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I am submitting herewith a thesis written by Jonathan Micah Duffey entitled "Investigations in Alpha Liquid Scintillation Spectrometry." I have examined the final copy of this dissertation for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Master of Science, with a major in Chemistry.

Geo. K. Schweitzer

George K. Schweitzer, Major Professor

We have read this thesis
and recommend its acceptance:

W E Bell

D. C. Klimfelter

Accepted for the Council:

Lee Minkel

Associate Vice Chancellor
and Dean of the Graduate School

INVESTIGATIONS IN ALPHA LIQUID SCINTILLATION SPECTROMETRY

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ABSTRACT

A recently developed technique known as Photon/Electron-Rejecting Alpha Liquid Scintillation (PERALS) Spectrometry has made liquid scintillation a useful alternative to conventional alpha spectrometry techniques. The advantages of the PERALS method include ease of sample preparation and essentially 100% counting efficiency. The primary disadvantage is the relatively poor energy resolution as compared to solid state techniques. A significant improvement in resolution would likely make this technique superior to any other alpha counting technique available at this time.

Various modifications in the current PERALS scintillator solutions were investigated in an effort to detect any promising means for resolution improvement. Studies included the use of a number of different primary solvents, the effect of naphthalene concentration on resolution, and the use of liquid naphthalene derivatives as both primary and secondary solvent. Additional experiments included the effect of an adducting agent and a drying agent on a typical PERALS scintillator solution, and the influence of counting temperature on energy resolution.

Some solutions were prepared which appeared to yield greater light output, but no significant improvement in energy resolution was observed. Several solutions were found to be useful alternatives to PERALS scintillators.

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CHAPTER I

INTRODUCTION

A. Types of Radioactive Decay

Radioactive nuclides, or radionuclides, have neutron-proton combinations which are not stable. Radionuclides with such unstable nuclear structures will spontaneously change to achieve a more stable configuration. These spontaneous changes are known as radioactive decays [1].

1. Beta Emission

Neutron-rich radionuclides tend to undergo radioactive decay that will decrease the number of neutrons, thereby lowering the neutron to proton ratio. This usually occurs by the conversion of a neutron (n) within the nucleus into a proton (p^+), and is accompanied by the emission of a negative electron, known as a beta particle (β^-), and an antineutrino ($\bar{\nu}$). The equation is

$$n \longrightarrow p^+ + \beta^- + \bar{\nu}. \qquad (1)$$

The antineutrino carries energy but has no charge and negligible mass. Beta emission increases the atomic number (Z) by one, but the mass number (A) remains the same.

$$^{A}_{Z}E \longrightarrow {}^{A}_{Z+1}E^+ + \beta^- + \bar{\nu} \qquad (2)$$

As in all types of spontaneous nuclear decay, mass is converted to energy. This converted mass is known as the reaction energy and is shared by all the reaction products. The recoiling nucleus carries away a small part of this

energy, and the remainder is shared between the beta particle and the antineutrino. For this reason the energy of the beta particle may range from zero to a maximum that is equal to the reaction energy minus the recoil energy.

2. Positron Emission

Neutron-poor radionuclides with Z < 55 tend to lower the number of protons and increase the number of neutrons by emitting a positron (β^+), a positive electron. This occurs when a proton in the nucleus becomes a neutron, a process which is accompanied by the emission of a positron and a neutrino (ν).

$$p^+ \text{ ---> } n + \beta^+ + \nu \qquad (3)$$

The neutrino, like the antineutrino, carries energy but has no charge and negligible mass. Positron emission decreases Z by one and A remains unchanged.

$$^{A}_{Z}E \text{ ---> } ^{A}_{Z-1}E^- + \beta^+ + \nu \qquad (4)$$

Like the beta particle, the positron is emitted over a range of energy values from zero up to slightly less than the total reaction energy.

3. Electron Capture

Neutron-poor radionuclides with Z > 55 favor a process known as electron capture as a means of increasing the neutron to proton ratio. An extranuclear electron is captured by the nucleus and reacts with a proton to form a neutron. A neutrino is emitted from the nucleus in the process

$$p^{+} + e^{-} \longrightarrow n + \nu. \qquad (5)$$

The result is that Z is decreased by one and A remains the same, just as in positron emission. As a means of keeping charges in order, the electron to be captured may be shown separated from the neutral atom prior to capture by the nucleus.

$$^{A}_{Z}E^{+} + {}^{0}_{-1}e^{-} \longrightarrow {}^{A}_{Z-1}E + \nu \qquad (6)$$

Electron capture is followed by the emission of an X-ray as an outer electron falls into the hole produced in the inner shell when the electron is captured.

4. Alpha Emission

Proton-rich radionuclides tend to be unstable due to excess coulombic repulsion resulting from the large number of protons in the nucleus. These nuclides try to achieve stability by emitting an alpha particle (α^{++}), which is a helium-4 nucleus ($^{4}_{2}He^{2+}$). Alpha emission decreases A by 4 and decreases Z by 2. This is illustrated by the general equation

$$^{A}_{Z}E \longrightarrow {}^{A-4}_{Z-2}E^{2-} + \alpha^{++}. \qquad (7)$$

In this type of decay the reaction energy is shared between only two products, the recoil nucleus and the alpha particle. As a consequence of the law of conservation of energy and momentum, the energy is split between these two particles according to the inverse ratio of their masses [2]. The result is that alpha particles are essentially

monoenergetic, although alpha emitting nuclides may emit several alphas of different but well defined energies.

5. Gamma Emission

This type of decay occurs when a nucleus is in an excited, or metastable state. The excited nucleus then decays to the ground state with the emission of electromagnetic radiation known as gamma rays. They are identical to x-rays except that they come from within the nucleus and may be of much greater energy. Like alpha particles, gamma rays are monoenergetic emissions. Gamma emission usually follows the emission of α^{++}, β^{-}, and β^{+} particles as well as electron capture. The resulting change is energetic only, with no change in A, Z, or charge.

$$ {}^{A}_{Z}E^{*} \longrightarrow {}^{A}_{Z}E + \gamma \qquad (8) $$

Sometimes an excited nucleus transfers its excess energy to an extranuclear electron, causing the electron to be ejected in the process. This is known as a conversion electron and interacts with matter in a manner similar to that of a beta particle.

B. Alpha Counting Techniques

The most common methods for detecting radionuclide emissions are based on the ionization and/or excitation of some detection medium by the emitted particle or radiation [3]. The detection medium may be gas, liquid, or solid. Ionization occurs when an alpha particle, beta particle, positron, electron, gamma ray, or X-ray interacts with an

atom or molecule (A) of the detection medium and removes one (or rarely more) of its electrons, for example,

$$A \text{ ---> } A^{+} + e^{-}. \qquad (9)$$

The result is an ion pair, and the number produced depends upon the ionization energy of the detection medium, its physical state, and the type of ionizing radiation with which it interacts. Due to their greater masses and higher charges, alpha particles produce about 300 times more ion pairs per unit path length than do beta particles, positrons, or electrons. These in turn produce 10 to 1000 times more ion pairs per unit path length than do gamma rays and X-rays. All of these types of ionizing radiation produce on the order of 1000 to 2000 times more ion pairs per unit path length in liquids or solids than they do in gases [4].

Some of the more important types of radiation detectors for counting alpha particles are discussed briefly in the following sections [5].

1. Gas Ionization Detectors

a. Proportional Counters. The proportional counter is usually a cylindrical chamber with a thin window at one end and a central electrode consisting of a wire insulated from the walls of the chamber. A voltage of 250 to 500 volts is applied so that the wire is positively charged and the walls are negatively charged. The chamber is filled with a mixture of argon and methane, or more commonly, the

gas mixture is allowed to flow through the chamber at atmospheric pressure. Emissions entering the detector through the thin window produce ion pairs when they interact with the gas molecules. Under the influence of the applied voltage, the electrons are accelerated toward the positively charged wire and the cations are accelerated toward the negatively charged walls. On the way to the electrodes the accelerated ions collide with other gas molecules producing more ion pairs known as secondary ions. These may also collide with other gas molecules as they are accelerated toward the electrodes, producing still more ion pairs. The electrons, which are highly mobile, are collected in approximately 1 μsec, but collection of the less mobile positive ions may take as long as 5 μsec. The number of ion pairs collected may be as much as 10^3 - 10^4 times the number of original ion pairs produced.

The rapid collection of ions gives an electronic pulse which decays in approximately 5 μsec. The size of this pulse is proportional to the original number of ion pairs produced by the emission.

b. Geiger-Müller Counter. The Geiger-Müller counter is very much like the proportional counter in construction, but there are two major differences. A voltage of approximately 1000 volts, rather than 500 volts, is applied, and the composition of the gas mixture is usually different. Under the influence of the higher voltage, the interaction

of ionizing radiation with the gas molecules leads the detection chamber to approach saturation with ion pairs. No matter how many ion pairs are produced initially, the final number of ion pairs ($\sim 10^{12}$) is essentially the same. The pulse produced is of only one size, therefore, and is not proportional to the initial number of ion pairs produced.

2. Scintillation Counters

a. Solid Scintillation Counters. Solid scintillation counters consist of a solid material, known as a scintillator, which absorbs energy upon interaction with ionizing radiation and emits the energy as a flash of light. This material may be an inorganic crystal, an organic crystal, or a plastic. The scintillator is placed in contact with a photomultiplier tube (PMT). When the scintillator absorbs a radioactive emission, a flash of light consisting of multiple photons is given off very rapidly (< 1 μsec). The photons are directed toward the PMT where they strike the photocathode expelling electrons from the surface. The liberated electrons are multiplied by a factor of approximately 10^6 through successive interaction with a series of appropriately charged electrodes. The size of the pulse that results is proportional to the original number of ion pairs produced in the scintillator.

b. Liquid Scintillation Counters. The principle is similar for liquid scintillation counters except the scintillating material is a liquid solution. This solution

is usually an organic solvent such as toluene or dioxane with a small amount (2-8 g/L) of organic scintillator dissolved in it. The sample to be counted is incorporated into the solution. This is a significant advantage over counting methods which place the sample external to the detector because all of the nuclear emanations can interact with the detection medium. This interaction leads most often to ionization and/or excitation of solvent molecules, since they are present in greatest concentration. The excited solvent molecules then rapidly transfer this energy to the scintillator, or fluor, resulting in a flash of light that impinges upon a photomultiplier and leads to an electronic pulse.

