

MODERN TECHNIQUES AND APPLICATIONS IN CERENKOV COUNTING*

H. H. Ross
G. T. Rasmussen**

Analytical Chemistry Division
Oak Ridge National Laboratory
Oak Ridge, Tennessee, USA

ABSTRACT

Cerenkov counting, a relatively unknown technique in the laboratory five years ago, has recently become the method of choice for counting many beta-emitting nuclides on a routine basis. The interest in this method is due, in part, to the ease in employing conventional liquid scintillation counting equipment without modification. Unfortunately, this similarity in measurement routine and equipment has led some investigators to believe that procedures developed for organic scintillation counting are directly applicable to Cerenkov systems. Unfortunately, this is far from true. Therefore, the following presentation has a three-fold purpose. First, a general review of the Cerenkov physical process is presented. Particular attention is given to the mechanism of Cerenkov radiation production, energy input-output characteristics, and spacial phenomena. The unusual properties of Cerenkov systems and how they may be used to advantage in practical counting situations is stressed. Also, an attempt is made to delineate important points of departure between organic liquid scintillation and Cerenkov methods. A second objective is to describe special measurement techniques that have been applied to Cerenkov counting problems. Among those discussed are the use of waveshifters, solvent selection, quenching, and standardization procedures. Finally, we will present the results of an original study concerning a computer simulation of the Cerenkov process that we have developed to establish optimal counting conditions for dual isotope

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

**Former student participant in Great Lakes College Association program at ORNL.

experiments. This technique is particularly interesting because it appears to be generally applicable to both Cerenkov and conventional liquid scintillation counting procedures. Use of a simple computer program allows one to quickly set-up his instrument for optimum isotope separation and also to evaluate the probable limits of error in the measurement.

Introduction

In the span of just a few years, Cerenkov counting techniques have become well established for the rapid assay of many beta and beta-gamma emitting radionuclides. Several authors have suggested that it is the method of choice for certain isotopes. Among the advantages of the techniques are extreme simplicity of sample preparation, the ability to count in aqueous systems without the use of organic fluors, and the high detection sensitivity that can be obtained. Another important consideration is that conventional liquid scintillation counting equipment can be used without modification. Many of the factors that influence the successful application of Cerenkov counting to practical problems have already been described (1,2). This paper will attempt to both review and extend the state of Cerenkov counting technology.

Fundamental Considerations

Cerenkov radiation is produced when a charged particle passes through a transparent medium (the Cerenkov generator) at a relative phase velocity greater than the speed of light in the same medium. Upon entering the generator, the particle experiences a strong slowing force and, during this period of rapid de-acceleration, electromagnetic radiation is generated. Cerenkov radiation has been described as the particle electromagnetic "shock wave" that is analogous to the boom created by hypersonic aircraft. Theoretically, the Cerenkov spectrum extends from microwave to X-ray frequencies; the portion of major concern to practical counting procedures lies in the ultraviolet and blue spectral regions. The most familiar display of Cerenkov radiation is the blue glow surrounding the core of swimming-pool reactors.

The basic physical condition that must be met for the formation of Cerenkov radiation is:

$$\beta n > 1 \quad (1)$$

LIQUID SCINTILLATION COUNTING

For relativistic electrons, β can be related to electron energy (E) and then combined with Equation 1 to yield:

$$\left[n^2 - \left(\frac{n}{\frac{E(\text{KeV})}{511} + 1} \right)^2 \right]^{1/2} > 1 \quad (2)$$

Where: β = velocity of particle (v)/speed of light (c)

n = refractive index of Cerenkov generator

E = energy of particle inducing Cerenkov radiation

When Equation 2 is solved for E , using the condition of equality and the refractive index of water, the result indicates that an electron must exceed 263 KeV in order to produce a Cerenkov response. Since many radionuclides emit beta particles significantly above the 263 KeV threshold, the legitimacy of using Cerenkov radiation for isotope assay in aqueous systems is obvious. It must be noted, however, that the photon yield from the Cerenkov process is quite small. Calculations have been made to describe the number of photons and the spectral distribution that results from a Cerenkov event (1,2) but perhaps one gets the best feeling for the magnitude of photon intensity by noting that a 1 MeV electron in water yields about the same number of photons as does an average tritium disintegration in an organic scintillator (3). Table I lists the detection efficiencies of several nuclides that have been determined experimentally (1,2,3,4,5,6,7,8,9).

