Conf-741212--4

HIGH-RESOLUTION LIQUID SCINTILLATION METHOD FOR THE ANALYTICAL DETERMINATION OF ALPHA-EMITTERS IN ENVIRONMENTAL SAMPLES*

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ABSTRACT

Appropriate optical and electronic components used in conjunction with an improved scintillator solution allow alpha liquid scintillation spectroscopy with an energy resolution of 200 to 300 keV and a background of 0.01 to 0.005 cpm. Liquid-liquid extraction procedures allow selective extraction of nuclides of interest directly into the scintillator. Applications to environmental samples are illustrated.

*Research sponsored by the U. S. Atomic Energy Commission under contract with the Union Carbide Corporation.

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INTRODUCTION

Alpha counting by liquid scintillation methods and its inherent advantages of simple, easy sample preparation, 100% counting geometry, and elimination of sample self-absorption were recognized several years ago.¹⁻³ However, only limited use has been made of the technique, for several reasons. First, the alpha energy resolution obtainable with commercial beta liquid scintillation equipment is poor, usually about 1 MeV full peak width at half maximum height (FWHM), and although it has been shown possible with appropriate optical and electronic arrangements to improve the energy resolution obtainable to 200 or 300 keV,^{1,2} parts of the needed equipment are not commercially available.

Second, the problem of quenching has prevented the use of liquid scintillation as a reliable means of identifying alpha energies. Quenching (i.e., reduction of the scintillator's light output) in alpha counting does not usually decrease the alpha counting efficiency as it does beta counting efficiency; however, pulse-height response is diminished. Therefore, samples introduced into a scintillator with varying amounts of water, acid, or salts, for instance, would show different pulse heights for the same nuclide, making identification of the alpha energies difficult.

A third constraint on the use of liquid scintillation has been its background which is somewhat higher than that of surface barrier detectors. Finally, the above obstacles to the effective use of liquid scintillation as a means of alpha counting and identification have been aggravated by a general lack of information about the use of liquid scintillation for alpha counting and of methods ^{lack} ~~of~~ ^{for} sample preparation. Recent work at Oak Ridge National

Laboratory and elsewhere has alleviated these difficulties to some extent and thus has made liquid scintillation an attractive alternative method for alpha counting and identification. This paper describes some of these developments and certain applications to the determination of alpha-emitters in environmental samples.

EXPERIMENTAL

Apparatus and Instrumentation

A block diagram of the single phototube detector and the basic associated electronics may be seen in Fig. 1. RCA 4523 and EMI-9840A phototubes were used. The signal from the phototube is fed to a multichannel analyzer through an appropriate preamplifier and any good linear amplifier. Specific detector and electronics arrangements have been described in previous publications.⁴⁻⁶ Pulse shape discrimination electronics for gating the multichannel analyzer to count only alpha pulses has also been described in an earlier publication.⁷ Other similar arrangements may be used for pulse shape discrimination.

Reagents

Extractants that are to be incorporated into the scintillator to prepare the extractive scintillator need to be as highly purified as possible to minimize quenching effects. To date, di(2-ethylhexyl)phosphoric acid (HDEHP) has been the principal extractant used. As received from Union Carbide Chemicals, this material usually contains about 1% neutral impurities. In our work, this impurity content was reduced to < 0.5% (with no detectable amount, < 0.1%, of dibasic acid) by scrubbing a 0.5 M solution in toluene with water three or four times, conversion to the sodium salt, scrubbing with saturated sodium sulfate

solution three or four times, and reconversion to the acid form. The tertiary amine, Adogen 364, from Ashland Chemicals was purified by one-stage vacuum distillation.

The naphthalene used in the scintillator solution was resublimed in our laboratory. The scintillator used in most of this work was PBBO [2-(4'-biphenyl)-6-phenylbenzoxazole]; it was chosen from a large number of commercially available scintillators as providing the best pulse height and resolution.⁶ It was used in all cases at a concentration of 4 g/liter in a toluene solution containing 200 g of naphthalene per liter. In earlier work a scintillator consisting of extractant plus 7 g of (2,5-diphenyloxazole) (PPO), and 0.5 g of [1,4-bis-2-(4-methyl-5-phenyloxazole)] (Me₂POPOP) per liter was used; however, energy resolution was not as good with these solutions. All the scintillators were obtained from commercial sources and were used without further purification.