3. Solid State Counters

This type of detector utilizes a semiconductor material such as silicon or germanium to detect emissions from radionuclides. Various techniques are used to produce a region in the semiconductor known as a depletion layer. When the depletion region is bombarded with ionizing radiation, electrons and holes are produced. By placing the semiconductor material between metallic plates and applying a reverse bias voltage, the electrons and holes can be collected in a manner similar to the collection of ions in the proportional counter. The pulse produced upon collection of the ions is proportional to the number of electron-hole pairs produced by the emission [3,6].

C. Liquid Scintillation Counting

In 1950 Kallmann in Germany, Ageno and co-workers in Rome, and Reynolds and co-workers at Princeton demonstrated that certain organic solutions could be used as efficient scintillation counters. Their work led to the development of the liquid scintillation method of counting radioactivity. Since that time liquid scintillation techniques have been used to measure almost every type of radioactive decay that is known [7].

This counting technique is also known as the internal-sample method, because the sample and scintillator are intimately mixed in an organic solvent. The intimate relation of sample to detection medium results in a 4π detection geometry and essentially one hundred percent counting efficiency for alpha particles as well as very high counting efficiencies for beta particles [8].

1. Components of a Liquid Scintillation Counter

Two basic units make up a typical liquid scintillation counter: the detector assembly and the electronics. Modern instruments often include automatic sample changers and many are interfaced with computers for data manipulation [9].

a. The Detector Assembly. This portion of the instrument consists of the scintillation solution components and the optical components. These are discussed briefly below in the following paragraphs.

Excluding the sample, a liquid scintillator usually consists of a primary solvent in which is dissolved a small amount of primary solute and sometimes a secondary solute, known as a wavelength shifter. Both the primary and secondary solutes are known as fluors. An additional component known as a secondary solvent is often used to increase the solubility of the sample in the scintillating solution or to aid in the transfer of energy from the solvent to the fluor.

In liquid scintillation counting the solvent is much more than just a means of solubilizing the fluor and sample. Since there are many more solvent molecules than there are molecules of any other component, the gross majority of the initial excitations occur in the solvent molecules themselves. These excited solvent molecules must then be able to efficiently transfer their energy to the fluor molecules.

An efficient solvent, in addition to being a liquid at room temperature, is one in which excited states are easily produced upon interaction with ionizing radiation. These excited states must possess long lifetimes relative to the time required for the energy to be transferred to the fluor molecules. The solvent should also be one that will not absorb the light emitted by the fluor.

These requirements are usually met by the simple aromatic compounds because they are liquids at room

temperature and possess π electrons which require relatively little energy to be promoted into higher energy levels. They also possess small absorption coefficients for light emitted by the fluor. Thus, solvents such as toluene, *p*-xylene, and 1,2,4-trimethylbenzene (pseudocumene) are most often employed as primary solvents. In systems in which it is important for the solvent to be miscible with water, *p*-dioxane is often used as the primary solvent. However, it is not an aromatic compound and, therefore, is not as efficient as those listed above [10].

Secondary solvents are used for two main purposes: (1) to increase the solubility of the sample in the primary solvent, or (2) to improve the efficiency of the energy transfer from solvent to fluor.

Solvents such as ethanol or methanol may be added to an efficient primary solvent to increase the solubility of aqueous samples in the solution. Alternatively, compounds known as specific binding agents may be used to incorporate various substances into the primary solvent. For example, metal ions may be incorporated into the solvent by organophilic complexing agents such as dibutyl phosphate or dioctyl phosphate [9].

A secondary solvent may also be used to improve the energy transfer from solvent to fluor. Furst and Kallmann [11] found that the addition of large quantities of naphthalene to the primary solvent could significantly

improve the efficiency of energy transfer. The excited naphthalene molecules are often less easily quenched by impurities than are the excited primary solvent molecules [12].

The primary solute, or fluor, must be able to accept the energy from the excited solvent or secondary solvent (naphthalene) molecules and efficiently convert this energy to light. Generally, the solute molecules require less energy for excitation than the solvent molecules, so the process is not reversible.

Not only must the fluor efficiently emit light, but the emission spectrum of the fluor should closely match the sensitivity of the photocathode. It is also important that the fluor be soluble in a variety of solvents and that it be economical. The counting efficiency for a given scintillation solution generally increases with increasing fluor concentration up to a point. For this reason it is also desirable for the fluor concentration to reach maximum detection efficiency before exceeding the solubility limit in a particular solvent.

Approximately 500 compounds have been investigated as to their performance as primary solutes (fluors). The most efficient primary solutes consist of three or four aromatic or heterocyclic rings arranged in a linear fashion yielding a continuously conjugated molecule. These are classified as oligophenylenes, oxazoles, or oxadiazoles [9,10].

Early studies in liquid scintillation counting showed that the addition of very small amounts of a second solute could greatly increase the scintillation efficiency of certain solutions. These secondary solutes served to shift the wavelength of emission to a region that more nearly matched the sensitivity of the photocathodes used at that time. Nowadays secondary solutes (wavelength shifters) are seldom used since photocathodes have been developed that are much more sensitive in the regions of emission of primary solutes.

Wavelength shifters are still used, however, when the solution contains a strong absorber in the region of primary solute emission. In such a case the secondary solute shifts the maximum emission to a region which is not affected by the absorbing substance.

The most common secondary solutes have four or five aromatic or heterocyclic rings which are continuously conjugated. They are usually much less soluble than primary solutes and have average emission wavelengths which are 30 to 40 nm higher than those of most primary solutes [9,10].

The optical components of most liquid scintillation counters include two photomultipliers mounted in a light-tight shield on either side of the sample chamber. The sample vial is generally coupled to the photomultiplier surface by an ultraviolet-transmissive light guide. Both

sample chamber and light guide are coated with a reflective surface such as MgO or TiO_2.

The sample vial is usually made of low-potassium glass to decrease background contribution from the natural radioisotope ^{40}K. Teflon vials have also been proven effective [9].

b. The Electronics. This portion of a liquid scintillation counter generally consists of a stable high voltage power supply, two photomultiplier tubes in coincidence, a summing amplifier, a multichannel analyzer, and some type of display. Their arrangement can be illustrated by the simple block diagram shown in Figure 1 (p. 15) [9].

Output pulses from the PMT's pass to a coincidence unit, or gate. Single pulses are rejected as noise, but pulses arriving simultaneously, or very nearly so, are sent to a summing amplifier where coincident pulses are added together and fed to the multichannel analyzer. The multichannel analyzer is a pulse height analyzer for the purpose of rapidly sorting and counting pulses of different heights resulting from particles of different energy. This information can then be displayed in the form of a spectrum of particle energies that gave rise to the observed pulse heights. In most cases where only a single nuclide is being counted, pulses within a defined height range are integrated and are read out as a number [13].

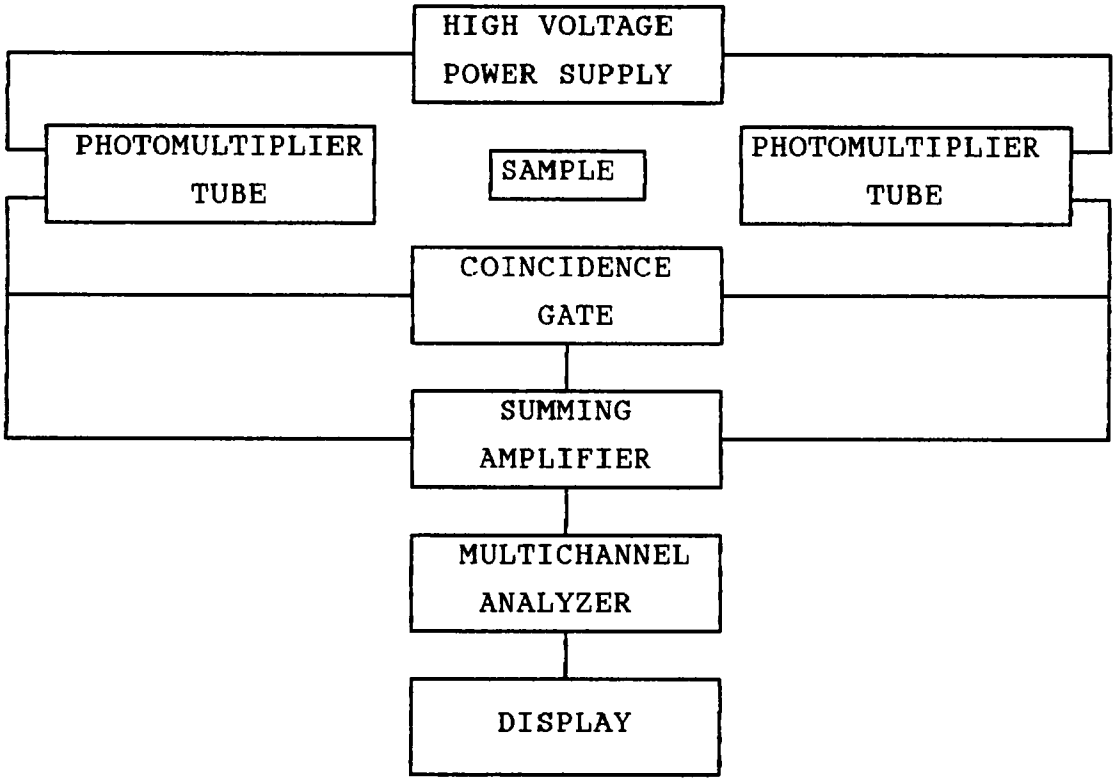


Figure 1. Block diagram showing the electronic components of a typical liquid scintillation counter.

