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Quantitative comparison of sample preparation methods for low-level alpha spectrometry

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QUANTITATIVE COMPARISON OF SAMPLE PREPARATION METHODS FOR LOW-LEVEL ALPHA SPECTROMETRY

by

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ABSTRACT

Quantitative Comparison of Sample Preparation Methods for Low-Level Alpha Spectrometry

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There are currently several widely accepted methods of sample preparation procedures for alpha spectroscopy. Alpha spectroscopy is becoming more important due to increased concentration on nuclear waste management, site decontamination and decommissioning, and environmental assessment. Due to increased emphasis on emergency response and preparedness, there is a strong desire to make the analysis of samples as quick and efficient as possible. Three methods evaluated in this project are electrodeposition, microprecipitation, and evaporation. Actinides are the main elements of concern, namely a tracer of ^{241}Am is used. Each method is itself optimized and evaluated quantitatively, and then the methods are compared against one another. Parameters such as energy resolution, sample yield and preparation time are evaluated to determine the most productive method for each scenario for preparing samples for alpha spectroscopy. Microprecipitation is the recommended due to the high yields produced and consistency of the results.

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CHAPTER 1

INTRODUCTION

1.I Alpha Spectroscopy

Alpha spectroscopy is a useful detection method for determining alpha emitting radionuclides in environmental samples. In modern times, alpha spectroscopy is becoming more important due to the shift from nuclear weapons development to nuclear waste management, site decontamination and decommissioning, and environmental assessment. Due to increased emphasis on emergency response and preparedness, there is a strong desire to make the analysis of samples as quick and efficient as possible. It is uncertain if and when the malevolent use of radioactive material, a severe nuclear accident or some other incident will occur. In order to recover as quickly and effectively from such an incident, rapid analysis methods need to be developed for alpha spectroscopy.

Alpha spectroscopy is a useful tool in the field of radiation detection for several reasons. It allows determination of isotopic composition of samples because of the ability to collect, store and create a spectrum of the energies of the particles emitted from an alpha source. Each isotope has one or more corresponding energies of the emitted alpha particle which can be used to identify the content of the sample. Unlike other types of decays, alpha decay results in a monoenergetic line spectrum that allows assignment of lines to individual transitions. This property not only provides for nuclide identification, but also quantification as well. Since each individual alpha particle reaching the detector is recorded, they will add up in "bins" in the multi-channel analyzer (MCA). The amount of events recorded at each particular energy is calculated as counts per second, which can then be converted to disintegrations per second using the known efficiency of the detector.

Because of 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. There should be no foreign matter in the source to attenuate the alpha particles. 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 length on the order of a few centimeters or less in air. Some parameters important for acceptable results are limiting self absorption, limiting absorption into 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.

The application of alpha spectroscopy has several potential problems that can compromise the validity of data and results and complicate detection. Sample preparation, no matter the method, can negatively affect the quality of the sample being measured. For environmental samples, collection of an alpha spectrum is complicated by low levels of radioactivity coupled with the limited range of the alpha particle. Because of this property, any excess matter contained in the sample, including the radionuclide itself if the sample is too thick, will attenuate the alpha particles. Foreign matter causes decreases in energy resolution. The sample needs to be as close to monatomic as possible with as little foreign matter in order to get the best results from alpha spectroscopy.

When samples are counted that have high activities, recoil contamination can become a problem that can lead to an increased background in the system after only a single sample has been counted. This issue can make decontamination of the detectors necessary after each use, which can become quite time consuming if there is a large amount of samples to be counted in the laboratory (Canberra 2001). When the samples are ready to be counted by alpha spectroscopy, the only parameters left to control are the background and efficiency of the detectors. Since detector efficiency can only be controlled by replacing a detector with a more efficient model, the background must be as low as possible, especially for environmental samples. Too much background can lead to radionuclides being undetectable if the samples have a very low specific activity. Usually, laboratories that analyze samples with varying activity levels will dedicate at the very least a few chambers to environmental level samples to avoid the time consuming task of cleaning the detectors before every sample. On today's market, the detectors with the highest efficiency run at about 37 % and are able to achieve energy resolutions as low as 10 keV.

1.2 Introduction of Methods

There are currently several accepted methods of sample deposition for alpha spectroscopy. The three main categories of sample deposition procedures are electrodeposition, microprecipitation, and evaporation. Each of these methods can be performed in several different ways. These three categories and the preferred methods will be discussed in detail in the following sections.

1.2.1 Electrodeposition

Electrodeposition is one of the most accepted methods of sample preparation for alpha spectroscopy. One of the most accepted methods is the Kressin method, developed in 1977 by Ivan Kressin. The Kressin method uses a self-buffered solution of sodium sulfate-sodium bisulfate as an electrolyte solution. When electrodepositing a 4 pCi sample of americium or plutonium, the method produced results of 102.4 % ± 3.4 recoveries for americium and 100.9 % ± 2 for plutonium with excellent spectral resolution for the alpha energies (Kressin 1977).

The process of electrodeposition involves adding a solution containing activity into an electrolytic solution then applying voltage to the deposition cell for a certain set current and a certain set amount of time. Some parameters important for electrodeposition that will be evaluated are the current, plating time, current density, applied voltage, and whether or not the planchets are electropolished and washed before the start of the electroplating process. The results are dependent upon the chemical properties of the element, especially the electrochemical potential and possible foreign material present in the solution. The electrochemical potential of the element, which depends on the nature of the ion; its chemical form, and its concentration, is very important. Aside from the radionuclide part of the sample, current density, material and design of the electrode and electrochemical cell are all important in optimizing the procedures (Zolotov 1990).

1.2.2 Electrodeposition Theory

The general basis behind electrodeposition is that electrochemical reactions allow radionuclides present as ions in solution to be deposited onto an electrode. This will 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 (MARLAP). The electrodeposition process discussed in this paper is nonspontaneous.

Deposition of actinides can be more difficult to control because of the decomposition of water and reactions of anions and cations at electrodes (Adolff and Guillaumont 1993). For this reason, each individual step of the electrodeposition process and each part of the sample solution must be examined to determine the best combination. Overall, the effectiveness of electrodeposition of trace components of actinides depends on the electrode potential, electrode surface area and material, properties of the electrolyte solution, duration of electrodeposition and temperature (Zolotov 1990).

The first step in the process of sample preparation for the Kressin method is to add 2 mL of 5 % $NaHSO_4$ and 0.5 mL of 70 % $HClO_4$ to the sample in a 30-50 mL beaker and heat at 180-200 °C until dryness. The 5 % $NaHSO_4$ is added to prevent tracer quantities of the actinides from baking onto the beaker during fuming (Kressin 1977). The 70 % $HClO_4$ drives off any organics found in the solution. As the fuming proceeds to dryness, the actinides remain in an acid salt that has formed the $NaHSO_4$. The $NaHSO_4$ will remain with the radionuclide sample and will act with as part of the electrolyte solution during the plating process.

In the next step, the beaker is rinsed with DI water to wash off anything that may have gotten onto the sides of the beaker above where the solution was. Next 1 mL of concentrated HCl is added and again heated until it is dry. This step is usually only performed twice, but it can be repeated as much as needed to get the acid salt to become white, which means the sample is pure and should have no organics that will interfere and cause resolution losses when the sample is counted by alpha spectroscopy. If the sample is not white, but has more of a wet translucent appearance, this indicates there may still be $HClO_4$ present (Kressin 1977).

Once the sample has cooled to room temperature and before the sample is ready to be added to the cell to be plated out, 3 mL of DI water is added and let sit for 10 minutes to allow for dissolution of the $NaHSO_4$. The pH of the solution at this point is only 0.9 which has proven too low for the electrodeposition process. A buffer must be added to the sample to raise the pH. The salt of an acid is an ideal buffer for that acid (Kressin 1977). Na_2SO_4 is an ideal buffering agent for $NaHSO_4$ which will bring the pH of the solution to between 1.5 and 2.5. The ideal pH for electrodeposition is approximately 2. Sodium sulfate is also an excellent electrolyte which acts to decrease the electrical resistance of the cell (Kressin 1977).

1.2.3 Microprecipitation

Microprecipitation is another common sample preparation method for alpha spectroscopy that rivals electrodeposition in sample yields. It is newer than the electrodeposition methods and some consider it to be the preferred method. Literature states that although the spectral resolution of microprecipitated samples is almost as good as electrodeposited samples, the microprecipitation procedures are much faster, more reliable, and generally give chemical yields greater than 98 % (Sill 1987).

The microprecipitation method that will be evaluated in this project is the CeF_3 method. In this method, a cerium carrier is added to a centrifuge tube containing the sample. Concentrated hydrofluoric acid is then added and swirled to mix. The solution is then left to drain onto a filter which is set up in an apparatus to which a vacuum is applied to speed the filtration process. When the sample has all been filtered through, the filter is then dried under an infrared lamp and mounted onto a planchet to be analyzed by alpha spectroscopy. Some parameters important for microprecipitation are the total amount of carrier used, fraction of the carrier in total solution, type of carrier, precipitation time, and the amount of hydrofluoric acid in the solution. Sources prepared by microprecipitation should be thoroughly dry before measurements to prevent self-absorption and scattering.

1.2.4 Microprecipitation Theory

During microprecipitation, insoluble compounds of a specific radionuclide are formed and isolated from other foreign ions in the solution. For this method, both the carrier and the hydrofluoric acid play important roles. The carrier is defined as a substance that is added in an appreciable amount, which, when associated with the tracer of a specified substance, in this case ^{241}Am, will carry the substance 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 down from solution by co-precipitation, associating it with an insoluble substance that precipitates from solution. The cerium carrier acts as the insoluble substance that will co-precipitate with the americium (MARLAP).

The hydrofluoric acid in the system automatically dissociates in water. The cerium carrier is cerium (III) nitrate hexahydrate. When the cerium (Ce^{3+}) combines with the fluorine atom (F^-) from the hydrofluoric acid, CeF_3 is formed. The rare earth fluorides are very effective scavengers of actinides in oxidation states III and IV, but not for actinides in oxidation states V and VI. Cerium is a lanthanide element that is highly insoluble in water when complexed with fluoride ions, thus a precipitate will be formed. The mass and size of these elements are comparable to actinides, making them better scavengers for precipitation.

The Gelman filter has an important role in the microprecipitation process as well. Excess solution is removed by the 0.1 micron filter while precipitate losses are minimized. The filters are washed with ethanol prior to the microprecipitation process to clean the filter and check for possible leaks in the apparatus. When the sample has been filtered through, the filter is again washed with ethanol in order to remove some excess water. The filters must be dried under an infrared lamp prior to counting by alpha spectroscopy in order to set the precipitate and eliminate excess water that can lead to attenuation of the alpha particles.

1.2.5 Evaporation

Evaporation is the third type of sample preparation method for alpha spectroscopy. It is a simpler procedure for sample preparation, therefore it does not require nearly as much time as the previously mentioned two methods. Due to the nature of this method, it is most commonly used when samples need to be quickly processed 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. Care must be taken to avoid sample loss onto the hot plate due to unacceptable pipetting methods or a hot plate temperature that is too high and could cause sputtering of the sample. Some parameters important for evaporation are the temperature of the hot plate, drying time, method of addition and planchet geometry. The most common problem with this method is the possibility of non-uniform sample spreading on the planchet or the sample not being thin enough, causing self-attenuation.

1.2.6 Evaporation Theory

This method is considered more primitive than electrodeposition and microprecipitation due to the fact that there are no chemical techniques performed on the sample to remove any contaminants. Anything left on the planchet after evaporation will cause unwanted, unaccounted for attenuation. Peak tailing on the low energy end of the peak will occur because particles will reach the detector with lower energies. Since the alpha particles are being attenuated, they will hit the detector with an energy less than the characteristic energy of the isotope they were emitted from. The attenuation only slows down the alpha particles, which is why the high end energy of the peak is usually almost vertical. The less of a tailing the peak has on the low energy end, the better the energy resolution of the sample is which will make it much easier for identification and quantification the sample.

1.3 Objective of Research

This research project will examine and compare the three sample preparation methods for alpha spectroscopy mentioned above. Each of the methods will be optimized based on yield, energy resolution, and time. The best procedure for each of the three methods will then be compared and a selection can be made as to which procedure is best for each possible scenario, whether it be emergency response or routine sample analysis. A standard solution of ^{241}Am in dilute hydrochloric acid will be used for each method in order to concentrate solely on the sample deposition aspect of sample preparation. Using the same radionuclide standard for each method allows for easier comparison between the three methods.

For data analysis purposes, there are several goals of this research project. The first goal is to obtain the best possible spectral resolution. This is important due to the fact that many alpha emitting isotopes emit alpha particles in energies in very close proximities to other isotopes, some on the range of 10-20 keV. Most detectors cannot obtain spectral resolutions better than 12 keV so sample preparation must be as clean as possible to eliminate as much attenuation as possible in the sample itself. Another goal is to obtain the best possible yield. For the sake of counting statistics, a high yield must be obtained in order to shorten the length of time the sample will need to be counted for. If approximately 10,000 counts are obtained under a peak, the counting error will be an acceptable 1 %. The reduction of sample preparation time is also a goal of this research project. 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 sample preparation can be optimized to a certain extent, however, without compromising the sample thinness or cleanliness.

The last and possibly most important or all-encompassing goal of this research project is to be able to assign the best method of sample preparation to each task that needs to be completed. If a task involves radionuclide identification, a method with a high energy resolution is needed to make sure there is no peak blending. A task that needs to achieve a quantification of the radionuclide needs to be performed using a method that produces the best sample yield. If time is of most concern and the energy resolution and yield don't need to be optimized, a method is needed that can be performed in the least amount if time.

CHAPTER 2

MATERIALS AND METHODS

2.1 Materials

A list of materials used for all experiments can be found in appendix II.

2.2 Electrodeposition

2.2.1 Apparatus

The equipment used for the electroplating process consists of a 12 volt electrodeposition unit with a current range from 0 to 2.0 amps and an electrodeposition cell. The electrodepositor is a piece of equipment providing a current to an anode and cathode placed in the cell in order to deposit the sample onto the planchet. Components of the electroplater include the power supply box, resistance adjustment knobs, meters to monitor the resistance, a toggle switch for each of the twelve stations which reverses the current for the option of electropolishing or electrodeposition, and a platinum electrode. All of this can be seen labeled in Figure 2.1 below.

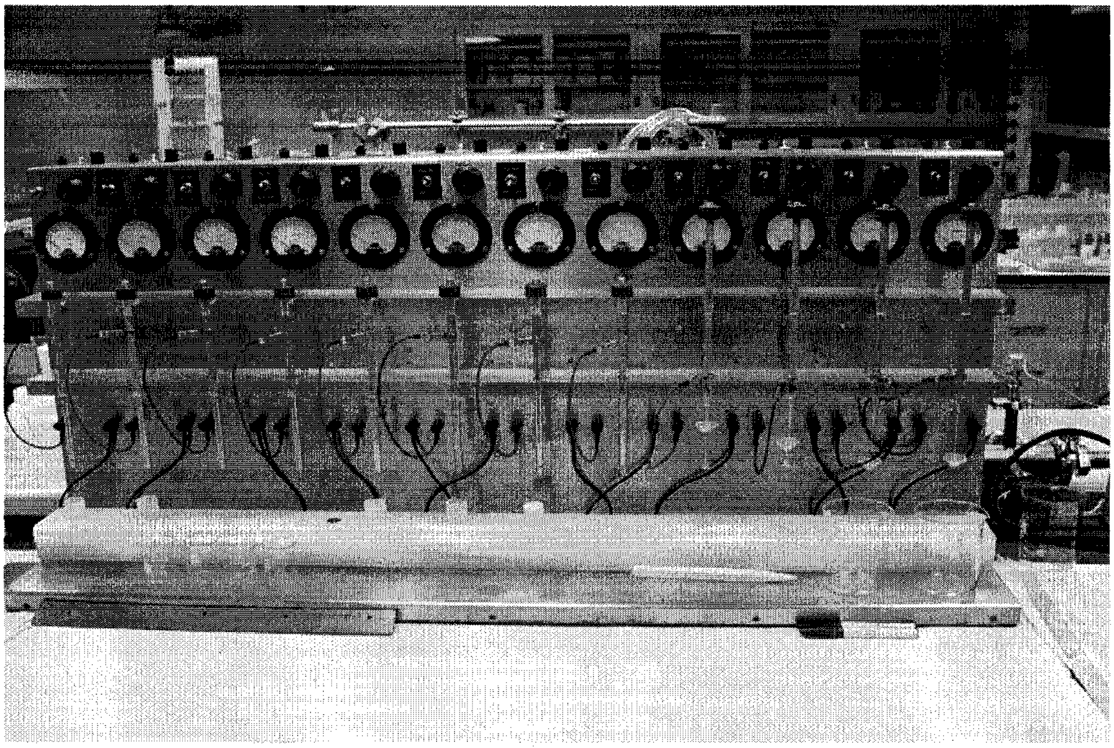

Figure 2.1. Electrodeposition Apparatus.