Solvents

The selection of a solvent for organic liquid scintillation counting is often a formidable task, especially if particular sample solubility requirements are needed. For Cerenkov counting, no such problems exist; virtually any transparent liquid can be used as the Cerenkov generator. The primary solvent requirement is that it transmit radiant energy in the blue and near ultraviolet spectral regions with little attenuation. Even here, some compromises can be made if one is willing to work at reduced counting efficiency. The actual choice of a solvent is most often determined by what is convenient for the samples and the chemistry involved. Equation 1 shows that, as the refrac-

Table I.
 Experimental Counting Efficiencies of Nuclides
 In Aqueous Systems

<u>Isotope</u>	<u>Range of Counting Efficiency (%)</u>	<u>Isotope</u>	<u>Range of Counting Efficiency (%)</u>
^{204}Tl	1.3 - 1.9	^{185}W	2.1
^{137}Cs	2.1	^{36}Cl	2.3 - 13
^{198}Au	5.4	^{170}Tm	5.6
^{210}Bi	6.8	^{47}Ca	7.5
^{40}K	14 - 25	^{24}Na	18
$^{90}\text{Sr}-^{90}\text{Y}$	22	^{86}Rb	23
^{32}P	20 - 48	^{90}Y	36 - 50
^{128}I	40 - 50	$^{144}\text{Ce}-^{144}\text{Pr}$	54 - 62
^{42}K	11 - 60	$^{106}\text{Ru}-^{106}\text{Rh}$	62 - 70

LIQUID SCINTILLATION COUNTING

tive index of the generator is changed, the detection threshold also changes. It has also been demonstrated that the use of highly refractive liquids will increase the photon yield for a given particle energy (10). Occasionally, use is made of these characteristics to select a solvent to enhance the counting efficiency of a given nuclide or to change the detection energy threshold.

The most widely used solvent for Cerenkov counting is water. It is highly transparent to the Cerenkov emission and can act as an efficient solvent for a wide variety of inorganic and organic materials. Other peripheral considerations are its low cost, and lack of toxicity and flammability. However, for many biological materials, other solvents are preferred. Table II lists experimental relative counting efficiencies for ^{32}P in various solvents (8,9). The change in the relative counting efficiency in the above table is a direct reflection of the variability of the index of refraction combined with any optical absorption properties of the solvents. As the index of refraction increases, the energy threshold is lowered and thus, more of the beta spectrum is included in the measurement. The photon yield is enhanced also. In some cases, small inconsistencies can be seen; this is probably the result of experimental error. There are many practical applications for the use of these special solvents. For example, it has been noted (8) that chloroform is used to extract lipids (a severe quenching situation in organic scintillators) and formic acid is used as a solvent for defatted tissue. Acetone (5%) in chloroform has been used for counting organic radiobromides (11). Additionally, a solvent can be selected to count a nuclide that cannot even be detected in water. The low energy emitter ^{99}Tc has been counted with very low efficiency in a 95% glycerol solution (1) and ^{14}C has been measured in α -bromonaphthalene (12). These techniques are, however, rather limited in their scope of application.

The effect of solvent volume has been adequately discussed in the literature (1,2,3,9,13,14) and will not be repeated in detail here. Most investigators agree in general, if not in detail, that counting volume is a parameter that must be controlled for reproducible results. In all of the counting systems tested that use a "standard" size liquid scintillation vial, the volume-efficiency curve appears to go through a maximum at about 10 ml. The main

Table II.
 Relative Counting Efficiencies Of ^{32}P In
 Various Solvents

<u>Solvent</u>	<u>Volume Ratio (v/v)</u>	<u>Relative Counting Eff. ($\text{H}_2\text{O}=1$)</u>
formic acid (98%)		0.96
formic acid-butyl acetate	1/1	1.00
methanol		1.08
chloroform		1.14
isopropanol-water	1/1	1.15
ethanol (95%)		1.16
ethanol-water	4/1	1.19
acetone		1.19
petroleum ether		1.21
chloroform-methanol	2/1	1.26
hexane		1.28
isopropanol		1.29
isopropanol-heptane	1/1	1.31
chloroform-isopropanol	2/1	1.32
heptane		1.38
benzene		1.59
toluene		1.66

LIQUID SCINTILLATION COUNTING

disagreement among authors is the magnitude of the efficiency shift with volume and the energy of the nuclide being counted. We feel that the variability in the volume effect can be directly related to the optical geometry of a particular counting system. Perhaps the one general rule that can be formulated is that each investigator must establish the volume-efficiency function for his own instrument so that acceptable volume tolerance limits can be assigned. For a given liquid sample, one would like to use the maximum possible volume to extend the lower limit of detection. However, it is quite clear that the volume effect is much more pronounced in Cerenkov counting than the usual organic techniques.

