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ADVANCES IN ALPHA LIQUID SCINTILLATION SPECTROMETRY

A Dissertation

Presented for the

Doctor of Philosophy

Degree

The University of Tennessee, Knoxville

Jonathan Micah Duffey

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DEDICATION

To my wife, Cheryl, and to my parents, Ted and Myrna, for their undying love and support during the completion of this work.

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ABSTRACT

With the introduction of the technique known as Photon/Electron-Rejecting Alpha Liquid Scintillation (PERALS) Spectrometry, pioneered by W. J. McDowell in the 1970's, liquid scintillation has become a useful alternative to conventional alpha spectrometry techniques. Despite many inherent advantages such as ease of sample preparation, greater than 99% counting efficiency, and low backgrounds, the technique has yet to gain widespread acceptance. This research consisted of two separate parts, both aimed toward increasing the usefulness and level of acceptance of PERALS spectrometry in the scientific community.

Part I of this work consisted of the development and testing of a new method for the determination of uranium in drinking water by PERALS spectrometry. In this method uranium was selectively extracted from an aqueous solution of DTPA into an aqueous-immiscible scintillation cocktail containing the extractant HDEHP. The extraction of uranium was found to be essentially quantitative under a wide variety of conditions. Under optimum conditions less than 1% of thorium, polonium, plutonium, americium, and radium were extracted. Because this method offered significant advantages in simplicity and speed over currently approved methods, it was proposed as an ASTM standard test method for uranium in drinking water and is currently awaiting final approval by ASTM.

Part II of this work involved the development and testing of a number of potentially more environmentally-safe extractive scintillator solutions which might replace current toluene/naphthalene-based solutions. Approximately 50 extractive scintillator solutions were prepared using various combinations of six different solvents and five commonly used fluors. Both pulse-shape distributions (time spectra) and pulse-height distributions (energy spectra) were recorded for each new scintillator solution and compared with those of a comparable toluene/naphthalene-based extractive scintillator. Based on the comparison of these spectra, the solutions were ranked according to their time and energy resolution capabilities. Observations regarding phase separation characteristics and long-term chemical stability were made for each solution. Also, alpha background measurements were conducted for a number of the test solutions. It was concluded that it is technically feasible to replace toluene/napthalene-based extractive scintillators with more environmentally-safe solutions with only minor losses in extractive scintillator performance.

TABLE OF CONTENTS

CHAPTER PAGE

INTRODUCTION 1

A. Background 1

B. Alpha Particle Detection 2

C. Photon/Electron-Rejecting Alpha Liquid Scintillation 6

D. Identification of the Problem 10

E. Proposed Research 12

PART I: DEVELOPMENT OF A RAPID PROCEDURE FOR THE MEASUREMENT OF URANIUM IN DRINKING WATER BY PERALS SPECTROMETRY

I. INTRODUCTION 15

A. Background 15

B. Review of Current Methods 26

II. EXPERIMENTAL METHODS AND MATERIALS 32

A. Apparatus 32

B. Reagents 34

C. Experimental Approach 35

D. Preparation of Test Solutions 38

E. Calculations and Propagation of Uncertainty 38

III. RESULTS AND DISCUSSION 42

A. Parameters Influencing Extraction Efficiency 42

B. Chemical Interferences 62

CHAPTER PAGE

C. Results of Interlaboratory Tests for the Proposed ASTM Test Method 73

IV. SUMMARY AND CONCLUSIONS 80

A. Summary 80

B. Conclusions 81

C. Future Work 81

PART II: DEVELOPMENT AND TESTING OF ENVIRONMENTALLY-SAFE EXTRACTIVE SCINTILLATORS FOR ALPHA LIQUID SCINTILLATION SPECTROMETRY

I. INTRODUCTION 84

II. EXPERIMENTAL METHODS AND MATERIALS 87

A. Selection of Test Solvents 87

B. Preparation of Scintillator Solutions for Testing 90

III. RESULTS AND DISCUSSION 93

A. Evaluation of Phase Separation Characteristics 93

B. Evaluation of Time Resolution Characteristics 95

C. Evaluation of Energy Resolution Characteristics 108

D. Evaluation of Alpha Background Count Rate 117

E. Evaluation of Chemical Stability 125

F. Work Beyond the Scope of This Study 128

IV. CONCLUSION 132

LIST OF REFERENCES 133

APPENDIX 140

CHAPTER PAGE

VITA..... 146

LIST OF TABLES

TABLE PAGE

I. PROPERTIES OF IMPORTANT ALPHA-EMITTING URANIUM ISOTOPES 16

II. TIME DEPENDENCE OF URANIUM EXTRACTION FROM 0.010 M DTPA SOLUTION AT pH 3.1 43

III. pH DEPENDENCE OF URANIUM EXTRACTION FROM 0.010 M DTPA SOLUTION 46

IV. pH DEPENDENCE OF THORIUM EXTRACTION FROM 0.010 M DTPA SOLUTION 49

V. pH DEPENDENCE OF POLONIUM EXTRACTION FROM 0.010 M DTPA SOLUTION 52

VI. pH DEPENDENCE OF PLUTONIUM EXTRACTION FROM 0.010 M DTPA SOLUTION 54

VII. pH DEPENDENCE OF AMERICIUM EXTRACTION FROM 0.010 M DTPA SOLUTION 55

VIII. EXTRACTION OF RADIUM FROM 0.010 M DTPA SOLUTION AT pH 3.0 56

IX. AVERAGE PERCENT EXTRACTION OF ALPHA-EMITTERS FROM 0.010 M DTPA SOLUTION AS A FUNCTION OF pH 57

X. EFFECT OF DTPA CONCENTRATION ON URANIUM EXTRACTION AT pH 3.0 59

XI. EFFECT OF DTPA CONCENTRATION ON AMERICIUM EXTRACTION AT pH 3.0 60

XII. EFFECT OF DTPA CONCENTRATION ON THORIUM EXTRACTION AT pH 3.0 61

XIII. URANIUM EXTRACTION AS A FUNCTION OF AQUEOUS-TO-ORGANIC PHASE VOLUME RATIO 63

TABLE PAGE

XIV. INFLUENCE OF CALCIUM ION CONCENTRATION ON URANIUM EXTRACTION FROM 0.010 M DTPA SOLUTION 65

XV. INFLUENCE OF CALCIUM ION CONCENTRATION ON THORIUM EXTRACTION FROM 0.010 M DTPA SOLUTION 66

XVI. INFLUENCE OF CALCIUM ION CONCENTRATION ON POLONIUM EXTRACTION FROM 0.010 M DTPA SOLUTION 67

XVII. INFLUENCE OF CALCIUM ION CONCENTRATION ON AMERICIUM EXTRACTION FROM 0.010 M DTPA SOLUTION 68

XVIII. AVERAGE PERCENTAGE EXTRACTION AS A FUNCTION OF CALCIUM ION CONCENTRATION 69

XIX. INFLUENCE OF FERRIC ION CONCENTRATION ON URANIUM EXTRACTION FROM 0.010 M DTPA SOLUTION 71

XX. INFLUENCE OF TOTAL PHOSPHATE CONCENTRATION ON URANIUM EXTRACTION FROM 0.010 M DTPA AT pH 3.0 74

XXI. INFLUENCE OF TOTAL OXALATE CONCENTRATION ON URANIUM EXTRACTION FROM 0.010 M DTPA AT pH 3.0 75

XXII. SUMMARY OF MULTIPLE SINGLE OPERATOR INTER-LABORATORY TEST FOR URANIUM IN DRINKING WATER 77

XXIII. SUMMARY OF ROUND-ROBIN INTERLABORATORY TEST FOR URANIUM IN DRINKING WATER 78

XXIV. OVERALL RESULTS OF INTERLABORATORY TESTS FOR URANIUM IN DRINKING WATER 79

XXV. SOME PROPERTIES OF SCINTILLATOR SOLVENTS INVESTIGATED 89

XXVI. SOME PROPERTIES OF FLUORS INVESTIGATED 91

XXVII. COMPARISON OF TIME RESOLUTION PROPERTIES 101

TABLE PAGE

XXVIII. EXTRACTIVE SCINTILLATORS IN ORDER OF DECREASING TIME RESOLUTION 106

XXIX. COMPARISON OF ENERGY RESOLUTION PROPERTIES 112

XXX. EXTRACTIVE SCINTILLATORS IN ORDER OF DECREASING ENERGY RESOLUTION 118

XXXI. EXTRACTIVE SCINTILLATORS RANKED ACCORDING TO COMBINED TIME AND ENERGY RESOLUTION 120

XXXII. SUMMARY OF EXTRACTIVE SCINTILLATOR BLANK COUNT RATES 123

XXXIII. COLOR INTENSITY OF EXTRACTIVE SCINTILLATORS AFTER SIX MONTHS OF STORAGE 126

XXXIV. TIME RESOLUTION DATA 141

XXXV. ENERGY RESOLUTION DATA 143

LIST OF FIGURES

FIGURE		PAGE
1.	Typical PERALS (a) pulse-shape distribution (time spectrum) and (b) pulse-height distribution (energy spectrum)	9
2.	Schematic of the uranium (4n + 2) decay series	18
3.	Schematic of the thorium (4n) decay series	20
4.	Schematic of the actinium (4n + 3) decay series	21
5.	Schematic representation of alpha-group spectral resolution with electrodeposited samples and semiconductor detectors assuming resolution of 20 keV FWHM	23
6.	Schematic representation of alpha-group spectral resolution with micro-coprecipitated samples and semiconductor detectors assuming resolution of 60 keV FWHM	25
7.	Flow diagram for the rapid determination of uranium in drinking water by PERALS spectrometry	37
8.	Uranium extraction with Alphaex from 0.010 M DTPA solution at pH 3.1 as a function of equilibration time	44
9.	Comparison of pulse-shape distributions in Alphaex and test scintillators	97
10.	Comparison of pulse-height distributions in Alphaex and test scintillators	109
11.	Comparison of normal uranium pulse-height distributions in solutions containing TOA as extractant	130

LIST OF SYMBOLS AND ABBREVIATIONS

A	activity
α-NPO	2-(1-naphthyl)-5-phenyloxazole
ASTM	American Society for Testing and Materials
bis-MSB	1,4-bis(2-methylstyryl)benzene
Bq	becquerel
butyl-PBD	2-(4-biphenylyl)-5-(4-*tert*-butylphenyl)-1,3,4-oxadiazole
CFR	Code of Federal Regulations
cm	centimeter
cpm	counts per minute
d	day
dpm	disintegrations per minute
DTPA	diethylenetriaminepentaacetic acid
ε	instrument detection efficiency
EPA	Environmental Protection Agency
FWHM	full peak width at half the maximum peak height
g	gram
HDEHP	bis(2-ethylhexyl)phosphoric acid
HVPS	high-voltage power supply
keV	kiloelectron volts
L	liter
M	moles per liter
MCA	multichannel analyzer
min	minute
mm	millimeter
MeV	megaelectron volts
mL	milliliter
μg	microgram
μL	microliter
μm	micrometer
NIM	nuclear instrument module
π	pi
PBBO	2-(4-biphenylyl)-6-phenylbenzoxazole
PCB	polychlorinated biphenyls
pCi	picocuries
PERALS	photon/electron-rejecting alpha liquid scintillation
PMT	photomultiplier tube
POPOP	1,4-bis(5-phenyloxazol-2-yl)benzene
ppb	parts per billion
ppm	parts per million
PPO	2,5-diphenyloxazole
ppt	parts per trillion

PSD	pulse shape discrimination or discriminator
ROI	region of interest
s	second
σ	standard deviation
SBIR	Small Business Innovation Research
t	count time
TOA	trioctylamine
TOPO	trioctylphosphine oxide
TPU	total propagated uncertainty
US DOE	United States Department of Energy
WHO	World Health Organization
y	year

INTRODUCTION

A. Background

Since its development in the 1950's, the radiation detection and measurement technique known as the liquid scintillation method has been used to detect and measure most types of radioactive decay.[1] This method involves intimately mixing a radioactive sample in a solution consisting of a fluorescent, organic solute, called a fluor or scintillator, and an organic solvent such as toluene or xylene. This liquid scintillator solution absorbs energy upon interaction with ionizing radiation and emits the energy very rapidly (~10^{-9} s) as a burst of photons, that is, a scintillation. The photons are directed toward a photomultipier tube (PMT) where they strike the photocathode expelling electrons from the surface. The number of electrons liberated by this process is multiplied by a factor of approximately 10^6 through successive interaction with a series of appropriately charged electrodes called dynodes. The resulting burst of photons is converted to a measurable electronic pulse, the size of which is proportional to the number of photons impinging upon the photocathode. The number of photons impinging upon the photocathode is proportional to the energy of the radioactive decay for a given type of decay particle, scintillator solution composition, and detector configuration. Because the radioactivity is contained within the scintillator solution, essentially all of the nuclear emanations can interact with the detection medium, thereby maximizing the efficiency of the

counting method for those radiations which deposit sufficient energy in the scintillator solution to permit detection.[2]

B. Alpha Particle Detection

Alpha decay is the emission of an alpha particle (a helium-4 nucleus, $^4He^{2+}$) from an unstable parent nucleus.[3] Unlike beta particles, which are emitted with energies between zero and some maximum value, alpha particles are essentially monoenergetic. Alpha-emitting nuclides emit one or more alpha particles of different but well defined energies, usually in the range of 4 to 8 MeV.[4] Because the alpha energy spectrum is characteristic of a particular nuclide, accurate measurement of the alpha energy spectrum of a sample may be used to identify the alpha-emitters present.

Alpha particles interact with the matter through which they pass to produce extensive ionization and excitation of orbital electrons, thus rapidly dissipating the kinetic energy of the alpha particles within a very short distance. The range of alpha particles in matter is a function of alpha particle energy and the density of the stopping material. A 5.0 MeV alpha particle has a range of approximately 3.5 cm in air and approximately 44 μm in water. In solids the range may vary from a few micrometers to a few tens of micrometers depending on the density of the material.[5]

The detection of alpha particles presents certain problems because of their very short range in matter. Radiation detectors used for measuring alpha

particles must allow the alpha particles into the sensitive portion of the detector with minimal energy loss in the insensitive portion of the detector. In addition, sources for alpha particle counting must be carefully prepared to minimize sample self-absorption, that is, alpha energy loss within the sample itself. This is especially true when one is interested in identifying and quantifiying specific alpha-emitting nuclides in the presence of others, because self-absorption leads to peak broadening and loss of energy resolution.[5]

Since it is often desirable to measure the alpha energy distribution as well as the count rate of a particular sample, high-resolution alpha spectrometry is usually the preferred means of alpha particle detection and measurement. This is most often accomplished with semiconductor radiation detectors, in part because of their excellent energy resolution capabilities.[6] These detectors consist of a semiconductor material such as silicon, in which a sensitive region known as a depletion layer is produced by one of several possible techniques. The interaction of ionizing radiation with the depletion layer results in the formation of electron-hole pairs. By placing the semiconductor material between a pair of electrodes and applying a reverse bias voltage, the electrons are rapidly collected at the positive electrode and the holes at the negative electrode. The size of the electrical pulse produced upon collection of the ions is proportional to the number of electron-hole pairs produced which, in turn, is proportional to the energy of the ionizing radiation impinging upon the depletion layer.[7]

Alpha spectrometry with solid samples and semiconductor detectors provides alpha counting efficiencies from 10 to 50%, backgrounds as low as 0.001 cpm under a given alpha peak, and energy resolution from about 15 keV to 130 keV FWHM (full peak width at half the maximum peak height).[8-10] The energy resolution is highly dependent on the quality of sample purification, the quality of source preparation, the distance of the source from the detector, and the detector area. Samples must be prepared as thin as possible to minimize sample self-absorption which leads to peak broadening and loss of counting efficiency. Also, the greater the distance from sample to detector and the smaller the detector area, the better is the resolution, but the lower is the counting efficiency.[6,11]

It was recognized very early in the development of the liquid scintillation counting technique that it could be used for the detection and measurement of alpha particle radioactivity. Flynn and Horrocks demonstrated in 1964 that the light output of a liquid scintillator solution is directly proportional to alpha particle energy over the range of 4 to 7 MeV.[12] Because the alpha-emitter is located in a closed vessel within the detection medium, the scintillator solution, there are several advantages to measuring alpha particles by liquid scintillation. These advantages include 4π detector geometry and no sample self-absorption, resulting in alpha-counting efficiencies near 100%; simplified source preparation, because self-absorption is not a problem; and little or no risk of detector contamination because the sample is contained in a sealed vessel.

Despite these obvious advantages, liquid scintillation was not recognized as a useful technique for measuring alpha particles until the 1970's. This is partly due to three major disadvantages ordinarily associated with liquid scintillation techniques: (1) poor energy resolution of 500 to 1000 keV FWHM, (2) interference from beta and gamma radiation within the sample and from background sources, (3) and variable levels of photon quenching from sample to sample resulting in spectral energy shifts.[2,13]

Conventional liquid scintillation techniques incorporate an aqueous sample into the organic solution with the aid of various solubilizing agents dissolved in the scintillator solution. However, this approach decreases the efficiency with which the alpha particle energy is converted into photons because the solubilizing agents, water, and certain water soluble species are quenching agents. A quenching agent is any species which reduces the number of photons produced in the scintillator solution and/or the number of photons striking the photocathode of the photomultiplier tube. A reduction in the number of photons produced will usually lead to a decrease in counting efficiency for beta particles, but normally only results in decreased pulse height and loss of energy resolution for alpha particles.[2,13]

Spectral interference from beta and gamma radiation occurs because the energy of beta particles and gamma rays, while typically much less than alpha particle energies, is converted to photons approximately ten times more efficiently than for alpha particles.[14] Because of this difference in energy

conversion, an electronic pulse generated from the emission of an 0.5 MeV beta particle may have the same magnitude as the pulse generated from a 5 MeV alpha particle, resulting in an overlap of the energy spectra of these two particles.

Variations in the composition of the aqueous sample introduced into the organic scintillator solution lead to variable levels of quenching in the sample. Samples exhibiting different levels of quenching will have different light outputs for a given particle energy. This variation in light output results in spectral energy shifts from sample to sample, making spectral energy calibration and peak identification difficult or impossible.[13]

C. Photon/Electron-Rejecting Alpha Liquid Scintillation

Beginning in the early 1970's, W.J. McDowell pioneered the development of a new system for the detection and measurement of alpha-particles by liquid scintillation which partially solved these three major problems.[13,15] This new system made use of the separation technique known as liquid-liquid, or solvent, extraction to incorporate alpha-emitting elements into the scintillator solution. This was accomplished by dissolving an organophilic complexing agent directly in the scintillator solution to form what is known as an "extractive scintillator solution". A portion of this extractive scintillator solution was then contacted with a portion of the aqueous phase containing ions of the alpha-emitting element or elements to be measured. Aqueous species forming a stable neutral complex or

ion pair with the organophilic extractant would tend to partition to the organic phase, and those which did not would tend to remain in the aqueous phase. For example, the extraction of a metal cation by an acidic organophilic extractant can be represented by Equation 1,

$$M^{n+} + \underline{nHA} \rightleftharpoons \underline{M(A)_n} + nH^+, \quad (1)$$

where M^{n+} indicates a metal cation of charge n, HA indicates the acidic organophilic extractant, and an underline denotes a species in the organic phase. By proper choice of the extractant and the aqueous phase conditions, selective extraction of the metal ions of interest could be obtained while minimizing the transfer of undesirable species to the scintillator solution.

McDowell's technique also utilized electronic pulse shape discrimination (PSD) to distinguish between pulses produced by beta or gamma events and pulses produced by alpha events. This is possible because pulses produced as a result of the interaction of alpha particles with the scintillator solution have longer decay times than those produced by the interaction of beta particles or gamma rays with the scintillator solution.[16-18] By electronically rejecting the beta and gamma pulses, the spectral interference from beta and gamma radiation can be greatly diminished. Together with detector modifications designed to maximize light collection, thus optimizing alpha-energy resolution, this technique called Photon/Electron-Rejecting Alpha Liquid Scintillation (PERALS®) spectrometry has become a valuable technique for alpha particle detection and measurement.

In its current configuration, the PERALS spectrometer provides greater than 99.9% rejection of beta/gamma pulses, nearly constant alpha counting efficiency of greater than 99%, and typical scintillator blanks of 0.03 to 0.003 cpm in a given alpha-particle energy region.[19] Instrument blanks, with no sample present are normally 0.001 cpm or less. Energy resolution is about 180 keV FWHM for a 4.78 MeV Ra-226 alpha particle under optimum conditions. Under routine conditions FWHM values are normally in the range of 200 to 300 keV, depending on the degree of sample quenching and the performance of the individual instrument, particularly the instrument's PMT.

Figure 1a) depicts a typical PERALS pulse shape distribution, or time spectrum for a mixture of natural uranium and ^{241}Am in an extractive scintillator solution. This figure illustrates the PERALS spectrometer's capability to distinguish electonically between pulses generated by beta or gamma decay events and pulses produced by alpha decay events. In this example the beta/gamma peak was generated primarily by an external ^{137}Cs gamma source. The approximate positioning of the pulse shape discriminator (PSD) relative to the beta/gamma peak and the alpha peak is also indicated. Figure 1b) shows a typical pulse height distribution, or energy spectrum, for the same sample. This figure illustrates the degree of energy resolution achievable with the PERALS spectrometer for a minimally quenched sample.

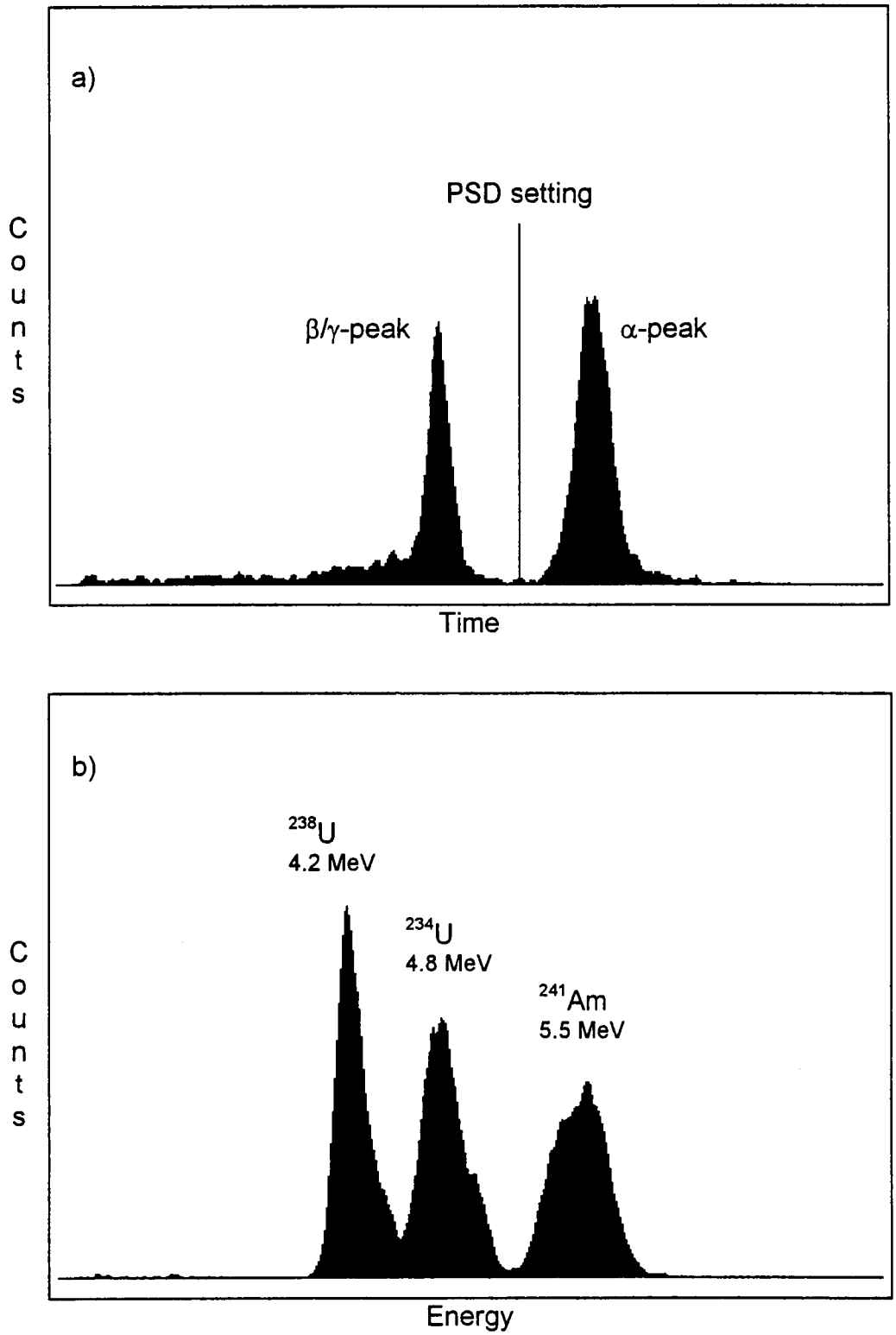


Figure 1. Typical PERALS (a) pulse-shape distribution (time spectrum) and (b) pulse-height distribution (energy spectrum).

D. Identification of the Problem

Since the development of PERALS spectrometry in the 1970's, alpha liquid scintillation counting has gained recognition as a useful analytical tool for the measurement of alpha-emitting nuclides. Consequently, procedures have been reported for the determination of polonium,[20,21] radon,[21,22] radium,[21-24] thorium,[25-28] uranium,[21,25-35] neptunium,[25,36] plutonium,[25,26,30,36-41] americium,[25,26,36] and curium[25,26,30] by PERALS spectrometry as well as by other types of alpha liquid scintillation counting. Many of the procedures have been shown to be faster, simpler, and just as sensitive and accurate as conventional alpha spectrometry using solid samples and semiconductor detectors. Thus, for certain applications, alpha liquid scintillation has proven a useful and rapid alternative to more traditional techniques of alpha spectrometry. However, advances in procedures for the determination of alpha-emitting elements and in the nature and performance of extractive scintillator solutions are still needed.

One area in which improvements are needed is in the separation of uranium from other alpha emitters and from a variety of matrix constituents prior to the measurement of its alpha-particle activity. Uranium occurs naturally throughout the earth's crust and natural waters.[42,43] However, its role in the production, testing, and use of nuclear weapons, and as a nuclear fuel source, has led to increased concern over environmental and human contamination by uranium isotopes.[10,44,45] Therefore, the determination of uranium is an important analytical measurement for reasons such as monitoring of public drinking water

systems and aqueous discharges from nuclear facilities;[44,46] environmental monitoring of air, water, and soil and assessment of environmental remediation efforts;[10,44,47-49] and bioassay measurements for the estimation of human radiation exposures and dosimetry calculations.[10,45,50] Uranium determination also plays an important role in assessment of decontamination and decommissioning efforts on uranium-contaminated materials and equipment.[51] Finally, the determination of uranium is vital to a variety of research applications in earth, marine, and environmental science programs.[52]

Another area of alpha liquid scintillation in which improvements could be made is in the replacement of hazardous scintillator solution components with components which are less hazardous or non-hazardous and potentially biodegradable. The two major components of extractive scintillators currently used in conjunction with PERALS spectrometry are toluene and naphthalene. Toluene serves as the primary solvent which, because it is the major component, is the species most likely to interact with particles of ionizing radiation as they pass through the solution.[53] Solvent molecules are excited to higher energy states and subsequently transfer this excitation energy to the fluor. The concentration of toluene in these solutions is approximately 7 M. Naphthalene is present at a concentration of 180 g/L (1.4 M) and aids in the efficient transfer of excitation energy from solvent to fluor.[54] The fluor is 2-(4-biphenylyl)-6-phenylbenzoxazole (PBBO), present at a concentration of 4.0 g/L (0.012 M). The solutions also contain from 30 to 60 g/L (0.1 to 0.2 M) of one of several

possible organophilic extracting agents which function to transfer certain metal ions from an aqueous solution into the scintillator solution under the appropriate extraction conditions.

The components of greatest concern are toluene and naphthalene for the following reasons: (1) they are currently listed as hazardous chemicals due to their low flashpoints and toxic nature, (2) people working with these solutions are more likely to be exposed to toluene and naphthalene than to the other components due to their relatively high vapor pressures, and (3) they are the components present in the greatest concentrations. Widespread acceptance and use of extractive scintillators and PERALS spectrometry has been hampered by the presence of toluene and naphthalene components and the hazardous mixed waste produced when radioactivity is added to the solution. Replacement of toluene and naphthalene with less hazardous or non-hazardous components with little or no loss of light output would result in more acceptable scintillator solutions which could be used by those who have chosen to eliminate hazardous chemicals such as toluene and naphthalene from their laboratories.

E. Proposed Research

This research effort consisted of two parts: (1) the development and testing of a new, rapid procedure for the determination of uranium alpha-particle activity in drinking water by PERALS spectrometry and (2) the development and testing of less hazardous extractive scintillator solutions for alpha liquid scintillation spectrometry. The first part was conducted as part of an effort to

obtain ASTM (American Society for Testing and Materials) approval for a uranium procedure using high-resolution alpha liquid scintillation spectrometry such as PERALS spectrometry.[29] The second part was conducted under an SBIR (Small Business Innovation Research) grant supported by the US DOE (United States Department of Energy).[55] The purpose of this work was to determine the feasibility of replacing the hazardous components of existing extractive scintillators, toluene and naphthalene, with components which are less hazardous and potentially biodegradable. These scintillators could be used for the measurement of uranium, as well as other alpha-emitting nuclides, by high-resolution alpha liquid scintillation techniques such as PERALS spectrometry.