The cell is the piece of equipment that holds the sample. It consists of a plastic scintillation vial with the bottom cut out, the vial cap, a rubber seal, a copper anode and a stainless steel planchet. Figure 2.2 shows the components of the cell and how it is assembled. Once the cell is assembled, it is set onto the electrodeposition unit and the platinum electrode is lowered into the cell.

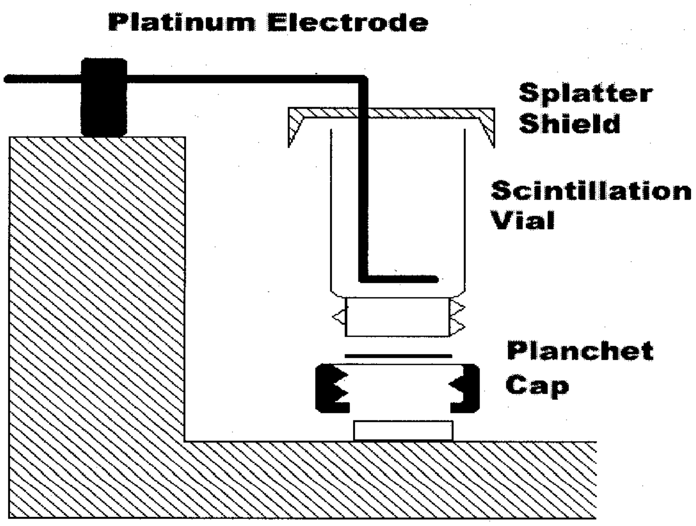

Figure 2.2. Electrodeposition Cell

2.2.2 General Method

The method of electrodeposition uses an electroplating apparatus and an electrolyte solution to deposit the sample onto a stainless steel planchet using an applied current. A 700 µL sample of ^{241}Am is first placed into a 50 mL beaker. Next, 2 mL of an electrolyte solution of 5% sodium bisulfate ($NaHSO_4$) and 0.5 mL of perchloric acid ($HClO_4$) are added to the beaker. The beaker is then placed on a hot plate at temperatures between 180°C and 200°C to drive off the perchloric acid. Complete removal of perchloric acid can be determined by when the sample stops fuming in a white color. Addition of the perchloric acid is done to drive off any organics in the solution that may later interfere with the purity of the sample. The beaker is then allowed to cool before rinsing with deionized (DI) water, adding 1 mL of hydrochloric acid (HCl) and placing it back on the hot plate to dry. After repeating the HCl addition and drying 2 to 3 times, the sample is allowed to cool again to room temperature before adding 3 mL of DI water. After the sample is left to dissolve for 10 minutes, 4 mL of 15 % sodium sulfate (Na_2SO_4) is added. Sodium sulfate is the second part of the electrolyte solution and acts as a buffer to maintain a pH of approximately 2 in the solution. The sample is then transferred to the electrodepositing cell. The beaker is rinsed with DI water and the rinse is also added to the cell.

Once the solution has been transferred to the cell and the cell is set up on the electrodepositor, the platinum wire which acts as the anode is lowered into the cell containing the solution, about 3-4 mm above the planchet. The spacing of the electrode determines the electric field which will affect how well the sample is electrodeposited onto the planchet. Also, if the platinum anode is lowered too far into the cell, this can create trapped bubbles which can interfere with the electrodeposition process. The electroplater is then switched on and set to the deposit setting. Each individual cell to be plated is switched on and the current is adjusted to 1.0 A. The current is monitored for approximately the first 15 minutes and again after 1 hour of plating time. Cells are also monitored for leakage throughout the process. Usually, the current holds steady after equilibrating for about 15 to 20 minutes. After the sample is allowed to plate out for 2 hours, 2 mL of 4 M potassium hydroxide (KOH) is added and left to plate for an additional 2 minutes. The current will jump when the KOH is added so care must be taken to keep the current adjusted to 1.0 A. The addition of the KOH is done to neutralize the acidic solution. The ^{241}Am tends to deposit as a hydroxide and the addition of the KOH will prevent the AmOH from dissolving back into the solution.

At the end of the plating run, the cell is disassembled and the planchet is then washed with 1 % ammonium hydroxide (NH_4OH). This is done to make sure the deposited surface of the planchet is neutralized and the americium is in the form of a hydroxide. The planchet is then heated on a hot plate until dry, and then it is ready for counting by alpha spectroscopy.

2.2.3 Washed Planchets

The Kressin method calls for the planchets to be washed prior to electrodepositing a sample onto them. Planchets are shipped with a plastic coating to protect the surface that the sample will be electrodeposited onto. Once the plastic is removed, the planchet is washed with acetone to remove any residue the plastic may have left on the planchet. Next, the planchet is washed with nitric acid (HNO_3) to remove any excess organics from the surface. Any substance that is not cleaned off of the planchet can interfere with the sample deposition and can cause attenuation of the alpha particles when they are being counted by alpha spectroscopy.

In this part of the study, comparisons were made to determine if washing the planchets before plating had any effect on the energy resolution of the sample or the sample yield. Several samples were electrodeposited onto washed planchets and the same number of samples were electrodeposited onto unwashed planchets.

2.2.4 Polished Planchets

The Kressin method also calls for the planchets to be electropolished before the sample is electrodeposited. This process involves adding 10 mL of a solution containing 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. For this process, for each cell containing a planchet to be electropolished, the toggle switch is set to the polish setting, which reverses the flow of the current, and a current of 1.0 A is applied for 15 minutes. This process is performed in order to make the surface of the planchet smoother for less attenuation of the alpha particles when counting by alpha spectroscopy.

Once the polishing step is complete, the cells can remain assembled with the planchet remaining a part of the cell. It is best if the cells are rinsed several times to remove all traces of the acidic solution and then refilled with a few mL of DI water until they are needed for the electrodeposition process. Unless leakage occurred from the cell during the electropolishing process, it is recommended that the cell remains assembled so that the electropolished portion of the planchet will be exactly the same surface that the sample will be electrodeposited onto. If the cell is disassembled, it is possible that some of the electrodeposition will occur on parts of the planchet that were not electropolished. In this part of the study, a comparison was made to determine if electropolishing the planchets before plating has any effect on the energy resolution of the sample or sample yield. Several samples were electrodeposited onto electropolished planchets and the same number of samples were electrodeposited onto planchets that had not been electropolished.

2.2.5 Time Study

It has been in question whether the sample really needs to be plated for a full 2 hours at 1.0 A. In order to answer this question, aliquots of sample solution are removed at various time intervals during the electrodeposition process. The Kressin method is used as described above using planchets that have been both washed and polished. Once the sample solution is transferred to the cell, the electroplating run is started as normal. For the first 30 minutes of electrodeposition, 50 μL or 100 μL aliquots are pipetted out of the cell every 5 minutes and added to a scintillation vial containing 10 mL of liquid scintillation cocktail. This process is repeated every 10 minutes for the second 30 minutes of electrodeposition time and every 20 minutes for the last 60 minutes of electrodeposition time. The final sample was taken after the addition of the potassium hydroxide. An aliquot is also taken before current is applied to the cell. Twice the quantity of sample from the general procedure is used in order to account for the aliquots being removed and to improve counting statistics. The amount of liquid in the cell was closely monitored throughout the electrodeposition process so that the total volume remained at 10 mL. If the level of solution reached below 10 mL, DI water was added to bring the sample volume back up to 10 mL.

Once all of the aliquots were collected, they were counted on a Perkin Elmer Tri-Carb Model 3100TR liquid scintillation counter, each for a period of one hour. The planchets were rinsed with 1 % ammonium hydroxide and then heated on a hot plate to dry, then counted by alpha spectroscopy on a Canberra Alpha Analyst. The results from the alpha spectroscopy of the planchets were compared to the results from the liquid scintillation samples to better determine the yield of the sample.

2.2.6 Current Study

Along with the time study, the main goal of the current study is to decrease the amount of time needed for the sample to plate out and to see the effects of changing the current on the electrodeposited sample. Using the Kressin method, the current was varied in increments of 0.2 A from 0.6 A to 1.4 A while keeping the plating time constant at 2 hours. Aliquots of 100 μL of sample were taken from the cell at the end of the electrodeposition run and counted by liquid scintillation. The electrodeposited planchets were counted by alpha spectroscopy and compared to the results from the liquid scintillation samples to get a more accurate yield measurement. As with the time study, care must be taken to monitor the solution level during the electrodeposition process. If the sample level drops below 10 mL from either evaporation or aliquot removal, DI water was added to maintain a total sample volume of 10 mL.

2.3 Microprecipitation

2.3.1 General Method

The experimental setup for the microprecipitation procedure uses two 100 mL polypropylene flasks. The second flask is used as a trap which is connected to a vacuum pump as seen in Figure 2.3. A 25mm 50 mL polysulfone funnel is connected to the top of the first flask using a rubber stopper to seal the flask. A 0.1 micron 25 mm diameter polypropylene Resolve filter is placed on the Gelman apparatus consisting of a polycarbonate base and metal screen between the bottom of the funnel and on top of the rubber stopper. Vacuum is applied to the system and the filter is prewetted with ethanol (C_2H_5OH) to check for leaks.

Once it is assured that there are no leaks, the system is rinsed with DI water. A 350 µL sample volume of ^{241}Am is added to a 50 mL centrifuge tube. Next, 0.1 mL of a cerium carrier, cerium (III) nitrate Hexahydrate ($Ce(NO_3)_3 6H_2O$) at a concentration of 0.00155 g mL^{-1} is added to the centrifuge tube. Next, 1.0 mL of 28 M hydrofluoric acid (HF) is added and then the whole solution is swirled to mix and left to sit.

After the solution has been left to sit for at least 30 minutes and the experimental setup is ready, the solution is poured into the funnel with vacuum applied. The solution runs through the filter and into the flask. Neither the ^{241}Am nor the CeF_3 will filter through and thus be left on the resolve filter. The filter is then washed with DI water and with ethanol for drying. Once the vacuum has been turned off and the pressure has gone up in the system, the resolve filter can be removed carefully with tweezers and placed in a plastic Petri dish to be dried under an infrared lamp. The filter is then mounted on a stainless steel planchet to be counted by alpha spectroscopy.

Figure 2.3. Microprecipitation Apparatus

2.3.2 Time Study

The method used calls for letting the solution sit for at least 30 minutes to precipitate out (Eichrom 2004). In order to determine if the precipitation time has an effect on yield or energy resolution, several samples are created with varying precipitation times. Precipitation times used in this part of the procedure range from 10 minutes to 60 minutes in 10 minute increments. The samples are then all prepared the same way as described for the general method and counted by alpha spectroscopy. Samples are compared to one another to determine the least amount of precipitation time that can be used to produce the best yield and energy resolution.

2.3.3 Amount of Carrier and Hydrofluoric Acid

Cerium fluoride is used as the primary carrier for the method. The amounts of cerium carrier and hydrofluoric acid are manipulated to see if there is any effect on the resulting spectra when the samples are counted by alpha spectroscopy. This is done by changing the total amount of cerium carrier as well as the amount of hydrofluoric acid while keeping the two in the same ratio used in the general method. Care is taken to not add too much of the carrier or it will interfere with the microprecipitation process or make the samples too thick for alpha spectroscopy.

2.3.4 Fraction of Cerium Carrier

In this part of the study, the amount of cerium carrier will be manipulated while the amounts of ^{241}Am and hydrofluoric acid are held constant. This is done to determine if there is any effect on the ability of the CeF_3 to carry the AmF_3 through the co-precipitation process.

2.3.5 Fraction of Hydrofluoric Acid

Hydrofluoric acid is a corrosive acid that requires extra training and personal protective equipment for its use. Due to these conditions, this part of the research is aimed at determining the minimum amount of hydrofluoric acid that can be used and still produce acceptable results when the sample is counted by alpha spectroscopy. As with the cerium carrier, the amount of hydrofluoric acid must be in the correct proportion to the rest of the solution and the amount of carrier in particular in order to avoid any interference with the microprecipitation process.

2.4 Evaporation

2.4.1 General Method

The liquid drop method for evaporation is used for this part of the study. The method involves placing a planchet onto a hot plate at a certain temperature and then pipetting an aliquot of the sample directly onto the planchet. The sample deposition is considered complete when the planchet is dry. The sample is then ready for counting by alpha spectroscopy. The setup for this procedure is shown in Figure 2.4 below. It should be noted that the planchets used for the evaporation method differ from those used in the electrodeposition method. The planchets for the evaporation method are lipped to prevent any sample loss from the sides of the planchets.

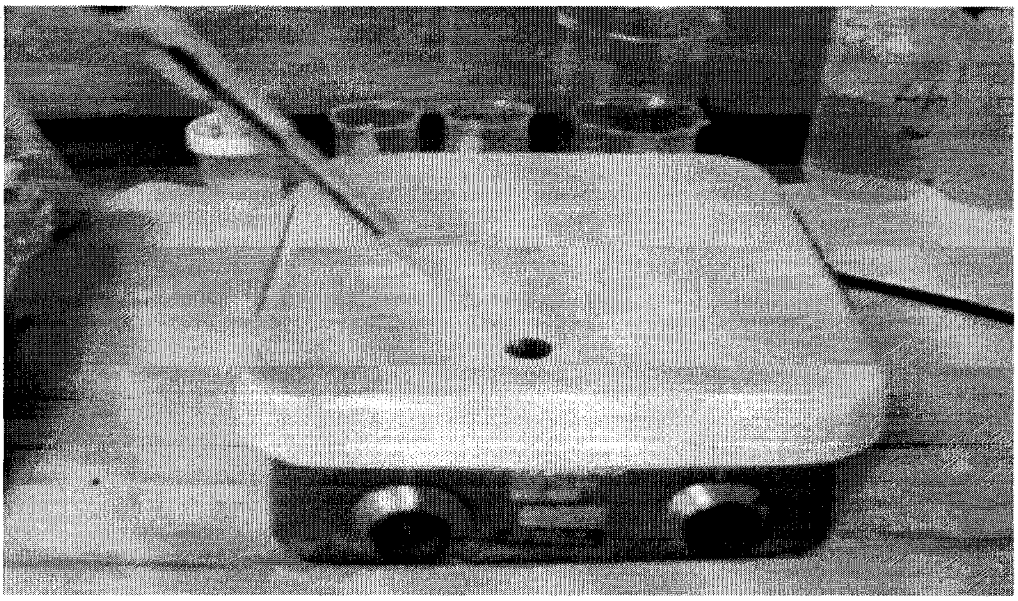

Figure 2.4. Evaporation Apparatus

A hot plate is used for this method and an Extech model number 42510 infrared thermometer is also used to monitor the planchet temperature since there are no temperature readings on the hot plate itself. The infrared thermometer has an accuracy of ± 2% of reading or ± 2 °C, whichever is greater, for the range of 18 °C to 28 °C. It should be noted that temperature tends to vary greatly on different locations on the hot plate.