Solid Cerenkov Generators

Thus far, the major consideration for Cerenkov generators has been liquids. There is no reason, however, that other transparent substances cannot be used. For large generating volumes, solids offer a number of advantages. Where Cerenkov detectors have been used to measure the radioactive products of an activation analysis, Lucite or Perspex generators have proven popular (15,16). One benefit of using these plastics is that they can be molded or machined into special shapes to suit the particular geometry required in the experiment. They also have excellent optical properties.

Other types of solids have also proven useful. One ^{32}P product was isolated on either paper or silica gel. For counting, the paper was suspended inside a counting vial and the response generated in the vial wall was counted. The silica gel was simply placed in the vial and the emission from the gel and the vial wall was measured (9). Results were good in both cases. In a similar experiment, a phosphorous compound was collected on a membrane filter and again suspended in the vial for counting (6). Other solid materials that have been used are polyethylene, sodium iodide, cesium iodide, quartz, ice, and crystals of many different types of organic compounds. With solids, as with liquids, the possible choices are almost limitless.

Geometry Effects

When Cerenkov radiation is generated, the emission takes place in a well defined spacial configuration. The practical effect of this phenomenon is covered in previously

cited literature. However, two items are worth noting as being very useful techniques for routine assays. It has been found (4,9,13) that by substituting polyethylene counting vials for glass, a >25% increase in the counting efficiency can be obtained. Another investigator (5) shows that by adding Cab-O-Sil to the liquid generator, an increase of 5-10% can be realized. In both of these methods, the increased counting efficiency is probably due to the diffusing effect that is introduced. Since most of the commercial counting systems utilize some type of coincidence circuitry, a positive indication in two phototubes is needed for a count to be registered. The geometry of Cerenkov emission is such that one phototube will be favored for a given decay event. Normal reflections in the counting chamber will help to partially alleviate this effect. The additional diffusing ability of the polyethylene vial or the Cab-O-Sil provides an even more uniform distribution of the emitted photons.

Quenching

The worker in organic liquid scintillation counting is well aware of two forms of quenching, chemical and color. Chemical quenching (chemical interference with molecular transitions in the organic fluor) does not exist in Cerenkov spectroscopy. This is evidenced by the fact that strong acids such as sulphuric, hydrochloric, and perchloric acids and a wide variety of inorganic anions and cations show no significant reduction in the counting efficiency when compared with samples counted in pure water (3,5,13, 17). Unfortunately, color quenching (partial or total absorption of emitted photons) continues to be a significant quenching parameter. As might be expected, most of the standard quench correction techniques have been tested with Cerenkov systems; the published results give less than a clear picture of what can be accomplished with these methods.

Samples may color quench by either ultraviolet or visible absorption. For example, the very common NO_3^- and NO_2^- ions are strong ultraviolet absorbing species and cause moderate to severe quenching problems (13). This substantially limits the use of nitric acid solutions in counting.

LIQUID SCINTILLATION COUNTING

Obviously, visibly colored solutions, especially reds and yellows, cause similar problems. One paper examines quench correction techniques in detail (18) and concludes that internal standard or de-colorization procedures are laborious, that the channels ratio method is too insensitive, and that the external standard is somewhat inaccurate but can possibly be used.

In spite of these findings, the external standard and the channels ratio method have both been used to obtain an assay correction of $98\% \pm 6\%$ (19). Another investigator pointed out that if one considers the variability of the sample vial, the external standard can yield results with errors of about $\pm 2\%$ (9). The channels ratio method has often been employed without difficulty. In one series of experiments designed to test various quench correction techniques for ^{42}K , the author found that the channels ratio was the best method (20).

