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ALPHA COUNTING AND SPECTROMETRY
-
USING LIQUID SCINTILLATION METHODS

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FOREWORD

The Committee on Nuclear and Radiochemistry is one of a number of committees working under the Board on Chemical Sciences and Technology of the Commission on Physical Sciences, Mathematics, and Resources of the National Academy of Sciences-National Research Council. Its members are drawn from academic, industrial, and government laboratories and represent the areas of nuclear chemistry, radiochemistry, and nuclear medicine.

The Committee has concerned itself with those areas of nuclear science which involve the chemist, such as the collection and distribution of radiochemical procedures, specialized techniques and instrumentation, the place of nuclear and radiochemistry in college and university programs, the training of nuclear and radiochemists, radiochemistry in environmental science, and radionuclides in nuclear medicine. A major interest of the Committee is the publication of the Nuclear Science Series of monographs on Radiochemistry and on Radiochemical Techniques. In 1982 a third series on Nuclear Medicine was initiated.

The Committee has endeavored to present monographs that will be of maximum use to the working scientist. Each monograph presents pertinent information required for radiochemical work with an individual element or with a specialized technique or with the use of radionuclides in nuclear medicine.

Experts in the various subjects have been recruited to write the monographs. The U.S. Department of Energy sponsors the printing of the series.

The current monograph is one of the series on Radiochemical Techniques which grew out of the need for compilations of specialized techniques and instrumentation in this field. The Committee is confident these publications will be useful not only to nuclear and radiochemists but also to research workers in other fields such as physics, biochemistry, or nuclear medicine who wish to use radiochemical techniques to solve specific problems.

Edward S. Macias, Chairman
Committee on Nuclear and Radiochemistry

PREFACE

Accurate quantitative assay of an alpha- or beta-emitting nuclide by radiometric methods has been a problem since the first use of radiation detection methods and remains a problem today. Both alpha and beta radiation are non-penetrating and are easily absorbed by any sample matrix with which the nuclide is mixed or, sometimes, by the nuclide itself. For beta-emitting nuclides the problems of sample self-absorption and sample/detector geometry have been attacked by a number of methods including sample dilution, 4π beta-gamma coincidence counting, internal gas counting, and liquid scintillation counting. The use of liquid scintillation for beta counting is very convenient and has been particularly valuable for low-energy beta emitters such as tritium and ^{14}C. These nuclides are extremely valuable tracers in biological and biomedical fields, and liquid scintillation is perhaps the most acccurate and certainly the most convenient way to quantify them. An industry has developed around the supplying of equipment and reagents for beta liquid scintillation work, and, indeed, liquid scintillation has become identified with tritium and ^{14}C counting.

Attempts to solve the counting problems of alpha-emitting nuclides have been concentrated on plate counting methods because excellent alpha energy resolution is available with these methods but also because it was possible to make the detectors used, gas ionization chambers and surface-barrier devices, insensitive to beta and gamma radiation. Although clean, laboratory-generated samples can be counted using beta liquid scintillation equipment and techniques, yielding nearly 100% counting efficiency and good accuracy, in most other types of samples there are problems with energy resolution and with separating the often unpredictable beta- and gamma-produced background. However, recent advances in detector design, sample preparation methods, and electronic pulse-shape discrimination now allow useful alpha spectra to be collected and beta-gamma backgrounds to be rejected. Coupling the technology of liquid-liquid extraction with that of liquid scintillation has allowed the development of the "extractive" scintillator with which the nuclide-of-interest can be phase-transferred into the scintillator, often without appreciably changing the composition or response characteristics of the scintillator. With these developments, practical application of liquid scintillation methods to alpha spectrometry is possible, and a broad range of potential applications exists for alpha liquid scintillation spectrometry.

ACKNOWLEDGMENTS

I am indebted to many people for help in making it possible to present this monograph and the information it contains. I can mention only a few here.

The initial use of liquid scintillation for alpha counting in our laboratory occurred in 1969 in connection with analyses required in separations science research. It was necessary to determine the concentrations of Am, Cm, Bk, Cf, and Es in aqueous and organic solutions to better than ± 1% accuracy for studies of the aqueous-phase complexes of these elements. It was not possible to obtain this counting accuracy with plate methods. **Donald L. Horrocks** is the person who pointed out that we could easily achieve that degree of accuracy with liquid scintillation methods. Much of the laboratory work on procedures was done by **G. N. Case** who has always had, and retains, an intense interest in the methods described here. **J.W. McKlveen** has also been keenly interested in liquid scintillation counting of alphas and has been responsible for sending a number of excellent students to work on this project in our laboratory. My supervisors at ORNL, **C. F. Coleman**, **A. P. Malinauskas**, and **R. G. Wymer**, along with our Department of Energy - Basic Energy Sciences sponsors, especially the late **W. J. Haubach**, deserve much credit for being tolerent of work that, I am sure, sometimes did not seem completely related to separation science. I believe the general value of this work to science will justify their patience. **C. F. Coleman** also deserves credit for many helpful suggestions and for help in calculating the theoretical shapes of alpha curves in liquid scintillation systems. Finally, I would like to acknowledge the help of my wife, **Betty**, in the typing, proofreading, and editing.

CONTENTS

I. INTRODUCTION

Liquid scintillation is an effective method for alpha counting and is attractive for that application because it is a 4π counting method, there are no problems of sample self-absorption (thus counting efficiency for alphas is virtually 100%), and because relatively simple methods of sample preparation can often be used. However, liquid scintillation has not been used much for alpha counting for a number of reasons. First, it was initially developed for beta counting, and the commercially available liquid scintillation equipment is almost exclusively designed for beta counting. Second, because of the ways in which alpha, beta, and gamma radiation interact with the scintillator there is a problem in controlling the background count level and in knowing accurately what that background count is. Third, there has not been an effective way of introducing the nuclide of interest to the scintillator without, at the same time, introducing variable amounts of undesirable materials, such as water, acids or salts, all of which have deleterious effects on the performance of the scintillator. In recent years, however, techniques and equipment have been developed for alpha liquid scintillation counting and spectrometry that solve many of the above problems, and these methods will be described in later sections.

It has been known that liquid scintillators could be used for the detection of alpha emitters almost from the initial development of the method. H.P. Kallmann first demonstrated the use of aromatic solvents containing dissolved scintillator solutes (fluors) as detectors for nuclear radiation in 1947.(1) Three years later M. Ageno and co-workers reported alpha as well as beta and gamma radiation produced scintillations in xylene solutions of naphthalene.(2) In 1954 Basson and Steyn further demonstrated the usefulness of liquid scintillation for alpha counting.(3) They devised a method of obtaining the absolute disintegration rate of an alpha emitter by taking advantage of the virtually 100% alpha counting efficiency of liquid scintillation and correcting the accompanying beta-gamma continuum by extrapolating to zero phototube voltage. A brief review of these early developments is given in a previous *Nuclear Science Series* publication.(4)

In the years following, the usefulness of liquid scintillation as a method of alpha counting and spectrometry has been demonstrated repeatedly and with increasing degrees of sophistication. A common approach to alpha liquid scintillation counting has been to use the readily available beta liquid scintillation equipment. This method is extremely useful for samples of known nuclide purity and known, preferably invariant, matrix composition, but samples of unknown composition suffer from unknown and variable quenching and background. Minimum backgrounds on beta liquid scintillation counters are usually of the order of 10 to 20 counts per minute (cpm) making this the approximate lower limit of detection with this equipment under the best conditions. Uncertainties in counting alphas by liquid scintillation methods due to background and quenching are much greater with samples of unknown composition. Although some standardization of sample composition can be effected by chemical pretreatment, this is not a practical solution in all cases or for all problems associated with alpha counting using beta liquid scintillation methods.

In addition to the variable quenching and background problems of beta liquid scintillation spectrometers, the alpha energy resolution encountered with such instruments is generally poor, and methods of improving energy resolution by liquid scintillation were sought. This quest has resulted in considerable success and has led to the development of detectors and electronics designed especially for alpha liquid scintillation spectrometry. Using such equipment it has been demonstrated(5-7) that useful alpha energy spectra can be obtained, although the energy resolution is not equal to that possible with surface barrier detectors and gridded ion chambers using properly prepared samples. Figure 1 shows the alpha spectrum of ^{232}Th and its daughters (not in secular equilibrium) obtained by the use of equipment and methods for alpha liquid scintillation spectrometry of the type to be described in later sections of this monograph.

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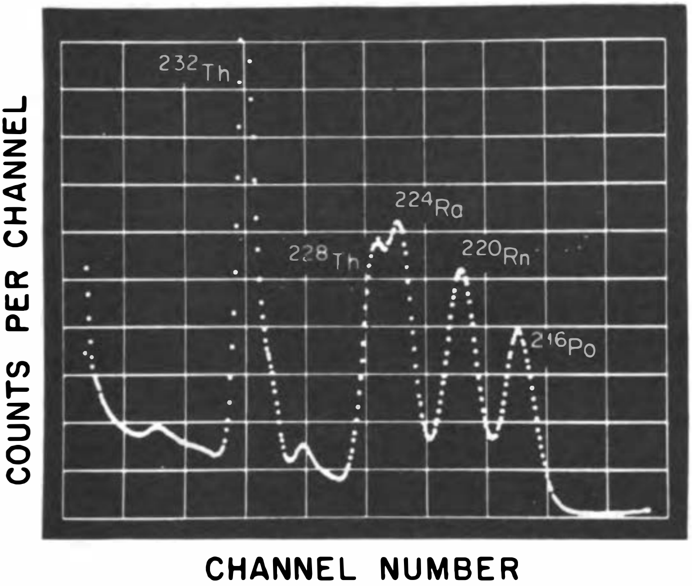

Fig. 1. Spectrum of ^{232}Th and Daughters (not at equilibrium) from an Alpha Liquid Scintillation Spectrometer. A small peak for ^{230}Th is visible to the right of the ^{232}Th peak (From Ref. 18).

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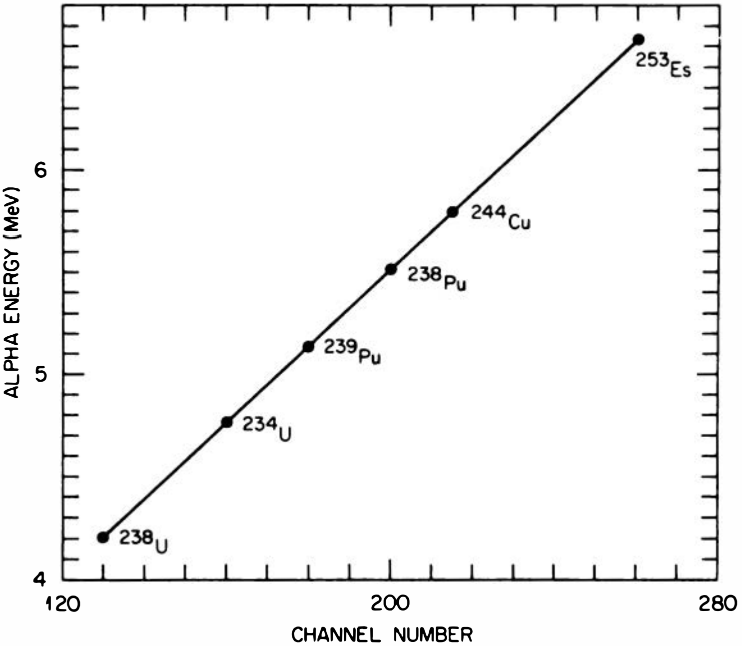

Fig. 2. Alpha Liquid Scintillation Spectrometer Calibration. Peak width at half maximum is about 200 keV at 4 MeV, 300 kev at 6 MeV.

With appropriate detectors and electronics the light output (and alpha peak position) of a liquid scintillator has been shown to be directly proportional to alpha energy to a useful degree over the range 4 to 7 MeV, an energy range that includes the alpha energies of most of the common nuclides (see Fig. 2),(6-8) providing the sample/scintillator mixture is of constant composition. The use of an organic-phase-soluble complex to introduce the alpha-emitting nuclide to the scintillator provides a method of assuring constant sample composition even though the original sample matrices may be very different and also allows a sample having advantages in energy resolution.(6-9) Even better energy resolution results from the use of an all-organic scintillator containing no aqueous-phase-accepting components but containing a solvent extraction or phase-transfer reagent. Thus, the nuclide can be introduced to the scintillator via liquid-liquid extraction techniques.(5-7, 10, 11)

The use of a sample of optimum size has been shown to be desirable for effective alpha energy resolution(6, 7, 12) along with efficient light collection and reflection to the phototube. Also, minimization of refractive index interfaces in the light collection system contribute markedly to the ability to obtain useful energy resolution.(5-7, 12-14)

Because of the fact that beta and gamma radiation also produce light in liquid scintillation systems, and more effectively than does alpha radiation, the background contribution from accompanying beta-gamma radiation, from beta-gamma emitting nuclides inadvertently incorporated into the scintillator with the alpha nuclide, and from gamma radiation from external sources has always been a serious problem in alpha liquid scintillation methods. Resulting beta-gamma backgrounds are variable, and reliable methods of predicting and subtracting them are not available. Chemical separations of unwanted nuclides and graphic or computer-aided stripping of the beta- and gamma-produced continuum from the alpha peak are both useful aids in dealing with beta-gamma background, but effective use of liquid scintillation for low-level counting was not possible until methods of electronically discriminating between beta- and gamma-produced pulses and alpha-produced pulses and rejecting the former were developed.(13, 15-17) Electronic pulse-shape discrimination allows controlled background count levels approaching those attainable with surface-barrier detectors.

A variety of levels of sophistication in alpha counting and spectrometry are possible using the developments referred to above. With beta liquid scintillation equipment and methods, energy resolution of about 1.0 MeV full peak width at half maximum height (FWHM) and a lower limit of detection of about 10 cpm is possible. With detectors and electronics designed for alpha liquid scintillation work, energy resolution of about 250 keV FWHM (for a 5 MeV alpha) and a lower limit of detection of 1 cpm is currently attainable. The addition of electronic pulse-shape discrimination allows the limit of detection to be lowered to 0.01 cpm or lower. These methods, and the results obtainable from them, will be examined in more detail in Sect. III of this monograph.

The material in the following sections is intended to be a practical introduction and guide to the use of liquid scintillation for alpha counting and spectrometry. Other works devoted to the development of the theory of liquid scintillation exist (see for example Refs. 19-21) and a minimum of such material is repeated here. Much remains to be learned and many improvements remain to be made in the use of liquid scintillation for alpha counting and spectrometry. It is hoped that this modest work will encourage others to continue development in the field.

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II. FACTORS INFLUENCING THE EFFECTIVENESS OF LIQUID SCINTILLATION FOR ALPHA SPECTROMETRY

A. RADIATION INTERACTION WITH THE SCINTILLATOR

The scintillator, basically a solution of a fluor in an organic solvent, responds differently to alpha radiation than to beta or gamma radiation. Ionizing radiation passing through a liquid scintillator leaves a trail of excited molecules, ionized molecules, radicals, and molecular fragments. Interactions are primarily with solvent molecules since they comprise by far the largest mole fraction in the solution and therefore the largest fraction of molecules in the path of the radiation. As soon as the ionized trail is produced in the solution, processes begin that dissipate the deposited energy. These include ion recombinations, ion-molecule reactions, and energy transfer. Energy transfer can be to a molecule that emits light (either directly or indirectly through other molecules) or to molecules that dissipate energy in nonradiative processes such as molecular vibration. Excited molecules can exist in any of several energy levels depending on the kind and degree of electron promotion, and these are referred to as S_1, S_2, S_3, etc. in order of increasing excitation.

1. Differences Due to Type of Radiation

The type of excitation produced and the density of the ionized molecules or fragments produced is different(1) for the different kinds of ionizing radiation. Beta and gamma radiation tend to produce excited or ionized molecules while alpha radiation tends to produce more radicals and molecular fragments. The specific ionization (number of ions produced per unit path-length) for gamma radiation and beta particles is much lower than is that of alpha particles. The path length within the scintillator for penetrating gamma radiation is usually determined by the boundaries of the sample container. The path length for 0.48 MeV beta particles (electrons) in the scintillator is approximately 1650 micrometers and that for 5.0 MeV alpha particles is approximately 50 micrometers. Gamma radiation and beta particles produce mainly singlet (S_1) excited molecules whereas alpha particles produce a larger proportion of triplet excited (S_3) molecules and other charged molecular fragments and ions. Triplet-excited molecules, molecular fragments, and ions discharge their energy more slowly than do singlet-excited molecules. The process appears to be diffusion controlled and requires 200 to 300 nsec while energy discharge by singlet-excited molecules requires only 1 to 2 nsec. These effects result in a situation in which a much larger part of the energy produced by alpha particles is lost to nonradiative processes than of that produced by beta or gamma radiation. Losses of this type have been referred to as "dynamic quenching". (2,3)

The phenomena referred to above produce two effects that are important in alpha liquid scintillation methods. First, the light-output/particle-energy relationship is different for the different radiation types. Gamma radiation and most beta particles are more effective in producing light than alpha particles. If we compare a 5 MeV alpha and a 0.5 MeV beta, we find that they produce about the same amount of light in a liquid scintillator (Fig. 3). Second, the durations and shapes of alpha-produced light pulses

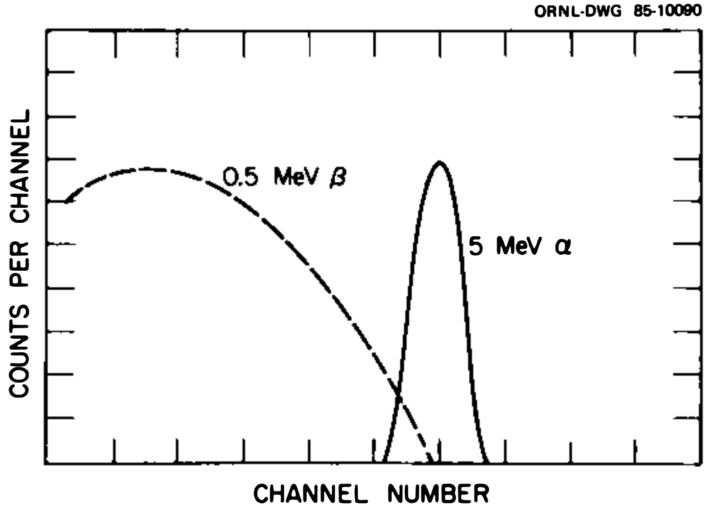

Fig. 3. Comparison of the Spectra Produced by a 5.0 MeV Alpha and a 0.5 MeV Beta.

are different from those produced by beta and gamma radiation. The alpha-produced pulse dies away and returns to zero more slowly than the beta- or gamma-produced pulse. This latter difference allows electronic discrimination between alpha-produced and beta- or gamma-produced pulses, a very important capability in alpha liquid scintillation spectrometry. It should be noted, however, that below about 200 keV the efficiency of light production by beta particles decreases (see Sect. 5 below). Thus the interference from low-energy betas and conversion electrons is not as severe as it otherwise might be.

2. Energy Transfer to Fluor

After production of the ionized material by the charged particle, the energy of ionization, initially largely in the solvent molecules, must be transferred to the fluor molecules where light can be produced. Although energy transfer can occur directly from solvent to fluor, the addition of a substance containing a high concentration of π electrons, such as naphthalene, improves the efficiency of energy transfer. Even with an energy transfer promoter, the total energy transfer is only a small fraction of that deposited in the scintillator. The energy output as light amounts to only about 0.04% of the total energy deposited by beta or gamma radiation in the 0.4 to 0.7 MeV energy range or 0.004% of that deposited by alpha radiation in the 4 to 7 MeV alpha range.

Gamma energy: Because of the difference in interaction and light production by the three types of radiation, the effective pulse-height distribution produced by each is different. Penetrating gamma radiation deposits a quantity of energy depending on the gamma-ray path length and energy. Low energy gammas deposit a larger fraction of their energy in the scintillator than do high energy gammas. The general type of pulse-height (energy) spectrum produced in a liquid scintillator by gamma energy is shown in Fig. 4a. The exact shape of the curve will depend on the energy distribution of the gamma source and whether it is internal or external to the scintillator, that is, the amount of energy absorbed before it reaches the scintillator; but the general shape is that shown, and the entire range of ordinary alpha energy response is covered.

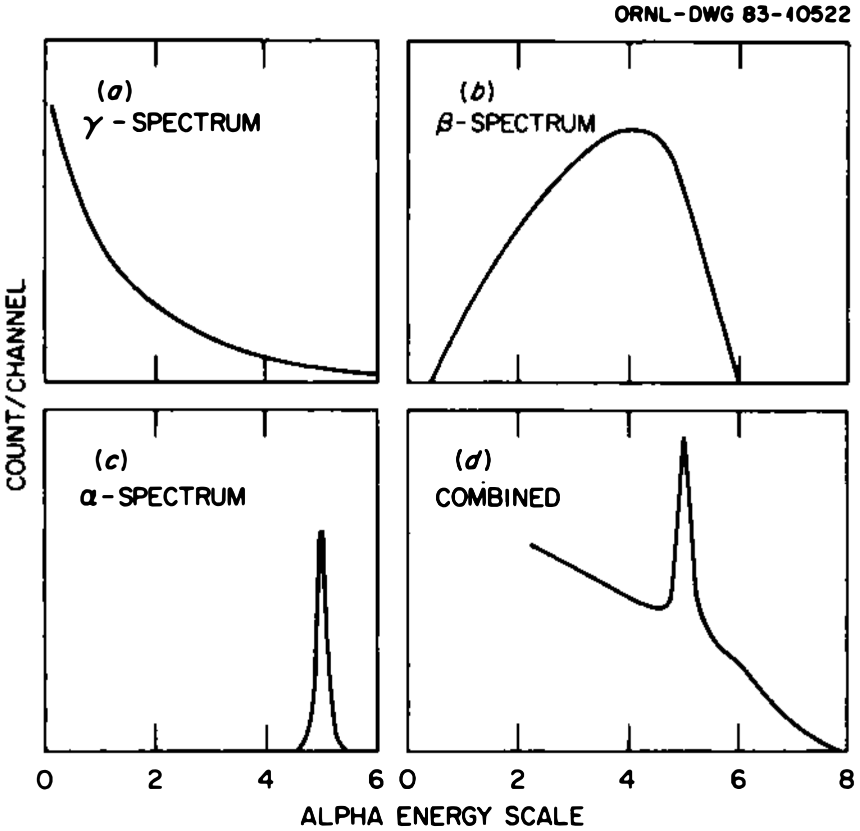

Fig. 4. The Spectra Produced in a Liquid Scintillator by: (a) Gamma Radiation, (b) Beta Radiation, ~0.6 MeV, (c) Alpha Radiation, ~5.0 MeV and, (d) All the above in the Same Sample

Beta energy is usually completely absorbed within the scintillator and its container. The light output is proportional to the beta energy within the range of energies of usual interest; thus, a meaningful energy or pulse-height spectrum is obtained; however, the energy distribution for individual betas is from zero to its maximum energy producing a pulse-height spectrum like that shown in Fig. 4b. Some beta pulses are always of such low energy that they do not produce sufficient light to be detected by the phototube; thus, the spectrum falls to zero before zero beta energy is reached. Note that the scale on the abscissa covers 0 to 6 MeV alpha energy response, and we have shown the spectrum produced by a 0.6 MeV beta. Thus, as was the case with the gamma-produced spectrum, the alpha response region is covered.

Alpha energy is also completely dissipated within the scintillator and its container, and as was noted in the introduction, the pulse-height in an alpha liquid scintillation spectrometer is proportional to the alpha energy in the energy range of the common alpha-emitting nuclides within experimental accuracy of the detection system. All of the alpha decays that occur *in the scintillator* are detected. Some of the alpha decays that occur within 50 micrometers of the sample vessel wall and go toward the wall will deposit some or all of their energy in the glass. The magnitude of this "wall effect" has been estimated for various size containers. For a 1.5 cm diameter vessel with 1 cm depth of scintillator, a partial and total energy loss of 0.4% of the alphas has been estimated.(4) For smaller containers, ~8 mm in diameter by 2 cm high, the wall effect can be estimated at 0.6%; however, some of these events are found in the low-energy tail of the alpha peak, and these can be included by integrating that tail. Ihle(4) has reported experimental wall losses less than 0.1%. At Oak Ridge an attempt was made to determine the experimental wall loss using a Bureau of Standards sample of U_3O_8 (Standard Reference Material 950b). Six separate weighed aliquots of a gravimetrically prepared solution of this standard were equilibrated with an extractive scintillator (see Sect. III C) in the vessel shown in Fig. 19. The results of the average of the 6 samples was 0.32% less than the standard value given. The standard deviation of this set of samples was 0.058% of their mean. The accuracy with which the standard sample value was known was given as ±0.02%. Taking a linear combination of the uncertainty of both the standard and the counting indicates that between 0.31% and 0.46% of the counts are lost in collisions with the wall of the sample tube. This gives an efficiency of counting between 99.69% and 99.54%. Using the mean of both the standard and experimental values gives a counting efficiency of 99.68%.