PART I

DEVELOPMENT OF A RAPID PROCEDURE FOR THE MEASUREMENT OF URANIUM IN DRINKING WATER BY PERALS SPECTROMETRY

CHAPTER I

INTRODUCTION

A. Background

As discussed in the previous chapter, the determination of uranium alpha-particle activity in water is an important measurement in many environmental and water quality monitoring programs as well as in a variety of research programs. Numerous procedures involving various chemical separation schemes designed to isolate uranium have been published. In the case of alpha spectrometry with semiconductor detectors, extensive purification of uranium from sample matrix elements is required in order to prepare the very low-mass samples needed to minimize sample self-absorption and to obtain good energy resolution. With the technique of alpha liquid scintillation spectrometry with extractive scintillators, it is often possible to selectively extract uranium directly into a scintillation cocktail from samples containing high concentrations of matrix elements, thus simplifying sample preparation. However, in both cases it is necessary to separate uranium from other radionuclides in the sample which may interfere with the uranium alpha particle spectrum to permit accurate quantification of uranium alpha activity.

Table I (p. 16) lists some properties of the six most important alpha-emitting uranium isotopes. Three of the isotopes, ^{234}U, ^{235}U, and ^{238}U, are

TABLE I

PROPERTIES OF IMPORTANT ALPHA-EMITTING URANIUM ISOTOPES

Isotope	Half-Life (y)	Natural Abundance	Principal Alpha Decay Energies (keV)[a]	Specific Activity (dpm μg^{-1})
232	72		5320 (69%) 5264 (31%)	4.8×10^{7}
233	1.59×10^{5}		4824 (84%) 4784 (13%) 4729 (1.6%)	2.14×10^{4}
234	2.45×10^{5}	0.0054%	4776 (72%) 4724 (27%)	1.38×10^{4}
235	7.04×10^{8}	0.72%	4598 (5.0%) 4556 (4.2%) 4396 (55%) 4370 (6%) 4364 (11%) 4325 (4.6%) 4217 (5.7%)	4.80×10^{0}
236	2.34×10^{7}		4494 (74%) 4445 (26%)	1.44×10^{2}
238	4.47×10^{9}	99.275%	4196 (77%) 4147 (23%)	7.46×10^{-1}

a. Minor alpha decay energies have been omitted.

naturally occurring and are the major isotopes of interest when determining uranium alpha-particle activity. Based on the percent natural abundance and the specific activity of each isotope, one can calculate that 1.0 μg of natural uranium is equivalent to 1.5 dpm of combined alpha-particle activity. The total activity consists of approximately 0.74 dpm (49%) each from ^{238}U and ^{234}U and 0.035 dpm (2.3%) from ^{235}U. The other three isotopes listed, ^{232}U, ^{233}U, and ^{236}U, are artificially produced isotopes which are not normally present at significant levels of activity in drinking water samples or other environmental samples. For this reason, and because its alpha-particle energies are widely separated from the energies of the next closest uranium alpha particles, ^{232}U is commonly used as an isotopic yield tracer to monitor chemical recovery of uranium for a given separation and measurement procedure.[6,11] In order for the yield correction to be valid, appropriate steps must be taken prior to separation to ensure isotopic equilibration of the tracer with uranium isotopes in the sample.[56]

Most naturally occurring alpha-emitters belong to one of three natural decay series: the uranium series, the thorium series, and the actinium series.[57,58] The members of the uranium series have mass numbers equal to $4n + 2$, where n is an integer. A schematic of this decay series is given in Figure 2 (p 18). The series begins with the most abundant uranium isotope, ^{238}U, and ends with the stable isotope, ^{206}Pb after eight alpha decay transformations and six beta decay transformations. In addition to ^{238}U this series contains the relatively long-lived alpha-emitters ^{234}U, ^{230}Th, ^{226}Ra, ^{222}Rn, and ^{210}Po,

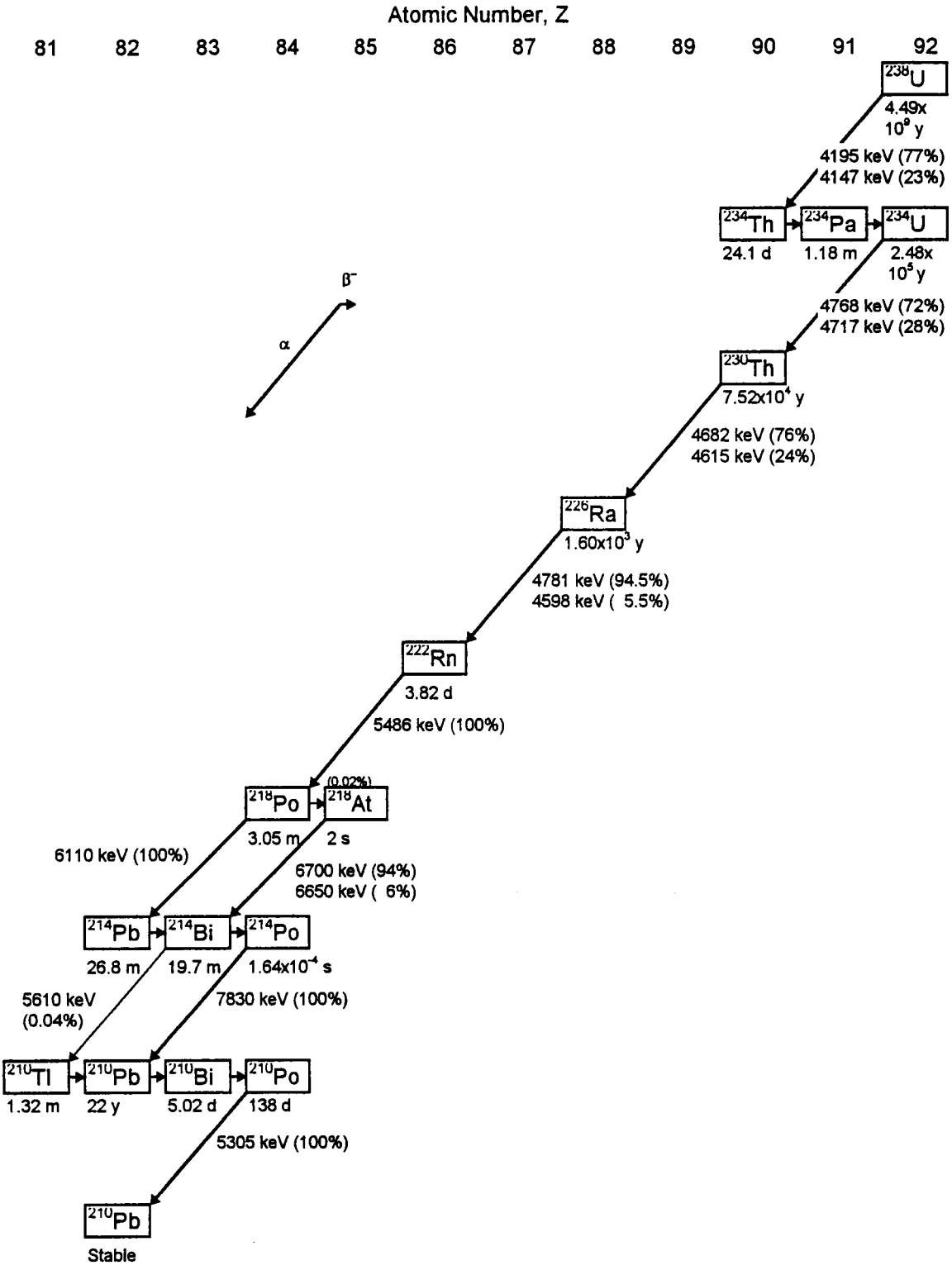


Figure 2. Schematic of the uranium (4n+2) decay series (after Ivanovich in ref. 58).

as well as several beta-emitters and short-lived alpha-emitters. The thorium ($4n$) series (Figure 3, p 20) begins with ^{232}Th (100% abundant) and ends with ^{208}Pb after six alpha decays and four beta decays. In addition to ^{232}Th, the most important alpha-emitters in this series include ^{228}Th, ^{224}Ra, and ^{220}Rn. The actinium ($4n + 3$) series begins with the second most abundant uranium isotope, ^{235}U (formerly actino-uranium), and following seven alpha decays and four beta decays ends with the stable isotope ^{207}Pb (Figure 4, p 21). Some other important alpha-emitters in this series include ^{231}Pa, ^{227}Th, ^{223}Ra, and ^{219}Rn.

Both uranium and thorium occur widely in the earth's crustal rocks, with average concentrations of about 4 ppm and 15 ppm, respectively.[59] Uranium occurs in sea waters in an average concentration of about 3.3 ppb, and in fresh waters in concentrations which vary widely from 0.01 to 5 ppb in surface waters to about ten times that in ground waters.[43] However, the thorium concentration in natural waters is extremely low at about 0.07 ppt.[43] Due to the widespread occurrence of uranium and thorium and to their positions in the natural decay series, uranium is always found in association with variable amounts of thorium and both uranium and thorium decay products. In addition to the naturally occurring alpha-emitters, several artificially produced alpha-emitters are often found in samples containing uranium. This is primarily a result of both controlled and accidental radioactive releases to the environment from the operation of nuclear reactors, reprocessing of spent nuclear fuel, the production and testing

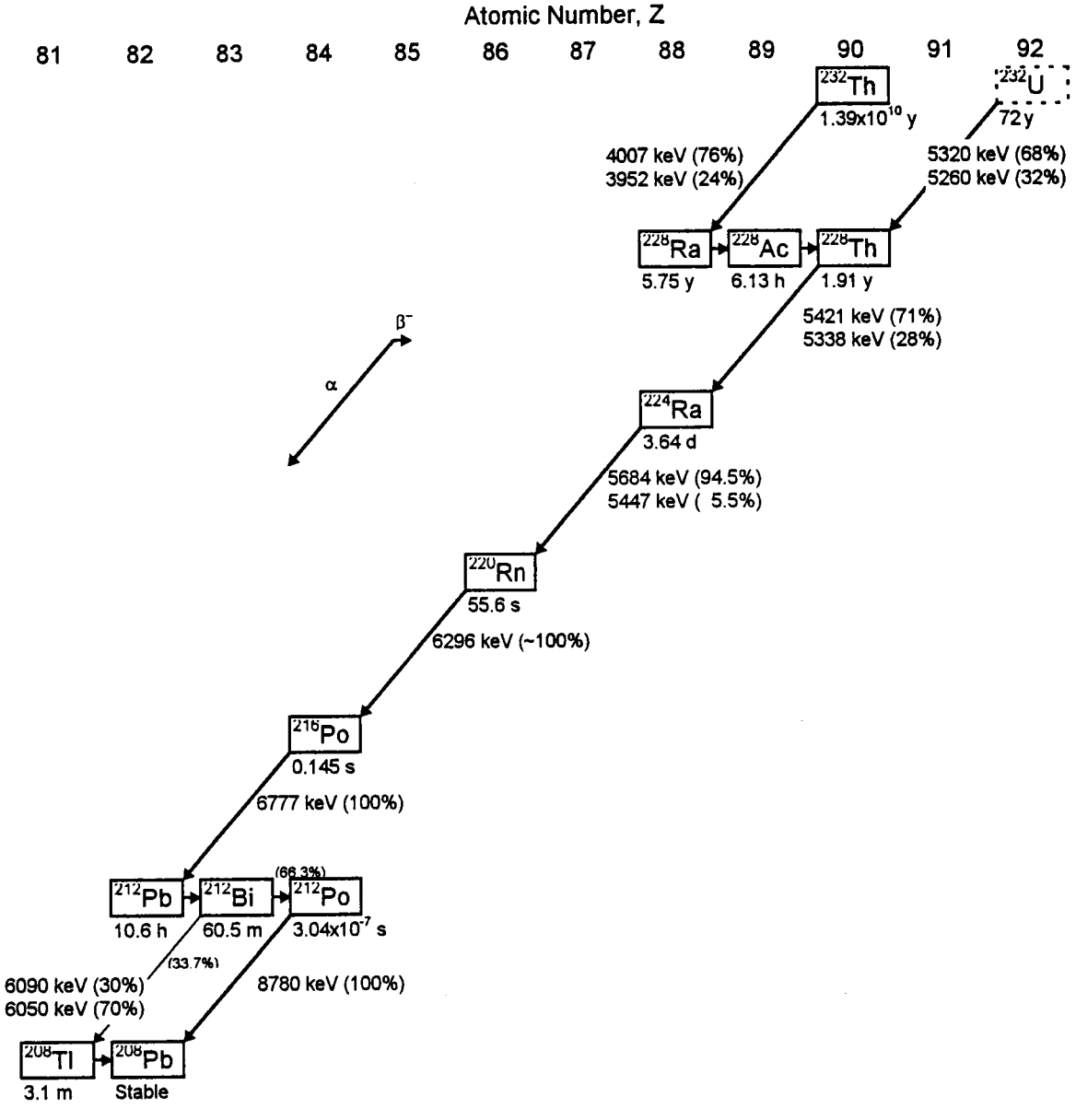


Figure 3. Schematic of the thorium (4n) decay series (after Ivanovich in ref. 58).

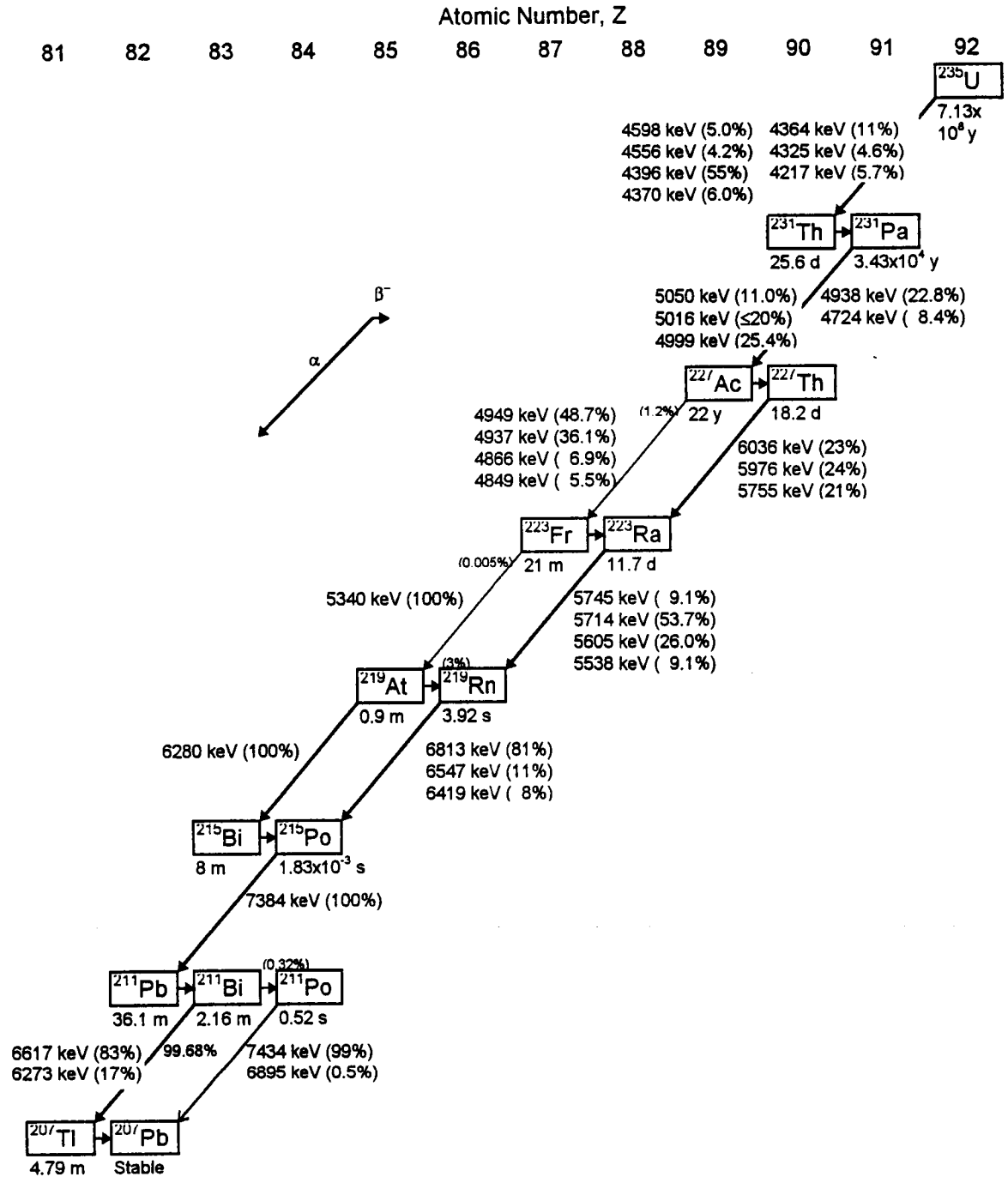


Figure 4. Schematic of the actinium (4n+3) decay series (after Ivanovich in ref. 58).

of nuclear weapons, and storage of nuclear wastes.[60] These radionuclides include, among others, ^{237}Np, $^{238\text{-}240}Pu$, and ^{241}Am. Thus, an analysis of alpha-particle spectral overlap for a given percent energy resolution could be useful in deciding which alpha-emitting elements must be chemically separated and which can be measured simultaneously.

Using semiconductor detectors and solid samples prepared by careful separation of the analyte(s) from matrix elements followed by electrodeposition onto a polished metal disk by an experienced operator, it is possible to achieve energy resolution of about 20 keV FWHM.[8,11] If the simplifying assumption is made that the alpha peaks are Gaussian-shaped, then the FWHM is equal to 2.35 standard deviations (σ) of the Gaussian distribution.[61] For adjacent Gaussian-shaped peak areas to be quantified with reasonable accuracy, the peak maxima should be at least 4σ apart.[62] Figure 5 (p 23) shows some of the more important alpha spectral groups of interest in the region of 3500 to 6500 keV. The vertical lines indicate relative intensity of the various alpha-particle energies for a given nuclide. The horizontal error bars indicate alpha-peak widths of $\pm 2\sigma$. Thus, alpha spectral groups having overlapping peak widths may not be sufficiently resolved to be measured simultaneously, and the elements should be chemically separated prior to sample preparation for accurate quantification of all peak areas. From Figure 5 (p 23) it can be seen that even with a resolution of 20 keV FWHM, there is some peak overlap of one or more uranium isotopes with one or more isotopes of all elements shown. There is only a slight degree

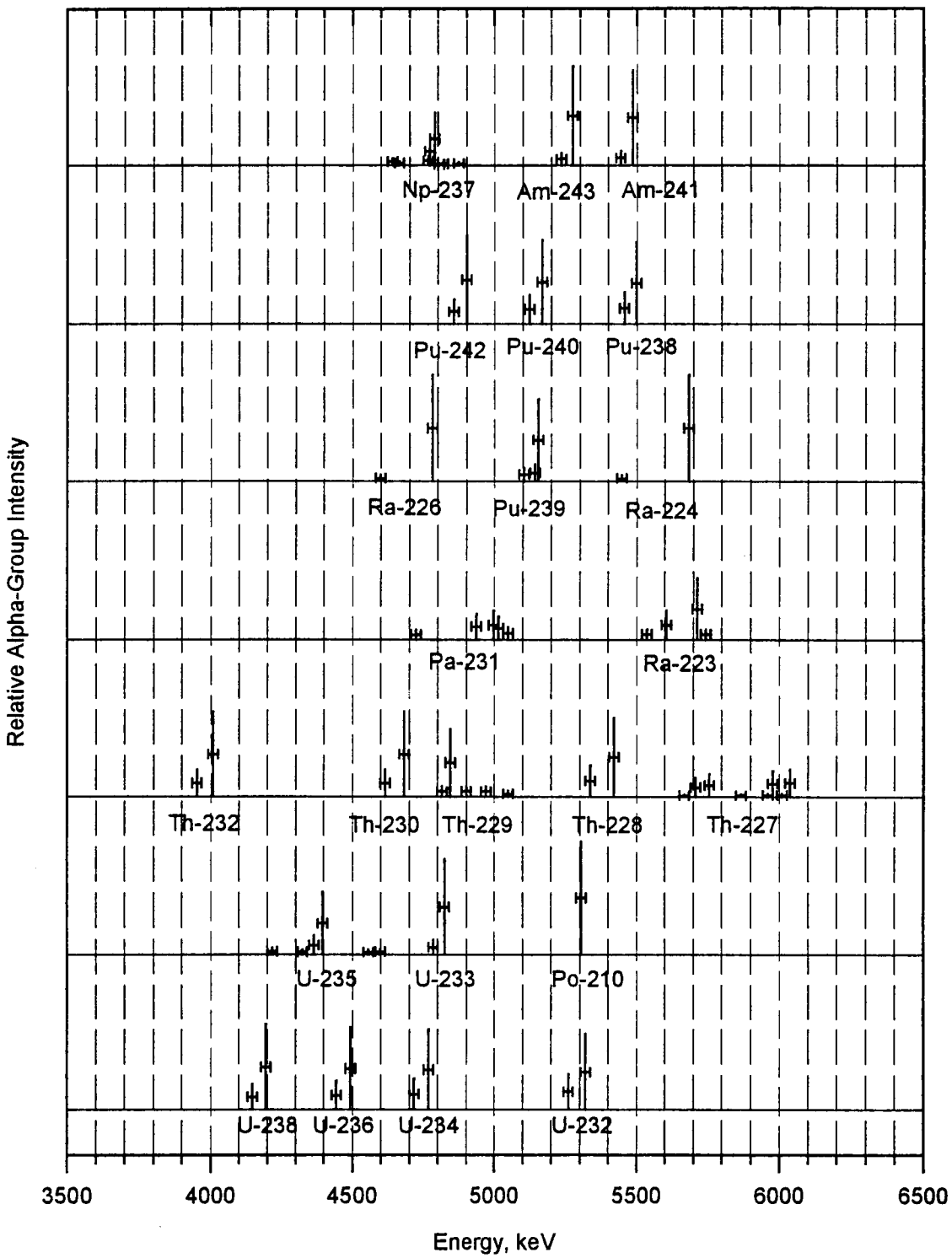


Figure 5. Schematic representation of alpha-group spectral resolution with electrodeposited samples and semiconductor detectors assuming resolution of 20 keV FWHM.

of overlap with the ^{231}Pa alpha group, and this small amount could be corrected for because the major portion of the group is resolved. Also, the only overlap between uranium and plutonium isotopes occurs between ^{233}U and ^{242}Pu, neither of which is naturally occurring, but both of which are sometimes used as isotopic tracers.

In practice it is difficult to obtain consistently energy resolution better than about 40 keV FWHM by electrodeposition during routine analyses. Using the much simpler and faster source preparation technique of micro-coprecipitation with an insoluble rare-earth fluoride (e.g., cerium or neodymium fluoride), energy resolution of 60 to 80 keV FWHM is easily and consistently obtainable.[63] Therefore, a more realistic comparison of spectral overlap might be that shown in Figure 6 (p 25), which illustrates the degree of alpha peak overlap expected for energy resolution of 60 keV FWHM. Here the overlap between uranium isotope peaks and other alpha peaks is clearly more pronounced than for 20 keV resolution. Specifically, the overlap between ^{233}U and ^{242}Pu is greater and there is some overlap between ^{234}U and ^{242}Pu, a potential interference which is of greater concern since ^{234}U is naturally occurring. Also, there is a significant degree of overlap between ^{234}U and ^{230}Th, both of which are naturally occurring radionuclides. These comparisons of spectral energy resolution indicate that to ensure minimal alpha spectral interference, uranium isotopes must normally be chemically separated from isotopes of thorium, neptunium, americium, polonium,

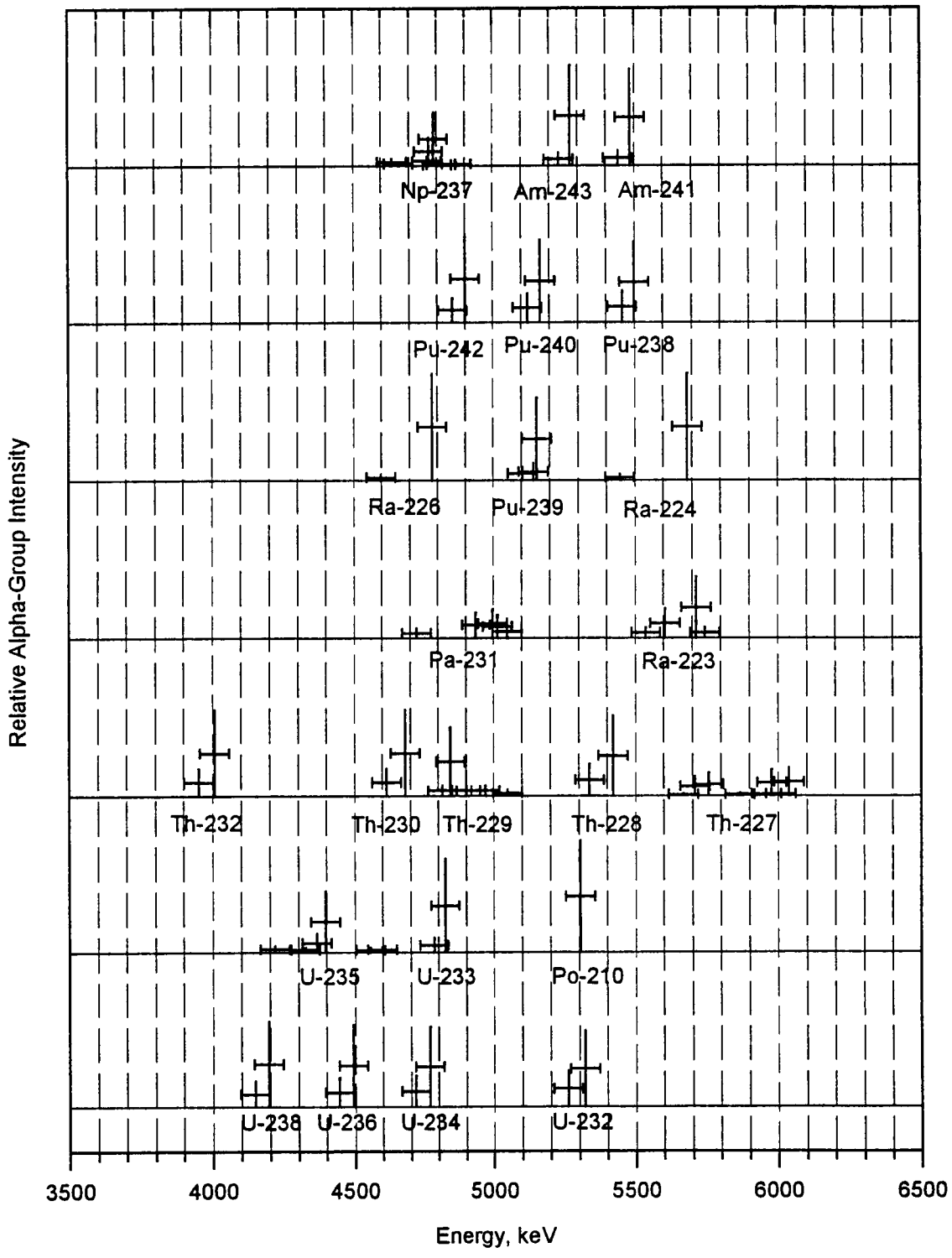


Figure 6. Schematic representation of alpha-group spectral resolution with micro-coprecipitated samples and semiconductor detectors assuming resolution of 60 keV FWHM.

and radium prior to source preparation. While it is possible to measure uranium isotopes in the presence of protactinium and plutonium, it is normal practice to perform chemical separations designed to purify uranium from all other common alpha-emitting elements as well as the bulk of non-radioactive matrix elements.

B. Review of Current Methods

At the time this research was begun, a procedure for the determination of uranium in water by PERALS spectrometry had been proposed by ETRAC Laboratories, Inc. and was undergoing evaluation as an ASTM standard method. However, initial single operator tests on drinking water samples containing uranium activities unknown to the operator were not successful. As a result, one of the primary goals of this research project was to develop a simple, rapid, and accurate procedure for the determination of uranium in water by PERALS spectrometry which could meet the requirements for approval by ASTM. During the course of this research, a new procedure for the determination of uranium in water by PERALS was developed and tested. This procedure was selected for continued evaluation by ASTM, and is awaiting final approval by ASTM Main Committee ballot at this time.

The current Environmental Protection Agency (EPA) standard method (908.0) for uranium in water by radiochemistry[64] utilizes a ferric hydroxide coprecipitation step to preconcentrate uranium as well as some other metal ions from one liter of water. Separation of uranium from matrix elements and other

alpha-emitters is achieved by anion exchange chromatography on a strongly basic anion exchange resin such as Dowex 1x4 or equivalent. The hydroxide precipitate is dissolved in 8.0 M HCl and the solution is passed through the column. Interferences are removed with a series of column elutions, and the purified uranium is eluted with 0.10 M HCl. This solution is evaporated to dryness and the salts converted to nitrates by evaporating three times with 5-mL portions of concentrated HNO_3. The residue is dissolved in 4.0 M HNO_3, evaporated in a planchet, flamed, and counted by gas-flow proportional counting. Because no alpha-energy resolution is involved in this technique, it is not possible to use an internal isotopic yield tracer, and an isotopic ratio must be assumed in order to calculate a mass concentration of uranium.

The ASTM standard test method for isotopic uranium in water by radiochemistry (D 3972)[65] is very similar to the EPA method, but the separated uranium is electrodeposited onto a stainless steel disk and counted by solid state alpha spectrometry. In this case the excellent energy resolution of solid state detectors allows use of an internal isotopic yield tracer (^{232}U) as well as accurate quantification of most uranium isotopes of interest. However, the electrodeposition step requires over one hour to complete and chemical recoveries can be erratic. Overall counting efficiencies, taking into account variations in detector efficiency and chemical recovery, can range from a high of about 35% to less than 10%.

