To the Graduate Council:

I am submitting herewith a thesis written by David W. Burkett entitled "Evaluation of Two Procedures for Assaying Uranium in Soil." I have examined the final copy of this thesis for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Master of Science, with a major in Nuclear Engineering.

Lawrence F. Miller
Dr. L.F. Miller, Major Professor

We have read this thesis
and recommend its acceptance:

Jon. K. Schweitzer

Peter J. Lin

Accepted for the Council:

Carolyn Winkel
Associate Vice Chancellor
and Dean of The Graduate School

EVALUATION OF TWO PROCEDURES FOR ASSAYING URANIUM IN SOIL

A Thesis

Presented for the

Master of Science

Degree

The University of Tennessee, Knoxville

David W. Burkett

August 1994

DEDICATION

This thesis is dedicated to my wife, Mary Lee Curtis Burkett, and my parents, John and Lenell Burkett.

ACKNOWLEDGMENTS

I would like to thank my committee members, Dr. L. Miller, Dr. P. Groer, and Dr. G. Schweitzer, for their comments and assistance with my thesis. Rose Boll and John Duffy deserve special thanks for helping me with the chemistry portion of this thesis. I would like to thank Dr. Kerlin and the Institute of Nuclear Power Operation for their financial support. I also want to thank my wife, Mary Lee, for being patient and understanding during the first two years of our marriage while I was obtaining my Master's degree. Special thanks to my parents for encouraging me to go to college and for teaching me that I could do anything I put my mind to.

ABSTRACT

This research project evaluated two procedures for preparing soil samples for alpha counting. The first procedure is the Environmental Protection Agency's (EPA) procedure which is an adsorption precipitation method. The soil is digested with acid and the uranium is coprecipitated with a lanthanum fluoride precipitation. The lanthanum fluoride precipitation is filtered out of solution and counted. The second is a potassium fluoride (KF) fusion procedure which was developed from papers written by Drs. Claude and David Sill. The soil is fused into a pyrosulfate cake which is subsequently dissolved in 2M hydrochloric acid. The uranium is coprecipitated out of solution with barium sulfate and redissolved into solution. Then it is precipitated out of solution in a lanthanum fluoride coprecipitation. The precipitant is filtered and counted. A byproduct of this research was the setting up of a alpha counting laboratory and a chemistry laboratory.

Three different soil samples were analyzed with both the EPA and the potassium fluoride fusion procedures. The soil samples are from Fernald and were part of a blind test of laboratories in the United States. Both the EPA and the potassium fluoride fusion procedures yielded results which were statistically equivalent to the results obtained from the laboratories in the blind test.

Both procedures yielded results which were statistically equivalent for these soil samples. The EPA procedure takes approximately three days to prepare a sample for alpha counting. The potassium fluoride fusion procedure can prepare a sample for alpha counting in approximately six hours. Thus, the potassium fluoride fusion procedure has the advantage of being much quicker than the EPA procedure.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

LIST OF ABBREVIATIONS

1. g: gram
2. ^{0}C: degree celsius
3. pCi: picoCurie
4. ml: milliliter
5. M: molar
6. TIOA: triisooctylamine
7. mg: milligram
8. EDTA: ethylenediaminetetraacetic acid
9. KEDTA: potassium ethylenediaminetetraacetic acid
10. NIM: nuclear instrumentation module
11. MCA: multichannel analyzer
12. PC: personal computer
13. V: voltage
14. MeV: megaelectronvolt
15. V/M: volts per meter
16. ADC: analog to digital converter
17. mV: millivolt
18. EPA: Environmental Protection Agency
19. dpm: disintegrations per minute

CHAPTER I

INTRODUCTION

1.1 Need for Improving Procedures

The ability to perform alpha spectroscopy on soil samples is a valuable tool in environmental restoration. Being able to extract uranium and other actinides from soil to perform alpha spectroscopy is useful for conducting site characterizations. Improving these types of procedures will provide better results for site characterization and possibly even better ways to clean up sites contaminated with uranium and other actinides.

1.2 Statement of Project

The purpose of this project was to evaluate two different procedures for extracting uranium from soil and to use alpha counting for determining the activity of the uranium in the soil. The first procedure which this project evaluated was the Environmental Protection Agency's (EPA) procedure. The second procedure is a potassium fluoride fusion procedure.

The EPA's procedure is an adsorption coprecipitation method. Soil samples are first reduce to ash in an oven at 550^{0}C for seventy-two hours. After the soil was ashed an aliquot of the ashed sample was digested in acid. The

uranium is dissolved into ten percent triisooctylamine (TIOA) and p-xylene. The uranium is coprecipitated with a lanthanum fluoride precipitation and filtered out of solution. This procedure is discussed in detail in chapter III.

The potassium fluoride fusion procedure fuses the soil into a pyrosulfate cake which is subsequently dissolved in 2M hydrochloric acid. The uranium is coprecipitated with barium sulfate. After centrifuging out the coprecipitants, the uranium is redissolved in solution. The uranium is finally coprecipitated in a lanthanum fluoride precipitation and filtered out of solution. This procedure is discussed in detail in chapter IV.

1.3 Problems with Performing Alpha Spectroscopy

An alpha particle can be very easily absorbed. A piece of paper or just a few millimeters of air will absorbed an alpha particle. An alpha particle produced by an uranium atom in a raw soil sample would be absorbed by the rest of the sample before it would have a chance to interact with a detector. Therefore to perform alpha spectroscopy on a soil sample the uranium must be extracted from the rest of the soil to prevent the rest of the soil from absorbing the alpha particle.

One problem with extracting the uranium from the soil is not knowing what is in the soil sample. Since every soil

sample is different, an effective procedure must separate every possible interferant from the uranium.

Once the uranium has been extracted from the soil, the uranium has to be deposited in way which will allow the alpha particles to escape from the source and interact with an alpha detector. This means the uranium must be deposited in a very thin layer which must be near the surface of the source to prevent the alpha particles from being self absorbed.

1.4 Goals of the Project

The goal of this project was to evaluate two procedures, the EPA procedure and the potassium fluoride fusion procedure. The side benefits of this project are the establishment of an alpha spectroscopy laboratory and a chemistry laboratory to extract uranium from soil.

CHAPTER II

MATERIALS AND METHODS

2.1 Purpose

This section includes a description of how to set up, operate, and calibrate the necessary equipment for this research. Also, a brief discussion on how the equipment works is presented here.

2.2 Equipment Set Up and Description

The alpha spectroscopy equipment used in this research consists of a personal computer based multichannel analyzer (PC based MCA), a Tennelec 256 alpha spectroscopy system with a surface barrier alpha detector, and a vacuum pump. The surface barrier detector used for the EPA procedure and the thorium spectra from the potassium fluoride fusion procedure was an EG&G Ortec model number BR-19-150-100. The surface barrier detector used for the potassium fluoride fusion procedure was an EG&G Ortec model number BU-021-450-100. The Tennelec 256 alpha spectroscopy system contains a high voltage power supply, preamplifier, linear amplifier, bias amplifier, and a discriminator. Therefore, the Tennelec 256 nuclear instrumentation module (NIM) is the only module required. The PC MCA card is produced by EG&G

Ortec and the Maestro II emulator software is used to operate the MCA card.

The vacuum pump is a Direct Torr vacuum pump model number 8811 which can pull a vacuum of 100 microns of mercury. A vacuum of this magnitude is necessary to get good alpha spectra, since alpha particles lose energy traveling through air. Any air in the vacuum chamber leads to absorption in the air which degrades the resolution of the alpha spectra.

The Tennelec 256 alpha spectroscopy system is easily set up. Place the Tennelec 256 NIM into a NIM bin. Connect the PC based MCA to the energy port on the back of the Tennelec 256 NIM. Attach the vacuum hose from the vacuum pump to the vacuum port on the back of the Tennelec 256.

The voltage on the surface barrier detector must be set to the recommended voltage of the detector manufacturer. A digital multimeter is required to perform this operation. On the back of the Tennelec 256 NIM, there are three test points which are marked DET, HV, and GND. Connect the ground wire from the multimeter to the test point marked GND. The positive wire from the multimeter is now connected to the test point marked HV. The high voltage control for the Tennelec 256 alpha spectroscopy system is on the back of the NIM module. Turn the high voltage control on the Tennelec 256 until the recommended voltage can be read on the multimeter. Then tighten the lock nut to insure the

voltage is locked in place.

2.3 Operation and Calibration

While using the Tennelec 256 alpha spectroscopy system, always turn the MARKER/BIAS/OFF switch to OFF before venting or evacuating the chamber. This will prevent the surface barrier detector from being damaged. The PC based MCA can now be calibrated as follows.

1) Set the range on the Tennelec 256 alpha spectroscopy system to a range consistent with the expected alpha particle energy.
2) Turn the MARKER/BIAS/OFF switch to OFF and turn the VENT/HOLD/PUMP control to VENT.
3) Open the door to the vacuum chamber carefully.
4) Use a pair of tongs to pick up the standard calibration source (^{239}Pu was used for this experiment) and place it in the source holding shelf. Always use a pair of tongs when handling an alpha source since touching the source could damage it.
5) Insert the shelf in the fourth slot from the top, since this is the closest to the detector the shelf can be placed.
6) This is also the position where the prepared soil samples will be counted.
7) Close the door to the vacuum chamber and turn the VENT/HOLD/PUMP control to PUMP.

8) Allow the chamber to evacuate for ten minutes.

9) Count the standard ^{239}Pu alpha source for fifteen minutes or until a statistical numbers of counts have been counted.

10) Turn the MARKER/BIAS/OFF switch to OFF and the VENT/HOLD/PUMP control to VENT.

11) Remove the shelf from the chamber, and using tongs, place the standard ^{239}Pu alpha source back in its box.

12) Repeat the above steps except this time use the standard ^{241}Am alpha source instead of the standard ^{239}Pu alpha source.

13) Locate the high energy side of the lower peak and move the cursor there. This lower peak is ^{239}Pu with energies 5.16 MeV, 5.14 MeV, and 5.11 MeV. Notice there is only one peak; the reason for this is the energies are too close together for the surface barrier detector to resolve. The high energy side of the lower peak has an energy of 5.16 MeV.

14) Press Alt C to bring up the calculate menu.

15) Press Alt C again to calibrate the PC based MCA.

16) Enter 5.16 as the energy.

17) Now, move to the cursor to the high energy side of the high peak which is ^{241}Am. The energies of the ^{241}Am alphas are 5.49 MeV and 5.44 MeV. Press Alt C to bring up the calculate menu.

18) Press Alt C to calibrate.

19) Enter 5.49 as the energy of this peak.

20) Enter MeV for the characters. The PC based MCA is now calibrated.

Operation of this system is straight forward.

1) Place the sample to be counted in the source holding shelf.

2) Turn the VENT/HOLD/PUMP control to VENT and insert the shelf into the fourth slot from the top.

3) Evacuate the chamber by turning the VENT/HOLD/PUMP control to PUMP and wait ten minutes.

4) While waiting set the count time. Press Alt P to bring up the presets menu.

5) Press Alt R to set the real time to 172,800 seconds (forty-eight hours).

6) When the chamber is finished being evacuated turn the VENT/HOLD/PUMP control to HOLD and the MARKER/BIAS/OFF switch to BIAS and start counting.

2.4 Band Structure

In order to explain how the surface barrier detector works a brief discussion of band structure, n-type material, and p-type material is required.

The term band is used since the electrons in the shells of atoms do not have discrete energies but instead have a range of energies. The valence band is the highest energy level which electrons normally possess. The conduction band

is the next higher energy level for the electrons after the valence band. In the conduction band, electrons are free to move.

A material is a conductor if the valence band is not completely full which means the conduction band usually contains electrons. An insulator has a completely full valence band with a band gap greater than five electron volts to the conduction band. A semiconductor has a completely full valence band like an insulator but the band gap is less than five electron volts (Knoll 338-339).

2.5 N-type Semiconductors

N-type semiconductors have free electrons to move around in the conduction band. This is accomplished by taking a group IV element like germanium which has four valence electrons and doping it with a group V element such as phosphorus which has five electrons in the valence band. The phosphorus uses four of its valence electrons to produce covalent bonds with four germanium atoms. The fifth electron from the phosphorus atom is unpaired. This gives the material an extra electron which resides in the forbidden gap at an energy level called the donor level. In reality a hyperpure n-type semiconductor is not actually doped, it possess's natural impurities which act as the doping material. N-type semiconductors are more rare than p-type semiconductors.

The energy difference between the donor level and the conduction band is small enough that thermal excitation will cause a large number of these electrons to move to the conduction band. Now, there are more electrons than holes and the conductivity is determined by the electrons (Knoll 343-345).

2.6 P-type Semiconductors

P-type semiconductors have extra holes to capture electrons. The germanium crystal is doped with a group III element such as boron, which only has three electrons in the valence band. Boron can only form three covalent bonds and where the fourth bond should be a hole is produced. If an electron is captured by this hole it creates a covalent bond. The electron which filled the hole resides in the forbidden band in an energy level called the acceptor level. In reality a p-type semiconductor is not actually doped, it possess's natural impurities which act as the doping material.

The energy difference between the acceptor level and the valence band is small enough that thermal excitation will fill some of these holes. The germanium crystal doped with boron will not have nearly enough electrons to fill all of these holes. Therefore, the holes will determine the conductivity of the material (Knoll 345-346).

2.7 Junction Detectors

A junction detector is produced when a n-type semiconductor and a p-type semiconductor are in contact with each other and a reverse bias is applied. The reverse bias produces a depletion region, which is the sensitive volume of the detector. The magnitude of the electric field produced by this reverse bias is 10^7V/M (Knoll 359). With an electric field of this magnitude the charge produced by the alpha particle interactions can be collected quickly. Thus, a junction detector can be used with relatively high count rates.

2.8 Surface Barrier Detectors

A surface barrier detector is a junction detector. The most common way which a surface barrier detector is produced is by oxidizing the surface of a n-type semiconductor. The oxidized surface is now a p-type semiconductor which is covered with a thin layer of gold to be the cathode. The n-type semiconductor is covered with aluminum to serve as the anode and a reverse bias is used to produce the depletion region which serves as the sensitive volume of the detector.

2.9 Detection Basics

In the absence of radiation, the resistance is great enough that there is no current. When an alpha particle

interacts with a surface barrier detector, it produces ion pairs which are partly composed of valence electrons and gives these electrons the necessary energy to move into the conduction band. These electrons are free to move in the conduction band. The potential applied across the surface barrier detector moves the holes toward the gold cathode and the electrons toward the aluminum anode which produces a charge pulse.

2.10 Preamplifiers

A major function of the preamplifier is to change the charge pulse from the detector into a voltage pulse which the amplifier can process. This voltage pulse is directly proportional to the energy of the ionizing radiation deposited in the detector. The voltage of the output pulse can be calculated with equation 2.1:

$$V = \frac{Q}{C} \qquad (2.1)$$

where: V is the voltage of the output pulse, Q is the charge collected by the detector, and C is the capacitance of the system.

The capacitance of the system needs to be kept constant, so the voltage will accurately show the correct charge collected. The capacitance of the preamplifier is

much greater than the capacitance of the detector. This is to compensate for the inherent changes in the capacitance of the detector.

The output pulse from the preamplifier is called a tail pulse. The tail pulse has a rapidly rising leading edge and a slowly decaying tail. Most of the pertinent information is in the leading edge and the rest of the pulse contains the information about the dead time. The rise time is the time required for the pulse to reach its maximum amplitude. Generally, the rise time is equal to the charge collection time of the detector.

2.11 Amplifiers

The amplifier increases the sizes of the pulses from the preamplifier so the analog to digital converter (ADC) can read them. The sizes of the pulses are increased by a multiplication factor such as 100 and not by an additive factor. This amplification also increases the range of the pulses. For example, a 1mV pulse would be increased to 100mV and a 20mV pulse would be amplified to 2V. Thus, the amplifier expands the range of the pulses.

The amplifier also does pulse shaping. The tail pulse which is the output pulse from the preamplifier is converted to a more gaussian pulse. The first stage of the pulse shaping in the amplifier is to work on the tail of the tail pulse. A differentiator circuit is used to quickly pull the

tail down to baseline. The second stage of pulse shaping in the amplifier is to work on the leading edge on the tail pulse. The leading edge needs to rise more slowly. This is accomplished with an integrator circuit. Now, the pulse has a more gaussian shape.

2.12 Quantum Numbers and Electron Structure

A discussion on quantum numbers and electron structure is necessary to explain the oxidation states of ions and why they change. The changing of oxidation states is important in the EPA procedure because it is used to extract the uranium from the aqueous acid phase into the ten percent TIOA in p-xylene leaving the majority of the soil components behind.