2.4.2 Time and Temperature Study

The time and temperature study is conducted to optimize the method itself for the specific hot plate used in the experiment. Essentially, the aim is the determination of the best temperature for the given hot plate that will dry the sample in the shortest amount of time without any sputtering due to overheating. This is important because if the sample is overheated, some of it may sputter off of the planchet causing yield losses and contamination of the hotplate.

2.4.3 Method of Addition Study

The main question in this part of the study is to determine whether there is an effect on yield and energy resolution depending on how the sample is added to the planchet. For the method of addition there are two possibilities, full volume addition and drop by drop addition. Full volume addition is when the full 350 μL sample is added to the planchet at the same time, while drop by drop addition requires the 350 μL sample to be added in drops in different locations spread across the planchet. Data sets will be created for samples that are added as a full volume addition and as drop by drop addition.

2.5 Liquid Scintillation Counting

2.5.1 System Specifications and Parameters

The system used is a Perkin Elmer model 3100TR liquid scintillation counter. A counting protocol has been set up that includes several parameters to optimize the liquid scintillation counting. Count time is set for 60.0 minutes per sample with the count mode set to normal and the pre-count delay set to 0. Background subtraction is set to "off" but is performed manually after the count is complete. This is performed by subtracting the number of counts per minute of a blank from that of the sample. The blank was counted along with the rest of the samples. The 2 sigma % terminator is set to on for any region and the low CPM threshold is set to off, since the samples in this experiment are not considered low CPM.

2.5.2 General Counting Procedure

The samples are loaded into a cartridge with the blank first, standard solution next and all of the samples following. The cartridge is loaded into the liquid scintillation counter and a protocol with the above conditions is loaded. Once the samples are done counting, a report is printed out with information including counts per minute, count time and amount of quench. For liquid scintillation counting, the amount of quench in the sample determines the yield of the sample. If the SIS quench level is above 500, it can be assumed that the liquid scintillation counter has 100 % efficiency for that set of alpha particle emitting samples. The background is then subtracted from the CPM for each sample for the final result. Results from liquid scintillation counting in this research project are used to determine the activity in solution during the electrodeposition process for the time and current study. The results are also used to determine the activity of the standard solution to use in the yield calculations. The standard solution has a purity of > 99 % so contributions from ^{237}Np can be neglected.

2.6 Alpha Spectroscopy

2.6.1 System Specifications and Parameters

The system used is a Canberra Alpha Analyst model 7200-04 with 12 detectors available for data collection. An Edwards 2 stage vacuum pump is used to evacuate the chambers for counting. The detectors are Canberra Passivated Implanted Planar Silicon (PIPS) detectors with an active volume of 450 mm^2 with an electronic resolution of 10.2 keV. The MCA is run by GENIE 2000 alpha analyst software from Canberra.

2.6.2 General Counting Procedure

Samples are loaded in the Teflon planchet holders are 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, is used for all of the samples counted in this project because it is far enough away from the detector to obtain better energy resolution due to the solid angle and close enough to obtain acceptable detector efficiency.

Once the samples are loaded, the chambers are evacuated to a pressure of 0.200049 torr. Count times are set for 3 hours which allows at least 10,000 counts to be recorded under the peak for each sample. This results in a counting error of 1 % or less. If samples are used with differing activities from those in the above procedures, count time must be adjusted so the count error remains at or below 1 %.

Electrodeposited standard sources were used to perform system calibrations before samples were counted. The data for the standard sources can be seen in Tables A and B in Appendix III. Using the information from the calibration, the ^{241}Am peak is set to the known decay energy of 5.485 MeV and then the channel number and energy of another known radionuclide, in this case ^{210}Po, is set to correspond with the data from the standard electrodeposited source used for calibration. Once the energy to channel ratios are set, the software calculates the energy resolution of the ^{241}Am peak. Information that is collected from the software for data analysis includes energy resolution (FWHM) in keV, live time, and number of counts recorded with error.

CHAPTER 3

RESULTS AND DISCUSSION

3.1 Data Analysis

3.1.1 Alpha Spectroscopy

Each of the detectors on the alpha spectrometer are calibrated monthly using an electroplated ^{239}Pu standard with a ^{241}Am peak. The standard had an activity level of 0.0054 μCi on 29 May 1991 and is labeled "HRC 118." Measurements are taken at each shelf level in the detection chamber starting at level 2 and working down to level 10. The efficiency of every detector is calculated at each shelf level. Shelf levels are approximately 2.5 mm apart.

As mentioned earlier, samples are counted on the alpha spectrometer for a sufficient period of time to obtain at least 10,000 counts under the peak for good statistical data. Electrodeposition and evaporation samples are counted on the fourth shelf level while microprecipitation samples are counted effectively at the 3.5 shelf level because of their unique geometry consisting of the Eichrom filters being mounted to the bottom of lipped planchets.

3.1.2 Yield

For each sample, the detector, number of counts with error, and live measurement time were recorded. The disintegrations per second (DPS) of the sample was calculated by using Equation 3.1 below. This equation is used assuming a 100 % radiation yield for that alpha transition.

DPS = CPS/eff

where CPS = counts per second

Eff = detector efficiency at the corresponding shelf level

Equation 3.1

After the DPS is calculated, the yield can be calculated using Equation 3.2.

Yield = (DPS/Activity)*99.4 %

where Activity is the amount of activity in the standard solution added to the sample

Equation 3.2

The 99.4 factor is used to convert the final result to percentage rather than a fraction. It is multiplied by 99.4 instead of 100 due to the fact that ^{241}Am decays due to alpha radiation 99.4 % of the time. The yields for all data from each method were calculated this way.

3.1.3 Energy Resolution

The same electroplated ^{239}Pu standard mentioned above was used for energy resolution calculations. Centroid channel numbers of the ^{239}Pu and ^{241}Am peaks from the electroplated standard are noted for use in calibrating the samples. After a sample was counted, an energy only calibration was performed. The channel numbers for ^{239}Pu and

^{241}Am for each detector were entered as calibration points for the samples. This essentially sets the energy to channel ratio so the energy resolution can be calculated by the alpha acquisition (GENIE 2000) software.

3.1.4 Liquid Scintillation Counting

In order to determine the amount of activity in the ^{241}Am standard, an aliquot of the standard solution was taken using a liquid scintillation detector. The same quantity of the standard solution is taken as is added to the samples used for electrodeposition and microprecipitation and counted by liquid scintillation counting. The quench level of the sample was always low enough to assume an efficiency of 100 % for the liquid scintillation counter. Liquid scintillation samples were counted for either 60 minutes or two sigmas, whichever occurred first. A blank sample of 10 mL of liquid scintillation cocktail was counted every time a sample was counted to determine the background. This data was then used as the known activity for each sample to calculate the yield.

3.2 Electrodeposition

3.2.1 General Method

The results for the general method include samples in which the planchets have been both washed and electropolished, as the general method calls for. Eight samples were created using the general method. When counted by alpha spectroscopy, an average yield of 99 ± 14 % was obtained with an energy resolution of 45 ± 21 keV. These results were calculated using only six of the eight samples created since two of the data points were removed after mathematically being determined as outliers.

3.2.2 Washing and Electropolishing

Eight samples exist for each combination of washed and polished planchets. The four combinations are washed polished (W-P), washed unpolished (W-UP), unwashed polished (UW-P), and unwashed unpolished (UW-UP).

Of the eight samples for the washed polished study, two were removed as they were statistically considered outliers. The resulting energy resolution was 45 keV ± 21 keV. The yield was calculated to be 99 ± 14 %. Only one outlier was removed in the washed unpolished data set. An energy resolution of 32 ± 12 keV and a yield of 61 ± 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 ± 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 ± 21 %. Results are summarized in Table 3.1 and plotted in Figures 3.1 – 3.2. The data for each individual sample, including outliers, can be seen in Tables C-F in Appendix IV.

Table 3.1. Average yield and energy resolution results for each data set for washed and electropolished planchet study.

Sample ID	**Energy Resolution**	**Yield**
Washed Polished	45 ± 21 keV	99 ± 14 %
Washed Unpolished	32 ± 12 keV	61 ± 8 %
Unwashed Polished	59 ± 9 keV	60 ± 20 %
Unwashed Unpolished	44 ± 18 keV	73 ± 21 %

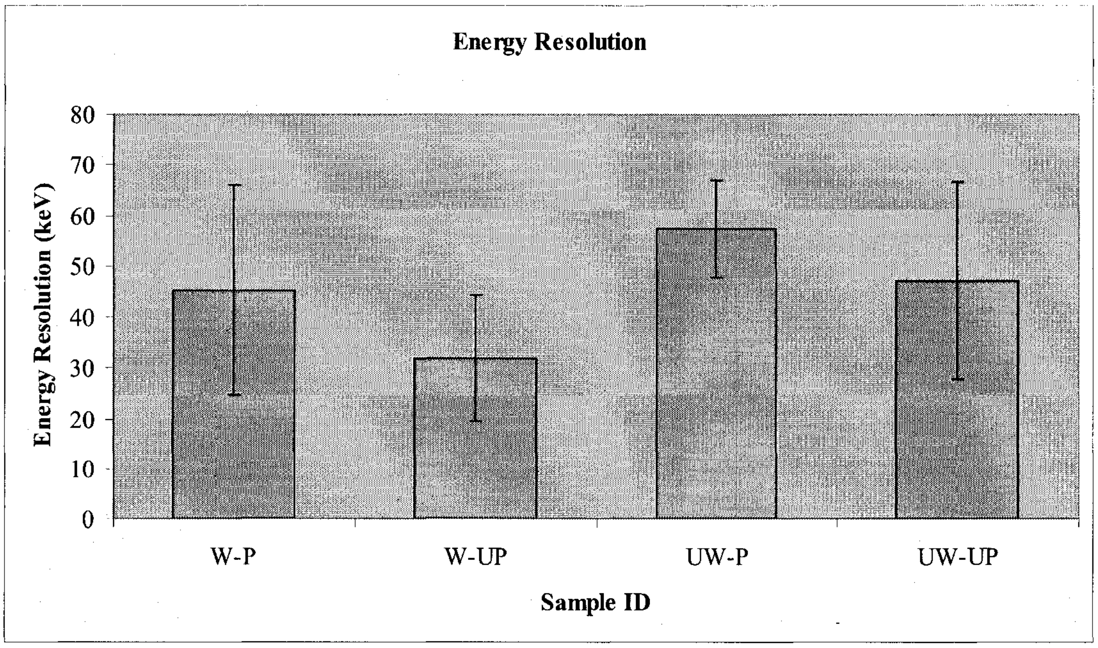

Figure 3.1. Average energy resolution for electrodeposited samples with different planchet pretreatments procedures. Washed polished (W-P), washed unpolished (W-UP), unwashed polished (UW-P), and unwashed unpolished (UW-UP).

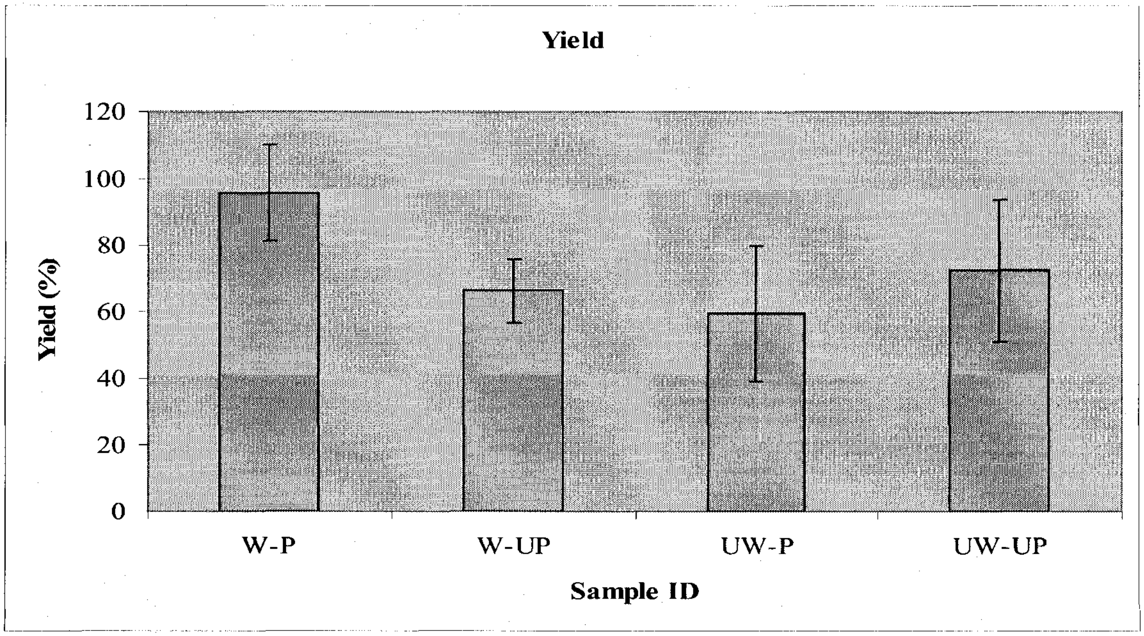

Figure 3.2. Average energy resolution for electrodeposited samples with different planchet pretreatments procedures.

3.2.3 Time Study

Four samples were created taking 50 μL aliquots and four samples were created taking 100 μL aliquots at given times during the electrodeposition process. During the 30 minutes of electrodeposition, samples were taken every five minutes, with the first aliquot taken before any current was applied. Aliquots were taken every ten minutes for the second 30 minutes and then every 20 minutes during the last hour of electrodeposition. Each aliquot was placed into a scintillation vial containing 10 mL of liquid scintillation cocktail and then counted, along with a blank and standard, by liquid scintillation counting. Results are plotted in Figures 3.3 – 3.4. The data for each individual sample, including outliers, can be seen in Tables G-N in Appendix IV.

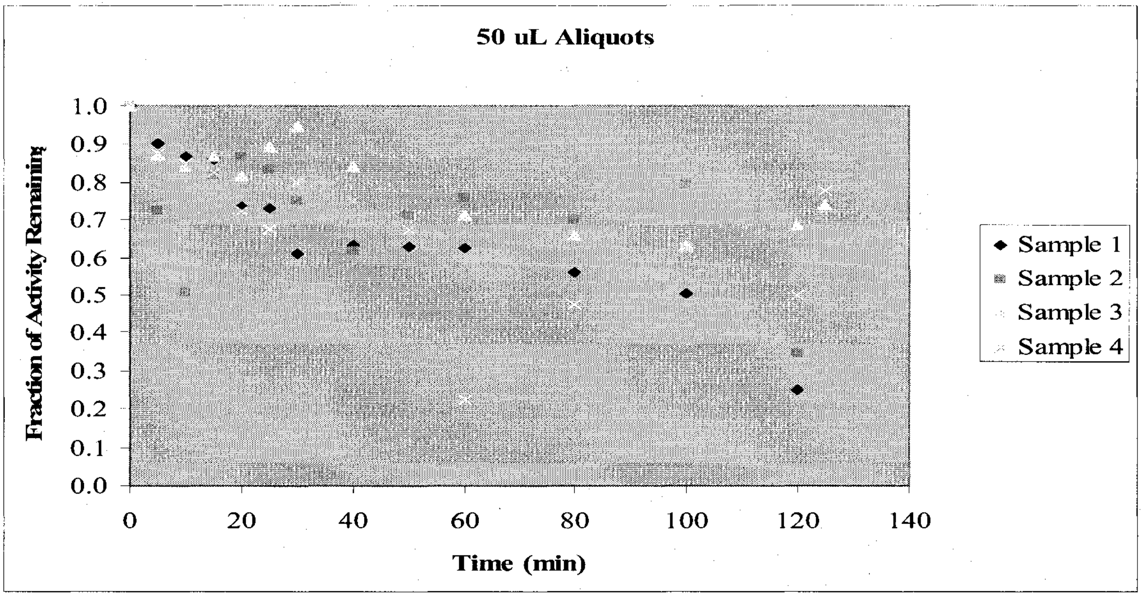

Figure 3.3. Fraction of activity remaining in the electrodeposition cell as a function of deposition time (50 μL aliquots).