A number of authors have demonstrated in recent years that alpha-liquid-scintillation offers an attractive alternative for measuring alpha-particle activity. The use of an extractive scintillator containing trioctylamine sulfate as the extractant (ETRAC Laboratories' Uraex® extractive scintillator) for the selective extraction of uranium from water samples containing sulfuric acid and sodium sulfate, followed by alpha counting by PERALS spectrometry was proposed and tested by Lowry[21] and Leyba, *et al.*.[33] However, the presence of greater than 100 ppm nitrate ion or greater than 1000 ppm chloride ion was found to interfere with the extraction of uranium by tertiary amine sulfates.[33] This makes direct extraction impractical for water samples which have been preserved with either HNO_3 or HCl, as is common practice for standard water sampling procedures. Because the boiling points of HNO_3 and HCl are significantly lower than that of H_2SO_4, these interferences can be eliminated by complete evaporation of the sample in the presence of H_2SO_4 until fumes of SO_3 are observed.[66]

The uranium procedure originally proposed to ASTM by ETRAC Laboratories, Inc. utilized this approach of evaporation, conversion to sulfate salts, and selective extraction with the tertiary amine-based extractive scintillator. During testing of this procedure, however, recovery of uranium was found to be inconsistent. Also, the fact that polonium was to some degree extracted along with uranium by the tertiary amine sulfate extractive scintillator prevented the use of ^{232}U (5.32 MeV) as a yield tracer because of the potential interference from ^{210}Po (5.30 MeV).

In an effort to alleviate the interference from HNO_3 and HCl, a technique was developed whereby uranium was preconcentrated from up to one liter or more of water by coprecipitation with $Fe(OH)_3$, as in the standard EPA and ASTM procedures. The precipitate was then separated by decantation and centrifugation and washed twice with dilute ammonium hydroxide (NH_4OH) to remove the bulk of NO_3^- and Cl^- ions. The washed precipitate was dissolved in a solution of H_2SO_4 and Na_2SO_4, and uranium was extracted with the tertiary amine sulfate extractive scintillator. This procedure resulted in consistently high uranium recoveries and was moderately simple to perform. However, polonium was found to coprecipitate with ferric hydroxide as well and some polonium was subsequently extracted along with uranium. It was found that the polonium could be removed and measured by first dissolving the precipitate in dilute HNO_3/HCl solution and extracting polonium with the tertiary amine extractive scintillator. Uranium did not extract under these conditions. Then ferric hydroxide was reprecipitated by the addition of ammonium hydroxide and the procedure continued as described previously. Although this modification eliminated the polonium inteference, the procedure was deemed too cumbersome and this approach was not pursued further.

Venso, *et. al.*,[67] reported the measurement of uranium in drinking water by direct extraction from one liter of water at pH 1.0 with 20 mL of scintillator solution containing bis(2-ethylhexyl)phosphoric acid (HDEHP) as the extracting agent followed by liquid scintillation counting. Counting on a Beckman LS 6000

system with PSD circuitry allowed near 100% counting efficiency and backgrounds as low as 0.75 cpm. The uranium recoveries were near quantitative, but the extraction under these conditions was not selective for uranium because HDEHP, a liquid cation exchanger, will extract many higher valence cations under these conditions.

Abuzeida, *et.al.*,[34] described a method for selectively extracting uranium (as uranyl, UO_2^{2+}) with an extractive scintillator containing HDEHP from aqueous solutions containing diethylenetriaminepentaacetic acid (DTPA). The DTPA functioned as a masking agent to inhibit the extraction of non-uranium radionuclides of the uranium and thorium decay series relative to the extraction of uranium. This is possible because DTPA forms a weaker complex with the linear uranyl ion ($O=U=O^{2+}$) than it does with simple cations, presumably due to steric hindrance from the uranyl oxygens.[68] This selective extraction technique made possible the accurate determination of uranium alpha-activity in geological samples containing all members of the uranium and thorium decay series by a liquid scintillation counter without any PSD capabilities. Uranium extraction was found to be independent of pH value in the range of pH 1.5 to 3.0. Some thorium was found to extract across a pH range of 1.0 to 4.0 with a minimum amount of thorium extracted at pH 3.0. However, the percentage of thorium extracted was not quantified in this article.

Because of its simplicity, potential for great selectivity for uranium,and its compatibility with the existing techniques used in conjunction with the PERALS

spectrometer, the method of Abuzeida[34] was selected for further testing. The procedure was adapted to the analysis of larger volumes of water samples and tested extensively to determine the degree of interference from other alpha-emitters and some other species commonly found in drinking water. As part of the ASTM approval process, two interlaboratory tests of this method were conducted. The experimental details and results are given in the following chapters.

CHAPTER II

EXPERIMENTAL METHODS AND MATERIALS

A. Apparatus

A Cole Parmer Model 05800-05 digital solution analyzer in conjunction with an Orion gel, semimicro, combination pH electrode was used for all pH measurements. Extractions were performed in 125-mL Teflon, pear-shaped, separatory funnels; 50-mL conical plastic centrifuge tubes; or 250-mL glass separatory funnels. Sample counting tubes consisted of 10-mm by 75-mm borosilicate glass culture tubes closed by placing a cork in the mouth of the tube or by placing a vinyl cap over the mouth of the tube or, in some instances, over both the cork and the mouth of the tube.

In order to remove dissolved oxygen, a chemical quenching agent, all samples were sparged prior to counting with dried, toluene-saturated argon, thus improving PSD and energy resolution. This was accomplished with a sparging gas conditioner manufactured by ETRAC Laboratories, Inc., Oak Ridge, Tennessee. Argon gas (99.999%) was first flowed through a gas drying tower containing $CaSO_4$ (6 to 8 mesh) to remove traces of water (also a chemical quench agent). The dried argon was then bubbled through a gas washing bottle containing toluene to saturate the argon with toluene and thus minimize sample evaporation while sparging. The toluene was kept free of water by the presence

of sodium metal. The outlet of the gas washing bottle was connected to a disposable Pasteur pipet which served as the sparging lance for the sample.

An ORDELA Model 8100AB PERALS spectrometer was used for all alpha-activity measurements. The spectrometer consisted of an integrated PMT detector and a light-tight sample chamber built to accommodate a 75-mm by 10-mm culture tube in a hemispherical counting chamber. The hemispherical surface was made highly reflective by coating it with barium sulfate dispersed in a small amount of binder. The reflective surface served to direct light from the sample tube onto the face of the PMT which comprised the flat side of the counting chamber. The cell was filled with light-coupling silicone oil to couple the sample to the PMT, improving light collection and, thus, resolution. The spectrometer was housed in a standard nuclear instrument module (NIM) bin and was connected to a high-voltage power supply (HVPS) and a multichannel analyzer (MCA) with a maximum of 4096 channels.

The detection circuitry consisited of a linear amplifier, and PSD circuitry with an adjustable low-level time discriminator. Each incoming pulse was converted to an amplified voltage pulse for energy analysis and a pulse-shape signal with a pulse height proportional to the duration of the incoming pulse. The PSD system measured the duration of each incoming pulse and the resulting time signals were converted to voltage pulses with heights proportional to time. These time pulses were analyzed by a single channel analyzer, and a gate pulse was generated for each one above the low-level discriminator setting.

The requirement of time coincidence between the gate pulses and appropriately delayed voltage pulses allowed only alpha pulses (those with longer decay times) to be selected for energy analysis. An MCA was used for pulse-height analysis of the coincidence pulses in order to generate an alpha-particle energy spectrum. This also enabled the time separation between beta/gamma pulses and alpha pulses to be recorded as a time spectrum. In either case it was possible to integrate electronically the entire spectrum or any portion of it. The instrument was capable of rejecting > 99.9% of pulses from beta and gamma events and had an alpha counting efficiency of 99+% when the PSD was properly adjusted and the volume of scintillator counted was 1.00 mL.[19]

B. Reagents

Radioactive tracer stock solutions of natural uranium had been prepared from an historic sample of triuranium octoxide (U_3O_8) by dissolution in nitric acid to yield a solution of uranyl nitrate. Tracer solutions of ^{241}Am, ^{210}Po, ^{238}Pu, ^{226}Ra, and ^{230}Th were obtained from Isotope Products Laboratories, Burbank, California. They were diluted with either dilute nitric acid or dilute hydrochloric acid solution to obtain stock solutions of each isotope which were further diluted to obtain working solutions. The calculated activities of the working solutions were confirmed by extraction under conditions known to give quantitative extraction for each element and by alpha-counting in the PERALS spectrometer.

In general the uncertainty in the activity of tracer solutions was from 3% to 5% at the 95% (2σ) confidence level.

The extractive scintillator used for these studies contained 64 g/L of HDEHP which had been purified by precipitation/recrystallization, 180 g/L naphthalene, and 4.0 g/L PBBO in toluene. This extractive scintillator is available from ETRAC Laboratories, Inc. as Alphaex®. The reducing agent, ascorbic acid, was 100% pure crystalline vitamin C from KAL®. All other reagents used were of analytical grade.

C. Experimental Approach

The technique of Abuzeida[34] was modified and used to develop a fast, simple, reliable, and accurate method for the measurement of uranium alpha-activity in drinking water by PERALS spectrometry. Additional studies were conducted to determine the optimum conditions for quantitative uranium extraction while extracting a minimum amount of some other alpha-emitters: ^{241}Am, ^{238}Pu, ^{210}Po, ^{226}Ra, and ^{230}Th.

The procedure was as follows: A 200-mL water sample was acidified with 0.50 mL each of concentrated HNO_3 and concentrated HCl and the beaker covered with a watchglass. The solution was heated to boiling on a hot plate and boiled gently for 5 to 10 min to drive off radon and to destroy any HCO_3^- ion present. The heat was reduced and evaporation continued until the sample volume was 40 to 50 mL. The sample was allowed to cool to room temperature

and either 5.0 mL of 0.10 M DTPA solution or 1.0 mL of 0.50 M DTPA solution was added to achieve a DTPA concentration of approximately 0.010 M. The solution pH was adjusted to 3.0 ± 0.1 by the addition of 6.0 M NaOH solution or 6.0 M NH_4OH solution while stirring continuously. The sample was transferred to a 125-mL separatory funnel, the beaker was rinsed twice with a total of 5 to 10 mL of distilled water, and the rinses were added to the separatory funnel. An accurately known volume (1.520 ± 0.007 or 2.000 ± 0.007 mL) of extractive scintillator was added to the separatory funnel, and the funnel was capped tightly. Equilibration of the sample and extractive scintillator was achieved by inverting the funnel by hand about once per second for 3 to 5 min. The phases were allowed to separate from 10 to 30 min, the aqueous (lower) phase was removed, and 1.000 ± 0.005 mL of the organic phase was transferred to a 10-mm by 75-mm borosilicate glass culture tube with a 1000 μL automatic pipet. The sample was sparged as described previously (p 32), the tube closed with a plastic cap or cork or both, and the sample was counted in the PERALS spectrometer.

Alternatively uranium was preconcentrated from larger water volumes by coprecipitation with ferric hydroxide, as in the EPA and ASTM methods, or with calcium phosphate. The precipitate was then dissolved in a small volume of concentrated HNO_3 and HCl and the procedure continued as above following the evaporation step. The flow diagram in Figure 7 (p 37) illustrates both the evaporation and ferric hydroxide coprecipitation procedures. In some

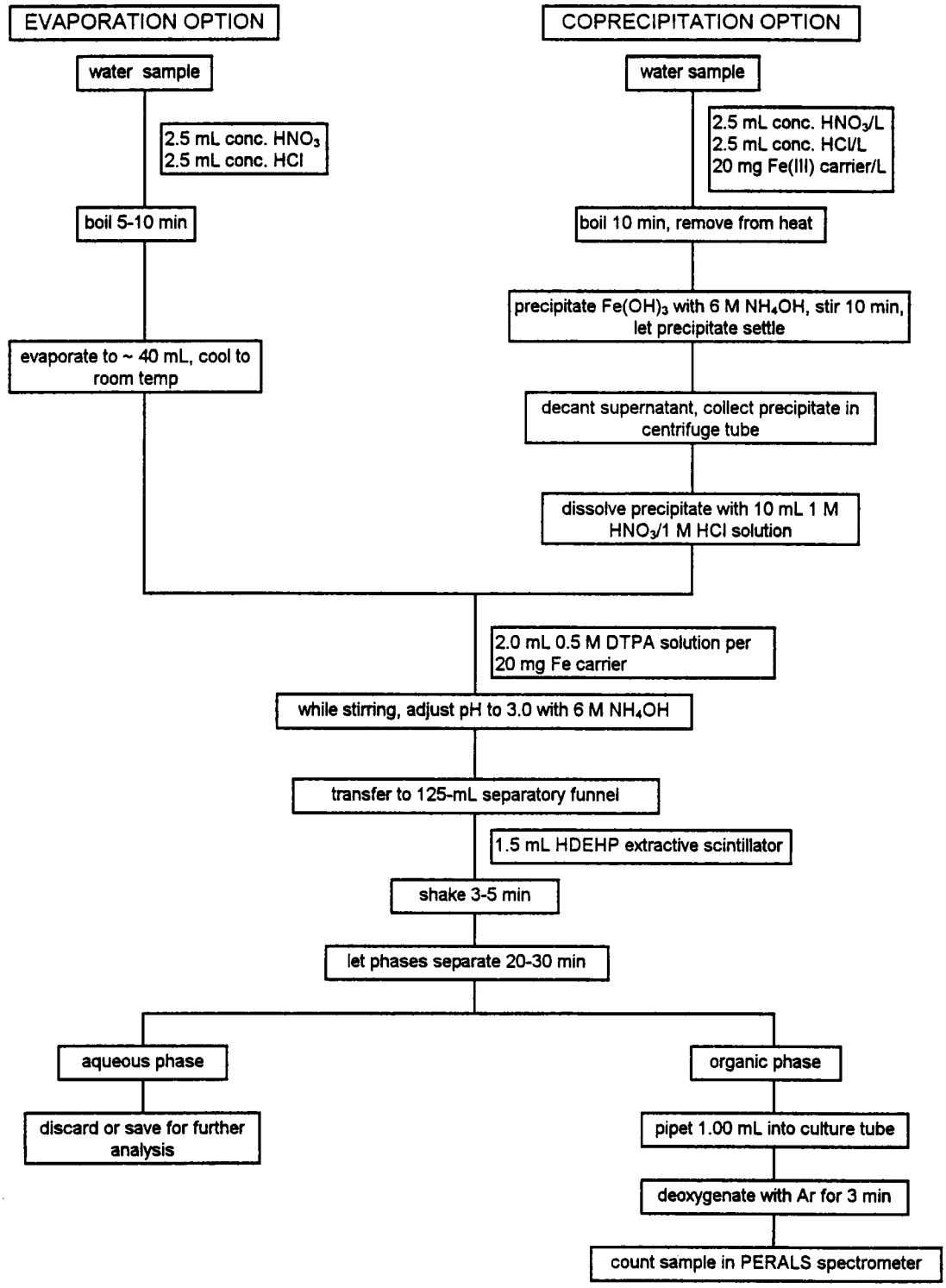


Figure 7. Flow diagram for the rapid determination of uranium in drinking water by PERALS spectrometry.

experiments uranium was extracted without preconcentration from up to 200 mL of aqueous solution.

D. Preparation of Test Solutions

For studies of the extraction dependence on various parameters, 100.0 to 1000 mL of solution was prepared in distilled water with the desired amounts of acid, radionuclides, DTPA, and interfering cations or anions. The pH was adjusted to the desired value with either 6.0 M NaOH solution or 6.0 M NH_4OH solution. An appropriate volume (50.0 ± 0.2 mL except in the case of aqueous phase volume dependence studies) of this solution was transferred to a 125-mL separatory funnel and extracted and counted as above. Alternatively individual 50 ± 1-mL samples were prepared under the desired conditions and extracted and counted as above.

E. Calculations and Propagation of Uncertainty

For experiments designed to determine the influence of various parameters or interferences on extraction efficiency, the activity A (dpm) of a given radionuclide extracted under a specific set of conditions was calculated according to Equation 2,

$$A = G_S \cdot V_{OT} \cdot V_{OC}^{-1} \cdot t^{-1} \cdot \varepsilon^{-1} \cdot 60, \qquad (2)$$

where G_S is the number of gross counts in the nuclide(s) energy region of interest (ROI), V_{OT} is the total volume of organic phase added, V_{OC} is the volume

of organic phase counted, t is the count time in seconds, ε is the instrument detection efficiency (0.996 cpm/dpm), and 60 is the conversion from dps, or becquerel (Bq), to dpm. Background counts were not subtracted in these experiments for one of two reasons: (1) the background count rate was negligible compared to the sample count rate or (2) fluctuations in background count rate due to the location of an external neutron source prohibited accurate or meaningful background subtraction.

The total propagated uncertainty (TPU) σ_A associated with the measured activity A depends on the square root of the number of counts measured and the relative uncertainty of each of the other measured terms in Equation 2 (p 38). Because of the accuracy with which time is measured, the uncertainty associated with the count time is so small as to be ignored. Thus σ_A may be estimated at the 95% confidence level by Equation 3,

$$\sigma_A = 2 \cdot \left[\left(G_S + G_S{}^2 \left[(\sigma_{V_{OT}})^2 + (\sigma_{V_{OC}})^2 + (\sigma_\varepsilon)^2 \right] \right)^{1/2} \left(V_{OT} \cdot V_{OC}{}^{-1} \cdot t^{-1} \cdot \varepsilon^{-1} \cdot 60 \right) \right], \quad (3)$$

where $\sigma_{V_{OT}}$ is the relative uncertainty in the total volume of organic phase added (1.520 ± 0.007 or 2.000 ± 0.007), $\sigma_{V_{OC}}$ is the relative uncertainty in the volume of organic phase counted (1.000 ± 0.005), and σ_ε is the relative uncertainty in the instrument counting efficiency (0.995 ± 0.003).

The percentage of a given nuclide(s) extracted or recovered, %R, under a specific set of conditions was calculated according to Equation 4,

$$\%R = (A_t)\cdot(A_0)^{-1}\cdot 100\%, \quad (4)$$

where A_t is the activity extracted and A_0 is the activity added. σ_R, the 2σ TPU associated with the percentage recovery was calculated according to Equation 5,

$$\sigma_R = \left[(\sigma_{A_t})^2 + (\sigma_{A_0})^2\right]^{1/2}\cdot \%R, \quad (5)$$

where σ_{A_t} is the relative TPU associated with the activity extracted and σ_{A_0} is the relative uncertainty of the added activity.

For the multiple single operator interlaboratory test, the uranium activity concentration U_C in $pCi\cdot L^{-1}$ was calculated for each sample according to Equation 6,

$$U_C = (G_S - B_S)\cdot V_{OT}\cdot V_{OC}{}^{-1}\cdot V_S{}^{-1}\cdot t^{-1}\cdot \varepsilon^{-1}\cdot 27, \quad (6)$$

where G_S is the number of counts in the uranium ROI for the sample, B_S is the number of counts in the uranium ROI for the reagent blank, V_S is the volume of sample analyzed (L), t is the count time for the sample and the reagent blank, and 27 is the conversion factor from Bq to pCi. For the second interlaboratory test, a ^{232}U yield tracer was added to each sample and U_C values were calculated by Equation 7,

$$U_C = (G_S - B_S)\cdot V_S{}^{-1}\cdot R^{-1}\cdot t^{-1}\cdot 27 \quad (7)$$

and Equation 8,

$$R = (G_T - B_T)\cdot T_a{}^{-1}\cdot t^{-1}, \quad (8)$$

where R represents the combined fractional chemical recovery and counting efficiency of ^{232}U tracer, G_T is the number of counts in the ^{232}U ROI for the sample, B_T is the number of counts in the ^{232}U ROI for the reagent blank, and T_a is the activity of added tracer in Bq.

CHAPTER III

RESULTS AND DISCUSSION

A. Parameters Influencing Extraction Efficiency

1. Equilibration Time

The equilibration time necessary to achieve quantitative transfer of uranium from the aqueous phase to the Alphaex organic phase was determined for the procedure outlined in Part I, Chapter II. Individual 50 ± 1-mL samples of 0.010 M DTPA solution containing 265 ± 12 dpm of natural uranium were prepared. The samples were agitated by hand with 1.520 ± 0.007 mL of extractive scintillator for times varying from 15 s to 360 s. The extractions were performed in 125-mL separatory funnels by inverting the funnels about once every second. Each analysis was repeated at least three times, and in each case the aqueous phase pH after extraction was 3.1 ± 0.1. Following equilibration, the phases were allowed to separate for 10.0 min. The aqueous phase was drained from the funnel and discarded to waste. One (1.000 ± 0.005) mL of the organic phase was removed to a culture tube, deoxygenated, and counted in the PERALS spectrometer for 1800 s.

The results of these experiments are given in Table II (p 43). Background count rates, typically 0.003 to 0.03 cpm, were not subtracted because they were insignificant relative to the sample count rates. In Figure 8 (p 44), the average

TABLE II

TIME DEPENDENCE OF URANIUM EXTRACTION
FROM 0.010 M DTPA SOLUTION AT pH 3.1

Sample	Equilibration Time (s)	DPM Added (± 2σ)	Gross Counts[a]	Count Time (s)	DPM Extracted (± 2σ TPU)	Percent Extracted (± 2σ TPU)
JD383A	15	265 ± 12	3877	1800.00	198 ± 7	75 ± 5
FC791A	15	265 ± 12	4061	1800.00	207 ± 7	78 ± 5
FC791B	15	265 ± 12	4399	1800.00	224 ± 7	85 ± 5
JD383A	30	265 ± 12	4804	1800.00	245 ± 8	93 ± 5
FC792A	30	265 ± 12	5032	1800.00	256 ± 8	97 ± 6
FC792B	30	265 ± 12	5043	1800.00	257 ± 8	97 ± 6
FC771	60	265 ± 12	4939	1800.00	252 ± 8	95 ± 6
FC793A	60	265 ± 12	5150	1800.00	262 ± 8	99 ± 6
FC793B	60	265 ± 12	5178	1800.00	264 ± 8	100 ± 6
FC772	120	265 ± 12	5150	1800.00	262 ± 8	99 ± 6
FC794A	120	265 ± 12	5180	1800.00	264 ± 8	100 ± 6
FC794B	120	265 ± 12	5178	1800.00	264 ± 8	100 ± 6
FC773	240	265 ± 12	5264	1800.00	268 ± 8	101 ± 6
FC795A	240	265 ± 12	5092	1800.00	259 ± 8	98 ± 6
FC795B	240	265 ± 12	5029	1800.00	256 ± 8	97 ± 6
FC796A	360	265 ± 12	5137	1800.00	262 ± 8	99 ± 6
FC796B	360	265 ± 12	15312	5400.00	260 ± 5	98 ± 5
FC796C	360	265 ± 12	5132	1800.00	262 ± 8	99 ± 6
JD385A	360	265 ± 12	15869	5400.00	270 ± 5	102 ± 5

a. Background counts were not subtracted

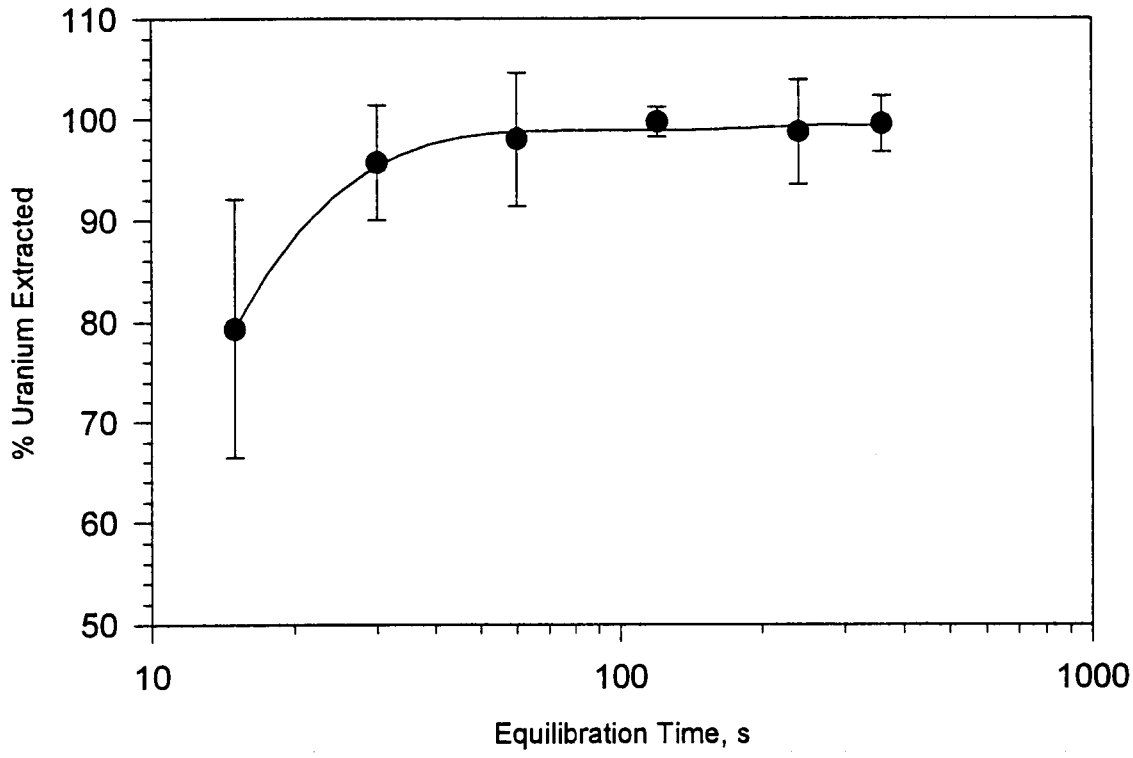


Figure 8. Uranium extraction with Alphaex from 0.010 M DTPA solution at pH 3.1 as a function of equilibration time.

percentage of uranium extracted is plotted against equilibration time. The error bars indicate the 95% confidence limits for each average percent extraction value. Approximately 79% uranium extraction was observed for the shortest equilibration time of 15 s. Over 96% of uranium was extracted within 30 s, and the extraction was found to be complete within 60 s to 120 s. Even so, all subsequent extractions were performed for a minimum of 180 s.

2. Solution pH Value

The influence of aqueous phase pH on extraction of uranium, thorium, polonium, plutonium, americium, and radium by Alphaex from 0.010 M DTPA solution was investigated to determine the optimum pH for extraction. Ideally, the optimum extraction pH is that at which quantitative uranium extraction is achieved while a minimum amount of other alpha-emitting elements are extracted.

a. Uranium: Solutions of natural uranium, with activities ranging from 2.7 ± 0.1 dpm mL^{-1} to 5.8 ± 0.3 dpm mL^{-1}, in 0.010 M DTPA were prepared at pH values of 1.0, 2.0, 3.0, 4.0 and 5.0. Fifty (50 ± 1 or 50.0 ± 0.2) mL of each solution was equilibrated with 1.520 ± 0.007 mL of extractive scintillator for times ranging from three to five minutes. The phases were allowed to separate for 10 to 30 minutes, and 1.000 ± 0.005 mL of the organic phase was taken for counting. Average uranium recoveries were found to be quantitative within experimental error at all pH values investigated (Table III, p 46). However, at pH values 4.0 and 5.0 phase separation was much slower than at lower pH values.

TABLE III

pH DEPENDENCE OF URANIUM EXTRACTION
FROM 0.010 M DTPA SOLUTION

Sample	Equilibrium pH	DPM Added (± 2σ)	Gross Counts[a]	Count Time (s)	DPM Extracted (± 2σ TPU)	Percent Extracted (± 2σ TPU)
FC521A[b,c]	1.0 ± 0.1	290 ± 16	10006	4261.72	215 ± 7	74 ± 5
FC521B[b,c]	1.0 ± 0.1	290 ± 16	10039	3384.02	272 ± 9	94 ± 6
FC521C[b,c]	1.0 ± 0.1	290 ± 16	9991	4157.80	220 ± 7	76 ± 5
FC521D[b,c]	1.0 ± 0.1	290 ± 16	10805	3268.80	303 ± 10	104 ± 7
FC62A[b,c]	1.0 ± 0.1	153 ± 6	5821	3600.00	148 ± 6	97 ± 6
FC62B[b,c]	1.0 ± 0.1	153 ± 6	3345	3600.00	164 ± 7	107 ± 7
FC62C[b,c]	1.0 ± 0.1	153 ± 6	5918	3600.00	151 ± 6	98 ± 6
FC62D[b,c]	1.0 ± 0.1	153 ± 6	5826	3600.00	148 ± 6	97 ± 6
JD3119A[d]	1.0 ± 0.1	134 ± 6	5230	3600.00	133 ± 5	99 ± 6
JD3119B[d]	1.0 ± 0.1	134 ± 6	5248	3600.00	133 ± 5	100 ± 6
JD3119C[d]	1.0 ± 0.1	134 ± 6	5229	3600.00	133 ± 5	99 ± 6
FC522A[b,c]	2.0 ± 0.1	290 ± 16	9990	3043.58	301 ± 10	104 ± 7
FC522B[b,c]	2.0 ± 0.1	290 ± 16	9991	3059.04	299 ± 10	103 ± 7
FC522C[b,c]	2.0 ± 0.1	290 ± 16	10009	3029.62	303 ± 10	104 ± 7
FC523A[b,c]	3.0 ± 0.1	290 ± 16	10037	3195.66	288 ± 9	99 ± 7
FC523B[b,c]	3.0 ± 0.1	290 ± 16	9984	2952.94	310 ± 10	107 ± 7
FC523C[b,c]	3.0 ± 0.1	290 ± 16	9986	3090.26	296 ± 10	102 ± 7
FC524A[b,c]	4.0 ± 0.1	290 ± 16	9981	3177.44	288 ± 9	99 ± 7
FC524B[b,c]	4.0 ± 0.1	290 ± 16	10008	3404.38	269 ± 9	93 ± 6
FC524C[b,c]	4.0 ± 0.1	290 ± 16	10007	3199.08	286 ± 9	99 ± 7
JD3145A[d]	4.0 ± 0.1	168 ± 7	6467	3600.00	164 ± 6	98 ± 6
JD3145B[d]	4.0 ± 0.1	168 ± 7	6666	3600.00	170 ± 6	101 ± 7
JD3145C[d]	5.0 ± 0.1	168 ± 7	6573	3600.00	168 ± 6	100 ± 6

a. Background counts were not subtracted.

b. Replicate 50-mL samples were prepared individually.

c. Approximately 0.20 ± 0.05 g of ascorbic acid was added to the sample.

d. Either 200.0-mL or 250.0-mL test samples were prepared and 50.0-mL aliquots extracted.