2. Quenching

In liquid scintillation counting any reduction of efficiency in the process of energy transfer and/or reduction in the number of photons produced is known as quenching [9]. The overall result is to reduce detection efficiency. There are several ways in which quenching may occur.

a. Chemical Quenching. The absorption of energy from the excited solvent or solute molecules before photons are emitted is known as chemical quenching. Any nonfluorescent component of the scintillation solution is a potential quencher, since it may rob excited molecules of energy without emitting light. Severe quenching occurs in the presence of oxygen, water, halogenated compounds, and other polar compounds. The sample being counted may contribute to quenching as well.

b. Color Quenching. Quenching may also occur once photons are emitted if the solution is colored. This is known as color quenching. Most scintillation solutes emit photons with wavelengths from 370 to 430 nm (violet to blue violet) [10]. Therefore, yellow green or yellow solutions, which absorb violet to blue violet light, have the greatest potential for color quenching.

c. Dilution Quenching. When addition of the sample to the scintillating solution results in a significant decrease in fluor concentration, dilution quenching becomes

a problem. For this reason it is advantageous to use a fluor which produces maximum light output over a range of concentrations that can be obtained before exceeding the solubility limit.

d. Self-quenching (Concentration Quenching). Solute self-quenching is a problem with certain types of solutes. It occurs when an excited solute molecule interacts directly with an unexcited solute molecule. Upon separation of the two molecules, the excitation energy is shared between them, but neither possesses enough energy to emit a photon. The probability of this type of interaction increases with increasing solute concentration and so may be called concentration quenching.

e. Optical Quenching. Sample conditions such as phase separation of the scintillation solution, partial freezing of the solution, or fogging of the sample vial's exterior may result in decreased photon detection. These effects are known as optical quenching [9].

3. Background

Background events in liquid scintillation counting may derive from many sources. There are two major types of these sources: those events produced in the scintillator solution and those events which result from sources having no connection with the solution [14]. The major contributors to background events are discussed briefly in the following sections.

a. Noise. The spontaneous emission of electrons from the photocathode and dynodes in the PMT results in background events known as noise. Noise is a characteristic of individual phototubes and is a random process. Most of these events are eliminated by the use of two photomultipliers in coincidence because the chance of noise pulses occurring in two different photocathodes simultaneously is very small.

b. Cross Talk and Gas Discharges. A light-producing event which occurs in one PMT and is seen simultaneously by the other is known as cross talk. An event of this type will result in a coincident pulse and, therefore contribute to background. Electrical discharges, Cerenkov radiation, natural radioactivity in the materials of the PMT, and gas discharges from residual gas in the PMT may all be light-producing events.

Residual gas in the PMT may also be ionized during the amplification of an actual pulse and thereby give rise to a second pulse known as an afterpulse. There is a high probability that such afterpulses will be coincident, since they result from true coincident events.

c. Cerenkov and Cosmic Radiation. The interaction of high-energy cosmic radiation with the scintillation solution, the PMT's, or materials in the vicinity of the liquid scintillation counter can produce secondary electrons, γ rays, X-rays, and Cerenkov radiation. These

may each contribute to background counts under the proper conditions. Secondary electrons, due to their relatively low energy, will usually only contribute to background when produced in the scintillation solution. Since most materials in the solution are made of low Z elements, the probability of their interacting with high-energy γ rays or high-energy X-rays is relatively low [14].

Cerenkov radiation is produced when high-energy electrons entering a medium exceed the speed of light in that medium and consequently release their excess energy as a blue-white light [4]. A fraction of these photons may be of the same energy as the scintillator photons and so will be counted with good efficiency.

d. Natural Radioactivity. All of the materials used to make the liquid scintillation counting system will likely contain some amount of natural radioactivity. Of particular concern are the primary solvents. Solvents produced from present era sources will contain ^{14}C and ^{3}H in the same amounts as found in the present environment. For this reason solvents should be produced from sources which are old enough to contain essentially no ^{14}C or ^{3}H.

e. Chemiluminescence and Photoluminescence. Some chemical reactions lead to the emission of photons in a process known as chemiluminescence. When this occurs in the liquid scintillation solution, the photons that are produced will contribute to the observed background counts. The

number and duration of background counts resulting from chemiluminescence depend on the rate of the chemiluminescent reaction or reactions. The result is a variable background for which it is difficult to correct.

Photoluminescence, the production of photon-producing species by light, may also contribute to background events. When these species are produced in the walls of the vial, or in the cap, they may be very long-lived since they are not deactivated by collision processes in the solution [14].

D. Alpha Liquid Scintillation Counting

Very early in the development of liquid scintillation counting it was recognized that this technique could be a useful method for counting alpha particles. Flynn and Horrocks demonstrated in 1964 that the light output of a liquid scintillator is directly proportional to the energy of an alpha particle over the range of 4 to 7 MeV. Most common alpha-emitting nuclides emit alphas with energies in this range [15].

There are several advantages to counting alpha particles by liquid scintillation. Because the alpha-emitter is within the detection medium, the problems of self-absorption and detector geometry associated with external sample techniques are eliminated. This simplifies sample preparation and allows counting efficiencies approaching one hundred percent. It also means improved reproducibility between samples of the same type.

Despite the advantages provided by an internal sample, liquid scintillation was not recognized as a useful technique for counting alpha particles until recently. This is partly due to three major disadvantages associated with ordinary liquid scintillation techniques: (1) poor energy resolution, (2) interference from beta and gamma radiation within the sample and from background sources, and (3) variable scintillator response to quenching.

In 1964 Horrocks and Studier obtained low resolution alpha energy spectra by incorporating an aqueous sample into an organic scintillator with an emulsifying agent. Further investigations showed that energy resolution could be improved by using an organic-soluble complexing agent to incorporate the sample in the scintillating solution, and even better resolution could be obtained if an all-organic scintillator was used [15].

Although the normal energy range for beta and gamma radiation (0.0 - 1.0 MeV) is much lower than that for alpha radiation, their energy spectra are often overlapping. This is because beta radiation and gamma radiation of a given energy produce more light in a liquid scintillator than does alpha radiation of equal energy [16]. Since the beta and gamma radiation may come from various sources, such as the alpha nuclide decay chains, sample impurities, or external sources, the degree of interference may vary from sample to sample. In addition, the magnitude of interference by beta

and gamma radiation is often great enough to make accurate measurement and sometimes location of the alpha peaks difficult or impossible.

When alpha-emitting samples are prepared in the same way as are beta-emitting and gamma-emitting samples, quenching constitutes a serious problem, both in energy resolution and identification. This results from the addition of components of the aqueous solution, in addition to the alpha-emitters, to the organic scintillator. Not only does quenching degrade the resolution by addition of aqueous solutions to scintillating solutions, but, since the type and amount of quenchers may vary widely from sample to sample, the position of the energy spectrum is shifted such that peak identification is difficult or impossible [15].

A recently developed technique has partially solved some of the problems discussed above. This was accomplished by modifications in the configuration of the liquid scintillation counter itself, the use of all-organic scintillators and organic extractants, improvements in detectors and electronic pulse height analysis, and the use of electronic pulse-shape discrimination to eliminate interfering beta/gamma pulses. This technique is known as PERALS (Photon/Electron-Rejecting Alpha Liquid Scintillation) Spectrometry [17] and, as the subject of this research, will be discussed in detail in the next chapter.

E. Proposed Research

Although the problems of interfering beta and gamma radiation and variable quenching are largely eliminated by the PERALS technique, there is always the desire to improve resolution. The current obtainable energy resolution is typically between four and six percent full peak width at half the maximum peak height [18]. It is possible that further improvements in energy resolution may be obtained by (1) altering the scintillator solutions, (2) improving the photomultiplier tube, or (3) improving the electronics.

It is the purpose of this research to attempt to improve the energy resolution by altering the scintillator solutions. This will be done by (1) altering the components of the scintillator solution, (2) using a drying agent to remove water from the organic phase, and (3) altering the counting temperature of the sample.

CHAPTER II

PERALS SPECTROMETRY

A. Overview

McDowell [17,18] has developed the technique known as Photon/Electron-Rejecting Alpha Liquid Scintillation (PERALS) Spectrometry for the accurate determination of alpha-emitting nuclides and the detection of low levels of activity in environmental samples. This technique makes use of all-organic scintillator solutions containing an organic extracting agent for incorporating the alpha-emitting nuclides into the scintillator solutions. The optical components of the detector assembly have been designed to provide optimum alpha energy resolution. The technique of electronic pulse-shape discrimination makes possible the rejection of almost one hundred percent of the interfering pulses from beta and gamma radiation.

B. Mechanisms of Time Delay

The effectiveness of the PERALS technique is largely due to its ability to distinguish between pulses produced by beta/gamma radiation and pulses produced by alpha particles. This differentiation of electronic pulses is possible because of the nature of the scintillation phenomenon.

For a given scintillation event, the intensity of photons produced as a function of time is the result of a fast (prompt) component and a slow (delayed) component

[19,20,21]. The fast component is produced by the fluorescence decay of excited solute molecules primarily in the first excited singlet state, S_1, to the ground state, S_0,

$$S_1 \text{ ---> } S_0 + h\nu. \qquad (1)$$

Although some excited state solute molecules are formed by direct interaction with the ionizing radiation, the gross majority are formed by the rapid transfer of energy from excited solvent molecules to the primary (or secondary) solute. The fast scintillation component has a decay time equal to the fluorescence lifetime of the scintillating molecule, usually 1-3 nsec [21,22]. The transfer of energy from solvent to solute is very rapid (on the order of 10^{-11} sec), therefore, essentially no photons are emitted by the solvent [23].

It has been shown that the slow scintillation component is due to the interaction of two molecules in the first excited triplet state, T_1, to produce an excited singlet state molecule and a ground state molecule,

$$T_1 + T_1 \text{ ---> } S_1 + S_0, \qquad (2)$$

followed by fluorescence from the first excited singlet state,

$$S_1 \text{ ---> } S_0 + h\nu. \qquad (3)$$

Because two excited triplet state molecules must physically interact, the decay time of the slow component is diffusion controlled and is on the order of 200-300 nsec in an

aromatic solvent at room temperature [20]. The intensity of photons emitted from an organic scintillator solution as a function of time is shown in Figure 2 (p. 27) [22]. This diagram illustrates how the fast and slow components contribute to the total scintillation intensity.