3. Alpha Energy Resolution

On Fig. 4c the liquid scintillation spectrum of a hypothetical 5 MeV alpha is plotted as it would appear on an alpha liquid scintillation spectrometer. The full peak width at half maximum height (FWHM) shown here is 250 keV, a degree of alpha energy resolution attainable with presently available scintillators, phototubes, and electronics. It is not known whether this is the ultimate resolution possible with liquid scintillators or not, but it is about the best obtained by several workers.(5-8) Further, it is not certain what factors limit the attainable resolution. Percentage-wise, the 200 to 300 keV resolution for 4.0 to 6.0 MeV alpha radiation is slightly better than that attainable for gamma radiation with a sodium iodide crystal and phototube suggesting that the reproducibility of the phototube output for a given light input determines the peak width. The characteristics of the phototube that may limit pulse reproducibility for a given amount of light are photocathode nonuniformity and the statistical scatter of size of the electron cascade initiated by photons striking the photocathode. The latter is known to be an important factor limiting the intrinsic response variations in the phototube.(9) These considerations suggest that better resolution could be obtained with a more sensitive photocathode despite the fact that the extra sensitivity is not needed for detection of the large, alpha-produced light pulse. They also suggest that the development of a photocathode of more uniform sensitivity would allow improved resolution. Gamma, X-ray, and conversion electron (see 5 below) radiation in coincidence with alpha pulses can change the shape of the observed alpha peak somewhat and affect the FWHM slightly, usually less than 10%. Peak position appears to be affected very little.

4. Composite Spectrum

The different interactions of the three types of radiation with the liquid scintillator that are described above produce an effect that is very unfortunate for alpha spectrometry by liquid scintillation. Fig. 4d shows the effect of combining in one scintillator-sample a gamma emitter, a beta emitter, and an alpha emitter. The alpha peak now sits atop of what may be called a beta-gamma continuum. This phenomenon is the origin of serious beta-gamma interference with alpha counting and spectrometry by liquid scintillation methods and is perhaps their most serious single problem. Methods of dealing with this problem will be described later.

5. Conversion Electrons

In the majority of alpha-emitting nuclides not all of the alpha emissions are of sufficient energy to leave the daughter nuclide immediately in the ground state (see Appendix iv). Thus, most alpha spectra consist of a group of alpha energies that differ by a few KeV. These may be seen using carefully prepared samples and high-resolution surface-barrier or gridded ion chamber detectors. Typically, a small fraction of the alpha decays leave the daughter nuclide in the ground state while a much larger fraction leads to various excited states of the daughter nuclide. The excited nuclei then go to the ground state with the release of gamma radiation, conversion and Auger electrons, and x-rays. The half-lives of these excited states are very short, usually of the order of a few nanoseconds or less and thus are within the time resolution period of the scintillator and detector. Under these conditions one could expect that whatever light output resulted from the photon and electron components of the decay would be combined with that produced by the alpha decay. Since photon and electron decays produce light more effectively than do alpha particles, these summation pulses would be expected to be larger (collected in higher-energy channels of the multi-channel analyzer, MCA) than the primary (ground-state-going) alpha pulse.

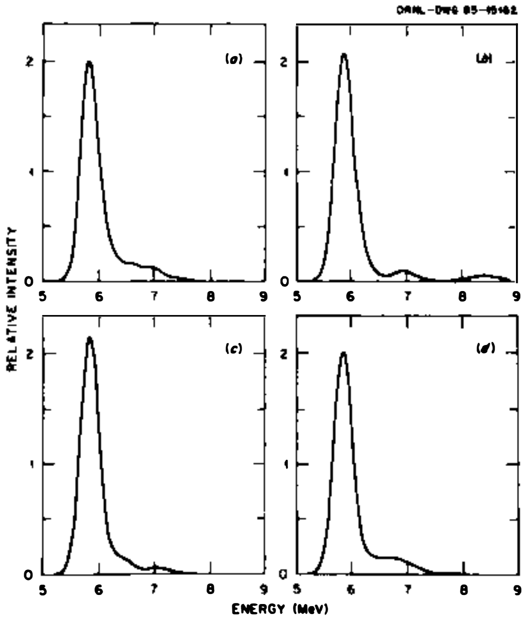

Fig. 5. Experimental and Calculated Liquid Scintillation Alpha Spectra of ^{249}Cf: a. Experimental (PERALS) spectrum. b. Calculated using a semi-theoretical model for conversion and Auger electrons, which assumes that they are as effective in light production as are beta particles (photons ignored). c. Calculated with a similar model in which the curve of (a) was used to evaluate the parameters (photons ignored). d. The same model for the electrons as in (c), with also a semi-theoretical model for gammas and x-rays, the curve of (a) again being used to evaluate the parameters.

This "conversion electron effect" would be expected to produce shoulders or tailing on the high energy side of the liquid scintillation peak. Many actual liquid scintillation alpha peaks are slightly skewed to the high energy (right) side, but it is often difficult to detect this skew by observation of the spectrum on the MCA.

Observation of actual liquid scintillation alpha spectra suggested that the light produced by conversion electrons was not as great as that which might be expected assuming the conversion electrons were as effective as beta particles in the 0.4 to 1.0 MeV energy range. The information available in the literature on the actual light-producing efficiency of low-energy electrons or betas is scant. It is known, however, that light production efficiency in anthracene decreases below 200 keV,(10) and at 1 keV the efficiency is about the same as that of a 4 MeV alpha.(11,12)

Figure 5 shows actual and calculated(13) peaks for ^{249}Cf, a nuclide in which the effect of conversion electrons is large. In this figure, the ordinate "Relative Intensity" is scaled so that the area under the peak is approximately unity. Figure 5a is the actual experimental (PERALS spectrometer) spectrum. The other three spectra were calculated from compiled(14,15) decay diagrams and data by means of a computer program written to develop the cascade of all significant paths to the ground state in terms of subdivided probability fractions and accumulated "effective energy" increments. The Guassian curve for the individual (fraction, energy)-pairs were then summed by the program to give the total peak. Figure 5b includes the calculated effects of conversion and Auger electrons (but not photons) by means of a model based on the electron/anthracene data compiled by Brooks (1956, quoted in Fig. 6.1 of Birks(16)). The satelite peaks that result from shifts of electron-affected pulses to unrealistically high energies show that the conversion and Auger electrons must be considerably less effective than "independent" beta particles in light production. It seems reasonable that the explanation for this low light-producing efficiency is the same as for alpha particles, i.e., "ionization quenching";(2,3) that is, quenching by the same high density cloud of ionized and excited molecules produced by the nearly coincident alpha particle. Since the foregoing model does not reproduce a realistic spectrum, it was modified by adjusting its parameters in an attempt to fit the actual spectrum. In Fig. 5c the ratio of light-producing effectiveness of electrons to that of alphas was taken as:

1 for $E \leq 0.001\,\mathrm{MeV}$,
$(1000E)^{0.29149}$ for $E = 0.001$ to 0.250, inclusive,
and 5 for $E \geq 0.250$.

Comparison of the resulting curve, Fig. 5c, with 5a shows that the shoulder is not high enough nor flat enough, presumably because the contribution from photons is still missing. It is almost certain that high-energy gammas escape from the small sample vial without much interaction. A model for the fraction absorbed was developed from attenuation data in water and carbon(14) and adjusted quantitatively to fit the actual spectrum:

Fraction of photons absorbed:
$= 1 - (0.67 + 0.025 \mathrm{\ in\ } E^{(L-0.8E)}, \quad E \leq 0.4\,\mathrm{MeV}$
$= 0.0085(E^{-1.86}), \quad 0.4 < E$
Effective $E_{photon} / E_{alpha} = 2.5$

where L is the mean path length within the scintillation sample; with the vial and sample size used for 5a it is estimated to be 0.43 cm. A spectrum calculated from the completed model is shown in 5d. It is considered that this model reasonably satisfactorily "postdicts" the actual spectrum.

The following general observations about the effect of conversion electrons (etc.) on alpha liquid scintillation spectra can be made:

1) For a single pure nuclide there will be no effect on the total alpha count recorded. The gamma- or electron-produced pulse either adds light to that of the "parent" alpha pulse, making no change in the count, or the light appears as separate low-energy beta-gamma-type pulses. If the latter is true it is rejected either by energy or pulse-shape discrimination.

2) The alpha liquid scintillation peak for each nuclide will have its own unique shape. While several alpha liquid scintillation curves have been

calculated, the result of these calculations must, so far, be considered tentative.(13) The semi-theoretical model developed for approximating the shape of liquid scintillation spectra has not yet been refined by fitting to a sufficient number of actual spectra.

3) It is often difficult to judge visually whether an alpha liquid scintillation peak is symmetrical or not.

4) In estimating the areas of partially merged peaks by doubling the outer half of each peak, a larger error is usually incurred in locating the peak maximum than is contributed by the peak asymmetry.

In practical analytical work we have never encountered a situation in which conversion electrons caused a problem, although it seems reasonable that shoulders like those on ^{249}Cf could be mistaken for a contaminating alpha. For analyses based on standards, it does not appear likely that conversion electron effects will produce problems. In the identification of nuclides, they could cause problems if comparison spectra of pure nuclides are not available. At present, obtaining standard spectra is hindered by difficulties in obtaining (radiometrically) pure nuclides. A program of obtaining and publishing high-resolution liquid scintillation spectra of all the alpha-emitting nuclides would be a valuable project.

The values of calculated percent peak assymmetry given in Appendix iv will be of value in the interpretation of some liquid scintillation spectra, although it should be noted that not all the calculations were done using the model tested against actual spectra. The assymmetries calculated by the simple model considering only conversion electrons will be larger than those shown by experimentally produced spectra.

B. SCINTILLATOR/SAMPLE COMPOSITION

1. Aqueous Accepting Scintillator

A great variety of liquid scintillation "cocktails" exist, their composition depending on their purpose. Aqueous-accepting scintillators generally contain alcohol or dioxane to facilitate the incorporation of aqueous samples in the toluene solution of organic fluor. Sometimes they also contain a detergent for this purpose. Such scintillators can be successfully used for alpha liquid scintillation work when aqueous samples of known composition containing a single nuclide are to be assayed. The best energy resolution is not possible with these scintillators nor is effective electronic beta-gamma discrimination possible.

2. Aqueous Immiscible Scintillators

All-organic scintillators contain no aqueous-accepting components and are therefore usually more efficient light-producers. Radionuclides must be introduced to these scintillators as organic-soluble compounds. A number of workers have introduced alpha-active nuclides to all-organic scintillators as complexes with compounds normally used as liquid-liquid extraction reagents.(4-8, 17-19) Examples of such organic-phase soluble complexers are bis(2-ethylhexyl)phosphoric acid, trioctylphosphine oxide, various high molecular weight amine salts, and high molecular weight branched carboxylic acids.

A further development arising naturally from introducing nuclides into the scintillator via extractants was to include the extractant as part of the scintillator solution.(5,20-23) This allows extraction of the nuclide directly into the scintillator from an aqueous sample. Such extractions can be quantitative, can concentrate the nuclide 10-fold or more, and can often be reasonably selective for the nuclides or group of nuclides of interest. These effects allow reduction of background and/or quenching problems and permit increased sensitivity of nuclide detection.

Quenching: In any sample-containing scintillator solution, any of the components in the mixture can profoundly affect its light-producing characteristics. In the scintillator solution, energy is first imparted to the solvent molecules by ionizing radiation and then must be transferred to the fluor, and the fluor must emit light which must leave the sample and act upon the photocathode of the multiplier phototube to produce the pulse that is counted. Quenching, as the term is commonly used, refers to interference with any of the steps of energy transfer. Some, but not all, of the ways in which this can occur are:

1) the solvent molecule fails to transfer energy to the scintillator;

2) the excited scintillator transfers its energy to a non-light-producing molecule;

3) the light is absorbed in the solution before it can reach the phototube. (Processes 1 and 2 can be called chemical quenching while process 3) can be called color quenching.)

4) energy transfer is interferred with by a high concentration of ionized or fragmented molecules. This has been referred to as "dynamic or ionization quenching.(2,3,16)

A fifth kind of quenching, less commonly mentioned, may be called "inclusion quenching" and occurs when radioactive atoms are included inside solid particulate or colloidal material. This phenomenon does not occur often but can result in count loss in alpha as well as beta counting. It should be suspected when alpha counting does not approach very close to 100% efficiency. All of the other quenching mechanisms result only in a shift of the alpha peak to the left on the energy or pulse-height scale.

Interference with energy transfer to the fluor, light production by the fluor, or light transmission to the phototube by the extractants themselves can be minimal. In general, cation exchangers such as alkyl/aryl phosphoric and carboxylic acids produce almost negligible quenching effects, amine sulfates are low quenchers, but amine nitrates and chlorides are very severe quenchers. The quenching properties of neutral extractants such as tributyl phosphate and trioctylphosphine oxide depend strongly on the aqueous medium from which the extraction is made since they extract acids; and if that medium is acid nitrate or chloride, these acid anions introduced to the scintillator can cause severe quenching. Fig. 6(24) shows the quenching characteristics of several useful extractants.

Water, oxygen, heavy metals, most chlorine-containing compounds, and many oxygen-containing compounds are usually called chemical quenchers; colored compounds, especially blue and uv absorbers, are color quenchers. In addition to causing a decrease in light output, most chemical quenchers affect the light pulse duration and tend to shorten the pulses and decrease the difference between beta- and gamma-produced pulses and alpha-produced pulses. This occurs partly because the triplet-excited molecules interact preferentially with quenching molecules because of their long half-life. Thus, chemical quenching is detrimental to any attempt to separate alpha from beta-gamma pulses by pulse-shape discrimination.

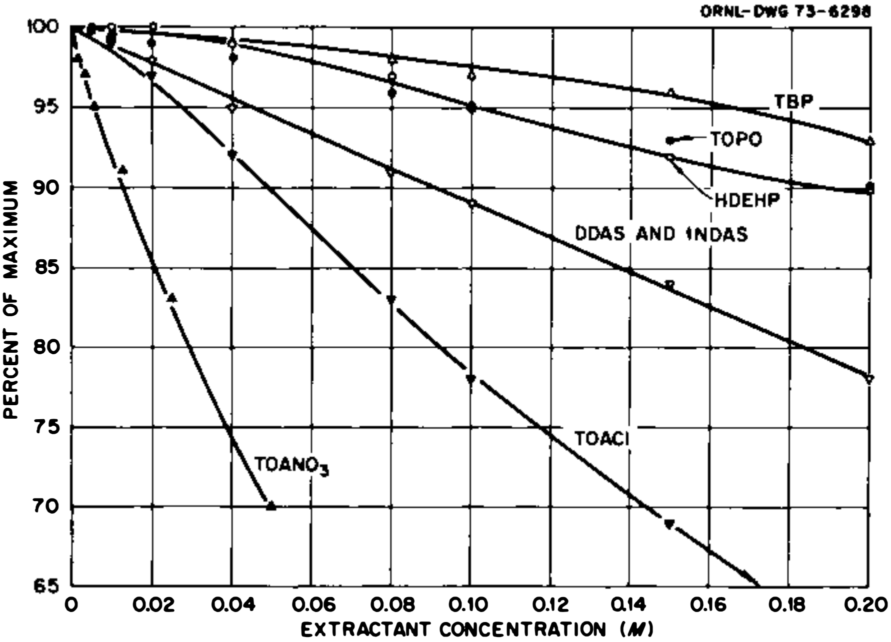

Fig. 6. The Quenching Effect of Various Extractants: TBP = tributylphosphate, TOPO = trioctylphosphine oxide, DDAS = didecylamine sulfate, 1NDS = 1-nonyldecylamine sulfate, TOACl = trioctylamine chloride, and $TOANO_3$ = trioctylamine nitrate.

In alpha counting and spectrometry by liquid scintillation, quenching usually does not result in a loss of counts as it does in beta counting (although this can happen in very severe chemical and color quenching and in inclusion quenching); but the light output, and consequently the pulse-height response, of the scintillator is decreased, and in addition, the alpha energy resolution and pulse-shape resolution capabilities of the scintillator are decreased. Thus in order to obtain the maximum amount of information (pulse-height and pulse-shape) from the scintillator, the amount of quenching substances in a scintillator should be kept to an absolute minimum.

3. Effects of Fluors

The quantity of useful light produced by a scintillator for a given alpha energy is strongly dependent on the type of fluor and its concentration. Increasing the concentration of the fluor increases the light output up to a point, after which adding additional fluor often results in less light production, an effect usually attributed to self quenching by the fluor (see Fig. 7).(25) The relative light-producing efficiency of several scintillators,(26) with and without naphthalene present as an energy transfer promoter is indicated by relative peak position in Table 1. These comparisons were all made at the same instrument gain settings. Thus, these numbers are a direct measure of the relative light production by the various scintillators and have a direct relationship to the energy resolution obtainable with that scintillator since energy resolution is directly proportional to the square root of the quantity of light collected by the phototube (see following section). A somewhat more direct measure of differences in resolution produced by

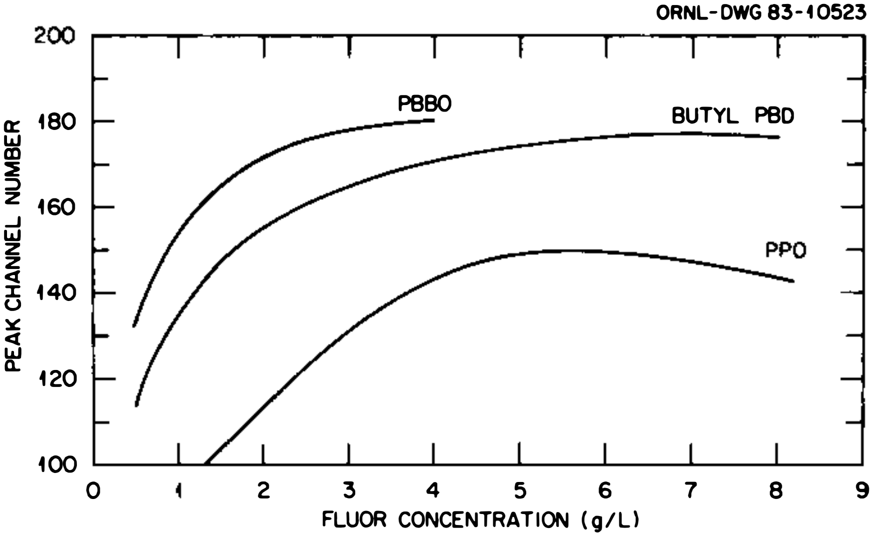

Fig. 7. Relative Pulse-Height Produced by Three Scintillators as a Function of Scintillator (Fluor) Concentration: The nuclide used was ^{233}U.

TABLE 1

Peak Position and Peak Separation Comparison for some Commercially Available Fluors based on $^{238-234}U$ Alpha Peaks

Fluor	Normalized Relative Peak Position (Ch. No.)	Peak/Valley Height Ratio
For Fluor alone (4 g/L) in Toluene		
PBBO	2.82	2.70
Butyl PBD	2.76	2.61
PBD	2.76	2.60
PPO	2.82	2.11
αNPO	2.00	2.27
BBOT	1.71	1.72
POPOP	1.00	1.30
Bis MSA	1.59	1.62
DPA	1.23	1.35
For Fluor (4g/L) + Naphthalene (200 g/L) in Toluene		
PBBO	3.18	3.78
Butyl PBD	2.53	2.83
PBD	2.12	1.91
PPO	2.47	2.50
αNPO	2.41	2.51
BBOT	2.29	2.61
POPOP	2.41	2.76
Bis MSA	1.71	1.73
DPA	1.71	1.73

the various scintillators is the peak to valley height ratio in the spectra. These ratios are also shown in Table 1. This work was done about 15 years ago, and it is possible that more effective fluors now exist.

4. Energy Transfer Agents

The addition of naphthalene, substituted naphthalenes, and similar aromatic compounds to the scintillator solution increases the efficiency of the transfer of energy from the solvent to the fluor. In the case of naphthalene, the light output of the scintillator solution (at constant instrument gain) increases up to saturation (Fig. 8). From the relationship between light intensity and resolution (see Sect. C), an increase in resolution with increased

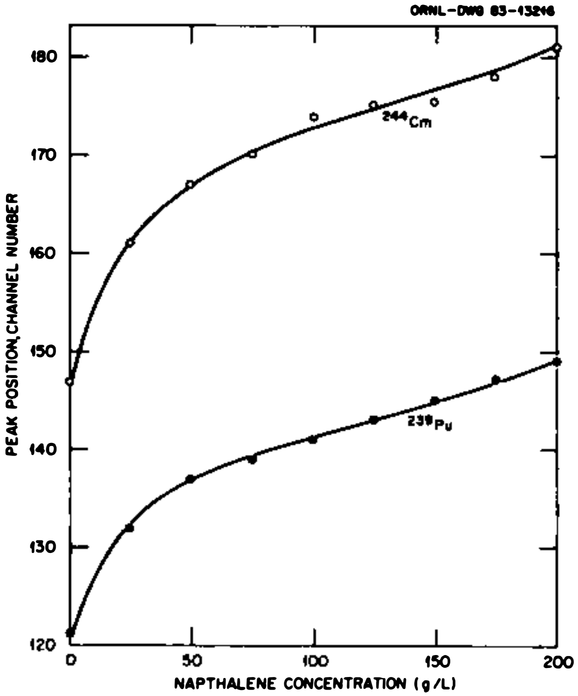

Fig. 8. The Effect of Naphthalene on the Light Output of a Fluor

light intensity would be expected. There is a small increase in peak separation varying from 26 channels with no naphthalene to about 33 channels at high naphthalene concentration; however, it is not possible to attribute this increase in peak separation solely to a resolution increase since there is an overall increase in gain that can also produce increased peak separation. There does, however, also appear to be an improvement in the ability to resolve alpha pulses from beta and gamma pulses due to the naphthalene. The time spectra shown in Fig. 9 show the time separation in a scintillator without naphthalene (Fig. 9a) compared with one containing 200 g/L of naphthalene (Fig. 9b).

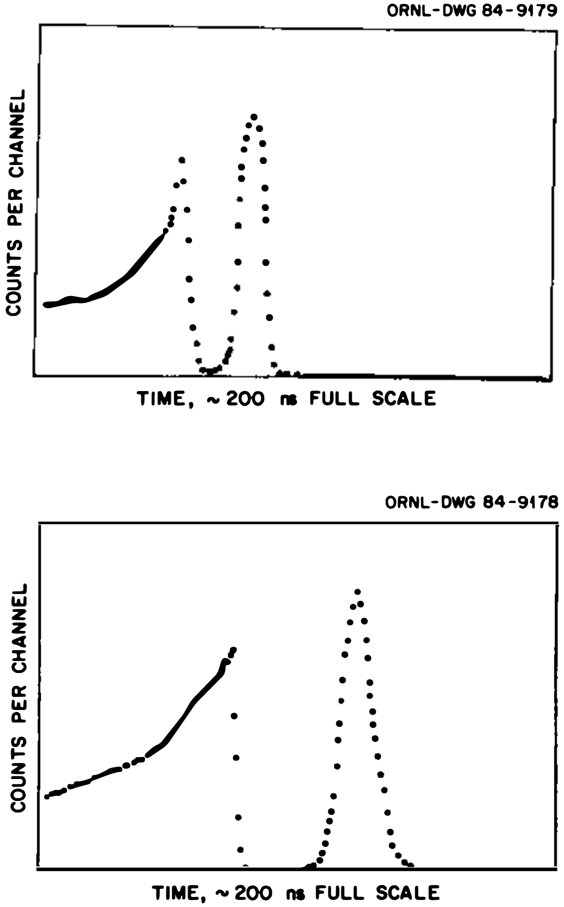

Fig. 9. The Effect on Pulse-Shape (Time) Resolution due to Naphthalene Concentration in the Scintillator. a. No naphthalene in the scintillator, b. 200g/L in scintillator.

It should be remembered, however, that under the best conditions, the overall transfer of energy from the ionizing radiation to the fluor is not efficient; and the factor of approximately 10 in the efficiency of light production by betas and gammas over that by alphas remains a serious problem in liquid scintillation counting in that alpha, beta, and gamma radiation all produce pulses that overlap in the same region (see Sect. II A). Scintillator compositions appear to have little or no effect on the ability to separate alpha pulses from beta or gamma pulses by energy resolution. As noted above, however, the addition of naphthalene does improve the ability to electronically discriminate between alpha and beta or gamma pulses on the basis of pulse duration.

5. Diluents

In general, aromatic diluents appear to be much superior to other types in liquid scintillation systems. A variety of aromatic compounds have been tested as replacements for toluene. These have included xylenes, trimethylbenzenes, and various substituted naphthalenes.(26–28) These solvents showed small improvements over distilled-in-glass toluene saturated with naphthalene in solvent and energy transfer characteristics. Since pure toluene is readily available, the advantages in improved performance have generally not been considered worth the additional expense and trouble in most practical applications.

6. Mixed Fluors

Scintillators containing mixtures of fluors that have been tested were always less effective in pulse-height response than the best single-fluor scintillators. Thus, mixed fluors are probably not an advantage in alpha liquid scintillation. Their purpose is to shift more light into the sensitive region of the phototube when the amount of light available is very small, as in tritium counting. Alpha particles produce much more light than tritium betas, and in addition, modern phototubes respond to shorter wavelength light than those that were available when most beta liquid scintillation cocktails were developed.

C. SAMPLE/REFLECTOR/PHOTOTUBE GEOMETRY

Efficient light production is not as necessary for alpha counting as for soft beta counting from the viewpoint of counting efficiency. It is relatively easy to obtain light collection sufficient to approach 100% counting efficiency with alphas; but since the energy resolution depends on the amount of light per pulse received by the phototube, according to the equation:

$$R = k\sqrt{n}$$

where n represents the number of photons collected, efficient light collection is important in liquid scintillation alpha spectra if spectra of useful resolution are to be obtained. Thus, in order to obtain the best energy resolution in liquid scintillation an efficient scintillator and reflector are necessary.

1. Phototube Characteristics and Positioning

Commercial beta liquid scintillation equipment usually has dual phototubes facing each other with the sample supported between them (Fig. 10).