There are four quantum numbers which describe the state of an electron. The first quantum number is n. The second quantum number is ℓ. The third is m_ℓ. Lastly, the fourth quantum number is m_s.

The first quantum number n is important since it determines the energy level of the electron. As n increases, the energy of the electron also increases. The greater the energy of the electron the further away from the nucleus it is. The quantum number n must take on integer values starting with 1.

Each energy level has sublevels. These sublevels are the second quantum number ℓ. The quantum number ℓ must also

take on integer values. These values start with 0 and go to (n-1). Thus, the quantum numbers n and ℓ are related. In chemistry the sublevels are designated with letters such as s, p, d, and f. The sublevel s has a ℓ quantum number equal to 0. The p sublevel has quantum number ℓ=1 and so on.

sublevel	s	p	d	f
quantum number	0	1	2	3

Each sublevel has $2\ell+1$ orbitals. These orbitals have the quantum number m_ℓ which has integer values of -l to l. The quantum numbers ℓ and m_ℓ are related. When ℓ is 0 or the sublevel is s, m_ℓ is equal to 0. When ℓ is 1 or the sublevel is p, m_ℓ can be -1, 0, or 1. All of the orbitals with in a sublevel have approximately the same energy.

The fourth and final quantum number which is related to n, ℓ, or m_ℓ describes the spin of the electron. The quantum number is m_s and only has two possible values +1/2 or -1/2. If electrons have the same value for m_s they have parallel spins. If electrons have different values for m_s then they have opposed spins. Each orbital can have two electrons but they must have opposed spins.

2.13 Oxidation States

Atoms, by sharing electrons can acquire eight electrons in their valence shell. These atoms with eight electrons in their valence shell are very stable. Another stable state for atoms is when all the orbitals of a sublevel have one

electron in them and the electrons have parallel spin. Yet, another stable state for atoms is when a sublevel is empty.

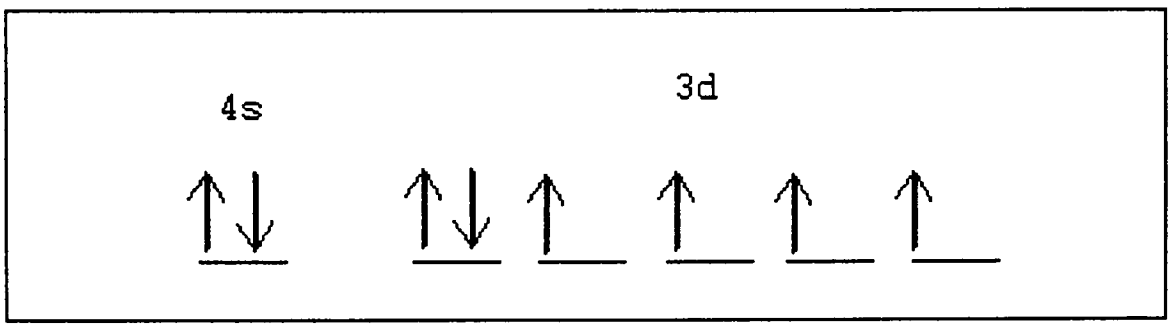


Figure 2.1 Valence Shell of Fe

Iron is a typical component of soil which will act as an actinide when the precipitation occurs if it is not reduced from +3 to +2, so let's look at its oxidation state. Iron typically has an oxidation state of +2 or +3. The reason for these states can be found by looking at the valence shell of iron (see figure 2.1). The two electrons in the 4s orbital are given up for a more stable empty orbital which yields the +2 oxidation state. Now, all of the 3d orbitals have one electron in them except for one orbital. The sublevel would be more stable if all the orbitals were half filled. Therefore, Fe^{+2} gave up the electron with the opposed spin in the 3d orbital which would yield the +3 oxidation state.

Since the objective of the research is to extract uranium from soil, let's examine its oxidation states. First, examine the valence shell of uranium (see figure 2.2). Uranium will give up either or both electrons in the

7s orbital which would yield an oxidation number of +1 or +2 to reach a more stable state. Notice the 6d sublevel only has one electron in it. Uranium will give up that electron to have an empty sublevel which is a stable state. This action will yield the +3 oxidation state of uranium. In reality, the U^{+3} is the first obtained oxidation state of uranium. The 5f sublevel has three electrons and each time uranium gives up one of these electrons it gets a little bit closer to the more stable empty sublevel. The removal of these electrons yields the oxidation states +4, +5 (rare), and +6.

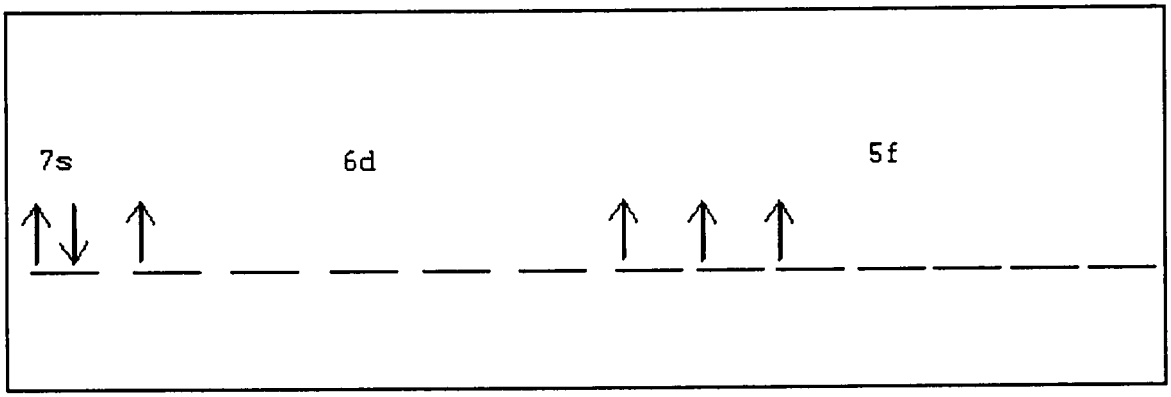


Figure 2.2 Valence Shell of U

2.14 Data Analysis

The amount of uranium recovered from the soil was determined by the recovery of the tracer. The recovery of the ^{232}U tracer was calculated with equation 2.2 where: R is the recovery, C_p is the count rate of the ^{232}U, A_c is the activity of the ^{232}U, and E is the efficiency of the

detector.

$$R=\frac{C_p}{A_c E}. \qquad (2.2)$$

Now, the activity of the isotopes in each sample can be calculated with equation 2.3 where: A_I is the activity of the isotope, C_I is the count rate of the isotope, E is the efficiency of the detector, and R is the recovery.

$$A_I=\frac{C_I}{RE}. \qquad (2.3)$$

Substituting equation 2.2 into equation 2.3 yields,

$$A_I=\frac{\frac{C_I}{E}A_c}{\frac{C_p}{E}}. \qquad (2.4)$$

The propagation of error for A_I is given by,

$$\sigma_{A_I}^2=\left(\frac{\partial A_I}{\partial C_p}\right)^2\sigma_{C_p}^2+\left(\frac{\partial A_I}{\partial C_I}\right)^2\sigma_{C_I}^2+\left(\frac{\partial A_I}{\partial A_c}\right)^2\sigma_{A_c}^2+\left(\frac{\partial A_I}{\partial E}\right)^2\sigma_E^2. \qquad (2.5)$$

The fractional uncertainty is,

$$\Sigma_{A_I}=\left(\Sigma_{C_p}^2+\Sigma_{C_I}^2+\Sigma_{A_c}^2+2\Sigma_E^2\right)^{\frac{1}{2}}. \qquad (2.6)$$

Since the activity of the tracer is known and pipeting reproducibility is high, Σ_{Ac} is very small and will be considered to be 0.01. The fractional uncertainty in the efficiency is assumed to be 0.03. Thus, the fractional uncertainty can be calculated with

$$\Sigma_{A_I}=\left(\frac{1}{C_p t}+\frac{1}{C_I t}+2(0.05)^2+(0.01)^2\right)^{\frac{1}{2}}. \qquad (2.7)$$

The uncertainty in the activity can be calculated with

$$\sigma_{A_I}=\Sigma_{A_I}A_I. \qquad (2.8)$$

CHAPTER III

EPA PROCEDURE AND DISCUSSION

3.1 Introduction

The purpose of this procedure is to extract uranium isotopes from soil samples. Once the uranium isotopes are extracted from the soil, alpha spectroscopy will be performed on the prepared samples to identify and quantify the uranium isotopes in the soil samples.

The soil sample is reduced to ash in an oven at 550°C for seventy-two hours. A ^{232}U tracer is added to one gram of ashed sample and the silicates are removed from the sample with hydrofluoric acid. The uranium is dissolved into ten percent triisooctylamine (TIOA) in p-xylene leaving most of the remaining soil components behind in the aqueous acid phase. Then the uranium is extracted from the TIOA with nitric acid and coprecipitated with a lanthanum carrier. The sample is filtered through a membrane filter with suction and assayed by alpha spectroscopy.

3.2 Reagents and Reagent Preparation

The following list identifies the necessary reagents needed to prepare a soil sample with the EPA procedure. Also included are instructions on how to prepare some of the

reagents.

1. Crystalline ascorbic acid. Procedure requires≈2g/sample.
2. 12M hydrochloric acid (37 percent HCl). Procedure requires≈50ml/sample.
3. 9M hydrochloric acid. Dilute 750 ml of 12M hydrochloric acid to 1 liter with water. Procedure requires≈500ml/sample.
4. 1M hydrochloric acid. Dilute 83 ml of 12M hydrochloric acid to 1 liter. Procedure requires≈70ml/sample.
5. 29M hydrofluoric acid (48 percent HF). Procedure requires≈40ml/sample.
6. 3M hydrofluoric acid. Dilute 104 ml of 29M hydrofluoric acid to 1 liter with water in a plastic graduated cylinder. Store in a plastic bottle. Procedure requires≈5ml/sample.
7. Polished Nickel Foil. 15 cm x 1 cm x 0.1 mm
8. 16M nitric acid (70 percent HNO_3). Procedure requires≈100ml/sample.
9. 0.1M nitric acid. Dilute 6 ml of 16M nitric acid to 1 liter with water. Procedure requires≈100ml/sample.
10. 12M perchloric acid (70 percent $HClO_4$). Procedure requires≈70ml/sample.
11. Lanthanum carrier, 0.1 mg La^{+3}/ml. Dissolve 0.0779 g $La(NO_3)\bullet 6H_2O$ per 250 ml 1M hydrochloric acid. Procedure requires≈1ml/sample.

12. 20 percent reagent grade titanium trichloride. Procedure requires≈200μl/sample.
13. Triisooctylamine (TIOA). Procedure requires≈20ml/sample.
14. P-xylene. Procedure requires≈200ml/sample.
15. 10 percent TIOA in p-xylene. Dilute 100 ml of TIOA to 1 liter with p-xylene.
16. ^{232}U tracer solution 5 to 30 dpm/ml. Procedure requires≈1ml/sample.

3.3 EPA Procedure and Discussion

The following is a discussion on how to prepare a soil sample for alpha spectroscopy with the EPA procedure.

1. Place 5 g of soil sample in ceramic dish. Ash in muffle furnace, gradually raise the temperature to 550°C and maintain for seventy-two hours.

Heating the soil sample at 550°C for seventy-two hours removes the water and decomposes organics by changing them into other carbon compounds, carbon dioxide and water vapor.

2. Weigh 1 g of ashed sample and place it in a teflon beaker. Add 1 ml of ^{232}U tracer.

A known amount of ^{232}U (approximately 5 to 30 dpm/ml) is added to the soil sample as a tracer. When the uranium is extracted from the sample, the ^{232}U tracer will also be extracted. Since the activity of the ^{232}U tracer is known, the uranium yield can be calculated.

3. Add 20 ml of 29M hydrofluoric acid to the sample and evaporate to dryness. Repeat once.

The silicates are the most difficult material to remove from the soil. In order to remove the silicates, concentrated hydrofluoric acid is employed. When concentrated hydrofluoric acid is added to the ashed sample, the silicates complex with the fluoride ions to form SiF_4 and SiF_6^{-2}. The SiF_6^{-2} decomposes to SiF_4. When evaporated to dryness, the silicon fluoride complex is released in the form of SiF_4.

4. Add 5 ml each of 12M perchloric acid and 9M hydrochloric acid to the sample; evaporate to dryness. Repeat once.
5. Add 10 ml of 12M hydrochloric acid to sample and transfer to a 600 ml glass beaker; evaporate to dryness. Repeat once.
6. Add 300 ml of 9M hydrochloric acid to sample to dissolve it and heat to 50°C.

The uranium will form a complex anion in the form $UO_2Cl_x^{-n}$ which dissolves in the aqueous acid phase. This is accomplished be adding 9M hydrochloric acid and 12M perchloric acid to the ashed sample. The 9M hydrochloric acid provides an abundance of chloride ions for the complexing reaction to occur. The addition of the hydrochloric acid also produces metallic chlorides of the other metals in the soil sample. The 12M perchloric acid

removes the last of the organics.

7. Place 50 ml of 9M hydrochloric acid and 100 ml of 10 percent TIOA in 1 liter separatory funnel. Shake well. Wait for separation of phases and discard lower aqueous acid phase.
8. Add sample to the separatory funnel and shake well for two minutes. Vent the funnel to prevent pressure build up.
9. Allow phases to separate. Drain off lower aqueous acid phase and discard it.
10. Add 50 ml of 9M hydrochloric acid to the aqueous sample in the funnel and shake well.
11. Allow phases to separate. Drain off lower aqueous acid phase and discard it.
12. Repeat steps 10 and 11.

The uranium is now extracted from the aqueous acid phase into an organic solvent which is ten percent TIOA in p-xylene. TIOA consists of a nitrogen atom surrounded by three carbon chains. The nitrogen also has a pair of free electrons which attract a hydrogen atom to become a complex cation (see figure 3.1). The complex uranium anion is attracted to the complex organic cation. This TIOA-UO_2Cl_x complex is now neutral and organic like. Thus, the uranium is removed from the aqueous acid phase into the organic xylene phase and most of the remaining soil components are left behind in the aqueous acid phase.

13. Add 100 ml of 0.1M nitric acid to the separatory funnel and shake well for two minutes. This strips the uranium from the TIOA.

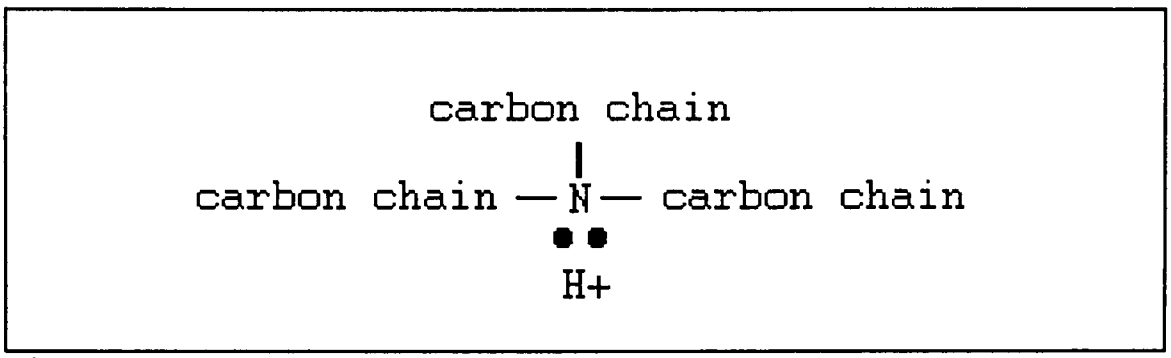


Figure 3.1 TIOA-H complex ion

14. Allow phases to separate. Drain off lower aqueous acid phase and save.
15. Repeat steps 13 and 14. Combine the saved solutions which are now refereed to as the sample solution.

By adding aqueous 0.1M nitric acid, the uranium is stripped from the TIOA. The addition of dilute nitric acid reduces the concentration of chloride ions in the solution causing the uranium chloride complex to dissociate which puts the uranium in the form of UO_2^{+2} cation. Since the UO_2^{+2} is a cation, the complex is broken and the UO_2^{+2} is in an aqueous acid phase again.

16. Place the sample solution in a clean separatory funnel.
17. Add 100 ml of p-xylene to the sample solution and shake well. This will remove any remaining TIOA.
18. Allow phases to separate. Drain off lower aqueous acid phase into a beaker and save. Discard remaining

p-xylene.

