed and polished. Once the sample solution was transferred to the cell, an aliquot was taken from the solution and the deposition was started as usual. During the first 30 minutes of electrodeposition, aliquots were taken out of the cell every 5 minutes and added to scintillation vials containing 10 mL of liquid scintillation cocktail. The process was repeated every 10 minutes during the second 30 minutes of electrodeposition time and every 20 minutes during the last 60 minutes of electrodeposition time. A final aliquot was taken after the addition of the potassium hydroxide. For this study twice the amount of stock solution (1.4 mL) was used to obtain a reasonable level of activity in the aliquots. The amount of liquid in the cell was closely monitored throughout the electrodeposition process to keep the volume of solution in the cell constant. If necessary, DI water was added to bring the sample volume back up to 10 mL. All of the aliquots collected were assayed for one hour using a liquid scintillation counter. The planchets were rinsed with 1 % ammonium hydroxide, heated on a hot plate to dry and counted by alpha spectroscopy. The results from the alpha spectroscopy performed on the planchets were compared to data obtained using the liquid scintillation.

4.4 Microprecipitation

4.4.1 General Method

The microprecipitations were carried out using the general procedure published by Eichrom Technologies, Inc. [8]. The initial experimental setup for the microprecipitation procedure consisted of two 100 mL polypropylene flasks connected by a piece of vacuum tubing. This setup is shown in Figure 4.4. A vacuum pump is connected to the second flask which served as a trap to prevent any liquid from entering the pump. A 25mm diameter 50 mL polysulfone funnel with a polycarbonate base and metal screen was connected to the top of the first flask using a rubber stopper. A 0.1 micron 25 mm diameter polypropylene Resolve filter was placed on the metal screen in filter apparatus. Vacuum was applied to the system and the filter was prewetted with ethanol (C_2H_5OH) to check the setup for leaks. Afterwards the system was rinsed with DI water.



Figure 4.4 Single Position Filtration Apparatus

In later experiments a Millipore Model 1225 sampling manifold was used. This manifold allowed the filtration of up to 12 samples in parallel. Figure 4.5 shows a schematic drawing of the manifold as well as a diagram illustrating the assembly of the manifold. The filters were placed on the support screens between the support plate and the top plate. A 15 mL centrifuge tube to collect the filtrate was placed in the tube rack under each filtration position used. Filtration positions that were not used were blocked using rubber stoppers.

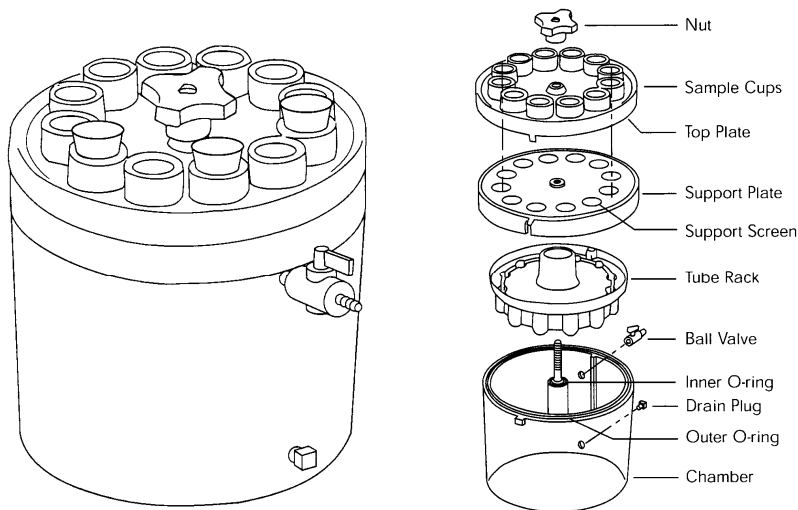


Figure 4.5 Diagram of Millipore Model 1225 Sampling Manifold [9]

350 μL of the ^{241}Am stock solution was placed in a 50 mL centrifuge tube. 0.1 mL of cerium carrier, consisting of $0.00155 \text{ g}\cdot\text{mL}^{-1}$ cerium (III) nitrate hexahydrate ($\text{Ce}(\text{NO}_3)_3\cdot 6\text{H}_2\text{O}$) was added to the same centrifuge tube. Next, 1.0 mL of 28 M hydrofluoric acid (HF) was added and the solution was swirled gently to mix. As a result a precipitate formed. The tube was placed in a water bath kept at $25 \text{ }^\circ\text{C}$ and left to sit for 30 minutes. At the end of the 30 minutes the solution was poured into the funnel with vacuum applied. The solution passed through the filter and was collected in flask while the precipitate remained on the filter. The filter was subsequently washed with DI water and with ethanol. The vacuum was turned off and the residue filter was removed carefully with tweezers once the system had returned to ambient pressure. The filter was placed in a plastic Petri dish and dried under an infrared lamp. The filter was then mounted on a stainless steel planchet and assayed by alpha spectroscopy.

4.4.2 Variation of Amount of Carrier and Hydrofluoric Acid Used

The microprecipitation procedure as published by Eichrom Technologies, Inc. calls for the use of 0.1 mL of cerium carrier solution with a concentration of $0.00155 \text{ g}\cdot\text{mL}^{-1}$ $\text{Ce}(\text{NO}_3)_3\cdot 6\text{H}_2\text{O}$ [8]. This corresponds to a total cerium mass of 0.05 mg. Two sets of experiments were carried out to study the influence of total carrier mass and total amount of hydrofluoric acid added on the performance of the microprecipitation. In the first set of experiments, the amount of cerium carrier added was varied while the amount of hydrofluoric acid added was held constant. In separate experiments 0.1, 0.05, 0.025, 0.01

and 0.005 mL of the carrier solution was added to the americium stock solution, while the amount of hydrofluoric acid was kept constant at 1 mL. The amount of carrier added corresponded to a total cerium mass of 0.05, 0.025, 0.0125, 0.005 and 0.0025 mg, respectively. Five precipitations were carried out for each different amount of carrier solution. In the second set of experiments the same volumes of carrier solutions were used, however in this case the amount of hydrofluoric acid added was reduced to keep the ratio between the volume of carrier and hydrofluoric acid constant. As a result corresponding volumes of 1, 0.5, 0.25, 0.1 and 0.05 mL of hydrofluoric acid were added to the americium stock solution. Again, five precipitations were carried out for each combination of carrier solution and hydrofluoric acid. The other parameters of the process were kept the same as described for the general procedure. The dried filters were mounted on a stainless steel planchet and assayed by alpha spectroscopy.

4.4.3 Investigation of the Influence of Precipitation Temperature

The microprecipitation as described in the general method was carried out at a controlled temperature of 25 °C. Precipitations were also carried out at elevated temperatures to determine the influence of temperature on method performance. Five centrifuge tubes were placed in a water bath kept at 30, 35, 40, 45 and 50 °C, respectively. 350 µL of ²⁴¹Am stock solution, 25 µL of cerium carrier solution and 1 mL of HF were added to each tube and the solution was swirled gently to mix. Each tube was left to sit for 30 minutes before the solution was filtered. Filtration of the sample was conducted as described for the general procedure. The dried filters were mounted on a stainless steel planchet and assayed by alpha spectroscopy.

4.4.4 Study of the Effect of Precipitation Time

The published method used requires that at least 30 minutes are allowed for the complete formation of the precipitate before the sample is filtered [8]. To determine the influence that precipitation time has on method performance, several samples were created with varying precipitation times. Based on the results from the previous experiments 25 µL of carrier solution and 1 mL of hydrofluoric acid solution were used for these experiments and all precipitations were carried out at a temperature of 25 °C. The precipitation times used were 10, 20, 30, 45, 50 and 60 minutes as well as 2, 4, 8, 16 and 24 hours. Five precipitations were performed for each given precipitation time. Filtration of the sample was conducted as described for the general procedure. The dried filters were mounted on a stainless steel planchet and assayed by alpha spectroscopy.

5. RESULTS AND DISCUSSION

5.1 Evaporation

5.1.1 General Method

For the general evaporation method 350 μL of ^{241}Am stock solution was pipetted in the center of a planchet that was placed on a hot plate kept at about 120 $^{\circ}\text{C}$. Four samples were created using this method with an average energy resolution of 74 ± 13 keV and an average yield of 83 ± 9 %.

5.1.2 Effect of Evaporation Temperature

Six samples were created at each heat setting on the hot plate. The heat setting used on the plate ranged from 3.0 to 4.4 and were increased in increments of 0.2. The results are listed in Table 5.1 and shown graphically in Figures 5.1 – 5.3

Table 5.1. Average energy resolution, yield and evaporation time as a function of hot plate temperature.