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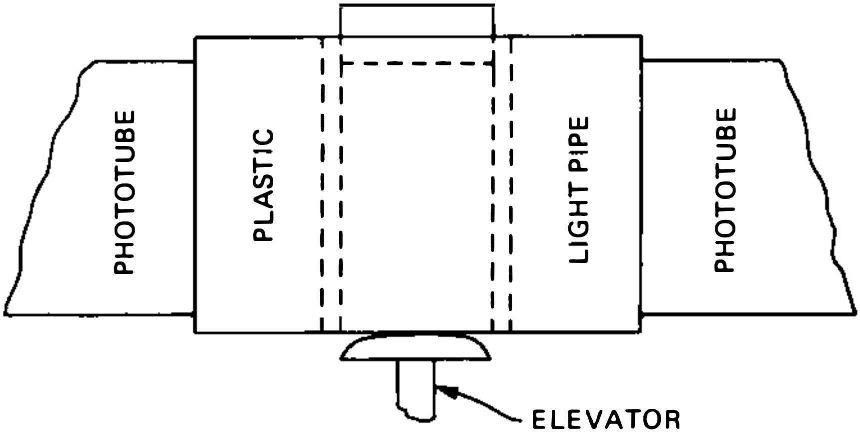

Fig. 10. The Usual Sample/Phototube Arrangement in a Beta Liquid Scintillation Spectrometer

A clear plastic material commonly serves as a light pipe between the sample and the phototubes, and sample changing mechanisms usually necessitate an air gap between the light pipe and the sample vial. Refractive index discontinuities with the attendant light refraction and scattering at these points causes the loss of some light resulting in broadening of line width and loss of pulse-shape information. These losses do not appear to cause problems in beta counting and spectrometry but do cause serious peak broadening and pulse-shape distortion if alpha spectrometry is attempted with this equipment. Numerous attempts to modify beta liquid scintillation equipment to obtain good energy and pulse-shape resolution have failed.

Whereas dual phototubes and phototube cooling are a necessity for very soft beta counting (such as tritium betas) by liquid scintillation, they are not necessary for alpha counting and spectrometry. Random, low-energy pulses produced by thermal electrons interfere with tritium counting, but such pulses lie below the pulses produced by even 3 MeV alphas. Thus a simple detector comprised of one phototube and a reflector/sample-holder appears to be quite adequate for alpha liquid scintillation spectrometry. A cross-section drawing of such an arrangement may be seen in Fig. 11.

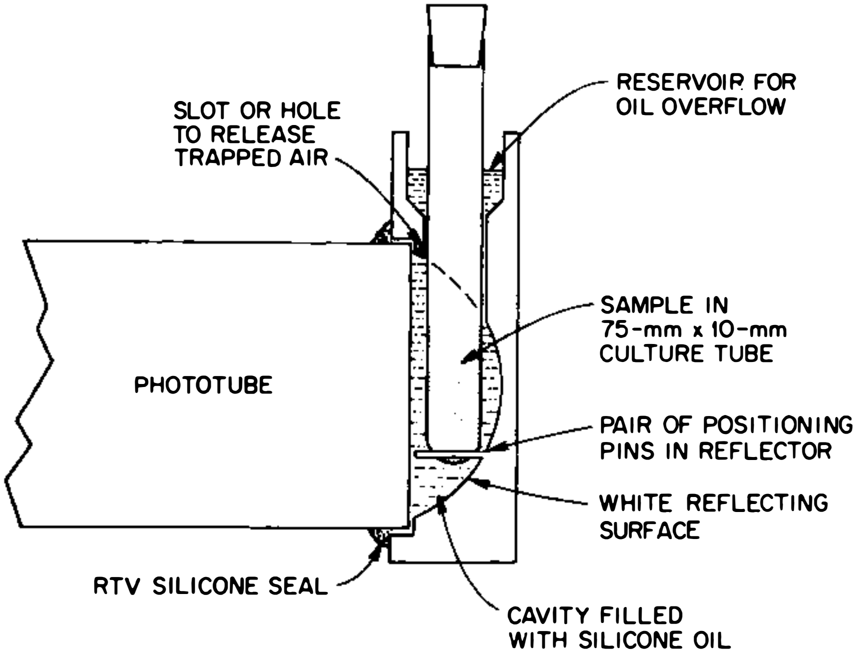

Fig. 11. Cross Section of a Single-Phototube Detector/Reflector/Sample Holder found Suitable for Alpha Liquid Scintillation Spectrometry

Two facing phototubes can be slightly more effective in light collection than a single phototube, but the difference between two phototubes and a single phototube with a well-designed reflector is very small.(29) Dual phototubes involve problems of phototube matching and summation circuits that are best avoided since they can cause degradation of spectral and timing information.

The spectral match between the light output of the fluor and the sensitivity of the phototube is also very important. As much of the fluorescence spectrum of the fluor should fall within the sensitivity curve of the phototube as possible. This is not as difficult to accomplish as formerly because of the wide spectral response of phototubes now available. Suppliers of phototubes generally provide spectral response curves for their products, and fluorescence emission curves are usually available from the vendors of fluors.

As was mentioned in Sect. A, certain characteristics of the phototube may limit pulse reproducibility and thus the resolution that the system can attain. These include the lack of photocathode uniformity and the statistical reproducibility of the electron cascade initiated by photons striking the photocathode.(9,30,31) It is possible that better resolution could be obtained with a more sensitive photocathode and by the development of a phototube with a more uniformly sensitive photocathode.

2. Reflector

In addition to the effective collection of light, the reflector for alpha liquid scintillation spectrometry appears to be required to spread light from each scintillation event as evenly as possible over the face of the phototube (photocathode area). This is necessary because the photocathode differs in response from one region to another.(7,30-32) Figure 12 shows a plot of the sensitivity of two typical 52 mm photocathodes produced by scanning with a 1.5 mm light spot. Variations in sensitivity by factors of 2 to 3 are seen. Thus, if light from an alpha event interacts primarily with a small area of the photocathode, differences in pulse-height of up to 200% are possible for the same amount of light, resulting in serious alpha peak broadening. Variations of 20 to 30% are easily seen by placing a scintillation source at various locations on the face of a phototube.

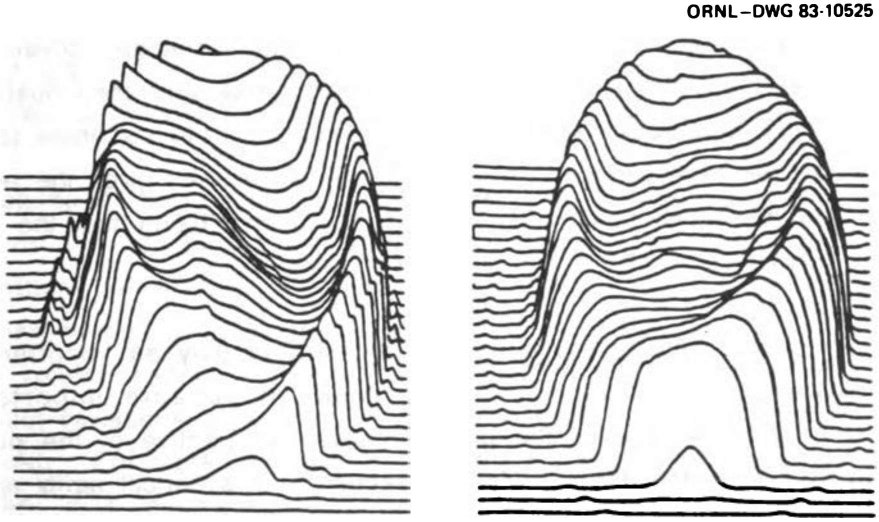

Fig. 12. Variations in Sensitivity of two Typical 52 mm Phototubes

In general, a highly reflective diffuse white surface has been found desirable for good alpha energy and pulse-height resolution. All polished specular reflectors have been found to give poorer energy resolution than diffuse white reflectors where energy resolution was a consideration. The reason for this effect probably derives from the uneven response of photocathodes and the tendency of the specular reflectors to focus light on a small area.

Tests of a variety of white reflective materials have indicated that the nature of the reflective surface is critical to good energy resolution and pulse-shape discrimination. Both magnesium oxide and barium sulfate surfaces have been found suitable when prepared from finely divided, highly purified material.(26) Barium sulfate has slightly better reflectivity and has the added advantage that a white reflective coating composed of barium sulfate in an ethyl alcohol and water vehicle with a small amount of polyester resin binder is commercially available from Eastman Organic Chemicals. This material can be sprayed onto the reflector with an air brush or similar aspirator. Three to six coats are required. Magnesium oxide surfaces can be prepared by coating the reflector with sodium silicate, covering the sodium silicate with finely powdered magnesium oxide and then dusting off the excess. This process also must be repeated four to six times to build up a suitable reflective surface. No commercial white paint gives the effective reflectivity of these two coatings, the reason probably being that the binder in most paints absorbs blue and uv light.

The shape of the reflector surface also appears to play an important role in energy and time resolution.(26,32) Again it appears important to spread the light evenly over the photocathode irrespective of the position of the alpha event within the sample. A section of a spherical cavity appears to be a near optimum, if not a precisely optimum, reflector shape for use with a flat circular photocathode. This has been demonstrated both empirically and mathematically.(7,29,32)

3. Sample Geometry

Sample size and shape must also be considered when attempting to optimize the collection of pulse-height and pulse-shape information from alpha liquid scintillation samples. Basically the sample needs to be small enough so that light from alpha events buried most deeply in the sample will not suffer appreciable absorption on its way to the photocathode and will thus show an intensity not measurably different from that of an event very near the sample surface. A very small spherical sample volume is probably ideal for these considerations(7) but is difficult to prepare on a routine practical basis. Large samples and thin samples spread out over the phototube face suffer from light absorption and photocathode inhomogeneity problems, respectively, as would be expected. A number of sample container sizes and shapes have been tested in combination with a variety of reflector configurations. A detector-reflector arrangement like that shown in Fig. 11 appears to give optimum pulse-height and pulse-shape resolution and is consistant with the theoretical evaluation of the problem by Hanschke.(7) The use of a 10 X 75 mm pyrex culture tube is a practical compromise between an ideal small, spherical sample cell and a larger, perhaps easier-to-prepare sample. The difference in performance between a spherical sample and the 1 mL sample in the culture tube is slight, and the culture tubes are available and easy to pipette into and handle. One mL fills the tube to a depth of about 2 cm and is a convenient sample size that can be conveniently and accurately measured.

The volume of sample in a 1 mL culture tube as described above has no effect on the counting efficiency of the sample if it is less than 1.5 mL, i.e. within the area of the reflector (see Fig. 11). The pulse-height response produced by a given alpha energy is, however, affected slightly by the volume and/or the vertical positioning of the sample in the detector. Maximum variations of 9 channels (with one channel ≈ 10 keV) have been observed. For work in which accurate calibration of the energy scale is required, it is recommended that the same sample volume always be used and that a pair of 0.5 mm diameter positioning pins be installed in the reflector (and coated with reflectance material) so that the bottom of the culture tube is supported in a reproducible position and the 1 mL sample is approximately in the center of the reflector-phototube assembly.

D. ELECTRONICS/PULSE-HEIGHT (ENERGY) RESOLUTION

The light pulse produced by the interaction of the ionizing alpha, beta, or gamma radiation with the scintillator must be processed electronically in a manner to derive the desired information from it. For beta liquid scintillation counters and spectrometers, there is little need for superior energy resolution because beta spectra are broad curves from zero to e-max. Stability and reproducibility are required, but narrow peak width is not. Thus, circuits for beta liquid scintillation counting are generally stable and reproducible but are not designed for energy resolution. Similarly, since there is no need for pulse-shape information in beta counting, no provisions are made to retain and process time (or pulse-width) information. Largely because of the electronics limitations, commercial beta liquid scintillation counters are suitable for alpha counting only if: 1. the nuclide is known (as in laboratory designed experiments) or it is known from prior chemistry that only alpha emitters are present, 2. the count rate is 50 counts per minute (cpm) or greater, and 3. quenching is constant for all samples. Some attempts have been made to improve the electronics of commercial beta liquid scintillation spectrometers. These efforts have usually been limited in success in improving pulse-height (energy) resolution by the limits imposed by scintillator composition and sample-reflector-phototube geometry.(21)

The electronics requirements for optimum pulse-height resolution from a liquid scintillation detector are easily met. Standard linear amplifiers and preamplifiers in the Nuclear Instrumentation Module (NIM) configuration are available from a number of manufacturers. The units designed for gamma spectrometry with sodium iodide crystal detectors work well with liquid scintillation detectors. A bin (NIM bin) with power supply is required to operate such units. A block diagram of the interconnection of the detector, preamplifier, and linear amplifier is shown in Fig. 13.

Although this arrangement can operate a scaler alone, it is much more useful to send the amplifier output to a multichannel analyzer (MCA) with spectrum-region-integrating ability. This allows the position of the desired alpha peak to be observed and the possibility of other interferring alpha, beta, or gamma radiation to be monitored routinely as samples are run since a spectrum is collected for each sample.

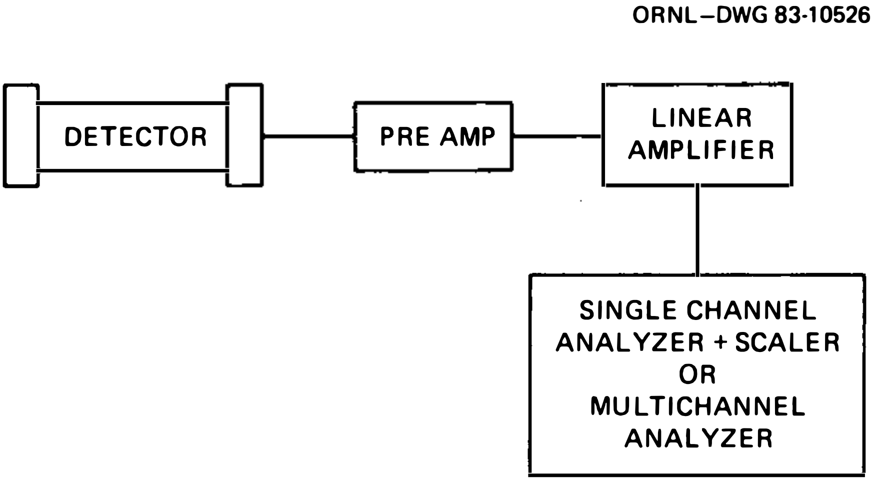

Fig. 13. Simple Arrangement for Alpha Liquid Scintillation Spectrometry (From Ref. 3)

The electronic system outlined above will allow the collection of spectra with energy resolution as good as can be produced by the detector and scintillator; however, it does not provide any ability to reject beta- or gamma-produced pulses, and spectra frequently look like that shown in Fig. 14 (see also Fig. 4d, Sect. II A) in which the alpha peak is underlain by a continuun produced by the beta and gamma radiation. If count rates are sufficiently long so that counting statistics in both the alpha peak and the beta-gamma continuum are good, the beta-gamma background may be estimated by averaging the counts per channel on each side of the peak (regions b and c in Fig. 14) and multiplying that value by the number of channels in region a. This method is described in more detail in Sect. III B.

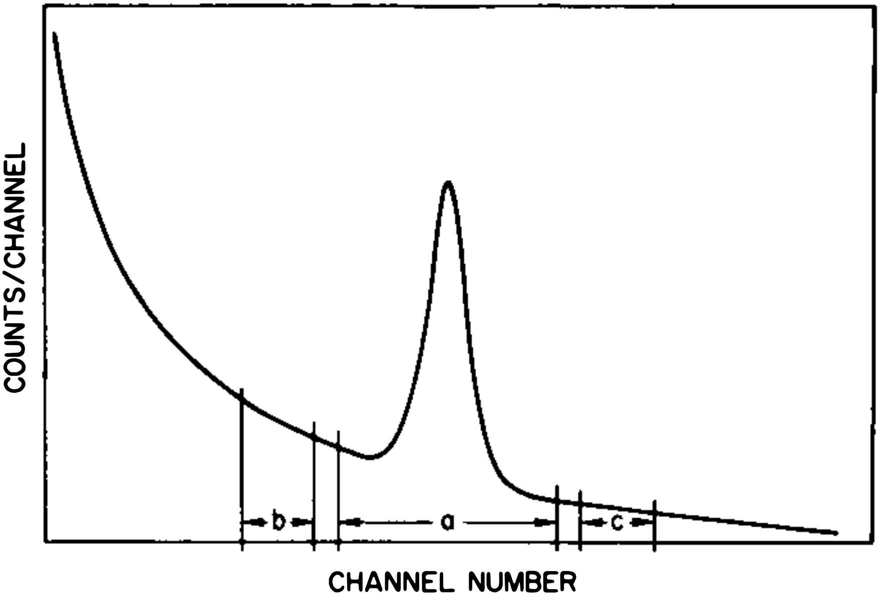

Fig. 14. A Simple Graphical Method of Estimating Beta-Gamma Background. The average count per channel in b+c is multiplied by the number of channels in a and subtracted from the total count in a.

Because beta- and gamma-produced pulses are slightly shorter in duration than alpha-produced pulses (see Fig. 21, Sect. III D), it is possible to sort the two types of pulses electronically and count whichever is desired. Electronic pulse-shape discrimination can be very efficient in rejection of beta and gamma pulses. It has been used extensively in separating neutron-produced and gamma-produced pulses and in nuclear time-of-flight experiments; so the technology is, in general, well developed. Certain modifications in electronics are necessary for efficient rejection of beta- and gamma-produced pulses from alpha spectra, and some of these will be described in Sect. III D.

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III DISCUSSION OF METHODS

A. USING BETA LIQUID SCINTILLATION INSTRUMENTATION AND AQUEOUS-ACCEPTING SCINTILLATORS FOR ALPHA COUNTING

1. Instrumentation

The commercially available instruments and aqueous-accepting scintillators that are designed for beta counting can be used without modification for alpha counting, and the results are satisfactory for certain applications. The amplifier gain on the beta liquid scintillation counter should be set at about 1/10 the setting used for ^{14}C counting. The use of an MCA on the output of the counter is extremely useful for determining if the alpha peak is in the region being counted. Such an arrangement is virtually a necessity for careful work and for situations in which quenching may vary from sample to sample. In many instruments the pulse-height output does not come through the upper and lower discriminators, so the spectral energy range observed on the MCA does not reflect the discriminator settings. The ability to visually monitor the effect of discriminator settings is very valuable; thus, it is desirable to try to acquire this capability. Usually, in such cases, it is possible to take the logic pulse sent to the scaler (often output as a "ratemeter" signal) and shape and delay it appropriately for the MCA gate input. Since these logic signals have passed the discriminators, this will allow only those pulses to record that are within the window defined by the discriminators.

2. Procedures

Alpha counting in a beta liquid scintillation spectrometer is most useful where samples are known to contain a single nuclide, the count rate is relatively high (> 50 cpm), and the sample matrix is relatively free of quenchers and of constant composition. Assuming that the gain and windows are set correctly on the counter, the procedure for alpha counting with beta liquid scintillation equipment is essentially the same as beta counting; a sample in solution is pipetted into the scintillation vial, the scintillator added, the vial is shaken and then placed in the counter and counted. Adding a known amount of the same alpha emitting nuclide and recounting is usually a reliable method of checking for count loss due to quenching. The simplicity of this procedure makes it very attractive, and it can be used effectively in a variety of situations especially for samples generated in laboratory research projects. Under ideal conditions counting accuracy is better than that of plate-counting methods. Accuracy of alpha counting by liquid scintillation methods is often limited only by counting statistics. Errors due to sample placement and sample self absorption usually do not exist. Perhaps the most useful area of application for this method of alpha counting is in the assay of samples from experimental work in the laboratory in which the identity and purity of the nuclide are known, in which the sample count rates will always be relatively high (a few hundred cpm or more), in which the half-life of the nuclide is consistent with the time-scale of the experiment, and in which daughters of the nuclide will not add background beta-gamma or (other) alpha-emitters that behave differently in the experiment.

3. Limitations

The principal limitations and disadvantages of alpha counting with beta liquid scintillation equipment and solutions are:

a. The real background count (counts recorded other than those from the alpha-emitting nuclide of interest during the sample count period) will always be high (15 to 25 cpm or more) and will vary as the quenching changes, as the amount of all other radionuclides added with the sample changes, and as the purity of the alpha nuclide changes.

b. Energy resolution ability is relatively limited. in general, resolution of 0.6 to 1 MeV FWHM can be expected.

c. Quenching resulting in a shift of the peak from a given alpha energy and possible loss of alpha counts under extreme conditions. These will vary widely with sample composition. The nitrate and chloride ions are particularly severe quenchers. Water, alcohol and acetone are among other substances commonly occuring in samples that also quench severely.

Because of the above basic limitations of alpha counting using beta liquid scintillation equipment and solutions, low count-rate samples or samples in which the identity of the nuclide is unknown cannot be assayed with much reliability. Further, the purity and decay characteristics of all nuclides counted in this way should be examined carefully for potential problems. Methods have been devised that deal with background problem to some degree,(1-4) but they are limited in what they can accomplish. In addition quenching and nuclide identification problems remain.

B. USING BETA LIQUID SCINTILLATION INSTRUMENTATION AND AN AQUEOUS-IMMISCIBLE EXTRACTIVE SCINTILLATOR

1. Methods and Advantages

Several of the problems associated with the procedure outlined in Part A above are made less severe by the use of a water-immiscible scintillator containing an extractant or phase-transfer agent to transfer the nuclide of interest into the scintillator by solvent extraction techniques followed by counting in the beta liquid scintillation spectrometer. If, for example, an extractant reasonably selective for actinides is used, the aqueous phase can generally be separated from the scintillator or allowed to remain in the scintillation vial as experimental conditions require, whichever is practical considering the aqueous sample volume. Moderate levels of beta activity in the aqueous phase have little effect on the scintillator; however, unextracted gamma activity is a problem since it can interact strongly with the scintillator and add to the background.

If the extractant is chosen so as to be more or less selective for the ion or molecule of interest, other materials that cause variable quenching or variable background can often be rejected. Also, little or no acid or water, salt or other solutes are added to the scintillator in this way, thus allowing the scintillator-sample to be more constant and reproducible in composition. Although energy resolution is not improved much due to the limitations of the equipment, energy response is more reproducible sample to sample. Thus, an alpha peak for the same nuclide can usually be expected to produce the same light-pulse response, i.e., to appear in the same place on the energy scale, in every sample. A number of workers have used the combination of extractive scintillator and beta liquid scintillation spectrometer with good results.(5-7)

2. Limitations

The limitations and disadvantages of using an extractive scintillator in combination with beta liquid scintillation spectrometer are:

a. Energy resolution ability is very limited and possibilities for identifying nuclides by energy are almost non-existent.

b. Pulse-shape discrimination between alpha and beta-gamma pulses is not possible, and a variable background due to co-extracted beta-gamma emitters and/or daughter nuclides will exist (background is always high, 10–20 cpm). This problem can be dealt with to some extent by extrapolation of the beta-gamma continuum under the alpha peak and subtraction as is seen in Fig. 14. The alpha-peak region is integrated using the same number of channels on either side of the midpoint. This is the total alpha count plus background, TC. A region of 10 to 20 channels on either side of the integrated alpha peak is then chosen (same number on each side) and integrated. The average count per channel is calculated from the sum of the counts in each side region. These two values are then averaged. This average is then multiplied by the number of channels in the region integrated for the alpha peak. This number, derived from the two side-region counts, can be used as a background count, BC. The net alpha count is then TC − BC. The statistical uncertainty of the value obtained contains the uncertainties in both the alpha region count and the side region count (used as a background) according to the equation:

$$\sigma = 1/T \sqrt{TC + BC}$$

where TC = total alpha region count (sample + background), BC = background count derived from the side regions, and T = count time. It should be remembered that such a procedure introduces additional statistical error due to the background and always requires collection of a full spectrum with integration of three areas of that spectrum.

One other limitation with this counting method occurs when samples contain relatively large amounts of non-extractable gamma emitters. In such samples, the aqueous phase must always be cleanly separated from the scintillator since this gamma activity can produce pulses in the scintillator that will record in the alpha region of the spectrum.

The procedure using an extractive scintillator in a beta liquid scintillation counter is effective for the laboratory-generated samples in which the nuclide is known but in which the matrix may vary, in other samples in which chemical separation steps (including extraction into the scintillator) give a sufficient separation and perhaps identification, and in samples in which only gross alpha is required. In all cases, the total count must be equal to or greater than the counter background (usually 10–20 cpm) and beta-gamma background contribution must be low.

C. USING ALPHA LIQUID SCINTILLATION INSTRUMENTATION AND AN AQUEOUS-IMMISCIBLE EXTRACTIVE SCINTILLATOR

The use of instrumentation designed for alpha liquid scintillation spectrometry in conjunction with a scintillator/sample of the proper composition and size will allow the collection of alpha energy spectra of useful resolution (200 to 300 keV FWHM) and improved background identification and quantification. If instrumentation (detector and electronics) designed for alpha liquid scintillation is used, it is desirable to use an "extractive" scintillator (a water immiscible organic solvent in which both a fluor and a solvent extraction or phase-transfer agent are dissolved). The use of such a scintillator allows one to place the nuclide in solution in the small volume of scintillator and to control the composition of the scintillator/sample. The scintillator/sample can thus be expected to be reproducible in both pulse-height reponse and alpha energy resolution. The combination of aqueous-accepting scintillator and alpha liquid scintillation instrumentation is not considered here because the superior performance of the extractive scintillator is necessary to obtain the advantages of the improved instrumentation.