The aqueous acid phase needs to have all of the TIOA removed, since the presence of any TIOA will complex uranium and lower the yield of uranium. This a accomplished by adding 100 percent p-xylene to the aqueous acid phase and separating the two layers again.

19. Evaporate the sample solution to dryness but do not over heat since the sample could be cooked into the beaker.
20. Add 100 ml of 16M nitric acid to the sample and evaporate to dryness. Do not over heat since the sample could be cooked into the beaker.
21. Add 5 ml each of 9M hydrochloric acid and 12M perchloric acid to the sample and evaporate to dryness. Repeat once.
22. Add 10 ml of 12M hydrochloric acid to sample and evaporate to dryness. Repeat once.

The sample is cleaned with nitric acid, perchloric acid, and hydrochloric acid. This decomposes any remaining TIOA or organics in the sample. The addition of the 12M hydrochloric acid removes the remaining nitric acid and switches the uranium to chloride complexation.

23. Add 50 ml of 1M hydrochloric acid to sample and warm to dissolve sample residue.
24. Heat the sample solution to 80°C while stirring and add 50 mg of ascorbic acid. Do not over heat.

25. Suspend polished nickel strip in solution for two hours to remove polonium.
26. Remove nickel strip and evaporate sample solution to dryness.

Any polonium (Po^{+2}) in the sample needs to be removed. Since polonium emits an alpha particle with energy 5.30 MeV which is the same energy as the alpha particle emitted from the ^{232}U tracer. Ascorbic acid is added to the sample solution which reduces Fe^{+3} to Fe^{+2} to prevent interference. A polished nickel strip is suspended in the solution to remove the polonium by plating the polonium out on the nickel strip.

27. Add 15 ml of 1M hydrochloric acid to sample solution and heat to 50°C.
28. Add ascorbic acid to the sample solution until the yellow color disappears; this reduces the iron in the sample solution.

When the solution is heated to dryness after the polonium is removed, if there is iron in the sample solution, it needs to be reduced from Fe^{+3} to Fe^{+2} to eliminate it as an interferant. The Fe^{+3} will act as an actinide when the precipitation occurs. This can be accomplished by adding ascorbic acid to the sample solution.

29. Reduce the uranium by adding 200 μl of 20 percent titanium trichloride.
30. Add 1 ml of lanthanum carrier and 5 ml of 3M

hydrofluoric acid. Mix well and set aside for half an hour to precipitate LaF_3 carrying uranium.

The uranium needs to be put into a form which will allow the alpha particles to escape from the surface of the sample. The way this is accomplished is with adsorption precipitation. Before adsorption precipitation can occur the UO_2^{+2} must be reduced to U^{+4} which is achieved with the addition of titanium trichloride to the sample solution. The adsorption precipitation is achieved when the lanthanum carrier and 3M hydrofluoric acid are added to the solution. If white precipitants can be seen, then either too much uranium is present in the sample to count which might contaminate the surface barrier detector or too much lanthanum is present which leads to self-adsorption of the alpha particles.

31. Filter sample through membrane filter using suction.
32. Rinse sample beaker with 10 ml of water and filter the water. Rinse sample beaker with ethanol and filter the ethanol.
33. Remove clamp and top of filter with suction on and allow the membrane to dry.
34. Mount membrane on holding paper and count sample for forty-eight hours.

The preceding procedure was taken from the Environmental Protection Agency (Environmental Protection Agency).

CHAPTER IV

POTASSIUM FLUORIDE FUSION PROCEDURE AND DISCUSSION

4.1 Origin of Potassium Fluoride Fusion Procedure

The potassium fluoride fusion procedure used in this research project was compiled from articles written by Dr. Sill. The procedure was compiled from articles in Nuclear and Chemical Waste Management, Waste Management, and Analytical Chemistry. The articles in Nuclear and Chemical Waste Management are entitled "Determination of Radium-226 in Ores, Nuclear Wastes and Environmental Samples by High-Resolution Alpha Spectrometry" (Sill 239-256) and "Precipitation of Actinides as Fluorides or Hydroxides for High-Resolution Alpha Spectrometry" (Sill 201-215). The article in Waste Management was entitled "Determination of Actinides in Nuclear Wastes and Reference Materials for Ores and Mill Tailings" (Claude and David Sill 219-229). The articles in Analytical Chemistry are entitled "Determination of Thorium and Uranium Isotopes in Ores and Mill Tailings by Alpha Spectroscopy"(Sill 618-621) and "Determination of Gross Alpha, Plutonium, Neptunium, and/or Uranium by Gross Alpha Counting on Barium Sulfate" (Sill 1452-1459).

4.2 Basic Procedure

The purpose of this procedure is to extract uranium isotopes from soil samples. Once the uranium isotopes are extracted from the soil, alpha spectroscopy will be performed on the prepared samples to identify and quantify the uranium isotopes in the soil samples.

The uranium is separated from the alpha absorbing materials and other radionuclides in the soil sample. The uranium in the soil sample is fused with potassium fluoride forming a pyrosulfate cake and subsequently dissolving the pyrosulfate cake in 2M hydrochloric acid. The uranium was coprecipitations with cerous hydroxide ($Ce(OH)_3$) and barium sulfate ($BaSO_4$). A ^{232}U tracer is added to one gram of sample for accurately determining the uranium yield. The prepared sample is assayed by alpha spectroscopy.

4.3 Reagents and Reagent Preparation

The following list identifies the necessary reagents needed to prepare a soil sample with the potassium fluoride fusion procedure. Also included are instructions on how to prepare some of the reagents.

1. Anhydrous potassium fluoride. Procedure requires 0.5g/sample.
2. Potassium hydrogen fluoride.
3. Potassium nitrate.

4. Mixed flux is prepared in the following way. Procedure requires 3.5g/sample.

    a. Weigh 100 g of anhydrous potassium fluoride and place in a mixing container.

    b. Weigh 70 g of potassium hydrogen fluoride and place in mixing container.

    c. Weigh 2 g of potassium nitrate and place in mixing container.

    d. Mix ingredients completely and place in storage container.

5. Barium chloride dihydrate (0.45 percent). Dissolve 0.45 g of barium chloride dihydrate in 100 ml of water. Procedure requires 4ml/sample.

6. Anhydrous potassium sulfate.

7. Concentrated sulfuric acid. Procedure requires 4ml/sample.

8. ^{232}U tracer solution. Accurately calibrated to 5 to 30 dpm/ml. Procedure requires 1ml/sample.

9. Seeding suspension which is prepared in the following way. Procedure requires 1ml/sample.

    a. Add 50 ml of 0.45 percent barium chloride dihydrate, 12 g of anhydrous potassium sulfate, and 6 ml of concentrated sulfuric acid to a 250 ml Erlenmeyer flask.

    b. Evaporate the solution until the barium sulfate just redissolves. Do not allow much

of the sulfuric acid to evaporate.

c. Cool the flask.

d. Add 80 ml of water.

e. Heat the solution to boiling.

f. After cake dissolves cool the flask to room temperature and dilute to 100 ml.

g. Shake solution thoroughly before each use.

10. 12M hydrochloric acid (37 percent HCl). Procedure requires 2ml/sample.

11. 2M hydrochloric acid. Dilute 167 ml of 12M hydrochloric acid to 1 liter. Procedure requires 35ml/sample.

12. Carborundum. Procedure requires 3 small chips/sample.

13. Ammonium iron (II) sulfate hexahydrate. Procedure requires 2.5g/sample.

14. 0.05M EDTA.

15. Potassium hydroxide.

16. 20 percent titanium trichloride. Procedure requires 1ml/sample.

17. 10M potassium hydroxide which is prepared in the following way. Procedure requires 3ml/sample.

    a. Weigh 28.05 g of potassium hydroxide.

    b. Dissolve the potassium hydroxide in 50 ml of water.

18. 0.05M KEDTA at a pH of 10.6 which is prepared in the following way. Procedure requires 6ml/sample.

a. Weigh 0.5 g of potassium hydroxide.

b. Dissolve the potassium hydroxide in 50 ml of 0.05M EDTA.

c. Add dropwise 10M potassium hydroxide until a pH of 10.6 is obtained.

19. 16M nitric acid (70 percent HNO_3). Procedure requires 100ml/sample.

20. 29M hydrofluoric acid (48 percent HF). Procedure requires 5ml/sample.

21. Anhydrous sodium sulfate. Procedure requires 2g/sample.

22. 0.25M potassium hydroxide which is prepared in the following way. Procedure requires 5ml/sample.

    a. Weigh 0.7 g of potassium hydroxide.

    b. Dissolve the potassium hydroxide in 50 ml of water.

23. Lanthanum carrier, 0.1 mg La^{+3}/ml. Dissolve 0.0779g $La(NO_3)_3 \cdot 6H_2O$ per 250 ml 1M hydrochloric acid. Procedure requires 1ml/sample.

4.4 Potassium Fluoride Procedure and Discussion

The following is a discussion on how to prepare a soil sample for alpha spectroscopy with the potassium fluoride fusion procedure.

1. Weigh 1 g of sample and place in platinum dish.

2. Add 1 ml of ^{232}U tracer to the platinum dish.

The soil sample is placed in a platinum dish, since the procedure uses 29M hydrofluoric acid and heats the sample to high temperatures with a blast burner. The ^{232}U tracer is added to the sample for the purpose of determining the yield of uranium from the sample.

3. Add 0.5 ml 16M nitric acid; carefully smell for hydrogen sulfide.
4. If no hydrogen sulfide is being evolved, add 3 ml of 29M hydrofluoric acid. If hydrogen sulfide is present add excess 16M nitric acid and evaporate to dryness before adding 29M hydrofluoric acid.
5. Evaporate to near dryness.

A half a milliliter of 16M nitric acid is added to the sample to test for the presence of sulfide in the sample. If no hydrogen sulfide is evolved from the sample, then no sulfur is present in the sample as S^{-2}. If hydrogen sulfide is evolved from the sample, then excess 16M nitric acid is added to remove the sulfide from the sample. The addition of 29M hydrofluoric acid removes silicates from the soil.

6. Weigh 3.5 g of mixed flux and place in platinum dish.
7. Mix sample and mixed flux thoroughly.
8. Heat the mixture with a blast burner until the sample turns clear.
9. Let the platinum dish cool on a stainless steel plate for approximately 30 seconds.
10. Add 4 ml of concentrated sulfuric acid. (NOTE: Have a

container with cold water near by to cool the dish if the reaction becomes too violent.)

11. When the reaction begins to stop, gently heat the platinum dish with the blast burner until the evolution of gas is restored. (NOTE: Do not over heat.)
12. When the evolution of gas has stopped and the solid cake has disappeared, add 0.5 g of anhydrous potassium fluoride to the platinum dish.
13. Gently heat the platinum dish with the blast burner and continuous swirling until the evolution of gas stops.

A mixed flux of anhydrous potassium fluoride, potassium fluoride, and potassium nitrate is added to the sample. The potassium nitrate is in the mixed flux to lower the melting point of the potassium fluoride and the anhydrous potassium fluoride. The potassium fluoride and the anhydrous potassium fluoride provide fluorine for the removal of silicates from the sample. The addition of more anhydrous potassium fluoride goes to remove any remaining silicates from the sample.

14. Add 2 g anhydrous sodium sulfate and continue to gently heat with the blast burner until a clear fusion is obtained.
15. Remove the platinum dish from the heat and wait for the sample to solidify.
16. When the sample has become a solid pyrosulfate cake place the platinum dish in a pan of cool water and let

the sample cool to room temperature.

17. Break the cooled sample by gently flexing the sides of the platinum dish and place the sample in a 100 ml beaker.

Two grams of anhydrous sodium sulfate is added to the sample and heated with a blast burner until a clear fusion is formed. The sample is allowed to cool to room temperature which forms a pyrosulfate cake.

18. Add three small chips of carborundum to the 100 ml beaker.
19. Pour 35 ml of boiling 2M hydrochloric acid in the platinum dish and then pour it into the 100 ml beaker.
20. Heat the solution to boiling over a flame produced by the blast burner. (NOTE: Swirl the solution to keep the beaker from breaking.)
21. Remove the 100 ml beaker from the flame.
22. Cover the 100 ml beaker with a watch glass and boil on a hotplate for approximately 3 minutes.
23. Add 5 drops of 25 % ammonium iron (II) sulfate hexahydrate.
24. Begin reheating the solution to boiling with blast burner.

The addition of thirty-five milliliters of boiling 2M hydrochloric acid keeps the calcium sulfate in solution.

25. Add 1 ml of seeding suspension.
26. Add 1 ml of 0.45 percent barium chloride dropwise to

the solution as it is being heated and swirl the solution after the addition of the barium chloride. Heat the sample to boiling.

27. Repeat step 26 three more times.

A seeding suspension which consists of 0.45 percent barium chloride dihydrate, anhydrous potassium sulfate and 18M sulfuric acid is added to the sample. The 0.45 percent barium chloride dihydrate and the anhydrous potassium sulfate provide barium and sulfate for the barium sulfate coprecipitation respectively. The barium sulfate coprecipitation removes the thorium from the sample since thorium would act as an interferant. Three milliliters of 0.45 percent barium sulfate solution is added to the sample one milliliter at a time to start the barium sulfate coprecipitation.

28. Keep a beaker half full with boiling water, to be used in the centrifuge tubes.
29. Transfer the solution to four 10 ml centrifuge tubes.
30. Centrifuge for 2 minutes. Stop the centrifuge as quickly as possible.
31. Pour the top liquid from each of the centrifuge tubes into a beaker and wash the walls of each tube with water.
32. Add 4 ml of water to each centrifuge tube and repeat steps 30-31.

The sample is transferred to centrifuging tubes and

centrifuged. The purpose of centrifuging the sample is to remove all the coprecipitants from the sample since thorium is a coprecipitant (see appendix E for more details). The washing of the centrifuge tube walls and repeated centrifuging of the sample is to insure all the coprecipitants are removed from the sample.

33. Wash the barium sulfate precipitant out of the centrifuge tubes with water and pour into a 250 ml beaker to be discarded.
34. Evaporate the supernate in the beaker to near dryness.
35. Pour 35 ml of boiling 2M hydrochloric acid in the platinum dish and then pour it into the 100 ml beaker.
36. Heat the solution to boiling over a flame produced by the blast burner. (NOTE: Swirl the solution to keep the beaker from breaking.)
37. Remove the 100 ml beaker from the flame.
38. Cover the 100 ml beaker with a watch glass and boil on a hotplate for approximately 3 minutes.
39. Add 400μl of 20 percent titanium trichloride. The titanium trichloride reduces the uranium.
40. Begin reheating the solution to boiling with blast burner.

The addition of thirty-five milliliters of boiling 2M hydrochloric acid keeps the calcium sulfate in solution.

41. Add 1 ml of seeding suspension.
42. Add 1 ml of 0.45 percent barium chloride dropwise to

the solution as it is being heated and swirl the solution after the addition of the barium chloride. Heat the sample to boiling.

43. Repeat step 42 three more times.

A seeding suspension which consists of 0.45 percent barium chloride dihydrate, anhydrous potassium sulfate and 18M sulfuric acid is added to the sample. The 0.45 percent barium chloride dihydrate and the anhydrous potassium sulfate provide barium and sulfate for the barium sulfate coprecipitation respectively. Three milliliters of 0.45 percent barium sulfate solution is added to the sample one milliliter at a time to start the barium sulfate coprecipitation.

44. Keep a beaker half full with boiling water, to be used in the centrifuge tubes.
45. Transfer the solution to four 10 ml centrifuge tubes.
46. Centrifuge for 2 minutes. Stop the centrifuge as quickly as possible.
47. Pour the top liquid from each of the centrifuge tubes into a beaker to be discarded and wash the walls of each tube with water.
48. Add 4 ml of water to each centrifuge tube and repeat steps 46-47.
50. Add 6 ml of 0.05M KEDTA to the 250 ml beaker and swirl.
51. Place the 250 ml beaker in a beaker of boiling water

for 3 minutes.

52. Add 1 drop of 10M potassium hydroxide and 1 drop of 20 percent titanium trichloride.
53. Add 2 ml of 10M potassium hydroxide to the 250 ml beaker and swirl.
54. Heat the 250 ml beaker in the hot water bath for 5 minutes.
55. Remove the solution from the hot water bath and let cool.
56. Centrifuge the solution for 5 minutes.
57. Remove the top liquid and discard.
58. Wash the walls of the centrifuge tube with water.
59. Add 0.5 ml of 0.25M potassium hydroxide and stir with a stirring rod.
60. Wash the stirring rod with 5 ml of 0.25M potassium hydroxide.
61. Swirl the centrifuge tube to resuspend the precipitate.
62. Centrifuge the solution for 5 minutes.
63. Remove the top liquid and discard.