Sample	Temperature ($^{\circ}\text{C}$)	Evaporation Time (M:SS)	FWHM (keV)	Yield (%)
3.0	101 ± 2	$7:43 \pm 1:00$	63 ± 8	96 ± 15
3.2	107 ± 3	$6:08 \pm 0:14$	54 ± 9	84 ± 3
3.4	110 ± 3	$7:03 \pm 0:57$	77 ± 10	80 ± 4
3.6	115 ± 1	$6:08 \pm 0:56$	69 ± 7	82 ± 10
3.8	124 ± 3	$5:01 \pm 0:07$	79 ± 16	84 ± 8
4.0	128 ± 4	$4:53 \pm 0:22$	86 ± 15	94 ± 6
4.2	134 ± 3	$4:39 \pm 0:39$	79 ± 14	84 ± 6
4.4	138 ± 3	$4:07 \pm 0:15$	74 ± 14	92 ± 6

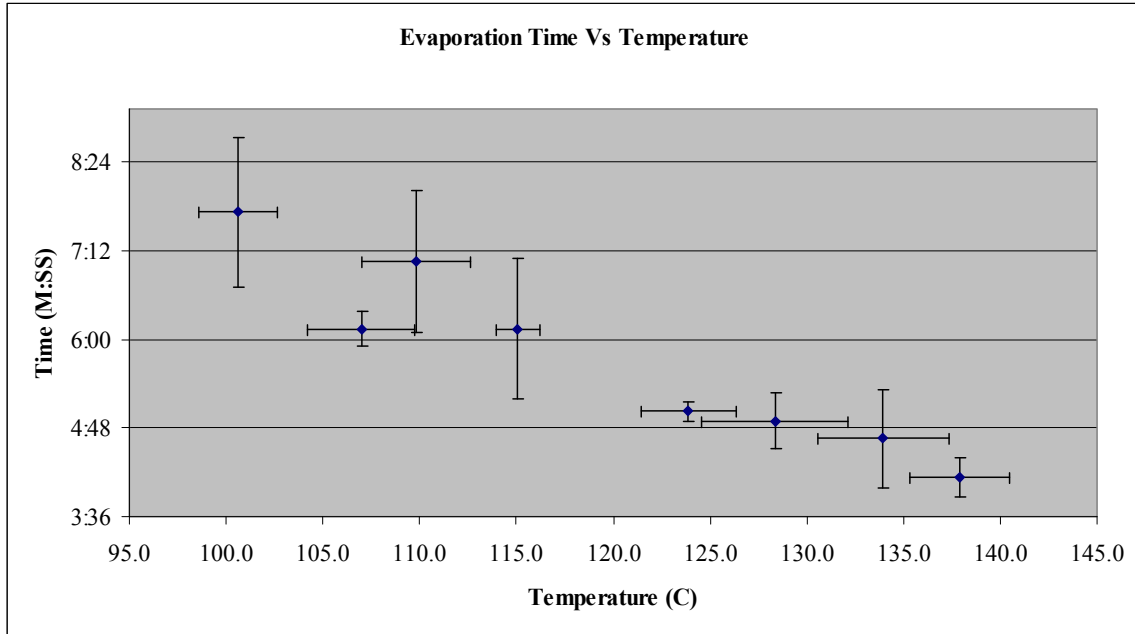


Figure 5.1. Average time for complete sample evaporation as a function of temperature.

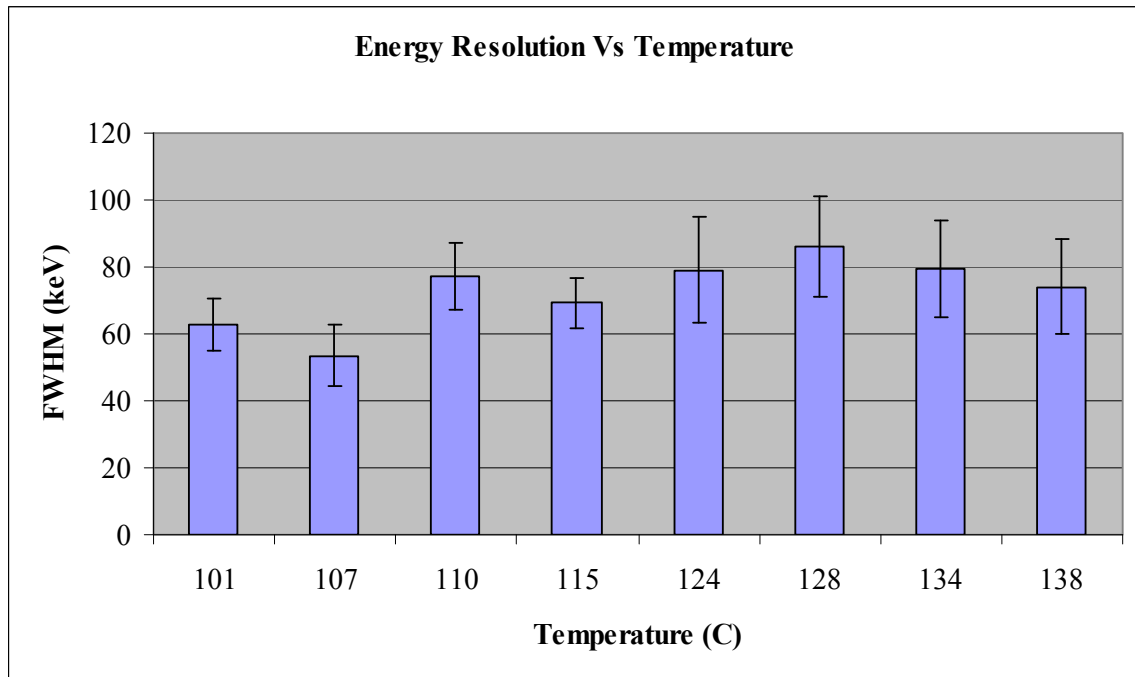


Figure 5.2. Average energy resolution as a function of temperature.

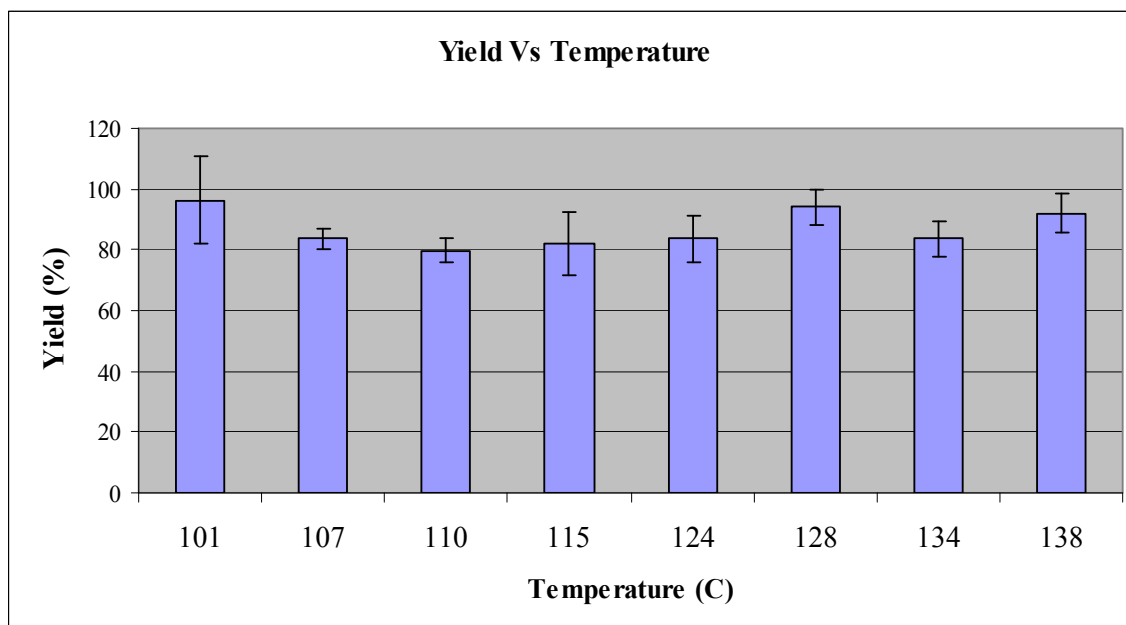


Figure 5.3. Average sample yield as a function of temperature.

5.1.3 Effect of Method of Addition

Two methods were studied for addition of the sample to the planchet for evaporation: full volume addition and drop by drop addition. Based on the results of the temperature study, all samples prepared to investigate the effect of addition method were created at a heat setting of 4.4, which corresponds to a temperature of about 135-140°C. The average energy resolution for full volume addition was calculated to be 74 ± 14 keV with an average yield of 92 ± 6 %. The average energy resolution for drop by drop addition was calculated to be 56 ± 5 keV with an average yield of 56 ± 15 %.