1. Equipment

The types of detector and electronics suitable for alpha liquid scintillation spectrometry have been discussed in Sect. II C and D. The detector, complete with the light-tight enclosure, is shown in Fig. 15; and a drawing of the detector is shown in Fig. 11, Sect. II C. Appropriate electronics for connection to this detector may be seen in the block diagram in Fig. 13. The detector is not commercially available at this writing but is easily constructed. The cost of parts and material is about $500, and the cost of labor will vary but should not be more than $1000. Shop drawings are available (as report No. CAPE-2825 from: DOE Office of Scientific and Technical Information, Technical Information Center, P.O. Box 62, Oak Ridge, TN 37831). Actually, any light-tight box with a lid will serve as a detector enclosure. High voltage cut-off switches actuated by the latch and door are highly desirable as bright light can damage the phototube if it is exposed while voltage is applied.

The immersion fluid between the phototube and reflector is important in obtaining good energy resolution. A non-volatile, non-aqueous fluid with

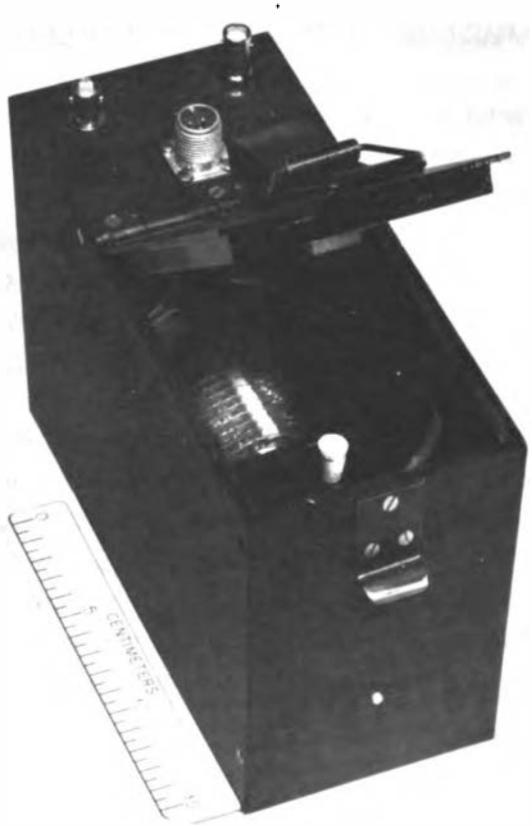

Fig. 15. A Photograph of an Alpha Liquid Scintillation Detector

uv-transmitting properties and a refractive index near that of the sample tube and phototube face is desirable for this application. Low-viscosity (50 cs.) silicone oils (polysiloxanes) and some mineral oils are suitable, although the refractive indices of mineral oils do not match that of glass as well as those of silicone oils.

A sample changer has been designed(8) for this type of detector; and other designs are no doubt possible, but a better solution to counting large numbers of samples may be to multiplex several detectors to a data collecting point, a method frequently used in plate alpha counting methods. Sample changers are not effective with low count-rate samples requiring several hours of counting, and manual sample changing of intermediate and high count-rate samples is not a serious chore. Further, observation of spectra as they accumulate can probably detect enough errors in sample preparation and instrument setting to save as much time in the long-run as does the sample changer.

2. Counting-Sample Preparation

Samples for the alpha liquid scintillation detector are best prepared by liquid-liquid extraction techniques. An aqueous solution of the nuclide up to 10 mL in volume is contacted with 1 to 1.5 mL of an extractive scintillator; and a measured volume of the scintillator, usually 1 mL, is placed in a 10 X 75 mm Pyrex culture tube for counting. An effective scintillator composition(9) is:

PBBO, [2-(4'-biphenylyl-6-phenylbenzoxazole)] - 4g
or αNPO, [2-(1-naphthyl)-5-phenyloxazole)] - 5g
Naphthalene, scintillation grade ----- 160 to 200g
Extractant - 0.1 to 0.3 gram molecular weight
Toluene or *p*-xylene, distilled in glass, to make 1 liter.

The scintillator αNPO is slightly less effective than PBBO in light production (and thus presumably in energy resolution) ability (9) but is slightly more soluble in toluene than is PBBO. The final steps in sample preparation are illustrated in Fig. 16. Equilibrations are usually carried out in a small

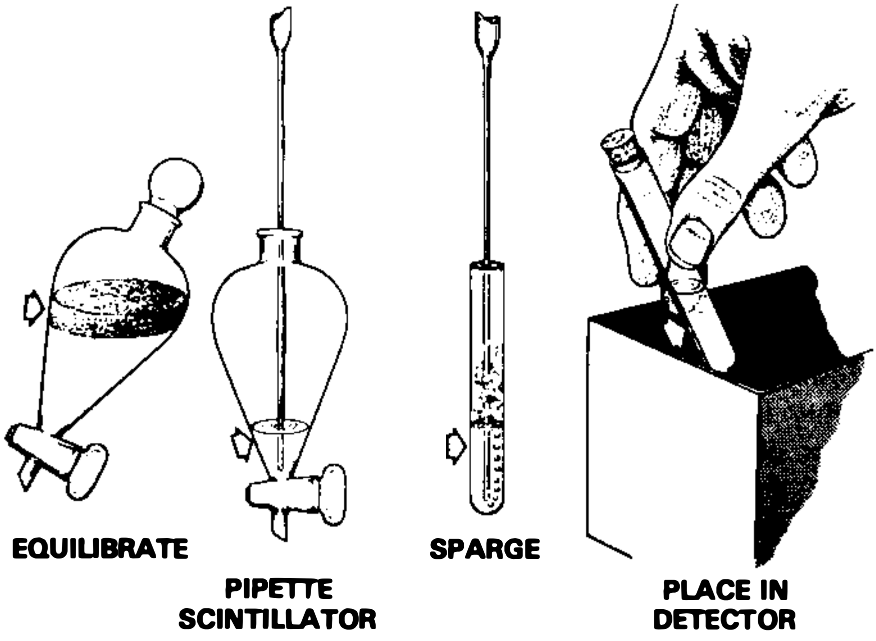

Fig. 16. The Final Steps in Preparing a Sample for Alpha Liquid Scintillation Spectrometry. The arrows indicate the extractive scintillator in the various steps.

separatory funnel, the aqueous phase drained away, the scintillator-sample transferred to a vial and then pipetted into the culture tube for deoxygenation and counting. All of the components of the extractive scintillator and the substances extracted into the scintillator should be color-free to avoid any color quenching and should be free of any substances that produce chemical quenching in order to obtain good energy resolution with the improved detector. A discussion of quenching has been given in Sect. II, but the importance of minimizing quenching in a system where alpha energy separation and identification is an object should be emphasized. Many reagents used in the extractive scintillator are available in a sufficiently pure form to use as received. Others will require purification. For most of the extraction reagents, molecular distillation using a spinning-cone molecular still is the recommended method of purification. In this type of still the substance to be distilled is heated only briefly as it is spun across the heated surface of the cone thus minimizing thermal degradation of high molecular weight compounds. Bis(2-ethylhexyl)phosphoric acid can be purified by precipitation of the copper salt(10) if it is not sufficiently pure as received.

Sparging the sample with an oxygen-free gas for 1 to 2 min is important to improve energy resolution and to allow pulse-shape discrimination (see next section). Disposable, 9-inch Pasteur pipettes make excellent sparging lances and are also very useful for the non-quantitative transfer of the scintillator and small amounts of other liquids. Any of several gases can be used for deoxygenation of the scintillator. Gases having a density near, or slightly greater than, that of air are desirable since there is a greater tendency for such gases to remain in the tube over the sample while the sparging lance is withdrawn and the culture tube is stoppered; thus, helium is not recommended. Gases that have been used successfully are argon, nitrogen, methane, carbon monoxide and acetylene. It is desirable to saturate the sparging gas with the solvent used in the scintillator, toluene or p-xylene, so that sparging will not evaporate solvent from the sample. An arrangement like that shown in Fig. 17 is suggested for this purpose. Multiple, automatic sparging units like that shown in Fig. 18 would be desirable where a large number of samples are to be prepared. Tubes that have been deoxygenated and sealed with corks covered with a thin film of RTV (room-temperature-vulcanizing) silicone sealer usually remain unchanged in their pulse-height and pulse-shape response for periods of about 24 to 48 hours. Samples sealed in glass will remain unchanged for years. A simple closure for the sample tube made of a material less permeable to oxygen than cork would be a desirable improvement.

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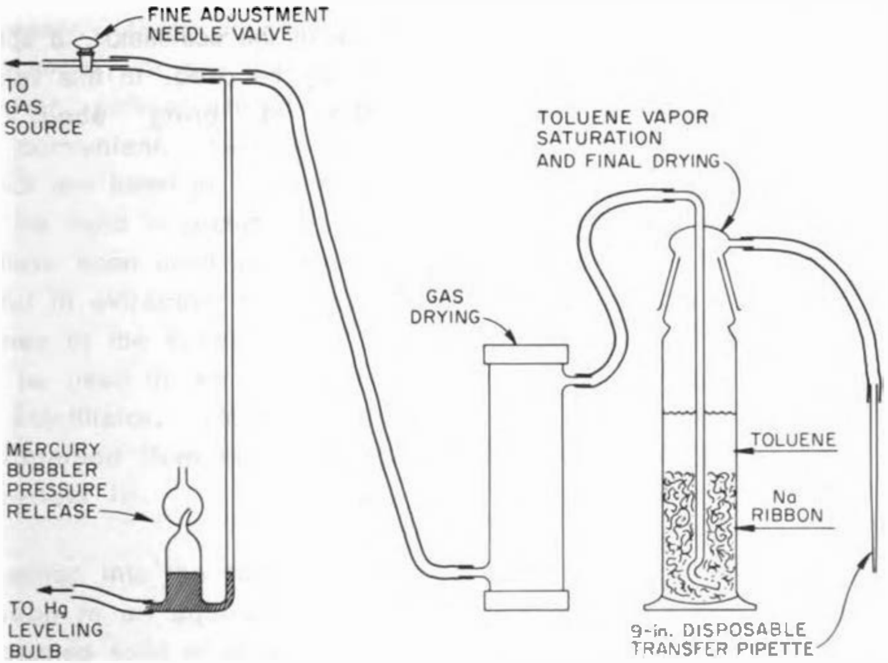

Fig. 17. An Apparatus for Drying Gas and Saturating the Gas Stream with Toluene for Deoxygenation of Liquid Scintillation Samples

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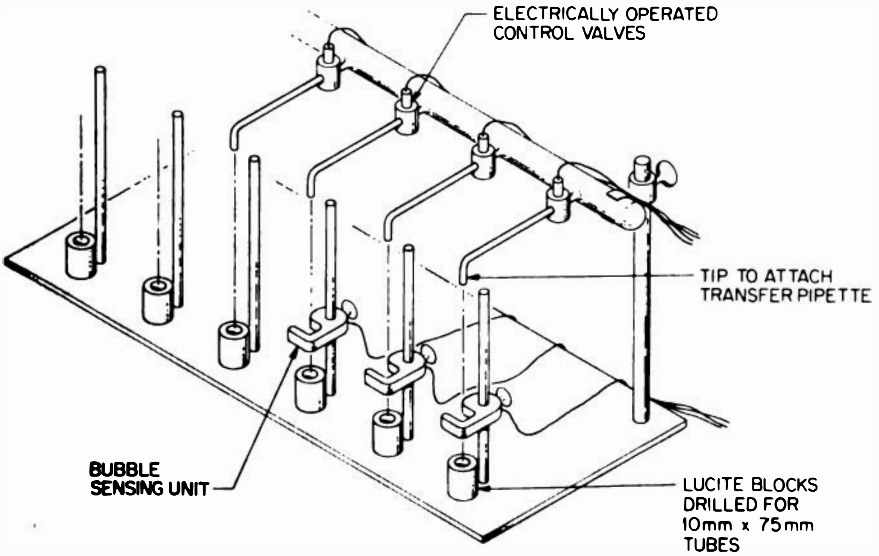

Fig. 18. A Multiple Automatic Sparging Device. The gas flow is controlled by the LED-phototube bubble-sensing device.

Where it is important to recover all of the nuclide in the scintillator, a special equilibration vessel like that shown in Fig. 19 may be used. In this vessel, the oxygen-free sparging gas is used to bring about the equilibration and deoxygenation of the sample at the same time. After equilibration, the aqueous phase is removed by connecting a hypodermic syringe to the transfer pipette that had been used as a sparging lance. Finally, the walls of the vessel and the transfer pipette are washed down with a few drops of scintillator. The vessel may be broken off just underneath the enlarged portion for counting, or an extended counting chamber can be built on the detector to accomodate the enlarged top if the procedure is to be routine. Preliminary designs have been made for such a detector. The vessel and procedure described allow the recovery of 100% of the activity in the sample and the removal of the possibility of one volumetric (pipetting) error from the procedure. Ten duplicate aliquots of a uranium-233 sample with a count rate of 42 cpm that were extracted and deoxygenated in this way gave a standard deviation of 0.42 or 1%. An automatic sparging unit, a conceptual design of which is shown in Fig. 18, could be used for the combined equilibration/deoxygenation.

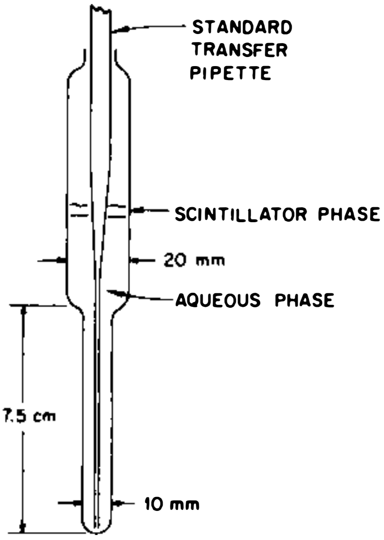

Fig. 19. A Special Vessel in which Equilibration and Deoxygenation can be Accomplished Simultaneously and in which the Sample can also be Counted.

Samples in their original solutions may or may not be suitable for direct extraction into the scintillator. In some cases preliminary separations are necessary. These preliminary separations can be precipitations, ion exchange separations, or any of the quantitative separations of analytical chemistry; however, solvent extraction techniques have been found rapid, accurate, and convenient. Several useful extractants and typical elements that they extract are listed in Table 2, Appendix i, part 5a. All the compounds listed can be used in preliminary separations, and several of them (marked with *) have been used successfully in scintillators. The extractants found most useful in extractive scintillators are bis(2-ethylhexyl)phosphoric acid, the amines in the sulfate form, and trioctyl phosphine oxide. Any extractant can be used in the scintillator so long as it does not cause quenching of the scintillator. More specific information on the use of extractants can be obtained from the literature. A list of useful references is given in Appendix iii.

Extraction into the scintillator presupposes that the nuclide is in true ionic solution in an aqueous medium. The nuclide cannot be extracted from suspended solid or colloidal material. Extractions also will not be successful in many cases if the aqueous phase contains organic (or in some cases inorganic) complexing materials. In many cases obtaining a complete ionic solution is the most difficult part of the analytical procedure; but this problem is, of course, not unique for alpha liquid scintillation procedures. All good quantitative alpha assay methods (in which the alpha is counted) require complete sample dissolution. Most standard methods of sample dissolution are applicable to this problem, and these methods can be found in standard analytical chemistry texts and references.

3. Principles of Solvent Extraction

Solvent extraction is an integral and very important part of the alpha nuclide assay scheme with liquid scintillation methods; and it is important to pay attention to the conditions under which an extractant is effective, in general and for a given substance. The concentration of the organic phase extractant is important. The distribution coefficient, D, is the ratio of the concentration of the extracted element in the organic phase to that in the aqueous phase ($[M]org/[M]aq$). It is directly dependent on the extractant concentration, sometimes on a power of the extractant concentration if more than one extractant molecule is involved in the organic phase complex. For the cation exchange extractants, such as the alkyl phosphoric acids, the equilibrium aqueous phase pH is usually an important controlling factor. The distribution coefficient, D, varies inversely with the equilibrium aqueous hydrogen ion concentration. This may be readily seen from the following equations in which HA is used to indicate an organic-phase-soluble acid.

$$M^{+i} + iHA \rightarrow MA_i + iH^+ \qquad (1)$$

The concentration quotient, Q, of this reaction is:

$$Q = \frac{[MA_i][H^+]^i}{[M^{+i}][HA]^i} \qquad (2)$$

But the ratio $[MA_i]/[M^{+i}]$ has been defined as D and thus,

$$Q = \frac{D[H^+]^i}{[HA]^i} \qquad (3)$$

or

$$D = Q[HA]^i/[H^+]^i \qquad (4)$$

In this very simple case it may be seen that D is directly proportional to the extractant concentration to the i power and inversely proportional to the hydrogen ion concentration to the i power. In many actual systems the power dependence of the extractant concentration is not i but is modified by dimerization or higher order association of the extractant and by involvment of the acid form of the extractant, HA, in the organic phase complex. The hydrogen ion dependence is usually straightforward.

Equation 4 may be rewritten to give;

$$\log D = \log Q + i\log[HA] - i\log[H+] \qquad (5)$$

from which it is seen that

$$\log D = \log Q + i\log[HA] + ipH \qquad (6)$$

Thus for each unit change in pH, D would be expected to change by a factor of 10 to the i power. Thus for the uranyl ion, UO_2^{2+}, a change of 1 pH unit would change D by 100 while for thorium or plutonium (IV) the same change would change D by 10,000.

The neutral and anionic species extractants, such as TBP, TOPO, and the amine salts, are not sensitive to pH in the same way but do suffer a decrease in extraction power with increasing acidity, generally because of the competing extraction of the acid. Reagent dependences of these extractants behave generally the same as those of the cation exchangers. Since the neutral species and anion exchange extractants extract a complex molecule or ion composed of the metal ion and aqueous anions, extraction is usually highest when the concentration of the appropriate complex ion is a maximum. This is typically 2 to 6 *M* nitrate, 4 to 8 *M* chloride, or 1 to 2 *M* sulfate. Phosphate and fluoride do not usually form complex species that are extractable. Perchlorate forms only extremely weak associations with metal ions; thus, extractions from perchlorate with neutral and anionic species extractants are not usually possible except with another complexing anion present. The neutral extractants are generally more selective than the cation exchangers, although a considerable degree of selectivity can often be obtained with the cation exchange extractants by aqueous-phase pH adjustment.

The degree to which the radionuclide is quantitatively transferred to the scintillator depends both on the value of the distribution coefficient, D, and the ratio of the extractive scintillator volume to the aqueous sample volume, V_{scint} / V_{aq}. If the phase ratio is 1, for example, a distribution coefficient of 100 will give a recovery of 99% since the concentration ratio (and the total quantity ratio) scintillator/sample will be 100/1; thus, the amount in the scintillator over the total will be 100/101 = 0.99. An equal phase ratio is not usually desirable, however, since the scintillator volume to be used is ca. 1 mL. With a sample size of 10 mL the distribution coefficient needs to be 1000 to obtain the same % recovery since the % recovery is equal to the total amount in the organic phase divided by the total amount in both phases. In terms of the distribution coefficient and volume this is:

$$\% \text{ recovery} = \frac{100DV_{org}}{DV_{org} + V_{aq}} . \qquad (7)$$

It is usually not difficult to chose an extractant and the conditions to obtain the desired recovery since extraction coefficients of over 1000, in fact over 10,000, are reasonably common for most of the actinides.

4. Advantages

The improved energy resolution obtainable with alpha spectrometry using a sample prepared via the extractive scintillator and the detector and electronics designed for alpha spectrometry is shown in Fig. 20.

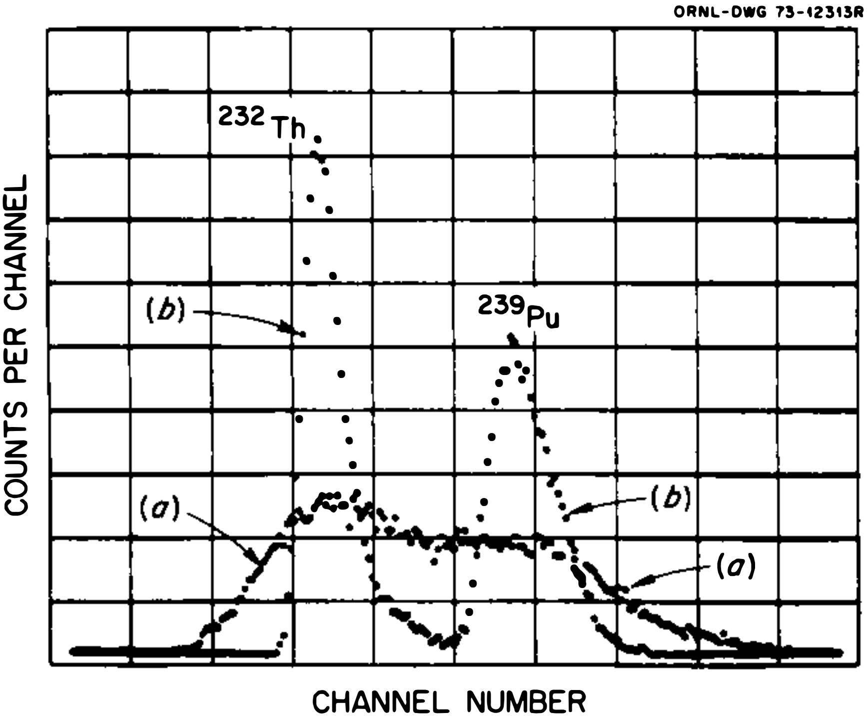

Fig. 20. A Direct Comparison on a Same-Scale Basis of Resolution Obtained by a Beta Liquid Scintillation Spectrometer (a) and an Alpha Liquid Scintillation Spectrometer (b) (From Ref. 2)

In this illustration the spectra from the alpha liquid scintillation spectrometer and a beta liquid scintillation spectrometer are directly compared on a same-scale basis. The high-performance extractive scintillator was used in both cases. The resolution with the beta liquid scintillation equipment would have been even worse if the usual aqueous-phase-accepting scintillator and aqueous sample had been used.

In addition to allowing a useful degree of nuclide identification by energy calibration of the MCA scale, the more narrow well-defined alpha peaks allow better determination of the presence of any interfering radiation and better quantification of the background count arising from the beta-gamma continuum. The technique for background subtraction used is that shown in Fig. 14, Sect. II D. With reasonable shielding a blank background of about 1.0 cpm is normal if Pyrex culture tubes are used. The use of quartz tubes will reduce this background to 0.3 cpm, and a quartz-faced phototube will reduce the background one to two tenths more.

5. Remaining Problems

The disadvantages of alpha spectrometry using the extractive scintillator and alpha liquid scintillation instrumentation compared to the approach using beta liquid scintillation equipment and an aqueous-accepting scintillator might be considered to be the necessity for special instrumentation and more chemical steps in sample preparation, but such a comparison of the two liquid scintillation methods as applied to alpha assay is not valid. Much more information is obtained by the extra steps and special equipment. The appropriate applications for the two methods are quite different. In comparison with other alpha assay methods, all methods of direct alpha assay require solids to be placed in solution and the alpha-emitting nuclide to be isolated, and all require special instrumentation. Sample preparation procedures for the liquid scintillation methods are often less complicated and time-consuming than those for methods using solid samples. The really valid disadvantage that one can attribute to alpha counting and spectrometry by the combined extractive scintillator - alpha liquid scintillation methods described above is the presence of the beta-gamma background that must be dealt with by graphical or other indirect methods. This problem is largely eliminated by the use of electronic pulse-shape discrimination techniques that will be described in the following section.

D. USING ALPHA LIQUID SCINTILLATION INSTRUMENTATION, AN AQUEOUS-IMMISCIBLE EXTRACTIVE SCINTILLATOR AND ELECTRONIC PULSE-SHAPE DISCRIMINATION

The most troublesome problem in alpha counting and spectrometry using liquid scintillation methods is the interference of beta and gamma pulses with the alpha count and spectrum. As has been indicated before, beta and gamma radiation produce pulses overlapping the alpha-response region and come from a variety of sources, sometimes as part of the decay chain of the nuclide of interest itself. Electronic pulse-shape discrimination (PSD) provides a satisfactory solution to this problem. The fact that the pulse decay time or pulse-shape of the alpha pulses is different from that of beta- and gamma-produced pulses (see Figure 21) allows electronic

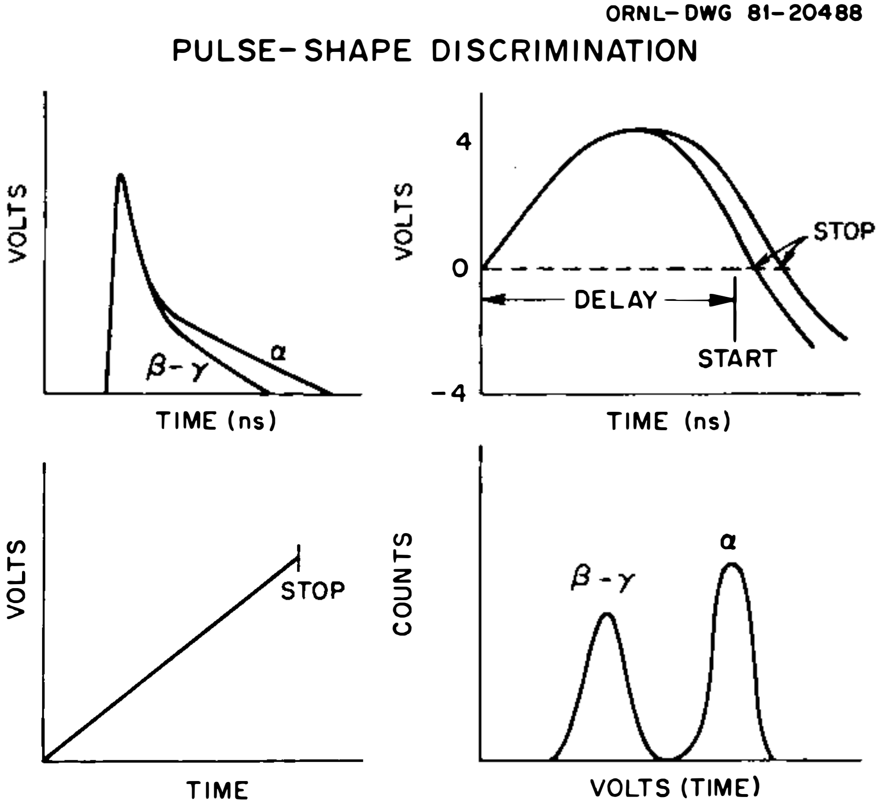

Fig. 21. Pulse-Shape Discrimination. This is possible because the detectable portion of alpha-produced light pulses (upper left) last about 30 nanoseconds longer than beta- or gamma-produced pulses. Since the integrated pulses (upper right) are about a microsecond long, the beginning of timing is delayed for about 800 nanoseconds. A voltage ramp (lower left) is then started and rises linearly with time until the pulse crosses zero. The spectrum of these voltage pulses (lower right) represents alpha (right) and beta-gamma pulses (left).

rejection of beta and gamma pulses. However, it should be noted that conversion electrons that are part of many alpha decay schemes in some cases cannot be rejected by pulse-shape discrimination because they occur within very short times (300 nsec or less) after the alpha decay. Light from these conversion electrons is thus a potential source of asymmetry in the liquid scintillation alpha peak because the light produced by the more-efficient-light-producing electron may be added to that produced by the alpha particle. Practice does not indicate that the problem is as serious as theory would predict, however. This will be discussed further in following paragraphs.

