

## THEORY AND APPLICATION OF CERENKOV COUNTING

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### ABSTRACT

The production of Cerenkov radiation by charged particles moving through a transparent medium (the Cerenkov generator) is a strictly physical process that is virtually independent of the chemistry of the medium. Thus, it is possible to calculate easily all of the important parameters of the Cerenkov process such as excitation threshold, emission intensity, spectral distribution, directional characteristics, and time response. The results of many of these physical effects are unknown in conventional liquid scintillation spectroscopy and, therefore, many unique assay techniques have been developed as a result of their consideration. This paper will discuss the theoretical basis of the Cerenkov process, explore the unusual characteristics of the phenomenon, and demonstrate how these unusual characteristics can be used to develop equally unusual counting methodologies. Particular emphasis will be directed toward an analysis of published data (obtained with conventional liquid scintillation instrumentation) that would be difficult or impossible to obtain with other counting techniques. Also discussed is a new type of sample vial that uses an isolated waveshifting system. The device was specifically designed for Cerenkov counting.

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Admiring, in the gloomy shade,  
Those little drops of light.

Edmund Waller

## INTRODUCTION

Although the concept of counting a radionuclide dissolved in a liquid via Cerenkov radiation was demonstrated by Belcher (1) over 20 years ago, it is only within the last five years that a significant number of real applications have appeared in the open literature. This lack of interest was most probably due to the difficulty in measuring the very feeble emission generated by beta particles in the range of 0.5 to 2.0 MeV. For example, a 1.0 MeV beta particle in water dissipates only about 1 KeV of energy in the 300 to 700 nm spectral region (perhaps 30-45 photons). Add to this tenuous photon emission the limited spectral sensitivity and conversion efficiency of early photomultiplier tubes, and the experimental difficulties become obvious. Other problems, such as dark current (S/N), directional considerations, and noisy electronics only compounded the dilemma. However, new instrumentation concepts and components for liquid scintillation counting have changed the situation significantly; high sensitivity Cerenkov counting has become a routine operation in many laboratories.

Jelley (2) has written an excellent account of the theory and application of Cerenkov radiation. The major application and instrumentation emphasis is, however, directed toward problem areas in high energy physics. More recent discussions (3-5) cover the general area of using commercially available liquid scintillation spectrometers for the assay of dissolved nuclides in small, conventional samples. These papers describe a wide range of experimental conditions that include typical detection efficiencies, instrument set-up, quenching effects, threshold energy response, sample volume, and directional considerations. All of these papers emphasize three important considerations peculiar to Cerenkov counting - energy discrimination, chemical quenching, and the absence of conventional scintillation fluors in the system. A view of these special characteristics reveals the unique application areas of Cerenkov spectroscopy.

Energy discrimination

Perhaps the most unusual aspect of Cerenkov counting is the presence of an energy threshold effect that is solely a function of the refractive index of the Cerenkov generator - solid, liquid, or gas. The result of this effect is that particles below the energy threshold create no photon emission; particles above the threshold do generate a photon emission which becomes greater as the initial energy of the particle becomes further separated from the threshold energy. The threshold energy for electrons (betas) in any medium can be approximated using Equation 1:

$$E_T = 511 \left( \frac{1}{\sqrt{1 - \frac{1}{n^2}}} - 1 \right) \quad (1)$$

where  $E_T$  = threshold energy (KeV)  
 $n$  = refractive index

The actual threshold energy cannot be calculated exactly using Equation 1 because, in real systems, the change of refractive index as a function of wavelength must be considered along with the spectral sensitivity of the experimental photon detector. However, one sees in Table I that the electron energy threshold varies over a rather narrow range (using  $n_D$ ) for a considerable change in refractive index. Thus, for practical purposes,  $E_T$  at  $n_D$  is fairly realistic. But, it should be noted that some materials exhibit significant changes in refractive index in spectral regions (UV) where phototubes are sensitive. In these cases, major shifts can be observed in the energy threshold (6).