5.2 Electrodeposition

5.2.1 General Method

The general method called for electrodeposition for 2 hours at 1.0 A on planchets that had both been washed and electropolished. Six samples were created using this method with an average yield of 99 ± 14 % and an average energy resolution of 45 ± 21 keV.

5.2.2 Effect of Planchet Washing and Electropolishing

Four combinations of planchet pretreatment were investigated to determine the influence of washing and electropolishing on method performance. These combinations were washed polished (W-P), washed unpolished (W-UP), unwashed polished (UW-P), and unwashed unpolished (UW-UP). Eight samples were prepared for each combination of washed and polished planchets.

Of the eight samples for the washed polished study, two were removed as they were statistically considered outliers. The remaining samples showed an average energy resolution was $45 \text{ keV} \pm 21 \text{ keV}$. The yield was calculated to be 99 ± 14 %. Only one outlier was removed for the washed unpolished data set. An energy resolution of 32 ± 12

keV and a yield of $61 \pm 8 \%$ were obtained. Seven of eight samples were used in the unwashed polished data set. The energy resolution was calculated to be 59 ± 9 keV and the yield was calculated to be $60 \pm 20 \%$. The unwashed unpolished data included seven of eight samples, with one omitted as an outlier. The energy resolution was calculated as 44 ± 18 keV with a yield of $73 \pm 21 \%$. Results are summarized in Table 5.2 and plotted in Figures 5.4 – 5.5.

Table 5.2. Average yield and energy resolution obtained for different planchet pretreatments

Sample ID	FWHM (keV)	Yield %
Washed Polished	45 ± 21 keV	$99 \pm 14 \%$
Washed Unpolished	32 ± 12 keV	$61 \pm 8 \%$
Unwashed Polished	59 ± 9 keV	$60 \pm 20 \%$
Unwashed Unpolished	44 ± 18 keV	$73 \pm 21 \%$

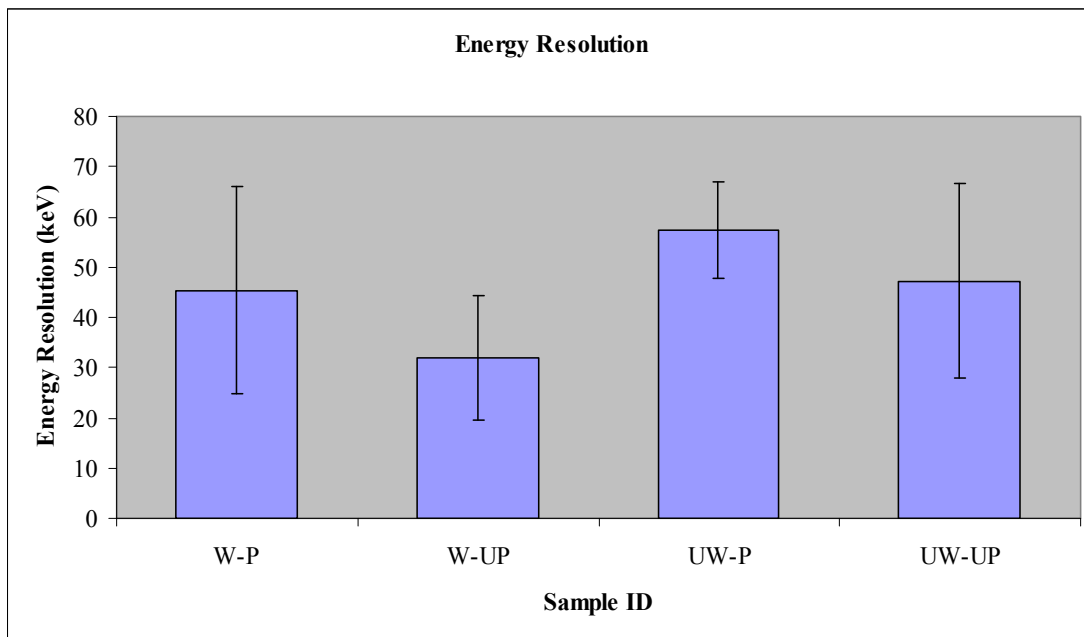


Figure 5.4. Average energy resolution for electrodeposited samples prepared with different planchet pretreatments procedures. (Washed polished (W-P), washed unpolished (W-UP), unwashed polished (UW-P), and unwashed unpolished (UW-UP))

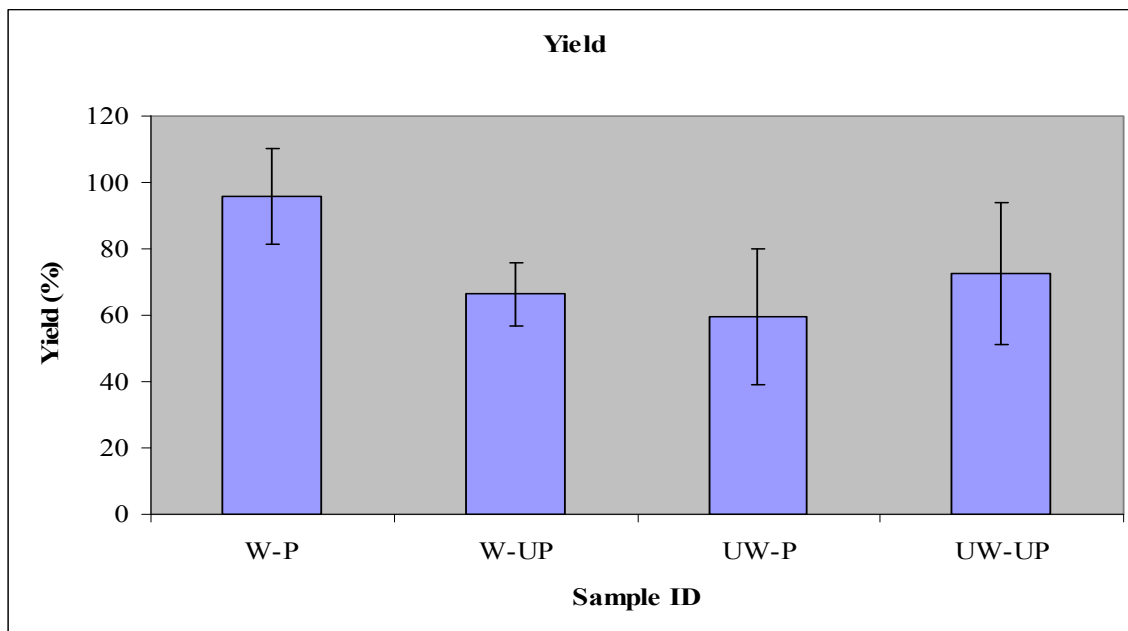


Figure 5.5. Average deposition yield for electrodeposited for electrodeposited samples prepared with different planchet pretreatments procedures.

5.2.3 Influence of Deposition Current

Four samples were created for each current setting of 0.6, 0.8, 1.0, 1.2, and 1.4 Ampere, respectively. The Kressin method was used for all samples. Planchets were washed and electropolished before the electrodeposition process. At the end of each electroplating run, after the KOH was added, a 100 μ L aliquot was taken from each cell. The aliquot was then added to 10 mL of liquid scintillation cocktail and counted by a liquid scintillation counter. In addition the planchets were counted as usual by alpha spectroscopy. The volume in the cell was maintained at 10 mL in order to make activity concentration calculations as accurate as possible. The results are summarized in Table 5.3 and plotted in Figures 5.6 and 5.7.

Table 5.3. Average energy resolution and yield as a function of electrodeposition current.