The light-coupling oil used in the detector was Dow Corning 200 silicone oil. Its light transmission in a 1-cm cell was measured and found to be >99% over the range 4500 to 3400 Å, decreasing to 93% at 2500 Å. All other chemicals were the usual reagent grade.

RESULTS AND DISCUSSION

Following the early work of Horrocks^{1,2} we developed, several years ago, a liquid scintillation detector for alpha spectroscopy having better pulse-height resolution than commercially available beta liquid scintillation counters.⁴ However, the improved energy resolution could not be obtained with commercial liquid scintillation detectors because of inherent features of their optical and electronic systems.

The detector shown in Fig. 2 was the result of a large number of experiments with various arrangements of sample, reflector, and phototube. Although we did not test all possible combinations, this simple configuration was found, in our work, to give the maximum pulse height and best pulse-height resolution.

A diffuse, white reflective surface approximating a section of a sphere appears to be important in obtaining good pulse height and energy resolution. We believe this is due to the nonuniformity of the photocathode of the phototube. Such a reflector may integrate a flash of light from any portion of the sample over the entire tube face, thus averaging out any photocathode inconsistencies. Sources without a reflector give a much poorer pulse-height resolution, as also do sources backed by a specular reflector. Tests in which diffuse white reflectors of larger volume were used, with the sample located a greater distance from the photocathode, showed, at best, only marginally better energy resolution and were more cumbersome to handle. A direct comparison of the alpha energy resolution of our detector system (with our electronics) and of a commercial beta liquid scintillation counter may be seen in Fig. 3.

In the course of using alpha liquid scintillation counting in studies of aqueous metal complexation^{8,9} it was found that incorporating the highly salted aqueous phases directly in a dioxane-base scintillator was not feasible. In contrast, extraction of the radionuclide from these aqueous phases into a scintillator containing a primary amine sulfate or an alkyl phosphoric acid allowed quantitative counting with a minimum of quenching. This work led to the development of the concept of the "extractive scintillator" and its use as the last step in the separation of the nuclide of interest from unwanted ions.

Figure 4 shows the quenching in percent of maximum pulse height produced by several extractants we have used.¹⁰ The use of the extractive scintillator confers several desirable characteristics on liquid scintillation as applied to alpha-emitting nuclides. Among these are: (1) convenience; nuclides can be extracted from an aqueous solution directly into a scintillator as the last step in a separation process. (2) Reproducible energy response; since the extraction process adds little or nothing to the scintillator except the radio-nuclide, the energy response of the scintillator can be standardized to permit identification of the nuclides. (3) Much lower background; the improved pulse-height response and the ability to use pulse shape discrimination provided by the improved scintillator system makes possible a much lower background.

Reduction of background by pulse shape discrimination is an important factor in making liquid scintillation counting useful for environmental survey work. A block diagram of the components presently used in our pulse shape discrimination work is shown in Fig. 5. Work is now underway in our laboratory to develop a simple-to-operate single-unit pulse shape discriminator. Such circuits time the pulses and use the difference in duration of the alpha- and the beta-produced pulses to identify the alpha pulses and gate the MCA for alpha pulses only. With the use of pulse shape discrimination and the high-resolution liquid scintillation detector, a background of 0.01 cpm or lower is easily attained.

Bubbling a gas such as argon, methane, hydrogen, or carbon monoxide through the sample for 10 to 15 min effectively removes oxygen and eliminates oxygen quenching of the scintillator, thus improving the time separation of beta-gamma and alpha pulses. Figure 6 shows the time spectrum before and after such

treatment. Figure 7 shows alpha energy spectra taken in the presence of a gamma source both with and without pulse shape discrimination. It is possible to eliminate >99% of the beta-gamma-produced pulses in this way. Background without pulse shape discrimination is 1.0 cpm with a Pyrex sample tube and 0.3 cpm with a quartz sample tube. The minimum background obtainable under an alpha peak with a commercial beta liquid scintillation counter is about 5 cpm.