1. Pulse-shape Discrimination (PSD)

The use of the detector, extractive scintillator, and preamplifier/amplifier described in the previous section in conjunction with pulse-shape discrimination provides what is currently the most effective method of alpha counting and spectrometry by liquid scintillation methods. This combination of approaches is called PERALS spectrometry for Photon-Electron Rejecting Alpha Liquid Scintillation spectrometry.(2) The technology of pulse timing and pulse-shape discrimination (PSD) is well established, having been developed for neutron spectrometry in the presence of intense gamma fields. Liquid scintillators are used for detectors in this application also. Applications to the separation of alpha-produced and beta- or gamma-produced pulses have been made only recently,(11-15) however, and commercial units designed specifically for that purpose are not available at this writing. Existing commercial units can be adapted to provide the necessary pulse-shape discrimination, however. Figure 22 shows a block diagram of such an arrangement.

The time pick-off unit senses the beginning of each pulse and sends a logic signal to the logic shaper and delay. Because the 30 to 40 nsec time-difference between the amplifier-integrated beta/gamma-produced and alpha-produced pulses is incorporated in a total pulse time of about one microsecond, the start signal to the time analyzer (time-to-pulse-height converter) must be delayed for approximately 0.8 microseconds (see Fig. 21). After delay, the start signal initiates a voltage ramp in the time analyzer that is stopped when the energy analog pulse falls to zero. The voltage on the time analyzer ramp at this time is then taken as a voltage analog of time. The resulting voltage pulses can then be displayed on

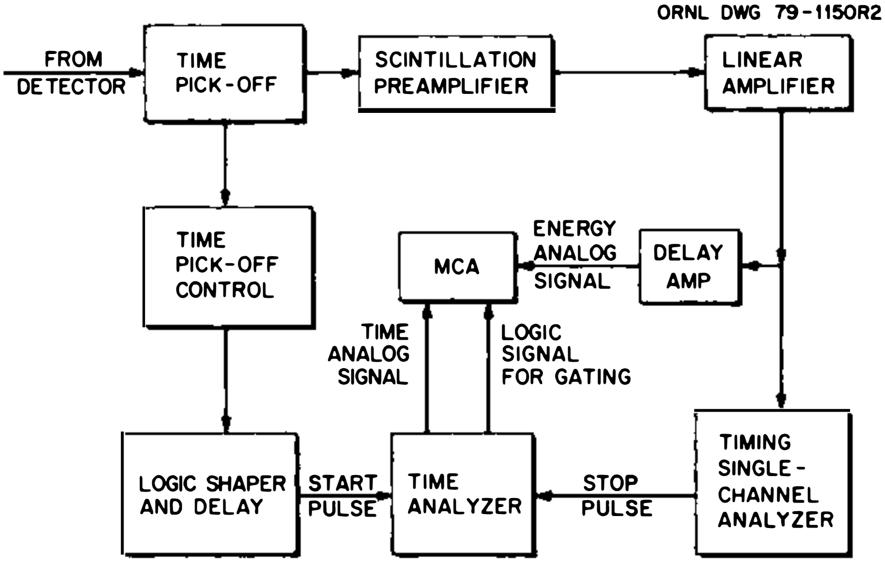

Fig. 22 A Block Diagram of a Pulse-Shape Discrimination (PSD) Circuit Assembled from Commercial Components

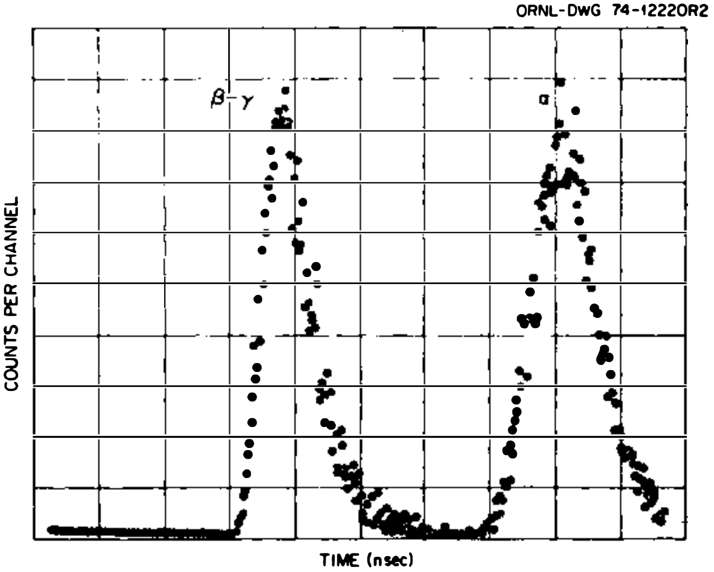

Fig. 23. A Time Spectrum Produced by a Set-up such as that shown in Fig. 22

an MCA as a time spectrum representing the relative pulse lengths of the beta-gamma and alpha pulses (see Fig. 23). A single channel analyzer (lower level discriminator) in the time analyzer, or following it, can then be adjusted to reject the beta- and gamma-produced pulses and accept only the alpha-produced pulses; thus, the logic signal generated will correspond only to alpha pulses. Sent to the gate input of an MCA, these logic pulses will allow only the alpha pulses to be recorded. Because time is consumed in deriving the voltage analog of pulse width, the gating signal will arrive at the MCA slightly later than the alpha energy pulse it is supposed to gate; thus, the energy analog pulse must be delayed by 100 to 200 nanoseconds in order to arrive at the proper time.

There have been numerous variations on the electronics arrangement described above for pulse-shape discrimination, most of them for gamma rejection in neutron spectrometry. Some of these time the pulse width at a small amount above zero crossing of the descending pulse and some time the rising portion of an integrated pulse. The basic principle in most of them is the same, however. In general, pulse-shape discrimination for quantitative alpha counting and spectrometry such as is being described here needs to be somewhat more precise and reliable than that normally used for neutron spectrometry. Improvements in pulse shape discrimination would make alpha liquid scintillation more useful for very low count rate samples.

Because the pulse-shape discrimination equipment described above is somewhat difficult to maintain in efficient operation by persons inexperienced with electronic timing equipment of this type (careful aligning of several pieces of electronic equipment is required), a simple one-NIM-wide pulse-shape discrimination unit has been designed by Thorngate.(15) This unit was designed specifically to do beta-gamma/alpha pulse-shape discrimination for a liquid scintillation system. Several useful improvements on this design were made by D. G. prater in 1981. A circuit diagram of the improved version may be seen in Fig. 29, Appendix i. Minor errors in the circuit shown in reference 15 are corrected in Fig. 29. This discriminator operates by converting each pulse to a square wave that retains the time information in the pulse width. A standard pulse, slightly shorter in duration than the beta-gamma pulses, is then subtracted from each pulse leaving remainders in which the fractional differences between the alpha and the beta-gamma pulses are larger than in the original pulses. The time-widths of these shortened pulses are then converted to voltage analogs that can be displayed on an MCA. As before, a lower level discriminator allows the alpha-produced pulses to be selected and their corresponding logic pulses to be sent to an MCA for gating.

The PSD unit designed by Thorngate(15) and Prater is simpler to operate and keep aligned than systems assembled from available electronic timing components but is not commercially available at the present time. A number of these units have been built by the Instrumentation and Controls Division of ORNL, and it is possible that arrangements could be made to have them build the units. If the intended users themselves have had electronics experience, they should be able to build their own PSD unit; alternatively, any competent electronics shop should be able to build the PSD unit. It is almost certain that further development could produce a PSD unit that is even more effective, reliable and convenient to use than those that are presently available. A small effort in this direction is currently in progress at Oak Ridge National Laboratory.

Pulse-shape discrimination requires that the PSD electronics work properly and that the detector, preamplifier, amplifier, PSD unit, delays, and the multichannel analyzer(s) are all connected in the proper manner and are working correctly. Pulse timing is an important part of the set-up requirements. Start and stop pulses must arrive at the time-to-pulse-height converter at the right times, and the information and gating pulses must arrive at the MCA within the interval specified for that particular instrument; thus, the use of an oscilloscope is necessary in placing the PSD set-up in proper working order.

Since the PSD characteristics of a liquid scintillator may vary slightly from sample to sample, it is desirable to be able to observe the PSD-generated time analog spectrum when necessary in order to adjust the discriminators for effective beta-gamma pulse rejection. For this purpose it is convenient to have two MCAs, one to record the energy (pulse-height) spectrum and one to record the time (pulse-shape) spectrum as is shown in the diagram in Fig. 24; however, a single MCA with a switching mechanism will serve.

Some illustrative time spectra are shown in Fig. 25. The spectrum 25a does not show pulse-shape discrimination sufficiently effective for quantitative

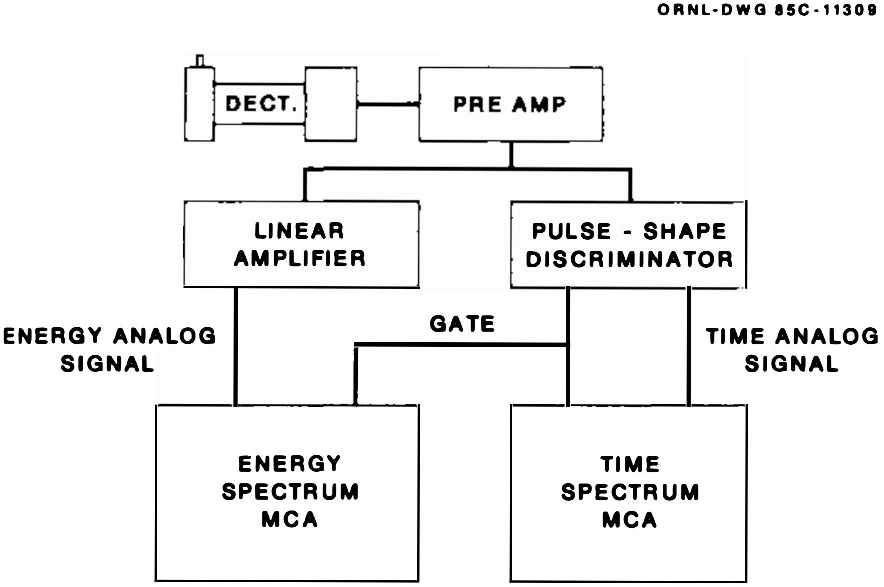

Fig. 24. A Block Diagram of an Arrangement to Monitor Energy and Time Spectra Simultaneously

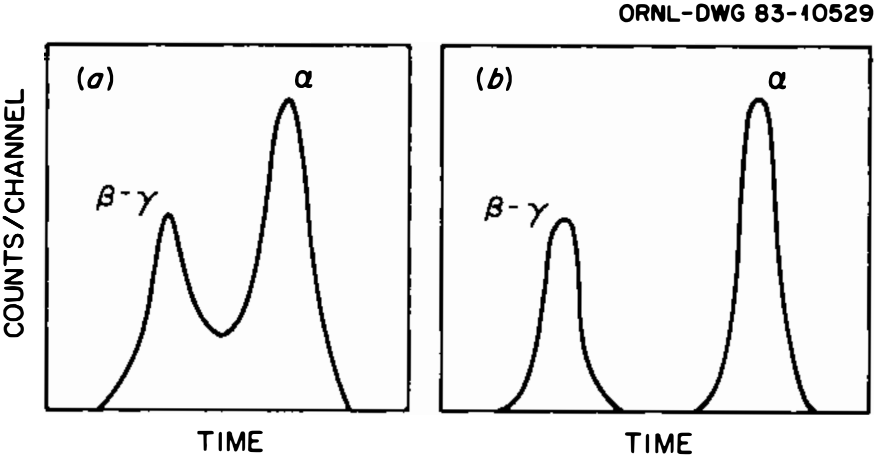

Fig. 25. Time Spectra Showing; (a) Ineffective Resolution of $\beta-\gamma$ and α pulses and (b) Good Pulse Resolution

rejection of beta and gamma pulses from an alpha spectrum while spectrum 25b shows a separation sufficient to select only alpha-produced pulses and reject others effectively. Assuming good instrumentation, ineffective PSD is usually due to oxygen, nitrate, chloride, alcohol, acetone, or other quenching material in the sample. If oxygen is the problem, additional sparging with an oxygen-free gas will usually solve the problem. If other quenching materials are present, the use of some other procedure in order to prepare a quench-free sample is indicated.

2. Pulse-Shape Discriminator Adjustment

In adjusting the cut-off for pulse-shape discrimination from a time spectrum (Fig. 25b), the count-rate of the sample may be too low to allow one to observe the time spectrum and adjust the setting of single-channel analyzer on the pulse-shape discriminator in any reasonable length of time. In such cases it is effective to bring a gamma source near the outside of the detector with the sample in place and set the pulse-shape discriminator so as to reject the pulses produced. Experience has shown that with this setting of the single-channel analyzer internally-produced beta and gamma pulses will also be rejected.

With properly prepared samples and a properly functioning PSD system, the rejection of beta-gamma pulses (with the exception of coincident conversion electrons) can be expected to be greater than 99.97% without measurable loss of alpha counts. A background blank, with a scintillator but no sample in the detector, will be between 0.002 and 0.02 cpm under a region corresponding to a 5 MeV alpha peak. The latter number is easy to obtain; the former requires careful instrument adjustment. A background taken in this way is a useful measure of how well the system is working and allows some comparison with background counts in other systems but can be misleading if applied to an actual sample, especially if the real sample contains any beta or gamma activity. Backgrounds obtained during sample counting with pulse-shape discrimination usually contribute less to the count error than the error due to counting statistics; however, for the best accuracy on very low count rate samples (< 0.1 cpm), an average baseline count per channel should be computed from regions taken symmetrically on either side of the alpha peak(s), and a background calculated from this value times the number of channels under the integrated alpha peak.

3. Spectrum Analysis and Integration

It should be emphasized here that every alpha event in a correctly prepared sample except for the 0.32% lost in the wall effect is counted, and the only other losses to be concerned with are those in sample preparation. Although in some cases it is possible to choose an isotope of the element to be determined that can be used as an internal standard, we have never used this approach to sample control. Instead, we have followed the protocol usual in many other analytical methods and developed procedures for 100% recovery with standard samples to be run at regular intervals to assure that the recovery remains what it should be. The integrated alpha peak (with wall-loss correction applied if desired) is then the total alpha count for that nuclide in that sample.

For samples with count rates higher than 1.0 cpm, background contributions will be 2% or less if the PSD equipment is working properly. Under these conditions single alpha peaks or peaks separated to the baseline may simply be integrated to give disintegrations per minute in the sample. Peaks that are not completely resolved may be handled by one of two methods that have been demonstrated to be successful.

a) Peaks produced by a single energy alpha (as for example from ^{210}Po) are perfectly Gaussian. Alpha decay schemes involving several alpha energies, x-rays, and conversion electrons may not produce absolutely symmetrical liquid scintillation peaks, but several common nuclides produce peaks that are approximately symmetrical. Theoretical calculations show (see Appendix iv) the nuclides ^{233}U and ^{238}U to be skewed about 1%, but this amount of assymmetry cannot be detected by integration on a multichannel analyzer. The uraniums 234 and 236 both give a calculated amount of skew of about 5%, but again the assymmetry cannot be detected in the spectrum. For these (and possibly other) nuclides integration from the mid-point to the outside base of any unresolved peak will give approximately half of the total count; thus, it is often possible to resolve merged peaks like those shown in Fig. 26a with acceptable accuracy and very little trouble.

Usually the use of the integrating function of modern multichannel analyzers will gives accurate results although it should be noted that considerable error, often the largest error, arises from the choice of the peak maximum. In fact, this uncertainty probably limits the accuracy of this method more

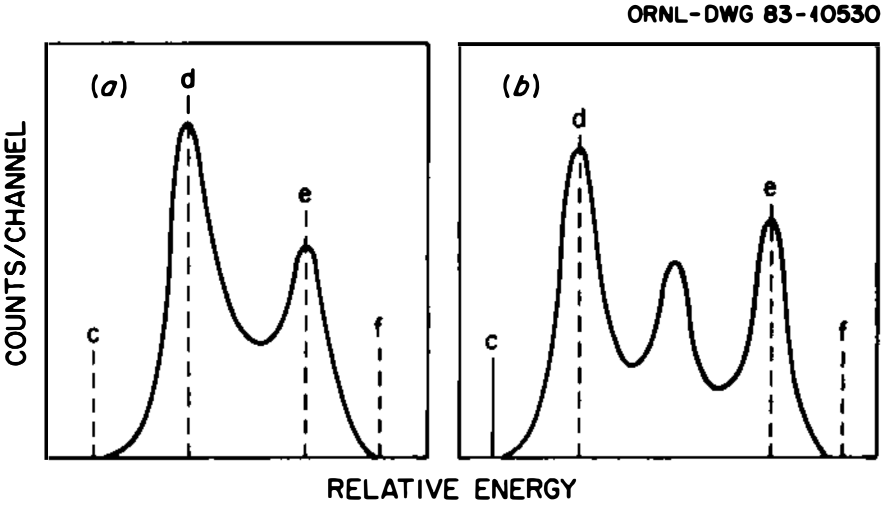

Fig. 26. Estimation of the Alpha Count in (a) Two and (b) Three Overlapping Alpha Peaks

severely than the assymmetry of the liquid scintillation peak caused by conversion electrons. Taking this technique one step further, three peaks such as are shown in Fig. 26b can be resolved by finding the total count under the outermost peaks as above and subtracting their sum from the total count under all three. Errors with this procedure are larger, of course, and errors also increase the larger the difference in size of the peaks and in the difficulty of identifying the apex of the peaks.

b) For complex spectra that cannot be resolved by the above simple approaches, computer curve resolution programs of the type commonly used for uv, visible, and infrared absorption spectra are sometimes applicable. The degree of assymmetry of the peaks (see Appendix iv and Sect. II A) should be taken into consideration in any such attempt.

4. Nuclide Identification

In many procedures the chemical steps used will assure that only one or a few nuclides are transferred to the scintillator; for example, a tertiary amine will extract plutonium(IV) very selectively from nitrate systems (Procedure 6, Appendix ii) or polonium can be separated easily from most other elements (Procedure 5, Appendix ii). In procedures designed to extract several nuclides, such as in the use of di(2-ethylhexyl)phosphoric acid (HDEHP) from solutions of pH 2, it is often desirable to identify the alpha peaks found. If the extractive scintillator and the aqueous phase from which the extraction is made are consistent from sample to sample and to standards, considerable reliance can be placed on the peak position - energy relationship, and energies can be estimated directly from channel number.

If differences in sample or scintillator composition have shifted the scintillator response, an effective way to calibrate the scale is to introduce two nuclides with widely separated alpha energies to the scintillator/sample in a small volume of extractive scintillator. If the added spike is less than 1 to 2% of the volume of the sample (10 to 20 microliters for a 1 mL sample), no change in scintillator response will occur due to the added material. The scale can then be calibrated for that sample directly from the position of the two known peaks.

If further refinement in nuclide identification is required, some of the sample in the scintillator may be dried on a planchette, the naphthalene, extractant and fluor driven off by heating and flaming, and a surface-barrier spectrum of the nuclides present obtained. Also, it may be possible to plate the nuclide from the scintillator onto a planchette by one of the following procedures. Where amines are the extractants, the addition of twice the sample volume of dimethylsulfoxide and 1 to 2 drops of 6 *M* HCl will usually produce a medium from which the trivalent and tetravalent actinides can be electroplated onto stainless steel by a current of 2.5 milliamps with a 250 to 300 volt potential. When HDEHP is the extractant, the addition of ethyl or isopropyl alcohol plus HCl will allow plating under similar conditions. A surface barrier spectrum from preparations on plates as described above can have energy resolution of the order of 20 keV FWHM. From this spectrum one can obtain more accurate nuclide identification by alpha energy. With nuclides of the same type, such as the trivalent actinides, activity ratios should be reliable. Thus, with the combination of the accurate total count from liquid scintillation and the identification and activity ratio from the surface-barrier detector spectrum, a combined quantification and identification better than by either method alone will be possible.

E. ACCURACY AND REPRODUCIBILITY

Reproducibility: Reproducibility of repetitive counting of the same prepared alpha sample by all liquid scintillation methods is determined by the statistics of counting. That is, if one has the mean of a large number of individual counts or a very long single count, the result of subsequent counts ± their square roots will include the original "true" value 68% of the time. Of course, since radioactive decay is itself a random process, we can never know an absolute rate of decay, only a very close approach to it. Stated another way; for a given count, $\bar{n}$, the "true" value will fall within $\bar{n} \pm \sqrt{\bar{n}}$ 68% of the time (the probability of it being outside these limits is only 32%). The quantity $\sqrt{\bar{n}}$ is called the standard deviation σ. The probability of the "true" value being outside 2σ is only 5% while the probability of being outside $1/2\ \sigma$ is 64%.

Because there is no problem of sample geometry reproducibility in most liquid scintillation detectors, the reproducibility of counts described above holds even when a sample is removed from the detector and replaced between counts. This is generally not true of surface barrier counting of alpha plates. Variations due to removing and replacing the plate are commonly 5 to 10%. Gas-flow proportional counters are much less sensitive to sample position. The reproducibility of a series of samples prepared separately and counted by liquid scintillation methods will depend primarily on the reproducibility of the chemical and volumetric steps used in the sample preparation if the count taken is large enough to give good counting statistics. An example of the reproducibility of multiple samples is given on page 46, Sect. III C.

Accuracy: The absolute accuracy of an alpha count can only be approached as was indicated above. With a total count of a single, pure nuclide sufficiently large that the standard deviation is only a small fraction of the total count; e.g., $\sqrt{\bar{n}} / \bar{n} < 10^{-3}$, the accuracy of the determination depends primarily on sample preparation and on the counting efficiency. Losses in sample preparation vary with the procedure. With the procedures described in Appendix ii recoveries are high. Extraction into the scintillator in all the procedures described is > 99.9% if conditions are right. Recoveries by the preliminary extractions are of the same magnitude. Thus, with all optimum conditions, losses in the separation procedures should be < 0.1%. However, the appropriate way to determine recovery under any specific set of conditions is to run standard samples of known nuclide concentration through the procedure. This, however, poses a problem because verified standards do not exist for many alpha-emitting nuclides. In fact, the highest accuracy quoted on an alpha emitting (solution) standard by the National Bureau of Standards is ± 1%. Better standards can be obtained by the use of weighable amounts of purified nuclides or mixtures of nuclides assayed by mass spectrometric methods. In an attempt at this laboratory to determine the overall accuracy of the extraction and counting procedure, a NBS sample of uranium oxide (Reference Material 950b) was used. Six weighed aliquots of a gravimetrically prepared solution were equilibrated with an extractive scintillator in the apparatus shown in Fig. 19. The aqueous phase was removed, and the total organic phase was counted. The mean of these determinations was 99.68% of the standard value with a standard deviation of ±0.058% of the mean. The absolute assay of the uranium oxide was quoted as being known to ±0.020%.

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IV. SUMMARY

Liquid scintillation techniques allow counting (detection and quantification) of non-penetrating alpha and beta radiation in ways that are usually more accurate and reproducible and are often easier than other methods. When the radionuclide is in homogeneous true solution in an appropriate organic liquid containing a compound (fluor) that produces light when excited by ionizing radiation, every ionizing event that produces a quantity of light sufficient to be detected by the multiplier-phototube is recorded. For alpha radiation this is virtually 100% (99.68%) of the events. The advantages of liquid scintillators have been exploited for beta counting because self-absorption problems for some of these nuclides are so severe in other counting methods that beta counting by these methods is of limited usefulness. The use of liquid scintillation for alpha counting has been much less used because other usable methods were developed, because both beta and gamma radiation interfere with alpha counting in liquid scintillation, and because equipment and methods to take full advantage of the capabilities of liquid scintillation in alpha counting and spectrometry have not been readily available.