Current (A)	FWHM (keV)	Yield (%)
0.6	90 \pm 31	63 \pm 9
0.8	124 \pm 52	86 \pm 13
1.0	86 \pm 1	84 \pm 10
1.2	121 \pm 11	87 \pm 9
1.4	72 \pm 5	83 \pm 14

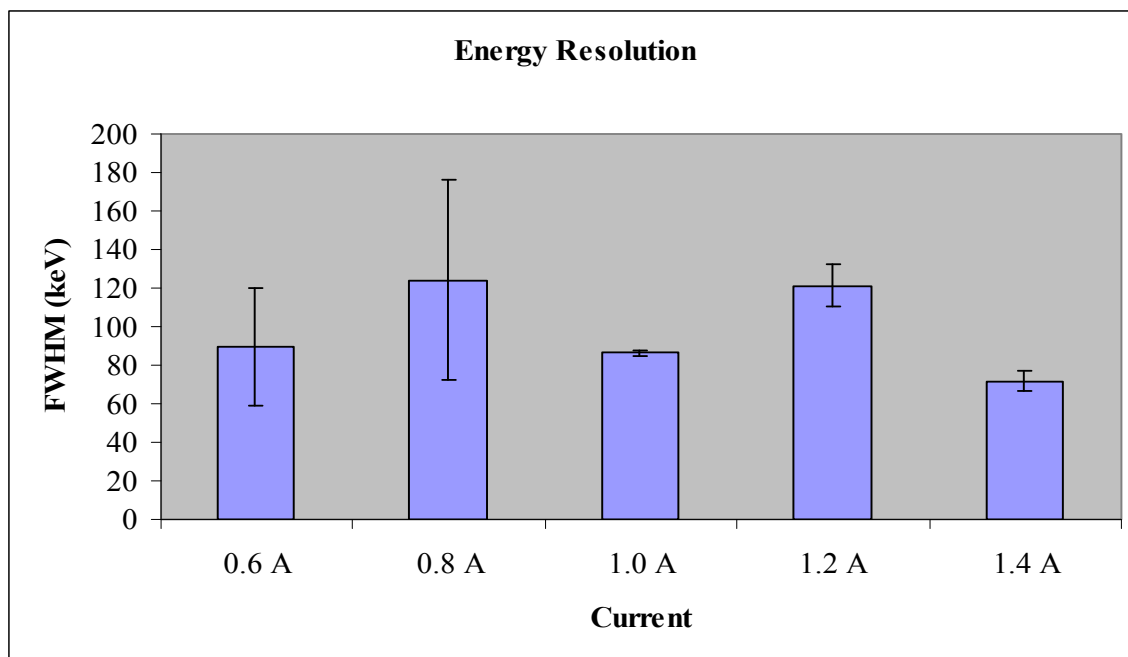


Figure 5.6. Average energy resolution as a function of electrodeposition current.

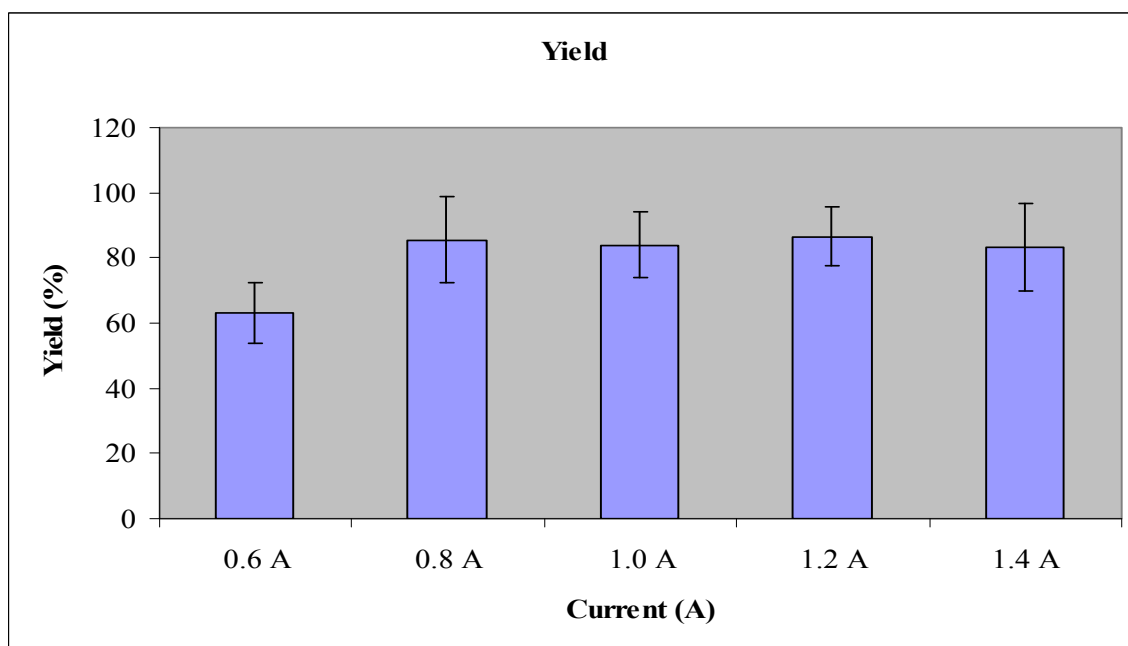


Figure 5.7. Average deposition yield as a function of electrodeposition current.

cell was interrupted each time an aliquot was taken. An interruption of current can cause the precipitate to redissolve and therefore directly affect the electrodeposition process. For the yield analysis of the electrodeposited samples created for alpha spectroscopy, the total amount of activity removed with the aliquots must be taken into consideration. Another aspect that must be considered is that the sum of the yields of the electrodeposited sample counted by alpha spectroscopy and the yield of the liquid scintillation sample cannot be greater than 100 %. Total yields of less than 100 % could be due to activity losses to the electrodeposition cell or electrode. The results for the FWHM and the deposition yield are summarized in Table 5.4 together with the yield determined by LSC measurements and the calculated total yield.

5.3 Microprecipitation

5.3.1 General Method

Five samples were created following the general cerium fluoride procedure as published by Eichrom Technologies, Inc. The precipitations were carried out at a temperature of 25 °C and the precipitate was left to settle for 30 minutes before filtration. The average energy resolution of the four samples was 37 ± 2 keV. The average yield of the four samples was calculated to be 85 ± 2 %.

5.3.2 Variation of Amount of Carrier and Hydrofluoric Acid Used

The microprecipitation procedure as published by Eichrom Technologies, Inc. calls for the use of 0.1 mL of cerium carrier solution with a concentration of $0.00155 \text{ g}\cdot\text{mL}^{-1}$ $\text{Ce}(\text{NO}_3)_3\cdot 6\text{H}_2\text{O}$ [8]. This corresponds to a total cerium mass of 0.05 mg. Two sets of experiments were carried out to study the influence of total carrier mass and total amount of hydrofluoric acid added on the performance of the microprecipitation. In the first set of experiments, the amount of cerium carrier added was varied while the hydrofluoric acid added was held constant. In separate experiments 0.1, 0.05, 0.025, 0.01 and 0.005 mL of the carrier solution was added to the americium stock solution, while the amount of hydrofluoric acid was kept constant at 1 mL. The amount of carrier added corresponded to a total cerium mass of 0.05, 0.025, 0.0125, 0.005 and 0.0025 mg, respectively. Five precipitations were carried out for each different amount of carrier solution. In the second set of experiments the same volumes of carrier solutions were used, however in this case the amount of hydrofluoric acid added was reduced to keep the ratio between the volume of carrier and hydrofluoric acid constant. As a result corresponding volumes of 1, 0.5, 0.25, 0.1 and 0.05 mL of hydrofluoric acid were added to the americium stock solution. Again, five precipitations were carried out for each combination of carrier solution and hydrofluoric acid. The other parameters of the process were kept the same as described for the general procedure. The dried filters were mounted on a stainless steel planchet and assayed by alpha spectroscopy. The results are listed in Table 5.5 and Table 5.6 and displayed graphically in Figures 5.9 – 5.12.

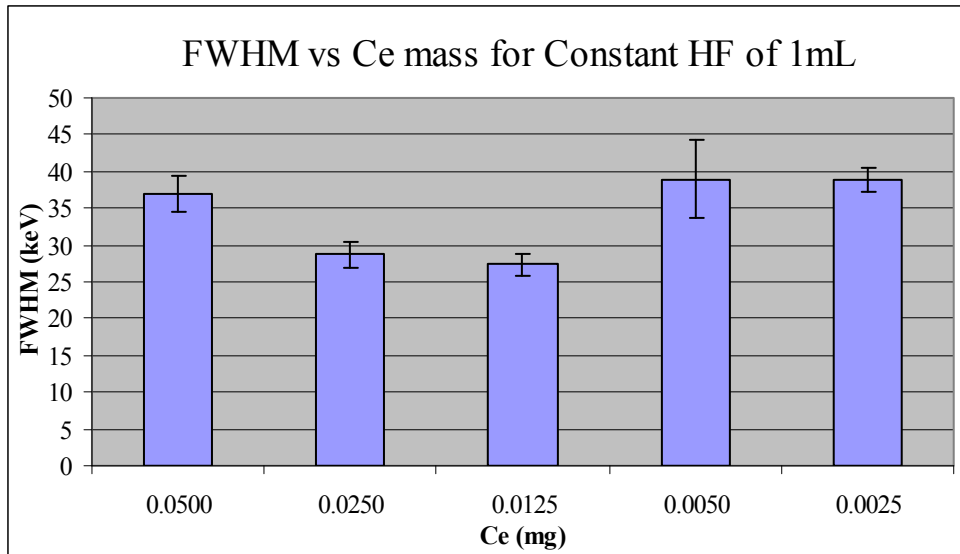


Figure 5.9. Average energy resolution as a function of cerium mass for precipitations using a constant amount of hydrofluoric acid (1 mL)