Two important observations have been made by Horrocks [20]: (1) the decay times of the fast and slow components are almost independent of the nature of the exciting particle, and (2) the ratio of the intensity of the fast component to the intensity of the slow component decreases as the specific ionization (energy loss by the particle per path length) of the exciting particle increases. Since alpha particles have a higher specific ionization than do beta particles or gamma rays, the ratio of fast component to slow component is less when the scintillator solution is excited by alpha particles than when it is excited by beta particles or gamma rays. This means that more time is required for a given fraction of the total scintillation intensity to be detected when the scintillation event is produced by an alpha particle than when it is produced by a beta particle or a gamma ray [18,22]. Figure 3 (p. 28) illustrates how the scintillation intensity as a function of time differs for solutions excited by beta/gamma radiation (primarily fast component) and solutions excited by alpha particles (primarily slow component) respectively. One can clearly see that the time required to reach a certain

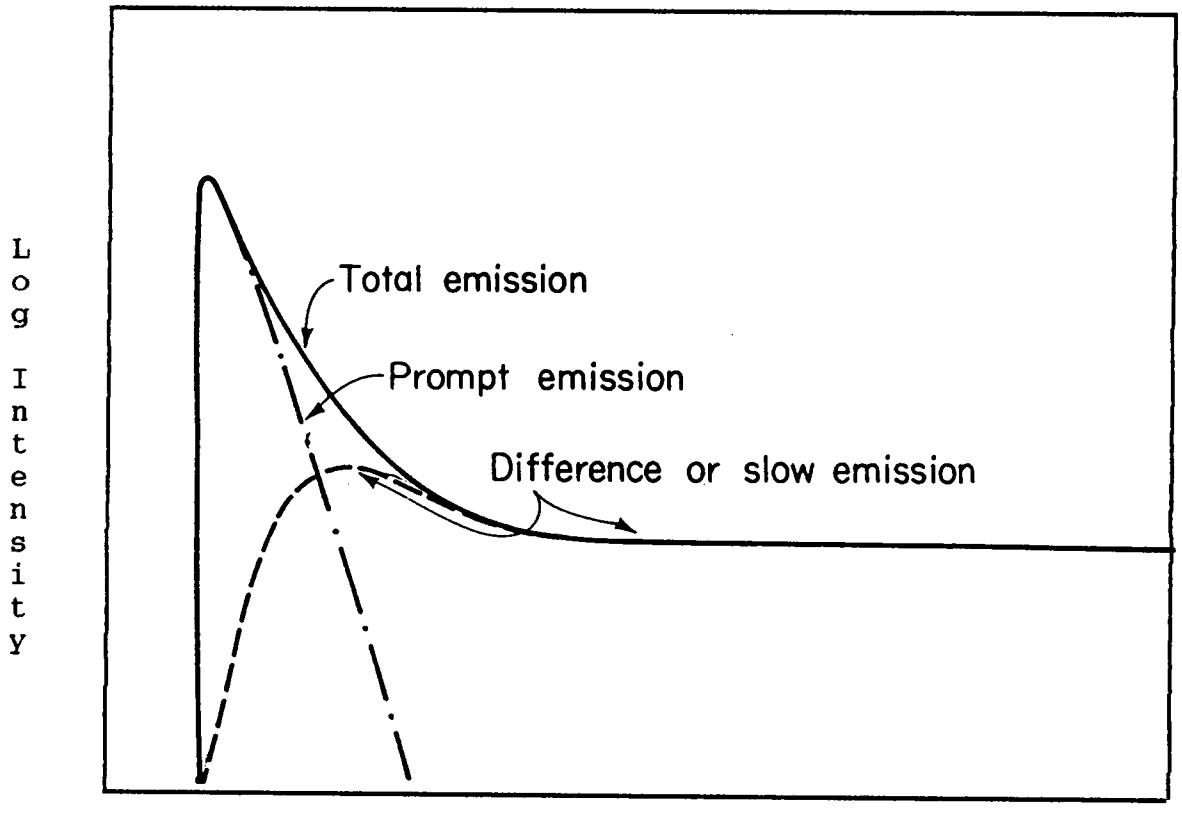
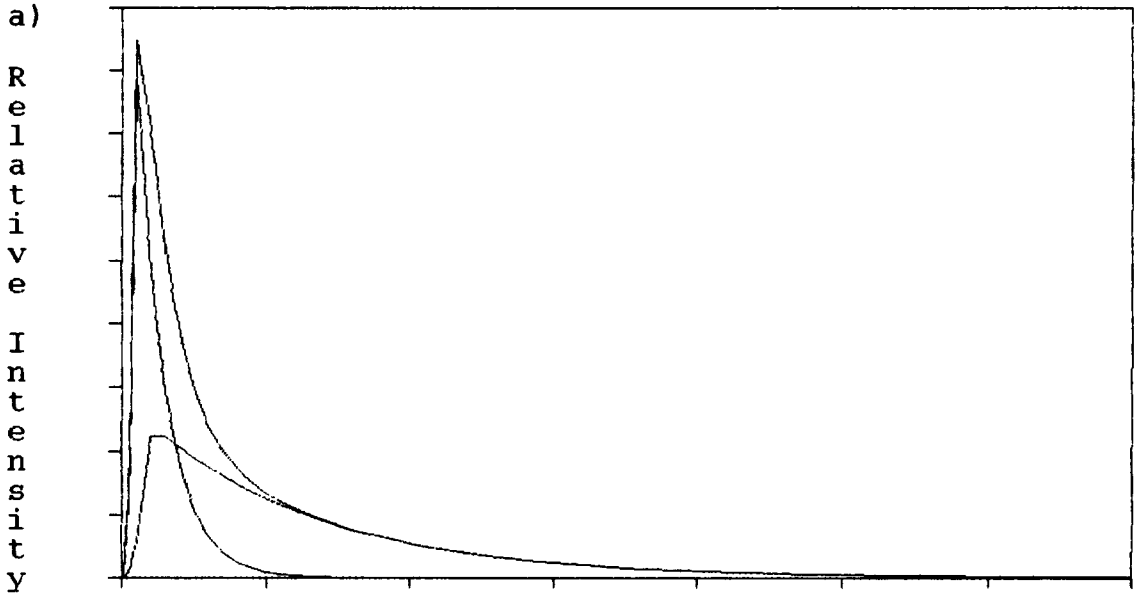


Figure 2. The scintillation intensity from an organic scintillator solution as a function of time showing the division of the total intensity into the fast and slow components.



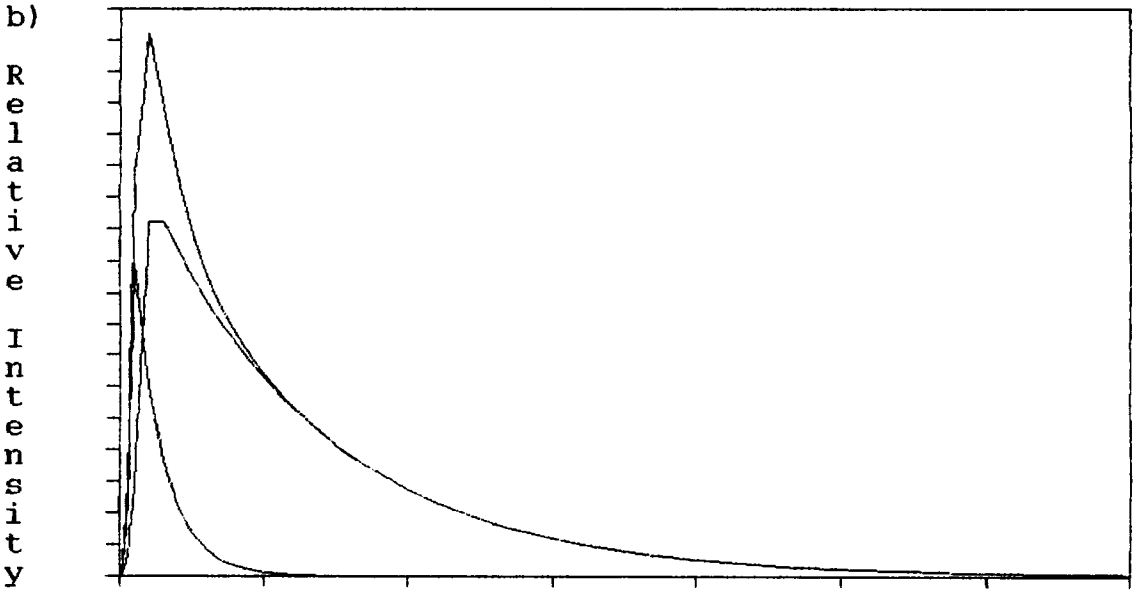


Figure 3. Comparison of scintillation efficiency in solutions excited by (a) beta/gamma radiation and (b) alpha radiation showing the division of the total intensity into the fast and slow components.

fraction (e.g. 80%) of the total integrated intensity is greater for alpha than for beta/gamma radiation. This property is the basis for the technique of pulse-shape discrimination of alpha pulses from beta and/or gamma pulses [22].

Electronic circuits used for pulse-shape discrimination are usually based on one of three different methods for distinguishing between pulses with different ratios of fast and slow components. Daehnick and Sherr have described a method which involves the measurement and comparison of the amplitudes of the slow and fast components of the pulse. A second method, described by Kuchnir and Lynch, uses an electronic circuit capable of measuring the time required for the pulse to reach a predetermined fraction of its total integrated intensity. The third method is known as the zero crossing technique. This method uses an electronic circuit to measure the time required for the doubly differentiated dynode pulse to cross the x-axis, the crossing time being dependent on the type of exciting particle [22].

The electronic circuit used in the PERALS pulse shape discrimination system is designed to measure the duration of incoming pulses. The time signals which are generated are then converted to voltages with pulse heights proportional to time. Time pulses with heights above an adjustable, low-level discriminator generate a gate pulse for pulse height

analysis while pulses with heights below the discriminator setting are rejected [18,24].