Other less common techniques have been developed to deal with the color quenching problem. One worker has found that the degree of quenching can be related to the optical absorption of the sample as measured on a spectrophotometer (5). An interesting technique is the development of the "Cerenkov insert" (21,22). Here, the sample is placed in a thin-wall opaque holder which is then suspended in a transparent generating solution. Color quenching is completely avoided but, because of self absorption in the sample, high counting efficiency can only be obtained with energetic emitters.

It is clear from the above discussion that many different procedures can be used for color quench correction. No one technique (except perhaps the internal standard) appears to be universally applicable. It is suggested that each sample type be treated as an individual situation and that the best correction method be selected on the basis of experimental tests.

Waveshifters

All of the above discussion has been centered on the direct measurement of the Cerenkov emission. As noted previously, a significant portion of this emission occurs in the ultraviolet spectral region. These frequencies are easily absorbed in glass sample vials, in the face of glass photomultiplier tubes, or in the solvent itself. A second problem is the directional nature of the Cerenkov emission

described under geometry effects. If the ultraviolet photons can be converted to the visible region and if these photons could be given an isotropic spacial distribution, the counting efficiency should be distinctly improved.

A possible answer to both of these problems rests in the use of a waveshifting compound in the Cerenkov generator similar to the use of POPOP in organic systems. Many investigators have already studied the characteristics and applications of waveshifting compounds and found them to be highly desirable (3,4,7,17,23,24,25,26). Table III lists some of the compounds that have been employed in both organic and aqueous media.

Although a significant increase in the counting efficiency can be obtained when using one of these compounds, it must be remembered that when they are employed, the system is no longer a purely Cerenkov process. Thus, the problem of chemical quenching becomes possible and large changes in the observed response can result. It is also true that visible quenchers can become more significant in a waveshifted system. The benefits of using a waveshifter must be carefully weighed against the possible deleterious side effects that may appear. Most authors agree, however, that waveshifters are particularly desirable when measuring low-energy emitters.

Applications

Cerenkov radiation has been employed in virtually every field of isotope assay problem. Samples such as plant and animal tissue, isotope preparations, environmental materials, reactor effluents, and biomedical fluids have been examined with excellent results. These applications are well documented in the open literature and will not be repeated here. However, some methods will be described that make use of the unusual properties of Cerenkov radiation and illustrate the unique characteristics that make the technique particularly valuable.

Since there is a distinct energy threshold below which no Cerenkov emission occurs, it is possible to determine the activity level of a small amount of an energetic nuclide in the presence of a much larger amount of a weaker emitter. This type of analysis can be performed with little or no interference from the predominant species. The simultaneous determination of ^{33}P and ^{32}P was accomplished by combining the techniques of Cerenkov and organic

LIQUID SCINTILLATION COUNTING

Table III.

Waveshifting Compounds Used Successfully In
Cerenkov Counting Systems

2-amino-6,8-naphthalene-disulfonic acid
2-naphthalene-3,6-disulfonic acid
2-naphthalamine-6,8-disulfonic acid
2-naphthol-3,6-disulfonic acid
2-naphthol-6,8-disulfonic acid
7-amino-1,3-naphthalene-disulfonic acid
4-methylumbelliferone
 β -naphthol
 β -naphthylamine
sodium salicylate

scintillation counting (27). First, the sample was assayed in an aqueous Cerenkov system to determine the ^{32}P concentration; ^{33}P was found to count with $< 0.01\%$ efficiency (probably zero). Then the sample was counted in an organic scintillator to determine total ^{33}P and ^{32}P . Subtracting the ^{32}P Cerenkov value from the total yielded the correct amount of each isotope. In a similar way, the ^{80}gBr and $^{80\text{m}}\text{Br}$ isotopes were counted successfully in the presence of ^{82}Br with only a small interference (11).

Both solid and liquid Cerenkov generators have been used for measuring the products from an activation analysis (7, 15, 16, 28, 29, 30). A particularly important aspect of this application is the very fast response of the detector; pulse pile-up and summation problems are greatly minimized. Some of the elements that have been determined are Be, Li, B, F, I, and O_2 . The role of Cerenkov detectors in charged particle activation has been summarized (31). Some of the more unusual applications of Cerenkov detectors include the use of the ^{36}Cl emission to determine particle size (32), the absorption of Cerenkov photon emission to follow radiolysis in solution (33, 34), the determination of the refractive index of liquid orthodeuterium by comparing its Cerenkov response with that of hydrogen (35), and the analysis of gaseous ^{85}Kr (36).