In the initial experiments, individual samples were prepared by adding the following reagents to between 35 and 40 mL of distilled water: 0.50 mL each of concentrated HNO_3 and concentrated HCl, 0.200 to 1.000 mL of the appropriate tracer solution, and either 5.000 mL of 0.10 M DTPA solution or 1.000 mL of 0.50 M DTPA solution. The solution pH was adjusted to the desired value with 6.0 M NaOH solution while stirring continuously. The solution was then diluted to 50 ± 1 mL and approximately 0.20 ± 0.05 g of ascorbic acid was added to the sample prior to extraction with 1.520 ± 0.007 mL of Alphaex extractive scintillator solution. Initially it was thought that the addition of ascorbic acid, a common reducing agent, would function to reduce any ferric ion present in the sample to ferrous ion, thereby minimizing the chance of iron hydroxide precipitation upon pH adjustment or extraction of ferric ion by Alphaex. Later experiments showed that this step was not necessary, and it was eventually eliminated from the procedure.

Using samples prepared individually as described above, some inconsistencies were observed in uranium recovery at pH 1.0 and 4.0 (see Table III, p 46, samples FC521A, FC521B, FC521C, and FC521D and FC524B). In these experiments, two out of four replicates at pH 1.0 showed recoveries of only about 75% and one out of three replicates at pH 4.0 indicated only 93% uranium recovery. Additional individually-prepared replicates of the experiment at pH 1.0 all gave recoveries of about 100%.

In some later studies, either 200.0- or 250.0-mL sample test solutions were prepared in the same manner as the individually-prepared 50-mL samples described previously. Aliquots of 50.0 ± 0.2 mL were taken for replicate extraction experiments. The triplicate sample set at pH 1.0 consisting of samples JD3119A, JD3119B, and JD3119C and the duplicate sample set at pH 4.0 consisting of samples JD3145A and JD3145B were prepared in this manner. The observed uranium recoveries in these experiments were quantitative and much more consistent than for the individually-prepared samples. Based on these results, experiments FC521A and FC521C were rejected as outliers when calculating the average uranium recoveries at pH 1.0 (Table IX, p 57). Experiment FC524B was included in the average calculation at pH 4.0.

b. Thorium: Abuzeida had previously reported that a minimum amount of thorium was extracted from DTPA solutions at pH 3.0.[34] Therefore, a pH value of 3.0 was originally chosen as the optimum pH for maximum uranium extraction and minimum extraction of other alpha-emitters. To verify this the percentage of ^{230}Th extracted from 0.010 M DTPA solutions of pH 2.0, 2.5, 3.0, and 3.5 was determined in the same manner as for uranium. Thorium activities ranged from 0.96 ± 0.04 dpm mL^{-1} to 3.82 ± 0.12 dpm mL^{-1}. The experimental results are given in Table IV (p 49). It was noticed during the course of these experiments that reagent blank counts varied more than usual due to the occasional presence of a neutron source in the counting room. Because it was not possible

TABLE IV

pH DEPENDENCE OF THORIUM EXTRACTION
FROM 0.010 M DTPA SOLUTION

Sample	Equilibrium pH	DPM Added (± 2σ)	Gross Counts[a]	Count Time (s)	DPM Extracted (± 2σ)	Percent Extracted (± 2σ TPU)
JD386A[b]	2.0 ± 0.1	191 ± 6	190	3600.00	4.8 ± 0.8	2.5 ± 0.4
JD386B[b]	2.0 ± 0.1	191 ± 6	134	3600.00	3.4 ± 0.6	1.8 ± 0.4
JD387A[b,c]	2.0 ± 0.1	191 ± 6	102	3600.00	2.6 ± 0.6	1.4 ± 0.3
JD387B[b,c]	2.0 ± 0.1	191 ± 6	115	3600.00	2.9 ± 0.6	1.5 ± 0.3
JD3120A[b]	2.5 ± 0.1	48 ± 2	38	7200.00	0.48 ± 0.16	1.0 ± 0.4
JD3120B[b]	2.5 ± 0.1	48 ± 2	570	60000.00	0.87 ± 0.08	1.82 ± 0.18
JD3120C[b]	2.5 ± 0.1	48 ± 2	26	7200.00	0.33 ± 0.12	0.7 ± 0.3
FC58A[c,d]	3.0 ± 0.1	191 ± 6	46	3600.00	1.2 ± 0.4	0.61 ± 0.18
FC58B[c,d]	3.0 ± 0.1	191 ± 6	26	3600.00	0.7 ± 0.3	0.35 ± 0.14
JD388A[b]	3.0 ± 0.1	191 ± 6	8	3600.00	0.20 ± 0.14	0.11 ± 0.08
JD388B[b]	3.0 ± 0.1	191 ± 6	5	3600.00	0.13 ± 0.12	0.07 ± 0.06
JD3134A[b]	3.5 ± 0.1	76 ± 3	7	3600.00	0.18 ± 0.14	0.23 ± 0.18
JD3134B[b]	3.5 ± 0.1	76 ± 3	9	3000.00	0.11 ± 0.08	0.15 ± 0.10

a. Background counts were not subtracted.

b. Either 200.0-mL or 250.0-mL test samples were prepared and 50.0-mL aliquots extracted.

c. Approximately 0.20 ± 0.05 g of ascorbic acid was added prior to extraction.

d. Replicate 50-mL samples were prepared individually.

to verify consistently a reagent blank count rate which was applicable for each test sample, background counts were not subtracted from any of these test samples or for other alpha-emitters tested. Therefore, it is possible that some of the percent extraction values reported for interfering alpha-emitters are higher than the true values.

With the exception of samples FC58A and FC58B, all of the thorium samples extracted were 50.0 ± 0.2-mL aliquots taken from either 200.0- or 250.0-mL test solutions. Samples FC58A and FC58B also contained 0.20 ± 0.05 g of ascorbic acid, as did samples JD387A and JD387B. The percentage of thorium extracted in experiments FC58A and FC58B was slightly higher than for the other two experiments at pH 3.0. However, no significant difference in thorium extraction was observed between JD387A and JD387B and the other two experiments at pH 2.0. The percentage of thorium extracted was found to decrease from a high of 1.8 ± 1.0 at pH 2.0 to a low of 0.19 ± 0.12 at pH 3.5. The average percent extraction at pH 3.0 was 0.3 ± 0.5. If the individually-prepared samples, FC58A and FC58B, are discarded, the average percent extraction at pH 3.0 is 0.09 ± 0.06 and there is no difference between thorium recovery at pH 3.0 and pH 3.5. These experiments confirm Abuzeida's results which indicated minimum thorium extraction at pH 3.0.

c. Polonium: The extraction of polonium was investigated at pH values 2.0, 2.5, and 3.0 for 0.010 M DTPA solutions containing from 0.94 ± 0.04 $dpm \cdot mL^{-1}$ to 38.0 ± 1.2 $dpm \cdot mL^{-1}$ of ^{210}Po. Less than 1% of ^{210}Po was extracted

in all but three experiments: FC57C, FC57D, and JD3120C (Table V, p 52). In experiments FC57C and FC57D an average of 5.0 ± 1.2% polonium extraction was recorded at pH 2.0. This is in contrast to an average of 0.1 ± 0.3% extraction for four other experiments at this pH value which were performed in an attempt to reproduce these results: samples JD386A, JD386B, JD386C, and JD387D. Samples FC57C and FC57D were prepared individually and contained 1909 ± 58 dpm of ^{210}Po per 50-mL sample. Ascorbic acid was also added prior to extraction in these experiments. The other four samples were 50.0 ± 0.2-mL aliquots taken from larger samples and contained either 115 ± 4 or 114 ± 4 dpm of ^{210}Po per 50.0-mL aliquot. Ascorbic acid was added to two of the four samples in an attempt to determine if the percentage of polonium extracted was affected by the presence of ascorbic acid. No significant difference was observed between the four samples at pH 2.0. However, at pH 2.5 about 10 to 15 times more polonium was extracted in the experiment in which ascorbic acid was added, JD3120C. Extraction experiments at pH 3.0 also indicated significant, although smaller, differences between samples containing 1900 ± 60 dpm ^{210}Po compared to samples containing less than 200 dpm ^{210}Po. It was not possible to say whether the difference was due to the greater concentration of polonium, the way in which the samples were prepared, or the addition of ascorbic acid. Because less than 1% extraction was recorded for all samples at pH 3.0, no additional investigations were performed to determine the reason for the observed differences.

TABLE V

pH DEPENDENCE OF POLONIUM EXTRACTION
FROM 0.010 M DTPA SOLUTION

Sample	Equilibrium pH	DPM Added (± 2σ)	Gross Counts[a]	Count Time (s)	DPM Extracted (± 2σ)	Percent Extracted (± 2σ TPU)
FC57C[b,c]	2.0 ± 0.1	1900 ± 60	4080	3600.00	104 ± 4	5.4 ± 0.3
FC57D[b,c]	2.0 ± 0.1	1900 ± 60	3470	3600.00	88 ± 4	4.6 ± 0.3
JD386A[d]	2.0 ± 0.1	115 ± 4	0	3600.00	0 ± 0	0 ± 0
JD386B[d]	2.0 ± 0.1	115 ± 4	2	3600.00	0.05 ± 0.08	0.04 ± 0.06
JD387A[c,d]	2.0 ± 0.1	114 ± 4	8	3600.00	0.20 ± 0.14	0.18 ± 0.13
JD387B[c,d]	2.0 ± 0.1	114 ± 4	12	3600.00	0.4 ± 0.3	0.32 ± 0.19
JD3120A[d]	2.5 ± 0.1	47 ± 2	8	7200.00	0.10 ± 0.08	0.22 ± 0.15
JD3120B[d]	2.5 ± 0.1	47 ± 2	28	60000.00	0.04 ± 0.02	0.09 ± 0.03
JD3120C[d,e]	2.5 ± 0.1	47 ± 2	61	7200.00	0.8 ± 0.2	1.6 ± 0.5
FC57A[b,c]	3.0 ± 0.1	1900 ± 60	614	3600.00	15.6 ± 1.4	0.82 ± 0.07
FC57B[b,c]	3.0 ± 0.1	1900 ± 60	378	3600.00	9.6 ± 1.0	0.50 ± 0.06
FC57F[b,c]	3.0 ± 0.1	1900 ± 60	331	3600.00	8.4 ± 1.0	0.44 ± 0.05
FC57E[b,c]	3.0 ± 0.1	191 ± 6	3	3600.00	0.08 ± 0.08	0.04 ± 0.05
JD388A[d]	3.0 ± 0.1	113 ± 4	2	3600.00	0.05 ± 0.08	0.05 ± 0.06
JD388B[d]	3.0 ± 0.1	113 ± 4	9	3600.00	0.23 ± 0.16	0.20 ± 0.14

a. Background counts were not subtracted.

b. Replicate 50-mL samples were prepared individually.

c. Approximately 0.20 ± 0.05 g of ascorbic acid was added prior to extraction.

d. Either 200.0- or 250.0-mL test samples were prepared and 50.0-mL aliquots extracted.

e. Approximately 0.30 ± 0.05 g of ascorbic acid was added prior to extraction.

d. Plutonium: The percentage of plutonium extracted from 0.010 M DTPA solution was investigated at pH 2.0 and 3.0. Table VI (p 54) gives the results of these experiments. The observed percent extraction values for plutonium were similar to those obtained for thorium, with an average of 1.9 ± 0.9% extraction at pH 2.0 and an average of 0.4 ± 0.3% extraction at pH 3.0. No significant difference was observed between experiments in which ascorbic acid was added and experiments in which no ascorbic acid was added.

e. Americium: The extraction of americium from 0.010 M DTPA solution was studied at pH 2.5 and 3.0. The results are given in Table VII (p 55). Less than 1% extraction of ^{241}Am was observed at both pH values. Experiment FC60A was rejected as an outlier when calculating the average percent americium extraction at pH 3.0.

f. Radium: The extraction of radium from 0.010 M DTPA solution was investigated at pH 3.0 only (Table VIII, p 56). With the exception of experiment FC61A, less than 1% of the added radium activity was found to extract at this pH. Since it could not be repeated, experiment FC61A was rejected as an outlier and was not included in the calculation of the average percent extraction.

Table IX (p 57) gives the average percent extraction and 95% confidence limits for each element at the various pH values investigated. The number of measurements from which the average value is calculated is given in parentheses. The extraction of uranium from 0.010 M DTPA solution is

TABLE VI

pH DEPENDENCE OF PLUTONIUM EXTRACTION
FROM 0.010 M DTPA SOLUTION

Sample	Equilibrium pH	DPM Added (± 2σ)	Gross Counts[a]	Count Time (s)	DPM Extracted (± 2σ)	Percent Extracted (± 2σ TPU)
JD3139A[b]	2.0 ± 0.1	51 ± 3	486	60000.00	0.74 ± 0.06	1.46 ± 0.15
JD3139B[b]	2.0 ± 0.1	51 ± 3	65	7200.00	0.8 ± 0.2	1.6 ± 0.5
JD3139C[b]	2.0 ± 0.1	51 ± 3	54	3600.00	1.4 ± 0.4	2.7 ± 0.8
JD3139D[b]	2.0 ± 0.1	51 ± 3	75	7200.00	1.0 ± 0.3	1.9 ± 0.5
FC58C[c,d]	3.0 ± 0.1	44 ± 4	9	3600.00	0.23 ± 0.16	0.5 ± 0.4
FC58D[c,d]	3.0 ± 0.1	44 ± 4	2	3600.00	0.05 ± 0.08	0.12 ± 0.16
JD3141A[b]	3.0 ± 0.1	51 ± 3	89	36000.00	0.23 ± 0.04	0.44 ± 0.10
JD3141B[b]	3.0 ± 0.1	51 ± 3	85	36000.00	0.22 ± 0.04	0.42 ± 0.09

a. Background counts were not subtracted.

b. Either 200.0- or 250.0-mL of sample solution was prepared and 50.0-mL aliquots extracted.

c. Replicate 50-mL samples were prepared individually.

d. Approximately 0.20 ± 0.05 g of ascorbic acid was added prior to extraction.

TABLE VII

pH DEPENDENCE OF AMERICIUM EXTRACTION
FROM 0.010 M DTPA SOLUTION

Sample	Equilibrium pH	DPM Added (± 2σ)	Gross Counts[a]	Count Time (s)	DPM Extracted (± 2σ)	Percent Extracted (± 2σ TPU)
JD423B[b]	2.5 ± 0.1	27 ± 2	23	14400.00	0.15 ± 0.07	0.6 ± 0.3
FC60A[c]	3.0 ± 0.1	260 ± 16	74	3600.00	1.9 ± 0.5	0.72 ± 0.18
FC60B[c]	3.0 ± 0.1	260 ± 16	4	3600.00	0.10 ± 0.10	0.04 ± 0.04
FC63A[c]	3.0 ± 0.1	260 ± 16	6	3600.00	0.15 ± 0.12	0.06 ± 0.05
FC63B[c]	3.0 ± 0.1	260 ± 16	5	3600.00	0.13 ± 0.12	0.05 ± 0.04

a. Background counts were not subtracted.

b. A 200.0-mL sample was prepared and a 50.0-mL aliquot extracted.

c. Replicate 50-mL samples were prepared individually.

TABLE VIII

EXTRACTION OF RADIUM FROM 0.010 M DTPA SOLUTION AT pH 3.0

Sample	Equilibrium pH	DPM Added (± 2σ)	Gross Counts[a]	Count Time (s)	DPM Extracted (± 2σ)	Percent Extracted (± 2σ TPU)
FC61A[b]	3.0 ± 0.1	193 ± 12	211	3600.00	5.4 ± 0.8	2.8 ± 0.5
FC61B[b]	3.0 ± 0.1	193 ± 12	0	3600.00	0 ± 0	0 ± 0
FC61C[b]	3.0 ± 0.1	193 ± 12	8	3600.00	0.20 ± 0.14	0.11 ± 0.07
FC61D[b]	3.0 ± 0.1	193 ± 12	13	3600.00	0.33 ± 0.18	0.17 ± 0.10
FC61E[b]	3.0 ± 0.1	193 ± 12	47	3600.00	1.2 ± 0.4	0.62 ± 0.19

a. Background counts were not subtracted.

b. Replicate 50-mL samples were prepared individually.

TABLE IX

AVERAGE PERCENT EXTRACTION OF ALPHA-EMITTERS FROM 0.010 M DTPA SOLUTION AS A FUNCTION OF pH

	Radionuclide Average Percent Extraction					
pH	Natural U	^{230}Th	^{210}Po	^{238}Pu	^{241}Am	^{226}Ra
1.0	99 ± 3 (9)	—	—	—	—	—
2.0	104 ± 2 (3)	1.8 ± 0.8 (4)	2 ± 3 (6)	1.9 ± 0.9 (4)	—	—
2.5	—	1.2 ± 1.4 (3)	1 ± 2 (3)	—	0.6 ± 0.3 (1)	—
3.0	103 ± 10 (3)	0.3 ± 0.4 (4)	0.3 ± 0.4 (6)	0.4 ± 0.3 (4)	0.05 ± 0.03 (3)	0.2 ± 0.5 (4)
3.5	—	0.2 ± 0.5 (2)	—	—	—	—
4.0	98 ± 8 (5)	—	—	—	—	—
5.0	100 ± 6 (1)	—	—	—	—	—

essentially quantitative in the pH range of 1.0 to 5.0 while less than 1% of thorium, polonium, plutonium, americium, and radium are extracted at pH 3.0.

3. DTPA Concentration

The percentage of uranium, americium, and thorium extracted from either 50 ± 1 mL or 50.0 ± 0.2 mL of aqueous solution at pH 3.0 was measured as a function of DTPA concentration. Extractions were performed with no DTPA added and at DTPA concentrations of 0.0010 M, 0.010 M, and 0.10 M. Higher DTPA concentrations were not investigated in this study due to the limited solubility of DTPA in water at pH 3.0. Uranium extraction was found to be quantitative at all DTPA concentrations tested (Table X, p 59). The percentage of americium extracted decreased from almost 90% with no DTPA added to less than 0.1% with 0.0010 M and higher concentrations of DTPA (Table XI, p 60). Although thorium is known to be strongly extracted by toluene solutions of HDEHP from more acidic solutions (pH 0.5 to 2),[69] less than 10% of thorium was extracted at pH 3.0 even with no added DTPA (Table XII, p 61). This is probably because Th^{4+} is partially hydrolyzed at pH 3 and, therefore, is not extracted as strongly as a simple M^{4+} cation would be. Less than 1% thorium extraction was observed for all solutions to which DTPA had been added.

4. Aqueous Phase Volume

The percentage of uranium extracted from 0.010 M DTPA solution was measured as a function of aqueous phase volume. In each case the aqueous phase pH was 3.0 ± 0.1. No attempt was made to preequilibrate either phase

TABLE X

EFFECT OF DTPA CONCENTRATION ON
URANIUM EXTRACTION AT pH 3.0

Sample[a,b]	[DTPA]	DPM Added (± 2σ)	Gross Counts[c]	Count Time (s)	DPM Extracted (± 2σ)	Percent Extracted (± 2σ TPU)
JD399A	—	134 ± 6	5392	3600.00	137 ± 5	103 ± 6
JD399B	—	134 ± 6	5224	3600.00	133 ± 5	99 ± 6
JD399C	—	134 ± 6	5278	3600.00	134 ± 5	100 ± 6
JD3102A	0.0010	134 ± 6	5268	3600.00	134 ± 5	100 ± 6
JD3102B	0.0010	134 ± 6	5466	3600.00	139 ± 5	104 ± 6
JD3102C	0.0010	134 ± 6	5373	3600.00	137 ± 5	102 ± 6
JD3119A	0.010	134 ± 6	5230	3600.00	133 ± 5	99 ± 6
JD3119B	0.010	134 ± 6	5248	3600.00	133 ± 5	100 ± 6
JD3119C	0.010	134 ± 6	5229	3600.00	133 ± 5	99 ± 6
JD3104A	0.10	134 ± 6	5291	3600.00	135 ± 5	101 ± 6
JD3104B	0.10	134 ± 6	5385	3600.00	137 ± 5	102 ± 6
JD3104C	0.10	134 ± 6	5300	3600.00	135 ± 5	101 ± 6

a. Either 200.0- or 250.0-mL samples were prepared and 50.0-mL aliquots extracted.

b. Each 50.0-mL aliquot also contained 1050 ± 40 dpm Am-241. The ^{241}Am alpha peak (5.48 MeV) was well resolved from the ^{234}U alpha peak (4.77 MeV).

c. Background counts were not subtracted.

TABLE XI

EFFECT OF DTPA CONCENTRATION ON AMERICIUM EXTRACTION AT pH 3.0

Sample	[DTPA]	DPM Added (± 2σ)	Gross Counts[a]	Count Time (s)	DPM Extracted (± 2σ)	Percent Extracted (± 2σ TPU)
JD399A[b,c]	—	1050 ± 40	32083	3600.00	817 ± 22	78 ± 4
JD399B[b,c]	—	1050 ± 40	33309	3600.00	849 ± 23	81 ± 4
JD399C[b,c]	—	1050 ± 40	33129	3600.00	844 ± 23	80 ± 4
JD399D[b,c]	—	1050 ± 40	37534	3600.00	956 ± 26	91 ± 5
FC761[d]	—	260 ± 8	9482	3600.00	242 ± 8	93 ± 5
FC762[d]	—	260 ± 8	9915	3600.00	253 ± 8	97 ± 5
FC763[d]	—	260 ± 8	9822	3600.00	250 ± 8	96 ± 5
JD3102A[b,c]	0.0010	1050 ± 40	24	3600.00	0.6 ± 0.3	0.06 ± 0.02
JD3102B[b,c]	0.0010	1050 ± 40	28	3600.00	0.7 ± 0.3	0.07 ± 0.03
JD3102C[b,c]	0.0010	1050 ± 40	22	3600.00	0.6 ± 0.3	0.05 ± 0.02
FC60A[d]	0.010	260 ± 16	74	3600.00	1.9 ± 0.5	0.72 ± 0.18
FC60B[d]	0.010	260 ± 16	4	3600.00	0.10 ± 0.10	0.04 ± 0.04
FC63A[d]	0.010	260 ± 16	6	3600.00	0.15 ± 0.12	0.06 ± 0.05
FC63B[d]	0.010	260 ± 16	5	3600.00	0.13 ± 0.12	0.05 ± 0.04
JD3104A[b,c]	0.10	1050 ± 40	5	3600.00	0.13 ± 0.12	0.01 ± 0.01
JD3104B[b,c]	0.10	1050 ± 40	9	3600.00	0.23 ± 0.16	0.02 ± 0.01
JD3104C[b,c]	0.10	1050 ± 40	11	3600.00	0.28 ± 0.16	0.03 ± 0.02

a. Background counts were not subtracted.

b. Either 200.0- or 250.0-mL samples were prepared and 50.0-mL aliquots extracted.

c. Each 50.0-mL aliquot also contained 134 ± 6 dpm natural uranium. The ^{241}Am alpha peak (5.48 MeV) was well resolved from the ^{234}U alpha peak (4.77 MeV).

d. Replicate 50-mL samples were prepared individually.

TABLE XII

EFFECT OF DTPA CONCENTRATION ON
THORIUM EXTRACTION AT pH 3.0

Sample	[DTPA]	DPM Added (± 2σ)	Gross Counts[a]	Count Time (s)	DPM Extracted (± 2σ)	Percent Extracted (± 2σ TPU)
FC761[b,c]	—	191 ± 6	359	3600.00	9.2 ± 1.0	4.8 ± 1.1
FC762[b,c]	—	191 ± 6	587	3600.00	15.0 ± 1.3	7.8 ± 1.5
FC763[b,c]	—	191 ± 6	512	3600.00	13.0 ± 1.2	6.8 ± 1.3
JD424A[d]	0.0010	56 ± 2	16	7200.00	0.20 ± 0.10	0.36 ± 0.18
JD424B[d]	0.0010	56 ± 2	25	14400.00	0.16 ± 0.06	0.28 ± 0.11
FC58A[b]	0.010	191 ± 6	46	3600.00	1.2 ± 0.4	0.61 ± 0.18
FC58B[b]	0.010	191 ± 6	26	3600.00	0.7 ± 0.3	0.35 ± 0.14
JD388A[d]	0.010	191 ± 6	8	3600.00	0.20 ± 0.14	0.11 ± 0.08
JD388B[d]	0.010	191 ± 6	5	3600.00	0.13 ± 0.12	0.07 ± 0.06
JD425A[d]	0.10	68 ± 2	13	14400.00	0.08 ± 0.04	0.12 ± 0.07
JD425B[d]	0.10	68 ± 2	18	14400.00	0.11 ± 0.06	0.17 ± 0.08

a. Background counts were not subtracted.

b. Replicate 50-mL samples were prepared individually.

c. Each 50-mL aliquot also contained 260 ± 8 dpm ^{241}Am. The ^{241}Am alpha peak (5.48 MeV) was well resolved from the ^{230}Th alpha peak (4.69 MeV).

d. Either 200.0- or 250.0-mL samples were prepared and 50.0-mL aliquots extracted.

prior to the extraction step. In all experiments either 1.520 ± 0.007 mL or 2.000 ± 0.007 mL of extractive scintillator was added to the appropriate aqueous phase. After equilibration 1.000 ± 0.005 mL of organic phase was removed for counting. In a few cases the ionic strength of the aqueous phase was adjusted by adding enough sodium nitrate ($NaNO_3$) to make the solution 1.0 M in $NaNO_3$. The results of these experiments are given in Table XIII (p 63). In all cases uranium recovery was quantitative within experimental uncertainty.

B. Chemical Interferences

1. Calcium Ion

The four most common metal ions in natural waters are Ca^{2+}, Mg^{2+}, Na^{+}, and K^{+}, with concentrations usually decreasing in that order.[70] The influence of Ca^{2+} concentration on the extraction efficiency of various alpha-emitters was studied because, of the four ions mentioned above, Ca^{2+} is typically the most prevalent, it is most strongly extracted by toluene solutions of HDEHP,[69] and it is most strongly complexed by DTPA.[71] Therefore Ca^{2+} poses the greatest potential for interference in both the extraction of uranium by Alphaex and in the masking of the extraction of other alpha-emitters with DTPA.

The extraction of uranium, thorium, polonium, and americium from 50 ± 1 mL or 50.0 ± 0.2 mL of 0.010 M DTPA solution at pH 3.0 was measured as a function of Ca^{2+} concentration. The Ca^{2+} concentrations investigated ranged from 0.010 M to 1.0 M (i.e., from 20 mg to 2,000 mg in 50 mL of solution), up to

TABLE XIII

URANIUM EXTRACTION AS A FUNCTION OF AQUEOUS-TO-ORGANIC PHASE VOLUME RATIO

Sample	Aqueous Volume (mL)	Organic Volume (mL)	Phase Ratio	DPM Added (± 2σ)	Gross Counts[a]	Count Time (s)	DPM Extracted (± 2σ)	Percent Extracted (± 2σ)
JD418D	4.00	2.00	2.00	27 ± 1	12625	55944.00	27.2 ± 0.7	101 ± 5
JD418B	25.0	2.00	12.5	168 ± 7	5071	3600.00	170 ± 6	101 ± 6
JD418C	25.0	2.00	12.5	168 ± 7	5085	3600.00	170 ± 6	101 ± 6
JD418A	25.0	1.52	16.4	168 ± 7	6665	3600.00	170 ± 6	101 ± 6
JD419C	50.0	2.00	25.0	67 ± 3	8355	14400.00	70 ± 2	104 ± 6
JD419A	50.0	1.52	32.9	67 ± 3	5290	7200.00	67 ± 3	100 ± 6
JD419B	50.0	1.52	32.9	67 ± 3	3774	5000.00	69 ± 3	103 ± 6
JD419H	125	1.52	82.2	168 ± 7	13058	7200.00	166 ± 5	99 ± 5
JD426A	200	2.00	100	268 ± 11	8343	3600.00	279 ± 8	104 ± 6
JD419F[b]	200	2.00	100	268 ± 11	8108	3600.00	271 ± 8	101 ± 6
JD419G[b]	200	2.00	100	268 ± 11	8110	3600.00	271 ± 8	101 ± 6
JD426B	200	1.52	132	268 ± 11	11141	3600.00	283 ± 9	106 ± 6

a. Background counts were not subtracted.

b. Solution contained 1.0 M $NaNO_3$.

200 times greater than the excessive limit established by the World Health Organization (WHO) International in 1958, and up to 100 times that typically found in the ocean.[70] At all calcium concentrations studied the uranium extraction (Table XIV, p 65) was quantitative within experimental uncertainty.

The average percentage of thorium extracted from samples containing 0.010 M Ca^{2+} was 1.4 ± 0.8% for individually-prepared replicate samples and 0.12 ± 0.08% for replicates taken from a large batch of solution (Table XV, p 66). The individually-prepared samples also contained 0.20 ± 0.05 g of ascorbic acid and about four times more ^{230}Th than the batch samples. The reason for the ten-fold difference in percentage extraction between the two types of samples was not determined in this work. Less than 1% thorium extraction was observed for samples containing 0.10 M and 1.0 M Ca^{2+}. The average percentage of polonium (Table XVI, p 67) and americium (Table XVII, p 68) extracted was less than 1% at all Ca^{2+} concentrations investigated. The polonium extraction experiment FC74B was rejected as an outlier when calculating the averaged percentage extraction values.