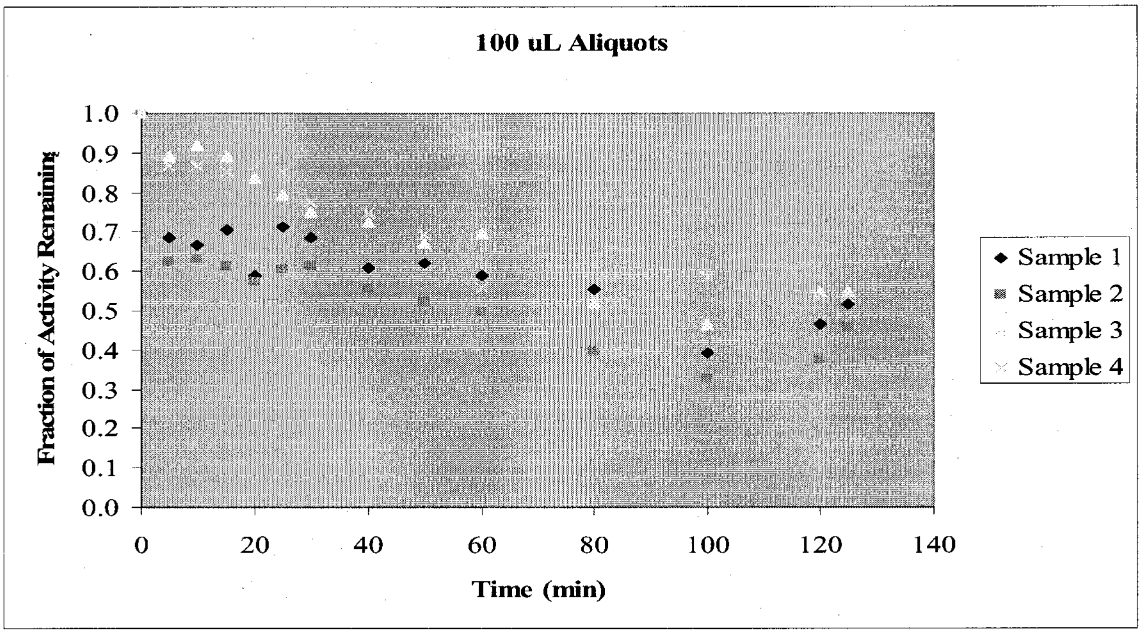

Figure 3.4. Fraction of activity remaining in the electrodeposition cell as a function of deposition time (100 μL aliquots).

As seen by Figures 3.3 and Fig. 3.4, some activity still remains in the solution after the electrodeposition process is complete. This is most likely due to the fact that the current through the cell was interrupted each time an aliquot was taken. An interruption of current could cause the precipitate to redissolve directly affecting 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. Results are summarized in Table 3.2.

Table 3.2. Average energy resolution and yield of electrodeposited samples counted by alpha spectroscopy as a function of deposition time. This table also includes liquid scintillation counting yield of samples and the total yield for each sample.

Sample	FWHM (keV)	Yield (%)	LSC Yield (%)	Total Yield (%)
50 μL #1	75.0	48.3	24.9	73.2
50 μL #2	46.0	39.7	34.6	74.3
50 μL #3	26.0	3.6	74.0	77.6
50 μL #4	30.6	10.5	78.0	88.5
100 μL #1	35.7	8.5	51.0	59.5
100 μL #2	79.4	21.5	46.0	67.5
100 μL #3	56.0	48.4	55.0	103.4
100 μL #4	91.5	52.0	53.0	105.0

3.2.4 Current Study

Four samples were created for each current setting of 0.6, 0.8, 1.0, 1.2, and 1.4 amps. The Kressin method was used for all samples using planchets that were washed and electropolished before the electrodeposition process. At the end of each electroplating run, after the KOH was added, a 100 μL 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. The planchets were then counted as usual by alpha spectroscopy. 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 3.3 and plotted in Figures 3.5 and 3.6. The data for each individual sample can be seen in Tables O – S in Appendix IV.

Table 3.3. Average energy resolution and yield results as a function of electrodeposition current.

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

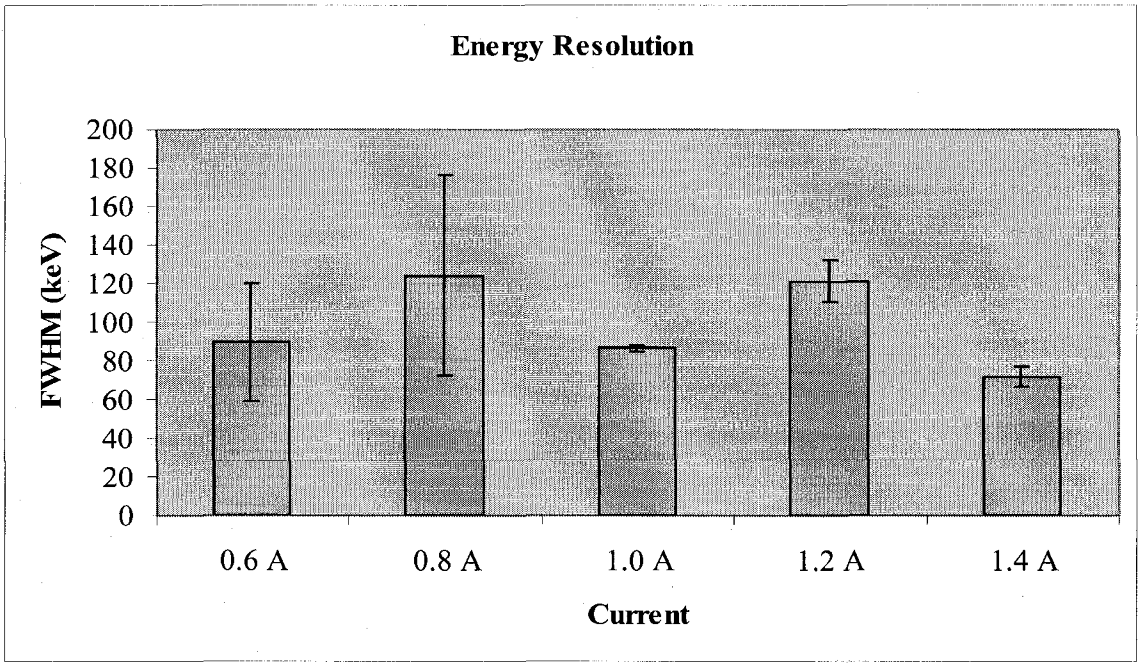

Figure 3.5. Average energy resolution as a function of electrodeposition current.

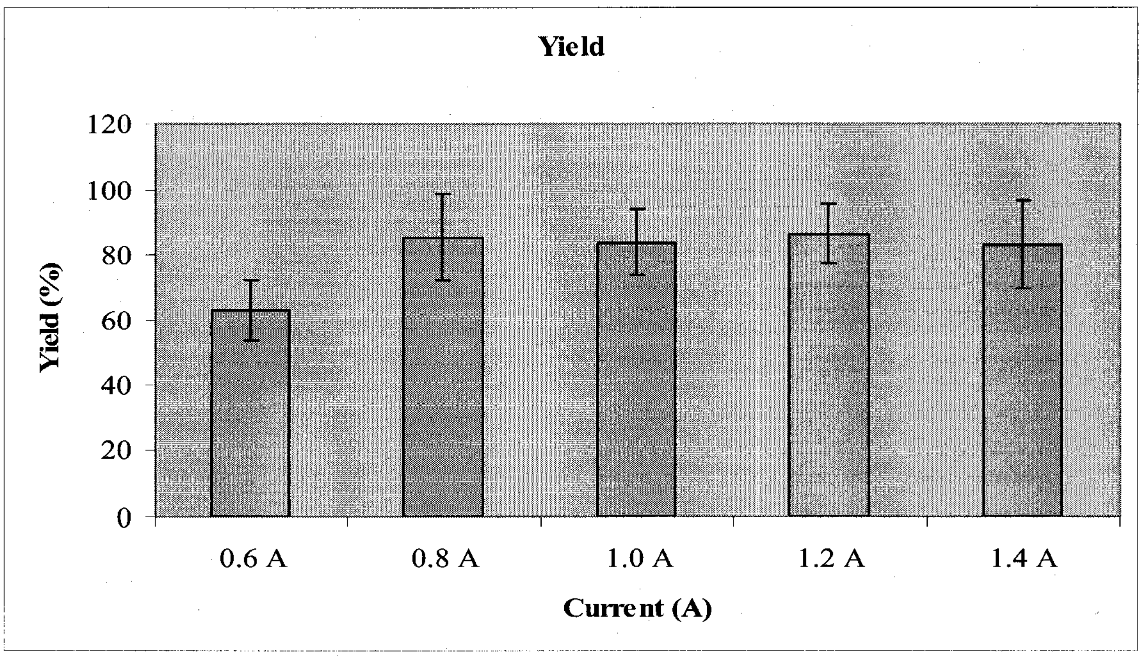

Figure 3.6. Average yield as a function of electrodeposition current.

3.3 Microprecipitation

3.3.1 General Method

For the general method, four samples were created following the general cerium fluoride procedure, allowing 30 minutes for precipitation. The average energy resolution of the four samples was 36 ± 7 keV. The average yield of the four samples was calculated to be 102 ± 8 %.

3.3.2 Time Study

In this part of the study, four samples were created for each different precipitation time of 10, 20, 30, 40, 50 and 60 minutes. The samples were then all processed by vacuum filtration in the same manner as the general method. Results are shown in Table 3.4 and Figures 3.7 – 3.8. All data points are shown in Tables T – Y in Appendix IV.

Table 3.4. Average energy resolution and yield as a function of precipitation time.

time (min)	FWHM (keV)	yield (%)
10	55 ± 18	109 ± 7
20	55 ± 20	133 ± 10
30	36 ± 7	125 ± 10
40	51 ± 13	116 ± 15
50	58 ± 33	118 ± 7
60	57 ± 22	116 ± 6

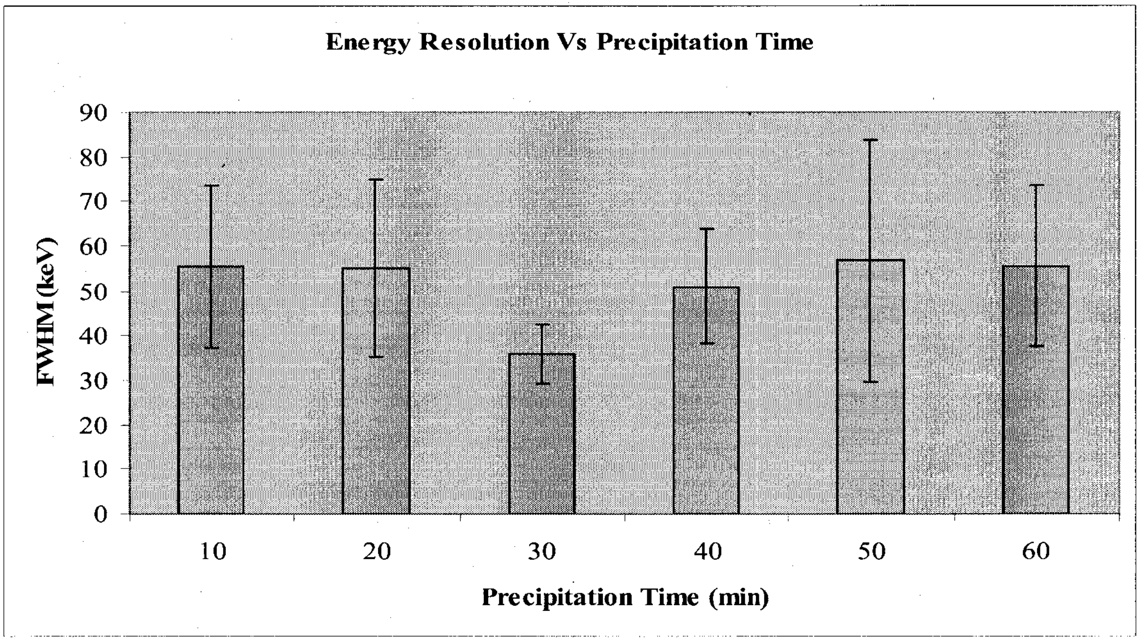

Figure 3.7. Average energy resolution as a function of precipitation time.

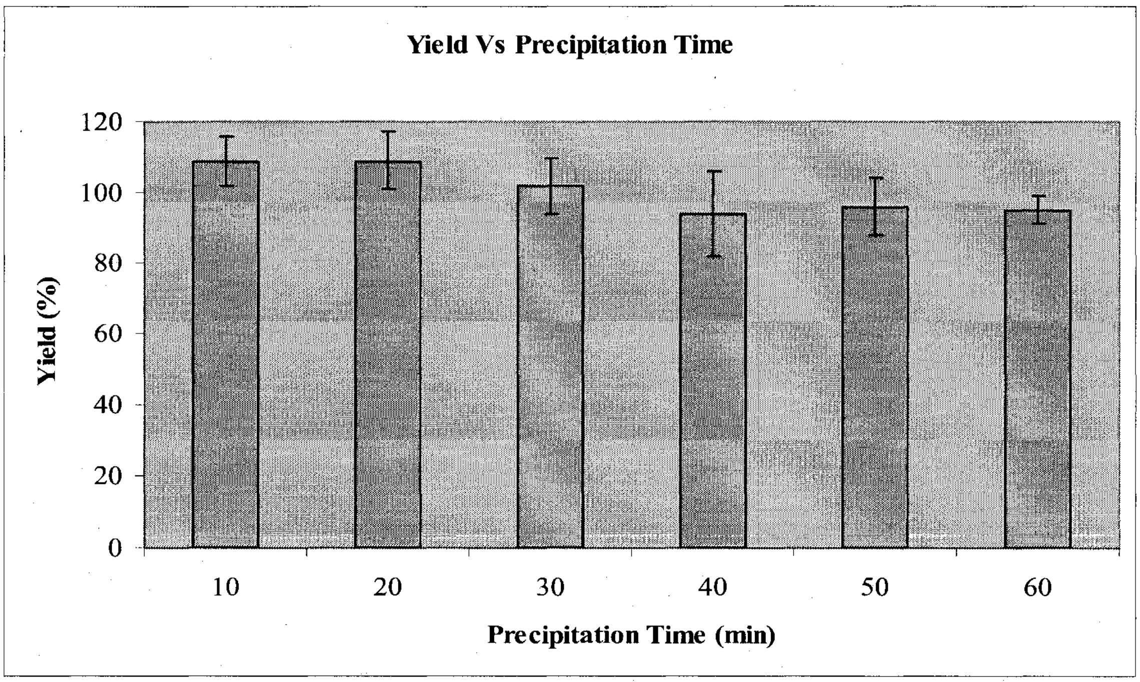

Figure 3.8. Average yield as a function of precipitation time.