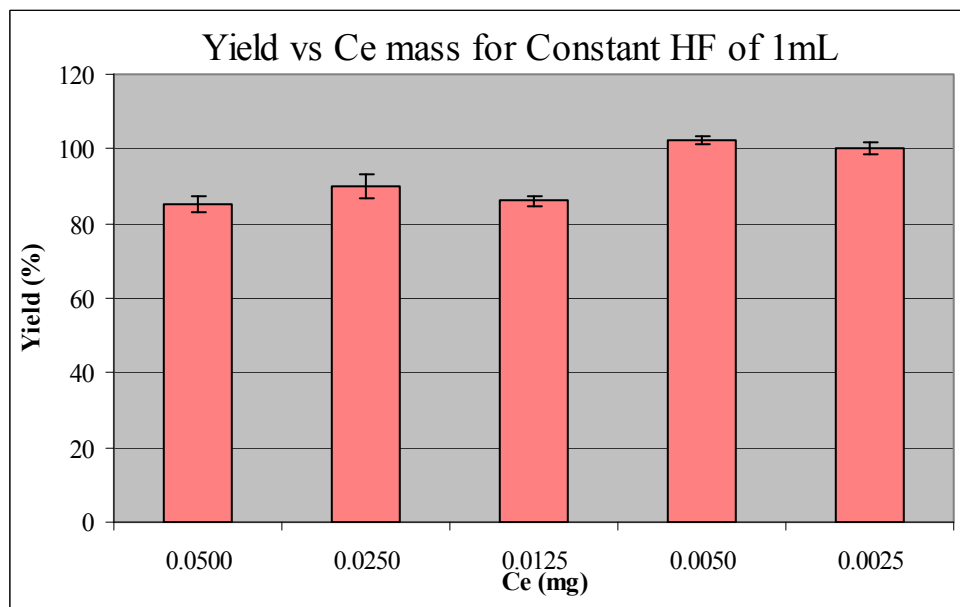


Figure 5.10. Average deposition yield as a function of cerium mass for precipitations using a constant amount of hydrofluoric acid (1 mL)

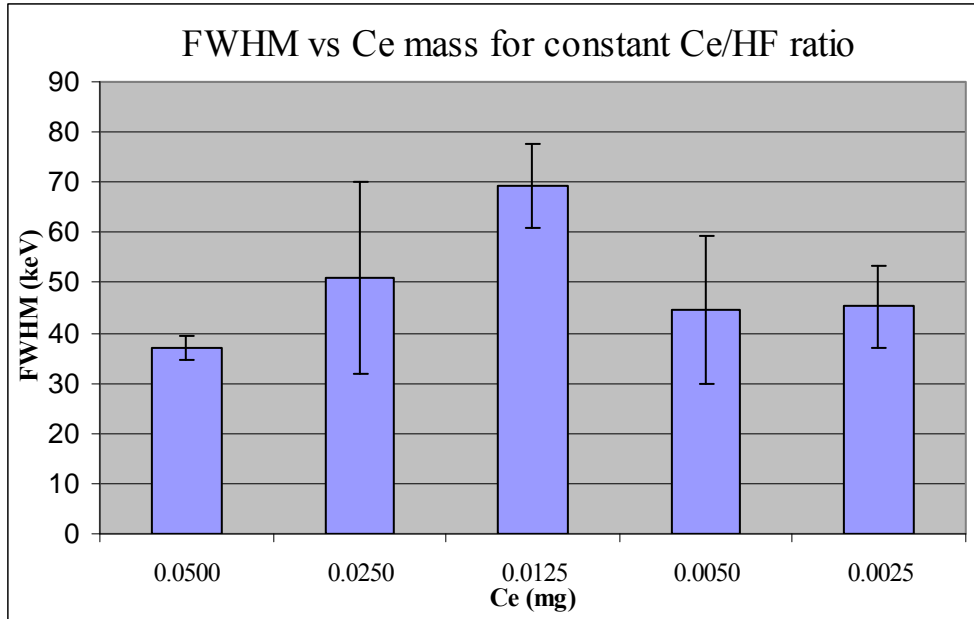


Figure 5.11. Average energy resolution as a function of cerium mass for precipitations using a constant ratio of carrier to hydrofluoric acid.

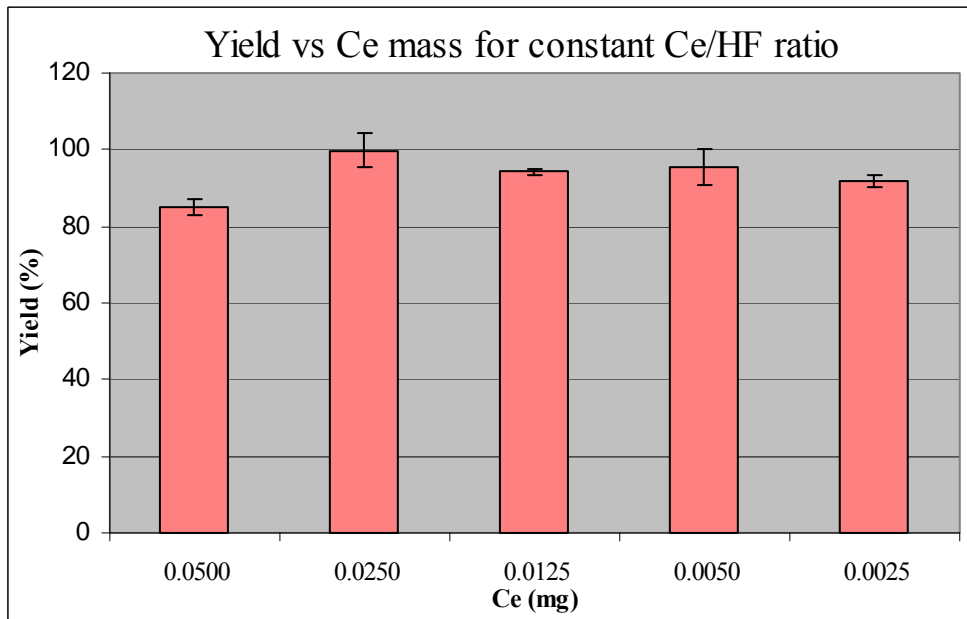


Figure 5.12. Average deposition yield as a function of cerium mass for precipitations using a constant ratio of carrier to hydrofluoric acid.

Table 5.5. Average energy resolution and deposition yield as a function of cerium mass for precipitations using a constant amount of hydrofluoric acid (1 mL).

Amount of Ce (mg)	FWHM (keV)	Yield (%)
0.0500	37 ± 2	85 ± 2
0.0250	29 ± 2	90 ± 3
0.0125	27 ± 2	86 ± 1
0.0050	39 ± 5	102 ± 1
0.0025	39 ± 2	100 ± 2

Table 5.6. Average energy resolution and deposition yield as a function of cerium mass for precipitations using a constant ratio of carrier to hydrofluoric acid.

Amount of Ce (mg)	Amount of HF (μL)	FWHM (keV)	Yield (%)
0.0500	1000	37 ± 2	85 ± 2
0.0250	500	51 ± 19	100 ± 5
0.0125	250	69 ± 8	94 ± 1
0.0050	100	45 ± 15	96 ± 5
0.0025	50	45 ± 8	92 ± 1

5.3.3 Temperature Study

The microprecipitation as described in the general method was carried out at a controlled temperature of 25 °C. Precipitations were also carried out at elevated temperatures to determine the influence of temperature on method performance. Five centrifuge tubes were placed in a water bath kept at 30, 35, 40, 45 and 50 °C, respectively. 350 μ L of ^{241}Am stock solution, 25 μ L of cerium carrier solution and 1 mL of HF were added to each tube and the solution was swirled gently to mix. Each tube was left to sit for 30 minutes before the solution was filtered. Filtration of the sample was conducted as described for the general procedure. The dried filters were mounted on a stainless steel planchet and assayed by alpha spectroscopy. The results are summarized in Table 5.7 and plotted in Figures 5.13 and 5.14.

Table 5.7. Average energy resolution and deposition yield as a function of precipitation temperature.

