

## Cerenkov Counting and Other Special Topics

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### INTRODUCTION

Cerenkov light is electromagnetic radiation, normally in the near ultraviolet and visible parts of the spectrum, which is emitted when charged particles of sufficient energy pass through a dielectric medium. It was first observed as a bluish-white luminescence by Mme Curie in 1910 and studied experimentally during 1926–29 by the French radiochemist Mallett.<sup>1</sup> Further detailed experimental work was performed by the Russian Cerenkov,<sup>2</sup> whose results were explained theoretically by Frank and Tamm.<sup>3</sup>

Practical use of the effect awaited the invention of the photomultiplier in the late 1940's. The first uses were in nuclear physics, and the application to radioassay came surprisingly late. In 1950 Belcher<sup>4</sup> observed a luminescence of low order from aqueous solutions of radioactive isotopes which he later<sup>5</sup> showed to be primarily Cerenkov emission. Little use appears to have been made of his work until the mid-1960's when, following a suggestion by Rapkin<sup>7</sup> and stimulated by the development of sensitive automatic liquid scintillation counting equipment and the subsequent demand for improvements in sample preparation, there were some sporadic reports of applications.<sup>6-12</sup> The method has since come into routine use for the assay of high-energy  $\beta$ -emitters and has been the subject of a number of fairly recent reviews.<sup>13-16</sup> In the present paper the more important features of the technique are summarised with emphasis on possible sources of error. More extended attention is given to those aspects which have received most attention during the past 3 years, namely, quench corrections and the use of wavelength-shifters, and finally the increasing number of applications are reviewed.

### NATURE OF THE CERENKOV EFFECT

When a charged particle, such as an electron, passes through a dielectric medium, local polarisation is produced along its path. Immediately after its passage the polarised molecules return to their quiescent state with the emission of electromagnetic radiation. Normally the light pulses will interfere destructively but if the velocity of the particle is greater than that of light in the medium it is possible for the wavelets to interfere constructively, in a similar manner to the

production of a shock wave from a supersonic aircraft. The resulting pulse of light is called 'Cerenkov emission'.

The light is highly directional, being emitted as a cone of radiation whose half angle  $\phi$  is given by:

$$\cos \phi = \frac{c}{vn} \quad (1)$$

where  $c$  is the velocity of light in vacuo,  $v$  the velocity of the particle in the medium and  $n$  the refractive index of the medium. Thus there is a threshold for emission given by:

$$v_{\min} = \frac{c}{vn} \quad (2)$$

An inverse relationship between  $v_{\min}$  and  $n$  exists, and for water  $v_{\min}$  corresponds to 0.263 MeV for electrons. The number of photons  $N$  emitted per unit path length  $x$  of an electron over a selected spectral region<sup>3</sup> is:

$$\frac{dN}{dx} = \frac{2\pi}{137} \left( \frac{1}{\lambda_2} - \frac{1}{\lambda_1} \right) \left( 1 - \frac{c^2}{v^2 n^2} \right) \text{ photons/cm} \quad (3)$$

where  $\lambda_1$  = upper limit of selected waveband (cm) and  $\lambda_2$  = lower limit. Values have been tabulated for water by Ross.<sup>17</sup> The intensity of the emitted light increases towards shorter wavelengths and extends into the near ultraviolet, where many photo-cathodes are very sensitive.

The pulse of radiation is very short (<1 ns) and is quite distinct from fluorescence and bremsstrahlung. A comprehensive treatment is given by both Jelley<sup>18</sup> and Marshall.<sup>19</sup>

The number of photons emitted in water by Phosphorus-32 is similar to that encountered in the measurement of Hydrogen-3 by liquid scintillation counting and for that reason standard liquid scintillation counting apparatus is suitable. Figure 1 shows experimentally determined Cerenkov spectra from Iodine-131 ( $\beta_{\max}$  0.61 MeV) and Phosphorus-32 ( $\beta_{\max}$  1.71 MeV) compared with the Hydrogen-3 spectrum using a typical scintillator cocktail. They are clearly comparable, but it is also obvious that the measurement of the lower-energy  $\beta$ -emitters by the Cerenkov method makes severe demands on the equipment.

## FACTORS AFFECTING COUNTING EFFICIENCY

Factors will now be summarised under convenient headings. Variations in them between samples, if not allowed for, will affect the accuracy of the method.

### 1 Basic factors

a. **Isotope energy.** The intensity of Cerenkov emission, and hence the detectability, is governed by the number of electrons emitted above the threshold value. For particular nuclides a theoretical maximum efficiency may be calculated<sup>16</sup> and these are given in Table 1 later in this paper. For reasons outlined below it is most unlikely that such high values will be obtained in practice.