One of the best examples of an application that takes advantage of the energy threshold effect is a demonstration of the rapid determination of phosphorus-32/33 mixtures by Brown (7). Analysis of these mixtures by liquid scintillation counting does not offer a sufficiently high degree of sensitivity or accuracy because of the relatively low energy resolution inherent with this method. However, in an aqueous Cerenkov system, phosphorus-33 lies below the energy threshold and thus yields no response at all; phosphorus-32, which lies well above the threshold gives a

Table 1

## CERENKOV ENERGY THRESHOLD FOR ELECTRONS IN VARIOUS SOLVENTS

<u>Solvent</u>	<u>n<sub>D</sub></u>	<u>Threshold (KeV)</u>
ethyl trifluoroacetate	1.31	283
water	1.33	263
ethyl alcohol	1.36	243
40% sucrose	1.40	219
toluene, 84% sucrose	1.50	174
bromoform	1.60	145
methylene iodide	1.76	111

strong reaction. Any counts observed in a phosphorus-32/33 mixture must be due only to the -32 contribution. (The response of -33 was experimentally determined to be <0.01%). By combining a Cerenkov count with a liquid scintillator count, Brown was able to determine mixtures of the phosphorus isotopes over an extremely wide range with errors usually less than 1.5%. The absolute accuracy of this method is limited mainly by the degree of uncertainty of phosphorus-33 liquid scintillation and the phosphorus-32 Cerenkov counting efficiency determinations.

The above example must be considered to be a "classic" since only one nuclide in the mixture gives any Cerenkov response while the other is completely masked. Nevertheless, many practical measurement systems have been developed where two (or more) nuclides have been assayed by taking advantage of the low detection efficiency of nuclides whose maximum beta energy lies above the threshold, but not significantly above. For example, thulium-170 with a beta energy maximum of almost 1 MeV counts with only about 5-6% efficiency. Using similar techniques, Randolph (8) has determined mixtures of Sr-89/90; Buchtela and Tschurlovits (9), Sr-89/90 and Y-90; and Ross (10), mixtures of Cl-36 and P-32. In each of these examples, some Cerenkov response was observed from every nuclide. The differences were sufficiently different, however, so that errors generally in the range of 5% were obtained over the span of mixture

concentrations that were studied. The energy threshold technique is clearly not strictly limited to the theoretical cut-off value.

### Chemical quenching

If any experimental parameter could be said to play a pivotal role in the success or failure of liquid scintillation counting, it must certainly be that of color and chemical quenching. The quenching phenomenon must be considered in virtually every aspect of the sample measurement - selection of cocktail formulation, sample preparation, instrument settings and correction procedures, etc. In almost one half of the liquid scintillation papers published in the last two years, a quenching problem and its solution was a major aspect of the investigation. In Cerenkov counting the situation is somewhat different; there is no known mechanism for chemical quenching to occur - it does not exist. This simple fact has virtually revolutionized the techniques used for sample preparation. Powerful chemical treatments that would be precluded from use with scintillation samples can be applied freely in Cerenkov systems. Dissolutions in strong acids, rapid molten salt fusions, and use of strong oxidants are all acceptable techniques. This new freedom for sample selection and processing has made a large impact on the recent growth of Cerenkov counting applications.

Although it is still true that color quenching effects can exist (and are in fact quite important), the ability to use strong chemical methods to treat samples can often completely eliminate color problems. A recent publication (11) describes the destruction of blood platelets by treatment with 0.5N sodium hydroxide and a subsequent direct count for P-32. The authors report that although the absolute counting efficiency is reduced from that obtained with scintillators, the advantages of a reduction in time, material, and expense are realized. They also note that the ease of sample recovery from the counting solution commends the approach to studies requiring subsequent analyses of the platelet lysate. Other recent examples of specific sample treatment include plant extracts and parts (12,13), gels (12), and biological materials in general (14).