In the past 10 to 15 years there have been many advances in alpha liquid scintillation methods. There are now several approaches to choose from:

1. Alpha-emitting nuclides can be introduced to the type of aqueous-accepting scintillator commonly used for beta counting and the resulting sample placed in a beta liquid scintillation counter. Many samples of reasonably high count-rate and of known nuclide composition can be assayed in this way. Variable interference by beta and gamma emitting nuclides and ambient gamma radiation is a problem as is the alpha-peak shift due to quenching materials added with the sample. Alpha energy discrimination is usually not possible.

2. Alpha-emitting nuclides can be transferred by liquid-liquid partitioning (solvent extraction) to an aqueous-immiscible solvent containing a solvent extraction reagent and this solution then mixed with an aqueous-immiscible scintillator solution. Alternatively, the extracting reagent and the fluor can be in the same solution initially and this "extractive scintillator" equilibrated with the aqueous sample. The resulting scintillator/sample from either method

is then counted in a beta liquid scintillation spectrometer. These procedures minimize problems of peak-shift due to quenching material in the sample (as in 1 above) and often, by selective extraction of the nuclide of interest, reduce problems of high background due to beta and gamma emitting nuclides in the scintillator/sample. Alpha energy separation/determination is still not possible and some background problems remain.

3. The alpha emitting nuclide in an extractive scintillator can be counted in a detector designed for alpha liquid scintillation spectrometry. Background count is lowered by this method by a factor of ~20, and the ability to deal with remaining background is improved. A useful degree of alpha energy resolution (200 to 300 keV, FWHM) is achieved, and spectra collected on a multichannel analyzer are useful for nuclide identification and for obtaining individual concentrations of mixed nuclides.

4. With electronic pulse-shape discrimination added to the system described above in 3, it is possible to reject most of the beta and gamma background (>99.9+%) and drastically lower the detection limit of alpha liquid scintillation. Detection limits and backgrounds approaching (or in some cases exceeding) those of surface-barrier detectors are achieved.

The alpha assay methods described above, especially in 3 and 4, can be much more accurate and reproducible than plate counting methods. Since there is no geometry reproducibility problem, accuracy is limited only by sample preparation and by counting statistics.

The work involved in sample preparation, even in methods 3 and 4 above, is usually less than that required for quantitative alpha counting by plate methods. The combination of liquid scintillation and solvent extraction allows many simple and effective nuclide separations to be made as a part of sample preparation. Opportunities for the development of many new and useful procedures exist.

Equipment for alpha liquid scintillation spectrometry is still in the development stages. Opportunities for improvements in energy resolution and in pulse-shape discrimination exist. These improvements are expected to occur as the demand for them increases.

V. APPENDIXES

APPENDIX I: EQUIPMENT AND REAGENTS

1. Beta Liquid Scintillation Spectrometer

Lists of current manufacturers of beta liquid scintillation counters/spectrometers may be found in any of several guides to scientific instruments. For use in alpha counting the following features are desirable:

1. The instrument should contain provisions for manually and continuously adjusting amplifier gain and upper and lower level discriminators.
2. Provisions for the output of pulses containing pulse-height or energy information should be present.
3. An output should be present that contains information as to whether the energy-analog pulse has passed the upper and lower discriminators or not.

The energy analog pulses may have already been selected by passing the discriminator, or the information as to which energy analog pulses have passed the discriminators may be contained in a separate pulse such as a scaler or ratemeter pulse. The purpose of having such outputs is to be able to see on a multichannel analyzer the energy spectrum that is being counted and to see the amount of unwanted background from beta-gamma or other alpha that has been eliminated by the discriminators. Alpha counting on beta liquid scintillation equipment without a multichannel analyzer (or without manually taking the spectrum of each sample) is subject to many errors because of peak shift due to quenching and because of unknown beta-gamma background.

A linear relationship between pulse-height and alpha energy is to be desired over a logarithmic relationship. A linear scale is easier to calibrate and elimination of unwanted low energy beta-gamma pulses is less troublesome.

2. Alpha Liquid Scintillation Spectrometer (PERALS Spectrometer)

A PERALS spectrometer consists of a detector, a high-voltage supply for the detector, a pulse-shape discriminator, a preamplifier, an amplifier, and a multichannel analyzer. The detector is presently not commercially available. A pulse-shape discriminator can be assembled from commercially available components or a more compact and convenient-to-operate unit can be constructed. A variety of suitable preamplifiers, amplifiers, and multichannel analyzers are on the market. Although large improvements in alpha energy resolution can be obtained through the use of the alpha liquid scintillation detector, the full potential of the alpha liquid scintillation method cannot be realized without the use of the pulse-shape discriminator. Descriptions of the detector and a pulse-shape discriminator follow.

a. Detector:

A cross-section of a suitable detector is shown in Fig. 11, Sect. II C, and a photograph of a model presently used in the author's laboratory is shown in Fig. 15, Sect. III C. Presented on the following pages (Fig. 27) are reductions of shop drawings from which the detector shown in Fig. 15 was constructed. Full-size drawings can be obtained as report No. CAPE-2825 from DOE Office of Scientific and Technical Information, Technical Information Center, PO Box 62, Oak Ridge, TN 37831. The critical parts of this device are the reflector and the phototube. A phototube having a high photocathode sensitivity is desirable since the statistical scatter of photoelectron production introduces the most variation in pulse reproducibility and consequently the largest contribution to the line width. Thus a sensitive photocathode contributes to improved energy resolution even though this degree of sensitivity is not needed for detecting the large light pulses produced by alpha particles.

The shape and the coating of the reflector are also important for reasons of optimizing alpha energy resolution (see Sect. II C). High reflectivity and evenly diffuse reflectivity contribute markedly to the energy resolution of the detector. Eastman white reflectance coating is presently the recommended reflecting material. The light-coupling material (oil) used in the space between the reflector and the phototube face also aids significantly in alpha energy resolution. The oil presently used in the author's laboratory is Dow-Corning 200 silicone oil having a viscosity of 50 cs. The shape of the box enclosing the detector and the manner of access to it are not important except that the box be light-tight, have high-voltage interlocks and be reasonably convenient.

b. Pulse-Shape Discriminator

The general principles of the application of pulse-shape discrimination (PSD) have been presented in Sect. III D, and a block diagram of a PSD system assembled from commercial electronic components is shown in Fig. 22. Such PSD circuits are, however, somewhat cumbersome and difficult to keep adjusted. A circuit was designed specifically for beta-gamma/alpha pulse-shape discrimination by J. H. Thorngate (present address Lawrence Livermore National Laboratory), and improvements were made by D. G. Prater of ORNL. Circuit diagrams for this PSD unit are shown below in Fig. 28, and a set of full-size prints and shop drawings may be obtained as report No. CAPE-2826 from:

DOE Office of Scientific and Technical Information
Technical Information Center
PO Box 62
Oak Ridge, TN 37831

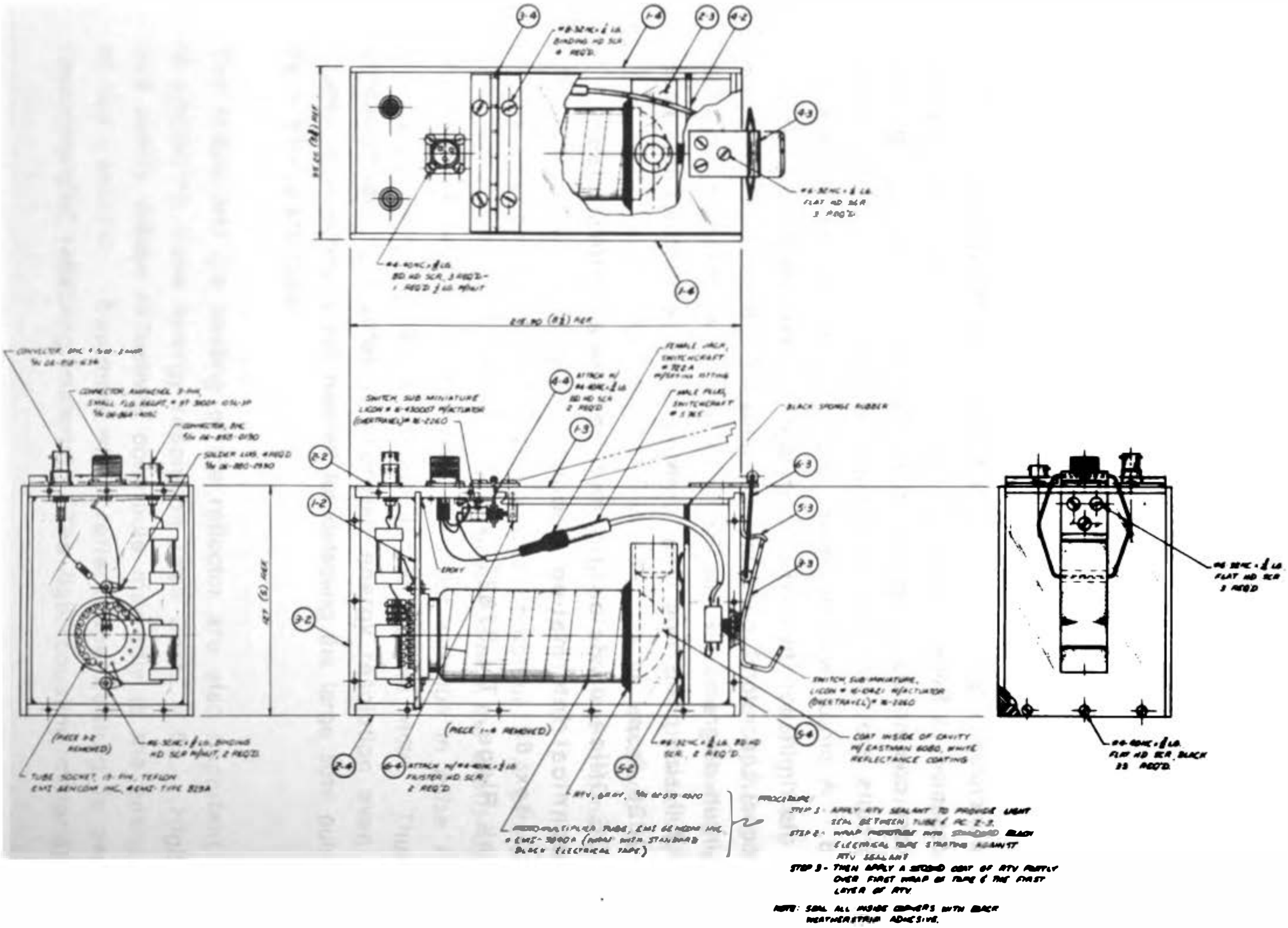


Fig. 27. Shop Drawings and Circuit Diagrams for the Construction of the PERALS Detector in use as of this Date. (1982 Design by the author)

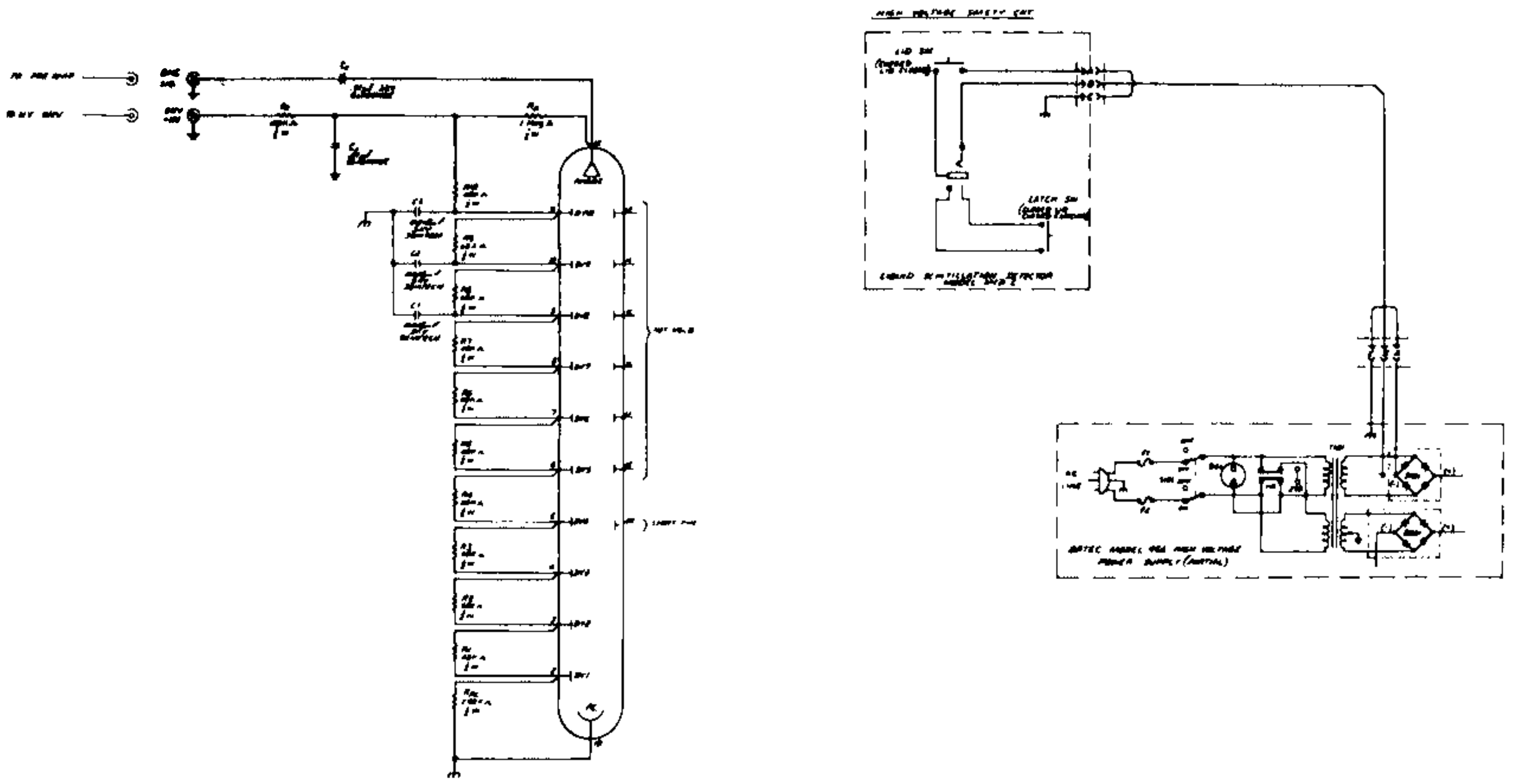


Fig. 27a. Phototube Divider Network and High-Voltage Supply and Connections

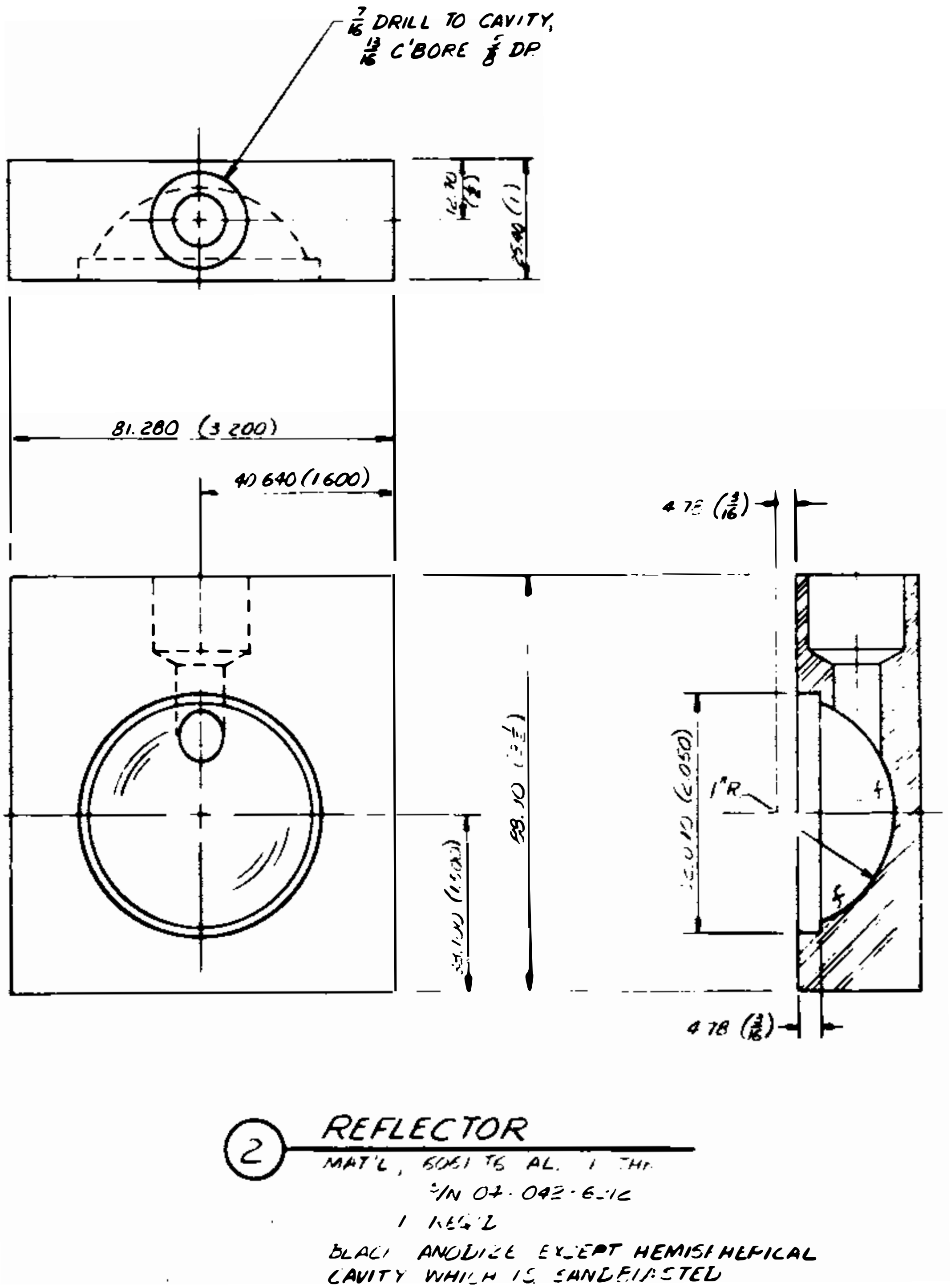
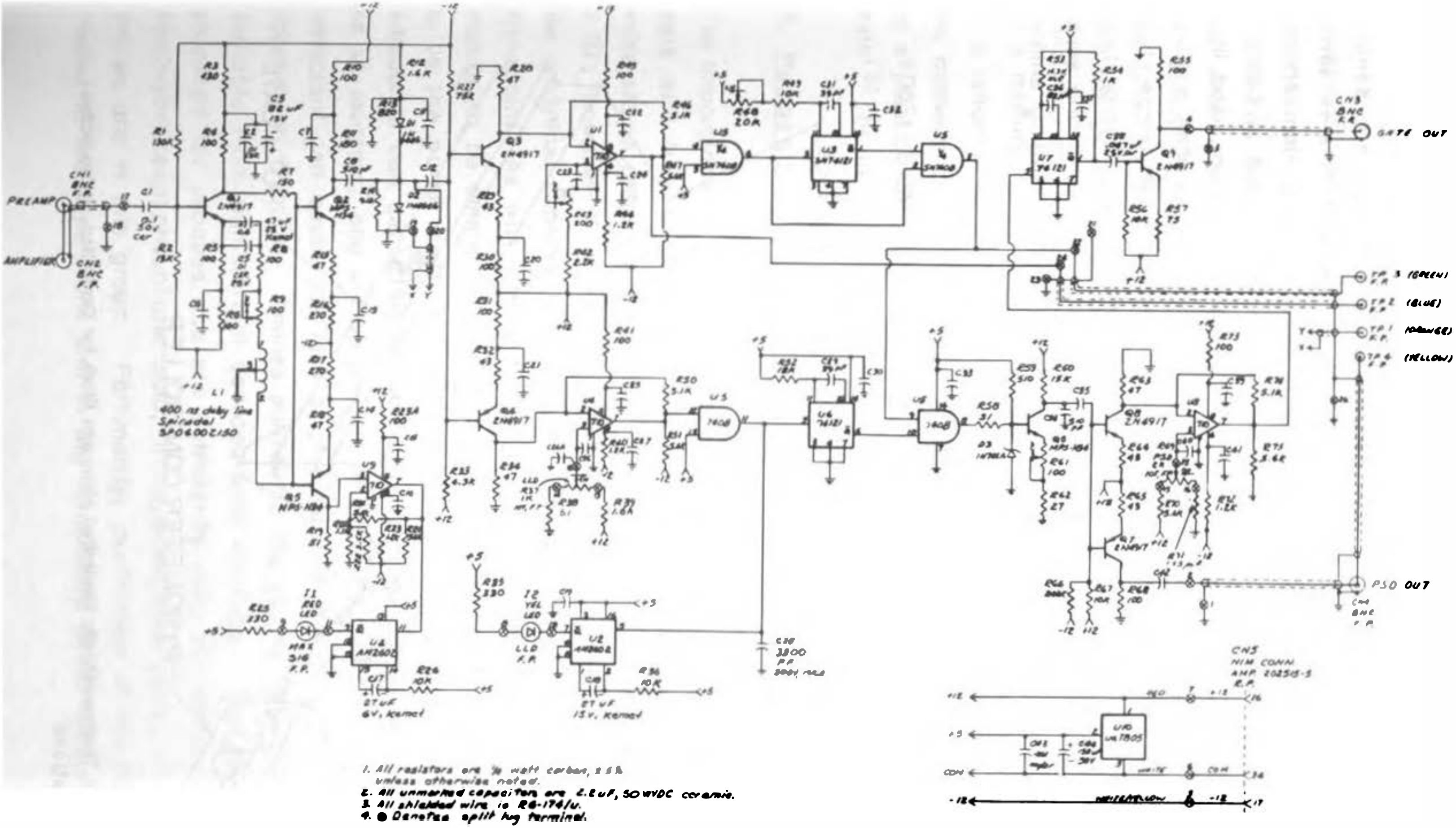


Fig. 27b. Reflector Construction Details. Positioning pins for the culture tube are not shown in this drawing (see Fig. 11).



1. All resistors are ¼ watt carbon, ± 5% unless otherwise noted.
2. All unmarked capacitors are 2.2 uF, 50 WVDC ceramic.
3. All shielded wire is RG-174/u.
4. ● Denotes split lug terminal.

Fig. 28. Circuit Diagram for a Single-Unit Pulse-Shape Discriminator. (Thorngate/Prater Design)

3. Aluminum-Block and Heat Lamp Evaporators

The most time-consuming steps in sample preparation for alpha liquid scintillation assay (as for any other alpha assay method) are sample dissolution and sample volume reduction. Much operator time is saved in these operations by the use of heat lamps or a controlled-temperature aluminum heating block like that shown in Fig. 29. The walls of beakers can thus be kept at nearly the same temperature as the bottom, and little or no refluxing occurs so that evaporation is faster. Also, it is often possible to control evaporation temperatures to avoid spattering. The temperature of the block or lamps can be adjusted to rapidly remove nitric, hydrochloric and hydrofluoric acids while leaving sulfuric, phosphoric and perchloric acids little affected. This makes the often necessary task of changing anions much simpler to accomplish.

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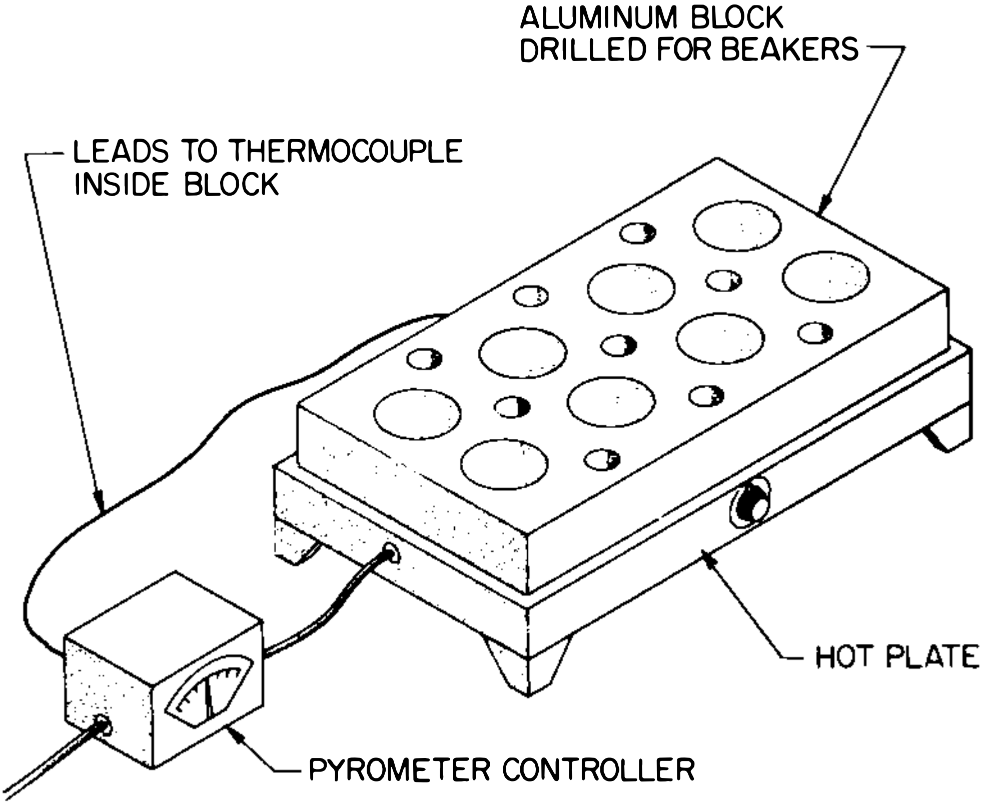

Fig. 29. A Thermostatically Controlled Aluminum Block for Controlled, Reproducible Evaporations

4. Sample Dissolution Equipment

Samples of organic materials or samples containing large quantities of organic materials must be ignited or wet-oxidized to destroy the organic material before dissolution. All of these samples may be ignited at 600 to 700°C after which the ash is dissolved. Care should be taken not to exceed 900°C. Refractory oxides of plutonium are produced at this temperature. Plant and animal tissues may be dissolved in concentrated nitric acid and small amounts of 30% hydrogen peroxide.(1) Mineral samples and soil samples containing minimal amounts of organic materials may be placed in solution in a mixture of concentrated nitric, hydrochloric, and hydrofluoric acids in a teflon-lined pressure vessel.(2) The Bureau of Mines has developed two methods of placing mineral samples in solution. Both use mild pressure in a plastic (polycarbonate) bottle and heating either in a boiling water bath(3) or in a microwave oven.(4)

5. Reagents

The importance of having all reagents that go into the extractive scintillator pure and free of color in order to obtain optimum pulse-height and pulse-shape response of the scintillator has been mentioned before (Sect. II B); however, it should be stressed here again. In addition, purity of the analytical separation reagents is important from an analytical accuracy standpoint. As with any analytical procedure, the smaller the amount of material to be determined and the more accurate the determination is desired to be the purer must be the reagents. Small amounts of impurities in extractants can cause the extraction of elements other than those desired. As an example, one or two percent of a primary amine in a tertiary amine extractant can cause the loss of plutonium in the procedure described in Appendix ii, Sect. 6. Amines purified to this degree have not been readily available from commercial sources until recently. Now some reagents produced for process use are sufficiently pure for analytical purposes. Bis(2-ethylhexyl)phosphoric acid, trioctylphosphine oxide, and some alkyl amines are in this group. Fortunately, purification of the other reagents needed in the separations and in the scintillators is not difficult. Molecular distillation in a spinning-cone molecular still has been found adequate in most cases and is recommended for distillation of the high molecular weight extractants to avoid decomposition. The material being distilled is heated for only a fraction of a second while it is on the distillation cone; thus, thermal degradation of the material is minimized. Most of the extractants undergo appreciable degradation in a still in which the entire batch remains heated in a still pot during the distillation even if vacuum distillation reduces the boiling point to 40 to 50°C.