C. Resolution Dependence

In addition to rejecting interfering pulses from beta/gamma radiation, the PERALS system provides useful energy resolution for alpha spectra. The minimum energy resolution obtainable with a given liquid scintillation detector is dependent upon a number of factors including (1) the number of photons produced per scintillation event, (2) the number of photons that reach the photocathode, (3) the number of photoelectrons ejected for each photon that strikes the photocathode, (4) the number of photoelectrons that impinge upon the first dynode, and (5) the total number of electrons produced by the photomultiplier tube. The greater the quantity of each of these factors, the better the resolution of the scintillation detector [25]. Factors (3), (4), and (5) pertain to the phototube and will not be altered in this research. Factors (1) and (2) depend on the nature of the scintillator solution and its components and are the main topic of this research.

All of the processes occurring in the scintillator solution are dependent on the nature of the scintillator solution and its components. These processes include ionization and excitation of solvent molecules leading to the production of both excited singlet and excited triplet states, the transfer of this energy to the scintillator

solute molecules, the emission of photons by the scintillator solute molecules, and the transmission of emitted photons out of the solution [21,23]. The scintillator solutions used in the PERALS system are designed to contain the optimum components for good time resolution (the differentiation of alpha pulses from beta/gamma pulses), good alpha energy resolution, and reproducibility of alpha energy spectra.

A typical PERALS scintillator solution consists of a primary solvent, a secondary solvent (energy transfer agent), a primary solute (fluor), and an organic extracting agent. The components that are currently in use are those that were found to provide the best time and energy resolution while at the same time allowing for an efficient solvent extraction of the radionuclides into the organic scintillator solution. Toluene is used as the primary solvent because it has a relatively high scintillation efficiency, is readily available and affordable, and is very slightly miscible with water solutions. It was found that both the time resolution and the energy resolution were enhanced by the addition of large amounts of naphthalene to the toluene solutions. The naphthalene is believed to aid in the transfer of energy from the solvent molecules to the fluor molecules. The primary scintillator solute used is 2-(4-biphenylyl)-6-phenylbenzoxazole (PBBO). Various organic extracting agents are employed depending on the desired

extraction characteristics for a particular scintillator solution [17,18,24].

D. Resolution Improvement

Any changes in the composition of the scintillator solution that result in more efficient production and transmission of photons to the photomultiplier tube should result in improved resolution. Such changes may consist of the substitution of various solvents for toluene, the substitution of certain solvents for both toluene and naphthalene, the substitution of various scintillator solutes for PBBO, the use of drying agents to remove traces of water from the solution, and the use of an adducting agent to displace water that might be bound to the extracted radionuclides.

Certain solvents are known to have greater scintillation efficiencies than toluene and should be investigated [10]. It is also possible that the energy transfer agent and/or the scintillator solute are more soluble in other solvents than in toluene. Increased concentrations of these components may result in increased photon production. Similarly, naphthalene derivatives which are liquids at room temperature may substitute for the combination of toluene and naphthalene [26].

Although PBBO was found to give the best resolution when the PERALS system was being developed, comparisons with other scintillator solutes were only made in toluene

solutions. The scintillator solute concentrations in that study were held constant at 4.0 g/L [27]. However, many scintillator solutes are more soluble than PBBO in toluene and in other solvents and should be tested at their optimum concentrations in each solvent. It is possible that the scintillation efficiencies of the solutes will differ in different solvents.

Since water is a strong quencher in liquid scintillator solutions it is important that the solution be essentially free of water. The use of organic extracting agents to incorporate the radionuclides into the scintillator solution eliminates much of the water from the solution. However, some water may remain bound to the metal cations and may contribute to quenching. It might be possible to remove this water by the use of an adducting agent which will displace the bound waters. Alternatively, a drying agent such as anhydrous magnesium sulfate might be used to remove unbound water from the organic solution.

In addition to altering the components of the scintillator solution, the effect of temperature on the resolution needs to be investigated. The slow component of the scintillation decay is diffusion controlled and, therefore, should be temperature dependent [20]. The effect of increasing and decreasing the counting temperature will be investigated to determine any trends in resolution.

CHAPTER III

APPARATUS AND TECHNIQUES

A. PERALS Instrument

1. Introduction

The instruments used in this research were the PERALS Model 8100AB, serial numbers 026, 074, and 007, manufactured by Oak Ridge Detector Laboratory, Inc. (ORDELA). They were constructed and used for the purpose of measuring alpha-particle spectra by the technique of liquid scintillation while rejecting signals from interfering beta/gamma radiation.

2. Components

Each PERALS spectrometer consisted of a light-tight sample cell built to accommodate a 75-mm x 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 cell was filled with a light-coupling oil (silicone oil) to couple the sample to the photomultiplier tube (PMT). A diagram of this cell is shown in Figure 4 (p. 35) [17].

A typical PMT used in a PERALS spectrometer was a 2-inch (51-mm) diameter, 10-stage, head-on type photomultiplier tube such as the Hamamatsu model R2154, designed for high energy physics experiments. The photocathode was of the bialkali type with a maximum

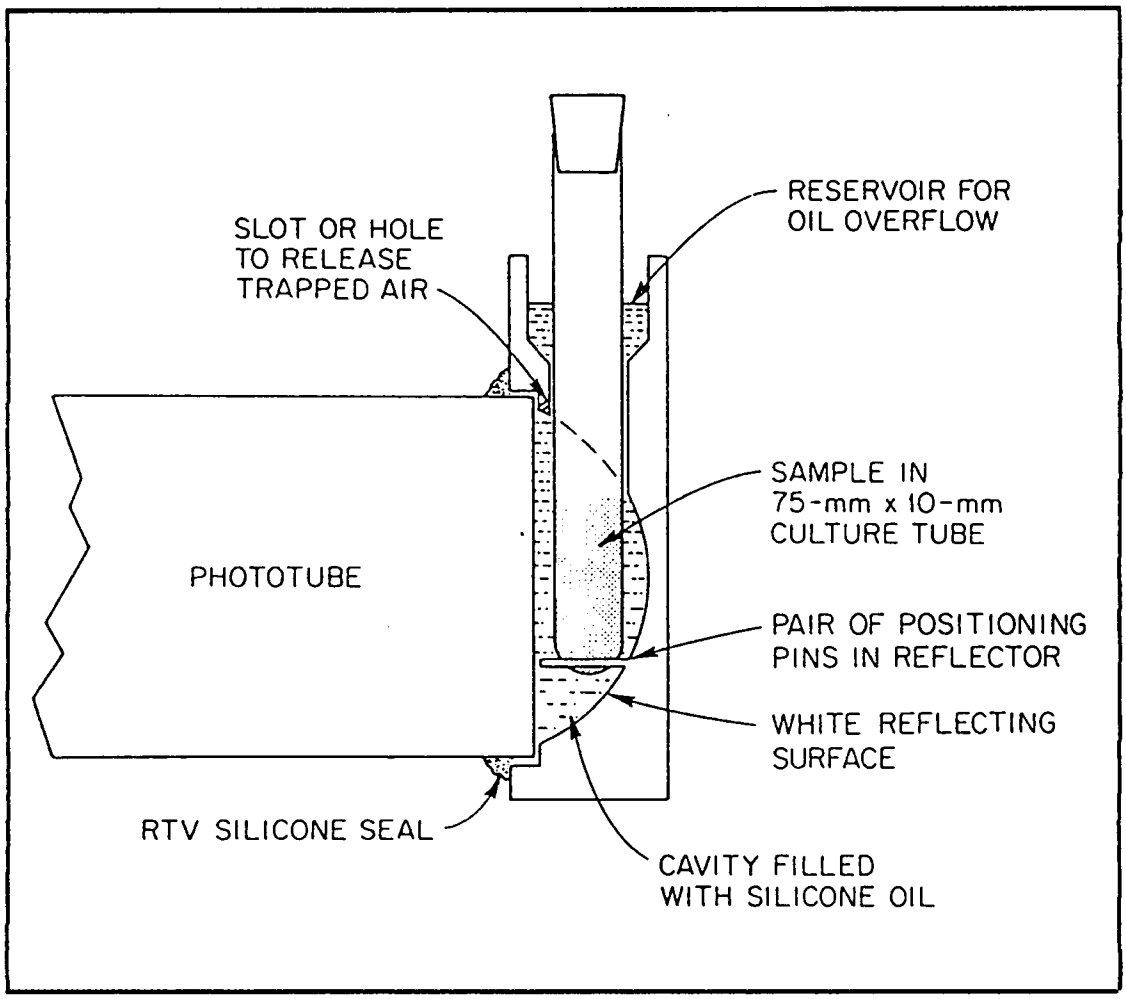


Figure 4. A cross section of a PERALS detector assembly.

wavelength response at 420 nm and a typical quantum efficiency of 25-30%.

The detection circuitry consisted of a preamplifier, a linear amplifier, and pulse-shape discrimination (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 long times) to be selected for energy analysis [24].

A multichannel analyzer (MCA) was used for pulse-height analysis of the coincidence pulses in order to generate an alpha-particle energy spectrum (Figure 5, p. 37). This also enabled the time separation between beta/gamma pulses and alpha pulses to be recorded as a time spectrum (Figure 6, p. 38). In either case it was possible to electronically integrate the entire spectrum or any portion of it.