Although forceful handling of samples to remove color quenching is possible, some investigators opt for a quench

correction technique when the quenching is not severe. Virtually all of the usual correction methods have been examined and, contrary to a report by Elrick and Parker (15), the channels ratio may be among the best (16, 17, 18, 19). An alternate solution that has been proposed to circumvent color problems is the use of a "Cerenkov insert" as described by Ballance and Johnson (20, 21). Here, the sample is contained in a small, opaque container and dipped into the Cerenkov generating medium. Energetic particles pass through the container and into the solution that creates the Cerenkov emission. Since the colored sample is not dissolved or dispersed in solution, color effects are avoided. However, here it must be asked what this technique actually accomplishes. The sample, which is a self-contained entity, is no longer free of self absorption effects. The result is that reduced counting efficiencies are observed when compared to homogeneous counting. The small size of the insert also obviates against another benefit of Cerenkov methods, the use of large samples for lowered detection limits. It would appear that any advantage gained by use of the insert could also be realized by substituting a conventional liquid scintillator for the Cerenkov medium, with a considerable enhancement of the detection efficiency. Thus it is difficult to discern the application area of this method.

### Spectral distribution, fluors, and counting efficiency

Since Cerenkov emission is solely the result of a rapid de-acceleration of a charged particle in a transparent medium, the use of conventional scintillation fluors is not necessary. This is the essential reason that chemical quenching does not occur in pure Cerenkov systems - there is simply nothing to chemically quench. The theoretical spectral output from a transparent medium ranges between its spectral transmission limits over the range where the refractive index is greater than one. The relative spectral yield varies as  $1/\lambda^3 d\lambda$  and is the reason that the familiar Cerenkov glow in swimming pool reactors always appears blue to the eye. Wider range detectors show that even greater emission occurs in the ultraviolet spectral region as predicted by theory.

The large majority of phototubes used for scintillation counting exhibit a significant drop in sensitivity in the ultraviolet region and, thus, much of the energy from a

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given particle event is not utilized for detection. For high-energy particles, this is not a significant problem; sufficient visible (and near UV) photons are generated to reliably trigger the phototube and counting circuits. However, for particles only marginally above the energy threshold, there is not a sufficient number of detectable photons and the observed counting efficiency is reduced proportionately. It appeared obvious to many investigators that the use of a wavelength shifter in the Cerenkov medium could be used to recover and use much of the wasted ultraviolet radiation. The use of such a material would also destroy the directional characteristic of the emission and further enhance the detection efficiency (22).

Early work by Herberg and Marshall (23) demonstrated two materials that gave a significant gain in water. The better of the two, 2-amino-6, 8-naphthalenedisulfonic acid, gave an increase in pulse height of 30%. This compound has been widely used since its utility was first demonstrated. Another significant increase in pulse height (as much as 100%) was shown to result from the use of 4-methylumbelliferone by Porter (24). A large number of other water soluble compounds have been proposed with various levels of success; many of these materials were examined in detail with regard to efficiency gain, stability, and other experimental parameters (22).

An important comment must be made at this point. Although the use of a wavelength shifting compound can result in a significant increase in counting efficiency in ideal systems, in practice, one must exercise a great deal of care when they are used. The reason for this is that once such materials are added to the Cerenkov generator, the system becomes a hybrid Cerenkov-scintillation medium. As a result, many of the advantages described earlier cannot be attained. The most important factor is the realization that chemical quenching of the waveshifter can occur. Thus, much of the freedom in sample pre-treatment is lost and, along with it, the convenience of the "pure" Cerenkov method. Is there a way to "... have your cake and eat it too?" The answer is yes.