Precipitating the hydroxides is the next process in this procedure. The hydroxide precipitation is accomplished by executing the following steps. The addition of 0.05 KEDTA, 10M potassium hydroxide, and 20 percent titanium trichloride to the solid sample while heating it. The sample must also be centrifuged. The resulting precipitants are cerium hydroxide, titanium hydroxide, and uranium

hydroxide.

64. Wash the walls of the centrifuge tube with water.

65. Add 0.5 ml of hydrochloric acid to the centrifuge tube.

66. Dilute with 2 ml of water.

67. Centrifuge the solution for 5 minutes.

68. Pour the top liquid into a 250 ml beaker.

The uranium needs to be put back into solution. This can be done with the addition of 12M hydrochloric acid. The 12M hydrochloric acid complexes the uranium.

69. Add 0.5 ml 12M hydrochloric acid and 5 ml of water.

70. Add excess 20 percent titanium trichloride.

71. Add 1 ml of lanthanum carrier

72. Add 1 ml of 29M hydrofluoric acid.

73. Filter sample through membrane filter using suction.

74. Remove clamp and top of filter with suction on and allow the membrane to dry.

75. Mount membrane on holding paper and count sample for forty-eight hours.

The uranium needs to be put into a form which will allow the alpha particles to escape from the surface of the sample. The way this is accomplished is with adsorption precipitation. Before adsorption precipitation can occur the UO_2^{+2} must be reduced to U^{+4} which is easily achieved with the addition of titanium trichloride to the sample solution. The adsorption precipitation is obtained when the lanthanum carrier and 3M hydrofluoric acid is added to the solution.

If white precipitants can be seen, then either too much uranium is present in the sample to count which might contaminate the surface barrier detector or too much lanthanum is present which leads to self-adsorption of the alpha particles.

CHAPTER V

RESULTS AND CONCLUSIONS

5.1 The Soil Samples

Three different soil samples and a blank spike of ^{232}U were processed with both procedures. The samples came from Fernald and were part of a blind test in which the samples were sent to laboratories around the country. The results were compiled by Dr. L. F. Miller (Personal Communications). The samples are identified with the numbers 7941, 7354, 7100. Samples 7941, 7354, and 7100 were each prepared in the following way for the EPA procedure. Approximately five grams of the soil sample was weighed and then ashed. From the ashed sample an aliquot of approximately one gram was prepared with the EPA procedure. From the same soil samples (not the ashed sample) an aliquot of approximately one gram of soil was prepared with the potassium fluoride fusion procedure.

5.2 Data from the EPA Procedure

Figures 5.1-5.6 show the alpha spectra for the samples prepared with the EPA procedure. These prepared samples were counted for 48 hours. Sample 7100 was ran three times with the EPA procedure, so the samples have been labeled 7100a, 7100b, and 7100c. Data taken from the spectra are

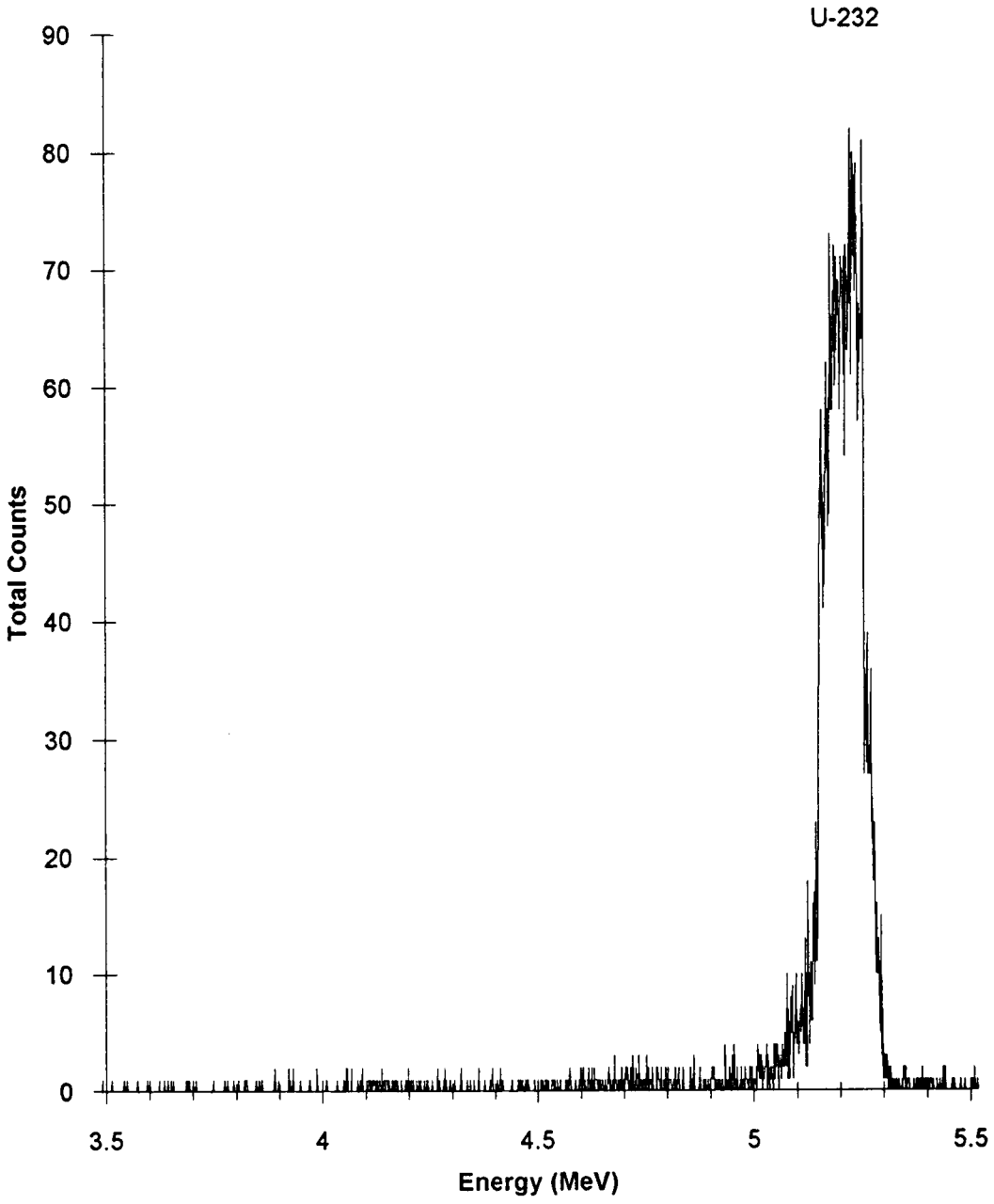


Figure 5.1 Blank spike with 19.86 dpm of ^{232}U processed by the EPA procedure.

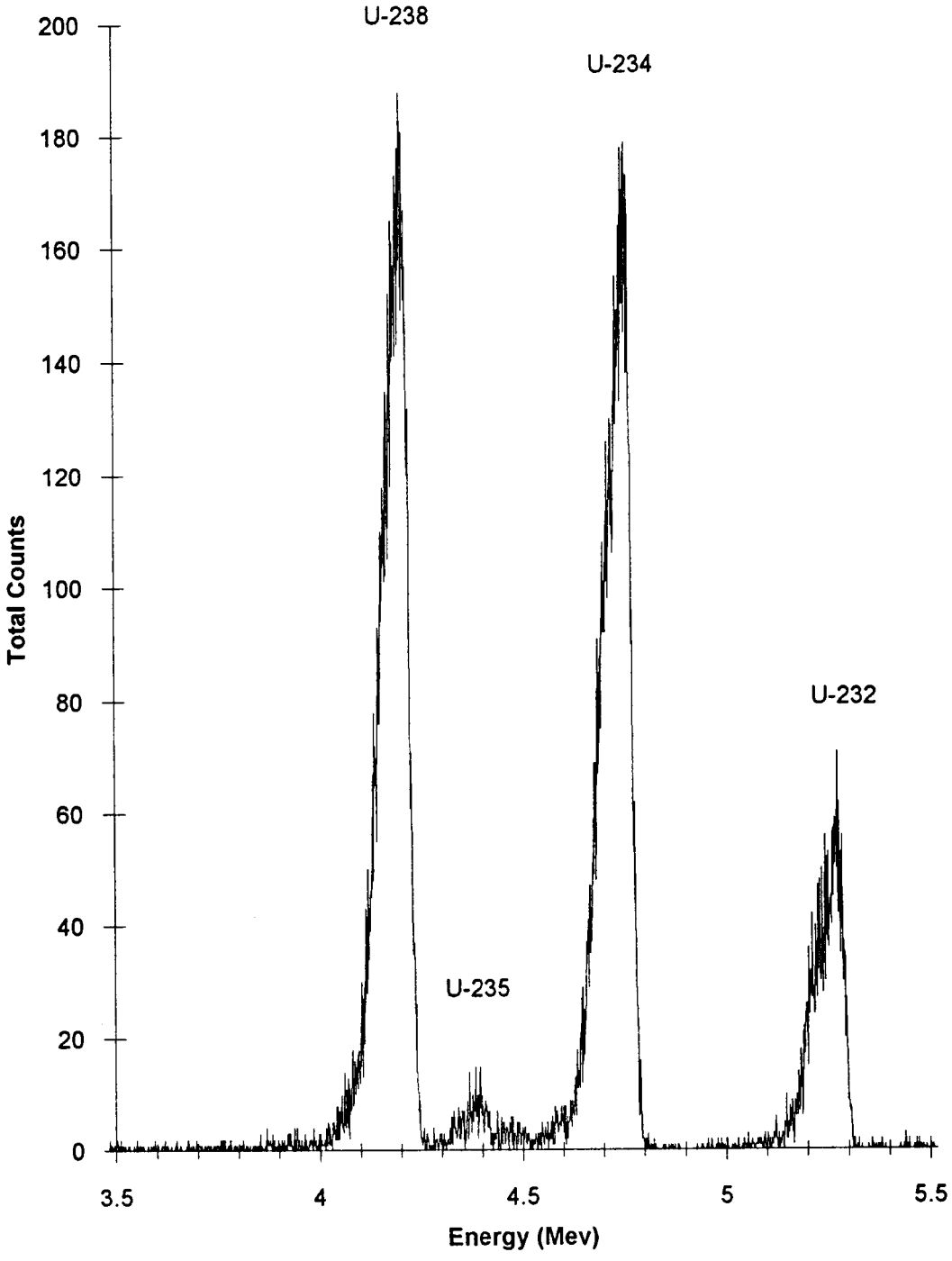


Figure 5.2 Soil sample 7100a spiked with 19.86 dpm of ^{232}U processed by the EPA procedure.

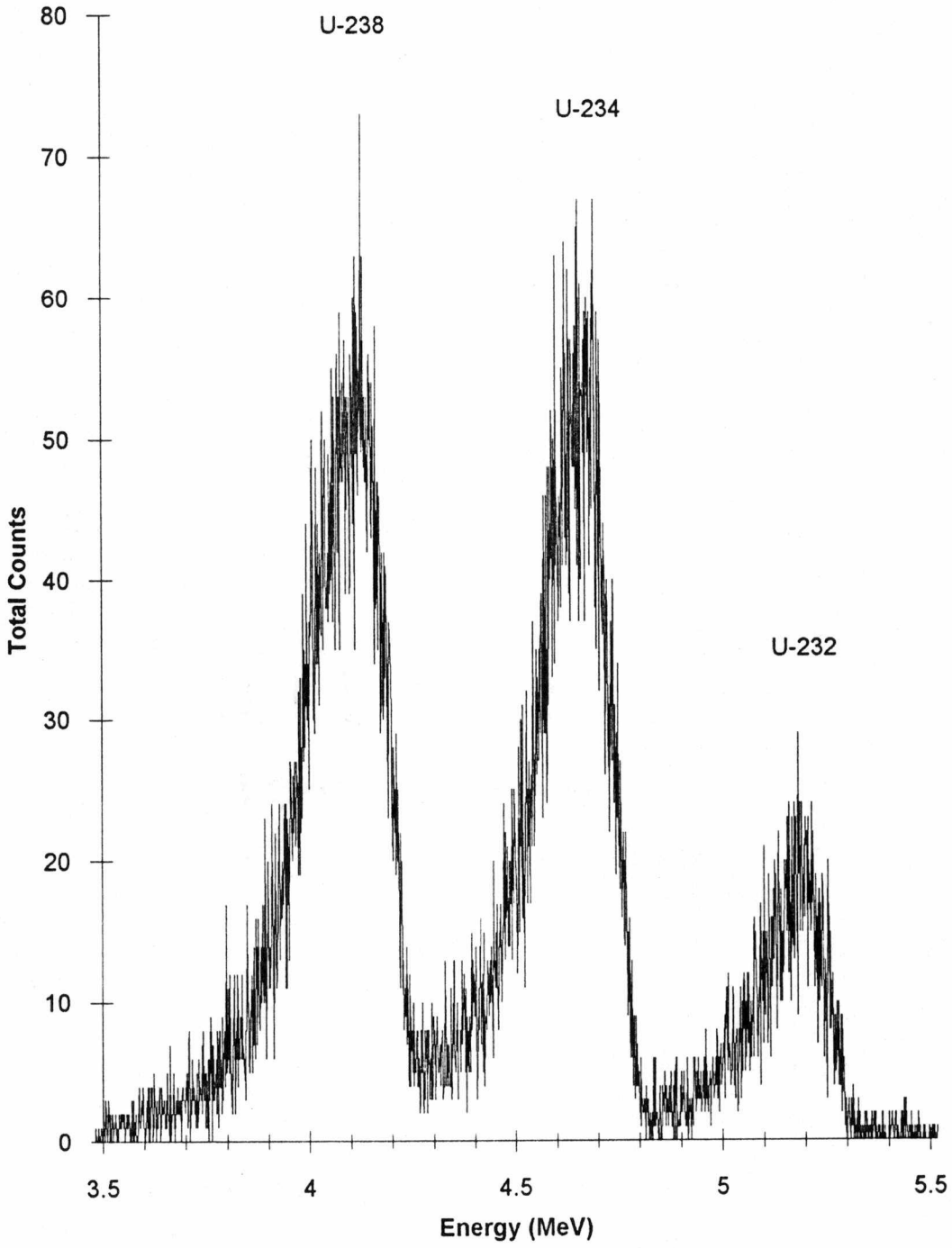


Figure 5.3 Soil sample 7100b spiked with 19.86 dpm of ^{232}U processed by the EPA procedure.

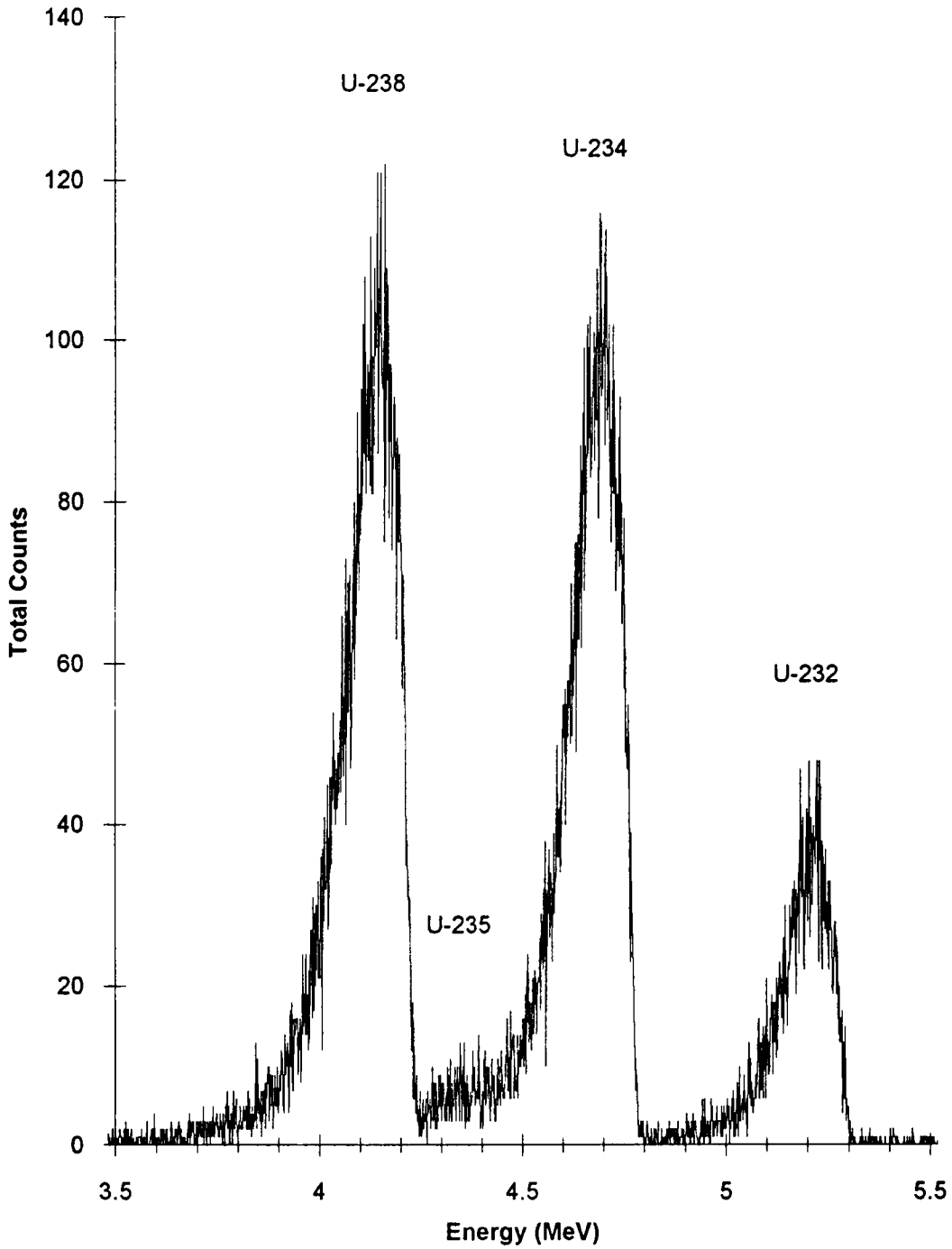


Figure 5.4 Soil sample 7100c spiked with 19.86 dpm of ^{232}U processed by the EPA procedure.