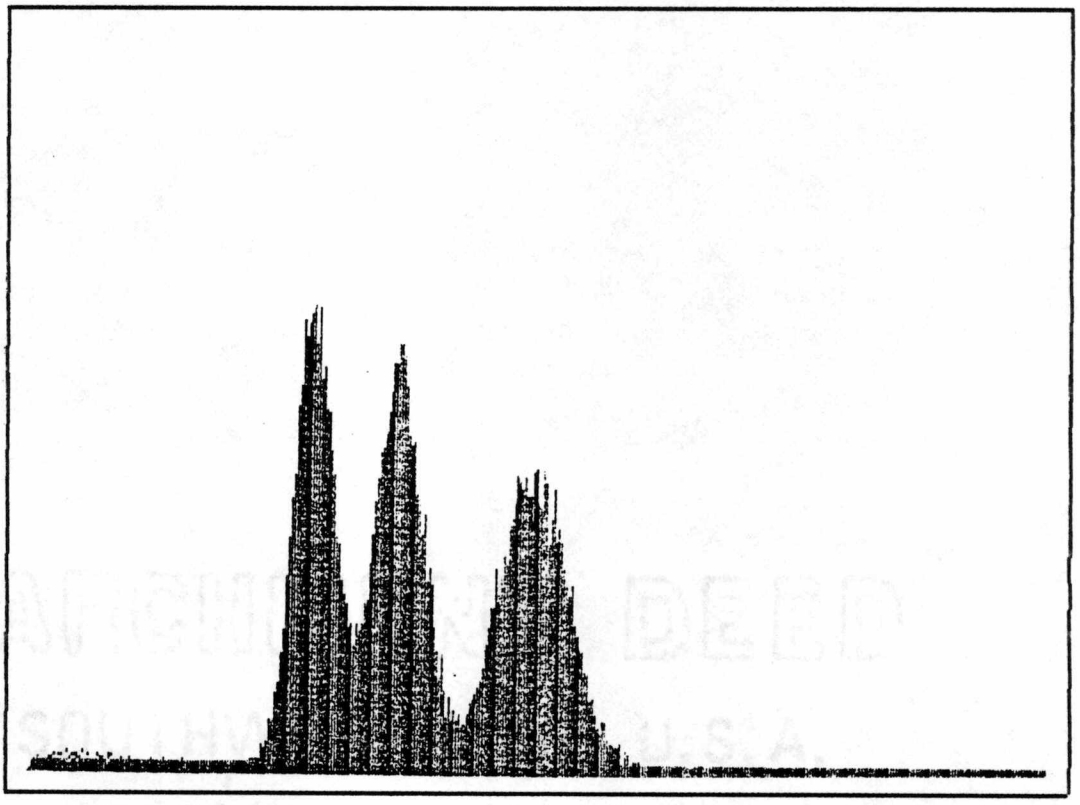


Figure 5. A typical PERALS alpha-energy spectrum for U-238 (left), U-234 (middle), and Am-241 (right) in ALPHAEX.

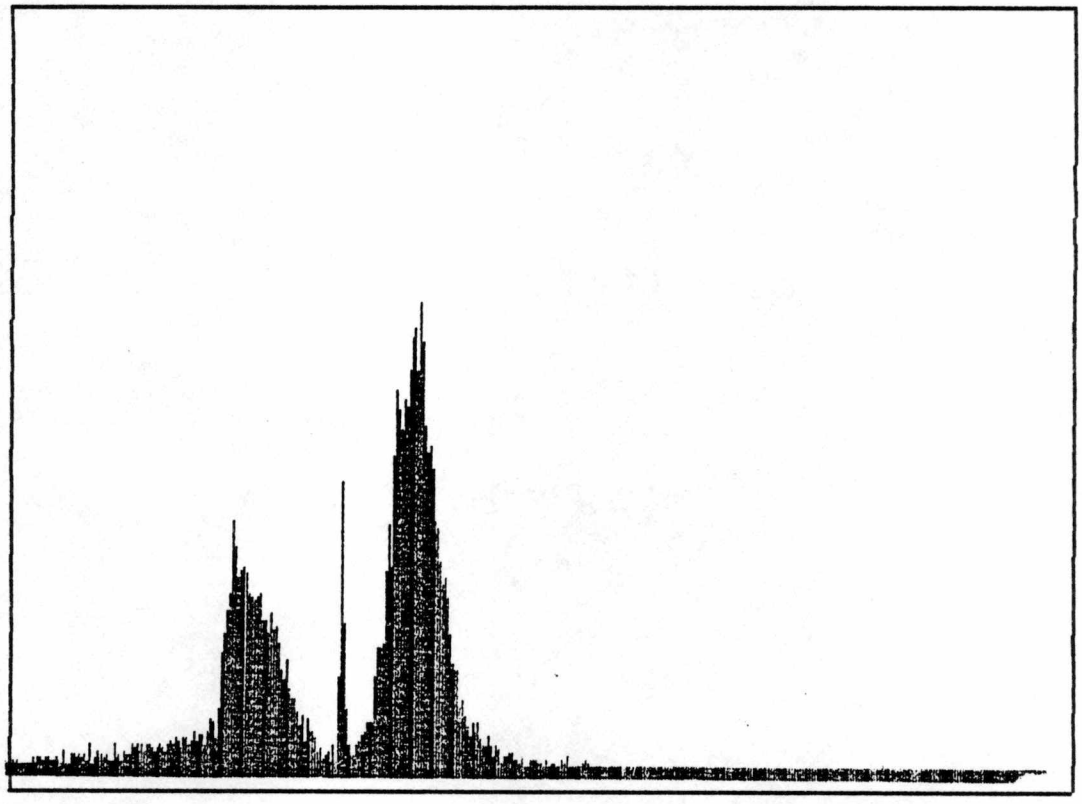


Figure 6. A typical PERALS time spectrum for U-238, U-234, and Am-241 in ALPHAEX showing alpha pulses on the right and beta/gamma pulses on the left.

3. Resolution

The resolutions of the three instruments varied due to slight differences in the PMT's. A resolution check was made on each instrument using a Ra-226 counting reference standard. Serial number 074 was found to give consistently higher resolutions than serial number 026. Serial number 007 consisted of an early model instrument which had been reconstructed with an improved PMT. Resolutions measured with this instrument were the best seen on any PERALS system manufactured to this date.

The methods for determining energy resolution varied depending upon the software available with the three instruments. Two indicators of energy resolution were utilized in this research: peak to valley ratio and percent energy resolution. In addition, the channel number of the Am-241 peak maximum was used as an indication of the light output of a solution, since in general, the greater the light output of a given solution, the greater the pulse heights, and the higher the peak channels.

The peak to valley ratio was determined by dividing the height of the U-238 peak by the height of the valley between the U-238 and U-234 peaks. The peak heights and valley heights for spectra obtained were taken as the maximum number of counts/channel of the U-238 peak and the minimum number of counts/channel in the valley between the two uranium peaks.

The percent energy resolution was calculated as the full peak width at half the maximum peak height (FWHM, KeV) multiplied by 100, then divided by the peak energy (KeV). The first instrument, serial number 026, had no software package and required hand calculation of the FWHM, which was determined at the point half way between the peak maximum and the baseline. The other instruments, serial numbers 074 and 007, determined the FWHM of the peaks using computer-generated Gaussian peaks which when combined would yield the original spectrum.

B. Scintillator Solutions

All of the scintillator solutions investigated in this research consisted of a primary solvent, a scintillator solute (fluor), an organic complexing agent, and usually a secondary solvent (energy transfer agent), which was naphthalene or a naphthalene derivative. The various chemicals used for each type of component are listed in Table I (p. 41) along with their sources and purities as stated when received. The diethylbenzene consisted of a mixture of the *meta*- and *para*- isomers, and the diisopropyl-naphthalene was a mixture of unspecified isomers. Chemicals were used without further purification except as indicated below.

The diisopropylnaphthalene was highly colored and had to be distilled in a high-vacuum molecular still. The

TABLE I

CHEMICALS USED IN SCINTILLATOR SOLUTIONS

Chemical	Source	Purity
Primary solvent		
Toluene	Baxter	99.9%
1-Methylnaphthalene	Aldrich	98%
2-Ethylnaphthalene	Aldrich	99+%
Pseudocumene	Eastman Kodak	Unspecified
Mesitylene	Eastman Kodak	98%
p-Xylene	J. T. Baker	Reagent
Cumene	Eastman Kodak	99%
Diethylbenzene	Eastman Kodak	Technical
Diisopropylnaphthalene	Koch Refining	Unspecified
Secondary Solvent		
Naphthalene	J. T. Baker	Reagent
1-Methylnaphthalene	Aldrich	98%
Primary Solute		
2-(4-Biphenylyl)-6-phenyl benzoxazole	Ciba-Geigy	Unspecified
Complexing Agent		
bis-(2-Ethylhexyl) phosphoric acid	ETRAC	Purified
Trioctyl phosphine oxide	Cyanamid	Unspecified

purified solvent was clear but retained a faint yellow color.

Scintillator solutions containing no energy transfer agent were prepared by weighing enough HDEHP into a volumetric flask to give a concentration of 60.0 (or 70.0) g/L. Enough PBBO was weighed into a plastic weighing boat to give a concentration of 4.0 g\L. The PBBO was transferred into a beaker containing a few milliliters of the desired solvent, and the residual PBBO was rinsed into the beaker with a small amount of the same solvent. The mixture was stirred (and heated, if necessary) until all of the PBBO had dissolved. Upon cooling to room temperature, the solution was transferred with rinsing to the volumetric flask containing the HDEHP. The flask was shaken to achieve thorough mixing and the solution was diluted to the mark with the appropriate solvent. Scintillator solutions were prepared to give a total volume of 10 mL, 25 mL, 50 mL, or 100 mL, depending on the availability of the solvent. Table II (p.43) includes a list of these scintillator solutions and their constituents.

Scintillator solutions containing naphthalene were prepared in the same manner except the naphthalene was first scrubbed with a nitric/phosphoric acid mixture. This procedure consisted of dissolving the desired amount of naphthalene in the appropriate solvent. The resulting solution was combined in a separatory funnel with an acid

TABLE II

SCINTILLATOR SOLUTIONS CONTAINING NO ADDED NAPHTHALENE

Scintillator Solution	Solvent	PBBO Conc (g/L)	HDEHP Conc (g/L)
ES106	1-Methyl-naphthalene	4.0	70.0
ES113-0	Toluene	4.0	70.0
ES120-PDC	Pseudocumene	4.0	70.0
ES120-MES	Mesitylene	4.0	70.0
ES157	2-Ethyl-naphthalene	4.0	60.0
ES163-CUM	Cumene	2.0	60.0
ES163-DEB	Diethyl-benzene	2.0	60.0
ES175-DIPN	Diisopropyl-naphthalene	4.0	60.0

mixture consisting of one part concentrated nitric acid, two parts concentrated phosphoric acid, and six parts distilled water. This mixture was shaken for several minutes and the phases allowed to separate completely. The acid was drained off, and the organic phase was washed twice with distilled water to remove the remaining acid. The scrubbed naphthalene solution was then used to prepare scintillator solutions as previously described. Table III (p. 45) includes a list of naphthalene-containing scintillator solutions and their constituents.