Temperature (°C)	FWHM (keV)	Yield (%)
25	28 ± 2	101 ± 2
30	35 ± 4	93 ± 1
35	31 ± 3	94 ± 2
40	30 ± 3	102 ± 10
45	34 ± 2	110 ± 2
50	30 ± 2	107 ± 1

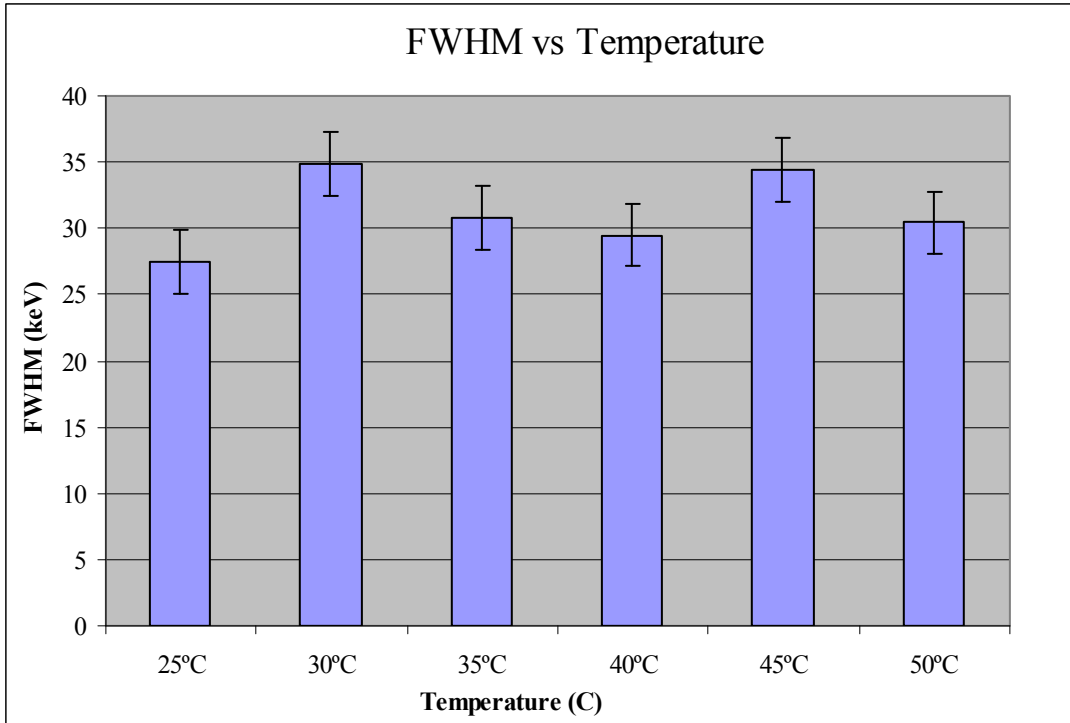


Figure 5.13. Average energy resolution as a function of precipitation temperature.

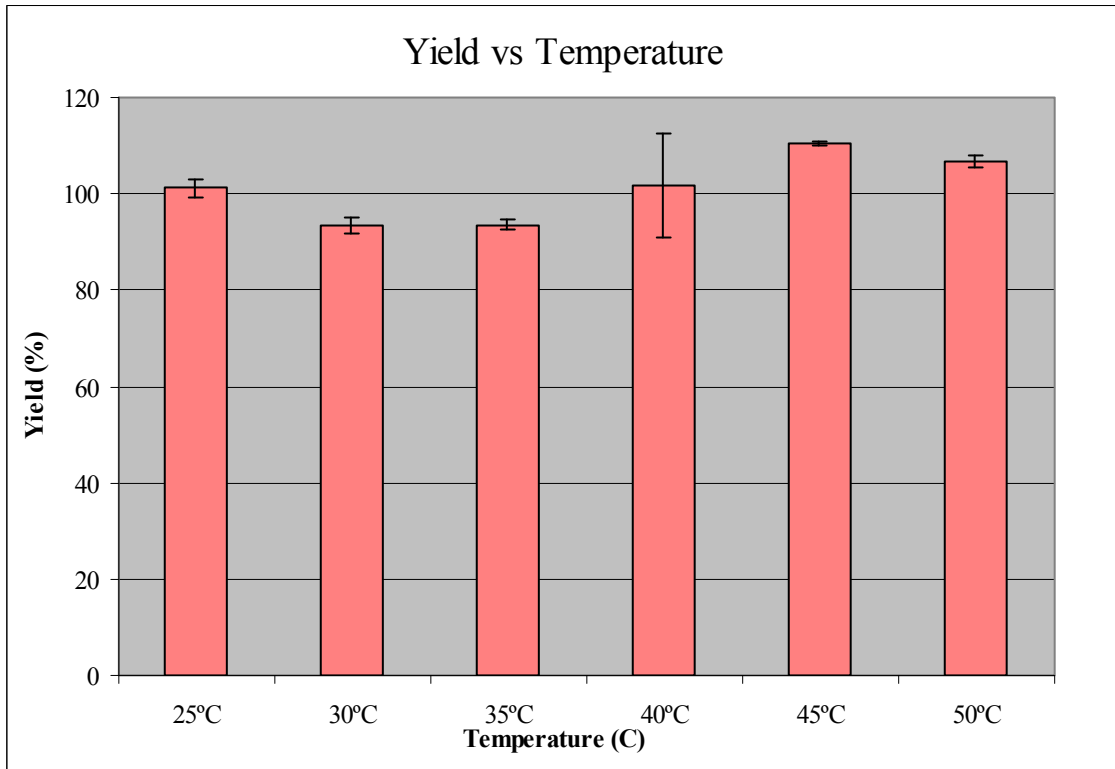


Figure 5.14. Average deposition yield as a function of precipitation temperature.

5.3.4 Effect of Precipitation Time

To determine the influence that precipitation time has on method performance, samples were created with varying precipitation times. Five samples were created for each precipitation time of 10, 20, 30, 45, 50 and 60 minutes as well as 2, 4, 8, 16 and 24 hours. The samples were then all processed by vacuum filtration in the same manner as described for the general method. Results are shown in Table 5.8 and Figures 5.15-5.16.

Table 5.8. Average energy resolution and yield as a function of precipitation time.

Time	FWHM (keV)	Yield (%)
10 min	35 ± 4	86 ± 7
20 min	35 ± 3	88 ± 5
30 min	28 ± 2	101 ± 2
40 min	28 ± 3	90 ± 1
50 min	28 ± 2	87 ± 5
60 min	33 ± 1	90 ± 1
2 hr	32 ± 3	87 ± 1
4 hr	31 ± 2	89 ± 2
8 hr	39 ± 5	90 ± 1
16 hr	41 ± 1	86 ± 5
24 hr	37 ± 2	86 ± 8

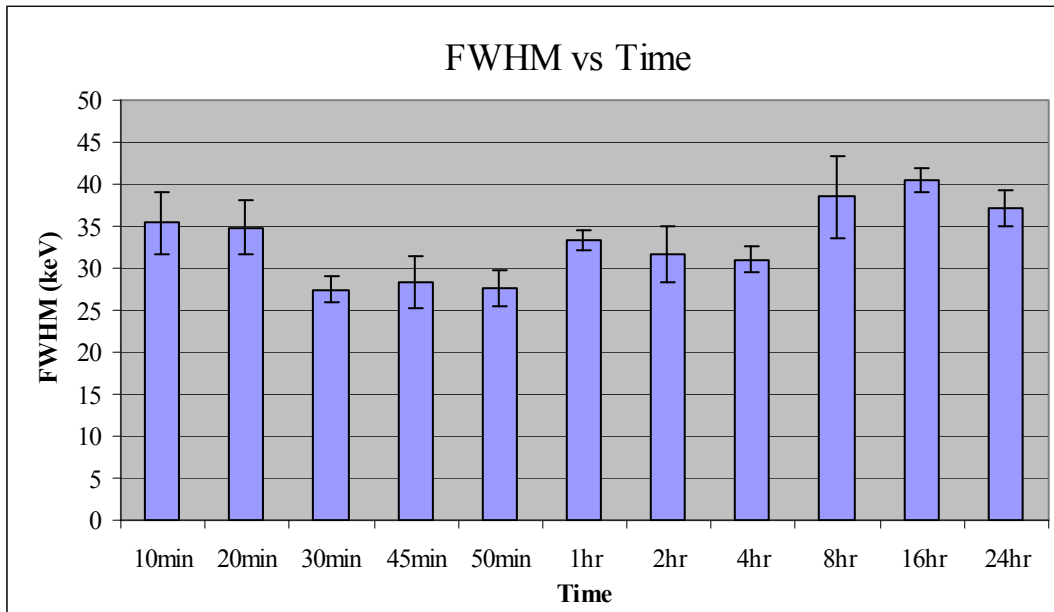


Figure 5.15. Average energy resolution as a function of precipitation time.