3.3.3 Amount of Carrier and Hydrofluoric Acid

The amounts of cerium carrier and hydrofluoric acid used for precipitation were varied in this part of the study, keeping the ratio between the two the same, i.e. if the amount of cerium carrier was reduced from 100 μL to 50 μL, the volume of hydrofluoric acid was reduced from 1 mL to 0.5 mL. Four data sets were created for this part of the study, with volumes of cerium carrier solution of 50 μL, 25 μL, 10 μL, and 5 μL and corresponding hydrofluoric acid volumes of 0.5 mL, 0.25 mL, 0.1 mL and 0.05 mL respectively. Results are shown in Table 3.5 and in Figures 3.9 – 3.10. All data points can be seen in Tables Z – CC in Appendix IV.

Table 3.5. Average energy resolution and yield as a function of cerium carrier amount.

Data Set	FWHM (keV)	Yield (%)
0.00775 mg Ce	86 ± 17	101 ± 3
0.003875 mg Ce	56 ± 5	113 ± 2
0.00155 mg Ce	60 ± 18	101 ± 2
0.000775 mg Ce	41 ± 10	105 ± 5

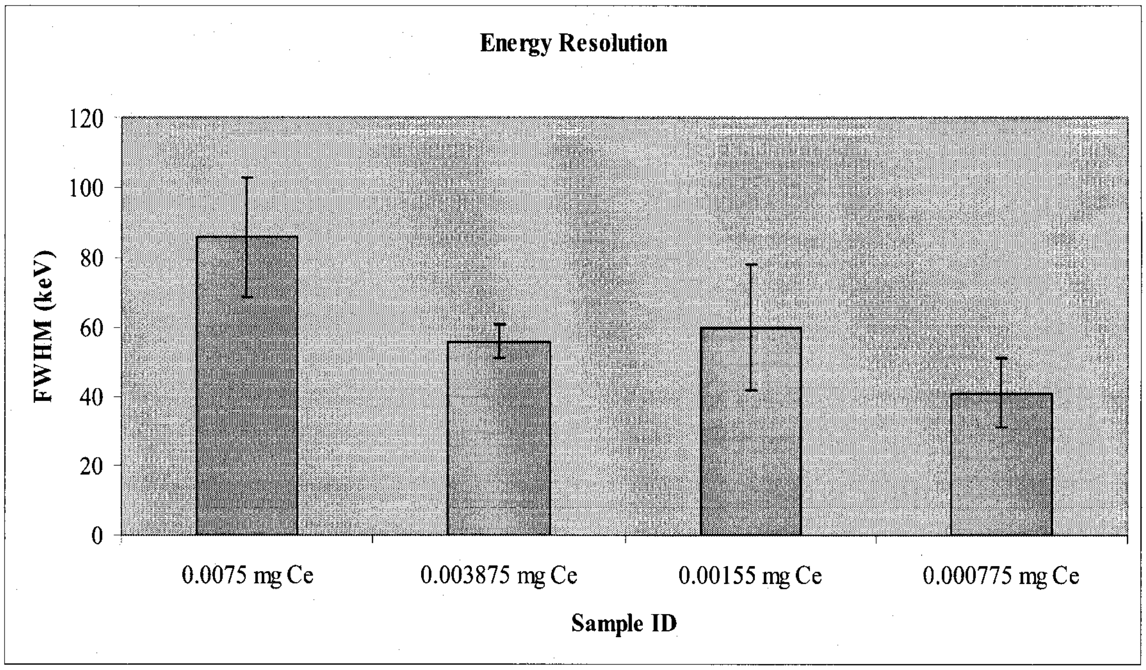

Figure 3.9. Average energy resolution as a function of the amount of cerium carrier.

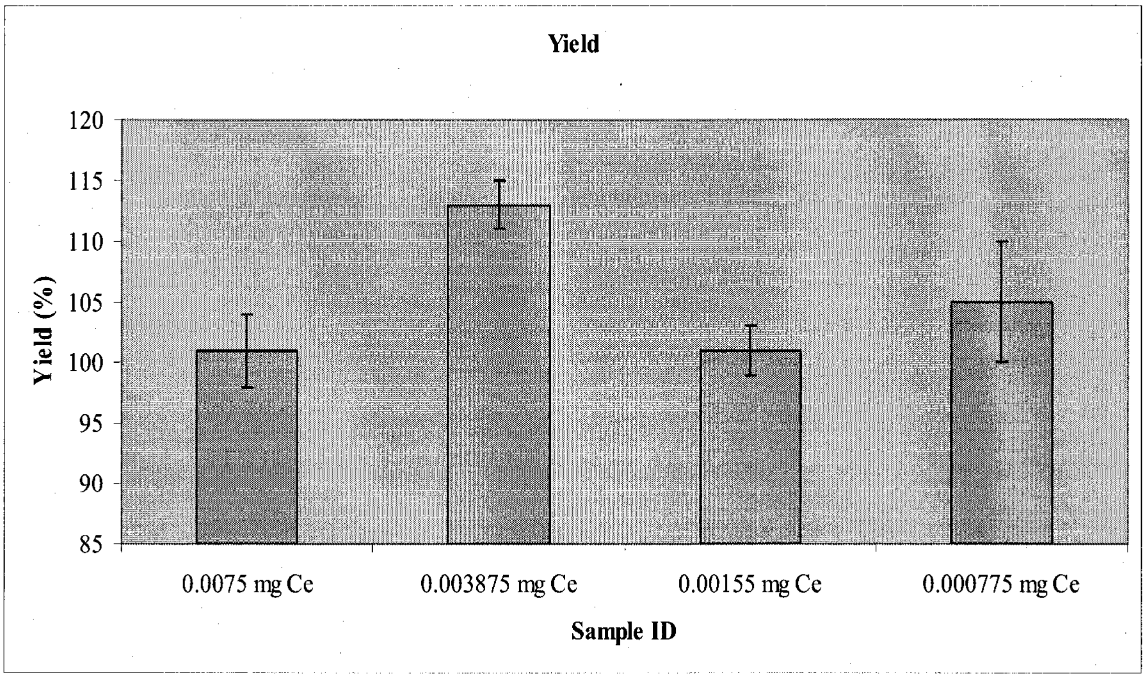

Figure 3.10. Average yield as a function of the amount of cerium carrier.

3.3.4 Fraction of Carrier

The fraction of cerium carrier in total solution was varied in this part of the experiment. While the ^{241}Am and HF volumes were held constant, the volumes of cerium (III) nitrate used were 100 μL, 50 μL, and 10 μL. Results are displayed in Table 3.6 and in Figures 3.11 – 3.12. All data for this study can be seen in Tables DD – FF in Appendix IV.

Table 3.6. Average energy resolution and yield for each data set of the fraction of carrier study.

mol Ce^{3+}	mol F^-	FWHM (keV)	Yield (%)
1.98E-04	1.56E+01	27 ± 2	98 ± 6
1.02E-04	1.56E+01	41 ± 6	105 ± 4
2.09E-05	1.56E+01	36 ± 7	102 ± 14

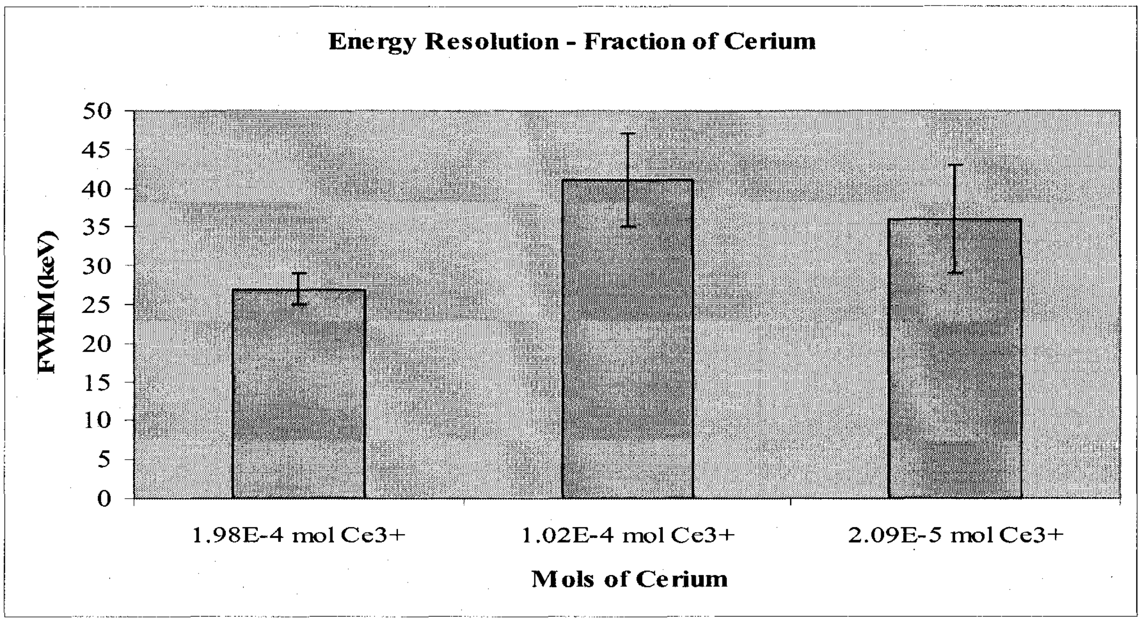

Figure 3.11. Average energy resolution for microprecipitation as a function of the fraction of cerium carrier in solution.

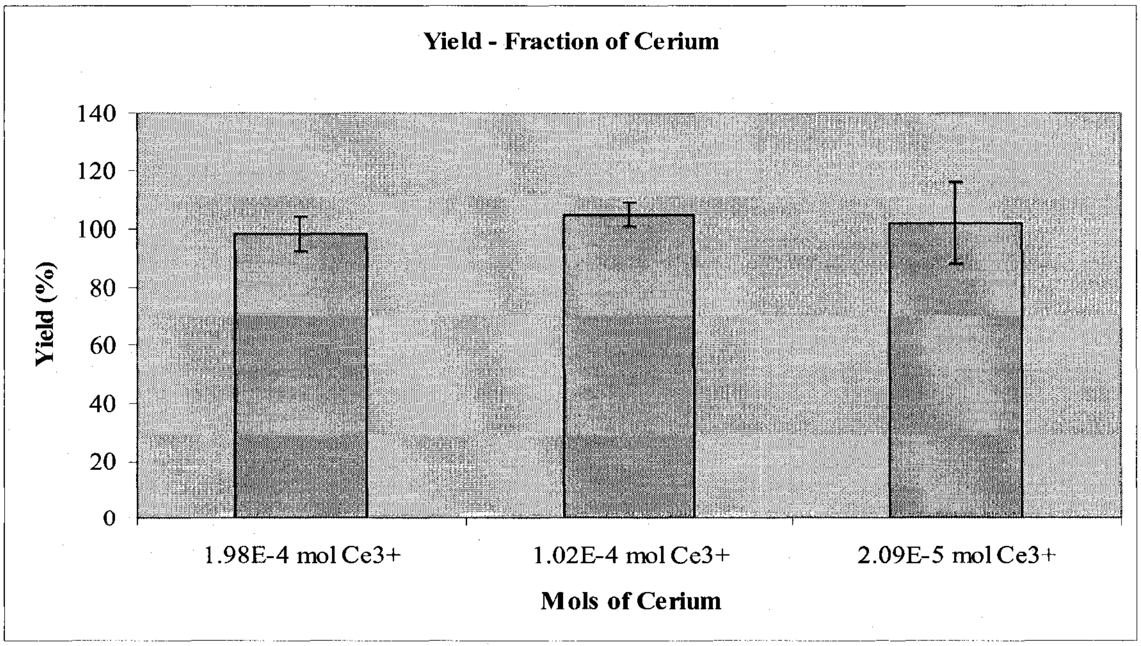

Figure 3.12. Average yield for microprecipitation as a function of the fraction of cerium carrier in solution.

3.3.5 Fraction of Hydrofluoric Acid

The fraction of hydrofluoric acid in total solution was also varied. While the ^{241}Am and cerium (III) nitrate volumes were held constant, the volumes of hydrofluoric acid used were 1.0 mL, 0.50 mL, and 0.10 mL. Results are shown in Table 3.7 and in Figures 3.13 – 3.14. All data for this study can be seen in Tables GG – II in Appendix IV.

Table 3.7. Average energy resolution and yield as a function of the fraction of HF in solution.

mol F^-	mol Ce^{3+}	FWHM (keV)	Yield (%)
1.56E+01	1.98E-04	57 ± 5	90 ± 3
1.08E+01	1.98E-04	50 ± 14	104 ± 8
3.11E+00	1.98E-04	36 ± 7	102 ± 14

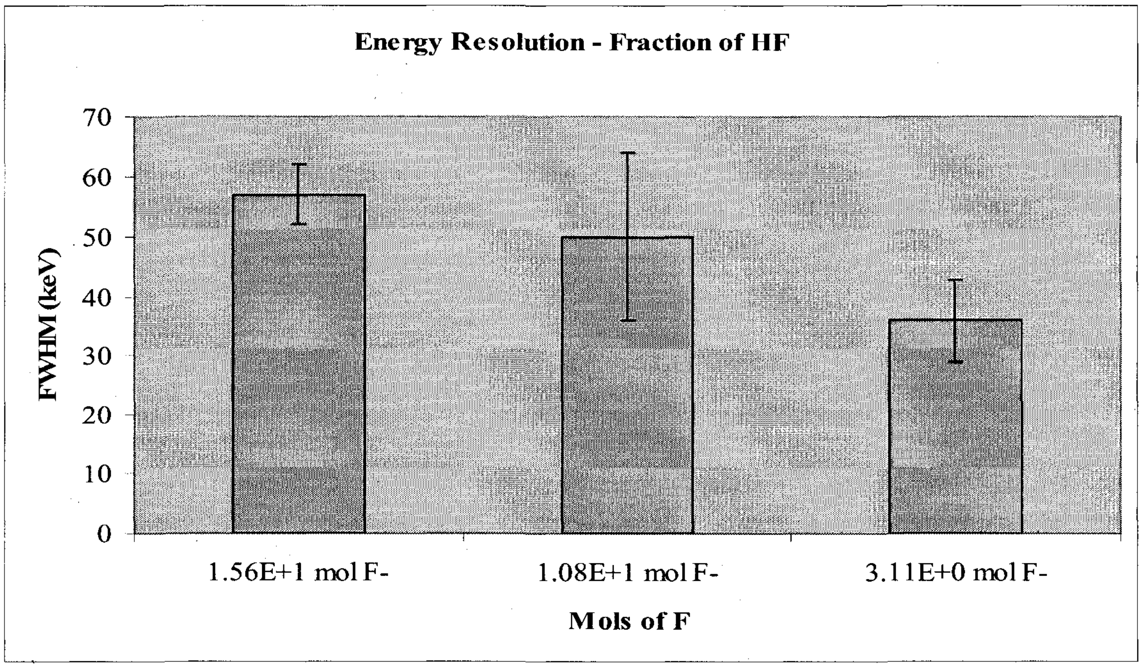

Figure 3.13. Average energy resolution for microprecipitation as a function of the fraction of HF in solution.