Scintillation grade naphthalene is sufficiently pure as purchased as are the fluors and the solvent toluene. It is hoped that chemical suppliers will find it profitable to make available more highly purified versions of some of the other reagents needed in these procedures in the near future.

a. Extractants:

Table 2 lists some selected solvent extraction reagents and gives an indication (necessarily incomplete) of their extraction behavior. Some of these are suitable for use in the scintillator and are marked with "*". Some others are colored or quench for other reasons. Table 3 lists some suppliers from which these reagents may be obtained. Other suppliers may exist of which we are not aware.

TABLE 2

General Properties of Selected Extraction Reagents

Type	Examples	Metals Extracted
Cation Exchange	Dinonyl or didodecyl naphthalene sulfonic acid	All cations extracted even from acidic solutions; not selective.
	Bis(2-ethylhexyl) phosphoric acid(a) *	Alkalis and alkaline earths weakly extracted; pH 4-6. Lanthanides/actinides(III) strongly extracted; pH 3-5. Actinides(IV) very strongly extracted; pH to 0.5.
	Neo-tridecanoic acid (branched carboxylic)*	Weak extractant at pH 4-7; Multivalent ions slightly better.
	Thenoyltrifluoroacetone	Pu(IV) from 1-3 *M* HNO_3 Th(IV) at pH >1, U(VI) at pH >2 Np(IV) at pH >0.5 Trivalent lanthanides at pH >3 Many other Elem.(III) extracted.
	Hydroxyoximes	Not selective for actinides; Most used as extractants for Cu.
	8-Hydroxyquinoline	Extracts many ions pH 3-6. Not very selective. Quenching.

(a) Compound successfully used in author's laboratory.

*Reagents usable in scintillator.

TABLE 2 (Continued)

Type	Examples	Metals Extracted
Ion Pair coordinators	Primary alkyl amine of MW ≥ 300(b)*	From nitrate; Au(III) From chloride; Po(IV) From sulfate; Fe(III), Y, Zr, Nb(V) Tc(VII), Pd(II), In(III), Sn(II), Eu, Hf Ta(V), Re(VII), Os(IV), Mo(VI) Pu(IV), U(IV), Th
	Secondary alkyl amine of MW ≥ 300* (Much variation in extraction with structure)	From nitrate; Au(III) Fe(III), Ga(III) Sb(V), Au(III), Cd From sulfate; Zr, Nb(V), Mo(VI) Tc(VII), Pd(II), Ta(V), Re(VII), Os(IV)
	Tertiary alkyl amine of MW ≥ 300(c)*	From Nitrate; Tc(VII), Au(III), Th, U(VI), Pu(IV) From sulfate; U(VI)
	Quat. ammonium compound MW ≥ 300*	From nitrate; Mo(VI), Tc(VII), Eu, Au(III), Hg(II), Bi(III), Th, U(VI) From chloride; Fe(III), Zn, Ga(III), Mo(VI), Pd(II), Cd, In(III), Sn(IV), Sb(V), Sb(III), Au(III), Hg(II), Po(IV), U(VI) From sulfate; Mo(VI), Tc(VII), Ta(V), Re(VII), Os(IV), Pd(II)

No extraction from perchloric acid.

Perchloric acid can be used to strip all amines.

(b) 1-nonyldecylamine and "Primene-JMT" used successfully.

(c) Trioctylamine, "Alamine-336", and "Adogen-464" used successfully.

* Reagents usable in scintillator

TABLE 2 (Continued)

Type	Examples	Metals extracted
Neutral coord.	Trioctyl phosphine oxide[(d)*]	From nitrate; U(VI), Zr, Tc(VII), Au(III), Th, Np(IV)(VI), Pu(IV)(VI), Pa, Hf
		From chloride; Au(III), Zn, Zr, Sn(IV), Sb(III), Cr(VI), Mo(VI), Fe(III), Th, U(IV)(VI), Pu(IV)(VI), Ga(III), Nb, Bi
		From sulfate + minimal nitrate or chloride U(IV), In(III), Cr(VI), Ce(IV)
	Tributyl phosphate	From nitrate; U(VI), Pu(VI)(IV), Np(VI)(IV), Os(VI), W, Th, Sc, Lu, Y
		From chloride; Au(III), Tl(III), Fe(III), Zr, Nb, Ga, Ta, Te(IV), W, Np, Sb, Mo, Hf, Sc, Re, In, Pa
		From sulfate; Re, Tc, Os
	Diethyl ether	From Nitrate; U(VI) [coef. ≈1]
	Polyethers	From nitrate; Hg, Th, Pa, U(VI)
	Methyl isobutyl ketone	From nitrate; U(VI), Tc(VII), Hg
		From chloride; Au(III), Ga

(d) Compound used successfully in author's laboratory.

*Reagents used in scintillator.

Table 3. Some Sources of Solvent Extraction Reagents

Reagent Type Name	Source
Carboxylic acids	
Versatic	
Naphthenic	Shell Chemicals Exxon Chemicals (Various Sales Offices)
Sulfonic Acids	King Industries P.O. Box 588 Science Road Norwalk, CO 06852
Phosphorus Acids	
Bis(2-ethylhexyl) phosphoric	Mobil Chemical Co. Industrial Chem. Div. Richmond, VA 23261
2-Ethylhexyl phosphonic acid mono(2-ethylhexyl) ester	Diahachi Chemical Co. Ltd. JAPAN
Beta-Diketones	
Thenoyltrifluoacetone	General Chemical Suppliers
Primary Amines	
1-Nonyldecylamine	Armak Chemicals Custom Preparation
Primene JMT	Rohm and Haas

Table 3 (continued)

Reagent Type Name	Source
Secondary Amines	
Amberlite LA-1, LA-2	Rohn and Haas
Adogen 283	Sherex Chemical Co. P.O. Box 646 Dublin, OH 43017
Others	Mars Chemical Co. 762 Marietta Blvd. Atlanta, GA 30318
	Armak Chemicals Box 1805 Chicago, IL 60690
	Henkel Corp. 1301 Jefferson Street Hoboken, NJ 07030
Tertiary Amines	
Alamine 336	General Mills
Azamine 10B	Mars Chemical Co.
Adogen 364, 363	Sherex Chemical Co
Phosphine Oxides	
Trioctyl	General Chem. Suppliers

b. Fluors

Listed below in Table 4 are several useful fluors for liquid scintillation. Both the commonly-used acronyms and the chemical names are included. There appears to be considerable difference in the fluors in regard to the amount of energy resolution they can produce, the over-all pulse height they produce, and the improvement that the addition of an energy transfer agent such as naphthalene can produce. Some of the comparisons done at ORNL are shown in Table 1, Sect. II B; however, these results were obtained several years ago,(5) and better fluors and better methods of comparing them may be available today. A recent recheck of the comparison between PBBO and butyl-PBD, however, confirmed the superior performance of PBBO.

Table 4. Fluors

Acronym	Chemical Name
PBBO	2-(4'-biphenylyl)-6-phenylbenzoxazole
Butyl-PBD	2-(4'-tert.-butylphenyl)-5-(4''-biphenylyl)-1,3,4-oxadiazole
αNPO	2-(1-Naphthyl)-5-phenyloxazole
PBD	2-(4-biphenylyl)-5-phenyl-1,3,4-oxadiazole
DPA	9,10-diphenylanthracene
PPO	2,5-diphenyloxazole
BBOT	2,5-bis(5'-tert.-butyl-2-benzoxazole)thiophene
BisMSB	p-bis(o-methylstyryl)benzene
POPOP	2,2'-p-phenylenebis[5-phenyloxazole]

APPENDIX II: SELECTED PROCEDURES

There appear to be many potential applications for alpha liquid scintillation techniques, even in their present state of development. Although the energy resolution attainable with liquid scintillation is not as good at present as that which can be produced under good conditions by some plate counting methods, quantification of the alpha count will nearly always be better with liquid scintillation because there are no problems of sample self-absorption or sample geometry. Improvements in energy resolution and in pulse-shape discrimination, both of which appear achievable with moderate additional research and development, would allow many more uses.

Many of the procedures below use perchloric acid. It is an ideal reagent from several viewpoints; (1) Nitric, hydrochloric and hydrofluoric acids can be driven off from the sample by heating to perchloric acid fumes. (2) Perchloric and nitric acid together will effectively and safely destroy small amounts of organic material in the samples that would otherwise cause serious quenching problems in the scintillator. (3) Perchlorate systems are non-complexing and provide the ideal system from which to extract into the HDEHP and other cation exchange extractive scintillators. Those who have developed these procedures are aware of the potential hazards of perchloric acid, as those who use them should be. However, with due care the risk is minimal, and the advantages to be gained are great. No acceptable substitute for the use of perchloric acid has been found in many procedures.

Commercially-available 72% perchloric acid more properly called perchloric acid dihydrate, $HClO_4 \cdot 2H_2O$, is a perfectly stable chemical that will not explode, detonate, or deteriorate on storage. The boiling temperature of this composition is 203°C. More dilute solutions will expel water until this composition and this boiling temperature is reached. Perchloric acid dihydrate or solutions of it are not strong oxidizing agents at room temperature. Ferrous ion is stable in perchlorate solutions at these temperatures. Hot perchloric acid solutions are, however, strong oxidants and react explosively with many organic materials. Alcohols in particular should not be heated with perchloric acids. In using perchloric acid to destroy organic materials, the initial reaction mixture should contain more concentrated nitric acid than perchloric acid. An excess of nitric acid should be maintained until the solution is clear and only small amounts of organic matter remain. If organic solids are present, the sample should be digested with concentrated nitric acid and 30% hydrogen peroxide until all solids are dissolved into a clear solution before perchloric acid is added.

All of the procedures described below are designed to be quantitative with 100% of the nuclide expected to to be extracted into the extractive scintillator. Because of this, none of the procedures use an internal tracer although in some cases this would be possible. Quality control of the analyses is expected to be maintained by the use of standard samples run at intervals as is usual for many other kinds of assays. Accuracy and reproducibility in all cases are expected to be determined by the accuracy of the volumetric manipulations and by counting statistics.

1. Actinides in Laboratory Samples

Alpha emitting nuclides of known purity that are used as tracers can often be assayed using a beta liquid scintillation spectrometer. The ease and the accuracy with which this can be done depend on the level of activity being assayed, the nature of the other ions present, and the physical and chemical form of the sample.

a. Reagents:

Aqueous-accepting scintillator: Any commercial scintillator that is compatible with the aqueous samples.
Extractive scintillator: Prepare a solution of 60 g bis(2-ethylhexyl)phosphoric acid, 180 g naphthalene and 4 to 6 g PBBO, PPO, or α-NPO fluor in toluene diluting to 1L. After the solution has been stirred for 1-2 hours allow it to set for several hours or overnight and filter to remove any undissolved fluor.

b. Procedure:

For liquids, aqueous or organic, that are of the same composition over a sample set, that contain little or no quenching materials (nitrates, chlorides, alcohols, acetone, organic chlorides), and that all have a count rate higher than the blank background, counting can be done by pipetting an appropriate amount (ideally the same for every sample in order to keep the scintillator composition constant) of sample into the scintillator and counting at a gain that is about 10% of that used for ^{14}C. *Solids or samples containing solids cannot be assayed with any reliability.* Some method must be used to assure that the gain used places the alpha peak within the region detected by the spectrometer. A multichannel analyzer (MCA) connected to the beta liquid scintillator spectrometer as described in Sect. III A is useful for this purpose. Without an MCA the spectra should be taken by hand through a narrow window. These procedures are necessary for reliable counting since, if either edge of the peak is cut by the spectrometer detection limits, slight changes in the peak position due to instrument voltage change or to the sample due to quenching will cause larger changes in the count.

For liquids containing quenching materials, counting can still be successful if; 1. The same amount of quencher is added to each sample. In this case, the gain generally must be raised. Sometimes additional quencher must be added to the least-quenched samples. 2. The gain is readjusted for each different degree of quenching to bring the pulse within the region where it can be detected. Quenching must be severe in order to depress the alpha-produced light pulse to the point where it cannot be detected.

If beta or gamma emitters are present in the sample either as impurities or as daughters of the nuclide of interest, subtraction of a separately determined background will not be correct, and a method of determining the background for each sample will be necessary. Graphic or computer analysis of a spectrum from each sample is often helpful (see Sect. III D).

As a general rule the net alpha count rate of the sample must be at least as large as the blank background count of the spectrometer (at the same gain and window settings) in order to be able to have meaningful counting statistics. This requirement usually limits the practical lower counting limit for a beta-liquid scintillation spectrometer to about 20 cpm.

Many of the problems associated with quenching in assaying laboratory samples can be eliminated by the use of an aqueous-immiscible extractive scintillator (see Sect. II B). An aqueous sample of up to 8 mL adjusted to pH 3 may be added to a 20-mL scintillation vial containing 10 ml of the scintillator. The two phases are then equilibrated, and the sample is counted in the beta-liquid scintillation spectrometer. Beta emitting impurities that are unextracted do not interfere; however, unextracted gamma emitters do. Most problems associated with the assay of laboratory-produced samples can be avoided by the use of extraction and the PERALS spectrometer as described in Sect. III C.

Solid samples must be placed in solution before applying any of these procedures. Alpha particles emitted in the interior of plant or animal tissue, soil or dust particulates, or even colloidal materials, will not be counted because the alpha particle will be absorbed before it reaches the scintillator.

2. Counting on Glass-Fiber Filters

Alpha activity on glass fiber filters can sometimes be counted with good accuracy, and even with fair alpha energy resolution and beta-gamma rejection, in liquid scintillation media. If the alpha activity is present without beta-gamma activity and without much inert solids, a rough idea of the alpha activity present can be obtained by placing the filter material in an all-purpose scintillator and counting it in a beta liquid scintillation counter. This technique is useful for assay of relatively clean "swipe" samples to check for suspected surface contamination. Relatively clean (only very light grey) air filter samples can also be counted in this way.

The same clean samples mentioned above can be run on a PERALS spectrometer and yield an energy spectrum good enough for some identification of nuclides and for excellent nuclide quantification. In addition, pulse-shape discrimination is usually good enough to reject most of the beta-gamma background. Filter discs up to 4.5 cm in diameter can be counted in this way. Push the filter material into a 10 x 75 mm culture tube using a glass rod. Add 1 mL of scintillator solution. HDEHP extractive scintillator appears to have some advantage in that it may dissolve some of the alpha-emiting material. Attach the culture tube to a short piece of rubber tubing on the outlet side of a three-way stopcock. Attach the other two sides to the inert gas supply shown in Fig. 17 and a water aspirator, respectively. Apply aspirator vacuum to the culture tube to remove air trapped in the filter fibers and then admit the inert gas. The filter should become transparent and virtually disappear. Repeat this procedure 2 or 3 times. Count the sample in a PERALS spectrometer. Samples count with nearly 100% efficiency apparently because the activity is on the surface of the filter fibers in a very thin layer. Answers are obtained quickly although accuracies and energy resolutions usually are not as good as with samples in solution.

3. Gross Alpha in Environmental Materials

Most alpha-emitting nuclides, with the notable exception of radium and radon, can be separated and counted with this procedure after the sample is placed in solution.

a. Reagents:

The extractive scintillator containing bis(2-ethylhexyl)phosphoric acid (HDEHP) is the only special reagent required for this procedure. The mixture is 60 g of HDEHP, 180 g of scintillation-grade naphthalene and 4.0 g of PBBO in 1 liter of distilled-in-glass toluene. After the solution has been stirred for 1 to 2 hours allow it to sit several hours or overnight and filter to remove any undissolved PBBO.

b. Procedure:

Place the sample in solution by a suitable method that leaves the system primarily in the chloride, nitrate or perchlorate anion form. Wet oxidation is often suitable for organic materials although drying, ashing and acid dissolution of the residue may be better in some cases, especially where the sample contains resinous materials that hinder the attack of acids (especially hydrofluoric acid) and oxidizing agents. Hydrogen peroxide and nitric acid are recommended as oxidizing agents rather than perchloric acid since a controlled amount of perchloric acid is to be added later. Soils and some ores also are often easier to dissolve if ignited first for the reasons cited above. Where the use of hydrofluoric acid is necessary to dissolve silicates, the use of a pressure vessel is recommended (see Appendix i).

When the sample is completely dissolved, add approximately 0.5 g of lithium perchlorate and 1.0 to 1.5 mL of 0.1*M* perchloric acid and evaporate at 160°C, using heat lamps or an aluminum block until boiling and evolution of hydrochloric or nitric acid ceases and the first signs of perchloric acid fumes appear (near 200°C). Be sure that the upper parts of the beaker are heated in order to drive off any perchloric acid condensed there. Cool the beaker and add 5 to 7 mL of water. When the sample dissolves, measure the pH of the solution. The pH should not be lower than 2.0. If it is, re-evaporate and heat to perchloric acid fumes again, then redissolve and again measure the pH. It is important that the chemist be able to recognize the fumes of perchloric acid and distinguish them from steam and nitric or hydrochloric acid fumes. It is recommended that a few trial runs be made that contain about a milliliter of concentrated perchloric acid before samples are attempted if one is not familiar with the use of perchloric acid. Since the only oxidizable organics present at this point would be the organic material entrained in the aqueous phase during the extraction, there would be little concern about the safety of this operation with perchloric acid; however, due care should always be taken when perchloric acid is used.

When the sample pH is between 2 and 3, transfer the sample to a separatory funnel. Do not increase the volume to more than 10 ml. Add a measured volume between 1.2 to 1.5 mL of HDEHP extractive scintillator and equilibrate for 1 to 2 minutes. Pipette 1 mL of the scintillator/sample into a culture tube and count. The special equilibration/counting vessel (Fig. 19) can be used here instead of a separatory funnel in which case 1.0 mL of extractive scintillator will be used and the total sample will be counted.

Exact procedures for placing in solution, evaporating to perchloric acid fumes and adjusting pH will vary with the sample material and will need to be adjusted and refined for each case. Extraction of all the alpha-emitting nuclide ions (except radium) will be quantitative at pH 2 to 3. The pH should not be higher than 3.5 or hydrolysis of some of the ions will occur. At pH lower than 1.5, incomplete extraction of some ions will occur. If plutonium is not present, the pH can be adjusted with sodium hydroxide, but plutonium will precipitate in local basic regions and will not be redissolved making that portion of the plutonium inextractable.

4. Uranium and Thorium in Phosphates

Uranium and thorium can be separated from phosphate-containing materials, such as fertilizers, bone, teeth, animal tissues and wastes, and phosphate chemicals including phosphoric acid, and counted separately by this procedure.

a. Reagents:

Uranium-extracting scintillator: Dissolve 96 g of Adogen 364 (molecularly distilled) in 600 mL of distilled-in-glass toluene and contact with 100 mL of 0.9 to 1.0 *N* H_2SO_4. To the equilibrated and separated organic phase add 180 to 190 g of scintillation-grade naphthalene and 4.0 grams of PBBO. Make to 1 liter with toluene. Stir for 1 to 2 hours and allow to sit overnight. Filter if any solids remain.

Thorium-extracting scintillator: Prepare as for uranium-extracting scintillator except use 70 to 75 g of 1-nonyldecylamine or other branched primary amine of similar molecular weight. (Solution should be 0.25 *N* in amine.) Most amines will require molecular distillation to purify and remove color.

Trioctylphosphine oxide (TOPO) extractant: Dissolve 77 g of TOPO in toluene to make a 0.2 *M* solution.

b. Procedure:

In general, the procedure involves six steps: 1. dissolution of the sample in nitric and perchloric acids, using hydrofluoric acid if necessary to break down silicates (in some cases perchloric acid can be replaced by 30% hydrogen peroxide if desired), 2. conversion of the resulting solution to a nitrate-perchlorate system containing sufficient aluminum to complex the phosphate, 3. extraction of the thorium and uranium with TOPO, 4. stripping of the thorium and uranium into an aqueous ammonium carbonate solution, 5. conversion of this solution to a sulfate system, and 6. extraction into the separate scintillators and counting. A more detailed description of the analytical procedure follows.

Dissolve a measured quantity of phosphate-containing material (amount depending on the concentrations of uranium and thorium expected) in 8.0

M HNO_3, using hydrofluoric acid if silicates are present. Heat, if necessary, to complete solution and then boil down to ca. 25 mL. Add about 25 mL of concentrated perchloric acid and heat the solution until perchloric acid fumes appear. Filter the warm solution through a glass frit and transfer it to a 125-mL separatory funnel. Dilute it to approximately 6 *M* acid and neutralize it to between 1 and 2 *M* acid with sodium hydroxide. In some samples, a precipitate of calcium sulfate is noted at this point, but it does not appear to affect the results. Add aluminum nitrate (ca. 25 g) to enhance the primary extraction for uranium and thorium and to complex phosphate and other interferring ions so as to ensure quantitative uranium and thorium recoveries. (For samples already in solution, such as phosphoric acid samples, the dissolution procedure is bypassed; enough aluminum nitrate is added to approach saturation, and the acidity is adjusted to 1 to 2 *M*.) Next, add a volume of 0.2 *M* TOPO in toluene equal to about one-half the aqueous-phase volume and equilibrate the two phases for 5 min. After phase separation is complete, discard the aqueous phase and wash the organic phase once with an equal volume of 0.5 *M* HNO_3 to remove extracted acid and undesirable salts. Double the volume of the organic phase by adding an alcohol such as isobutanol or 2-ethylhexanol to prevent solids formation in the subsequent stripping step.

Strip both the uranium and thorium from the organic phase by adding an equal volume of 0.5 *M* ammonium carbonate solution, shaking the separatory funnel for 10 min, and allowing the phases to separate. Drain the ammonium carbonate strip solution into a clean 100-mL beaker and boil down to 5 mL in a fume hood. Any excess ammonium carbonate is decomposed by heat to ammonia and carbon dioxide. To oxidize any organics add 2-mL volumes each of concentrated nitric and perchloric acids. The presence of nitric acid while the organic materials are being oxidized prevents possible formation of an explosive mixture of chloric and perchloric acids with oxidizable organic matter. Boiling with nitric acid present should continue (adding additional nitric acid if necessary) until the solution is water clear before it is allowed to evaporate to concentrated perchloric acid. It is helpful to place a ribbed watch glass on the beaker and allow the system to reflux to eliminate the remaining small amounts of colored organics (suspected to be humic acids in phosphate ores) that are present. These organic materials are difficult to destroy; however, the final solution must be colorless for effective pulse-height and pulse-shape resolution. When the refluxing solution becomes colorless, wash down the sides of the beaker with water and add 5 to 7 mL of 6.0 *M* H_2SO_4. Heat the beaker to 300°C to drive off all of the nitric and perchloric acids, leaving only a thin layer of sulfuric acid. This final evaporation procedure may be done in a muffle furnace or an aluminum block or, if care is exercised, over a flame. The uranium and thorium are now contained in a small volume of concentrated sulfuric acid solution.