2. Ferric Ion

The influence of Fe^{3+} concentration on extraction efficiency was also investigated, even though it is a minor constituent in drinking water (< 1.0 mg/L or < 2×10^{-5} M),[70] because it presents a great potential for interference due to its tendency to hydrolyze at pH values greater than 2.0 and because the resulting

TABLE XIV

INFLUENCE OF CALCIUM ION CONCENTRATION ON URANIUM EXTRACTION FROM 0.010 M DTPA SOLUTION

Sample	$[Ca^{2+}]$	DPM Added (± 2σ)	Gross Counts[a]	Count Time (s)	DPM Extracted (± 2σ)	Percent Extracted (± 2σ TPU)
FC66A	0.010	153 ± 6	6078	3600.00	155 ± 3	101 ± 6
FC66B	0.010	153 ± 6	6142	3600.00	156 ± 3	102 ± 6
FC66C	0.010	153 ± 6	6134	3600.00	156 ± 3	102 ± 6
FC72A	0.10	153 ± 6	5970	3600.00	152 ± 3	99 ± 6
FC72B	0.10	153 ± 6	5925	3600.00	151 ± 3	98 ± 6
FC72C	0.10	153 ± 6	6043	3600.00	154 ± 3	100 ± 6
JD379A[b]	1.0	168 ± 7	6758	3600.00	172 ± 3	102 ± 6
JD380A[b]	1.0	168 ± 7	6478	3600.00	165 ± 3	98 ± 6
FC781[b,c]	1.0	168 ± 7	6552	3600.00	167 ± 3	99 ± 6
FC782[b,c]	1.0	168 ± 7	6677	3600.00	170 ± 3	101 ± 6

a. Background counts were not subtracted.

b. Each 50-mL aliquot also contained approximately 1500 ± 90 dpm ^{210}Po. The ^{210}Po alpha peak (5.30 MeV) was well resolved from the ^{234}U alpha peak (4.77 MeV).

c. Approximately 0.20 ± 0.05 g of ascorbic acid was added to the aqueous solution prior to extraction.

TABLE XV

INFLUENCE OF CALCIUM ION CONCENTRATION ON THORIUM EXTRACTION FROM 0.010 M DTPA SOLUTION

Sample	$[Ca^{2+}]$	DPM Added (± 2σ)	Gross Counts[a]	Count Time (s)	DPM Extracted (± 2σ)	Percent Extracted (± 2σ TPU)
FC69A[b,c]	0.010	191 ± 6	85	3600.00	2.2 ± 0.5	1.1 ± 0.3
FC69B[b,c]	0.010	191 ± 6	33	3600.00	0.8 ± 0.3	0.4 ± 0.2
FC69C[b,c]	0.010	191 ± 6	148	3600.00	3.8 ± 0.7	2.0 ± 0.4
FC70A[b,c]	0.010	191 ± 6	146	3600.00	3.7 ± 0.7	1.9 ± 0.4
FC70B[b,c]	0.010	191 ± 6	112	3600.00	2.8 ± 0.6	1.5 ± 0.3
JD427A[d,e]	0.010	45 ± 2	3	7200.00	0.04 ± 0.05	0.1 ± 0.1
JD427B[d,e]	0.010	45 ± 2	6	5400.00	0.10 ± 0.09	0.2 ± 0.2
JD427C[c,d,e]	0.010	45 ± 2	9	14400.00	0.06 ± 0.04	0.1 ± 0.1
JD427D[c,d,e]	0.010	45 ± 2	3	7200.00	0.04 ± 0.05	0.1 ± 0.1
FC73A[b,c]	0.10	191 ± 6	40	3600.00	1.0 ± 0.4	0.5 ± 0.2
FC73B[b,c]	0.10	191 ± 6	38	3600.00	1.0 ± 0.4	0.5 ± 0.2
FC73C[b,c]	0.10	191 ± 6	99	3600.00	2.5 ± 0.6	1.3 ± 0.3
JD428A[d,e]	0.10	45 ± 2	5	7200.00	0.06 ± 0.06	0.14 ± 0.13
JD428B[d,e]	0.10	45 ± 2	14	14400.00	0.09 ± 0.05	0.20 ± 0.11
JD428D[d,e]	1.0	45 ± 2	7	17575.56	0.04 ± 0.03	0.08 ± 0.07
JD428E[d,e]	1.0	45 ± 2	3	14400.00	0.02 ± 0.03	0.04 ± 0.05

a. Background counts were not subtracted.

b. Replicate 50-mL samples were prepared individually.

c. Approximately 0.20 ± 0.05 g of ascorbic acid was added to the aqueous solution prior to extraction.

d. Either 200.0- or 250.0-mL of sample solution was prepared and 50.0-mL aliquots extracted.

e. Each 50.0-mL aliquot also contained 50 ± 3 dpm ^{241}Am. The ^{241}Am alpha peak (5.48 MeV) was well resolved from the ^{230}Th alpha peak (4.69 MeV).

TABLE XVI

INFLUENCE OF CALCIUM ION CONCENTRATION ON POLONIUM EXTRACTION FROM 0.010 M DTPA SOLUTION

Sample	$[Ca^{2+}]$	DPM Added (± 2σ)	Gross Counts[a]	Count Time (s)	DPM Extracted (± 2σ)	Percent Extracted (± 2σ TPU)
FC71A[b,c]	0.010	155 ± 6	43	3600.00	1.1 ± 0.4	0.7 ± 0.3
FC71B[b,c]	0.010	155 ± 6	44	3600.00	1.1 ± 0.4	0.7 ± 0.3
FC71C[b,c]	0.010	155 ± 6	76	3600.00	1.9 ± 0.5	1.2 ± 0.3
FC74A[b,c]	0.10	143 ± 6	20	3600.00	0.5 ± 0.3	0.4 ± 0.2
FC74B[b,c]	0.10	143 ± 6	248	3600.00	6.3 ± 0.8	4.4 ± 0.6
FC74C[b,c]	0.10	143 ± 6	62	3600.00	1.6 ± 0.4	1.1 ± 0.3
FC75A[b,c]	0.10	140 ± 6	22	3600.00	0.6 ± 0.3	0.4 ± 0.2
FC75B[b,c]	0.10	140 ± 6	30	3600.00	0.8 ± 0.3	0.5 ± 0.2
JD379A[d,e]	1.0	1498 ± 90	16	3600.00	0.4 ± 0.2	0.03 ± 0.02
JD380A[d,e]	1.0	1498 ± 90	15	3600.00	0.4 ± 0.2	0.03 ± 0.02
FC781[b,c]	1.0	1490 ± 90	143	3600.00	3.6 ± 0.6	0.24 ± 0.05
FC782[b,c]	1.0	1460 ± 88	311	3600.00	7.9 ± 1.0	0.54 ± 0.07

a. Background counts were not subtracted.

b. Replicate 50-mL samples were prepared individually.

c. Approximately 0.20 g of ascorbic acid was added to the aqueous solution prior to extraction.

d. Either 200.0- or 250.0-mL of sample solution was prepared and 50.0-mL aliquots extracted.

e. Each 50.0-mL aliquot also contained 168 ± 7 dpm natural uranium. The ^{234}U alpha peak (4.77 MeV) was well resolved from the ^{210}Po alpha peak (5.30 MeV).

TABLE XVII

INFLUENCE OF CALCIUM ION CONCENTRATION ON AMERICIUM EXTRACTION FROM 0.010 M DTPA SOLUTION

Sample	$[Ca^{2+}]$	DPM Added ($\pm 2\sigma$)	Gross Counts[a]	Count Time (s)	DPM Extracted ($\pm 2\sigma$)	Percent Extracted ($\pm 2\sigma$ TPU)
JD427A[b,c]	0.010	50 ± 3	4	7200.00	0.05 ± 0.05	0.1 ± 0.1
JD427B[b,c]	0.010	50 ± 3	0	5400.00	0 ± 0	0 ± 0
JD427C[b,c,d]	0.010	50 ± 3	4	14400.00	0.03 ± 0.03	0.05 ± 0.05
JD427D[b,c,d]	0.010	50 ± 3	1	7200.00	0.01 ± 0.03	0.03 ± 0.05
JD428A[b,c]	0.10	50 ± 3	1	7200.00	0.01 ± 0.03	0.03 ± 0.05
JD428B[b,c]	0.10	50 ± 3	2	14400.00	0.01 ± 0.02	0.03 ± 0.04
JD428D[b,c]	1.0	50 ± 3	15	17575.56	0.08 ± 0.04	0.2 ± 0.09
JD428E[b,c]	1.0	50 ± 3	7	14400.00	0.04 ± 0.04	0.09 ± 0.07

a. Background counts were not subtracted.

b. Either 200.0- or 250.0-mL of sample solution was prepared and 50.0-mL aliquots extracted.

c. Each 50.0-mL aliquot also contained 45 ± 2 dpm ^{230}Th. The ^{241}Am alpha peak (5.48 MeV) was completely resolved from the ^{230}Th alpha peak (4.69 MeV).

d. Approximately 0.20 g of ascorbic acid was added to the aqueous solution prior to extraction.

TABLE XVIII

AVERAGE PERCENTAGE EXTRACTION AS A FUNCTION OF CALCIUM ION CONCENTRATION

	Radionuclide Average Percentage Extraction			
$[Ca^{2+}]$	Natural U	^{230}Th	^{210}Po	^{241}Am
0.010	102 ± 2 (3)	0.8 ± 0.7 (9)	0.9 ± 0.8 (3)	0.04 ± 0.07 (4)
0.10	99 ± 3 (3)	0.5 ± 0.6 (5)	0.6 ± 0.6 (4)	0.03 ± 0.00 (2)
1.0	100 ± 3 (4)	0.06 ± 0.09 (2)	0.2 ± 0.4 (4)	0.1 ± 0.7 (2)

gelatinous precipitate has a strong tendency to adsorb other cations. It was also important to determine the amount of Fe^{3+} that could be tolerated by this uranium separation procedure because Fe^{3+} is commonly added to water samples at a rate of 20 to 25 mg L^{-1} and precipitated as the hydroxide to preconcentrate uranium and other radionuclides from large volumes of water. It was reasoned that if the presence of 20 to 25 mg of Fe^{3+} in the aqueous phase did not adversely affect the extraction of uranium by Alphaex or the masking effect of the DTPA, then it should be possible to combine preconcentration of uranium by ferric hydroxide coprecipitation with the selective extraction procedure under investigation.

The extraction of uranium from 50 mL of 0.010 M DTPA solution at pH 3.0 was measured as a function of Fe^{3+} concentration. The Fe^{3+} concentration studied ranged from 3.6×10^{-4} M (1.0 mg Fe^{3+} per 50 mL) to 1.1×10^{-2} M (31 mg Fe^{3+} per 50 mL). The results of these studies are given in Table XIX (p 71).

Test solutions were prepared by acidifying distilled water with 0.500 ± 0.005 mL each of concentrated HNO_3 and concentrated HCl per 50 mL of water, adding an appropriate amount of uranium tracer solution, the desired amount of Fe^{3+} from a solution of $FeCl_3$ containing 25.0 mg mL^{-1} Fe^{3+}, and enough 0.50 M DTPA to make the final solution 0.010 M. In each case the solution turned yellow upon the addition of DTPA. This color intensified and darkened as the pH was adjusted to 3.0 ± 0.1. When preparing test solutions containing more

TABLE XIX

INFLUENCE OF FERRIC ION CONCENTRATION ON URANIUM EXTRACTION FROM 0.010 M DTPA SOLUTION

Sample[a]	$[Fe^{3+}]$	DPM Added (± 2σ)	Gross Counts[b]	Count Time (s)	DPM Extracted (± 2σ)	Percent Extracted (± 2σ TPU)
JD3106A	0.00036	134 ± 6	5423	3600.00	138 ± 4	103 ± 5
JD3106B	0.00036	134 ± 6	5420	3600.00	138 ± 4	103 ± 5
JD3106C[c]	0.00036	134 ± 6	5148	3600.00	131 ± 4	98 ± 5
JD3106D[c]	0.00036	134 ± 6	5334	3600.00	136 ± 4	101 ± 5
JD3109A	0.0022	168 ± 7	6676	3600.00	170 ± 5	101 ± 5
JD3109B	0.0022	168 ± 7	6544	3600.00	167 ± 5	99 ± 5
JD3109C[c]	0.0022	168 ± 7	6517	3600.00	166 ± 5	99 ± 5
JD3109D[c]	0.0022	168 ± 7	6540	3600.00	167 ± 5	99 ± 5
JD3110A	0.0090	168 ± 7	6546	3600.00	167 ± 5	100 ± 5
JD3110B	0.0090	168 ± 7	6588	3600.00	168 ± 5	100 ± 5
JD3110C[d]	0.0090	168 ± 7	6589	3600.00	168 ± 5	100 ± 5
JD3110D[d]	0.0090	168 ± 7	6515	3600.00	166 ± 5	99 ± 5
JD3111A[e]	0.011	168 ± 7	3450	3600.00	168 ± 6	100 ± 5
JD3111B[e]	0.011	168 ± 7	3385	3600.00	165 ± 6	98 ± 5

a. Individual 50-mL samples were prepared.

b. Background counts were not subtracted.

c. Approximately 0.20 ± 0.05 g of ascorbic acid was added to the aqueous solution prior to extraction.

d. Each 50-mL aliquot also contained 260 ± 12 dpm ^{241}Am. The ^{241}Am alpha peak (5.48 MeV) was well resolved from the ^{234}U alpha peak (4.77 MeV).

e. Only 0.520 mL of organic phase was counted out of the total 1.520 mL.

than 1.0 mg Fe^{3+} per 50 mL it was necessary to adjust the solution pH with NH_4OH rather than NaOH to avoid precipitation of the gelatinous $Fe(OH)_3$.

Initially 0.20 ± 0.05 g of ascorbic acid was added to the aqueous phase just prior to extraction to reduce Fe(III) to Fe(II). However, no decolorization of the solution was observed, and it was concluded that the Fe(III) was complexed too strongly by the DTPA to be reduced to Fe(II). Eventually the addition of ascorbic acid was deemed unnecessary and deleted from the procedure.

Uranium extraction was quantitative within experimental error at all Fe^{3+} concentrations investigated. However, when the Fe^{3+} concentration (0.011 M) exceeded the DTPA concentration (0.010 M), some solid was collected at the aqueous/organic interface and less than 1.00 mL of organic phase was recovered for counting. Additionally, the extraction of uranium from a sample containing 250 mg Fe^{3+} in 75 mL water (6.0×10^{-2} M) and 6.7×10^{-2} M DTPA was measured and found to be quantitative also.

3. Dihydrogen Phosphate and Hydrogen Oxalate

The influence of total phosphate and total oxalate concentration on the extraction of uranium from 50 ± 1 mL of 0.010 M DTPA solution at pH 3.0 was investigated. At pH 3.0 the predominant phosphate species is $H_2PO_4^-$ (~88%) and the predominant oxalate species is $HC_2O_4^-$ (~92%). Both $H_2PO_4^-$ and $HC_2O_4^-$ form stable complexes with UO_2^{2+}. While neither species is ordinarily present to any significant degree in drinking water, it was desirable to determine what

concentration of each anion could be tolerated in the procedure without significant decrease in uranium extraction efficiency.

Table XX (p 74) gives the results of the total phosphate dependency studies. It was found that a total phosphate concentration up to approximately 0.17 M resulted in no significant loss of uranium extraction efficiency. As the total phosphate concentration was increased above this value the percentage of uranium extracted began to decrease. An average of 78% of uranium was extracted from 0.33 M total phosphate and an average of 54% was extracted from 0.50 M total phosphate.

The results of the total oxalate dependency studies are shown in Table XXI (p 75). $HC_2O_4^-$ was found to have a much more negative impact upon the extraction of uranium by Alphaex than $H_2PO_4^-$. Uranium was quantitatively extracted from DTPA solutions containing 0.0010 M total oxalate. However, only 55% uranium extraction was observed when the total oxalate concentration was increased to 0.010 M. Furthermore, uranium extraction decreased to 3.8% at total oxalate concentrations of 0.10 M.

C. Results of Interlaboratory Tests for the Proposed ASTM Test Method

Two interlaboratory tests of this method for uranium in drinking water were conducted in an effort to gain approval as an ASTM standard test method. For the first interlaboratory study, termed a multiple single operator test, ten

TABLE XX

INFLUENCE OF TOTAL PHOSPHATE CONCENTRATION ON URANIUM EXTRACTION FROM 0.010 M DTPA AT pH 3.0

Sample[a]	Total Phosphate (M)	DPM Added (± 2σ)	Gross Counts[b]	Count Time (s)	DPM Extracted (± 2σ)	Percent Extracted (± 2σ TPU)
JD3113A	0.062	168 ± 7	6509	3600.00	166 ± 6	99 ± 6
JD3113B	0.062	168 ± 7	6546	3600.00	167 ± 6	100 ± 6
JD3113C	0.17	168 ± 7	6383	3600.00	163 ± 6	97 ± 6
JD3113D	0.17	168 ± 7	6389	3600.00	163 ± 6	97 ± 6
JD3114A	0.33	168 ± 7	4949	3600.00	126 ± 5	75 ± 5
JD3114B	0.33	168 ± 7	5237	3600.00	133 ± 5	80 ± 5
JD3112A	0.50	134 ± 6	2760	3600.00	70 ± 4	52 ± 4
JD3112B	0.50	134 ± 6	2965	3600.00	76 ± 4	56 ± 4

a. Either 200.0- or 250.0-mL samples were prepared and 50.0 mL aliquots were extracted.

b. Background counts were not subtracted.

TABLE XXI

INFLUENCE OF TOTAL OXALATE CONCENTRATION ON URANIUM EXTRACTION FROM 0.010 M DTPA AT pH 3.0

Sample[a]	Total Oxalate (M)	DPM Added (± 2σ)	Gross Counts[b]	Count Time (s)	DPM Extracted (± 2σ)	Percent Extracted (± 2σ TPU)
JD430A	0.0010	335 ± 14	13445	3600.00	343 ± 11	102 ± 5
JD430B	0.0010	335 ± 14	13137	3600.00	335 ± 10	100 ± 5
JD420D	0.010	168 ± 7	7214	7200.00	92 ± 4	55 ± 3
JD420E	0.010	168 ± 7	7239	7200.00	92 ± 4	55 ± 3
JD420A	0.10	168 ± 7	503	7200.00	6.4 ± 0.6	3.8 ± 0.4
JD420B	0.10	168 ± 7	255	3600.00	6.5 ± 0.9	3.9 ± 0.6

a. Either 200.0- or 250.0-mL samples were prepared and 50.0 mL aliquots were extracted.

b. Background counts were not subtracted.

laboratories were provided with a small volume of three solutions containing different concentrations of natural uranium in 2.0 M HCl solution. The analysts were instructed to dilute 1.000 mL of each solution to a volume of 1.000 L with their own laboratory tap water and to follow the general procedure for drinking water samples outlined in Part I, Chapter II. Two of the samples also contained additional alpha-emitters as potential interferences. The participating laboratories were provided with enough DTPA and extractive scintillator to analyze each sample plus a tap water blank in triplicate. Five laboratories completed the analyses and submitted results which are given in Table XXII (p 77).

Following the successful completion of this test, an ASTM supported round-robin test of the proposed method was conducted. Instructions were essentially identical to those for the multiple single operator test with the exception that labs were instructed to dilute 10.00 mL of a concentrated sample to 1.000 L with their own tap water and to monitor chemical recovery by spiking each sample with an internal ^{232}U tracer. Again, there were three different concentrations of natural uranium and each activity level contained additional alpha-emitting nuclides. Seven laboratories completed the analyses and submitted results (Table XXIII, p 79). The overall results along with precision and bias data for both tests are given in Table XXIV (p 80). Both tests were determined by ASTM to be successful, and the proposed method was submitted for further editorial revisions and final approval by ASTM.

TABLE XXII

SUMMARY OF MULTIPLE SINGLE OPERATOR INTERLABORATORY TEST FOR URANIUM IN DRINKING WATER

Amount Added (pCi L^{-1})	Amount Found (pCi L^{-1})[a]				
	Lab 1	Lab 2	Lab 3	Lab 4	Lab 5
6.04[b]	5.7 ± 0.3	4.3 ± 1.0	5.5 ± 0.6	6 ± 10	6 ± 5
75.5[b]	75 ± 5	73 ± 5	76 ± 2	66 ± 35	73 ± 2
302	300 ± 12	310 ± 48	298 ± 18	281 ± 44	286 ± 2

a. Reported values are averages of triplicate analyses ± 95% confidence limits.

b. Samples also contained 37 pCi L^{-1} ^{210}Po, 52 pCi L^{-1} ^{226}Ra, and 50 pCi L^{-1} ^{230}Th.

TABLE XXIII

SUMMARY OF ROUND-ROBIN INTERLABORATORY TEST FOR URANIUM IN DRINKING WATER

Amount Added[b] ($pCi\ L^{-1}$)	Amount Found ($pCi\ L^{-1}$)						
	Lab 1	Lab 2	Lab 3	Lab 4	Lab 5	Lab 6	Lab 7
7.99	5 ± 2	7.7 ± 0.4	8 ± 3	8.0 ± 0.6	6 ± 2	8 ± 3	8.5 ± 0.4
89.3	88 ± 12	86 ± 10	95 ± 14	92 ± 12	92 ± 25	90 ± 14	88 ± 4
365	338 ± 50	350 ± 11	278 ± 47	377 ± 4	349 ± 47	387 ± 31	362 ± 0

a. Reported values are averages of triplicate analyses ± 95% confidence limits.

b. Samples also contained 50 $pCi\ L^{-1}$ ^{226}Ra and 52 $pCi\ L^{-1}$ ^{230}Th.

TABLE XXIV

OVERALL RESULTS OF INTERLABORATORY TESTS FOR URANIUM IN DRINKING WATER

Amount Added (pCi L^{-1})	Amount Found (pCi L^{-1})	Bias (pCi L^{-1})	% Bias	95% Confidence Limits (pCi L^{-1})
Multiple Single Operator Test				
6.04	5.48	-0.56	-9.3	0.94
75.5	72.6	-2.9	-3.8	3.7
302	295	-7	-2	9
Round-Robin Test				
7.99	7.44	-0.55	-6.9	0.50
89.3	90.2	0.9	1	2.4
365	349	-16	-4.5	15

CHAPTER IV

SUMMARY AND CONCLUSIONS

A. Summary

A new method for the measurement of uranium alpha-activity in drinking water by PERALS spectrometry has been developed that combines chemical separation and sample preparation into a single step. Uranium is selectively extracted from an aqueous solution containing approximately 0.010 M DTPA at pH 3.0 with an extractive scintillator containing HDEHP as the extractant. A portion of the organic phase is then counted in a PERALS spectrometer with an alpha-counting efficiency of 99+%, essentially 100% chemical recovery, and an overall efficiency of 67% or greater, depending on the volume ratio of extractive scintillator counted to total extractive scintillator used. The extraction efficiency of uranium—and in some instances thorium, polonium, plutonium, americium, and radium—as a function of equilibration time, solution pH, DTPA concentration, and aqueous-to-organic phase volume ratio was investigated. Also, the influence of several potential chemical interferences on the extraction of uranium was determined. Because this method offers significant advantages in simplicity and speed over currently approved methods, the method was proposed as an ASTM standard test method for uranium in drinking water, and two interlaboratory tests of the proposed method were conducted as part of the ASTM approval process.

B. Conclusions

The proposed method for the measurement of uranium in drinking water has been shown to be a simple, rapid, accurate, and robust alternative to existing procedures. The uranium extraction step was found to be complete with an equilibration time of only 60 s. Also, uranium extraction was quantitative in the pH range of 1.0 to 5.0 while less than 0.5% of thorium, polonium, plutonium, americium, and radium were extracted at pH 3.0. Uranium was quantitatively extracted from solutions containing up to 0.10 M DTPA at pH 3.0. Extraction of uranium from 0.010 M DTPA solution at pH 3.0 was quantitative at aqueous-to-organic phase volume ratios ranging from 2.00 to 132. Calcium ion concentrations as high as 1.0 M had no detrimental effect on uranium extraction or on the masking effect of DTPA on the extraction of thorium, polonium, or americium. Uranium extraction from 0.010 M DTPA solution was quantitative at ferric ion concentrations as high as 0.010 M. Total phosphate concentrations higher than ~0.15 M and total oxalate concentrations higher than ~0.0010 M were found to interfere with uranium extraction. Both interlaboratory tests were determined by ASTM to be successful, and the proposed method was submitted for further editorial revisions and final approval by ASTM.

C. Future Work

Some preliminary studies were conducted to demonstrate that the selective and quantitative extraction of uranium from DTPA solution could be

combined with an initial preconcentration step by either ferric hydroxide or calcium phosphate coprecipitation. These preliminary studies were successful, indicating that up to one or two liters of sample can be analyzed as quickly and easily as several hundred milliliters of sample by the evaporation procedure. In the case of ferric hydroxide coprecipitation it is necessary to add a slight excess of DTPA relative to the amount of iron present to avoid reprecipitation upon pH adjustment. If calcium phosphate coprecipitation is used, it is important to limit the amount of phosphate added to avoid potential interferences in the extraction of uranium. Additional studies are needed to perfect these modifications to the procedure and to verify that uranium selectivity is maintained.

While this research effort focused on the measurement of uranium in drinking water, this procedure offers great potential for the analysis of environmental water samples as well due to the relative lack of interference from many common matrix constituents. The presence of water-soluble organic acids will likely pose the greatest potential interferences to this method. Therefore, additional studies are needed to determine the degree of interference from such species and to investigate possible modifications to the procedure to eliminate these interferences.

PART II

DEVELOPMENT AND TESTING OF ENVIRONMENTALLY-SAFE EXTRACTIVE SCINTILLATORS FOR ALPHA LIQUID SCINTILLATION SPECTROMETRY

CHAPTER I

INTRODUCTION

The US DOE has identified a need for improved methods of monitoring environmental remediation efforts. An important aspect of this is the measurement of alpha-emitting nuclides in a wide variety of sample matrices.[47] The use of extractive scintillator solutions coupled with electronic pulse shape discrimination of beta/gamma background offers one of the most rapid and accurate techniques for the separation and measurement of alpha-emitters.[72] Extractive scintillator solutions were developed as a superior means of incorporating alpha-emitting elements into a liquid scintillator solution by the use of liquid-liquid extraction technology. An extractive scintillator solution contains an organophilic complexing agent in an aqueous-immiscible scintillator solution. With the proper choice of extractant and aqueous solution conditions, alpha-emitting elements can be phase-transferred quantitatively, and often selectively, from an aqueous solution to the scintillator solution. Concentration factors of 10 to 100 are possible with a single extraction step. More importantly, this technique minimizes the large and variable quench effects associated with aqueous-accepting scintillators, making it possible to eliminate efficiently beta/gamma background and achieve useful energy resolution (approximately 200 keV FWHM for a 4.78 MeV alpha particle).[72]

Despite its obvious advantages, extensive commercialization of this technique has been hampered because the extraction of radionuclides into current toluene/naphthalene-based scintillator solutions results in the production of an undesirable "mixed waste". Also, the low flash point of toluene (4.4°C) and the toxicity of both toluene and naphthalene make their use in some laboratory facilities undesirable and often unacceptable. To overcome these problems ORDELA, Inc., under the auspices of a Phase I US DOE/SBIR research grant, has developed and tested a number of non-hazardous, more environmentally-safe extractive scintillator solutions for the separation and measurement of alpha-emitters by alpha liquid scintillation coupled with electronic pulse shape discrimination. The development of these scintillator solutions was accomplished by the replacement of the hazardous toluene and naphthalene components with scintillation solvents which are less toxic, are nonflammable because of their higher flash points, and are not classified as hazardous materials.

Results obtained in Phase I research clearly demonstrate the technical feasibility of replacing toluene and naphthalene with one or more non-hazardous solvents having much higher flash points, lower vapor pressures, and lower toxicities than either toluene or naphthalene. Furthermore, the results prove that some of the replacement solvents result in little or no loss in desirable characteristics such as phase separation, time resolution, energy resolution, and low alpha background. Additional research will be required to (1) optimize the

chemical composition of a complete line of environmentally-safe solutions for maximum time and energy resolution and (2) verify their performance as efficient extractants for a number of different alpha-emitters under a variety of conditions simulating actual analysis conditions.

CHAPTER II

EXPERIMENTAL METHODS AND MATERIALS

The purpose of the Phase I research effort was to demonstrate the technical feasibility of developing useful extractive scintillator solutions in which the toluene and naphthalene used in currently available extractive scintillators were replaced by one or more non-hazardous scintillation solvents. The specific technical objectives were to (1) identify several promising non-hazardous scintillation solvents, and (2) develop extractive scintillator solutions with these solvents and to test their performance by evaluating phase separation characteristics, alpha backgrounds, time resolution, energy resolution, and chemical stability during storage. Experimental details and results are presented in the following sections.

A. Selection of Test Solvents

Selection of solvents for evaluation during Phase I was based on their previously reported or suggested use as efficient scintillation solvents, their high flash points and low vapor pressures, their low or moderate toxicity characteristics, their reported biodegradability and low bioaccumulation, their availability, and the fact that they are currently not regulated by the Environmental Protection Agency under the Resource Conservation and Recovery Act or the Clean Water Act. The solvents selected were

phenylxylylethane, diisopropylnaphthalene, monoisopropylbiphenyl, cyclohexylbenzene, 1-methylnaphthalene, and 2-ethylnaphthalene (Table XXV, p 89). Phenylxylylethane, diisopropylnaphthalene, and monoisopropylbiphenyl were obtained as technical or commercial grade mixtures of varying and indeterminate purity from Koch Chemical Company in Corpus Christi, TX. Cyclohexylbenzene, 1-methylnaphthalene, and 2-ethylnaphthalene were obtained from Sigma-Aldrich Chemical Company, Milwaukee, WI. Both phenylxylylethane and diisopropylnaphthalene are currently used as solvents for commercial environmentally-safe scintillation cocktails.