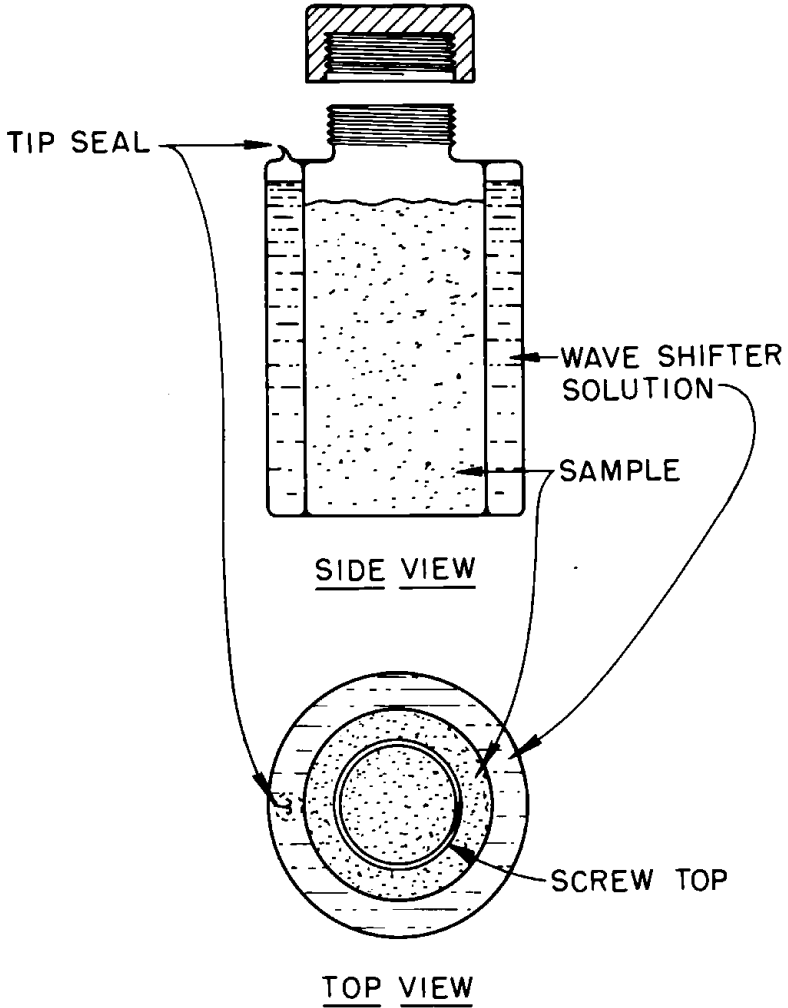
### MATERIALS AND METHODS

Baillon, et.al., (25) have demonstrated that an increase by about a factor of 3.4 in photoelectron emission from Cerenkov light can be obtained by coating a standard

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Figure 1

Quartz counting vial with isolated wavelength shifter compartment for Cerenkov counting



QUARTZ SAMPLE VIAL

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photomultiplier tube with a thin deposit of a wavelength shifter (lithium fluoride). Although the coating operation is straightforward and requires only simple manipulation, it does not appear to be a feasible approach for a general purpose liquid scintillation counting system. This work, however, suggested the design of a new type of counting vial specifically for Cerenkov measurements using a wavelshifter. The design of the vial is shown in Figure 1. The device consists of two concentric chambers. The outer chamber is used to contain a wavelength shifting solution that may be either organic or inorganic. In this work, the opening to the chamber was fitted with a stopper so that various waveshifting solutions could be tested. The inner chamber is used to hold the counting sample - about 10 ml maximum. The entire assembly is made of quartz so that efficient transfer of the ultraviolet radiation from the inner chamber to the shifter can take place. Since the quartz vial is definitely not a throw-away item, the inner chamber of the vial is lined with a thin ( $\approx$  1.8 mil) polyethylene bag. The use of this liner prevents radioactive contamination of the internal chamber surface yet permits a high degree of UV transmission. The construction of a similar all polyethylene vial appears feasible but this fabrication was not attempted.

Scintillators and other materials used in this study were scintillator or reagent grade. The strontium-89 radionuclide was prepared by irradiation of enriched strontium-88 nitrate (98% enrichment) in the Oak Ridge Research Reactor. The initial standardization of the tracer was carried out by  $4\pi\beta$  counting techniques. A Packard series 3000 liquid scintillation counter was used for the Cerenkov measurements. Maximum amplifier gain and wide window settings were used.