A series of scintillator solutions was prepared in toluene in which 1-methylnaphthalene was substituted for naphthalene. These scintillator solutions and their constituents are listed in Table IV (p. 45).

C. Sample Preparation

1. Step one

Two (2.000) mL of a solution containing 0.1 nCi/ml each of U-238 and U-234 and 0.1 nCi/ml of Am-241 was measured into a small screw-cap vial using a 5000-microliter automatic pipet.

2. Step two

Two (2.000) mL (sometimes 1.500 mL) of extractive scintillator was measured into the same vial using the automatic pipet.

TABLE III

SCINTILLATOR SOLUTIONS CONTAINING ADDED NAPHTHALENE

Scintillator Solution	Solvent	Naphthalene Conc (g/L)	HDEHP Conc (g/L)	PBBO Conc (g/L)
ALPHAEX	Toluene	180.0	60.0	4.0
ES113-90	Toluene	90.0	70.0	4.0
ES156	*p*-Xylene	180.0	60.0	4.0
ES160	*p*-Xylene	280.0	60.0	4.0
ES162	Pseudocumene	18.0	60.0	4.0
ES168	Pseudocumene	180.0	60.0	4.0
ES170	Diethyl-benzene	45.0	60.0	2.0
ES175-C	Cumene	45.0	60.0	2.0

TABLE IV

SCINTILLATOR SOLUTIONS CONTAINING 1-METHYLNAPHTHALENE IN TOLUENE

Scintillator Solution	1-Methyl-naphthalene Conc (g/L)	HDEHP Conc (g/L)	PBBO Conc (g/L)
ES116	600	70.0	4.0
ES117-180	180	70.0	4.0
ES117-90	90	70.0	4.0

3. Step three

The vial was shaken gently for four minutes to expand the interfacial area between the phases temporarily and extract the radionuclides into the organic phase. The sample was then allowed to stand several minutes to permit the phases to separate completely.

4. Step four

Using a 1000-microliter automatic pipet, 1.000 mL of the organic phase was transferred to a 75-mm x 10-mm glass culture tube.

5. Step five

The sample was sparged for two minutes with dried, toluene-saturated argon to remove moisture and dissolved oxygen. The culture tube was capped as the tip of the sparging pipet was removed.

D. Counting and Statistics

The 1.000-mL sample was placed in the sample cell and enough silicone oil was added to fill the chamber. The instrument was set for pulse-shape analysis, and the low-level time discriminator setting was adjusted for optimum rejection of beta/gamma pulses while minimizing loss of alpha pulses. A time spectrum (number of pulses vs. decay time of pulse) was recorded for each sample. The instrument was then set for pulse-height analysis and a preset count time of 1800 sec or 3600 sec was selected. An energy

spectrum (number of pulses vs. pulse height) was recorded for each sample.

For samples consisting of U-238, U-234, and Am-241, a typical spectrum consisted of $3.6144 \times 10^4 \pm 1.91 \times 10^2$ total counts ($5.4216 \times 10^4 \pm 2.33 \times 10^2$ if extracted with 1.500 mL of extractive scintillator) with an average of $1.2048 \times 10^4 \pm 1.10 \times 10^2$ counts per peak. This gives a 90% confidence limit of $[(1.64)(1.10 \times 10^2)(1.2048 \times 10^4)^{-1}] \times 100\% = 1.50\%$. Thus, any change in resolution (FWHM) less than 1.50% is meaningless. In actuality, fluctuations as large as 5% in FWHM values were observed for the same spectrum, depending on the selected region of interest.

Typical counts/channel values for the U-238 peak maximum (X) and the valley minimum (Y) were 400 counts/channel and 100 counts/channel respectively. The error (σ_Q) for the peak to valley ratio ($[X][Y]^{-1} = Q$) was given by [28]

$$\sigma_Q = Q[(\sigma_X)^2(X)^{-2} + (\sigma_Y)^2(Y)^{-2}]^{1/2}, \qquad (10)$$

or simply

$$\sigma_Q = Q[(X)^{-1} + (Y)^{-1}]^{1/2}. \qquad (11)$$

For the values given above the error is

$$\sigma_Q = 4.00[(400)^{-1} + (100)^{-1}]^{1/2} = 0.45. \qquad (12)$$

The channel numbers for the Am-241 peak maximum were estimated to be accurate to ± 5 channels. This estimation was based on examination of individual spectra as well as comparison of different spectra for the same sample.

CHAPTER IV

EXPERIMENTAL RESULTS

A. Pure Solvents

Scintillator solutions were prepared in a number of different solvents as described in Chapter III, section B. The first solutions prepared contained 70.0 g/L HDEHP while solutions prepared more recently contained 60.0 g/L. This change did not appear to affect the solution properties significantly. All of the solutions contained 4.0 g/L PBBO with the exception of the cumene and diethylbenzene solutions. The solubility of PBBO was limited to 2.0 g/L in these solutions.

Samples were prepared with each solution as described in Chapter III, section C. Each sample was counted on one of the three PERALS units described previously, and time and energy spectra were obtained for each one. The peak to valley ratio, percent energy resolution, and the channel number of the Am-241 peak maximum were measured for each sample. These values were compared with those measured for a sample extracted with ALPHAEX and counted on the appropriate instrument. These data are listed in Table V (p. 49).

B. Solvents Plus Naphthalene

As stated previously (p. 11), the addition of relatively large quantities of naphthalene to a scintillator

TABLE V

COMPARISON OF ALPHAEX WITH SCINTILLATOR SOLUTIONS CONTAINING NO ADDED NAPHTHALENE

Scintillator Solution	Peak to Valley Ratio	Am241 Peak Maximum (Channel #)	% Resolution	
			U238	Am241
Scintillator Solutions Tested on PERALS Unit 026				
ALPHAEX	2.5 ± 0.3	131 ± 5	7.5%	8.8%
ES113-0	2.1 ± 0.2	115 ± 5	9.7%	10.3%
ES120-PDC	2.1 ± 0.2	119 ± 5	8.1%	9.5%
ES120-MES	1.7 ± 0.1	96 ± 5	9.0%	10.1%
Scintillator Solutions Tested on PERALS Unit 074				
ALPHAEX	4.6 ± 0.6	407 ± 5	5.6%	7.7%
ES163-CUM	1.4 ± 0.1	128 ± 5	5.4%	8.7%
Scintillator Solutions Tested on PERALS Unit 007				
ALPHAEX	10.1 ± 1.6	501 ± 5	3.9%	7.1%
ES163-DEB	2.0 ± 0.2	206 ± 5	5.9%	7.5%

solution has been shown to improve the scintillation efficiency of many solutions [12]. However, the maximum useful solubility of naphthalene in toluene was limited to about 180 g/L. In order to investigate the effect of naphthalene concentrations greater than this, a liquid naphthalene derivative, 1-methylnaphthalene, was used instead of naphthalene, since its solubility in toluene was not limited.

The effect of naphthalene concentration on the measured resolution of a series of toluene solutions was investigated. Table VI (p. 51) lists the scintillator solutions, naphthalene or 1-methylnaphthalene concentrations, and resolutions measured for each solution.

In addition to 1-methylnaphthalene, the naphthalene derivatives 2-ethylnaphthalene and diisopropylnaphthalene are also liquids at room temperature. These solvents were used to prepare scintillator solutions with the highest naphthalene concentration attainable for a solution (~1000 g/L). Table VII (p. 52) compares the resolutions measured for these solutions with the data for ALPHAEX.

Scintillator solutions containing naphthalene were also prepared in solvents other than toluene. The naphthalene concentration varied depending on its maximum solubility in each solvent. The data for these solutions are given in Table VIII (p. 53).

TABLE VI

EFFECT OF ENERGY TRANSFER AGENT (ETA) CONCENTRATION ON RESOLUTION MEASUREMENTS IN TOLUENE SOLUTIONS COUNTED ON PERALS UNIT 026

Scintillator Solution	ETA Conc (g/L)	Peak to Valley Ratio	Am241 Peak Maximum (Channel)	Percent Resolution	
				U238	Am241
Solutions Containing Naphthalene					
ES113-0	0.0	2.1 ± 0.2	114 ± 5	9.7%	10.3%
ES113-90	90.0	2.5 ± 0.3	132 ± 5	7.3%	9.3%
ALPHAEX	180.0	2.5 ± 0.3	131 ± 5	7.5%	8.8%
Solutions Containing 1-Methylnaphthalene					
ES117-90	90.0	2.5 ± 0.3	133 ± 5	8.2%	9.4%
ES117-180	180.0	2.6 ± 0.3	136 ± 5	6.9%	9.4%
ES116	600.0	2.5 ± 0.3	142 ± 5	8.0%	9.2%

TABLE VII

COMPARISON OF ALPHAEX WITH SCINTILLATOR SOLUTIONS PREPARED WITH NAPHTHALENE-DERIVATIVE SOLVENTS

Scintillator Solutions	Peak to Valley Ratio	Am241 Peak Maximum (Channel #)	% Resolution	
			U238	Am241
Scintillator Solutions Tested on PERALS Unit 026				
ALPHAEX	2.5 ± 0.3	131 ± 5	7.5%	8.8%
ES106	2.8 ± 0.3	147 ± 5	8.0%	8.3%
Scintillator Solutions Tested on PERALS Unit 074				
ALPHAEX	4.6 ± 0.6	407 ± 5	5.6%	7.7%
ES106	5.0 ± 0.7	432 ± 5	5.6%	8.2%
ES157	4.0 ± 0.5	481 ± 5	4.6%	7.6%
Scintillator Solutions Tested on PERALS Unit 007				
ALPHAEX	10.1 ± 1.6	501 ± 5	3.9%	7.1%
ES175-DIPN	4.2 ± 0.5	358 ± 5	4.5%	8.6%