All of the solvents chosen have flash points significantly higher than toluene (Table XXV, p 89). According to the definitions of "flammable liquid" and "combustible liquid" in the Code of Federal Regualtions (29 CFR 1910.1200), 1-methylnaphthalene is a combustible liquid, and the other five test solvents are neither flammable nor combustible. Most are reported to be only slightly to moderately toxic. Because of the much higher flash points and lower vapor pressures, the fire and inhalation hazards associated with using these solvents in the laboratory are significantly reduced and are not normally expected to be a concern. Phenylxylylethane, diisopropylnapthalene, and monoisopropylbiphenyl are among compounds that have been proposed as PCB replacements in dielectric fluids.[73,74] Their bioaccumulation and biodegradation characteristics have been well recorded.[75-77] Of the three solvents, monoisopropylbiphenyl is

TABLE XXV

SOME PROPERTIES OF SCINTILLATOR SOLVENTS INVESTIGATED

Solvent (Letter Designation)	Flash Point (°C)	Vapor Pressure (mm Hg at 25°C)	Relative Scintillation Yield	Specific Gravity	Percent Purity	$ kg^{-1}
Toluene (T)	4.4	28	100	0.866	99.99	12.57
Naphthalene (N)	79	1[a]	—	1.162	99+	45.72
Phenylxylylethane (P)	145	4×10^{-4}	110	0.985	97-100	4.40
Diisopropylnaphthalene (D)	149	5×10^{-4}	112	0.949	50-70	1.60
Monoisopropylbiphenyl (I)	149	5×10^{-4}	—	0.989	95	4.40
Cyclohexylbenzene (C)	98	—	103	0.950	98	420.00
1-Methylnaphthalene (M)	82	—	—	1.001	95	98.10
2-Ethylnaphthalene (E)	104	—	—	0.992	99+	2540.00

a. Vapor pressure at 53°C.

reported to be the most biodegradable, being 80% degraded in river water in two days and 100% degraded in sewage sludge in less than seven days. Phenylxylylethane and diisopropylnapthalene are somewhat less biodegradable. Cyclohexylbenzene, 1-methylnaphthalene, and 2-ethylnaphthalene are considerably more expensive than the three technical mixtures from Koch Chemical Company, and they are somewhat more expensive than toluene and naphthalene. In this respect they are not as attractive as potential replacements for toluene and naphthalene. However, some previous work with 1-methylnaphthalene[2] and 2-ethylnaphthalene[41] indicated that their scintillation properties were as good or better than the toluene/naphthalene combination; therefore, they were included in this study primarily for the sake of comparison with the more affordable solvents. Also, because they are liquid derivatives of naphthalene, they should serve as energy transfer agents in scintillator solutions.

B. Preparation of Scintillator Solutions for Testing

Approximately 50 extractive scintillator solutions were prepared using various combinations of the six solvents listed above and five commonly used fluors (Table XXVI, p 91). POPOP, commonly used as a secondary fluor, was originally selected for use in this study. However, because of its poor solubility, no scintillator solutions were developed using this fluor.

Because of the very large number of possible combinations of solvents and fluors, the development of new scintillator solutions was not strictly systematic. Rather, initial choices for combinations of solvents and

TABLE XXVI

SOME PROPERTIES OF FLUORS INVESTIGATED

Fluor, Common Name (Letter Designation)	λ max (nm)	Quantum Yield	Optimum Concentration (g L^{-1})
2-(4-biphenylyl)-5-(4-*tert*-butylphenyl)-1,3,4-oxadiazole, butyl-PBD (a)	385	0.69	12
2-(1-naphthyl)-5-phenyloxazole, a-NPO (b)	395	—	0.05-0.2
2-(4-biphenylyl)-6-phenylbenzoxazole, PBBO (c)	395	0.79	0.1-0.5
2,5-diphenyloxazole, PPO (d)	375	0.83	3-7
1,4-bis(5-phenyloxazol-2-yl)benzene, POPOP (e)	415	—	0.05-0.2
1,4-bis(2-methylstyryl)benzene, bis-MSB (f)	425	—	1.5

fluors were based on previous knowledge of optimum energy transfer agent and solute concentrations. As newly developed solutions were evaluated, additional combinations of solvents, energy transfer agents, and solutes were tried based on the results that had been obtained.

For convenience and ease of identification, each new scintillator solution was named by the upper case letter designation of the primary solvent, the upper case letter designation of any secondary solvent (energy transfer agent) used followed by the concentration in g L^{-1}, and the lower case letter designation of the fluor(s) used followed by the concentration in g L^{-1} of each fluor added. For example, solution PI200d7f1.5 contains 200 g L^{-1} monoisopropylbiphenyl, 7.0 g L^{-1} PPO, and 1.5 g L^{-1} bis-MSB in phenylxylylethane. Each solution contains 64 g L^{-1} HDEHP as the extractant unless otherwise noted. As suggested by one reviewer of the Phase I grant proposal, some solutions were also prepared which contained extractants other than HDEHP. These other extractants were trioctylphosphine oxide (TOPO), trioctylamine (TOA) and Primene JM-T—a mixture of high-molecular weight primary amines. One solution utilizing naphthalene as an energy transfer agent, PN180b4, was prepared and tested for comparison with otherwise identical solutions containing liquid derivatives of naphthalene.

CHAPTER III

RESULTS AND DISCUSSION

A. Evaluation of Phase Separation Characteristics

Before development of extractive scintillator solutions was begun, it was decided to examine the phase separation characteristics of each solvent when equilibrated with 0.20 M $NaNO_3$ solution at pH 2.5. This was done at organic:aqueous volume ratios of 1:1, 1:10, and 1:100 for each solvent. As expected, because of the higher specific gravities and greater viscosities, none of the solvents separated from the aqueous phase as quickly or as cleanly as toluene solutions. However, phase separation without centrifuging was found to be essentially complete in most cases within 20 to 90 minutes. Usually the organic phase remained somewhat cloudy even when the aqueous phase was completely clear. The solvent 1-methylnaphthalene displayed some tendency to separate as two separate layers, one below and one above the aqueous phase. All of the solvents separated cleanly from the aqueous phase when centrifuged for two to three minutes.

As stated previously, most of the scintillator solutions prepared contained HDEHP as the organophilic extractant. Because the solvent and, if present, the energy transfer agent are the major components of extractive scintillator solutions, it was expected that the new scintillator solutions would exhibit similar phase separation characteristics as the solvents themselves. Under certain

extraction conditions even the toluene/naphthalene-based scintillator solutions exhibit problems in phase separation. However, when HDEHP is the extractant and the aqueous phase pH is 3.0 or less, phase separation is usually rapid and complete unless metal ions that readily hydrolyze are present in appreciable concentrations. Because all extractions with the new scintillator solutions were to be performed under controlled and favorable conditions, it was not anticipated that the extractant would have any significant effect on phase separation. As expected, no significant differences in phase separation were observed while performing the extractions necessary for time and energy resolution evaluation. With the exception of solutions containing only 1-methylnaphthalene as solvent and energy transfer agent, all test solutions separated cleanly after centrifuging for two to three minutes.

It is not expected that phase separation will be a significant problem in the use of the new scintillators. Most extraction procedures are carried out in vessels which can be centrifuged, and centrifuges are generally available at most laboratory facilities. When extractions must be performed in separatory funnels and cannot be centrifuged, it may be necessary to increase the ionic strength of the aqueous phase and allow several hours for complete phase separation.

B. Evaluation of Time Resolution Characteristics

The pulse-shape, or time, resolution of the new solutions was evaluated and compared to that of Alphaex—a toluene/naphthalene-based extractive scintillator containing HDEHP as the extractant. In each case 2.000 ± 0.007 mL of 0.35 M $NaNO_3$ solution at pH 2.5 containing 185 pCi of normal uranium and 95 pCi of ^{241}Am was extracted with 2.000 ± 0.007 mL of extractive scintillator solution for 5.0 minutes. The phases were allowed to separate for 10 to 30 minutes. Usually it was necessary to centrifuge the sample for several minutes to obtain complete phase separation. One (1.000 ± 0.005) mL of the organic phase was then placed in a 10-mm by 75-mm culture tube, sparged with dry argon for 3 min, and capped with a cork and vinyl cap. Subsequent counting of the samples indicated that extraction was essentially quantitative in all cases. All samples were counted on an ORDELA Model 8100AB PERALS Spectrometer (see Part I, Chapter II) with internal high voltage. The multichannel analysis (MCA) system consisted of the EG&G ORTEC Trump Card and Maestro II software.

A differential pulse-shape distribution (time spectrum) of the sample was measured for 600 s using an external ^{137}Cs gamma source to induce a consistent beta/gamma-pulse-shape distribution (β/γ-peak) approximately equal in amplitude to the alpha-pulse-shape distribution (α-peak). This was necessary because the extraction of ^{234}Th and ^{234}Pa, the beta-emitting daughters of ^{238}U, was incomplete at the pH value of 2.5 necessary for quantitative americium

extraction. The time spectra for all of the HDEHP-containing extractive scintillators tested were compared with the Alphaex time spectrum (Figure 9, p 97). The x-axis is channels (512 channels full scale) and corresponds to pulse decay time. The y-axis is counts per channel. The peak separation—the difference in time between the β/γ-peak centroid and the α–peak centroid—in Alphaex has been measured to be approximately 35 ns, thus the relative peak separation is an indication of the difference in decay time between α-pulses and β/γ-pulses. A greater difference in decay time between α-pulses and β/γ–pulses is desirable because the pulses can be separated more efficiently from each other electronically. However, if an increase in decay time difference is accompanied by a proportional increase in the width of the pulse-shape distributions (peak widths) the separation may not be improved.

In order to compare the time resolution for each scintillator solution in a consistent manner, the data from the MCA output was fed into a nonlinear curve-fitting program (PeakFit® by Jandel Scientific), and the β/γ-peaks and α-peaks were fitted as Gaussian functions. The peak centroid channel and the FWHM in channels of each β/γ- and α-peak are recorded in the Appendix in Table XXXIV (p 138). Uncertainties in peak centroids and FWHM values were found to be no more than ± 1.0 channel at the 95% confidence level based on five replicate measurements of a sealed Alphaex sample. The relative peak position (P_{rel}), relative peak separation (S_{rel}), relative peak edge separation (E_{rel}) and the peak

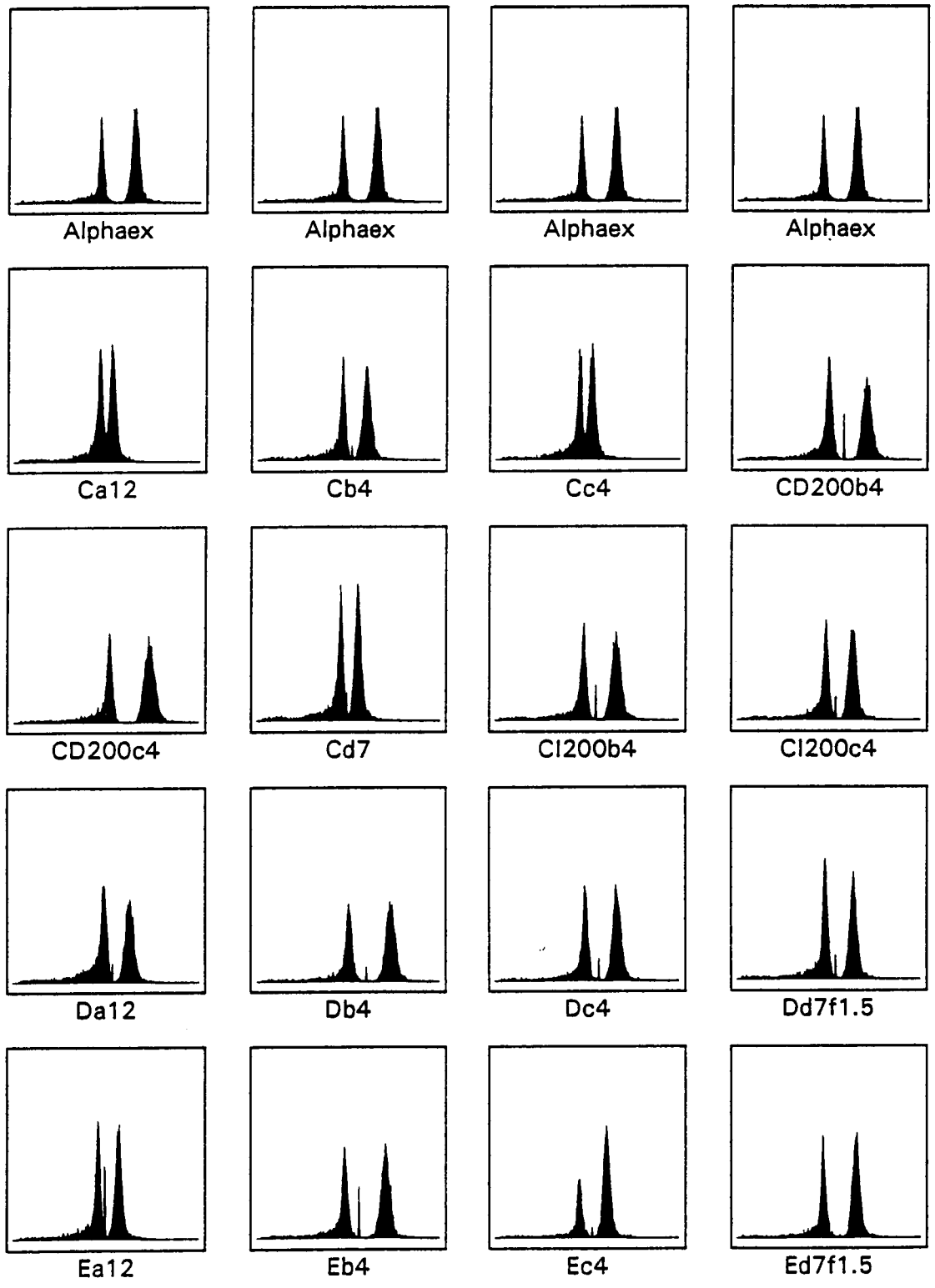


Figure 9. Comparison of pulse-shape distributions in Alphaex and test scintillators.

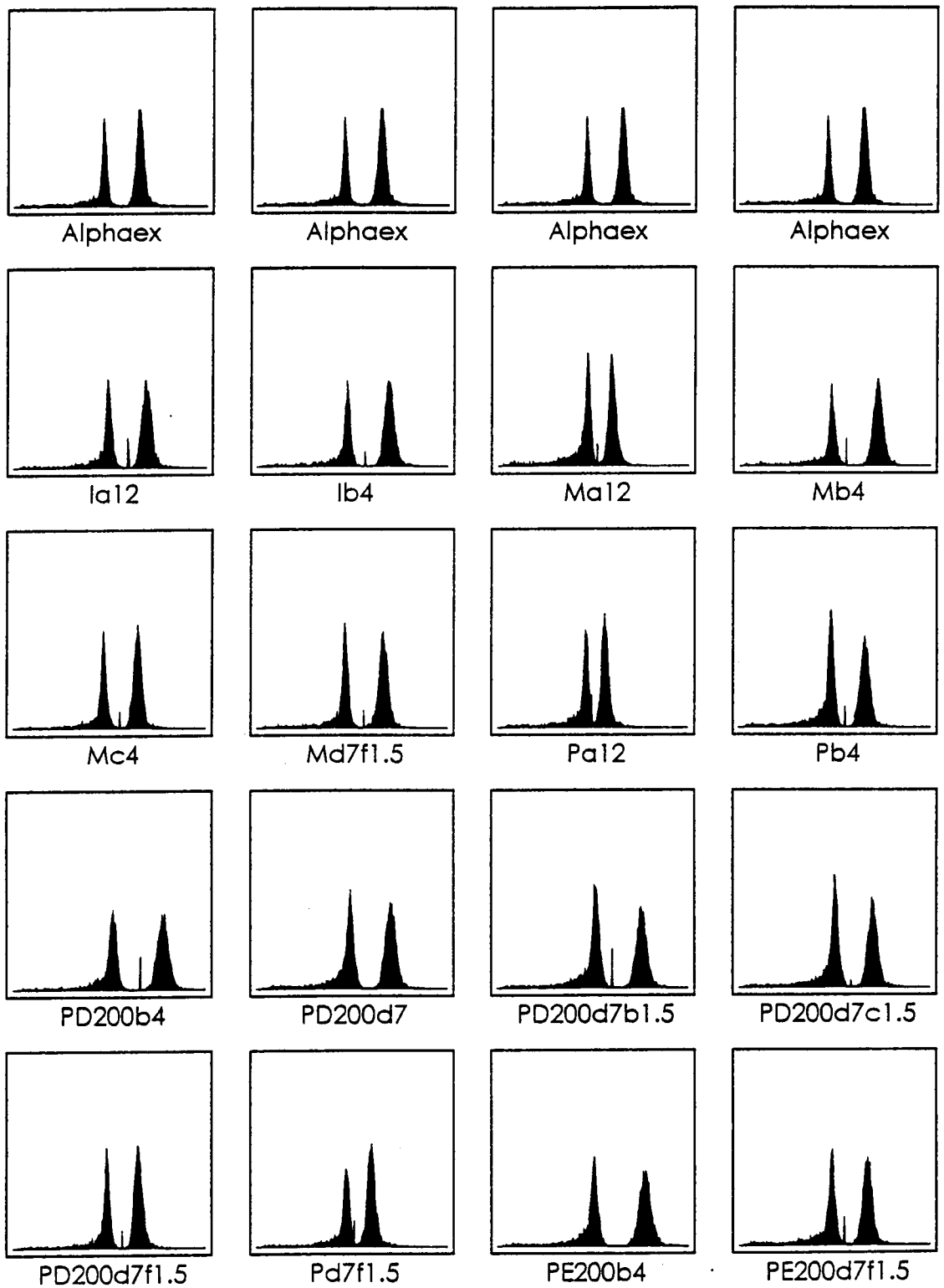


Figure 9. (Continued).

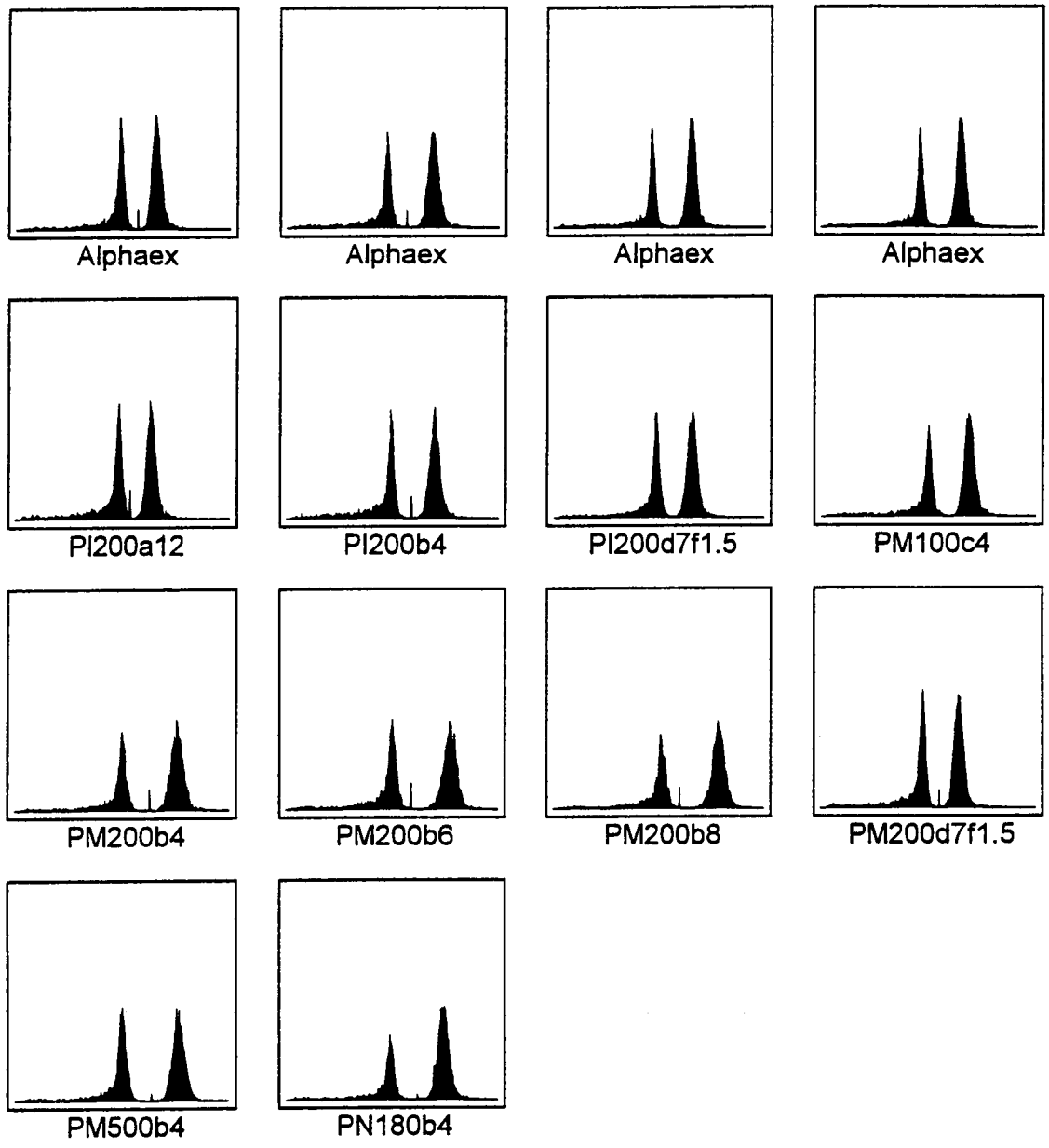


Figure 9. (Continued).

resolution (R) for Alphaex and for each new scintillator solution (Table XXVII, p 101) are discussed in the following paragraphs.

The relative peak position indicates the position of the β/γ- or α-peaks of each scintillator relative to their positions in Alphaex. The P_{rel} values for β/γ- (or α-) peaks were calculated according to Equation 9,

$$P_{rel} = C_{T\alpha\ (or\ \beta/\gamma)} \cdot (C_{A\alpha\ (or\ \beta/\gamma)})^{-1}, \quad (9)$$

where C_T and C_A are the α– or β/γ–peak centroids for the test solution and Alphaex, respectively. The propagated uncertainties were ± 0.01. From the data in Table XXVII (p 101) it is clear that while the β/γ-peak positions were all very nearly the same, the α-peak positions varied considerably. This probably indicates significant differences in α-pulse decay times for the different scintillator solutions.

Relative peak separation, S_{rel}, values were calculated according to Equation 10,

$$S_{rel} = (C_{T\alpha} - C_{T\beta/\gamma}) \cdot (C_{A\alpha} - C_{A\beta/\gamma})^{-1}. \quad (10)$$

The estimated propagated uncertainties were approximately ± 0.03. Although greater peak separation is desirable for more effective time resolution, peak separation alone is not a good indication of resolution because the peak widths are not taken into account.

The ability to resolve adjacent peaks depends not only on the separation of peak centroids but also on the peak widths. Therefore, perhaps a better indication of resolution is the distance between the right edge of the β/γ-peak

TABLE XXVII

COMPARISON OF TIME RESOLUTION PROPERTIES

Extractive Scintillator	Relative β/γ-Peak Position	Relative α-Peak Position	Relative Peak Separation	Relative Peak Edge Separation	Resolution
Alphaex	1.00	1.00	1.00	1.00	2.64
Ca12	1.00	0.82	0.37	-0.02	0.97
Cb4	1.01	0.92	0.70	0.45	1.66
Cc4	0.98	0.80	0.36	0.00	1.01
CD200b4	1.07	1.09	1.12	1.00	2.24
CD200c4	1.11	1.13	1.17	1.06	2.28
Cd7	0.99	0.85	0.50	0.20	1.33
Cl200b4	1.04	1.01	0.94	0.75	1.97
Cl200c4	1.04	0.97	0.79	0.56	1.78
Da12	1.05	0.96	0.76	0.43	1.54
Db4	1.09	1.13	1.22	1.16	2.45
Dc4	1.06	1.02	0.91	0.76	2.07
Dd7f1.5	1.04	0.98	0.84	0.70	2.08
Ea12	0.99	0.88	0.60	0.32	1.50
Eb4	1.03	1.08	1.19	1.17	2.59
Ec4	0.99	0.93	0.78	0.65	2.07
Ed7f1.5	1.02	1.00	0.97	0.93	2.48
Ia12	1.05	1.06	1.07	0.93	2.18
Ib4	1.04	1.06	1.13	1.08	2.47
Ma12	1.02	0.92	0.68	0.42	1.62
Mb4	1.05	1.11	1.28	1.30	2.70
Mc4	1.01	1.00	0.96	0.89	2.34
Md7f1.5	1.01	1.02	1.04	0.98	2.41
Pa12	1.01	0.87	0.52	0.20	1.31
Pb4	1.04	1.01	0.94	0.77	2.02

TABLE XXVII (CONTINUED)

Extractive Scintillator	Relative β/γ-Peak Position	Relative α-Peak Position	Relative Peak Separation	Relative Peak Edge Sepatation	Resolution
Pd7f1.5	1.03	0.93	0.66	0.37	1.53
PD200b4	1.12	1.20	1.39	1.34	2.48
PD200d7	1.07	1.08	1.10	0.93	2.11
PD200d7b1.5	1.11	1.16	1.28	1.20	2.40
PD200d7c1.5	1.08	1.07	1.05	0.91	2.15
PD200d7f1.5	1.05	1.00	0.88	0.76	2.16
PE200b4	1.09	1.18	1.42	1.38	2.53
PE200d7f1.5	1.05	1.03	1.00	0.84	2.10
PI200a12	1.03	0.97	0.81	0.59	1.84
PI200b4	1.08	1.08	1.07	1.04	2.53
PI200d7f1.5	1.04	1.00	0.91	0.75	2.04
PM100c4	1.09	1.06	0.99	0.87	2.18
PM200b4	1.08	1.16	1.36	1.34	2.56
PM200b6	1.10	1.19	1.43	1.42	2.61
PM200b8	1.11	1.20	1.44	1.42	2.57
PM500b4	1.09	1.17	1.40	1.40	2.64
PM200d7f1.5	1.04	0.99	0.89	0.76	2.14
PN180b4	1.08	1.14	1.30	1.29	2.60

and the left edge of the α-peak, or the peak edge separation. This distance depends on both the peak centroid separation and the peak widths. For a Gaussian-shaped peak, the peak width is generally taken as four standard deviations (4σ) of the peak[62] and the FWHM is equal to 2.35σ.[61] The greater the peak edge separation, the more efficient is the separation of β/γ- and α-pulses and the less crucial is the setting of the PSD. This is because pulses with decay times between the right edge of the β/γ-peak and the left edge of the α-peak will be spread over a greater number of channels the greater the peak edge separation, while the discriminator setting will be only one channel in all cases. The relative peak edge separation, E_{rel}, was calculated according to Equation 11,

$$E_{rel} = [(C_{T\alpha} - 0.85\alpha_T) - (C_{T\beta/\gamma} + 0.85\beta/\gamma_T)] \cdot [(C_{A\alpha} - 0.85\alpha_A) - (C_{A\beta/\gamma} + 0.85\beta/\gamma_A)]^{-1}, \quad (11)$$

where α_T or β/γ_T and α_A or β/γ_A represent the FWHM values of the α-peak or β/γ-peak for the test solution and Alphaex, respectively. The estimated uncertainties were ± 0.06 at the 95% confidence level.

For chromatographic peaks of approximately Gaussian shape, the degree of separation or resolution, R, of adjacent peaks has been defined as the distance between peak centroids divided by the average 4σ peak width.[62] By this definition, R = 1 corresponds to an approximate 3% overlap of peak areas

and R = 1.5 corresponds to an approximate 0.2% overlap. Thus, the greater the R value, the greater the degree of separation.

The above definition of resolution was used as an additional comparison of time resolution characteristics for all of the scintillator solutions tested. An R value was calculated for each extractive scintillator according to Equation 12,

$$R = (C_{\alpha} - C_{\beta/\gamma}) \cdot [0.85(\alpha - \beta/\gamma)]^{-1}, \qquad (12)$$

where α and β/γ stand for the FWHM values of the α- and β/γ-peaks, respectively. The propagated uncertainty associated with the calculation of R was estimated to be approximately $\pm$ 0.12 at the 95% confidence level.

The primary purpose of this portion of the study was to determine which, if any, of the newly developed scintillator solutions exhibit time resolution comparable to that of Alphaex. It can be seen from the spectra in Figure 9 (p 97) and the data in Table XXVII (p 101) that the degree of separation between β/γ- and α-pulses varies considerably, depending primarily on the presence or absence of an energy transfer agent and on the fluor used. Scintillator solutions containing the liquid naphthalenes—diisopropylnaphthalene (D), 1-methyl-naphthalene (M), and 2-ethylnaphthalene(E)—and monoisopropylbiphenyl (I) all exhibit better time resolution than solutions which do not contain one of these components. Also, in most cases solutions containing α-NPO (b) as the fluor exhibit better time resolution than comparable solutions containing other scintillators. In some cases this may have been due to the fact that the solubility

of PBBO (c) was limited in the solvents such as phenylxylylethane (P) and monoisopropylbiphenyl. However, both PBBO and α-NPO were quite soluble in the liquid naphthalenes, and in each of these instances solutions containing α-NPO showed better time resolution than solutions containing PBBO.

Although a number of the test solutions exhibited greater peak centroid separations and peak edge separations than Alphaex, the FWHM values were also usually greater. As a result, none of the test solutions was found to have an R value significantly greater than Alphaex, but many had R values very close to or equal to that of Alphaex. In summary, with the exception of solutions containing butyl-PBD as the fluor, the solutions containing either monoisopropylbiphenyl or one of the liquid naphthalenes as primary or secondary solvent were found to exhibit sufficient time resolution to make them useful replacements for Alphaex.