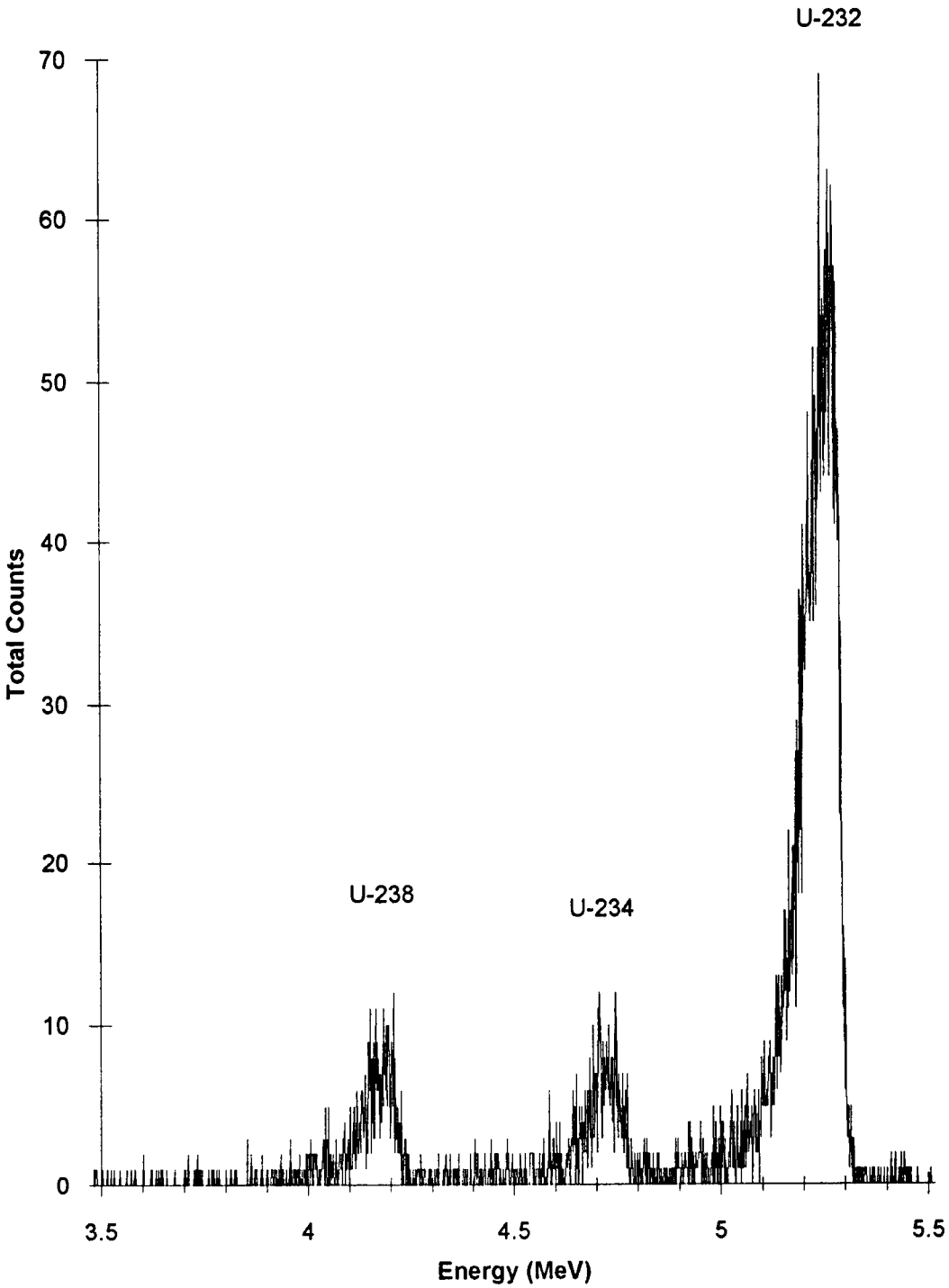


Figure 5.5 Soil sample 7941 spiked with 19.86 dpm of ^{232}U processed by the EPA procedure.

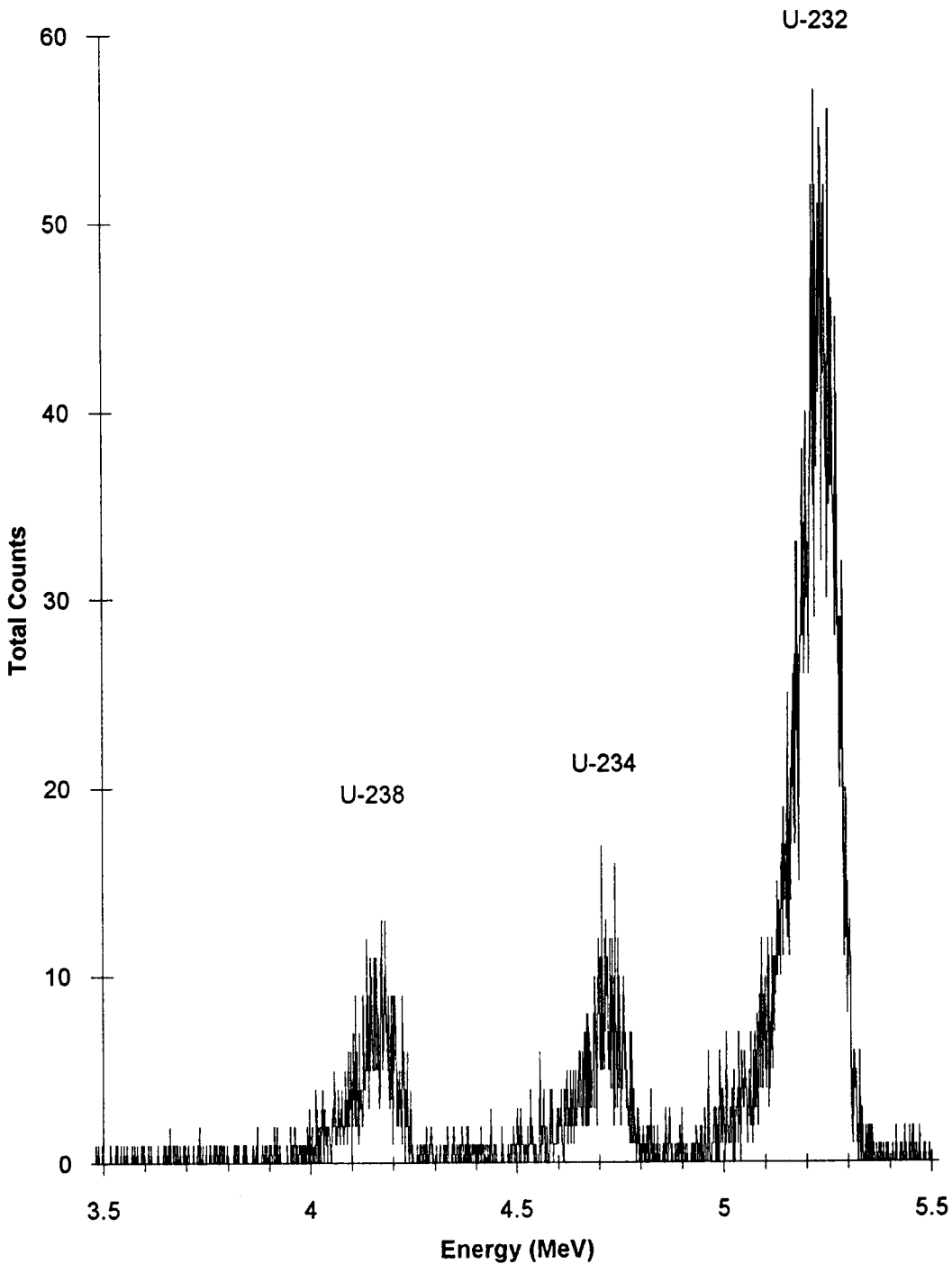


Figure 5.6 Soil sample 7354 spiked with 19.86 dpm of ^{232}U processed with the EPA procedure.

given in Table 5.1. In Table 5.2 the preashed weight of the soil, postashed weight of the soil, percentage of weight retained (Equation 5.1), aliquot of ashed sample, and aliquot of soil sample (Equation 5.2) is given.

$$\%WeightRetained=\frac{PostashedWeight}{PreashedWeight} \qquad (5.1)$$

$$AliquotofSoilSample=\frac{AliquotofAshedSample}{\%WeightRetained} \qquad (5.2)$$

5.3 Data from the Potassium Fluoride Fusion Procedure

Figures 5.7-5.10 show the alpha spectra for the soil samples prepared with the potassium fluoride fusion procedure. These prepared samples were counted for 24 hours. The blank spike processed with the potassium fluoride fusion procedure was 9.93 dpm of ^{232}U and one gram of iron(III) sulfate. Data taken from the spectra is given in table 5.3. In Table 5.4 the weight of each sample prepared with the potassium fluoride fusion procedure is given.

Table 5.1 Spectra Data from EPA Procedure(Total Counts)

Sample	Area Under ^{232}U Peak	Area Under ^{234}U Peak	Area Under ^{235}U Peak	Area Under ^{238}U Peak
Blank	6988±84	---	---	---
7100a	3896±63	11353±107	737±28	11555±108
7100b	3395±59	10122±101	---	11250±107
7100c	4850±70	13450±116	825±29	14847±122
7941	5099±72	756±28	---	709±27
7354	4984±71	976±32	---	883±30

Table 5.2 EPA Sample Weights

Sample	Preashed Weight g	Postashed Weight g	% Weight Retained	Aliquot Ashed Sample g	Aliquot Soil Sample g
7100a	5.07	4.40	86.8%	1.02	1.18
7100b	5.07	4.40	86.8%	1.04	1.20
7100c	1.10	---	---	---	---
7941	2.51	2.13	84.9%	1.02	1.20
7354	5.03	4.15	82.5%	1.00	1.21

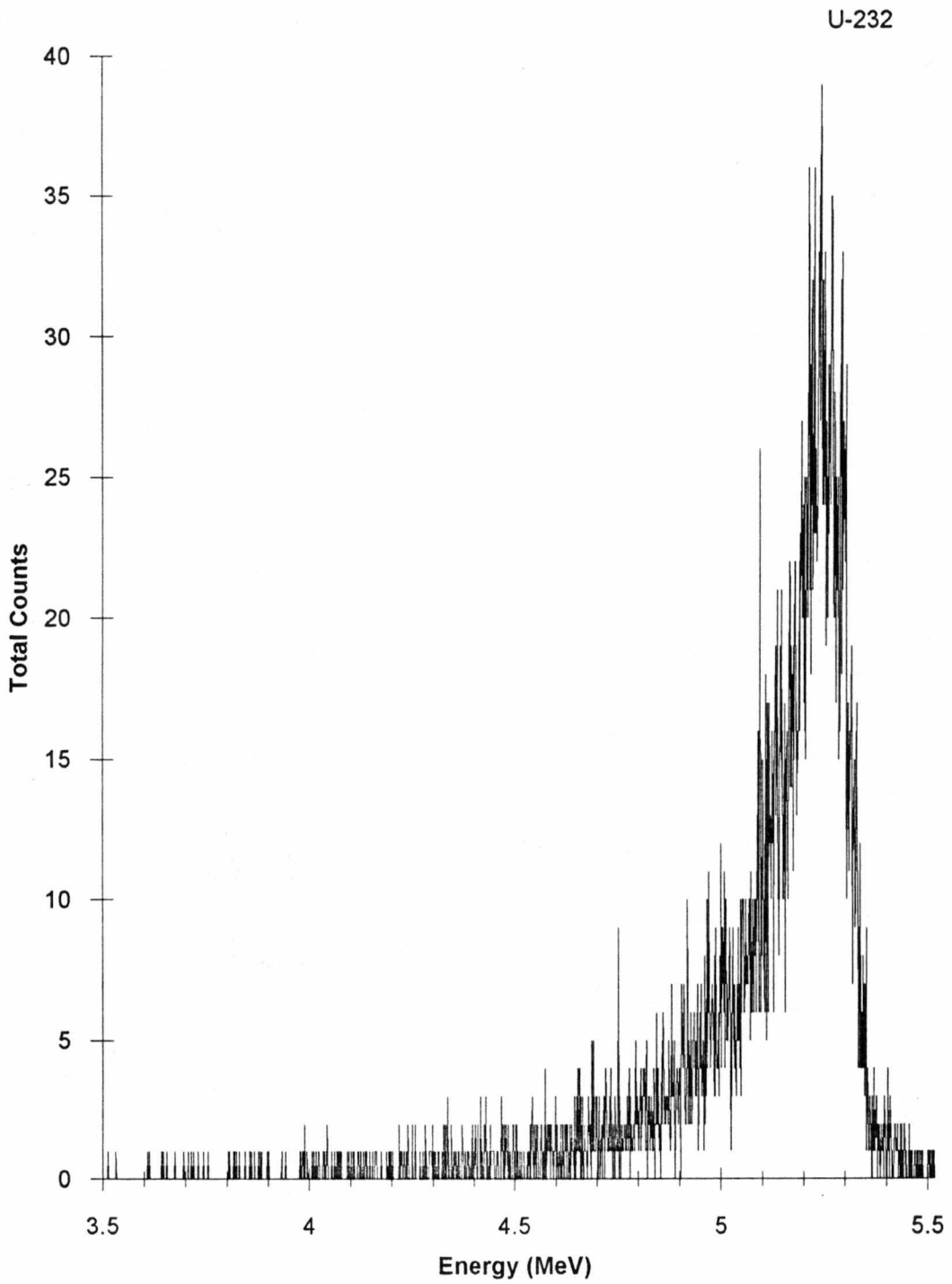


Figure 5.7 Blank spike with 9.93 dpm of ^{232}U processed by the potassium fluoride fusion procedure.