Dual Tracer Studies

In our laboratory, we have been concerned recently with the problem of determining two isotopes simultaneously in a Cerenkov system. The solution of this problem is somewhat more complex than that observed in organic scintillators because of the high degree of overlap in the Cerenkov spectra. For our study, we selected the isotopes ^{36}Cl and ^{32}P as being representative of a typical counting situation.

The effective determination of these two isotopes in a mixture requires that their Cerenkov spectra be sufficiently different to provide different relative counting efficiencies over two regions of the response function. If two single channel analyzers are set to count different portions of the response, it is possible by using a solution containing only chlorine-36, to determine counting efficiencies for this isotope in each channel. The efficiencies of phosphorous-32 in these same two channels can also be determined. Also, a count rate for a phosphorous-chlorine mixture can be determined in each of the two channels. Knowing the efficiency for each isotope in each

LIQUID SCINTILLATION COUNTING

channel and counting rates in each channel for a mixture, one can determine the disintegration rate of each isotope in the mixture using techniques developed previously for organic systems. The necessary equations are summarized in Table IV.

If the same stock solutions of phosphorus and chlorine are used to prepare samples containing a single isotope and also isotope mixtures, it is possible to determine the accuracy of a dual isotope measurement that is independent of the absolute accuracy of the stock solution assays. This quantity, hereafter referred to as the accuracy function, is the ratio of the experimentally determined disintegration rate of one isotope to the "known" disintegration rate for that isotope that is used in the calculations of the channel efficiencies. The accuracy function is a function of six variables which are the counting rates used to determine the efficiency of each isotope in each channel and the counting rates of the mixture in each channel. If the dual tracer method is effective, that is, if the equations describing the system are valid, the accuracy function for an isotope will equal 1 for the case where the amount of that isotope used is the same in both the sample used for the efficiency determination and the mixed sample. The accuracy function, appropriately, provides a convenient measure of the accuracy of the determination. It equals (or can be corrected to equal) one, when the system is "well-behaved," and deviations from unity indicate directly relative errors.

The equation for the accuracy function, because it is a function of six counting rates, can be used to estimate the effect of random statistical errors in specific gross counts on the precision of the determination. The variation in the accuracy function as a result of statistical variation in a given counting rate can be estimated as the product of the partial differential of the accuracy function with respect to that counting rate and the estimated error in the counting rate. The estimated error in the counting rate resulting from random statistical errors can be approximated as the product of the counting rate and the relative standard deviation of the gross count that was accumulated to determine that counting rate. A convenient estimate of the standard deviation of the gross count is its square root. The sum of the absolute values of the relative error in the accuracy function caused by random

Table IV.

Summary of Equations Used For Dual Isotope Analysis

$$\frac{G_{Cl,1}}{t_{Cl}^D D_{Cl}} = \frac{C_{Cl,1}}{D_{Cl}} = E_{Cl,1}$$

$$\frac{G_{Cl,2}}{t_{Cl}^D D_{Cl}} = \frac{C_{Cl,2}}{D_{Cl}} = E_{Cl,2}$$

$$\frac{G_{P,1}}{t_{P}^D D_{P}} = \frac{C_{P,1}}{D_{P}} = E_{P,1}$$

$$\frac{G_{P,2}}{t_{P}^D D_{P}} = \frac{C_{P,2}}{t_{P}^D D_{P}} = E_{P,2}$$

$$\frac{G_{M,1}}{t_M} = C_{M,1}$$

$$\frac{G_{M,2}}{t_M} = C_{M,2}$$

$$C_{M,1} = E_{Cl,1}^D D_{Cl} + E_{P,1}^D D_{P}$$

$$C_{M,2} = E_{Cl,2}^D D_{Cl} + E_{P,2}^D D_{P}$$

$$D^*_{Cl} = \frac{C_{M,1} E_{P,2} - C_{M,2} E_{P,1}}{E_{Cl,1} E_{P,2} - E_{Cl,2} E_{P,1}}$$