The extractive scintillator solutions were listed according to decreasing relative peak edge separation and decreasing resolution (Table XXVIII, p 106). The solutions in each category were then ranked from 1 to 43 and assigned an overall time resolution ranking based on an equally weighted combination of the first two categories. The solutions are listed in order of decreasing overall time resolution in the third column. It should be remembered that rankings are at best approximate and are meant to serve only as a rough guide. Because of the.

TABLE XXVIII

EXTRACTIVE SCINTILLATORS IN ORDER OF DECREASING TIME RESOLUTION

Extractive Scintillator	Relative Peak Edge Separation	Extractive Scintillator	Resolution	Extractive Scintillator	Overall Time Resolution
PM200b6	1.42	Mb4	2.70	PM200b6	1
PM200b8	1.42	Alphaex	2.64	PM500b4	1
PM500b4	1.40	PM500b4	2.64	Mb4	3
PE200b4	1.38	PM200b6	2.61	PM200b8	3
PD200b4	1.34	PN180b4	2.60	PE200b4	5
PM200b4	1.34	Eb4	2.59	PM200b4	5
Mb4	1.30	PM200b8	2.57	PN180b4	5
PN180b4	1.29	PM200b4	2.56	Eb4	8
PD200d7b1.5	1.20	PE200b4	2.53	PD200b4	8
Eb4	1.17	PI200b4	2.53	Alphaex	10
Db4	1.16	Ed7f1.5	2.48	PI200b4	11
Ib4	1.08	PD200b4	2.48	Db4	12
CD200c4	1.06	Ib4	2.47	Ib4	12
PI200b4	1.04	Db4	2.45	PD200d7b1.5	12
Alphaex	1.00	Md7f1.5	2.41	Ed7f1.5	15
CD200b4	1.00	PD200d7b1.5	2.40	CD200c4	16
Md7f1.5	0.98	Mc4	2.34	Md7f1.5	17
Ed7f1.5	0.93	CD200c4	2.28	CD200b4	18
Ia12	0.93	CD200b4	2.24	Ia12	19
PD200d7	0.93	Ia12	2.18	Mc4	20
PD200d7c1.5	0.91	PM100c4	2.18	PD200d7	21
Mc4	0.89	PD200d7f1.5	2.16	PM100c4	21
PM100c4	0.87	PD200d7c1.5	2.15	PD200d7c1.5	23
PE200d7f1.5	0.84	PM200d7f1.5	2.14	PD200d7f1.5	24
Pb4	0.77	PD200d7	2.11	PE200d7f1.5	25

TABLE XXVIII (CONTINUED)

Extractive Scintillator	Relative Peak Edge Separation	Extractive Scintillator	Resolution	Extractive Scintillator	Overall Time Resolution
Dc4	0.76	PE200d7f1.5	2.10	PM200d7f1.5	25
PD200d7f1.5	0.76	Dd7f1.5	2.08	Dc4	27
PM200d7f1.5	0.76	Dc4	2.07	Pb4	28
Cl200b4	0.75	Ec4	2.07	Dd7f1.5	29
Pl200d7f1.5	0.75	Pl200d7f1.5	2.04	Pl200d7f1.5	30
Dd7f1.5	0.70	Pb4	2.02	Ec4	31
Ec4	0.65	Cl200b4	1.97	Cl200b4	32
Pl200a12	0.59	Pl200a12	1.84	Pl200a12	33
Cl200c4	0.56	Cl200c4	1.78	Cl200c4	34
Cb4	0.45	Cb4	1.66	Cb4	35
Da12	0.43	Ma12	1.62	Da12	36
Ma12	0.42	Da12	1.54	Ma12	36
Pd7f1.5	0.37	Pd7f1.5	1.53	Pd7f1.5	38
Ea12	0.32	Ea12	1.50	Ea12	39
Cd7	0.20	Cd7	1.33	Cd7	40
Pa12	0.20	Pa12	1.31	Pa12	41
Cc4	0.00	Cc4	1.01	Cc4	42
Ca12	-0.02	Ca12	0.97	Ca12	43

uncertainty associated with each measurement there may be very little actual difference between, for example, a rank of 1 and a rank of 10. In all 3 categories the top 10 solutions—with the exception of Alphaex in the Resolution category—contained α-NPO (b) as the scintillator.

C. Evaluation of Energy Resolution Characteristics

Following measurement of the pulse-shape distributions, the same samples were used to measure the pulse-height distributions (energy spectra) of normal uranium and ^{241}Am in Alphaex and in each new scintillator (Figure 10, p 109). The abscissa represents energy and the ordinate is in counts per channel. Each sample was measured for 3600 s. From left to right the peak identities and α-energies are ^{238}U (4180 keV), ^{234}U (4770 keV), and ^{241}Am (5480 keV). As before, PeakFit was used to curve-fit the data from the MCA output to determine peak centroids and FWHM values. Uncertainties for peak centroids and FWHM values were found to be no more than ± 0.5 channels at the 95% confidence level. This data is recorded in Table XXXV (p 140) in the Appendix.

The energy resolution characteristics of all new scintillator solutions are compared to those of Alphaex in four ways (Table XXIX, p 112). The first comparison is by relative peak position, calculated for each α-peak as in Equation 9 (p 100). This is a measure of energy resolution because peak position is proportional to the light output of the scintillator, which in turn is a major factor in determining energy resolution. Usually, the greater the light output, the better the energy resolution. Estimated uncertainties are ± 0.01 at

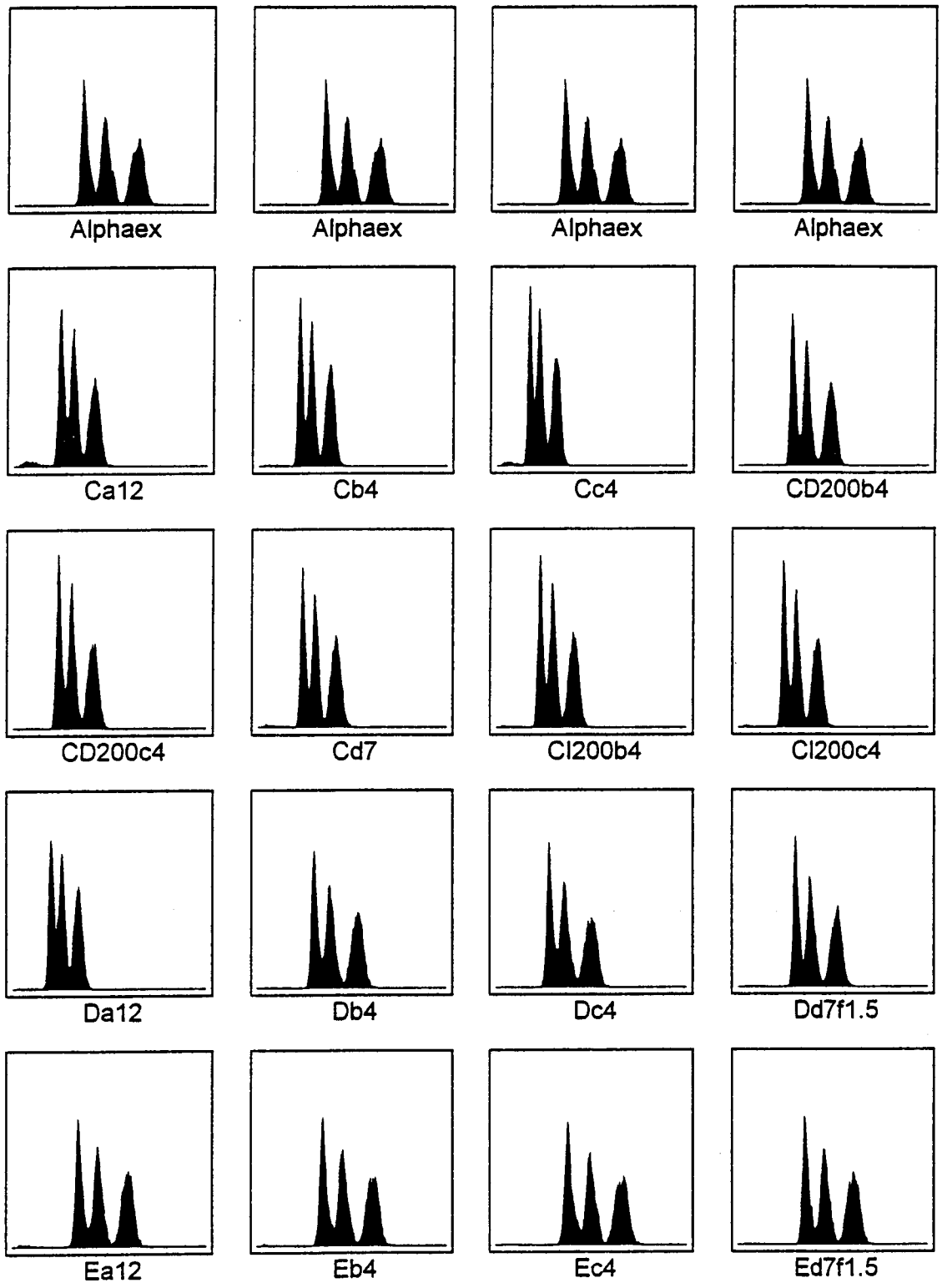


Figure 10. Comparison of pulse-height distributions in Alphaex and test scintillators.

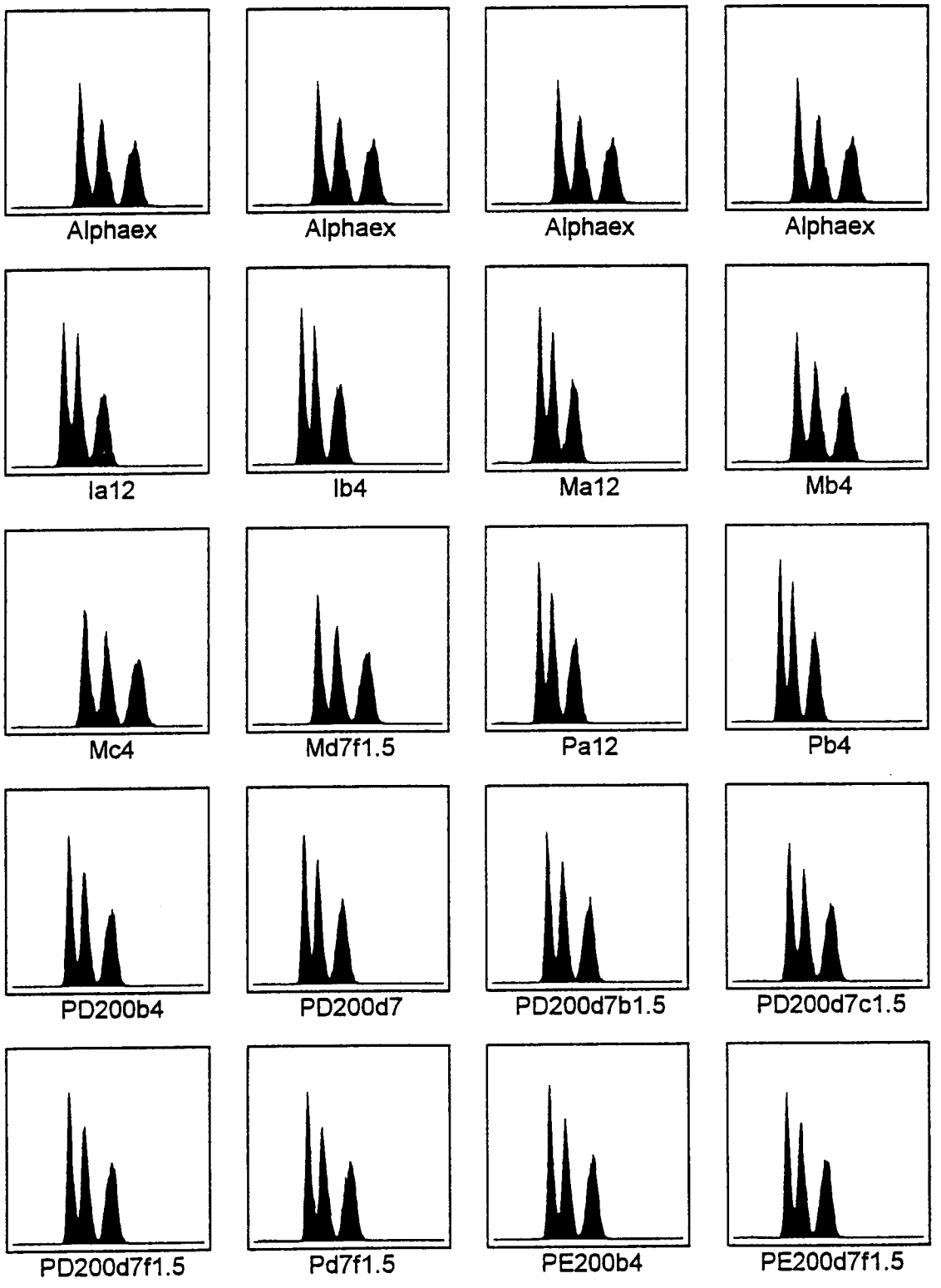


Figure 10. (Continued).

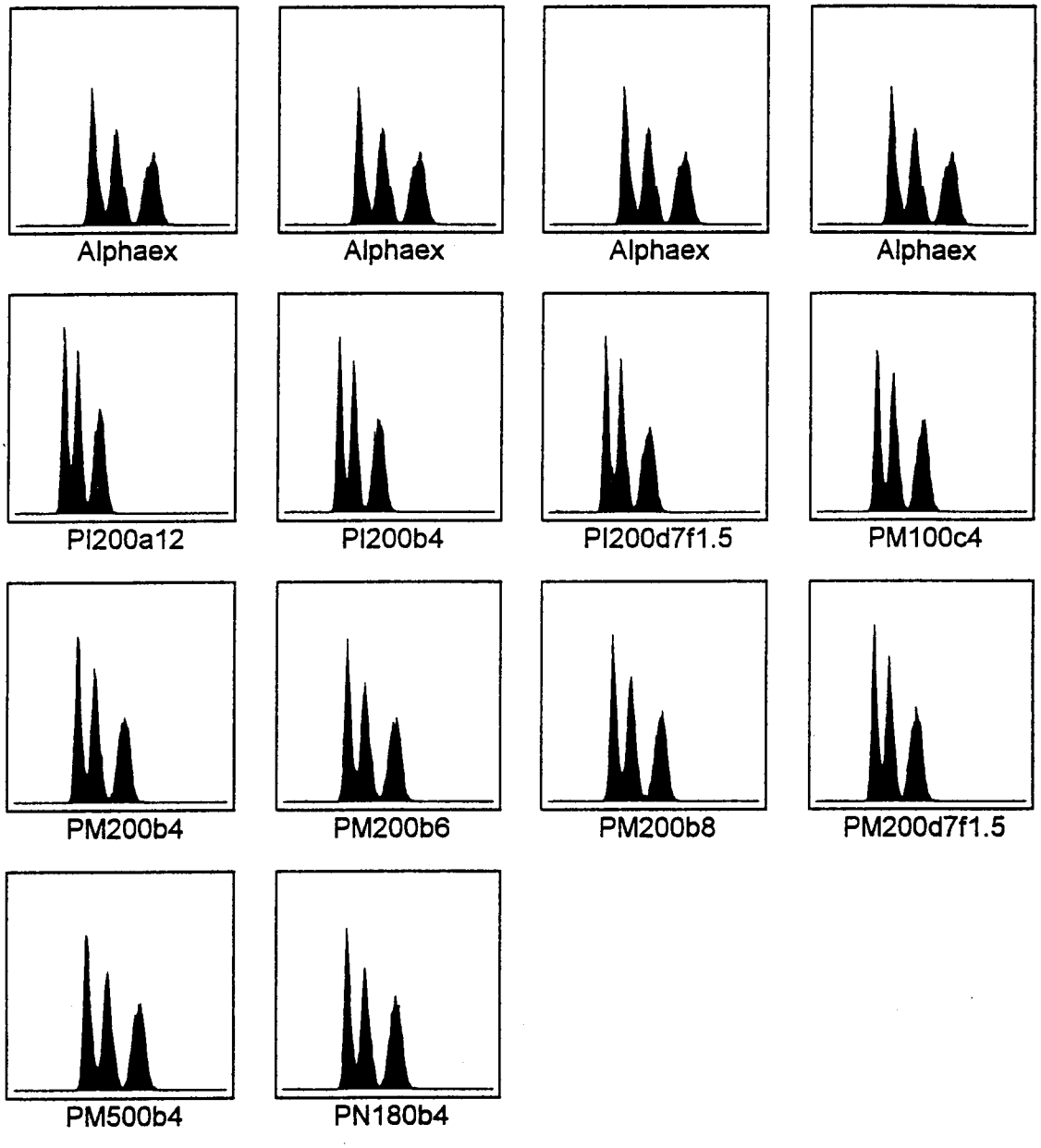


Figure 10. (Continued).

TABLE XXIX

COMPARISON OF ENERGY RESOLUTION PROPERTIES

Extractive Scintillator	Relative Peak Position[a]			Resolution[b]		Peak-to-Valley Ratio[c]		Percent Energy Resolution[d]		
	^{238}U	^{234}U	^{241}Am	^{238}U:^{234}U	^{234}U:^{241}Am	^{238}U:^{234}U	^{234}U:^{241}Am	^{238}U	^{234}U	^{241}Am
Alphaex	1.00	1.00	1.00	1.19	1.35	9.4 ± 1.5	34 ± 12	4.7	6.5	6.7
Ca12	0.68	0.66	0.66	0.96	1.15	3.2 ± 0.3	10 ± 1.6	5.8	7.1	9.1
Cb4	0.63	0.61	0.60	0.98	1.18	3.7 ± 0.4	13 ± 3	5.8	7.0	8.6
Cc4	0.51	0.50	0.50	0.90	1.08	2.7 ± 0.3	7.2 ± 0.9	5.9	7.9	9.3
CD200b4	0.79	0.77	0.77	1.06	1.30	5.0 ± 0.6	19 ± 4	5.3	6.2	8.1
CD200c4	0.67	0.65	0.66	1.05	1.19	4.3 ± 0.5	13 ± 3	5.4	6.5	8.9
Cd7	0.68	0.66	0.66	1.01	1.20	4.2 ± 0.4	15 ± 3	5.7	6.7	8.7
Cl200b4	0.67	0.65	0.65	1.00	1.19	4.1 ± 0.4	14 ± 3	5.6	6.9	8.6
Cl200c4	0.68	0.66	0.67	1.03	1.20	4.2 ± 0.4	15 ± 3	5.2	6.7	8.7
Da12	0.58	0.56	0.54	0.89	1.06	2.4 ± 0.2	5.9 ± 0.8	7.0	7.8	9.1
Db4	0.86	0.84	0.85	1.04	1.30	4.7 ± 0.6	16 ± 4	4.9	6.9	7.6
Dc4	0.79	0.77	0.78	0.98	1.19	3.8 ± 0.4	12 ± 3	4.9	7.2	8.8
Dd7f1.5	0.85	0.82	0.83	1.05	1.30	5.7 ± 0.7	18 ± 4	4.8	6.8	7.6
Ea12	0.96	0.95	0.94	1.18	1.38	6.4 ± 0.9	27 ± 8	5.1	6.2	6.7
Eb4	0.99	0.98	0.97	1.18	1.34	6.9 ± 1.0	24 ± 7	5.0	6.3	7.0
Ec4	1.07	1.06	1.04	1.24	1.32	8.4 ± 1.3	36 ± 13	5.0	6.2	6.9

TABLE XXIX (CONTINUED)

Extractive Scintillator	Relative Peak Position[a]			Resolution[b]		Peak-to-Valley Ratio[c]		Percent Energy Resolution[d]		
	^{238}U	^{234}U	^{241}Am	^{238}U:^{234}U	^{234}U:^{241}Am	^{236}U:^{234}U	^{234}U:^{241}Am	^{238}U	^{234}U	^{241}Am
Ed7f1.5	1.00	0.99	0.97	1.19	1.31	8.0 ± 1.2	26 ± 8	5.0	6.3	7.1
Ia12	0.76	0.73	0.75	1.01	1.23	3.6 ± 0.4	14 ± 3	5.3	6.6	8.9
Ib4	0.76	0.73	0.73	1.07	1.27	4.4 ± 0.5	20 ± 5	5.0	6.3	8.5
Ma12	0.72	0.70	0.68	0.98	1.16	3.3 ± 0.3	9.5 ± 1.5	6.5	6.6	9.1
Mb4	0.98	0.96	0.95	1.14	1.32	6.1 ± 0.8	23 ± 6	5.1	6.5	7.0
Mc4	1.07	1.06	1.04	1.23	1.36	7.7 ± 1.2	37 ± 13	5.2	6.1	6.7
Md7f1.5	0.99	0.97	0.95	1.19	1.36	8.4 ± 1.3	24 ± 7	4.9	6.2	6.9
Pa12	0.72	0.69	0.69	1.02	1.22	4.1 ± 0.4	14 ± 6	5.4	6.6	8.6
Pb4	0.73	0.70	0.70	1.07	1.30	4.6 ± 0.5	22 ± 5	5.4	6.1	8.2
Pd7f1.5	0.83	0.80	0.81	1.06	1.32	5.4 ± 0.6	22 ± 6	4.7	6.7	7.6
PD200b4	0.83	0.80	0.81	1.11	1.36	6.0 ± 0.7	26 ± 7	5.0	6.0	7.7
PD200d7	0.78	0.75	0.75	1.08	1.33	5.0 ± 0.6	20 ± 5	5.4	6.0	8.0
PD200d7b1.5	0.83	0.80	0.80	1.11	1.38	6.0 ± 0.7	30 ± 8	5.1	6.0	7.5
PD200d7c1.5	0.85	0.83	0.83	1.04	1.33	4.6 ± 0.5	18 ± 4	5.3	6.5	7.6
PD200d7f1.5	0.83	0.80	0.81	1.09	1.35	5.7 ± 0.7	26 ± 7	4.8	6.3	7.6
PE200b4	0.85	0.82	0.83	1.11	1.40	6.1 ± 0.7	30 ± 8	4.7	6.2	7.2

TABLE XXIX (CONTINUED)

Extractive Scintillator	Relative Peak Position[a]			Resolution[b]		Peak-to-Valley Ratio[c]		Percent Energy Resolution[d]		
	^{238}U	^{234}U	^{241}Am	^{238}U:^{234}U	^{234}U:^{241}Am	^{238}U:^{234}U	^{234}U:^{241}Am	^{238}U	^{234}U	^{241}Am
PE200d7f1.5	0.81	0.78	0.78	1.06	1.32	4.9 ± 0.6	19 ± 5	5.0	6.5	7.9
PI200a12	0.65	0.63	0.62	1.03	1.17	3.8 ± 0.4	13 ± 3	5.6	6.8	8.8
PI200b4	0.75	0.72	0.72	1.09	1.32	5.1 ± 0.6	26 ± 7	5.2	6.1	8.0
PI200d7f1.5	0.77	0.74	0.75	1.06	1.28	4.7 ± 0.7	23 ± 8	5.0	6.3	8.5
PM100c4	0.82	0.79	0.81	1.12	1.39	5.6 ± 0.7	38 ± 12	4.8	6.0	7.4
PM200b4	0.84	0.81	0.81	1.11	1.36	5.7 ± 0.7	30 ± 8	4.9	6.2	7.6
PM200b6	0.87	0.85	0.85	1.06	1.34	5.3 ± 0.6	22 ± 6	5.0	6.7	7.2
PM200b8	0.87	0.84	0.84	1.10	1.39	5.9 ± 0.7	23 ± 6	4.9	6.3	7.1
PM500b4	0.95	0.93	0.92	1.14	1.35	6.5 ± 0.9	36 ± 12	5.1	6.4	7.0
PM200d7f1.5	0.79	0.76	0.76	1.06	1.28	4.8 ± 0.5	32 ± 9	5.1	6.5	8.1
PN180b4	0.89	0.86	0.86	1.10	1.38	6.4 ± 0.8	33 ± 10	4.9	6.4	7.0

a. Estimated uncertainties ± 0.01 at the 95% confidence level.

b. Estimated uncertainties ± 0.03 at the 95% confidence level.

c. Uncertainties are 2σ counting uncertainties.

d. Estimated uncertainties ± 0.2% at the 95% confidence level.

the 95% confidence level. The second comparison is by resolution of adjacent peaks, where R is calculated as in Equation 11 (p 103), by dividing the peak centroid separation of adjacent peaks by the average 4σ peak width. Again, the higher the R value, the better the resolution. Estimated uncertainties are ± 0.03 at the 95% confidence level. The third means of comparison is by peak-to-valley ratios of adjacent peaks. These were calculated by first performing a five-point smoothing function (a function of the Maestro II MCA software) on the pulse-height distribution data, to minimize variations due to counting statistics. Then the number of counts at the maximum ordinate of the ^{238}U and ^{234}U peaks and the number of counts at the minimum ordinate of the ^{238}U:^{234}U and ^{234}U:^{241}Am valleys were recorded (Table XXXV, p 140).

For each pair of adjacent peaks, the peak-to-valley ratio was calculated by dividing the number of counts in the left-hand peak channel by the number of counts in the valley minimum channel. Because the data had been smoothed using the five-point smoothing function, it was assumed that the number of counts in each channel was actually known with a degree of uncertainty based on five times the number of counts recorded. This assumption was proved to be valid by determining the standard deviation of five replicate peak-to-valley ratio calculations for a sealed Alphaex sample counted for five 60-min intervals. These five peak-to-valley ratios were calculated without smoothing the spectra. The average ^{238}U:^{234}U and ^{234}U:^{241}Am peak-to-valley ratios calculated without smoothing the spectra were 10.0 ± 12% and 66 ± 34%, respectively, at the 95%

confidence level. When the spectra were smoothed the same ratios were calculated to be 8.1 ± 14% and 37 ± 33%, respectively, where the percent uncertainties were calculated at the 95% confidence level (2σ) according to Equation 13,

$$2\sigma = \text{ratio} \cdot 2[(5 \cdot N_{peak})^{-1} + (5 \cdot N_{valley})^{-1}]^{1/2}, \quad (13)$$

where N is the number of counts in the peak or valley channel. The uncertainty of this calculation was determined primarily by the number of counts in the valley minimum; therefore, the better the resolution, the larger is the peak-to-valley ratio and the greater is the uncertainty.

The fourth comparison is by percent energy resolution of each α-peak, where percent energy resolution (% R) is given by Equation 14,

$$\%R = (\alpha_{FWHM} \cdot E_{\alpha}^{-1})100\%, \quad (14)$$

where α_{FWHM} is the peak FWHM in keV and E_{α} is the α-particle energy in keV. The FWHM in keV was calculated by multiplying the FWHM in channels by the number of keV per channel for each sample energy spectrum. The estimated uncertainties are ± 0.2% at the 95% confidence level.

It can be seen from the spectra in Figure 10 (p 109) and the data in Table XXIX (p 112) that, with the exception of some solutions containing 1-methyl-naphthalene or 2-ethylnaphthalene as the only solvent, Alphaex is superior to all of the new scintillator solutions in terms of light output and energy resolution. However, in many instances the differences are slight, and it seems that most of

the newly developed solutions could replace Alphaex with only minor losses in energy resolution.