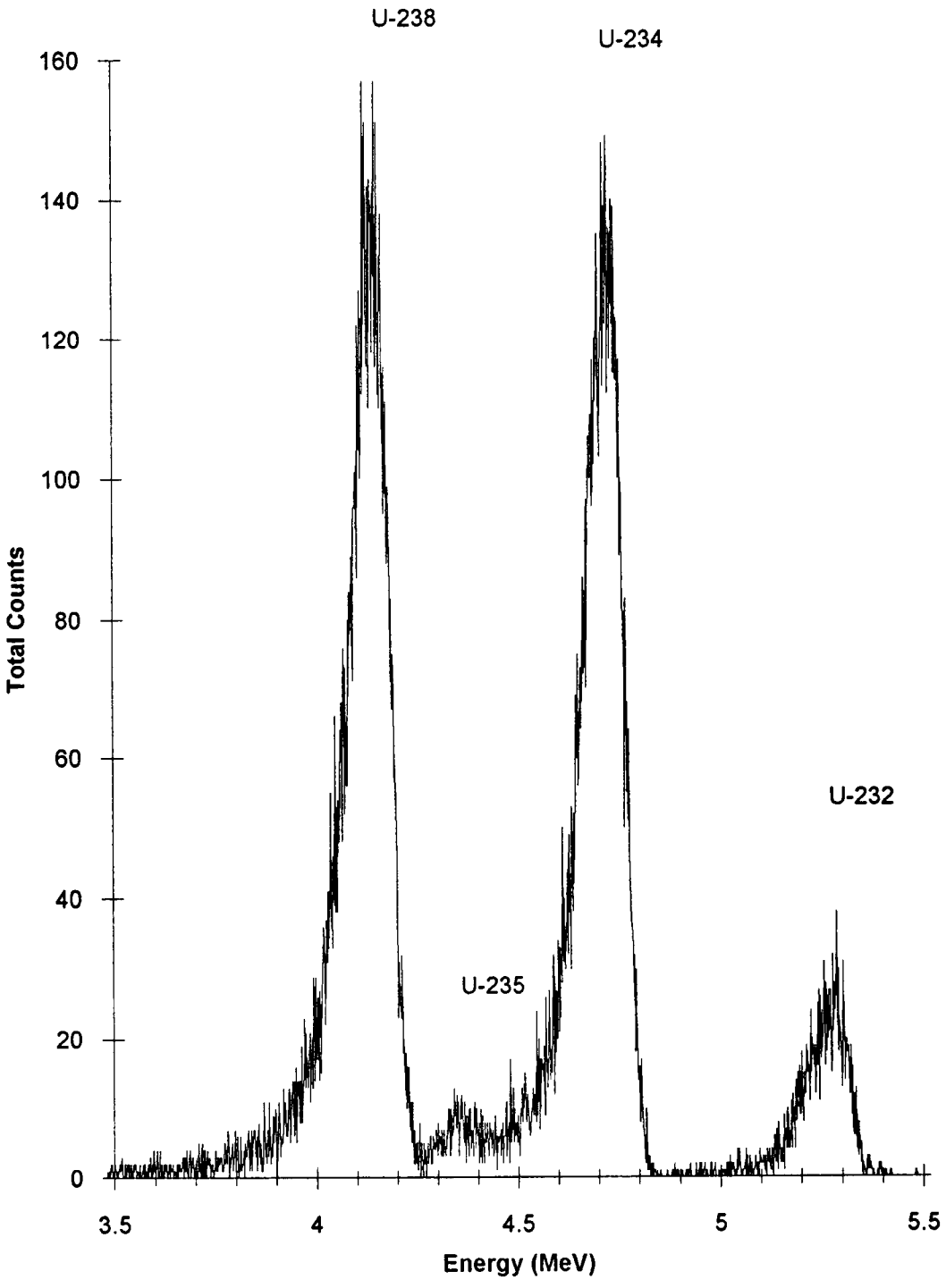


Figure 5.8 Soil sample 7100 spiked with 9.93 dpm of ^{232}U processed by the potassium fluoride fusion.

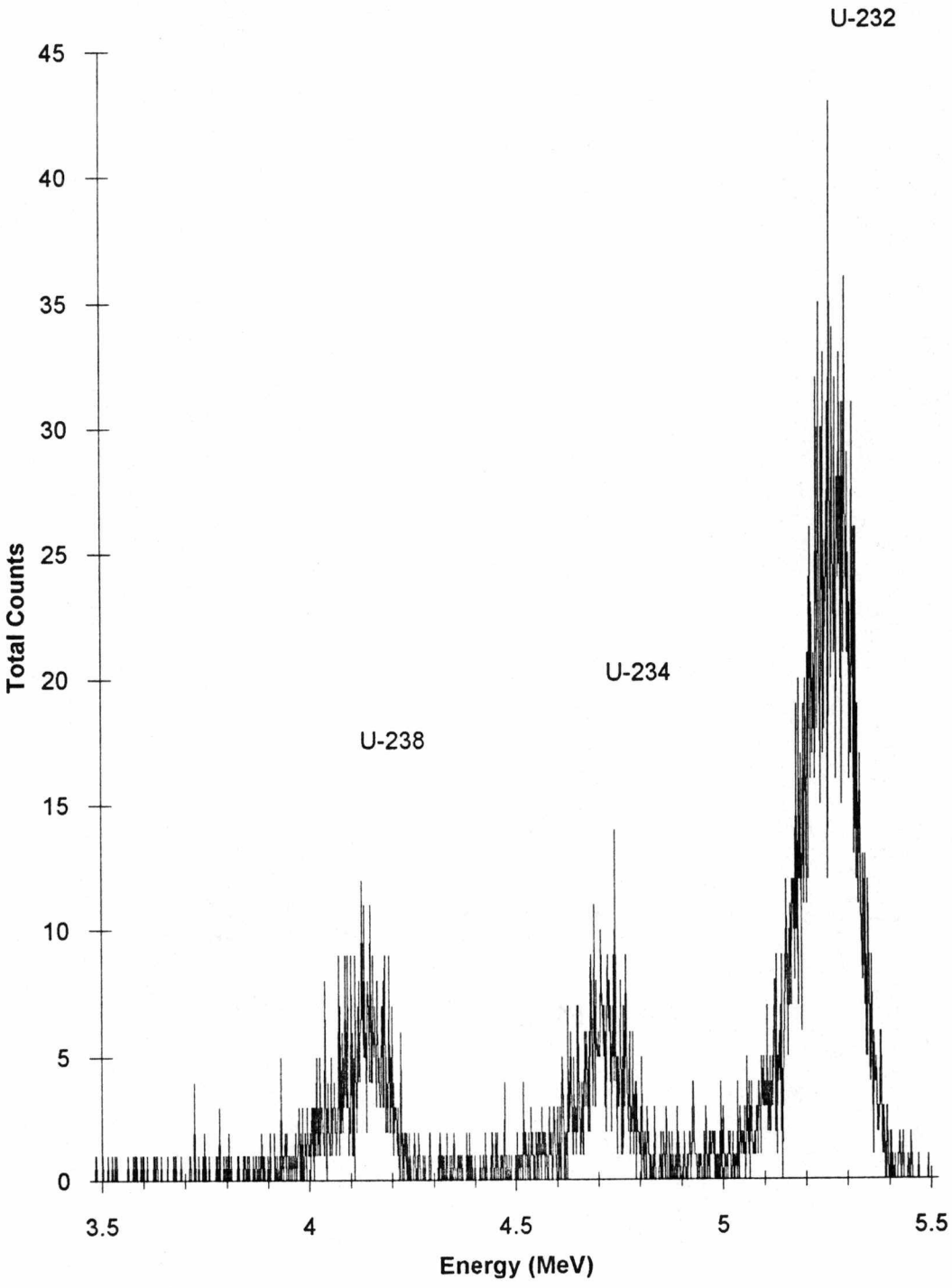


Figure 5.9 Soil sample 7941 spiked with 9.93 dpm of ^{232}U processed by the potassium fluoride fusion procedure.

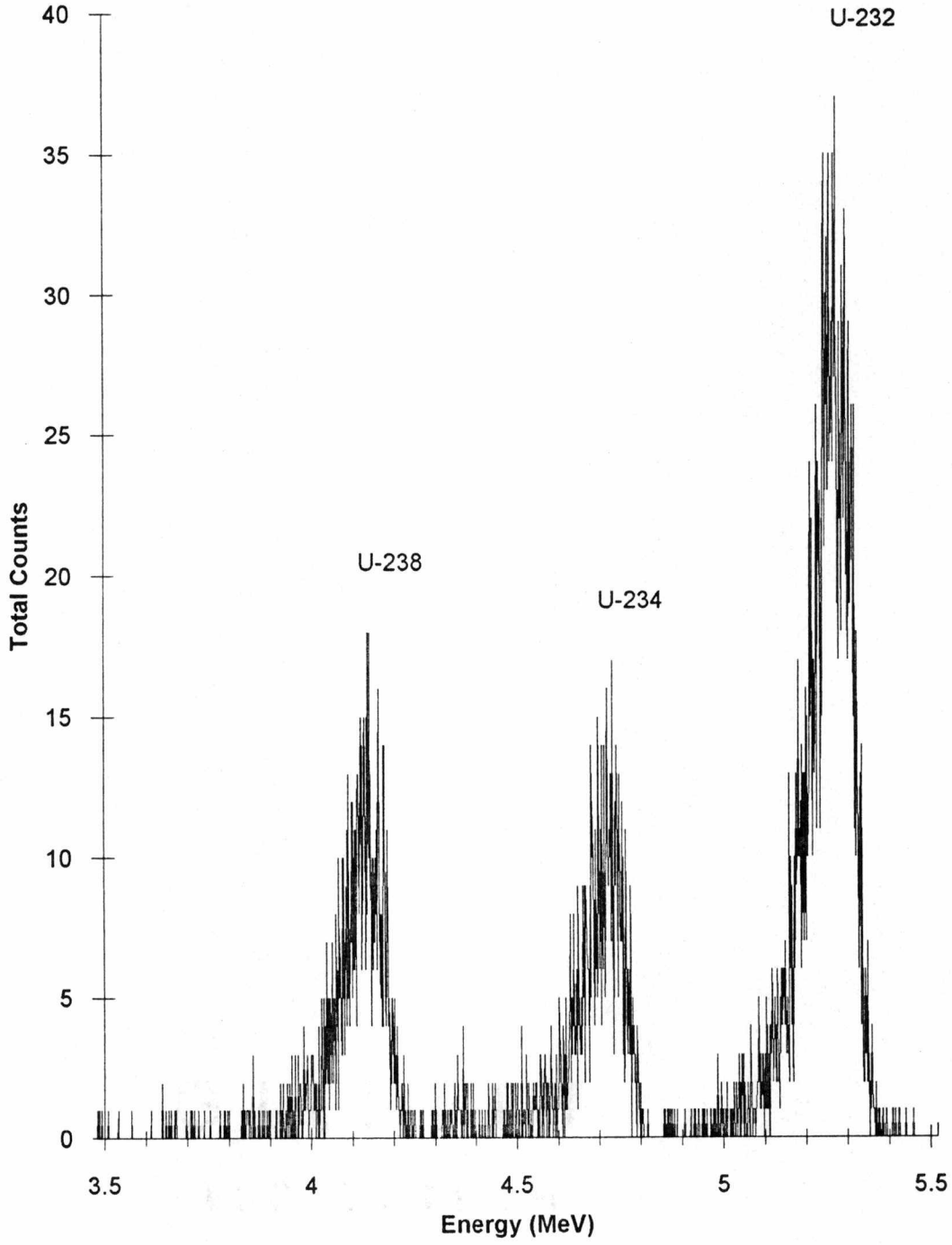


Figure 5.10 Soil sample 7354 spiked with 9.93 dpm of ^{232}U processed by the potassium fluoride fusion procedure.

Table 5.3 Spectra Data from Potassium Fluoride Fusion Procedure(Total Counts)

Sample	Area Under ^{232}U Peak	Area Under ^{234}U Peak	Area Under ^{235}U Peak	Area Under ^{238}U Peak
Blank	3768±62	---	---	---
7100	2526±51	13513±117	822±29	14607±121
7941	3370±59	768±28	---	819±29
7354	2850±54	1059±33	---	1145±34

Table 5.4 Potassium Fluoride Fusion Sample Weights

Sample	Weight of Soil
7100	1.06 g
7941	1.03 g
7354	1.01 g

5.4 Data Analysis

The amount of uranium recovered for both procedures is given in Table 5.5. These values given were computed with equation 2.2 from chapter II.

Table 5.5 Uranium Recoveries

Sample	EPA Procedure	Potassium Fluoride Fusion Procedure
Blank	76%	98%
7100	---	66%
7100a	43%	---
7100b	37%	---
7100c	53%	---
7941	56%	87%
7354	54%	74%

The sample activities for both the EPA procedure and the potassium fluoride fusion procedure were calculated with equation 2.4 from chapter II. The results are given in Tables 5.6 and 5.7.

The activities of each sample was normalized to one gram of soil. This was accomplished by dividing the activities given in Tables 5.6 and 5.7 by the amount of soil process by that particular procedure. The normalized sample

Table 5.6 Sample Activities for EPA Procedure

Sample	^{234}U (dpm)	^{235}U (dpm)	^{238}U (dpm)
Blank	---	---	---
7100a	57.9	3.8	58.9
7100b	59.2	---	65.8
7100c	55.1	3.4	60.8
7941	2.9	---	2.8
7354	3.9	---	3.6

Table 5.7 Sample Activities for Potassium Fluoride Fusion Procedure

Sample	^{234}U (dpm)	^{235}U (dpm)	^{238}U (dpm)
Blank	---	---	---
7100	57.4	3.2	53.1
7941	2.3	---	2.4
7354	4.0	---	3.7

activities is given in Tables 5.8 and 5.9. The uncertainty in the normalized sample activities was calculated with equation 2.8 from chapter II. The results from the blind test for the same soil samples are given in Table 5.10. In the Lab column of Table 5.10 RESL is the Radiological Environmental Science Laboratory and ITRSL is the International Technology Corp. Radiological Science Laboratory.

5.5 Conclusions and Recommendations

The normalized activities for ^{234}U, ^{235}U and ^{238}U are statistically no different for the soil samples for both the EPA and potassium fluoride fusion procedures. Therefore the EPA and potassium fluoride fusion procedures are statistically the same for these soil samples. The advantage the potassium fluoride fusion procedure has over the EPA procedure is that it is muck quicker than the EPA procedure

The results from the EPA procedure and the potassium fluoride fusion procedure are statistically no different from the results of the blind test. This is a good check for the results obtained in this research since the laboratories involved in the blind test are top laboratories in the United States.

Table 5.8 Normalized Sample Activities for EPA Procedure

Sample	^{234}U (dpm/g)	^{235}U (dpm/g)	^{238}U (dpm/g)
Blank	---	---	---
7100a	49.1±2.5	3.3±0.2	49.9±2.5
7100b	49.3±2.5	---	54.8±2.8
7100c	50.1±2.6	3.1±0.2	55.3±2.8
7941	2.5±0.2	---	2.4±0.2
7354	3.3±0.2	---	3.0±0.2

Table 5.9 Normalized Sample Activities for Potassium Fluoride Fusion Procedure

Sample	^{234}U (dpm/g)	^{235}U (dpm/g)	^{238}U (dpm/g)
Blank	---	---	---
7100	50.1±2.6	3.1±0.2	54.2±2.8
7941	2.2±0.2	---	2.3±0.2
7354	3.7±0.3	---	4.0±0.3

Table 5.10 Results from Other Laboratories

Sample	Lab	^{234}U(dpm)	^{235}U(dpm)	^{238}U(dpm)
7100	RESL	57.5	2.6	59.5
7100	ITRSL	66.2	0.9	85.9
7941	RESL	2.6	---	2.9
7941	ITRSL	2.4	---	3.9
7941	ITRSL	3.2	---	2.2
7354	RESL	3.3	---	3.7
7354	ITRSL	1.8	---	2.9

BIBLIOGRAPHY

BIBLIOGRAPHY

Knoll, Glenn F. Radiation Detection and Measurement. 2nd edition. New York: John Wiley & Sons, Inc., 1979, 1989.

Miller, L.F. Personal Communication.

Sill, Claude W. "Determination of Gross Alpha, Plutonium, Neptunium, and/or Uranium by Gross Alpha Counting on Barium Sulfate." Analytical Chemistry Vol. 52, No. 9 (1980): 1452-1459.

---. "Determination of Radium-226 in ores, Nuclear Wastes and Environmental Samples by High-Resolution Alpha Spectrometry." Nuclear and Chemical Waste Management Vol. 7 (1987): 239-256.

---. "Determination of Thorium and Uranium Isotopes in Ores and Mill Tailings by Alpha Spectrometry." Analytical Chemistry Vol. 49, No. 4 (1977): 618-621.

---. "Precipitation of Actinides as Fluorides or Hydroxides for High-Resolution Alpha Spectrometry." Nuclear and Chemical Waste Management Vol. 7 (1987): 201-215.

Sill, Claude W., and Sill, David S. "Determination of Actinides in Nuclear Wastes and Reference Materials for Ores and Mill Tailings." Waste Management Vol. 9 (1989): 219-229.

United States. Environmental Protection Agency. Radiochemical Determination of Thorium and Uranium in Ashed Samples. n.d.