TABLE VIII

COMPARISON OF ALPHAEX WITH SCINTILLATOR SOLUTIONS CONTAINING ADDED NAPHTHALENE

Scintillator Solution	Peak to Valley Ratio	Am241 Peak Maximum (Channel #)	% Resolution	
			U238	Am241
Scintillator Solutions Tested on PERALS Unit 026				
ALPHAEX	2.5 ± 0.3	131 ± 5	7.5%	8.8%
ES113-90	2.5 ± 0.3	132 ± 5	7.3%	9.3%
ES162	2.3 ± 0.3	133 ± 5	7.8%	8.5%
Scintillator Solutions Tested on PERALS Unit 074				
ALPHAEX	4.6 ± 0.6	407 ± 5	5.6%	7.7%
ES156	4.0 ± 0.5	448 ± 5	5.0%	7.8%
ES160	3.7 ± 0.5	451 ± 5	5.6%	7.9%
ES162	3.6 ± 0.5	349 ± 5	5.3%	8.7%
ES168	3.9 ± 0.5	380 ± 5	4.8%	7.9%
Scintillator Solutions Tested on PERALS Unit 007				
ALPHAEX	10.1 ± 1.6	501 ± 5	3.9%	7.1%
ES170-DEB	4.2 ± 0.5	263 ± 5	5.2%	8.0%
ES175-CUM	4.2 ± 0.5	299 ± 5	4.5%	8.6%

C. Scintillator Solutes

A portion of this research was intended to include an investigation of the relative efficiencies of various scintillator solutes in a number of different solvent systems. Previously, a study of this type had been done, but the solubilities of different scintillator solutes in the same solvent were not taken into account [27]. It was the intention of this research to determine the optimum scintillator solute concentrations for several different scintillators in a variety of solvents. Unfortunately, the research facility was unable to acquire any scintillator solutes other than PBBO in time to carry out this part of the investigation.

D. Adducting Agents

It was believed possible that water molecules remaining bound to the radionuclides after complexation by HDEHP and extraction into the organic phase might contribute to quenching, thereby degrading the resolution. The addition of an adducting agent such as trioctyl phosphine oxide (TOPO) to the extractive scintillator might serve to displace these waters from the metal ions. The free waters might then be removed more easily by sparging or by use of a drying agent.

One (1.000) mL of extractive scintillator containing HDEHP in toluene was combined in a small screw-cap vial with 1.000 mL of extractive scintillator containing TOPO in

toluene. This solution was used to extract 2.000 mL of an aqueous solution of U-238, U-234, and Am-241 as previously described in Chapter III, section C. The sample was counted on instrument number 074, and the resulting energy spectrum was compared with previous spectra for samples extracted with HDEHP toluene solutions only. The data are recorded in Table IX (p. 56). No significant improvement in resolution was achieved.

E. Drying Agents

Since it was still possible that unbound water in the organic phase was acting to degrade the resolution, an attempt was made to dry the organic phase more completely than could be achieved by sparging. Two (2.000) mL the aqueous U-238, U-234, and Am-241 solution was extracted with 2.000 mL of ALPHAEX in the usual manner. About 1.5 mL of the organic phase was transferred to a screw-cap vial containing a small amount of anhydrous magnesium sulfate powder. The mixture was swirled gently for one minute and allowed to sit for approximately one hour. One (1.000) mL of the liquid was removed and counted on instrument number 007. Table X (p. 56) includes the data for this experiment. Again there was no improvement in resolution.

F. Temperature Effects

Several attempts were made to investigate the relationship between temperature and resolution of a high

TABLE IX

COMPARISON OF ALPHAEX WITH SCINTILLATOR SOLUTION CONTAINING HDEHP AND TOPO

Scintillator Solution	Peak to Valley Ratio	Am241 Peak Maximum (Channel #)	% Resolution	
			U238	Am241
ALPHAEX	4.6 ± 0.6	407 ± 5	5.6%	7.7%
HDEHP/TOPO	4.4 ± 0.4	449 ± 5	5.1%	8.3%

TABLE X

COMPARISON OF ALPHAEX WITH DESSICANT-DRIED ALPHAEX

Scintillator Solution	Peak to Valley Ratio	Am241 Peak Maximum (Channel #)	% Resolution	
			U238	Am241
ALPHAEX	10.1 ± 1.6	501 ± 5	3.9%	7.1%
DRIED ALPHAEX	9.5 ± 1.6	510 ± 5	4.1%	6.5%

count (3700 cpm) Ra-226 counting reference sample. However, the PERALS instruments had no facility for controlling the temperature, and it was not possible to obtain any definitive results by simply pre-heating or pre-cooling the sample and sample chamber.

CHAPTER V

SUMMARY AND CONCLUSIONS

A. Summary

The development of the PERALS technique for measuring alpha-emitters has made alpha liquid scintillation spectrometry a practical and useful alternative to conventional solid state techniques. Its primary advantages include rapid and easy sample preparation, 4π detection geometry, accuracy, and sensitivity (0.001 cpm). The major disadvantage at this time is the relatively poor energy resolution compared to that attainable with solid state detection systems. This is, however, partially compensated by the use of highly specific liquid-liquid extraction techniques available with the PERALS system [17,18,24].

This research consisted of a number of investigations to determine if it was possible to markedly improve the energy resolution by altering the scintillator solution components. Studies included the use of a number of different scintillator solvents and the effect of naphthalene concentration on energy resolution. The use of liquid naphthalene derivatives as substitutes for solid naphthalene was investigated as well as their use as both solvent and energy transfer agent. Additional experiments include the use of an adducting agent and a drying agent to remove both bound and unbound waters from the scintillator

solution after extraction of the radionuclides. The effects of temperature on resolution were also investigated but no useful data were obtained.

B. Conclusions

From the data in Table V it can be seen that scintillator solutions prepared without naphthalene result in energy spectra with lower peak to valley ratios, less light output (lower Am-241 peak maximum channel numbers), and usually higher percent resolutions, that is, worse energy resolution. It is important to note that while ES163-CUM compared favorably with ALPHAEX in the percent resolution category, it gave a much lower peak to valley ratio and had a much lower light output as indicated by the distance to the last peak. For this reason the peak to valley ratio and Am-241 peak maximum channel number are believed to be much more indicative of practical resolution than are the percent energy resolution measurements.

Experiments involving the effect of naphthalene concentration on the resolution measured with toluene solutions are summarized in Table VI. There appears to be no significant increase in peak to valley ratio upon addition of naphthalene, in any concentration, to toluene. The distance to the last peak does increase significantly upon addition of naphthalene and continues to increase slightly as naphthalene concentration increases.

In contrast, comparison of the data for scintillator solutions in diethylbenzene with no naphthalene (ES163-DEB) from Table V and with naphthalene (ES170-DEB) from Table VIII reveals a marked increase in peak to valley ratio and light output. The percent resolution, meanwhile, remains relatively constant.

Comparison of ALPHAEX with scintillator solutions prepared from liquid naphthalene derivatives showed no significant differences in peak to valley ratio, with the exception of diisopropylnaphthalene (ES175-DIPN). This solution did not compare favorably with ALPHAEX, possibly due to the need for further purification. The distance to the last peak was found to be greatest for 2-ethyl-naphthalene (ES157) and 1-methylnaphthalene (ES106), thus indicating greater light output from these than from ALPHAEX solutions. However, the overall resolution did not appear to improve significantly. This was also the case for the *p*-xylene solutions (ES156 and ES160) listed in Table VIII.

In summary, alteration of the scintillator solutions as described above did not result in any significant improvement in energy resolution. Several different solutions were found to give resolution measurements comparable to those for ALPHAEX, and may be used in the future as alternative scintillator solutions in conjunction with the PERALS system. Solutions prepared with the liquid naphthalene derivatives are of particular interest due to

their higher flash points as compared to toluene solutions. These solvents may afford a more environmentally friendly scintillator than is available at this time.

C. Prospects

It remains to be seen whether any useful resolution improvement can be made by modifications to the scintillator solutions. Additional studies need to be done with a series of likely scintillator solutes measured at their optimum concentrations in the best solvents. These solvents should include toluene, *p*-xylene, pseudocumene, and the liquid naphthalene derivatives. Additional purification of these solvents may be necessary to achieve optimum results.

Initial experiments with adducting agents and drying agents were not encouraging, and it appears unlikely that any marked improvements in resolution will be made by their use. This was also true of the temperature experiments, although further studies must incorporate some means of controlling the temperature of the sample chamber.

It may be that the current solutions are nearing the maximum scintillation efficiency and light output of liquid scintillation systems. This is not to say that further resolution improvement is not possible, since the resolution was clearly increased by improvements in the PMT. Additional advances in the electronics are sure to lead to

increased resolution, even with no further improvements in the scintillator solutions.

Yang [29] has reported the use of a commercial solid scintillator to count alpha-emitting samples in a normal liquid scintillation counter. He reports counting efficiencies approaching 100% and greater light output than possible with normal scintillation cocktails. It is not clear, however, what type of resolution is possible with this system.

A potentially very useful experiment might be to incorporate the extracted alpha-emitting sample into a melted organic scintillator contained in a normal sample culture tube. After gradual cooling to produce an annealed crystal, the solid could be counted in a PERALS spectrometer to determine if greater light output and increased resolution are possible with a solid scintillator. Anthracene and *trans*-stilbene are efficient solid scintillators which might be used in such an experiment [30]. The absence of additional components and the more ordered structure of the crystal may result in greater scintillation efficiency than is possible with a liquid solution.

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VITA

Jonathan Micah Duffey was born in Roxboro, North Carolina on August 20, 1964. He graduated valedictorian of his class in May 1982 from Camden Central High School in Camden, Tennessee. 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 by Union University at their satellite campus in Memphis, Tennessee. In August 1988 he entered graduate school at the University of Tennessee in Knoxville.