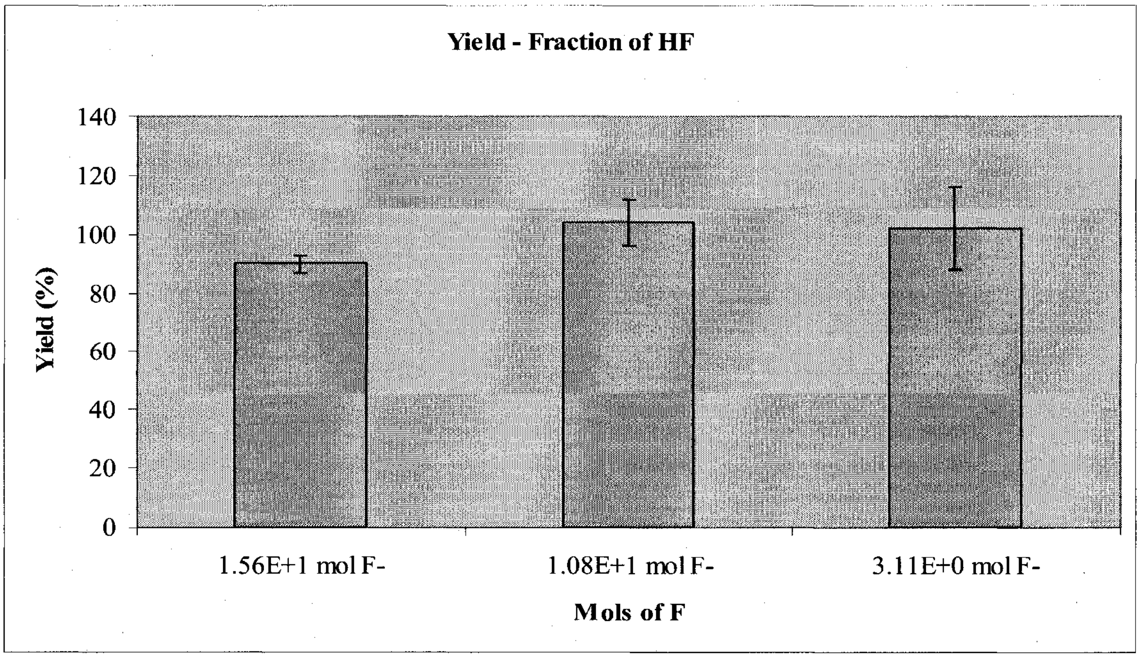

Figure 3.14. Average yield for microprecipitation as a function of the fraction of HF in solution.

3.4 Evaporation

3.4.1 General Method

The general method for the evaporation part of the study called for 350 μL of the ^{241}Am standard to be pipetted onto a planchet on a hot plate at about 120 °C. Four samples were created using this method with an average energy resolution of 74 ± 13 keV and an average yield of 83 ± 9 %.

3.4.2 Time and Temperature Study

Six samples were created at each heat setting on the hot plate from 3.0 to 4.4 in increments of 0.2. Results are listed in Table 3.8 and plotted in Figures 3.15 – 3.17. All data for this study can be seen in Tables JJ – QQ in Appendix IV.

Table 3.8. Average energy resolution and yield results as a function of time and temperature.

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

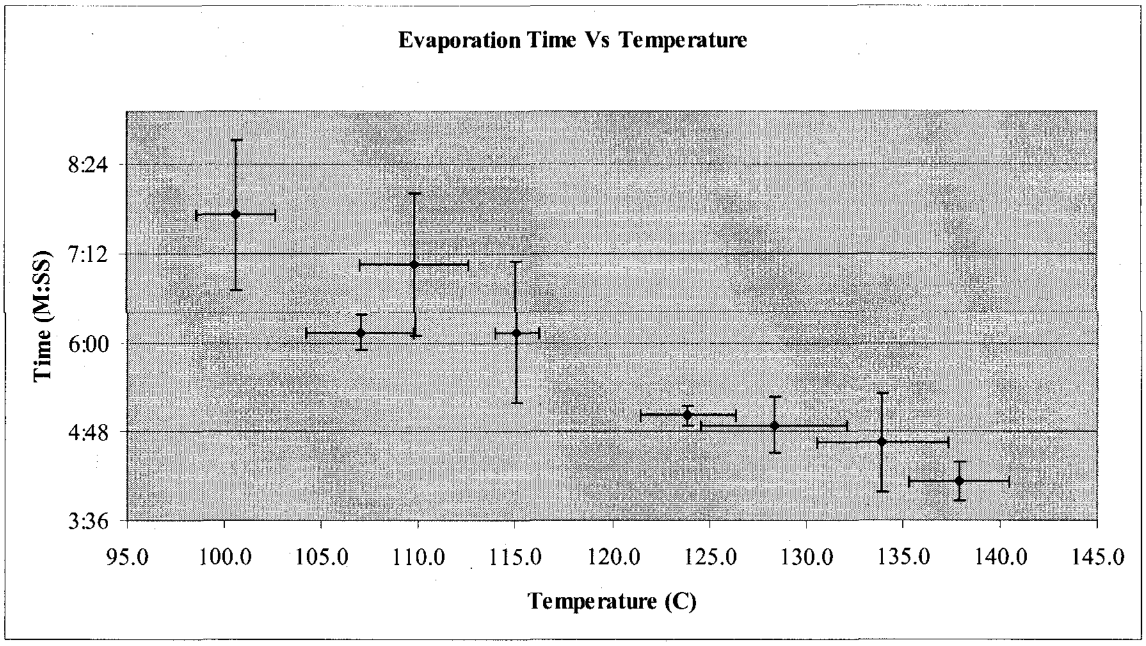

Figure 3.15. Average time for complete sample evaporation as a function of temperature.

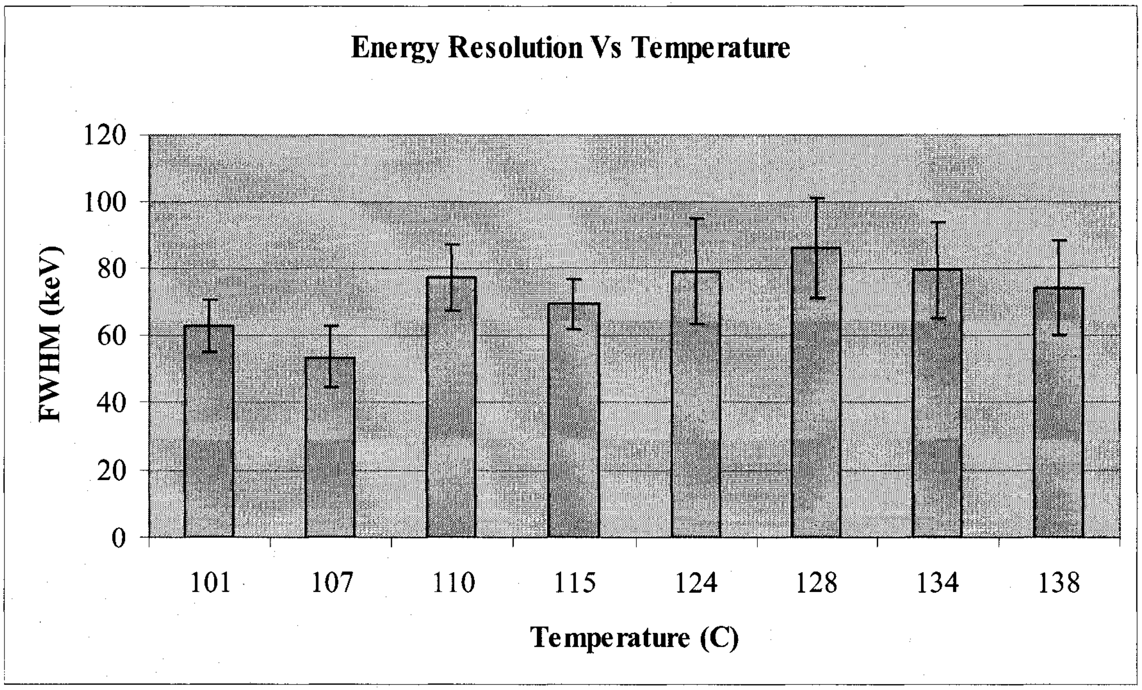

Figure 3.16. Average energy resolution as a function of temperature.

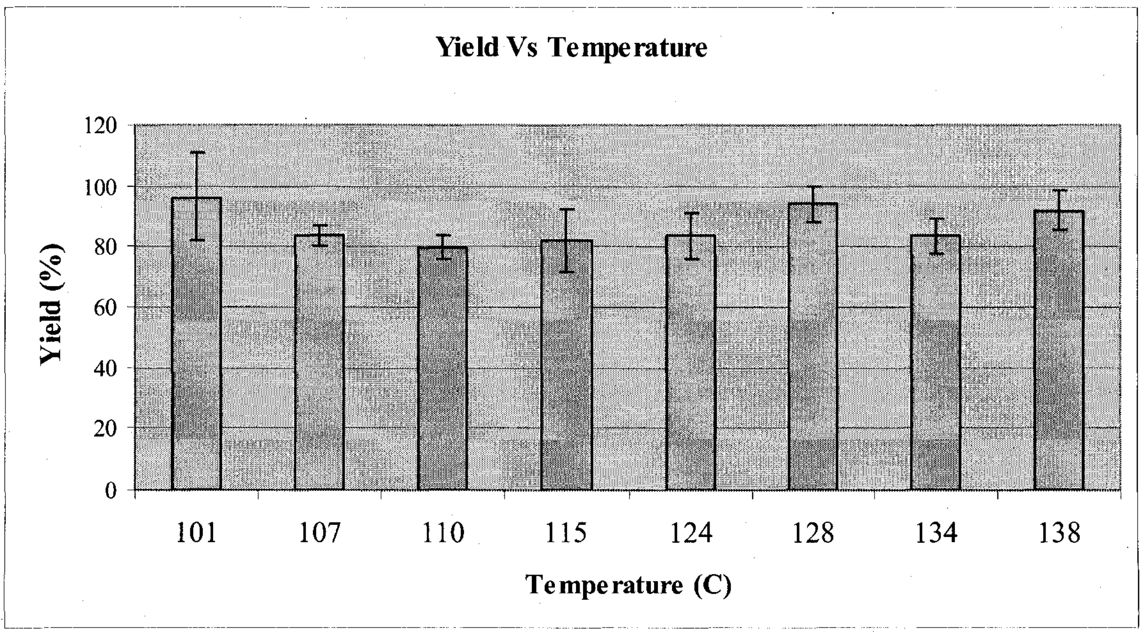

Figure 3.17. Average yield as a function of temperature.

3.4.3 Method of Addition

There are two methods of adding the sample to the planchet for evaporation; full volume addition and drop by drop addition. Since the quickest time has been determined in the time and temperature part of the study, all samples for the method of addition study were created at the 4.4 heat setting 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 %.

3.5 Discussion

3.5.1 Electrodeposition

The general method of the electrodeposition study was performed to become familiar with the process of electrodeposition, as well as to have baseline data to compare the rest of the samples to. Samples created using the general Kressin method had a very high average yield and an acceptable average energy resolution.

The point of the planchet pretreatment study was to determine if the washing and electropolishing processes are parts of the procedure that 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 investigation using a scanning electron microscope are necessary to confirm this. When the surface of a counting media is rougher, this leads to the sample not being uniformly deposited. Non-uniform deposition can result in losses in energy resolution due to scattering and attenuation. Samples with the best average energy resolution were samples that had been washed but not electropolished.

High yields produced on polished planchets are most likely due to the fact that the roughness caused by the electropolishing procedure creates more surface area for the sample to attach to. The highest average yield was achieved with planchets that were both electropolished and washed so that was the procedure that was continued to be used for the remainder of the electrodeposition study.

The time study for electrodeposition was performed 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 shows signs of an increase. This could be due to a number of factors such as the aliquot not being taken from the same area or inhomogeneous mixing of the sample. Longer deposition times need to be investigated 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. From the results shown for the rest of the electrodeposition experiments, the energy resolutions of the electrodeposited samples created in the time study are what should be expected.

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 a cause of not enough current being present to support the electrodeposition process. 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 the increased electrical flow through the cell which interferes with the deposition of the ^{241}Am onto the planchet.

3.5.2 Microprecipitation

As with the Kressin method for electrodeposition, the cerium fluoride method for microprecipitation was performed to become familiar with the process of microprecipitation as well as to have baseline data to compare the rest of the samples to. Samples created using the general cerium fluoride method had acceptable energy resolution results and exceptional yield results. The standard deviation of the samples was also much less than that of samples created by electrodeposition, proving microprecipitation to be more reliable.

The time study for microprecipitation was performed in order to determine the optimal precipitation time for the procedure. The lowest energy resolution was seen in the data set of samples that had a precipitation time of 30 minutes. Samples created with less time for the precipitate to form may have higher energy resolutions due to inhomogeneous sample deposition. The precipitate would form smaller clumps so there would be less of a chance of the whole filter area being covered with activity. If more precipitation time is allowed, the precipitate could form larger clumps which would lead to an increase in energy resolution because the thickness of the sample would lead to more attenuation.

Data for the yield of samples created with different precipitation times shows the best energy resolution for samples that were allowed to precipitate for 30 minutes. All of the yields are close to 100 % so precipitation time should not be of concern when trying to obtain the best results for yield.

In the part of the microprecipitation experiment where the amount of cerium carrier and hydrofluoric acid were varied, there is no real effect on the yield of the samples. All of the yields are around 100 % so no recommendation can be made on the optimal amount of cerium carrier and hydrofluoric acid to use to obtain better microprecipitation yields. The energy resolution, however, does change with the variations of solutions used. There is a general downward trend where the energy resolution improves with the decrease in cerium carrier and hydrofluoric acid used. Since the amounts were only varied in the range that would still allow the AmF_3 to be carried through the co-precipitation process with the CeF_3, the improved energy resolution at lower carrier and acid volumes is caused by a thinner sample with less interference of carrier.

The fraction of cerium carrier in total solution was varied to determine the effects on energy resolution and yield. Energy resolution was the lowest for samples with 0.01 mL of cerium carrier in total solution. This is due to the fact that there is not as much excess cerium to attenuate the sample. Yield results are similar for all fractions of cerium carrier in solution showing that the cerium carrier was kept above the level needed for the AmF_3 to co-precipitate.

The fraction of hydrofluoric acid in total solution was varied to determine effects on energy resolution and yield. A volume of 1.0 mL of hydrofluoric acid in total solution showed the best energy resolution and yield results. The worst energy resolution and yield results were seen in the samples with 0.1 mL of hydrofluoric acid, the least amount used in the study. This trend is most likely due to the fact that when the amount of hydrofluoric acid is reduced, there are less fluorine atoms available for the cerium and americium to complex with, showing losses in yield.

3.5.3 Evaporation

The general method for evaporation was performed in order to have data to compare for the rest of the evaporation studies. Average energy resolution was calculated to be approximately 74 keV, which is higher than the results for both the electrodeposition and microprecipitation. This is due to the fact that there is nothing done prior to evaporation to eliminate any matter on the planchets that might interfere with the sample spectrum. 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.

CHAPTER 4

ERROR ANALYSIS

4.1 Data Analysis

4.1.1 Standard Deviation Calculations

The standard deviation for all data is calculated using Microsoft Excel. The unbiased or "n-1" method is used for these calculations. The equation for standard deviation is shown in Equation 4.1 below:

$$\sigma = \sqrt{\frac{\Sigma(x-\bar{x})^2}{(n-1)}}$$

Equation 4.1

In this equation, x represents the sample, $\bar{x}$ is the sample mean and n is the number of samples. A standard deviation is calculated for the energy resolution and yield of each data set created in this project.

4.1.2 Removal of Outlying Data Points

In some cases during the course of this project, certain data points could be considered as outliers. An outlier is considered to be a data point that exists far from the mean. These points lead the average and standard deviation of the data set to be so far off, the results of the entire project could be changed. In order to determine if these outliers can be eliminated, mathematical analysis must be performed.

Chauvenet's criterion is the established condition for discarding data in such circumstances, which states that a data point should be discarded if less than half an event is expected to be farther from the mean than the suspect point (Bevington 2003). Since the elimination of an outlier has more of an effect on the standard deviation than the mean, care should be taken to make sure deleting a point won't lead to deletions of other points and so on.

4.2 Electrodeposition Experiments

4.2.1 Error during the Sample Preparation Process

There are several steps in the electrodeposition process that can introduce an error into the measurement. The two main contributions to the error are due to the experimenter and errors due to the equipment used. Potential sources of error will be discussed by following the method used for electrodeposition in chronological order.