Substituting for efficiency terms and dividing by D_{Cl}^D yields the accuracy function:

$$A_{Cl} = \frac{D^*_{Cl}}{D_{Cl}} = \frac{C_{M,1} C_{P,2} - C_{M,2} C_{P,1}}{C_{Cl,1} C_{P,2} - C_{Cl,2} C_{P,1}} ; \Delta A = \left[\frac{\partial A}{\partial C_{M,1}} \Delta C_{M,1} \right] +$$

$$\left[\frac{\partial A}{\partial C_{M,2}} \Delta C_{M,2} \right] + \left[\frac{\partial A}{\partial C_{Cl,1}} \Delta C_{Cl,1} \right] + \left[\frac{\partial A}{\partial C_{Cl,2}} \Delta C_{Cl,2} \right] + \left[\frac{\partial A}{\partial C_{P,1}} \Delta C_{P,1} \right] +$$

$$\left[\frac{\partial A}{\partial C_{P,2}} \Delta C_{P,2} \right] ; \Delta C_{M,1} = C_{M,1} \sqrt{\frac{G_{M,1}}{G_{M,1}}} , \text{ etc.}$$

Variables;

Subscripts;

- G: gross counts
- C: counting rate
- t: time of count
- D: disintegration rate "known"
- D*: experimentally determined disintegration rate
- A: accuracy function
- E: counting efficiency

- Cl: chlorine
- P: phosphorus
- 1: channel 1
- 2: channel 2
- M: mixture

LIQUID SCINTILLATION COUNTING

errors in the six counting rates provides an estimate of error based solely on the statistics of the system. Such an error estimate is quite useful in the selection of optimum channel combinations.

Chlorine-36 was obtained from the Isotopes Division at Oak Ridge National Laboratory, and the phosphorous-32 was prepared by irradiation of ammonium phosphate (dibasic) in the Oak Ridge Research Reactor. Conventional $4\pi\beta$ counting techniques were used to determine absolute disintegration rates. The basic instrumentation used was a Packard Tri-Carb Liquid Scintillation Spectrometer (3000 series). All data were collected with the instrument operating in a coincident pulse height distribution mode. Counts were taken at preset times to yield between 10^5 and 10^6 gross counts in most counting situations. Background, which was determined to be approximately 10 counts per minute over the entire single channel analyzer range for the experimental conditions used, was considered negligible in all cases. Samples were prepared to give a total volume of about 8 ml of aqueous solution and were counted in standard glass counting vials at 1° C.

To accumulate a set of data, five different solutions were prepared, one of each of chlorine-36 and phosphorous-32 separately and three mixtures of the two in which the activity ratios were approximately one to one, one to ten, and ten to one. The solutions containing only one isotope were used to determine counting efficiencies in selected channels, and the mixtures were counted to determine the accuracy of the method.

The major variable parameters in the determination of two isotopes in a mixture are the gain and discriminator settings for the two single channel analyzers. The adjustment of these variables defines the two channels which are used to assay the mixture. While methods for the selection of optimum gain and channel combinations have been reported for dual tracer studies with liquid scintillation systems, it was not readily evident that these methods could be extended to Cerenkov counting systems. For example, a useful technique to optimize gain settings in dual tracer liquid scintillation systems utilizes an "efficiency isotope A vs. efficiency isotope B" plot for varying gain settings (37). However, when this technique, known as an Engberg plot, was applied to the phosphorous-32/chlorine-36 Cerenkov system, it provided relatively

little guidance. (It should be noted that an Engberg plot for carbon-14 and tritium in liquid scintillation solutions prepared at the same time worked well for that combination of isotopes.) Experience indicated that a practical gain setting was one which allowed the entire spectrum of phosphorus-32, the stronger Cerenkov emitter, to be included completely in the range spanned by the single channel analyzer.

A more complex problem was that of selecting optimum channels for the simultaneous determination of the two isotopes. Any given channel may include a certain portion of each isotope's response spectrum, and thus it is possible to describe a channel in terms of the efficiencies that it defines for the two isotopes or in terms of the ratio of these efficiencies. In selecting channels, a variety of criteria may be applied. A channel may be set to maximize the chlorine/phosphorous efficiency ratio. Another channel may be set to minimize this ratio. Instead of counting efficiencies, ratios of other terms such as the figure of merit, which is the product of counting rate and efficiency, may be the basis for selecting channels. Another possibility is to select a channel which excludes entirely the lower energy β^- emitter, and counts only the stronger one. Selecting combinations of channels provides even more possibilities. Two channels may be selected so that they have a common boundary, no boundary, or boundary overlap.