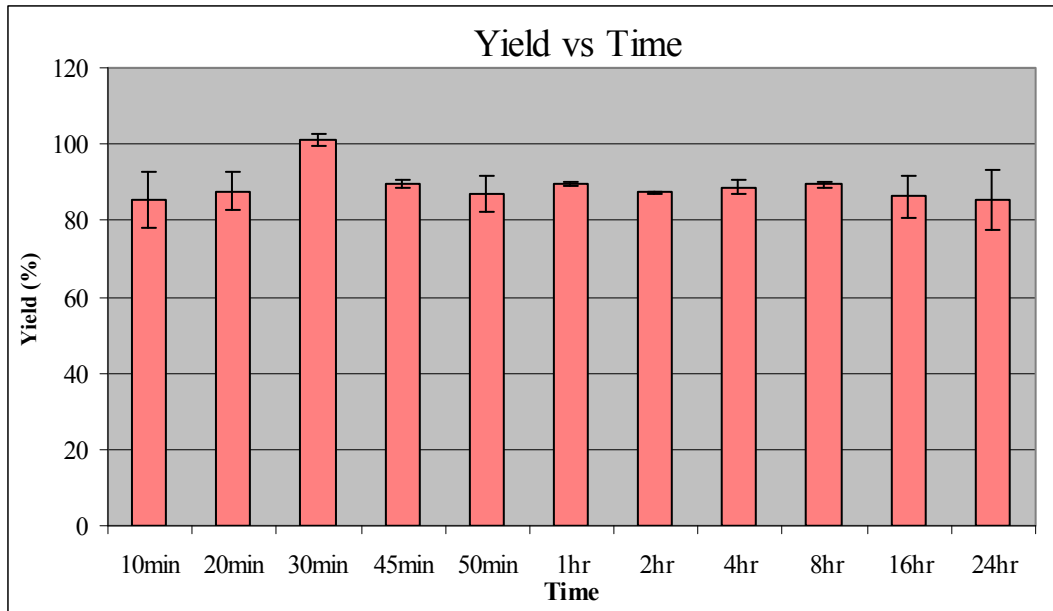


Figure 5.16. Average deposition yield as a function of precipitation time.

5.4 Discussion

5.4.1 Evaporation

Samples were prepared using the general method for evaporation to establish a baseline for method optimization. Average energy resolution of the samples prepared by the general procedure was approximately 74 keV, which is higher than the results obtained with both the electrodeposition and the microprecipitation method. This is due to the fact that this method does not include a step to eliminate any residual matter on the planchets that might interfere with the sample spectrum prior to evaporation. Yield results are approximately 83 %, which again is lower than the results for both electrodeposition and microprecipitation. Losses in yield during the evaporation process are likely caused by possible sputtering of the sample off the planchet during heating, even though this may not be visible to the naked eye.

The time and temperature study for evaporation was performed in order to determine the optimum hot plate temperature for evaporation and the evaporation time that corresponds to that temperature. As mentioned before, the ideal temperature is one that is hot enough to make the sample evaporate quickly, but not so hot that the sample sputters off the planchet leading to losses in yield. The highest temperature used for evaporation was approximately 138 °C since sputtering of water was seen at higher temperatures. Samples created at 138 °C are evaporated to dryness in approximately 4 minutes. No significant changes in energy resolution or yield are seen throughout the changes in temperature. This shows that samples can be evaporated at any temperature within the range without a measurable effect on the energy resolution and yield results.

In the last part of the evaporation study, the effects of the method of addition of the sample to the planchet were evaluated. The energy resolution for full volume addition samples was higher than that for drop by drop addition samples. When the sample is

added all at once, the energy resolution can worsen because any contamination present in the sample or on the planchet will be concentrated in the center of the sample, attenuating a greater percentage of particles. The yield for full volume addition samples was higher than that for drop by drop addition samples. A sample that is added to the planchet all at once with the full volume in the middle of the planchet will have a higher yield because there will be less sample loss to the edges of the planchets.

At a temperature of 138 °C the evaporation occurred in about 4 minutes. Washing of the planchet and addition of the sample will require a brief amount of time as well, but the total time required for sample preparation was significantly less than 10 minutes in all cases. Multiple planchets can be placed on the same hot plate to allow simultaneous handling of several samples. In this case however spatial variations in temperature on the hot plate need to be taken into account.

5.4.2 Electrodeposition

The general electrodeposition method as described by Kressin was used to obtain baseline data for comparison. Samples created using this general method had a very high average yield of $99 \pm 14\%$ and an acceptable average energy resolution of 45 ± 21 keV.

The objective of the planchet pretreatment study was to determine if the washing and electropolishing steps included in the procedure affect the energy resolution and yield results drastically. When energy resolution is a concern, it appears planchets that have been polished have a slightly worse energy resolution when compared to planchets that were not polished prior to the electrodeposition process. This is thought to be caused by the fact that, when viewed under an optical microscope, electropolished planchets seem to be rougher than planchets that have not been electropolished. Further investigations using a scanning electron microscope are necessary to confirm this. Increased roughness of the surface of a counting media can lead to the sample not being uniformly deposited. Non-uniform deposition can result in deterioration in energy resolution due to scattering and attenuation. Samples with the best average energy resolution were samples that had been washed but not electropolished.

Electrodeposition on polished planchets did however produce higher yields. This is most likely due to the fact that the roughness caused by the electropolishing procedure creates more surface area for the ions to attach to. The highest average yield was achieved with planchets that were both electropolished and washed. These conditions were therefore used for the remainder of the electrodeposition study.

The influence of deposition time was studied to determine whether the amount of electrodeposition time could be reduced without affecting the yield and energy resolution negatively. Generally, the amount of activity left in solution in the electrodeposition cell was at its lowest at around 100 minutes into the electrodeposition process. After 100 minutes of electrodeposition, the amount of activity in solution appears to increase again. This could be due to a number of factors such as the aliquots not being taken from the same area or inhomogeneous mixing of the sample. Longer deposition times need to be investigated in future experiments to confirm this. The last aliquot taken after the completion of the electrodeposition process should be representative of the amount of activity that was not plated out onto the planchet. The fraction of activity left in solution after the electrodeposition process added to the yield of the electrodeposited sample counted by alpha spectroscopy should not add up to more than 100 %. Although some of

the yields of the planchets counted by alpha spectroscopy may seem low, when the liquid scintillation data is added, the yields are more on the order of the electrodeposition results seen in the rest of the experiments. The average energy resolution measured for the samples created as part of the time study is comparable to that of samples prepared using the general method.

The electrodeposition current study was performed to determine the optimum current for electrodeposition that will produce the best energy resolution and yield results. Energy resolution results show no pattern corresponding to the specific current for each set of samples. Samples created at a current of 1.0 A showed the least statistical variation between samples while samples created at 0.6 A and 0.8 A showed a high statistical variation between samples.

The yield results showed more of a trend than the energy resolution results for the current study. Samples that were created with current settings of 0.8 A, 1.0 A and 1.2 A all showed similar results, all with yields from 84 – 87 %. The samples with the lowest yield were samples created at a current of 0.6 A. These samples had an average yield of only 63 %. The low yield is most likely caused by the current not being high enough to allow for complete deposition within 2 hours. At a current of 1.4 A, the yield starts to decrease from what is seen in the 0.8 – 1.2 A range. This is most likely caused by bubble formation from increased water electrolysis occurring in the cell which interferes with the deposition of the ^{241}Am onto the planchet.

The results of the time study showed that approximately 100-120 minutes are required for the electrodeposition process to reach completion. Additional time is required for the washing and polishing of the planchet before deposition as well as the washing and drying of the planchet after the deposition. However the largest amount of time in addition to the time required for the deposition is spent on the evaporation and conditioning of the sample solution before deposition. The exact time required depends on the sample volume as well as the number of evaporations that are required to, e.g. destroy all organic material present. Typically this will require another 1-2 hours of preparation time. The electrodeposition unit used in the experiments allowed for the simultaneous handling of up to 12 samples. Therefore a total of twelve samples could be produced in approximately 4 hours or less.

5.4.3 Microprecipitation

As with the Kressin method for electrodeposition, several samples were prepared using the general cerium fluoride method for microprecipitation to establish a baseline for comparison. Samples created using this method had an acceptable average energy resolution of 37 ± 2 keV and an exceptional average yield of $85 \pm 2\%$. The standard deviation of the samples was also much less than that of samples created by electrodeposition, proving microprecipitation to be more reliable.

The influence of carrier concentrations on energy resolution and yield was investigated at constant and variable concentrations of hydrofluoric acid. Reduction of the amount of carrier leads to an initial decrease in energy resolutions in those experiments for which the amount of hydrofluoric acid was kept constant at 1 mL. A minimum energy resolution is reached for the addition of 0.0125 mg of Ce. A reduction in carrier leads to less attenuation on the filter sample. The energy resolution increases however again for even lower amounts of carrier. On the other hand the highest precipitation yields are

obtained by the addition of 0.0050 of carrier added. This concentration is apparently still sufficient to form enough precipitate for the AmF_3 to co-precipitate.

The energy resolution shows an opposite trend in those experiments in which the hydrofluoric acid concentration was varied simultaneously with the carrier concentration. The energy resolution increases with decreasing acid and carrier concentrations until a maximum is achieved at a concentration corresponding to 0.0125 mg Ce and 0.25 mL of HF. The resolution decreases again for even lower amounts of carrier and acid. The yield results in these experiments show no discernable trend. The highest precipitation yield is obtained using 0.0250 mg of Ce and 0.5 mL of HF.