A toluene or xylene solution containing a single efficiency^t scintillator and nearly saturated with naphthalene has been found best for achieving maximum pulse height, energy resolution, and pulse shape discrimination. Of 12 commercially available scintillators tested, PBBO was shown to be the most effective.

Tests of this counting method for use in analyzing both soil and water for plutonium^{5,6} have given excellent results. The basic separation procedure includes: (1) placing the sample in solution in a nitrate medium, (2) adjusting the plutonium valence to IV with ferrous sulfate followed by sodium nitrite, (3) extraction of the plutonium into 0.3 M tri-n-octylamine nitrate, (4) stripping of the plutonium into 1.0 M perchloric acid, (5) removal of most of the perchloric acid by fusion in lithium perchlorate, and (6) dissolving the lithium perchlorate in water and extracting the plutonium into 0.5 to 1.5 ml of scintillator. This procedure requires about 45 min and separates plutonium cleanly from all other ions found in soil and water, including uranium and thorium. Greater than 99% of the plutonium in solution is usually recovered and counted. We are presently working on methods for analyzing plutonium in animal tissue and bone, and it is easy to modify the extraction procedure to recover almost any other alpha-emitting nuclide. In many cases, it is desirable to use chemical separations such as solvent extraction, ion exchange, or

precipitations to isolate the desired nuclides; in other cases, however, the 200- to 300-keV resolution available with this method allows more than one nuclide to be counted simultaneously. Figure 8, which shows part of the ^{232}Th decay chain, illustrates this possibility. Computer codes are available for separating partly merged peaks.⁶

Although relatively new, the techniques of combined liquid scintillation--solvent extraction described above frequently offer attractive alternatives to established separation and counting methods. Sample preparation is usually simpler and more rapid than that associated with other methods, notably electroplating for surface barrier detector counting. System reproducibility, energy resolution, and background levels are approaching values that make the methods competitive in identifying and counting environmental samples. Continuing research promises even further improvements in the method.

ACKNOWLEDGEMENT

The author wishes to acknowledge the excellent technical assistance of G. W. Case in this work.

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FIGURE CAPTIONS

1. High-Resolution Liquid Scintillation Spectrometer with Pulse Shape Discrimination.
2. Phototube and Reflector - Sample Holder Assembly. These two designs gave nearly identical performance.
3. Comparison of Energy Resolution Obtainable with (a) a Commercial Beta Liquid Scintillation Detector and (b) the ORNL Detector. The nuclides were ^{232}Th (4.01 MeV) and ^{239}Pu (5.15 MeV). The composition of the extractive scintillator solution was, per liter: 4 g of PBBO, 200 g of naphthalene, and 32 g of HDEHP in toluene.
4. Percent Quenching of PBBO Scintillator, 4 g/liter, in Toluene, by Several Extractants as a Function of Their Concentration. TBP = tri-n-butyl phosphate, TOPO = tri-n-octylphosphine oxide, HDEHP = di(2-ethylhexyl)-phosphoric acid, DDAS=di-n-decylamine sulfate, LNDAS = 1-nonyldecylamine sulfate, TOACl = Tri-n-octylamine chloride, TOANO₃ = tri-n-octylamine nitrate. Reprinted from Ref. 10, p. 797, by courtesy of Marcel Dekker, Inc.
5. Arrangement of Components Presently Used in Pulse Shape Discrimination Work.
6. Time Spectra of Alpha- and Gamma-Produced Pulses in PBBO-Naphthalene Scintillator (a) Before and (b) After Argon Bubbling.
7. Spectra of ^{239}Pu (5.15 MeV) and ^{244}Cm (5.80 MeV) in PBBO-Naphthalene Scintillator in the Presence of a Gamma Source (a) With and (b) Without Pulse Shape Discrimination.
8. Pulse-Height Spectrum of Thorium and Daughters in PBBO-Naphthalene Scintillator.

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Fig 5

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Fig. 3