To evaluate which combinations of which channels might be promising for application to the chlorine-36/phosphorous-32 Cerenkov system, an error analysis based on a number of different semi-hypothetical counting situations was initiated. The efficiencies of each isotope separately were determined over the whole range of the single channel analyzer in one-half volt increments. By summing the efficiencies of appropriate groups of increments, it was possible to predict efficiencies for both isotopes in hypothetical channels. Eight such channels were selected, and the efficiencies of phosphorous and chlorine associated with them were calculated. Each of these efficiencies was multiplied by 5×10^5 . The resulting numbers were assumed to correspond to counts that would be tallied for a specific isotope in a given channel if it were exposed to a solution of that isotope that yielded five hundred thousand disintegrations over any arbitrarily selected time period. The numbers themselves provided estimates of counts that

LIQUID SCINTILLATION COUNTING

might actually be observed in efficiency determinations for the particular isotope in selected channels. Adding the phosphorous and chlorine numbers for a channel predicted the count for a mixture of the two with a one-to-one activity ratio. Counts were also predicted for one-to-ten and ten-to-one activity ratios, so that each hypothetical channel had five numbers associated with it--one for chlorine, one for phosphorous, and one for each of three mixtures. By selecting combinations of these eight hypothetical channels it was possible to predict the errors in statistics for a particular combination of channels.

Of the twelve different combinations of these eight channels that were examined, the one for which the lowest errors on the basis of statistics were predicted, was a pair of channels with a common boundary in which the chlorine-36 efficiency was 3.0% in the lower channel and 0.53% in the upper channel, and the phosphorous-32 efficiency in the lower channel was 12.7% and in the upper channel 18.0%. An effort was made to duplicate these channels in the laboratory and to correlate the predicted and observed errors for the laboratory situation. The combination of channels found experimentally which closely approximated the hypothetical combination was a pair for which the phosphorous efficiencies were 13.0% in the lower channel and 17.7% in the upper channel. The chlorine efficiencies were 2.58% and .42% in the lower and upper channels respectively. Table V lists the predicted and observed errors for two combinations in laboratory trials. Another combination of hypothetical channels which was selected as being relatively good with respect to predicted error was also nearly duplicated in actual counting conditions, and these channels too showed roughly the same correlation between predicted and observed error. It must be remembered that predicted errors are maximum errors predicted on the basis of random errors in counting statistics while the observed errors reflect errors from all sources, such as errors in pipetting and variations in instrument response.

The data in Table V show that the largest error observed in any determination of phosphorus is <3%. The greatest observed error for chlorine (excluding the 10:1 P/Cl ratio) is <5%. Of course, predicted and observed errors can be reduced by extending the counting period.

In a preliminary way, we have applied this computer simulation technique to the more common situation of counting

Table V.
Comparison Of Experimental And Predicted Results For
Two Isotopes

Condition # 1

Sample	Activity Ratio (P/Cl)	Phosphorous-32 % Of Error		Chlorine-36 % Of Error	
		Observed	Predicted	Observed	Predicted
1	1:1	1.59	0.28	2.88	2.81
2	1:10	1.42	0.84	3.05	1.03
3	10:1	1.06	0.26	55.80	18.45
1	1:1	1.85	0.28	1.69	2.85
2	1:10	2.09	0.84	3.43	1.04
3	10:1	2.23	0.25	13.77	22.03

Condition # 2

Sample	Activity Ratio (P/Cl)	Phosphorous-32 % Of Error		Chlorine-36 % Of Error	
		Observed	Predicted	Observed	Predicted
1	1:1	1.50	0.40	3.25	3.89
2		2.12	0.39	4.39	4.16
3		1.80	0.39	0.07	4.03
4		1.36	0.40	1.70	3.95
5		1.85	0.39	0.99	4.07
1	1:10	2.78	1.23	1.23	1.50
2		2.78	1.23	1.33	1.49
3		1.95	1.24	2.50	1.49
4		2.40	1.24	1.88	1.50
5		2.24	1.23	1.62	1.50
1	10:1	1.55	0.36	0.02	34.03
2		2.19	0.35	32.51	50.32
3		1.64	0.36	8.70	31.85
4		1.61	0.36	12.32	38.89
5		1.63	0.36	18.79	42.16

LIQUID SCINTILLATION COUNTING

carbon-14 and tritium in organic scintillators. Over wide ranges of activity ratios and absolute activity levels, predicted and observed errors are in very close agreement. Thus, in our opinion, the computer simulation is generally applicable to the general problem of counting multiple isotopes that exhibit a continuous emission function. The great advantages of the method are the speed with which predictions can be obtained and the accuracy of those predictions.