In addition the effect of precipitation temperature on energy resolution and yield was investigated. No obvious relationship between either energy resolution or yield and temperature was discovered. The optimum energy resolution was measured for samples that were prepared at a temperature of 25 °C, while the highest precipitation yield was obtained for samples that were precipitated at 45 °C. An almost comparable yield was however already achieved at 25 °C and this would allow for a simplified precipitation at room temperature without the use of a water bath.

The influence of precipitation time was studied to determine the optimal time for the procedure. The lowest energy resolution was seen for samples with precipitation times ranging from 30 – 50 minutes. Samples created with shorter precipitation times exhibited a much higher energy resolution as well as a larger standard deviation. This might be indicative of an incomplete precipitate formation. Samples that were prepared with longer precipitation times showed an increased energy resolution as well, in particular those samples that were allowed to sit for more than 8 hours. A possible explanation for this effect could be that the dissolution and reprecipitation processes occurring on the surface of the precipitate preferentially involve CeF_3 . As a result the AmF_3 would slowly migrate to the inner parts of the precipitate, which would cause additional attenuation. The precipitation yield does not appear to follow an obvious trend in relation to the precipitation time. The highest yield is however achieved if the sample is allowed to settle for 30 minutes.

The initial precipitation experiments were conducted using a setup that allowed for the handling of only one filter at a time. The largest amount of time required for the method was spent on allowing the precipitate to settle. Addition of carrier and hydrofluoric acid, the filtration itself and the drying of the filter required only a small amount of additional time (10-15 minutes). Using a precipitation time of 30 minutes allowed for the preparation of a sample in 40-55 minutes. The use of a multiposition filtration manifold significantly increased the efficiency of the process. The manifold allowed for the simultaneous filtration of up to twelve samples. As a result, twelve sources could be prepared in under an hour.

6. CONCLUSIONS

Three methods of sample preparation for alpha spectroscopy were examined as part of this research project. Each method was scrutinized to optimize method performance while keeping the time required for sample preparation in mind. The process of electrodeposition was examined using the standard Kressin method as a starting point and the influence of parameters such as time, applied current and planchet preparation were investigated. For microprecipitation, the cerium fluoride method was used as standard and the parameters varied included precipitation time, amount of cerium carrier and hydrofluoric acid, fraction of cerium carrier in total solution and fraction of hydrofluoric acid in total solution. Evaporation was the third procedure compared and evaporation time, hot plate temperature, and method of sample addition were varied.

Evaporation was the method that required the least amount of chemistry to be performed on the samples before deposition onto the counting media. An evaporation temperature of approximately 140 °C was determined as the most effective. No dependency on evaporation or temperature was seen for energy resolution or yield results. For the best yield results, the sample should be added to the planchet at the same time in the center of the planchet. Evaporation was the fastest method examined, but the samples produced were inferior in regards to yield and resolution compared to the other methods investigated.

For the electrodeposition method, the procedure with the best yield results was the general method using planchets that had been both washed and electropolished prior to electrodeposition. The energy resolution was the best for planchets that had been washed but not electropolished. A study of the amount of radionuclide deposited over time showed that the fraction of activity in solution decreased steadily until about 100 minutes were reached. This study should be continued for longer electrodeposition times to determine the optimum deposition time. Variation of the deposition current led to the recommendation of keeping the current set between 0.8 A and 1.2 A for the best results in yield. The best energy resolution results were seen when the current was set at 1.0 A. Overall, samples prepared by electrodeposition showed superior energy resolution and acceptable yields; however the method was discovered to be lacking in reproducibility. The yield as well as energy resolution was found to vary significantly between samples, even though the deposition conditions were kept the same. Use of a multiposition electrodeposition unit allowed for the preparation of up to 12 samples in approximately 4 hours.

The microprecipitation method was studied by varying parameters such as the amount of cerium carrier and hydrofluoric acid, the precipitation temperature and the time that the precipitate was allowed to settle. For the general method involving a precipitation time of 30 minutes and solutions of 0.1 mL of cerium carrier and 1.0 mL of hydrofluoric acid, an average energy resolution of 37 ± 2 keV and a yield of $85 \pm 2\%$ was obtained. A study of the influence of the carrier and acid concentrations on energy resolution and yield revealed that the best results were obtained if the amount of hydrofluoric acid is kept at 1 mL. The best energy resolution was achieved by addition of 0.01225 mg of Ce, while the best yield was obtained by addition of 0.0050 mg of Ce. When the precipitation time was varied, the best energy resolution was seen for samples with a

precipitation time between 30 and 50 minutes. The highest yield was however achieved if the sample is allowed to settle for 30 minutes. Overall the reproducibility of the microprecipitation method was found to be far superior compared to the other methods. The use of a multiposition sampling manifold combined with a precipitation time of 30 minutes allowed for the preparation of 12 samples in less than one hour.

Based on the results of this study, microprecipitation was singled out as the most promising method for source preparation for alpha spectroscopy in emergency response situations. It was found to be a very reliable and robust method that allows for the fast preparation of samples with an excellent energy resolution and yield. While electrodeposition often yields samples with an even better energy resolution, it seems to be less robust and suffers from greater variations in reproducibility. In addition, the preparation of samples by electrodeposition takes almost four times as long as by microprecipitation. The evaporation method allows for an even faster source preparation; however it does not achieve the energy resolution or the yield that can be achieved by either of the other two methods. It should therefore only be used if a source needs to be prepared quickly with less of a concern for energy resolution and yield, or if the nuclides present in solution have already been identified.

7. FUTURE WORK

Each of the three methods investigated has the potential for further optimization and the influence of additional parameters should be investigated as part of a future project.

In the case of the evaporation method, the influence of the planchet geometry should be investigated; in particular the use of planchets with a ribbed bottom should be examined. In addition the possibilities of evaporation from organic solutions instead of aqueous solutions should be studied.

For the electrodeposition the relationship between deposition time and yield should be investigated for even longer deposition times to determine whether long deposition times will eventually lead to redissolution of the sample. In addition in the future this study should be repeated in such a way that aliquots are taken without the need to interrupt the current flowing through the cell. The influence of temperature on the deposition yield and energy resolution should be studied as well.

Several additional parameters should be investigated to finalize optimization of the microprecipitation procedure. The use of different carriers such as lanthanum and neodymium should be compared to the use of cerium. The influence of different interferences such as iron, calcium, phosphate and sulfate on method performance should be studied. Additional microprecipitations should be performed using solution volumes that are representative of those encountered in common separation schemes. And finally, precipitation from solutions containing multiple radionuclides should be investigated.

The distribution of radionuclides and possible interfering stable elements on the prepared sources should be examined using autoradiography and different microscopy techniques. This would allow an independent characterization of the amount of attenuating material, the homogeneity of radionuclide deposition and therefore the source quality itself.

8. REFERENCES

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9. APPENDIX I: CHEMICALS USED

Cerium (III) Nitrate Hexahydrate, 99.9%, Strem Chemicals

CAS 10294-41-4

Hydrofluoric Acid, 48-51%, J.T. Baker

CAS 7664-39-3

Titanium Chloride, 30% weight in 2N HCl, Acros Organics

CAS 7705-07-9

Nitric Acid, 4 molar, Fisher Scientific

CAS 7697-37-2

Acetone, Fisher Scientific

Potassium Hydroxide, J.T. Baker

CAS 1310-58-3

Phosphoric Acid, J.T. Baker

CAS 7664-38-2

Sulfuric Acid, >51% acid, J.T. Baker

CAS 7664-93-9

Perchloric Acid, 69-72%, J.T. Baker

CAS 7601-90-3

Hydrochloric Acid, J.T. Baker

CAS 7647-01-0

Sodium Sulfate, J.T. Baker

CAS 7757-82-6

10. APPENDIX II: MATERIALS USED

^{241}Am in 1 M hydrochloric Acid, 100 Bq mL⁻¹, Isotope Products

12 Volt Electrodeposition unit

Electrodepositing Cell

Flat 25 mm stainless steel planchets

Lipped 25 mm stainless steel planchets

25 mm diameter seals, part number 016F75Q, McMaster Carr

Variable volume VWR pipettors

100 μL Eppendorf pipettor

1000 μL Eppendorf pipettor

50 mL Centrifuge tubes

Gelman filter apparatus

Hot plate, Corning PC-101

Heat lamp

Petri dishes

Vacuum pump, Dry-fast, model number 2012B-01

2 stage vacuum pump, Edwards

Resolve filters 0.1 micron 25 mm polypropylene, Eichrom Technologies, Inc.

Infrared thermometer, Extech

Liquid Scintillation Counter, Perkin Elmer Tri-Carb, model 3100TR

Canberra Alpha Analyst Spectrometer, 450 mm² active area PIPS detectors