All of the HDEHP-containing scintillator solutions tested in this study were listed in order of decreasing ^{241}Am relative peak position—a measure of light output—and ability to resolve ^{238}U and ^{234}U peaks (Table XXX, p 118). The individual rankings from each category were then combined to give an approximate overall ranking in the last column. The extractive scintillators were also ranked according to their combined overall time and energy resolution rankings, with equal weighting given to each category (Table XXXI, p 120). Again, rankings are only approximate due to the uncertainties associated with the various measures of resolution. It should be noted that, except for a few of the lowest-ranked solutions, the energy resolution of all the solutions measured on the PERALS unit used in this study was better than the resolution measured for Alphaex on earlier model PERALS units which employed less efficient photomultiplier tubes.[2]

D. Evaluation of Alpha Background Count Rate

An important advantage of α-particle measurement by PERALS spectrometry and, to a lesser degree, other types of pulse-shape-discriminating liquid scintillation alpha spectrometry, is the low alpha background that can be achieved by this technique. Instrument backgrounds are as low as 0.001 cpm in the range of 4 to 8 MeV. However, a more useful background indicator is the activity measured with a normal sample tube and 1.00 mL of extractive

TABLE XXX

EXTRACTIVE SCINTILLATORS IN ORDER OF DECREASING ENERGY RESOLUTION

^{241}Am Relative Peak Position		^{238}U:^{234}U Peak Resolution		^{238}U:^{234}U Peak to Valley Ratio		Overall Energy Resolution	
Ec4	1.04	Ec4	1.24	Alphaex	9.4	Ec4	1
Mc4	1.04	Mc4	1.23	Ec4	8.4	Alphaex	2
Alphaex	1.00	Alphaex	1.19	Md7f1.5	8.4	Mc4	3
Eb4	0.97	Ed7f1.5	1.19	Ed7f1.5	8.0	Ed7f1.5	4
Ed7f1.5	0.97	Md7f1.5	1.19	Mc4	7.7	Md7f1.5	4
Mb4	0.95	Ea12	1.18	Eb4	6.9	Eb4	6
Md7f1.5	0.95	Eb4	1.18	PM500b4	6.5	Ea12	7
Ea12	0.94	Mb4	1.14	Ea12	6.4	Mb4	8
PM500b4	0.92	PM500b4	1.14	PN180b4	6.4	PM500b4	8
PN180b4	0.86	PM100c4	1.12	Mb4	6.1	PN180b4	10
Db4	0.85	PD200b4	1.11	PE200b4	6.1	PE200b4	11
PM200b6	0.85	PD200d7b1.5	1.11	PD200b4	6.0	PD200b4	12
PM200b8	0.84	PE200b4	1.11	PD200d7b1.5	6.0	PM200b8	13
Dd7f1.5	0.83	PM200b4	1.11	PM200b8	5.9	PM200b4	14
PD200d7c1.5	0.83	PM200b8	1.10	Dd7f1.5	5.7	PD200d7b1.5	15
PE200b4	0.83	PN180b4	1.10	PD200d7f1.5	5.7	PM100c4	15
PD200b4	0.81	PD200d7f1.5	1.09	PM200b4	5.7	PD200d7f1.5	17
PD200d7f1.5	0.81	PI200b4	1.09	PM100c4	5.6	PM200b6	18
Pd7f1.5	0.81	PD200d7	1.08	Pd7f1.5	5.4	Dd7f1.5	19
PM100c4	0.81	Ib4	1.07	PM200b6	5.3	Pd7f1.5	20
PM200b4	0.81	Pb4	1.07	PI200b4	5.1	Db4	21
PD200d7b1.5	0.80	CD200b4	1.06	CD200b4	5.0	PD200d7	22
Dc4	0.78	Pd7f1.5	1.06	PD200d7	5.0	CD200b4	23
PE200d7f1.5	0.78	PE200d7f1.5	1.06	PE200d7f1.5	4.9	PE200d7f1.5	23
CD200b4	0.77	PI200d7f1.5	1.06	PM200d7f1.5	4.8	PI200b4	23
PM200d7f1.5	0.76	PM200b6	1.06	Db4	4.7	PD200d7c1.5	26
Ia12	0.75	PM200d7f1.5	1.06	PI200d7f1.5	4.7	PM200d7f1.5	27

TABLE XXX (CONTINUED)

^{241}Am Relative Peak Position		^{238}U:^{234}U Peak Resolution		^{238}U:^{234}U Peak to Valley Ratio		Overall Energy Resolution	
PD200d7	0.75	CD200c4	1.05	Pb4	4.6	PI200d7f1.5	28
PI200d7f1.5	0.75	Dd7f1.5	1.05	PD200d7c1.5	4.6	Ib4	29
Ib4	0.73	Db4	1.04	Ib4	4.4	Pb4	29
PI200b4	0.72	PD200d7c1.5	1.04	CD200c4	4.3	CD200c4	31
Pb4	0.70	CI200c4	1.03	Cd7	4.2	Dc4	32
Pa12	0.69	PI200a12	1.03	CI200c4	4.2	CI200c4	33
Ma12	0.68	Pa12	1.02	CI200b4	4.1	Ia12	34
CI200c4	0.67	Cd7	1.01	Pa12	4.1	Pa12	34
Ca12	0.66	Ia12	1.01	Dc4	3.8	Cd7	36
CD200c4	0.66	CI200b4	1.00	PI200a12	3.8	PI200a12	37
Cd7	0.66	Cb4	0.98	Cb4	3.7	CI200b4	38
CI200b4	0.65	Dc4	0.98	Ia12	3.6	Ma12	39
PI200a12	0.62	Ma12	0.98	Ma12	3.3	Cb4	40
Cb4	0.60	Ca12	0.96	Ca12	3.2	Ca12	41
Da12	0.54	Cc4	0.90	Cc4	2.7	Cc4	42
Cc4	0.50	Da12	0.89	Da12	2.4	Da12	43

TABLE XXXI

EXTRACTIVE SCINTILLATORS RANKED ACCORDING TO COMBINED TIME AND ENERGY RESOLUTION

Extractive Scintillator	Overall Time Resolution	Overall Energy Resolution	Extractive Scintillator	Combined Ranking
Alphaex	10	2	PM500b4	1
Ca12	42	41	Alphaex	2
Cb4	35	40	Mb4	2
Cc4	42	43	Eb4	4
CD200b4	16	22	PN180b4	4
CD200c4	15	31	PE200b4	6
Cd7	40	36	PM200b8	6
Cl200b4	29	37	PM200b6	8
Cl200c4	34	33	PD200b4	9
Da12	36	42	Md7f1.5	10
Db4	11	21	PM200b4	10
Dc4	27	32	Ed7f1.5	12
Dd7f1.5	31	19	Mc4	13
Ea12	39	7	PD200d7b1.5	14
Eb4	9	6	Db4	15
Ec4	32	1	Ec4	16
Ed7f1.5	17	5	Pl200b4	17
Ia12	19	35	CD200b4	18
Ib4	14	30	PM100c4	18
Ma12	37	39	PD200d7	20
Mb4	4	8	PD200d7f1.5	20
Mc4	21	3	Ib4	22
Md7f1.5	17	4	CD200c4	23
Pa12	40	34	Ea12	23

TABLE XXXI (CONTINUED)

Extractive Scintillator	Overall Time Resolution	Overall Energy Resolution	Extractive Scintillator	Combined Ranking
Pb4	28	29	PD200d7c1.5	25
PD200b4	8	12	PE200d7f1.5	26
PD200d7	20	22	Dd7f1.5	27
PD200d7b1.5	11	16	PM200d7f1.5	28
PD200d7c1.5	21	26	Ia12	29
PD200d7f1.5	25	17	Pb4	30
Pd7f1.5	38	20	PI200d7f1.5	30
PE200b4	5	11	Pd7f1.5	32
PE200d7f1.5	24	25	Dc4	33
PI200a12	33	37	CI200b4	34
PI200b4	13	24	CI200c4	35
PI200d7f1.5	29	28	PI200a12	36
PM100c4	23	15	Pa12	37
PM200b4	7	14	Cb4	38
PM200b6	1	18	Cd7	39
PM200b8	3	13	Ma12	39
PM200d7f1.5	26	27	Da12	41
PM500b4	1	8	Ca12	42
PN180b4	5	10	Cc4	43

scintillator in the sample chamber—a scintillator blank. Scintillator blank activities are usually in the range of 0.01 to 0.03 cpm in the region of a given α-peak. This activity depends on several factors including alpha contamination of the scintillator solution reagents, alpha contamination of the sample tube, and the degree to which α-pulses can be distinguished from β/γ-pulses by a given instrument and in a given scintillator solution.

Scintillator blanks for approximately half of the solutions developed in this study were measured and compared to Alphaex. At least one solution prepared from each solvent was tested to confirm that there was no significant contamination in any of the solvents. The majority of the solutions tested utilized phenylxylylethane as the primary solvent because it is the most promising replacement solvent based on cost, available purity, and overall resolution characteristics.

Time and energy resolution evaluations revealed PSD settings and α-energy band positions varied considerably between solutions. For this reason scintillator blanks were measured using the same PSD settings and the same alpha regions of interest (ROI's) as for the solutions evaluated for time and energy resolution. Count times ranged from 60 to 1440 minutes. In some instances a sample was counted more than once or for different lengths of time (Table XXXII, p 123).

With the exception of solution Ca12, all of the measured blank count rates were less than or equal to those measured for Alphaex. The high count rate for

TABLE XXXII

SUMMARY OF EXTRACTIVE SCINTILLATOR BLANK COUNT RATES

Extractive Scintillator	Count Rate in ^{238}U ROI	Count Rate in ^{234}U ROI	Count Rate in ^{241}Am ROI	Count Time (min)
Alphaex	0.022 ± 0.008	0.021 ± 0.008	0.023 ± 0.008	1440
Ca12	0.10 ± 0.02	0.030 ± 0.011	0.016 ± 0.008	1000
CD200c4	0.02 ± 0.02	0.010 ± 0.012	0.017 ± 0.015	300
Dc4	0.05 ± 0.06	0.02 ± 0.04	0.05 ± 0.06	60
Dd7f1.5	0.03 ± 0.05	0.05 ± 0.06	0.03 ± 0.05	60
Ec4	0.02 ± 0.04	—	0.02 ± 0.04	60
Ia12	—	—	—	60
Ib4	0.010 ± 0.007	0.017 ± 0.009	0.018 ± 0.009	958
Mb4	—	—	—	60
Mb4	0.005 ± 0.005	0.004 ± 0.004	0.006 ± 0.005	1000
Pa12	0.03 ± 0.05	0.02 ± 0.04	0.02 ± 0.04	60
Pb4	—	0.03 ± 0.05	0.02 ± 0.04	60
Pb4	—	0.03 ± 0.05	0.02 ± 0.04	60
Pd7f1.5	—	—	0.02 ± 0.04	60
Pd7f1.5	—	—	—	60
Pd7f1.5	0.006 ± 0.005	0.003 ± 0.004	0.002 ± 0.003	1000
PD200b4	—	0.03 ± 0.05	0.02 ± 0.04	60
PD200b4	0.02 ± 0.04	0.02 ± 0.04	—	60
PD200d7f1.5	—	0.02 ± 0.04	0.05 ± 0.06	60
PD200d7f1.5	0.01 ± 0.03	—	—	70

TABLE XXXII (CONTINUED)

Extractive Scintillator	Count Rate in ^{238}U ROI	Count Rate in ^{234}U ROI	Count Rate in ^{241}Am ROI	Count Time (min)
PE200b4	0.03 ± 0.05	0.05 ± 0.06	0.08 ± 0.08	60
PE200b4	—	—	—	60
PE200d7f1.5	0.03 ± 0.05	0.02 ± 0.04	0.02 ± 0.04	60
PI200a12	0.08 ± 0.08	—	0.05 ± 0.06	60
PI200b4	0.03 ± 0.05	0.03 ± 0.05	—	60
PI200b4	0.03 ± 0.05	0.02 ± 0.04	—	60
PI200d7f1.5	—	—	0.05 ± 0.06	60
PM100c4	0.016 ± 0.009	0.008 ± 0.006	0.012 ± 0.008	900
PM100c4	—	0.02 ± 0.04	0.02 ± 0.04	60
PM100c4	—	0.02 ± 0.02	0.02 ± 0.02	173
PM200b4	0.05 ± 0.06	—	0.07 ± 0.07	60
PM200d7f1.5	0.03 ± 0.05	—	0.02 ± 0.04	60
PN180b4	0.011 ± 0.007	0.010 ± 0.007	0.013 ± 0.008	1000
PN180b4	—	—	0.02 ± 0.05	43

Ca12 in the ^{238}U ROI is most certainly due to the poor time resolution of this solution (see Figure 9, p 97, and Tables XXVII and XXVIII, pp 101 and 106, respectively). The lower count rate for solution Mb4 appears to be due to its superior time resolution properties and/or a lower level of alpha contamination. Any of the test solutions having adequate time resolution capabilities seem to exhibit scintillator blank count rates comparable to or slightly better than current solutions.

E. Evaluation of Chemical Stability

Two (2.000 ± 0.007) mL of each solution prepared in the initial stages of this study were placed in six different 2-dram, screw-cap vials. Three of the solutions were sparged with argon and capped and three were capped without sparging. One vial from each of these two sets was stored either in the light at room temperature, in the dark at room temperature, or in a refrigerator for the duration of the study. A number of solutions prepared in the later stages of this study were simply stored in a refrigerator without sparging.

After approximately six months all of the solutions were examined visually and assigned a number from 1 (no color) to 10 (intense color) according to the degree to which they had become colored (Table XXXIII, p 126). Observations over the course of the study and at the end of the study indicate at least three general conclusions: (1) most solutions developed less color when stored in the dark than when stored in the light; (2) most solutions containing the diiso-propylnaphthalene used in this study developed significant color within two or

TABLE XXXIII

COLOR INTENSITY OF EXTRACTIVE SCINTILLATORS AFTER SIX MONTHS OF STORAGE

Extractive Scintillator	Light		Dark		Refrigerator		Stock
	Sparged	Not Sparged	Sparged	Not Sparged	Sparged	Not Sparged	
Alphaex	1[a]	1	1	1	1	1	1
Ca12	1	1	1	1	1	1	2
Cb4	1	1	1	1	1	1	1
Cc4	2	2	1	1	1	1	1
CD200b4	-	-	-	-	-	-	3
CD200c4	-	-	-	-	-	-	3
Cd7	1	1	1	1	1	1	1
Cl200b4	-	-	-	-	-	-	1
Cl200c4	-	-	-	-	-	-	1
Da12	-	-	-	-	-	-	3
Db4	-	-	-	-	-	-	6
Dc4	8	8	7	7	7	7	5
Dd7f1.5	6	7	7	7	7	7	5
Ea12	-	-	-	-	-	-	1
Eb4	-	-	-	-	-	-	1
Ec4	2	2	1	1	1	1	1
Ed7f1.5	6	9	1	1	1	1	1
Ia12	8	4	3	4	1	2	2
Ib4	2	4	1	2	1	1	1
Ma12	-	-	-	-	-	-	1
Mb4	-	-	-	-	-	-	1
Mc4	5	5	2	2	1	1	1
Md7f1.5	8	8	3	3	1	1	1
Pa12	3	4	2	2	1	1	1

TABLE XXXIII (CONTINUED)

Extractive Scintillator	Light		Dark		Refrigerator		Stock
	Sparged	Not Sparged	Sparged	Not Sparged	Sparged	Not Sparged	
Pb4	3	3	1	1	1	1	1
PD200b4	4	5	3	3	3	3	3
PD200d7	-	-	-	-	-	-	3
PD200d7b1.5	-	-	-	-	-	-	4
PD200d7c1.5	-	-	-	-	-	-	4
PD200d7f1.5	4	5	2	2	1	1	1
Pd7f1.5	3	3	1	1	1	1	1
PE200b4	4	4	1	1	1	1	1
PE200d7f1.5	2	3	1	2	1	1	1
PI200a12	2	4	1	2	1	1	1
PI200b4	-	-	-	-	-	-	1
PI200d7f1.5	1	3	1	1	1	1	1
PM100c4	-	-	-	-	-	-	1
PM200b4	3	4	1	1	1	1	1
PM200b6	-	-	-	-	-	-	1
PM200b8	-	-	-	-	-	-	1
PM200d7f1.5	3	4	1	1	1	1	1
PM500b4	-	-	-	-	-	-	1
PN180b4	-	-	-	-	-	-	1

a. Color intensity rated from 1 (no color) to 10 (intense color).

three months, no matter how they were stored; (3) little difference was observed between sparged and unsparged solutions.

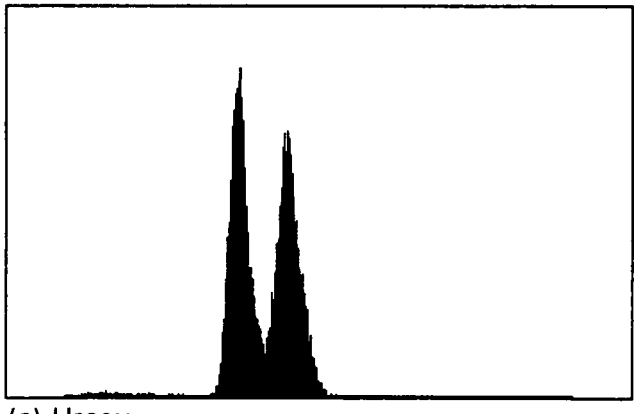
It is important from the standpoint of maintaining the best time and energy resolution that extractive scintillator solutions remain as color free as possible during storage to minimize color quenching. Extractive scintillator solutions tested in this study will remain color free longer when protected from light and possibly, but to a lesser degree, from oxygen. Many of the solutions tested are sufficiently stable under these storage conditions to make their commercialization practical. Even so, future investigations will examine the benefit of storage in nontransparent containers and the addition of chemical stabilizers to prolong storage life.

F. Work Beyond the Scope of This Study

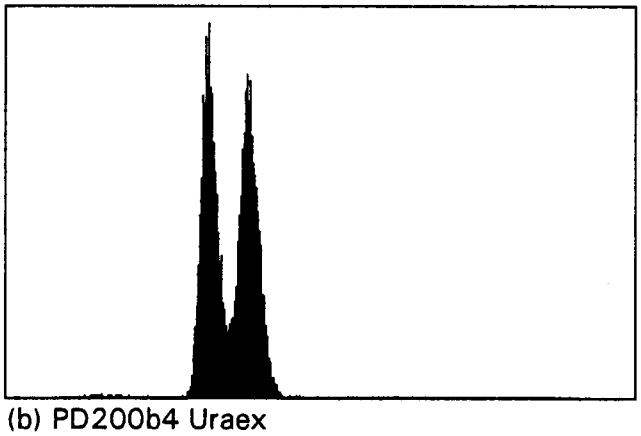
At the suggestion of the reviewers of the original proposal, two sets of solutions were prepared containing organophilic extractants other than HDEHP. One set of solutions contained 200 g L^{-1} diisopropylnaphthalene and 4.0 g L^{-1} α-NPO in phenylxylylethane (PD200b4), and the other contained 200 g L^{-1} isopropylbiphenyl and 4.0 g L^{-1} α-NPO in phenylxylylethane (PI200b4). In each set either 36 g L^{-1} of TOA, 60 g L^{-1} Primene JM-T, or 40 g L^{-1} TOPO was added as the extractant. These solutions correspond to the toluene/naphthalene-based extractive scintillators Uraex®, Thorex®, and Polex®, respectively, which are manufactured by ETRAC Laboratories, Inc..

All of these solutions remained colorless over the course of the study while stored in the dark. Extractions of uranium, thorium, and polonium with the Uraex-, Thorex-, and Polex-substitutes, respectively, were essentially quantitative in all cases. Time and energy resolution characteristics were similar to the HDEHP-containing solutions of similar composition. The energy spectra measured for normal uranium in Uraex, PD200b4 Uraex, and PI200b4 Uraex were measured (Figure 11, p 130). The nature of the extractant does not seem to be a significant factor in the selection of the best replacement solvent system.

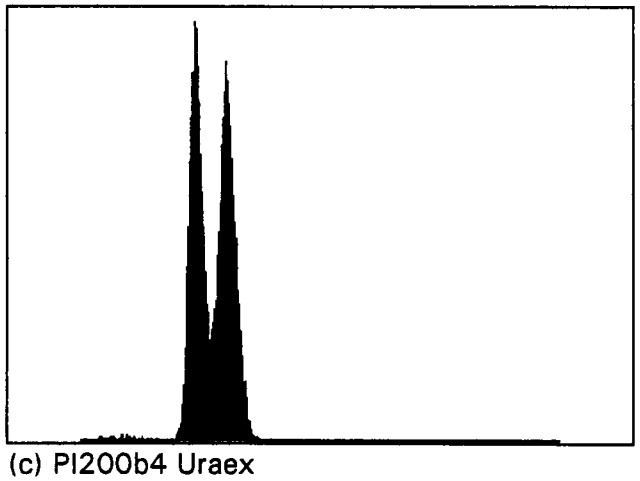
As stated previously, the extraction of nuclides at aqueous-to-organic phase ratios of 1.00 for the evaluation of resolution characteristics was quantitative in all instances after three to five minutes of equilibration. Additional extractions of uranium performed at phase ratios of approximately 33 were also quantitative after 5.0 minutes of equilibration. However, when an aqueous to organic phase ratio of approximately 65 was employed, only 86 ± 2% of the uranium was extracted by solution PM100c4 after 5.0 minutes of equilibration. Uranium is extracted quantitatively by Alphaex under the same conditions.[21,29,33] When the experiment was repeated and the phases were equilibrated for 10.0 minutes, 94 ± 3% of the uranium was extracted. Thus for large aqueous to organic phase ratios, longer equilibration times may be required to achieve complete extraction. It has not yet been determined if this is due to slower kinetics of the exchange reaction or simply the result of less intimate mixing of



(a) Uraex



(b) PD200b4 Uraex



(c) PI200b4 Uraex

Figure 11. Comparison of normal uranium pulse-height distributions in solutions containing TOA as extractant.

aqueous and organic phases because of the increased viscosity of the new solvents.

CHAPTER IV

CONCLUSION

Based on the results obtained in this study, it was concluded that it is technically feasible to replace toluene and naphthalene in current extractive scintillator solutions with nonhazardous, more environmentally-safe solvents and energy transfer agents with only minor losses in performance. Additional research will be required to optimize solution composition for maximum time and energy resolution, to improve long-term stability during storage, and to determine extraction characteristics for important alpha-emitting elements across a broader range of conditions.

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APPENDIX

APPENDIX

TABLE XXXIV

TIME RESOLUTION DATA

Extractive Scintillator	β/γ-Peak Centroid	α-Peak Centroid	Peak Separation	β/γ-Peak FWHM	α-Peak FWHM
Alphaex	191.0	267.0	76.0	13.7	20.2
Ca12	191.0	219.0	28.0	15.7	18.3
Cb4	193.0	246.0	53.0	15.0	22.6
Cc4	187.2	214.4	27.2	13.6	18.2
CD200b4	204.9	289.8	84.9	19.0	25.6
CD200c4	211.6	300.4	88.8	17.7	28.2
Cd7	188.7	226.9	38.2	15.7	18.1
Cl200b4	198.2	269.9	71.7	17.8	25.0
Cl200c4	199.4	259.5	60.1	16.9	22.8
Da12	199.8	257.5	57.7	20.1	24.0
Db4	208.3	300.7	92.4	18.5	25.8
Dc4	202.4	271.5	69.1	16.7	22.6
Dd7f1.5	198.5	262.0	63.5	15.8	20.2
Ea12	189.1	234.5	45.4	17.3	18.3
Eb4	197.6	287.8	90.2	16.9	24.1
Ec4	189.6	249.2	59.6	15.3	18.6
Ed7f1.5	194.1	267.9	73.8	14.7	20.3
Ia12	200.7	281.9	81.2	17.7	26.1
Ib4	198.0	283.8	85.8	16.2	24.6
Ma12	194.1	245.7	51.6	17.3	20.1
Mb4	200.4	297.4	97.0	17.3	24.9
Mc4	192.9	266.0	73.1	15.5	21.2
Md7f1.5	193.7	272.4	78.7	15.6	22.8
Pa12	192.1	231.6	39.5	16.6	18.8

TABLE XXXIV (CONTINUED)

Extractive Scintillator	β/γ-Peak Centroid	α-Peak Centroid	Peak Separation	β/γ-Peak FWHM	α-Peak FWHM
Pb4	198.8	270.6	71.8	17.3	24.5
PD200b4	213.7	319.6	105.9	21.5	28.8
PD200d7	204.2	287.9	83.7	20.3	26.3
PD200d7b1.5	212.9	309.8	96.9	20.5	27.0
PD200d7c1.5	207.1	287.0	79.9	18.8	24.9
PD200d7f1.5	201.1	268.0	66.9	15.2	21.3
Pd7f1.5	197.6	248.0	50.4	18.2	20.5
PE200b4	207.8	315.8	108.0	20.4	29.9
PE200d7f1.5	200.4	276.1	75.7	18.1	24.3
PI200a12	197.6	258.8	61.2	17.4	21.8
PI200b4	206.5	288.0	81.5	14.8	23.1
PI200d7f1.5	199.0	268.3	69.3	16.7	23.3
PM100c4	207.4	283.0	75.6	17.3	23.5
PM200b4	206.8	310.1	103.3	18.9	28.5
PM200b6	210.0	318.6	108.6	20.6	28.3
PM200b8	211.8	321.3	109.5	21.9	28.2
PM200d7f1.5	197.9	265.3	67.4	15.7	21.4
PM500b4	207.5	313.6	106.1	19.9	27.4
PN180b4	205.7	304.8	99.1	19.0	25.9

TABLE XXXVI

ENERGY RESOLUTION DATA

Extractive Scintillator	^{238}U Peak Centroid	^{234}U Peak Centroid	^{241}Am Peak Centroid	^{238}U FWHM	^{234}U FWHM	^{241}Am FWHM	^{238}U Peak Counts	^{238}U:^{234}U Valley Counts	^{234}U Peak Counts	^{234}U:^{241}Am Valley Counts
Alphaex	147.6[a]	192.2	260.0	17.0	27.0	32.2	339[b]	36	237	7
Ca12	100.5	126.5	171.1	13.3	18.5	27.3	420	132	370	36
Cb4	92.9	117.0	157.2	12.2	16.7	23.5	451	122	387	30
Cc4	75.4	95.6	129.9	10.4	15.9	21.5	482	176	429	60
CD200b4	117.1	147.4	200.4	14.3	19.2	28.6	406	81	334	18
CD200c4	98.8	125.6	170.7	12.6	17.4	27.2	469	108	391	30
Cd7	100.9	127.1	171.6	13.0	17.4	26.2	430	103	355	24
Cl200b4	99.2	124.9	168.3	12.5	17.6	25.4	464	112	387	28
Cl200c4	100.2	126.9	173.0	12.4	18.1	27.0	446	107	367	24
Da12	85.0	106.9	140.8	12.7	16.2	21.6	402	164	366	62
Db4	127.6	161.4	219.8	14.8	23.4	29.6	370	79	277	17
Dc4	117.1	147.7	203.6	13.8	23.0	32.2	391	102	284	24
Dd7f1.5	125.4	158.2	215.3	14.0	22.7	29.1	406	71	298	17
Ea12	141.4	181.9	244.0	16.9	23.6	29.3	347	54	273	10
Eb4	146.5	188.2	251.6	17.0	24.5	31.2	347	50	264	11
Ec4	157.3	204.0	270.4	18.2	26.0	33.2	334	40	251	7
Ed7f1.5	147.9	190.2	253.2	17.2	24.7	31.8	346	43	260	10
Ia12	111.8	140.9	193.8	14.0	19.9	30.6	400	112	360	25

TABLE XXXV (CONTINUED)

Extractive Scintillator	^{238}U Peak Centroid	^{234}U Peak Centroid	^{241}Am Peak Centroid	^{238}U FWHM	^{234}U FWHM	^{241}Am FWHM	^{238}U Peak Counts	^{238}U:^{234}U Valley Counts	^{234}U Peak Counts	^{234}U:^{241}Am Valley Counts
Ib4	111.8	140.3	191.0	13.0	18.4	28.6	427	96	373	19
Ma12	106.8	133.6	177.8	14.9	17.3	27.4	421	126	353	37
Mb4	144.8	185.3	247.4	16.9	24.8	30.4	352	58	273	12
Mc4	158.1	203.8	269.3	18.9	24.9	31.8	316	41	260	7
Md7f1.5	145.5	186.0	248.0	16.4	23.5	30.0	352	42	266	11
Pa12	105.8	132.7	179.4	12.8	18.1	27.0	438	108	354	26
Pb4	108.0	135.2	182.4	13.0	16.8	26.0	439	96	381	17
PD200b4	122.6	154.5	209.9	14.2	19.5	28.4	407	68	308	12
PD200d7	115.0	144.3	195.5	14.0	18.0	27.2	400	80	335	17
PD200d7b1.5	122.5	154.0	208.8	14.4	19.1	27.5	407	68	328	11
PD200d7c1.5	126.0	158.7	215.5	15.5	21.5	28.9	376	81	303	17
PD200d7f1.5	122.7	154.3	210.5	13.7	20.4	28.5	411	72	318	12
Pd7f1.5	122.0	153.9	210.7	13.5	21.9	28.7	406	75	307	14
PE200b4	125.5	158.1	215.1	13.7	20.7	27.2	419	69	326	11
PE200d7f1.5	119.4	149.8	203.9	13.7	20.2	28.2	394	80	311	16
Pl200a12	96.4	121.3	162.4	11.9	16.6	24.8	454	121	396	30
Pl200b4	111.0	138.6	186.9	12.8	17.1	25.8	427	83	368	14
Pl200d7f1.5	113.8	142.4	194.7	13.0	18.8	29.2	215	46	187	8
PM100c4	120.8	152.7	209.3	13.8	19.8	28.0	395	70	338	9
PM200b4	123.5	155.4	211.0	13.9	19.9	28.3	403	71	362	12

TABLE XXXV (CONTINUED)

Extractive Scintillator	^{238}U Peak Centroid	^{234}U Peak Centroid	^{241}Am Peak Centroid	^{238}U FWHM	^{234}U FWHM	^{241}Am FWHM	^{238}U Peak Counts	^{238}U:^{234}U Valley Counts	^{234}U Peak Counts	^{234}U:^{241}Am Valley Counts
PM200b6	129.1	162.8	220.2	14.8	22.5	28.0	395	74	289	13
PM200b8	128.7	162.2	219.6	14.6	21.2	27.3	404	69	302	13
PM200d7f1.5	116.3	145.9	197.8	13.5	19.5	28.1	427	88	351	11
PM500b4	140.3	178.8	239.4	16.5	23.3	29.6	378	58	288	8
PN180b4	130.8	165.3	223.8	14.8	22.1	27.8	393	61	296	9

a. All peak centroids and FWHM values in units of channels ± 0.5 channels.

b. All counts recorded after data was smoothed once. Counting uncertainties based on five times the number of counts recorded after smoothing.

VITA

Jonathan Micah Duffey was born in Roxboro, North Carolina on August 20, 1964. He attended the Benton County public schools in Camden, Tennessee and graduated valedictorian of his class in May 1982 from Camden Central High School. In May 1987 he received the B.S. degree in Chemistry with high honors from Union University in Jackson, Tennessee. From July 1987 to August 1988 he was employed as Laboratory Coordinator by Union University at their satellite campus in Memphis, Tennessee. In August 1988 he entered graduate school at the University of Tennessee in Knoxville where he received the M.S. degree in Chemistry in December 1993 before continuing in the doctoral program at the University of Tennessee. He entered the University of Tennessee College of Veterinary Medicine in August 1994. In January 1995 he left the College of Veterinary Medicine to begin work as Laboratory Supervisor for ETRAC Laboratories, Inc. in Oak Ridge, Tennessee. On October 28, 1995 he and Cheryl Laughter were married at St. Stephen's Episcopal Church in Oak Ridge, Tennessee. In October 1997 he left ETRAC Laboratories to become a Research Scientist at Eichrom Industries, Inc. in Darien, Illinois. He received the Ph.D. degree in Chemistry from the University of Tennessee in December 1998, while still employed by Eichrom Industries, Inc.