References

1. H. H. Ross, Anal. Chem. **41**, 1260 (1969).
2. R. P. Parker and R. H. Elrick in The Current Status of Liquid Scintillation Counting, P.110 (Edwin D. Bransome, Ed.). New York and London: Grune and Stratton (1970).
3. T. Iwakura, Radioisotopes (Tokyo) **18**, 500 (1969).
4. A. Laüchli, Int. J. Appl. Radiat. and Isotopes **20**, 265 (1969).
5. L. I. Wiebe, A. A. Noujaim, and C. Ediss, ibid. **22**, 463 (1971).
6. S. Mizuno, K. Eguchi, and K. Yano, Radioisotopes (Tokyo) **18**, 19 (1969).
7. F. L. Hoch, R. A. Kuras, and J. D. Jones, Anal. Biochem. **40**, 86 (1971).
8. M. K. Johnson, ibid. **29**, 348 (1969).
9. R. T. Haviland and L. L. Bieber, ibid. **33**, 323 (1970).
10. I. M. Frank and I. G. Tamm, Dokl. Akad. Nauk. SSSR **14**, 109 (1937).
11. G. P. Gennaro and K. E. Collins, J. Radioanal. Chem. **5**, 387 (1970).
12. H. H. Ross in The Current Status of Liquid Scintillation Counting, p.123 (Edwin D. Bransome, Ed.). New York and London: Grune and Stratton (1970).
13. J. R. Robinson, Int. J. Appl. Radiat. and Isotopes **20**, 531 (1969).
14. K. Asada, M. Takahashi, and M. Urano, Anal. Biochem. **48**, 311 (1972).
15. M. Wiernik and S. Amiel, Trans. Am. Nuc. Soc. **12**, 518 (1969).
16. H. R. Lukens, J. Radioanal. Chem. **1**, 349 (1968).
17. V. K. Haberer, Atomwirtschaft **10**, 36 (1965).
18. R. H. Elrick and R. P. Parker, Int. J. Appl. Radiat. and Isotopes **19**, 263 (1968).

19. J. R. Brownell and A. L'äuchli, ibid. 20, 797 (1969).
20. A. T. B. Moir, ibid. 22, 213 (1971).
21. P. E. Ballance and S. Johnson, Health Phys. 20, 447 (1971).
22. P. E. Ballance and S. Johnson, Planta 91, 364 (1970).
23. H. H. Ross in Organic Scintillators and Liquid Scintillation Counting, p.757 (D. L. Horrocks and C. T. Peng, Eds.). New York and London: Academic Press (1971).
24. E. Heiberg and J. Marshall, Rev. Sci. Instrum. 27, 618 (1956).
25. N. Porter, Nuovo Cim. 5, Series 10, 526 (1957).
26. G. Cosme, S. Jullian, and J. Lefrancois, Nucl. Instrum. and Methods 70, 20 (1969).
27. L. C. Brown, Anal. Chem. 43, 1326 (1971).
28. H. R. Lukens and J. E. Lasch, Int. J. Appl. Radiat. and Isotopes 15, 758 (1964).
29. J. P. Thomas and E. A. Schweikert, Radiochem. Radioanal. Lett. 9, 155 (1972).
30. M. Wiernik and S. Amiel, J. Radioanal. Chem. 5, 123 (1970).
31. F. Girardi, V. Camera, and E. Sabbioni, Radiochem. Radioanal. Lett. 2, 195 (1969).
32. J. Ashcroft, Int. J. Appl. Radiat. and Isotopes 20, 555 (1969).
33. Z. P. Zagorski and Z. Zimek, Nukleonika 15, 335 (1970).
34. Z. P. Zagorski and Z. Zimek, ibid. 16, 359 (1971).
35. D. S. Ayers, et. al., Physica 43, 105 (1969).
36. J. D. Buchanan, Radiochim. Acta 9, 218 (1968).
37. Y. Kobayashi and D. V. Maudsly in The Current Status of Liquid Scintillation and Counting, p.76 (Edwin D. Bransome, Ed.). New York and London: Grune and Stratton (1970).