APPENDICES

APPENDIX A

RADIOACTIVE CONTAMINATION SURVEY PROCEDURES

The chemical extraction of the uranium from the soil samples was done in room 203 of Pasqua Engineering Building. The activities involved in extracting the uranium from the soil was restricted to two main locations in that room. The first location was inside the hood and the second location was the area designated as the "work station" on the diagram of room 203 Pasqua.

The alpha spectroscopy done on the prepared samples was done in room 201 of Pasqua. The alpha counting activities of prepared soil samples was restricted to the alpha counting chamber of the Tennelec TC 256 alpha counting system.

During periods of active research in rooms 201 and 203 of the Pasqua building radioactive contamination surveys were conducted on a daily basis. These surveys were two fold; first a Geiger counter was used to survey the laboratory followed by a swipe survey of the laboratory. The results of the surveys were recorded and kept.

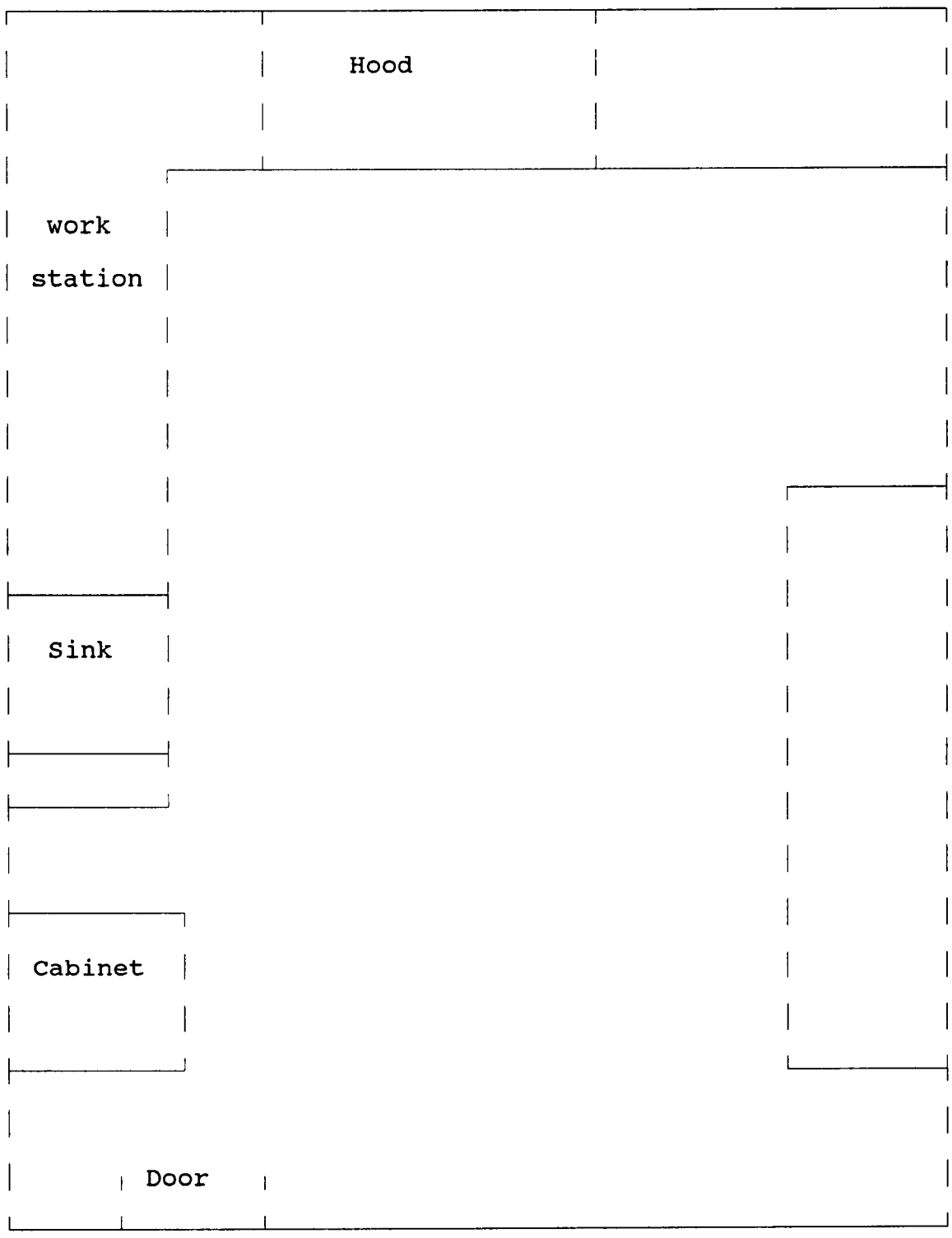
The Geiger counter surveys included the following areas: 1) the hood 2) the floor in front of the hood 3)the "work station" 4) the floor in front of the "work station" 5) the area around the alpha spectroscopy equipment and 6)

any potentially contaminated area. All research personnel frisked their hands and shoes each time they left the research area with the Geiger counter. Any time research personnel removed an item from the research area the item was surveyed with the Geiger counter and a swipe of the item was also be counted.

The swipe survey included the following areas: 1) the inside of the hood 2) the inside of the hood glass 3) the lip of the hood 4) the floor in front of the hood 5) the "work station" 6) the floor in front of the "work station" 7) the door knob to room 203 8) the door knob to room 201 9) the area around the alpha spectroscopy equipment 10) any potentially contaminated area. The swipes never covered an area of more than 100 square centimeters and was counted on the LSC in room 201 of Pasqua for one minute each. Any swipe with a count greater than 200 dpm will be decontaminated.

During research activities personnel working with radioactive material in room 203 of Pasqua wore latex gloves, laboratory coats, and eye protection at all times. When research personnel left room 203 of Pasqua, their latex gloves were removed and disposed of in the radioactive disposal drum and the laboratory coats and eye protection were removed before they left the area. Latex gloves were worn any time a radioactive source was being handled in room 201 of Pasqua.

Diagram of Pasqua 203



APPENDIX B

EPA PROCEDURE

B.1 Reagents and Reagent Preparation

1. Crystalline ascorbic acid.
2. 12M hydrochloric acid (37 percent HCl).
3. 9M hydrochloric acid. Dilute 750 ml of 12M hydrochloric acid to 1 liter.
4. 1M hydrochloric acid. Dilute 83 ml of 12M hydrochloric acid to 1 liter.
5. 29M hydrofluoric acid (48 percent HF).
6. 3M hydrofluoric acid. Dilute 104 ml of 29M hydrofluoric acid to 1 liter in a plastic graduated cylinder. Store in a plastic bottle.
7. Nickel Foil.
8. 16M nitric acid (70 percent HNO_3).
9. 0.1M nitric acid. Dilute 6 ml of 16M nitric acid to 1 liter.
10. 12M perchloric acid (70 percent $HClO_4$).
11. Lanthanum carrier, 0.1 mg La^{+3}/ml. Dissolve 0.0779 g $La(NO_3)\bullet 6H_2O$ per 250 ml 1M hydrochloric acid.
12. 20 percent reagent grade titanium trichloride.
13. Triisooctylamine (TIOA).
14. P-xylene.
15. 10 percent TIOA in p-xylene. Dilute 100 ml of TIOA to

1 liter with p-xylene.

16. ^{232}U tracer solution 19.86 dpm/ml.

B.2 Sample Preparation

1. Place 5 g of soil sample in ceramic dish for ashing.
2. Ash in muffle furnace, gradually raise the temperature to 550°C and maintain for seventy-two hours.
3. Weigh 1 g of ashed sample and place in a teflon beaker. Add 1 ml of ^{232}U tracer.
4. Add 20 ml of 29M hydrofluoric acid to the sample and evaporate to dryness. Repeat once.
5. Add 5 ml each of 12M perchloric acid and 9M hydrochloric acid to the sample; evaporate to dryness. Repeat once.
6. Add 10 ml of 12M hydrochloric acid to sample and transfer to a 600 ml glass beaker; evaporate to dryness. Repeat once.
7. Add 300 ml of 9M hydrochloric acid to sample to dissolve it and heat to 50°C.
8. Place 50 ml of 9M hydrochloric acid and 100 ml of 10 percent TIOA in 1 liter separatory funnel. Shake well. Wait for separation of phases and discard lower aqueous acid phase.
9. Add sample to the separatory funnel and shake well for two minutes. Vent the funnel to prevent pressure build up.

10. Allow phases to separate. Drain off lower aqueous acid phase and discard it.
11. Add 50 ml of 9M hydrochloric acid to the aqueous sample in the funnel and shake well.
12. Allow phases to separate. Drain off lower aqueous acid phase and discard it.
13. Repeat steps 11 and 12.
14. Add 100 ml of 0.1M nitric acid to the separatory funnel and shake well for two minutes. This strips the uranium from the TIOA.
15. Allow phases to separate. Drain off lower aqueous acid phase and save.
16. Repeat steps 14 and 15. Combine the saved solutions which are now refereed to as the sample solution.
17. Place the sample solution in a clean separatory funnel.
18. Add 100 ml of p-xylene to the sample solution and shake well. This will remove any remaining TIOA.
19. Allow phases to separate. Drain off lower aqueous acid phase into a beaker and save. Discard remaining p-xylene.
20. Evaporate the sample solution to dryness but do not over heat.
21. Add 100 ml of 16M nitric acid to the sample and evaporate to dryness. Do not over heat.
22. Add 5 ml each of 9M hydrochloric acid and 12M perchloric acid to the sample and evaporate to dryness.

Repeat once.

23. Add 10 ml of 12M hydrochloric acid to sample and evaporate to dryness. Repeat once.
24. Add 50 ml of 1M hydrochloric acid to sample and warm to dissolve sample residue.
25. Heat the sample solution to 80°C while stirring and add 50 mg of ascorbic acid. Do not over heat.
26. Suspend nickel strip in solution for two hours to remove polonium.
27. Remove nickel strip and evaporate sample solution to dryness.
28. Add 15 ml of 1M hydrochloric acid to sample solution and heat to 50°C.
29. Add ascorbic acid to the sample solution until the yellow color disappears; this reduces the iron in the sample solution.
30. Reduce the uranium by adding 200 μl of 20 percent titanium trichloride.
31. Add 1 ml of lanthanum carrier and 5 ml of 3M hydrofluoric acid. Mix well and set aside for half an hour to precipitate LaF_3 carrying uranium.
32. Filter sample through membrane filter using suction.
33. Rinse sample beaker with 10 ml of water and filter the water. Rinse sample beaker with ethanol and filter the ethanol.
34. Remove clamp and top of filter with suction on and

allow the membrane to dry.

35. Mount membrane on holding paper and count sample for forty-eight hours.

APPENDIX C

POTASSIUM FLUORIDE FUSION PROCEDURE

C.1 Reagents and Reagent Preparation

1. Anhydrous potassium fluoride.
2. Potassium hydrogen fluoride.
3. Potassium nitrate.
4. Mixed flux is prepared in the following way.
    a. Weigh 100 g of anhydrous potassium fluoride and place in a mixing container.
    b. Weigh 70 g of potassium hydrogen fluoride and place in mixing container.
    c. Weigh 2 g of potassium nitrate and place in mixing container.
    d. Mix ingredients completely and place in storage container.
5. 0.45 percent barium chloride dihydrate. Dissolve 0.45 g of barium chloride dihydrate in 100 ml of water.
6. Anhydrous potassium sulfate.
7. Concentrated sulfuric acid.
8. ^{232}U tracer solution 5 to 30 dpm/ml.
9. Seeding suspension which is prepared in the following way.
    a. Add 50 ml of 0.45 percent barium chloride dihydrate, 12 g of anhydrous potassium

sulfate, and 6 ml of concentrated sulfuric acid to a 250 ml Erlenmeyer flask.

b. Evaporate the solution until the barium sulfate just redissolves. Do not allow much of the sulfuric acid to evaporate.

c. Cool the flask.

d. Add 80 ml of water.

e. Heat the solution to boiling.

f. After cake dissolves cool the flask to room temperature and dilute to 100 ml.

g. Shake solution thoroughly before each use.

10. 12M hydrochloric acid (37 percent HCl).

11. 2M hydrochloric acid. Dilute 167 ml of 12M hydrochloric acid to 1 liter.

12. Carborundum.

13. Ammonium iron (II) sulfate hexahydrate.

14. 0.05M EDTA.

15. Potassium hydroxide.

16. 20 percent titanium trichloride.

17. 10M potassium hydroxide which is prepared in the following way.

    a. Weigh 28.05 g of potassium hydroxide.

    b. Dissolve the potassium hydroxide in 50 ml of water.

18. 0.05M KEDTA at a pH of 10.6 which is prepared in the following way.

a. Weigh 0.5 g of potassium hydroxide.

b. Dissolve the potassium hydroxide in 50 ml of 0.05M EDTA.

c. Add dropwise 10M potassium hydroxide until a pH of 10.6 is obtained (Sill 220).

19. 16M nitric acid (70 percent HNO_3).

20. 29M hydrofluoric acid (48 percent HF).

21. Anhydrous sodium sulfate.

22. 0.25M potassium hydroxide which is prepared in the following way.

a. Weigh 0.7 g of potassium hydroxide.

b. Dissolve the potassium hydroxide in 50 ml of water.

C.2 Sample Preparation

1. Weigh 1 g of sample and place in platinum dish.

2. Add 1 ml of ^{232}U tracer to the platinum dish.

3. Add 0.5 ml 16M nitric acid; carefully smell for hydrogen sulfide.

4. If no hydrogen sulfide is being evolved, add 3 ml of 29M hydrofluoric acid. If hydrogen sulfide is present add excess 16M nitric acid and evaporate to dryness before adding 29M hydrofluoric acid.

5. Evaporate to near dryness.

6. Weigh 3.5 g of mixed flux and place in platinum dish.

7. Mix sample and mixed flux thoroughly.

8. Heat the mixture with a blast burner until the sample turns clear.
9. Let the platinum dish cool on a stainless steel plate for approximately 30 seconds.
10. Add 4 ml of concentrated sulfuric acid. (NOTE: Have a container with cold water near by to cool the dish if the reaction becomes too violent.)
11. When the reaction begins to stop, gently heat the platinum dish with the blast burner until the evolution of gas is restored. (NOTE: Do not over heat.)
12. When the evolution of gas has stopped and the solid cake has disappeared, add 0.5 g of anhydrous potassium fluoride to the platinum dish.
13. Gently heat the platinum dish with the blast burner and continuous swirling until the evolution of gas stops.
14. Add 2 g anhydrous sodium sulfate and continue to gently heat with the blast burner until a clear fusion is obtained.
15. Remove the platinum dish from the heat and wait for the sample to solidify.
16. When the sample has become a solid pyrosulfate cake place the platinum dish in a pan of cool water and let the sample cool to room temperature.
17. Break the cooled sample by gently flexing the sides of the platinum dish and place the sample in a 100 ml beaker.

18. Add three small chips of carborundum to the 100 ml beaker.
19. Pour 35 ml of boiling 2M hydrochloric acid in the platinum dish and then pour it into the 100 ml beaker.
20. Heat the solution to boiling over a flame produced by the blast burner. (NOTE: Swirl the solution to keep the beaker from breaking.)
21. Remove the 100 ml beaker from the flame.
22. Cover the 100 ml beaker with a watch glass and boil on a hotplate for approximately 3 minutes.
23. Add 5 drops of 25 % ammonium iron (II) sulfate hexahydrate.
24. Begin reheating the solution to boiling with blast burner.
25. Add 1 ml of seeding suspension.
26. Add 1 ml of 0.45 percent barium chloride dropwise to the solution as it is being heated and swirl the solution after the addition of the barium chloride. Heat the sample to boiling.
27. Repeat step 26 three more times.
28. Keep a beaker half full with boiling water, to be used in the centrifuge tubes.
29. Transfer the solution to four 10 ml centrifuge tubes.
30. Centrifuge for 2 minutes. Stop the centrifuge as quickly as possible.
31. Pour the top liquid from each of the centrifuge tubes

into a beaker and wash the walls of each tube with water.

32. Add 4 ml of water to each centrifuge tube and repeat steps 30-31.
33. Wash the barium sulfate precipitant out of the centrifuge tubes with water and pour into a 250 ml beaker to discard.
34. Evaporate the supernate in the beaker to near dryness.
35. Pour 35 ml of boiling 2M hydrochloric acid in the platinum dish and then pour it into the 100 ml beaker.
36. Heat the solution to boiling over a flame produced by the blast burner. (NOTE: Swirl the solution to keep the beaker from breaking.)
37. Remove the 100 ml beaker from the flame.
38. Cover the 100 ml beaker with a watch glass and boil on a hotplate for approximately 3 minutes.
39. Add 400μl of 20 percent titanium trichloride.
40. Begin reheating the solution to boiling with blast burner.
41. Add 1 ml of seeding suspension.
42. Add 1 ml of 0.45 percent barium chloride dropwise to the solution as it is being heated and swirl the solution after the addition of the barium chloride. Heat the sample to boiling.
43. Repeat step 42 three more times.
44. Keep a beaker half full with boiling water, to be used

in the centrifuge tubes.