First, error can be introduced by incorrect or inaccurate pipetting. Two variable volume VWR pipettors are used for the sample preparation process for electrodeposition. The 1000 – 5000 μL pipettor has an accuracy of ± 0.6 – 0.5 % while the 100 – 1000 μL pipettor has an accuracy of ± 0.9 – 0.6 %. Any error in the pipetting will lead to incorrect quantities of stock solution added in the sample preparation process. This inaccuracy will propagate all the way through to the end of the electrodeposition process. Another source of error is introduced by heating the beaker for an insufficient amount of time. This can result in some of the perchloric acid being left in the sample. If this occurs, some organics may still be left in the beaker. This effect will also carry throughout the whole process and lead to sample attenuation during counting by alpha spectroscopy and possible reduction in yield. An indication that all of the perchloric acid has been driven off is given if the sample in the beaker is white in color. Translucence of the sample indicates that there is still perchloric left in the beaker.

After addition of 4 mL of 15 % Na_2SO_4 to the sample, it must be left to sit for a sufficient amount of time in order to ensure that the electrolyte solution has mixed completely with the sample and is ready for electrodeposition. The beaker must be rinsed well to make sure the entire sample is transferred into the electrodeposition cell to avoid losses in yield.

4.2.2 Error during the Electrodeposition Process

During the electrodeposition process, care must be taken to maintain the proper settings required for an ideal sample to be created. The current must be maintained at 1.0 A for the general method and at a constant setting during the experiments in which the current was varied. As shown by the results, the current does have an effect on the yield and energy resolution. It therefore must remain consistent with the method. Any deviations from the required current could affect the quality of the electrodeposited sample.

Even though the current can be controlled by the experimenter, fluctuations within the cell itself cannot be controlled. The general accuracy with which the current meters can be read is approximately 0.05 A. Poor electrical contacts in the system can lead to variations in the current during the two hours required for the electrodeposition process. Sometimes when monitoring the current, it may jump. This is caused by bubble formation in the solution which makes the current vary throughout the solution and can cause uneven electrodeposition. Also occurring in the cell is the fact that during the electrodeposition process, part of the electrolyte solution will be used up. This causes the current in the cell to decrease which will in turn affect the electrodeposition process.

Planchets used for electrodeposition can have an effect on the energy resolution and yield. Stainless steel planchets with a 25 mm diameter are used in this project. While stainless steel planchets are most commonly used for electrodeposition, planchets made of nickel and platinum have also been used for electrodeposition. Any change in the material of the planchet can have an effect on the energy resolution and yield of the sample.

Preparation of the planchets prior to electrodeposition of the sample is also a factor in the quality of the sample. Planchets that are electropolished before electrodeposition may show a greater standard deviation in results. Scratches on the surface of planchets can occur during electropolishing. These effects can be seen qualitatively under a microscope, but cannot be quantified. Washed planchets should have less variation in results as long as the washing process was performed sufficiently for each planchet.

4.3 Microprecipitation Experiments

As with electrodeposition, pipetting errors can occur during the microprecipitation process. For the microprecipitation, a 100 – 1000 μL variable volume VWR pipettor was used to transfer the ^{241}Am from the vial with stock solution to the centrifuge tube. The accuracy of the VWR pipettor is ±0.9 - 0.6 %. Eppendorf pipettors were used for the addition of the hydrofluoric acid and the cerium carrier. The accuracy of the 100 μL Eppendorf pipettor is ± 0.8 % and the accuracy of the 1000 μL Eppendorf pipettor is ± 0.6 %.

Another source of error depends on how well the centrifuge tube and microprecipitation apparatus are rinsed at the end of the filtration procedure. If any of the sample is left in the centrifuge tube or on the funnel, yield losses will occur. Unfortunately, there is no way this error can be quantified. Everything the sample came in contact with should therefore be rinsed at least twice.

A third source of error could be caused by any dirt or contamination the filters had present on them before the microprecipitation process. The filters are stored in the packaging they came in, protected by separate papers between each filter. Tweezers are used to transfer the filters from the package to the filtration apparatus. If there is any contamination on the tweezers, it could be transferred to the filter. Care is taken to minimize any outside contamination on the filters.

Other sources of error occur due to equipment inaccuracies of balances for the carrier preparation as well as experimenter error in time measurement. The accuracy of the balance used to measure out 0.155 g of solid cerium (III) nitrate is ± 0.01 g. The accuracy of the100 mL volumetric flask used to measure the DI water used to dilute the cerium (III) nitrate is ± 0.08 mL. A wall clock was used to determine the length of precipitation time. Experimenter error in time measurement is estimated to be ± 5 – 10 seconds.

4.4 Evaporation Experiments

Pipetting is again a possible source of error for the evaporation process. A 100 – 1000 μL variable volume VWR pipettor is used for this method which has an accuracy of ±0.9 - 0.6 %. The only washing done to the planchets prior to evaporation is done with water, therefore another source of error could be caused by any kind of organic material that may be on the planchet from either the manufacturer, or from handling them in the lab.

Any amount of organic material on the planchet has the ability to interfere with the alpha spectrum, causing errors in yield and energy resolution.

Time measurements are taken using a four channel digital timer from VWR. The accuracy of the timer is 0.01 %. Experimenter error also exists in time measurements since it is sometimes hard to visually determine if the sample is fully evaporated. Temperature measurements are taken using an Extech infrared thermometer with accuracy in the range of 18 °C to 28 °C of ± 2 % of the reading or ± 2 °C, whichever is greater. No accuracy was given outside of the temperature range listed above. Lastly, it should be noted that the temperature of the hot plate varies greatly, up to 30 °C, depending on the placement. This should have no effect on results since the temperature is measured directly at the planchet location, but should be noted anyway.

4.5 Alpha Spectroscopy Measurements

4.5.1 Statistical Error within the Detector

In the present day, silicon detectors for alpha spectroscopy systems are available that can produce energy resolution results greater than or equal to a full width at half of the maximum of 10 keV. Because of the properties of the silicon diode detectors, it is expected that charge carrier formation statistics will limit the achievable energy resolution (Knoll 2000). Using the Fano Factor, F, the ionization energy ε and the energy of the alpha particle E, the limiting FWHM can be calculated using the following equation:

$$\mathrm{FWHM}_{\mathrm{lim}} = 2.35\sqrt{FE\varepsilon}$$

Equation 4.2

The F value for silicon is 0.11, ε is equal to 3.62 eV and E of ^{241}Am is equal to 5.485 MeV. When these values are entered into the above equation, a value of 3.47 keV is obtained, which would be the best resolution that could be obtained by a silicon detector without any other interferences. Alpha particle energy resolution has been demonstrated at about 8 keV under very controlled laboratory conditions, but in general, a FWHM of less than 10 keV should not be expected in a laboratory setting (Knoll 2000).

4.5.2 Counting Error

The accuracy with which the yield of a sample can be determined depends strongly on counting statistics. The standard deviation of the count rate is determined by the following equation:

$$\sigma = \sqrt{N}$$

Equation 4.3

In this equation, σ is the standard deviation and N is equal to the number of counts. For a spectrum with 10,000 counts under the peak, the standard deviation will be 1 %. All of the samples created in this study were counted for a sufficient time to include at least 10,000 counts under the peak in order to achieve a standard deviation for the counting of 1 % or less

4.6 Liquid Scintillation Measurements

There are a several sources of error to be considered in liquid scintillation counting as well. Quenching occurs when there are any chemical or optical impurities in the sample. This can lead to decreases in counting efficiency. In order to minimize quenching, the sample should be as clear, colorless and homogeneous as possible. For the liquid scintillation counting performed in this project, a 100 % counting efficiency is assumed for samples that have an SIS quench level of greater than 500.

Another source of error in liquid scintillation counting is electronic noise created in the sample by static that could be present. If this occurs, pulses will be generated that could add to the spectrum. This can also occur if any light enters into the system. A solution to light interference is to allow the samples to dark adapt before counting. This was not done with the liquid scintillation samples created in this project due to the high count rate involved because it would have a minimal effect on the outcome of the data.

As with any other method of counting radioactive samples, the amount of time the sample is counted for is directly related to the counting error. In the liquid scintillation counting performed in this project, the protocol was set to count each sample for 60 minutes or until 2σ was reached. The only samples to reach 2σ before 60 minutes was up were the standard solutions. A standard solution of 100 μL of 100 Bq mL^{-1} ^{241}Am usually only needed to count for 2 – 3 minutes for a count rate of approximately 4000 counts per minute to be obtained.

CHAPTER 5

RECOMMENDATIONS FOR SAMPLE PREPARATION PROCEDURES

Recommendations to determine which method should be used are based upon the quality of the results that need to be obtained. When a sample containing radioactivity needs to be analyzed, it is more than likely it will need to be done either quickly or quantitatively. Depending on which outcome is desired, a method can be assigned to achieve that goal.

For samples that are being analyzed to identify which radionuclides are present, a procedure that produces the best energy resolution is required. The Kressin method for electrodeposition, when performed without varying any procedures produces an average energy resolution of 45 keV. Energy resolutions in this experiment were seen as low as 25 keV FWHM. Microprecipitation procedures show slightly higher energy resolutions with an average of around 55 keV. The general method, however, produced energy resolution results of approximately 35 keV. More samples would need to be created in order to have more conclusive results as to which of the two methods should be used to obtain the best energy resolution. If, however, time is of major concern as well as energy resolution, microprecipitation produces acceptable results in one quarter of the amount of time per sample as does electrodeposition.

For quantification of a radionuclide, a procedure that results in the highest yield is recommended. In this case, microprecipitation is the recommended procedure. Although electrodeposition can sometimes produce samples with yields averaging 90 %, microprecipitation samples come much closer to 100 %. Another factor making microprecipitation the recommended method for sample quantification is the fact that there are fewer chances for interferences to be introduced into the sample. The results of electrodeposition and evaporation samples are often much more varied than those of microprecipitation because of uncontrolled interferences. As mentioned above, the time to create a sample using the microprecipitation method is much shorter than electrodeposition. All of these reasons make microprecipitation the recommended method for producing high yield samples for alpha spectroscopy.

For fast analysis and samples where the yield and energy resolution are not a leading concern, evaporation is the recommended procedure. Evaporation is a very quick procedure that produces acceptable yield results, but samples usually have a poor energy resolution. Samples created by evaporation should not be used to identify radionuclides present in the sample without prior chemical separation due to the fact that many actinides have energies in close range with other actinides. Sometimes as little at 30 - 40 keV exists between two radionuclides and a sample created by evaporation would not produce good enough energy resolution results to discern the two peaks from each other. Sample yields of evaporated samples, on the other hand, rival those of electrodeposited samples with yields seen from 80 to 96 %. In case of a scenario where massive amounts of samples need to be quantitatively analyzed, evaporation could be used. Although sample counting times will increase, the preparation time of the samples would be much shorter than even microprecipitation.

CHAPTER 6

CONCLUSIONS

Three methods of sample preparation for alpha spectroscopy were examined in this research project. Each method was scrutinized to optimize the performance while keeping the time of sample preparation in mind. The process of electrodeposition was examined using the Kressin method and varying such parameters as time, applied current and planchet preparation. For microprecipitation, the cerium fluoride method was used and 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.

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 on the amount of solution deposited showed the fraction of activity in solution to decrease steadily over time until about 100 minutes of electrodeposition time. This should be continued with longer electrodeposition times in order to determine what the optimal amount of deposition time is. When the current was varied, results led to a 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.

The microprecipitation method was studied with varying parameters such as precipitation time, amount of cerium carrier and hydrofluoric acid, fraction of cerium carrier and fraction of hydrofluoric acid in total solution. 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 36 ± 7 keV and a yield of 102 ± 8 % was seen. When the amount of precipitation time was varied, the best energy resolution was seen for samples precipitated for 30 minutes. There was no conclusive relation of the yield to precipitation time. The best results for energy resolution when changing the amounts of cerium carrier and hydrofluoric acid in the solution were seen for 1.98E-4 mol of Ce^{3+}.

Evaporation was the method that involved the least amount of chemistry 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.

For identification of radionuclides using alpha spectroscopy, electrodeposition is the best method because of low energy resolution of samples created. When time is an issue, microprecipitation can be substituted for electrodeposition. If quantification of a sample is the main concern, microprecipitation produces the highest yields and therefore would be considered the best method. Samples that need to be analyzed quickly with less of a concern for energy resolution and yield should be prepared using evaporation.

Future work should be conducted for the microprecipitation procedure. This research showed that reducing the amount of hydrofluoric acid can have a positive effect on the energy resolution and yield. The amount of hydrofluoric acid used for this procedure should be examined more thoroughly in order to determine the optimum amount of hydrofluoric acid to use. The same should be done for the amount of cerium carrier used.

APPENDIX I

CHEMICALS

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

APPENDIX II

MATERIALS

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

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

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

Nitric Acid, 4 mol L^{-1}, Fisher Scientific

Acetone, Fisher Scientific

Potassium Hydroxide, 88.2%, J. T. Baker

Phosphoric Acid, 85-87 %, J. T. Baker

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

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

Hydrochloric Acid, 37-38 %, J. T. Baker

Sodium Sulfate, 99.0 %, J. T. Baker

Deionized water

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

Infrared thermometer, Extech

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

Canberra Alpha Analyst Spectrometer, 450 mm^2 active area PIPS detectors

APPENDIX III

CHEMICAL NAMES AND FORMULAS

HNO_3	Nitric Acid
H_3PO_4	Phosphoric Acid
H_2SO_4	Sulfuric Acid
$NaHSO_4$	Sodium Hydrogen Sulfate
$HClO_4$	Perchloric Acid
HCl	Hydrochloric Acid
Na_2SO_4	Sodium Sulfate
KOH	Potassium Hydroxide
NH_4OH	Ammonium Hydroxide
DI water	Dionized water
$Ce(NO_3)_3\ 6H_2O$	Cerium (III) Nitrate Hexahydrate
HF	Hydrofluoric Acid

APPENDIX IV

SUPPLEMENTAL TABLES

Table A. Calibration source data.

Source	Po-210	Source	Am-241
Energy	5.3044 MeV	Energy	5.485 MeV
Size	12.7 mm	Size	19.6 mm
Area	127 mm^2	Area	302 mm^2
Activity	4422 Bq	Activity	268 Bq
Origin	1-Aug-06	Origin	27-Apr-89
Time	392 days	Time	18.35 years
$t_{1/2}$	138.38 days	$t_{1/2}$	432.7 years
Lambda	0.0050079 days^{-1}	Lambda	0.00160157 years^{-1}
Activity	620.938 Bq	Activity	260.238 Bq

Table B. Alpha spectrometer calibration data for detectors 1A, 1B, 2A, 2B, 3A, 3B, 4A, and 4B.