### RESULTS

The strontium-89 nitrate tracer was dissolved in 0.1 N HCl. An aliquot of this solution was added to 10 ml of 0.01 N HCl and this sample was placed into the inner chamber of the vial and sealed with a screw cap. The aliquot was selected so that about 30,000 dpm were contained in the sample. The outer chamber was filled with various solutions with and without an added waveshifter. A count of the sample was made so that a total of at least 50,000 counts were collected in each test. The relative counting efficiency

was determined for each counting combination; the results are summarized in Table II.

Table II

RELATIVE COUNTING EFFICIENCY OF Sr-89  
USING AN ISOLATED WAVELENGTH SHIFTING VIAL

<u>Waveshifter Chamber Contents</u>	<u>Concentration</u>	<u>Relative Counting Eff.</u>
water	100%	1.00
ethanol	95%	1.02
benzene	100%	1.06
toluene	100%	1.07
dimethyl POPOP	0.7 gm/l in toluene	1.88
4-methyl- umbelliferone	0.5 gm/l in 75% ethanol	1.69
2-naphthol-3, 6-disulfonic acid-sodium salt	0.1 gm/l in water	1.59
$\beta$ -naphthol	0.1 gm/l in 50% ethanol	1.37
1-naphthylamine	0.1 gm/l in 50% ethanol	1.22

Three strong reagents (and powerful chemical quenchers in conventional scintillation mixtures) were added to the sample compartment during the tests with umbelliferone and dimethyl POPOP. One milliliter of concentrated sulfuric acid, 10% sodium hydroxide, and 30% hydrogen peroxide were each tested in separate experiments. In every case, no significant change in the relative counting efficiency was observed.

Another series of tests was designed to examine the effect of color quenching in the sample. Here, either the wavelength shifter dimethyl POPOP in toluene or plain water was used in the external compartment of the Cerenkov vial. Dye solutions were added to the sample compartment

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until a strong color component was visible. However, no attempt was made to determine the actual absorbances of the solutions since relative measurements were being made. Coloring agents used were water-soluble FD&C coal-tar dyes. The results obtained in these tests are shown in Table III.

Table III

THE EFFECT OF COLOR IN THE SAMPLE  
WHEN USING THE CERENKOV VIAL

<u>Color &amp; <math>\lambda</math> abs.<sub>max</sub></u>	<u>Waveshifter</u>	<u>Relative Counting Eff.</u>
None	None (Water)	1.00
FD&C yellow (400 nm)	None	0.62
FD&C yellow	DMPOPOP	0.91
FD&C red (510 nm)	None	0.57
FD&C red	DMPOPOP	1.09
FD&C blue (625 nm)	None	0.91
FD&C blue	DMPOPOP	1.83

all tests with Sr-89 tracer

## DISCUSSION

The results presented in Table II clearly demonstrate that the specially constructed Cerenkov vial can be used to significantly increase the detection efficiency of beta emitters by separating the sample and the wavelength shifting component. In the case of Sr-89, which is a moderately energetic emitter ( $E_{\max}=1.49$  MeV), a major increase is observed. Since previous work has indicated that waveshifting becomes more crucial with weaker emitters, an even greater increase could be projected for nuclides such as Cl-36 or Tm-170. A vital consideration is that use of the new vial design does not change the detection process from a true Cerenkov function. Thus, insensitivity to chemical quenching is preserved and virtually any form of sample dissolution and pre-treatment can be employed. Another prominent feature of the new vial is that the wavelength shifter can be used in a totally organic system.

This results in the ability to select more efficient fluor materials and those that match phototube spectral response more closely.

An additional aspect of the vial concept is the improved response when some visible color quenching remains in the sample (Table III). This is important because some biological materials resist complete decoloration using simple procedures. It is only fair to note that ultraviolet absorbers in the sample will clearly reduce the effectiveness of this technique. But, we have found that many of these materials are easily destroyed during the routine initial sample dissolution. The only real disadvantage of this method is that the volume of sample that can be conveniently handled is reduced by about a factor of two. However, in the majority of situations, sample size is not a limiting factor.

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