Transfer the aqueous sulfate solution with a water rinse to a small vial (ca. 20 mL), limiting the total volume in the vial to less than 7 mL. Adjust the pH of this solution to between 0.7 and 1.0 with sodium hydroxide (see Figs. 30 and 31), then transfer this aqueous sample to a 30-mL separatory funnel using 0.05 *M* H_2SO_4 as a rinse. Extract the uranium into a measured volume between 1.2 and 1.5 mL of the 0.25 *M* Adogen-364 sulfate extractive scintillator. Filter the remaining aqueous phase, now containing only thorium, and extract the thorium into the 0.25 *M* 1-nonyldecylamine sulfate extractive scintillator. A pipetted volume of the particular scintillator, now containing either the uranium or the thorium, is placed in a 10 X 75-mm

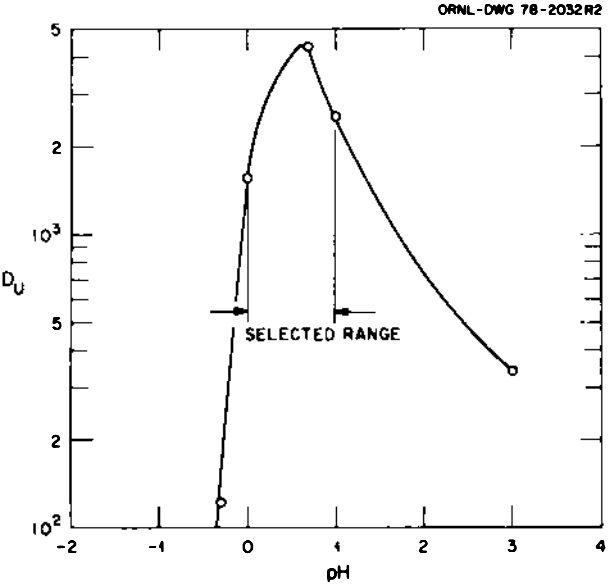

Fig. 30. Extraction of Uranium from a Sulfate System by Adogen-364 Extractive Scintillator as a Function of Aqueous-Phase pH

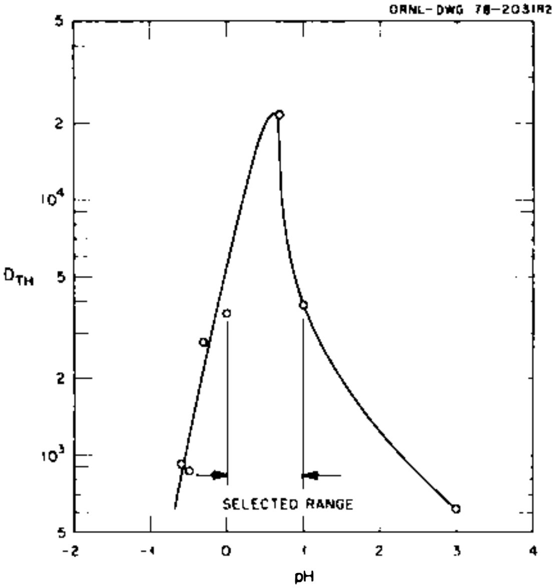

Fig. 31. Extraction of Thorium from a Sulfate System by 1-Nonyldecylamine Sulfate Extractive Scintillator as a Function of Aqueous-Phase pH

culture tube and bubbled with toluene-saturated argon for 2 min to minimize oxygen quenching to improve pulse-shape discrimination. Seal the sample with a cork covered with a thin film of room-temperature-vulcanizing silicone sealer and place it in a PERALS detector for counting. Accumulate a spectrum for a sufficient length of time to give counting statistics consistent with the degree of accuracy desired.

If the sample is normal uranium in secular equilibrium (It should be noted that in many cases uranium will not be in secular equilibrium because either it has been through an isotope separation process or because aggregate recoil coupled with natural geologic processes has disturbed the isotopic ratio.), exactly as many of the alpha decays should come from ^{234}U as from ^{238}U. In addition, each gram of natural uranium contains about 0.007 g of ^{235}U. In counting and integrating both peaks the ^{235}U will be included since it cannot be resolved. For most uses the total count can be converted to mass units by dividing the net count by two and employing the specific activity of the ^{238}U if the counts from ^{235}U are accounted for since the mass of ^{234}U is negligible. It can usually be considered that the calculated amount of uranium is 1.5% high because of the ^{235}U and the appropriate correction applied; however, for more accurate results a portion of the extracted sample should be dried on a planchette, flamed and counted on a surface barrier detector to establish the exact 238/235/234 ratio. To convert the net thorium alpha dpm per gram of sample to mass units, the specific activity of the respective thorium isotope (^{230}Th or ^{232}Th) is employed. The separate peaks for these two thorium isotopes can usually be integrated individually since their energies are 0.67 MeV apart.

Initial dissolution of a solid sample may be the most time-consuming step of the analysis, requiring a few minutes to a few hours, depending on the nature of the sample. Primary extraction, stripping, volume reduction, and the two extractions into appropriate scintillators require 2 to 3 h; of course, several samples can be run simultaneously.

Counting times of about 10 min are sufficient to determine the uranium activity in a 1-g sample of superphosphate fertilizer or apatite. The ^{230}Th activity associated with superphosphate fertilizer is lower, and 50-min counting times are necessary. Longer counting times will be necessary to obtain statistically meaningful results for samples containing smaller amounts of uranium and thorium.

Using a statistical treatment for low-activity samples,(6) detection thresholds and counting accuracies were determined at a 97.5% level of confidence from data given in reference 7. Without pulse-shape discrimination, the beta-gamma background is about 1 cpm. Assuming a 50-min counting time yields a minimum detectable true activity of 0.62 cpm. This corresponds to 0.28 pCi of uranium or thorium. With pulse-shape discrimination and 1000 min counting times, this detection threshold can be lowered to 0.017 cpm corresponding to 1.1 part/10^8 for ^{238}U, 6.9 part/10^8 for ^{232}Th in a 1-g sample. Concentration factors of at least 10 are easily achieved in the extraction and separation steps.

5. Polonium

^{210}Po, the daughter of naturally occurring ^{238}U, is a common alpha-emitting radionuclide found in biological and environmental materials. It is rated as a Class 1 radionuclide (very high radiotoxicity), yet few methods for accurately determining ^{210}Po have been developed. Most prior methods involve lengthy chemical separations and depend on auto-deposition onto silver disks and counting on a surface barrier detector. They also require the use of ^{208}Po or ^{208}Po tracers to determine ^{210}Po recovery and counting efficiency. The method described here using PERALS spectrometry in conjunction with solvent extraction separation is selective for polonium, is quantitative, is simple to apply, and avoids many of the problems present in previously described methods for polonium assay.(2)

a. Reagents:

The extractive scintillator is composed of trioctylphosphine oxide (TOPO), 77 g/L; naphthalene, scintillation grade, 180 g/L and PBBO, 4.0 g/L in distilled-in-glass toluene.

b. Procedure:

1). Inorganic solids: Place approximately 0.5 g of the sample (accurately weighed) in a Teflon-lined pressure vessel and add 2 mL each of concentrated hydrochloric, hydrofluoric and nitric acids. Seal the vessel and heat it in an oven to 140°C for about 2 hr. Remove the vessel from the oven, let it cool for about 1 hr and transfer the dissolved sample to a 250-mL Teflon beaker with about 5 mL of water. Add 5 mL of concentrated phosphoric acid. Using a hot-plate with a heat control, evaporate the solution to approximately 5 mL. Rinse down the beaker with about 5 mL of water and again evaporate to about 5 mL. The acid remaining in the sample should now mainly be phosphoric acid. Retention of hydrochloric acid will increase the extraction of uranium (see Fig. 32), but the uranium can be removed by a scrub (see below). Transfer the sample to a 30-mL separatory funnel with about 5 mL of water and add 1 mL of 0.1 M HCl. The solution should now be approximately 7.0 M H_3PO_4 - 0.01 M HCl. Add by pipette a known volume (usually in the range of 1.2 to 1.5 mL) of the extractive scintillator and shake the funnel on a wrist-action shaker for at least 30 min. Run off the aqueous phase and scrub the organic phase with about

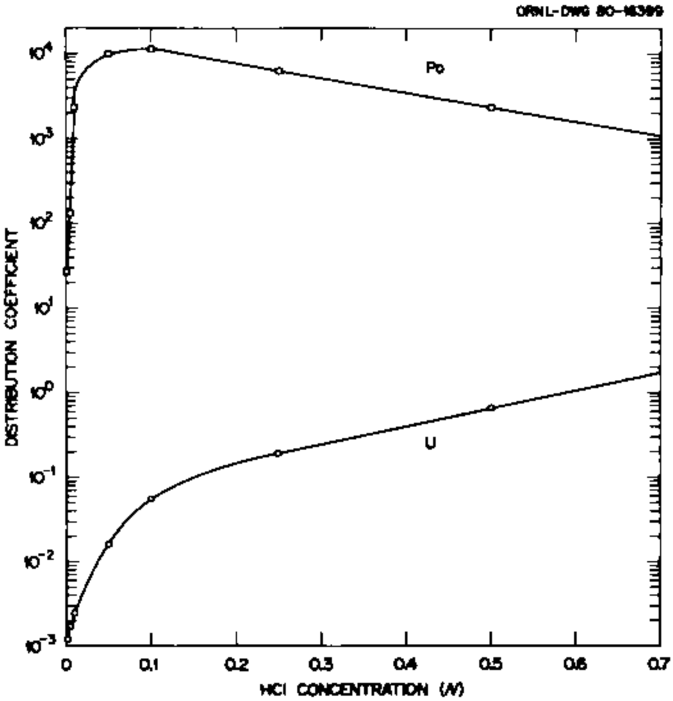

Fig. 32 Uranium Extraction from 7 M H_3PO_4 by TOPO Extractive Scintillator as a Function of Chloride Concentration (From Ref. 2)

5 mL of 7.4 *M* H_3PO_4– 0.001 *M* HCl to remove any co-extracted uranium. After the phases have separated, pipette 1.0 mL of the organic phase into a 10 X 75 mm culture tube. Deoxygenate the solution by bubbling argon, methane, propane or acetylene (presaturated with toluene) through it for about 2 min using a disposable transfer pipette as a sparging lance. (Deoxygenation is necessary if the beta and gamma pulses are to be discriminated from alpha pulses by the electronics.) Seal the sample with

a cork coated with a room-temperature-vulcanizing silicone sealer and count the ^{210}Po with a beta- gamma-rejecting PERALS spectrometer. Samples are generally stable for 48 hr when sealed as described. Good pulse-shape characteristics can be restored by repeating the sparging.

2). Organic solids: Plant and animal tissues and other materials that are organic or that contain organic materials can be dealt with as follows: evaporate excess water at low temperatures (near 100°C) in an oven or under heat lamps. Ignite the dried material at 600 to 800°C and dissolve the residue in HCl or as in "Inorganic solids" above if required. Once the sample is in solution, continue as in the main procedure. At present it is not known whether or not there is a risk of volatilizing polonium in the ignition step, but it is believed that the ash and salts retain any volatile forms of polonium.

3). Samples in aqueous solution: Combine measured quantity of the aqueous sample with 5 mL of concentrated phosphoric acid and 2 mL of concentrated hydrochloric acid in a 250-mL Teflon beaker. Apply the procedure given above for solid samples, starting wtth the evaporation step. Some aqueous samples may require or permit modified procedures: for example, analysis of a sample of about 6 *M* commercial (wet-process) H_3PO_4 needs only the addition of 0.1 *M* HCl, extraction, etc. before the scintillation counting.

Low level polonium samples can be counted with good accuracy even in the presence of high beta-gamma background as is demonstrated in Fig. 33.

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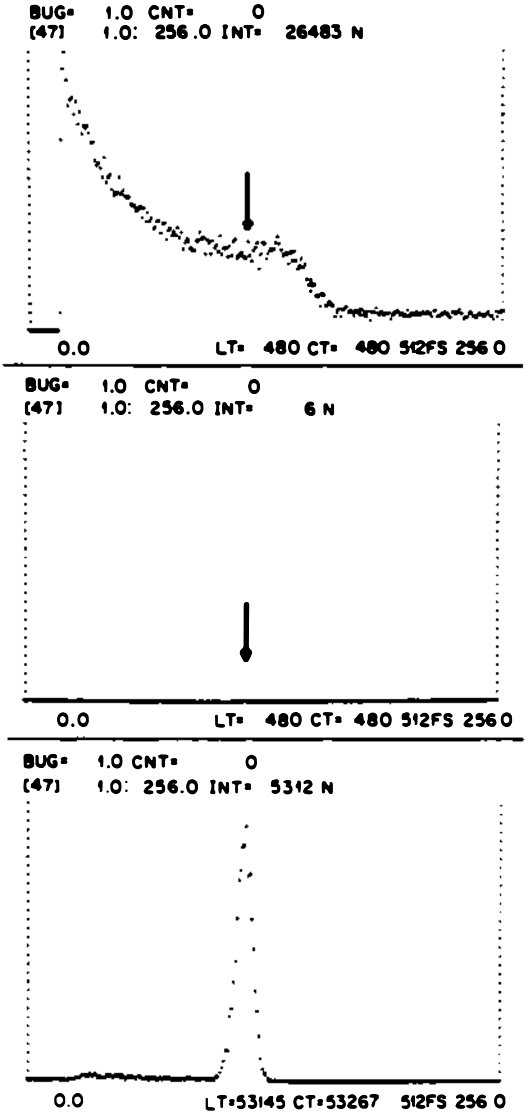

^{210}Po, ~ 1 ALPHA PER MINUTE

$^{152-154}$Eu, ~ 3300 BETAS AND GAMMAS PER MINUTE
8 MINUTES
(1 mℓ)

THE ARROW POINTS TO WHERE THE FEW ALPHA COUNTS ARE BURIED

EXACTLY THE SAME, WITH BETAS AND GAMMAS REJECTED BY PULSE-SHAPE DISCRIMINATION

COUNTING TIME INCREASED FROM 8 MINUTES TO 88 HOURS

RESULTS: 0.90 ^{210}Po α/min · mℓ
(4 X 10^{-13} Ci/mℓ)

Fig. 33. An Illustration of Low-Level Polonium Counting with the PERALS Spectrometer

6. Plutonium

Plutonium can be chemically separated from all other elements except neptunium and counted quantitatively by this procedure, and ^{237}Np can be separated by its energy difference from ^{239}Pu and ^{240}Pu.

a. Reagents:

Tertiary amine nitrate: The initial extractant in this procedure is 0.3 *M* high molecular weight tertiary amine nitrate ($TANO_3$) in toluene. Trioctylamine or one of the proprietary tertiary amines in the 300 or greater molecular weight range is suitable. It is important that there be no primary or secondary amine in the reagent. Primary amines will produce nitrosoamines in the nitrite valence adjustment step, and these compounds will complex plutonium so that it cannot be recovered in the stripping step. Both primary and secondary amine nitrates will extract unwanted elements.

Prepare the amine solution and equilibrate it with a 10% excess of an equivalent concentration of nitric acid. Do not use acid more concentrated than 1 *M*. If the amine nitrate solution is brown or pink, discard it and purify the amine reagent by molecular distillation.

Extractive scintillator (HDEHP): The preparation of this reagent is described in Procedure 3.

Sodium persulfate solution: Dissolve 2.5 grams of sodium persulfate in 50 mL of distilled water and add ~10 mg of silver chloride.

Alternative Extractive Scintillator (1NDAS): This scintillator, using 1-nonyldecylamine, is described in procedure 4.

b. Procedure:

Place the sample in solution in a medium that is 3 to 4 *M* total nitrate and 0.5 to 1.0 *M* acid. Perchlorate should not be present. Small amounts of sulfate (less than .01 *M*) do not interfere. Amounts of phosphate and fluoride to a few hundredths molar can be tolerated if 1 to 2 *M* of aluminum nitrate is present.

Add 50 to 100 mg of ferrous sulfate to the solution and warm. Allow the solution to cool to room temperature. At this point the plutonium should be reduced to valence III. Add 50 to 100 mg of sodium nitrite to the cooled solution and swirl. The oxidation state of the plutonium should now be IV, its most extractable form. Transfer the solution to a separatory funnel and contact it with not less than 1/4 of its volume of 0.3 *M* $TANO_3$. Equilibrate for 1 min by hand shaking or by turning at 30 rpm on an inverting rack. Drain away the aqueous phase. Retain if uranium analysis or other actinide analysis is desired. Wash the organic phase twice with not less than 1/4 its volume of 0.7 *M* HNO_3. Add these washes to the original aqueous phase if uranium analysis is desired. The distribution coefficient for uranium is approximately 1 in the original solution but is < 0.01 in this system; so any extracted uranium is repartitioned to the aqueous phase. Add to the organic phase in the separatory funnel an equal volume of 2-ethylhexanol and contact with a measured volume of 0.5 *M* $HClO_4$ – 0.5 *M* $LiClO_4$ equal to the original amine nitrate volume. Drain this aqueous solution into a beaker. Wash the organic phase in the separatory funnel twice with a solution that is 0.5 *M* $LiClO_4$ and 0.1 *M* $HClO_4$. Add these wash solutions to the original strip solution. Add a volume of concentrated nitric acid equal to 1/4 the volume of the total aqueous phase in the beaker. Evaporate in an aluminum block until nitric acid and water boiling ceases and the first dense, white fumes of perchloric acid appear. Rinse the sides of the beaker with a few drops of water and repeat the evaporation. (If the chemist is not familiar with the appearance of perchloric acid fumes a few trial runs of nitric and perchloric acid would be valuable.) Add 1 mL of the sodium persulfate solution and warm the beaker. This operation should place all of the plutonium in oxidation state VI. Make the volume to 5 mL with water. Measure the pH of this solution. If it is less than

1, re-evaporate, redissolve, and remeasure the pH. When pH is 1 to 2.5, extract with extractive scintillator. There should be no delay between this final evaporation and extraction into the scintillator. Plutonium disproportionates to a significant degree into oxidation states III, IV, V, and VI on standing in dilute acids for more than a very few minutes. The extraction coefficient of Pu(III) is much lower than is that of Pu(IV) and Pu(VI), and Pu(V) is not extractable (although the amount of (V) formed is small). Counting of the sample is performed as described elsewhere.

An alternative procedure for stripping the plutonium and re-extracting into the scintillator that does not use perchloric acid and is perhaps simpler follows:

Dilute the tertiary amine nitrate solution with an equal volume of 2-ethylhexanol or similar high molecular weight alcohol. Strip the diluted organic phase with 1/3 its total volume of 1 *N* H_2SO_4. Draw off the aqueous phase and evaporate to the first white sulfuric acid fumes. If any color is visible from charred organics that have been entrained in the organic phase, add 1 to 2 mL each of 30% H_2O_2 and concentrated HNO_3 and heat. Repeat until the final solution is free of color. Transfer with approximately 10 mL of water to a 30 mL seperatory funnel and extract with a measured quantity, 1.2 to 1.5 mL of the 1NDAS scintillator (see "Thorium extracting scintillator" in Procedure 4).

7. Nuclear Fuel Reprocessing Streams

Although at this writing little actual experimental work has been been done on the application of liquid scintillation to the determination of alpha activity in nuclear fuel reprocessing streams, it seems reasonable that with effective beta-gamma rejection and, in some cases, good chemical separation, very accurate determination of uranium and plutonium in fuel reprocessing streams can be made. In many cases accuracy will be limited only by counting statistics and by the accuracy with which the sample can be taken (weight or volume measured). Thus the accuracy of the counting procedure can approach the accuracy of gravimetric determinations.

The most difficult stream to analyze will probably be the first waste stream in the tributylphosphate extraction (PUREX) reprocessing scheme. This stream, usually called the "1AW" stream, contains most of the fission product beta and gamma activity and only small amounts of uranium and plutonium isotopes. It is important in fuel reprocessing accountability to know as accurately as possible the quantity of fissionable material in this stream. Presently used counting methods use surface-barrier detectors and give accurate ratios of several alpha energies but cannot determine the total quantity of a nuclide more accurately than ±5% because of sample-geometry-reproducibility and self-absorption problems. Calculations based on the amount of alpha and beta-gamma activities in the PUREX 1AW stream resulting from processing 160-day cooled pressurized water reactor (PWR) fuel(8) show that even under these severe conditions, alpha activity can be determined accurately. The ratio, curies of beta-gamma to curies of uranium, plutonium, and neptunium alpha activity, is 1.0×10^6 in the original solution. After extraction with a tertiary amine nitrate as described in the preceeding procedure, stripping, and re-extraction into the HDEHP extractive scintillator, the beta-gamma/alpha ratio is less than 100, a ratio that can easily be managed by pulse-shape discrimination. With a PERALS spectrometer, the spectrum obtained is expected to look similar to that shown in Fig. 34. Integration of the main peak and subtraction of the curve-fit or estimated contributions from the side peaks should allow determination of $^{239-240}$Pu with errors of less than 1% from interferences by other alpha and beta-gamma energies. The energies of ^{239}Pu and ^{240}Pu cannot be resolved even with surface barrier detector resolution.

Plutonium in PUREX dissolver solutions, product streams, and waste streams other than 1AW can be assayed in the same way as described above but with less severe chemical separation or pulse-shape discrimination problems. In general, alpha activity levels are such that count rates sufficient to give a statistical accuracy of counting of better than 1% is possible in a counting time of 10 min or less either by appropriate dilution of the original sample

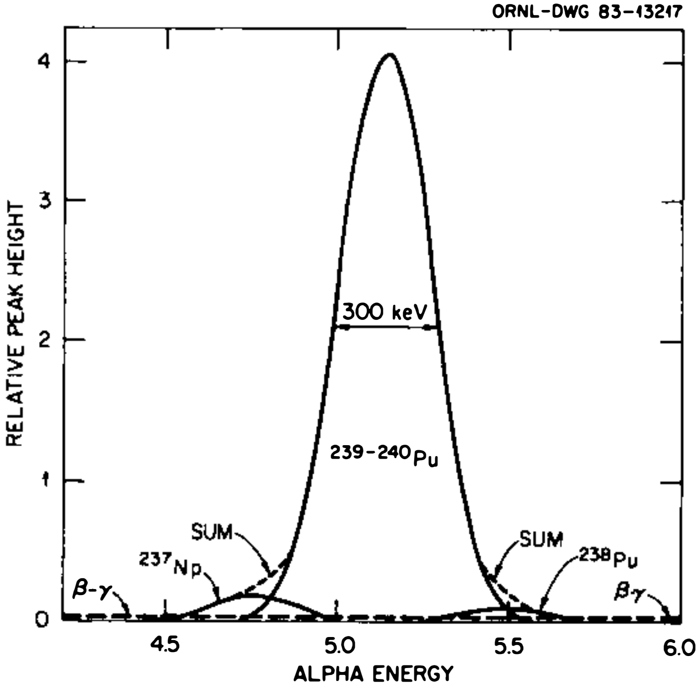

Fig. 34. Plutonium Alpha Spectrum Expected to be Obtained Using PERALS Spectrometry Based on Known Separation Factors in Extraction with Tertiary Amine Nitrate from PUREX 1AW Waste followed by Extraction into HDEHP Extractive Scintillator

(for dissolver solutions, product streams, etc.) or extraction of a relatively large sample (as in waste streams to be released). Count rates of 10^6 cpm can be easily counted without loss of count and count rates of 0.02 cpm can be easily and accurately counted. There are corrections for counting efficiency of 99.68% at most in either case.

A further refinement that makes use of both the good counting accuracy of liquid scintillation and the good energy resolution abilities of surface barrier detectors depends on the use of these two methods in tandem on the same sample. Using a separation method that removes monovalent and divalent elements will reduce beta-gamma activity in many sample solutions to the point where pulse-shape discrimination can reject this activity component effectively. Extraction into a scintillator and use of pulse-shape discrimination will now allow accurate determination of the total alpha activity but probably not resolution of the separate alphas if there are several. A small unmeasured portion of this extract dried on a planchette and heated to drive off volatile solids in the scintillator will provide a sample from which a surface barrier detector can accurately determine alpha energy ratios in the sample. The two assays, taken together, will allow more accurate determination of the quantities of the various nuclides than is possible with either method alone.

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APPENDIX iv: PROPERTIES OF SOME ALPHA-EMITTING NUCLIDES

NUCLIDE	HALF LIFE, yr	PRINCIPLE α ENERGY, MeV(%)	ENERGY AT CALC. PEAK MAXIMUM[a]	PERCENT PEAK ASSYMMETRY
^{222}Rn	0.010	5.49(99.9)	5.490	−0.26
^{226}Ra	1600	4.78(94.5)	4.783	+0.14 [b]
^{230}Th	80000	4.69(76.3)	4.696	+9.25
^{232}Th	1.4X10^{10}	4.01(77)	4.020*	+12.6
^{233}U	1.6X10^{5}	4.82(84.4)	4.831	+0.51
^{234}U	2.5X10^{5}	4.77(72.5)	4.781*	+7.9
^{235}U	7.1X10^{8}	4.40(55)	4.426*	+25.8
^{236}U	2.4X10^{7}	4.49(75)	4.508*	+4.6
^{238}U	4.5X10^{9}	4.20(77)	4.200	+1.1
^{237}Np	2.1X10^{6}	4.79(47)	4.824	+9.8
^{238}Pu	86	5.50(71.6)	5.513*	+2.0
^{239}Pu	24400	5.16(73.3)	5.162	+1.7
^{240}Pu	6580	5.17(73.5)	5.190*	+2.8
^{241}Am	458	5.49(85.2)	5.580	−0.25
^{243}Am	7400	5.28(87.9)	5.279*	+17.3
^{244}Cm	17.6	5.80(76.4)	5.815*	−1.2
^{249}Cf	360	5.81(84.4)	5.834	not appl.
^{250}Cf	13	6.03(84.5)	6.036*	+0.49

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[a] Calculated using parameters fitted to ^{249}Cf experimental spectrum (see Sect. II A5) except those marked with * which were calculated with a simple model considering only conversion electrons.

[b] calculated ignoring the satellite peak.