1A		**1B**	
Energy	**Channel**	**Energy**	**Channel**
4.197 MeV	410	4.197 MeV	412
4.788 MeV	497	4.788 MeV	496
5.156 MeV	551	5.156 MeV	551
5.485 MeV	599	5.485 MeV	600
2A		**2B**	
Energy	**Channel**	**Energy**	**Channel**
4.197 MeV	413	4.197 MeV	413
4.788 MeV	496	4.788 MeV	496
5.156 MeV	551	5.156 MeV	552
5.485 MeV	600	5.485 MeV	601
3A		**3B**	
Energy	**Channel**	**Energy**	**Channel**
4.197 MeV	409	4.197 MeV	410
4.788 MeV	496	4.788 MeV	495
5.156 MeV	550	5.156 MeV	551
5.485 MeV	600	5.485 MeV	600
4A		**4B**	
Energy	**Channel**	**Energy**	**Channel**
4.197 MeV	411	4.197 MeV	410
4.788 MeV	496	4.788 MeV	494
5.156 MeV	552	5.156 MeV	550
5.485 MeV	601	5.485 MeV	600

Table C. All energy resolution and yield data for washed polished electrodeposition.

sample	**detector**	**FWHM (keV)**	**yield (%)**
2	1B	64.360	104.74
3	2A	68.829	90.05
4	2B	35.471	93.51
5	1A	69.847	80.01
6	1B	87.896	120.22
8	2B	36.500	99.23

Table D. All energy resolution and yield data for washed unpolished electrodeposition.

sample	detector	FWHM (keV)	yield (%)
1	1A	30.258	13.79
2	1B	29.940	6.97
4	2B	63.169	97.16
5	2A	27.547	82.10
6	2B	39.072	75.71
7	1B	29.317	85.30
8	1B	36.274	89.67

Table E. All energy resolution and yield data for unwashed polished electrodeposition.

sample	detector	FWHM (keV)	yield (%)
1	1A	55.156	49.45
2	1B	57.969	31.21
3	2A	46.628	83.34
4	2B	56.228	75.86
5	2A	64.307	57.28
6	1B	76.357	79.84
8	2B	55.854	40.54

Table F. All energy resolution and yield data for unwashed unpolished electrodeposition.

sample	detector	FWHM (keV)	yield (%)
1	1A	70.851	89.16
2	1B	58.077	105.77
3	2A	35.670	88.31
4	2B	55.665	70.65
6	1B	33.334	40.82
7	2A	28.921	91.51
8	2B	22.725	94.12

Table G. All liquid scintillation data for 50 μL sample 1.

CPM	Bq	Total Bq Removed	Fraction Bq Remaining
33	76.45	0.55	1.00
30	69.00	1.05	0.90
29	66.22	1.53	0.87
29	65.73	2.02	0.86
25	56.25	2.43	0.74
25	55.83	2.85	0.73
21	46.55	3.20	0.61
22	48.40	3.57	0.63
22	48.03	3.93	0.63
22	47.67	4.30	0.62
20	43.00	4.63	0.56
18	38.40	4.93	0.50
9	19.05	5.08	0.25

Table H. All liquid scintillation data for 50 μL sample 2.

CPM	Bq	Total Bq Removed	Fraction Bq Remaining
37	85.72	0.62	1.00
27	62.10	1.07	0.72
19	43.38	1.38	0.51
31	70.27	1.90	0.82
33	74.25	2.45	0.87
32	71.47	2.98	0.83
29	64.28	3.47	0.75
24	52.80	3.87	0.62
28	61.13	4.33	0.71
30	65.00	4.83	0.76
28	60.20	5.30	0.70
32	68.27	5.83	0.80
14	29.63	6.07	0.35

Table I. All liquid scintillation data for 50 μL sample 3.

CPM	Bq	Total Bq Removed	Fraction Bq Remaining
38	126.67	0.63	1.00
33	110.00	1.18	0.87
32	106.67	1.72	0.84
33	110.00	2.27	0.87
31	103.33	2.78	0.82
34	113.33	3.35	0.89
36	120.00	3.95	0.95
32	106.67	4.48	0.84
74	246.67	5.72	1.95
27	90.00	6.17	0.71
25	83.33	6.58	0.66
24	80.00	6.98	0.63
26	86.67	7.42	0.68
28	93.33	7.88	0.74

Table J. All liquid scintillation data for 50 μL sample 4.

CPM	Bq	Total Bq Removed	Fraction Bq Remaining
40	133.33	0.67	1.00
35	116.67	1.25	0.88
34	113.33	1.82	0.85
33	110.00	2.37	0.83
29	96.67	2.85	0.73
27	90.00	3.30	0.68
32	106.67	3.83	0.80
30	100.00	4.33	0.75
27	90.00	4.78	0.68
9	30.00	4.93	0.23
19	63.33	5.25	0.48
25	83.33	5.67	0.63
20	66.67	6.00	0.50
31	103.33	6.52	0.78

Table K. All liquid scintillation data for 100 μL sample 1.

CPM	Bq	Total Bq Removed	Fraction Bq Remaining
105.00	175.00	1.75	1.00
72.00	120.00	2.95	0.69
70.00	116.67	4.12	0.67
74.00	123.33	5.35	0.70
62.00	103.33	6.38	0.59
75.00	125.00	7.63	0.71
72.00	120.00	8.83	0.69
64.00	106.67	9.90	0.61
65.00	108.33	10.98	0.62
62.00	103.33	12.02	0.59
58.00	96.67	12.98	0.55
41.00	68.33	13.67	0.39
49.00	81.67	14.48	0.47
54.00	90.00	15.38	0.51

Table L. All liquid scintillation data for 100 μL sample 2.

CPM	Bq	Total Bq Removed	Fraction Bq Remaining
101.00	168.33	1.68	1.00
63.00	105.00	2.73	0.62
64.00	106.67	3.80	0.63
62.00	103.33	4.83	0.61
58.00	96.67	5.80	0.57
61.00	101.67	6.82	0.60
62.00	103.33	7.85	0.61
56.00	93.33	8.78	0.55
53.00	88.33	9.67	0.52
50.00	83.33	10.50	0.50
40.00	66.67	11.17	0.40
33.00	55.00	11.72	0.33
38.00	63.33	12.35	0.38
46.00	76.67	13.12	0.46

Table M. All liquid scintillation data for 100 μL sample 3.

CPM	Bq	Total Bq Removed	Fraction Bq Remaining
73.00	121.67	1.22	1.00
65.00	108.33	2.30	0.89
67.00	111.67	3.42	0.92
65.00	108.33	4.50	0.89
61.00	101.67	5.52	0.84
58.00	96.67	6.48	0.79
55.00	91.67	7.40	0.75
53.00	88.33	8.28	0.73
49.00	81.67	9.10	0.67
51.00	85.00	9.95	0.70
38.00	63.33	10.58	0.52
34.00	56.67	11.15	0.47
40.00	66.67	11.82	0.55
40.00	66.67	12.48	0.55

Table N. All liquid scintillation data for 100 μL sample 4.

CPM	Bq	Total Bq Removed	Fraction Bq Remaining
75.00	125.00	1.25	1.00
65.00	108.33	2.33	0.87
65.00	108.33	3.42	0.87
64.00	106.67	4.48	0.85
65.00	108.33	5.57	0.87
64.00	106.67	6.63	0.85
58.00	96.67	7.60	0.77
56.00	93.33	8.53	0.75
52.00	86.67	9.40	0.69
42.00	70.00	10.10	0.56
40.00	66.67	10.77	0.53
44.00	73.33	11.50	0.59
40.00	66.67	12.17	0.53
40.00	66.67	12.83	0.53

Table O. All energy resolution and yield data for current setting at 0.6 A.

detector	sample	FWHM (keV)	yield (%)
1A	1	68.21	62.54
1B	2	76.57	54.34
2B	4	124.82	72.56

Table P. All energy resolution and yield data for current setting at 0.8 A.

detector	sample	FWHM (keV)	% yield
1B	2	133.35	70.99
2A	3	68.11	96.89
2B	4	170.83	88.91

Table Q. All energy resolution and yield data for current setting at 1.0 A.

detector	sample	FWHM (keV)	% yield
1A	1	85.16	92.01
1B	2	87.69	87.10
2A	3	85.93	72.91

Table R. All energy resolution and yield data for current setting at 1.2 A.

detector	sample	FWHM (keV)	% yield
1B	2	120.74	76.32
2A	3	132.16	89.57
2B	4	110.53	93.80

Table S. All energy resolution and yield data for current setting at 1.4 A.

detector	sample	FWHM (keV)	% yield
1A	1	68.08	73.67
2B	4	75.52	92.77

Table T. All energy resolution and yield data points for microprecipitation time of 10 minutes.

Sample	FWHM (keV)	Yield (%)
10.1	29.5	112.3
10.2	69.3	114.3
10.3	66.2	101.7
10.4	56.6	109.4

Table U. All energy resolution and yield data points for microprecipitation time of 20 minutes.

Sample	FWHM (keV)	Yield (%)
20.1	25.2	101.4
20.2	64.6	102.6
20.3	66.2	112.3
20.4	64.0	118.1

Table V. All energy resolution and yield data points for microprecipitation time of 30 minutes.

Sample	FWHM (keV)	Yield (%)
30-1	33.0	86.6
30-2	33.4	101.6
30-3	31.2	99.4
30-4	45.6	119.8

Table W. All energy resolution and yield data points for microprecipitation time of 40 minutes.

Sample	FWHM (keV)	Yield (%)
40-1	63.3	85.1
40-2	41.8	97.4
40-3	38.4	100.7
40-4	60.6	115.4

Table X. All energy resolution and yield data points for microprecipitation time of 50 minutes.

Sample	FWHM (keV)	Yield (%)
50-1	95.9	89.3
50-2	40.9	96.6
50-3	35.7	101.7
50-4	54.5	108.4

Table Y. All energy resolution and yield data points for microprecipitation time of 60 minutes.

Sample	FWHM (keV)	Yield (%)
60-1	79.6	91.1
60-2	54.3	94.6
60-3	36.8	100.1
60-4	51.4	100.1

Table Z. All energy resolution and yield data for 50 μL cerium carrier, 500 μL HF microprecipitation.

Sample	FWHM (keV)	Yield (%)
1	107.0	100.1
2	73.8	97.7
3	92.1	102.0
4	71.9	103.7

Table AA. All energy resolution and yield data for 25 μL cerium carrier, 250 μL HF microprecipitation.

Sample	FWHM (keV)	Yield (%)
1	53.4	113.1
3	52.3	114.3
4	60.8	110.5

Table BB. All energy resolution and yield data for 10 μL cerium carrier, 100 μL HF microprecipitation.

Sample	FWHM (keV)	Yield (%)
1	80.0	102.0
3	45.8	98.9
4	54.2	101.8

Table CC. All energy resolution and yield data for 5 μL cerium carrier, 50 μL HF microprecipitation.

Sample	FWHM (keV)	Yield (%)
1	40.5	110.3
2	26.8	107.2
3	47.1	104.4
4	49.3	99.5

Table DD. All energy resolution and yield data for 100 μL cerium carrier fraction of carrier in total solution microprecipitation study.

Sample	FWHM (keV)	Yield (%)
1	33.0	86.6
2	33.4	101.6
3	31.2	99.4
4	45.6	119.8

Table EE. All energy resolution and yield data for 50 μL cerium carrier fraction of carrier in total solution microprecipitation study.

Sample	FWHM (keV)	Yield (%)
1	41.9	110.2
2	48.4	103.0
3	38.1	105.0
4	34.2	101.7

Table FF. All energy resolution and yield data for 10 μL cerium carrier fraction of carrier in total solution microprecipitation study.

Sample	FWHM (keV)	Yield (%)
1	26.4	91.9
2	29.0	103.5
3	25.9	98.8

Table GG. All energy resolution and yield data for 1000 μL hydrofluoric acid fraction of carrier in total solution microprecipitation study.

Sample	FWHM (keV)	Yield (%)
1	33.0	86.6
2	33.4	101.6
3	31.2	99.4
4	45.6	119.8

Table HH. All energy resolution and yield data for 500 μL hydrofluoric acid fraction of carrier in total solution microprecipitation study.

Sample	FWHM (keV)	Yield (%)
1	30.9	111.9
2	64.0	93.8
3	52.0	109.0
4	54.7	100.1

Table II. All energy resolution and yield data for 100 μL hydrofluoric acid fraction of carrier in total solution microprecipitation study.

Sample	FWHM (keV)	Yield (%)
1	54.5	85.8
2	51.7	91.0
3	58.1	89.6
4	64.2	94.0

Table JJ. All energy resolution, yield, time and temperature data for heat setting 3.0.

Sample	Detector	FWHM (keV)	Yield (%)	Temperature ©	Evaporation Time (M:SS)
3.0.1	1A	69.012	76.193	100.2	6:22
3.0.2	1B	61.13	80.758	97.4	6:50
3.0.3	1A	66.6	128.845	103.6	7:34
3.0.4	1B	48.2	93.248	100.4	8:27
3.0.5	2A	63.7	123.235	101.6	8:02
3.0.6	2B	67.8	131.167	100.4	9:05

Table KK. All energy resolution, yield, time and temperature data for heat setting 3.2.

Sample	Detector	FWHM (keV)	Yield (%)	Temperature ©	Evaporation Time (M:SS)
3.2.1	1A	81.569	80.852	106.5	6:01
3.2.2	1B	62.025	80.010	103.6	6:25
3.2.3	3A	46.000	87.487	101.6	5:49
3.2.4	3B	49.300	87.487	105.8	6:05
3.2.5	4A	34.600	84.182	106.1	6:04
3.2.6	4B	47.900	82.287	104.4	6:09

Table LL. All energy resolution, yield, time and temperature data for heat setting 3.4.

Sample	Detector	FWHM (keV)	Yield (%)	Temperature ©	Evaporation Time (M:SS)
3.4.1	1A	93.81	76.71	114.2	5:54
3.4.2	1B	79.19	84.08	112.3	6:06
3.4.3	1A	68.90	80.59	108.4	7:07
3.4.4	1B	67.60	73.16	108.2	8:26
3.4.5	2A	72.40	82.36	107	7:45
3.4.6	2B	81.80	82.08	108.9	7:02

Table MM. All energy resolution, yield, time and temperature data for heat setting 3.6.

Sample	Detector	FWHM (keV)	Yield (%)	Temperature ©	Evaporation Time (M:SS)
3.6.1	1A	63.91	73.88	116.6	5:00
3.6.2	1B	67.17	77.91	115.8	5:15
3.6.3	3A	81.80	95.81	113.7	6:06
3.6.4	3B	73.80	85.49	115.6	6:40
3.6.5	4A	67.20	69.10	114.9	7:36
3.6.6	4B	61.50	89.95	113.9	6:14

Table NN. All energy resolution, yield, time and temperature data for heat setting 3.8.

Sample	Detector	FWHM (keV)	Yield (%)	Temperature ©	Evaporation Time (M:SS)
3.8.1	1A	56.47	71.78	122.3	4:49
3.8.2	1B	62.85	76.91	126.1	5:06
3.8.3	1A	93.70	91.25	121.8	4:55
3.8.4	1B	84.10	88.06	126.1	5:04
3.8.5	2A	83.00	87.07	126	5:09
3.8.6	2B	93.70	86.84	120.9	5:07

Table OO. All energy resolution, yield, time and temperature data for heat setting 4.0.

Sample	Detector	FWHM (keV)	Yield (%)	Temperature ©	Evaporation Time (M:SS)
4.0.1	1A	67.19	83.13	124.7	4:45
4.0.2	1B	85.35	93.49	132.4	5:07
4.0.3	3A	103.60	99.06	125.3	4:47
4.0.4	3B	82.30	98.48	129.2	4:32
4.0.5	4A	103.80	93.91	133.2	4:37
4.0.6	4B	74.60	96.47	125.3	5:33

Table PP. All energy resolution, yield, time and temperature data for heat setting 4.2.

Sample	Detector	FWHM (keV)	Yield (%)	Temperature ©	Evaporation Time (M:SS)
4.2.1	1A	79.06	74.94	128	5:35
4.2.2	2B	69.86	87.68	134.9	5:20
4.2.3	1A	78.30	91.79	133.1	4:25
4.2.4	1B	107.40	81.39	136.1	4:22
4.2.5	2A	70.40	82.30	138	3:49
4.2.6	2B	71.20	83.75	133.6	4:27

Table QQ. All energy resolution, yield, time and temperature data for heat setting 4.4.

Sample	Detector	FWHM (keV)	Yield (%)	Temperature ©	Evaporation Time (M:SS)
4.4.1	1A	71.12	84.44	134.4	3:58
4.4.2	1B	58.17	84.35	140	4:31
4.4.3	3A	85.20	96.79	138	3:47
4.4.4	3B	96.30	93.09	140.5	4:16
4.4.5	4A	68.60	98.64	139.4	4:02
4.4.6	4B	64.70	95.31	135.1	4:13

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