45. Transfer the solution to four 10 ml centrifuge tubes.
46. Centrifuge for 2 minutes. Stop the centrifuge as quickly as possible.
47. Pour the top liquid from each of the centrifuge tubes into a beaker to be discarded and wash the walls of each tube with water.
48. Add 4 ml of water to each centrifuge tube and repeat steps 46-47.
49. Add 6 ml of 0.05M KEDTA to the 250 ml beaker and swirl.
50. Place the 250 ml beaker in a beaker of boiling water for 3 minutes.
51. Add 1 drop of 10M potassium hydroxide and 1 drop of 20 percent titanium trichloride.
52. Add 2 ml of 10M potassium hydroxide to the 250 ml beaker and swirl.
53. Heat the 250 ml beaker in the hot water bath for 5 minutes.
54. Remove the solution from the hot water bath and let cool.
55. Centrifuge the solution for 5 minutes.
56. Remove the top liquid and discard.
57. Wash the walls of the centrifuge tube with water.
58. Add 0.5 ml of 0.25M potassium hydroxide and stir with a stirring rod.

59. Wash the stirring rod with 5 ml of 0.25M potassium hydroxide.
60. Swirl the centrifuge tube to resuspend the precipitate.
61. Centrifuge the solution for 5 minutes.
62. Remove the top liquid and discard.
63. Wash the walls of the centrifuge tube with water.
64. Add 0.5 ml of hydrochloric acid to the centrifuge tube.
65. Dilute with 2 ml of water.
66. Centrifuge the solution for 5 minutes.
67. Pour the top liquid into a 250 ml beaker.
68. Add 0.5 ml 12M hydrochloric acid and 5 ml of water.
69. Add excess 20 percent titanium trichloride.
70. Add 1 ml of lanthanum carrier
71. Add 1 ml of 29M hydrofluoric acid.
72. Filter sample through membrane filter using suction.
73. Remove clamp and top of filter with suction on and allow the membrane to dry.
74. Mount membrane on holding paper and count sample for forty-eight hours.

APPENDIX D

DECAY TABLES

Table D.1 ^{234}U Decay Table

Isotope	Decay	Energy (MeV)	Half-life
^{234}U	α	4.78,4.73	2.45E5y
^{230}Th	α	4.69,4.62	7.7E4y
^{226}Ra	α	4.78,4.60	1600y
^{222}Rn	α	5.49	3.82d
^{218}Po	α	6.00	3.05m
^{214}Pb	β^-		26.8m
^{214}Bi	β^-		19.9m
^{214}Po	α	7.69	163.7μs
^{210}Pb	β^-		22.26y
^{210}Bi	β^-		5.01d
^{210}Po	α	5.30	138.39d
^{206}Pb			stable

Table D.2 ^{232}U Decay Table

Isotope	Decay	Energy (MeV)	Half-life
^{232}U	α	5.32,5.26	70y
^{228}Th	α	5.42,5.34	1.19y
^{224}Ra	α	5.69,5.45	3.66d
^{220}Rn	α	6.29	55.6s
^{216}Po	α	6.78	0.145s
^{212}Pb	β^-		10.64h
^{212}Bi	β^-		7m
^{212}Po	α	8.78	0.30μs
^{208}Pb			stable

Table D.3 ^{238}U Decay Table

Isotope	Decay	Energy (MeV)	Half-life
^{238}U	α	4.20,4.15	4.47E9y
^{234}Th	β^-		24.10d
^{234}Pa	β^-		1.17m
^{234}U	α	4.78,4.73	2.45E5y

APPENDIX E

THORIUM SPECTRA

The original potassium fluoride procedure did not include step 34-48 of the present procedure. When the potassium fluoride fusion procedure was first ran the spectra on the following pages was produced. The peaks which are present are thorium peaks.

The reason the potassium fluoride fusion procedure yielded the thorium spectra is that the uranium remained in solution during the first barium sulfate coprecipitation. To correct this problem the supernate from the first barium sulfate coprecipitation was evaporated to near dryness. Then brought bach up into a 2M hydrochloric acid solution. The uranium was subsequently reduce with titanium trichloride and a second barium sulfate coprecipitation was used to bring down the uranium.

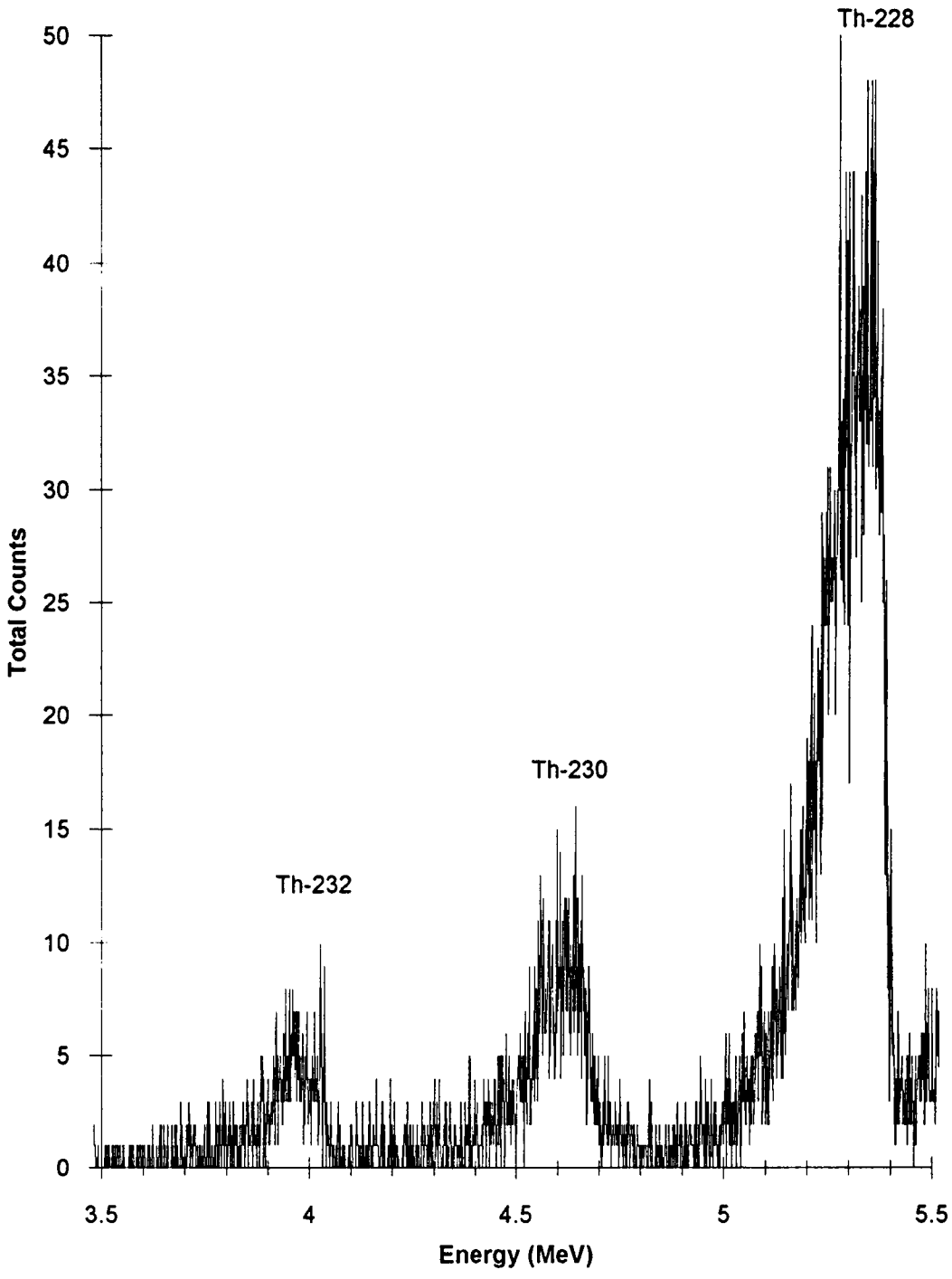


Figure E.1 Sample 7100 processed with the Potassium Fluoride Fusion Procedure after first coprecipitation.

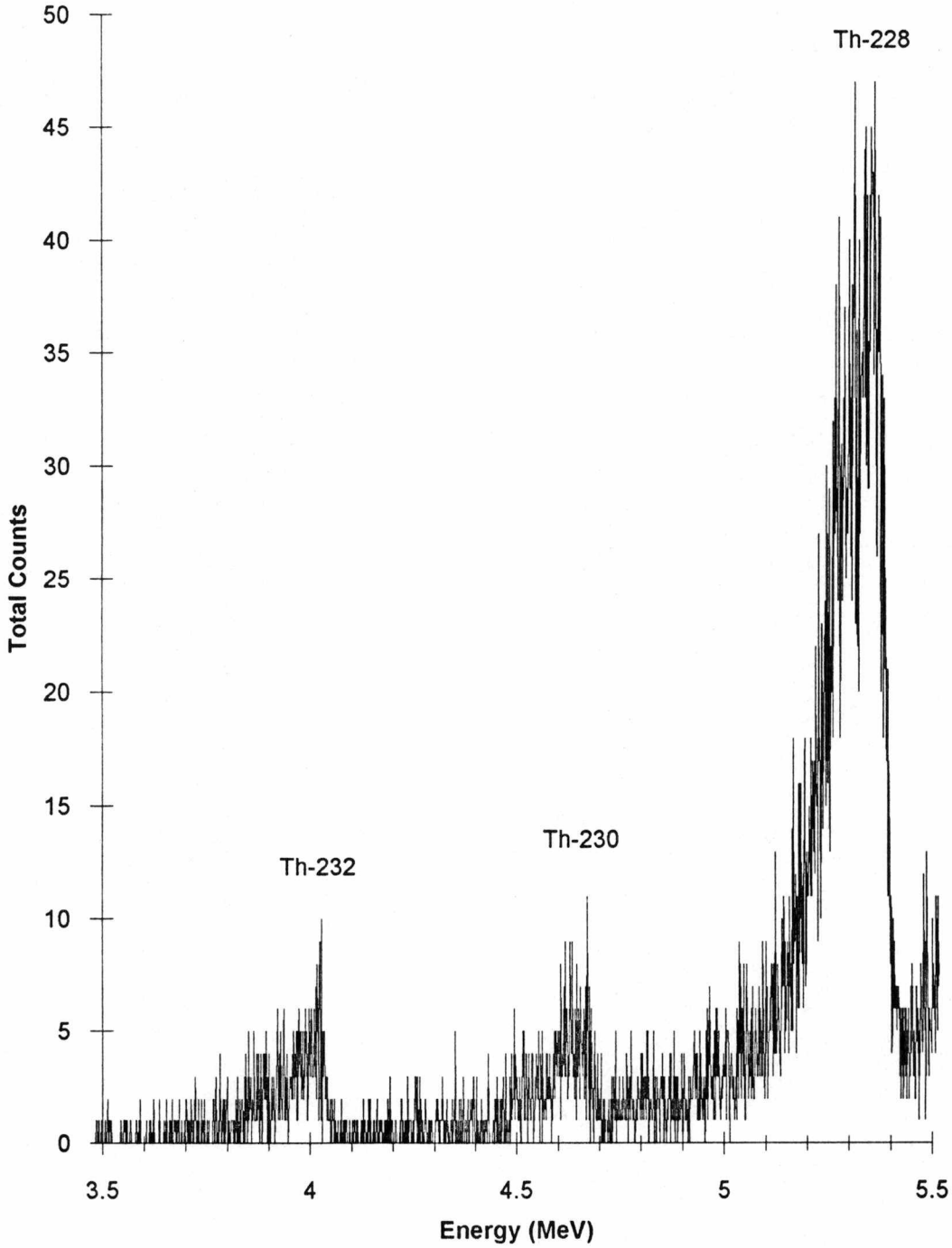


Figure E.2 Sample 7941 processed with the Potassium Fluoride Fusion Procedure after first coprecipitation.

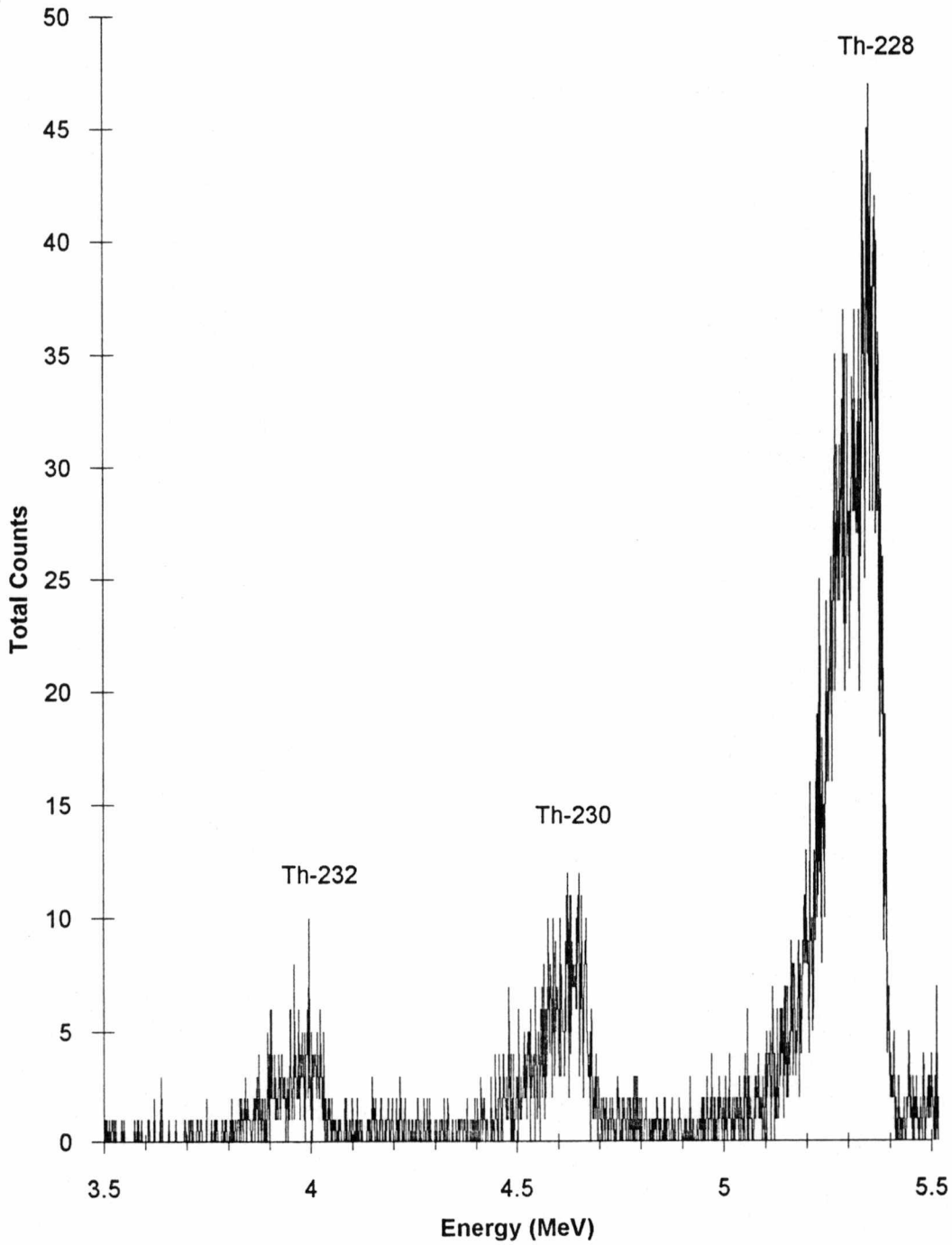


Figure E.3 Sample 7354 processed with the Potassium Fluoride Fusion Procedure after the first coprecipitation.

VITA

David Wayne Burkett was born in Greenville, Kentucky on May 23, 1970. He attended Greenville City Schools and graduated from Greenville High School in May, 1988. The following August, he entered Western Kentucky University where he earned his Bachelor of Science degree in Physics and Mathematics in May, 1992. In May, he also married Mary Lee Curtis Burkett. In August, they moved to Knoxville, Tennessee, where he entered graduate school at The University of Tennessee. In August, 1994, he received his Master of Science degree in Nuclear Engineering.