### 2 Instrumental factors

a. **Optical.** The directional nature of Cerenkov emission results in inefficient detection of the light by the normal twin-photomultiplier arrangement. This is particularly true for low-energy  $\beta$ -emitters, where the cone of emission is narrow and the number of available photons small. Experimental studies have been carried out by Ross.<sup>13</sup> In practice the collection of light may be improved by using plastic vials

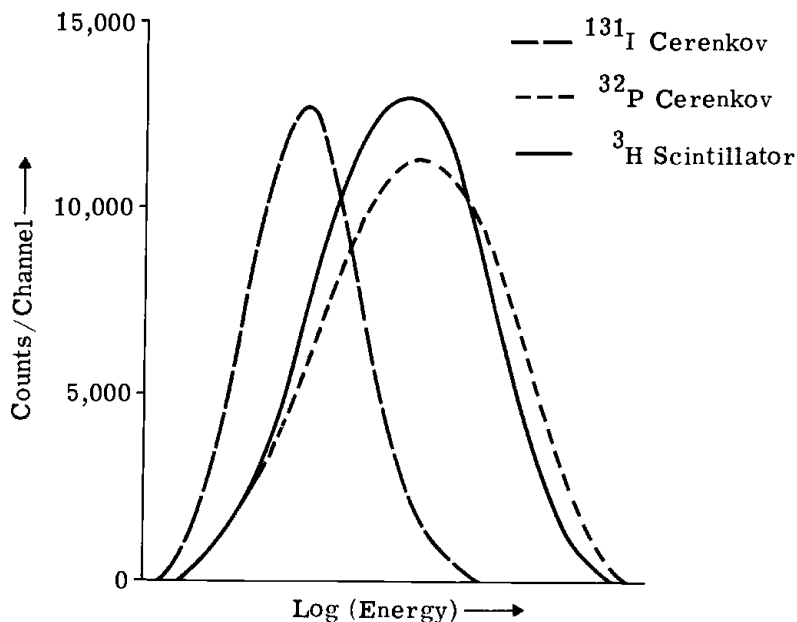


Fig. 1. Cerenkov spectra of unquenched aqueous solutions of Phosphorus -32 and Iodine-131, compared with the liquid scintillation spectrum of Hydrogen-3.

which cause greater light scattering than glass<sup>14,20,21</sup> and by the use of wavelength shifters (see Section 3 (d) below).

Greater efficiencies can be obtained if the coincidence condition is removed<sup>22,23</sup> but the background is considerably increased, as is the detection of chemiluminescence. Since a significant proportion of the Cerenkov light is in the near ultraviolet, the number of photons detected depends on the optical absorption characteristics of the vial, and quartz photomultiplier windows and plastic vials are better than glass. Variations between batches of vials can affect results.

**b. Type of photocathode.** As noted above, the number of photons detected is very dependent on the quantum and spectral sensitivity of the photocathode. Recent improvements have shown corresponding gains in counting efficiency.<sup>14</sup> Further advances are to be expected, but it must be noted that photocathodes matched to the peak emission of liquid scintillators are not necessarily best for the Cerenkov spectrum.

**c. Instrument settings.** In all types of counting systems the amplifier, E.H.T. and channel settings will considerably affect the performance. For the Cerenkov counting of most radionuclides the Hydrogen-3 settings will be satisfactory (see Fig. 1), but if the  $\beta$ -energy is particularly low or high, adjustments should be made.

### 3 Factors affected by sample preparation

**a. Refractive index of solvent.** As shown by Eqns. (2) and (3) the refractive index affects both the threshold energy and the number of photons emitted. An increase in refractive index will improve the efficiency, particularly for low-energy  $\beta$ -emitters. Using S-11 photocathodes a change in refractive index of 0.01 increases the

efficiency for Tellurium-204 ( $\beta_{\max} 0.77$  MeV) by as much as 10%, whilst for Phosphorus-32 ( $\beta_{\max} 1.71$  MeV) the increase is less than 1%.<sup>24</sup> The detection of a  $\beta$ -emitter as low in energy as Carbon-14 ( $\beta_{\max} 0.156$  MeV) by Cerenkov emission in  $\beta$ -bromonaphthalene has been reported by Ross,<sup>17</sup> presumably due to anomalous refractive dispersion.

**b. Density of solvent.** A decrease in density of the medium will result in a longer path length for the electrons with a corresponding gain in the number of photons emitted. A decrease of 7% in density has similar effects to an increase of 0.01 in refractive index, described above.<sup>24</sup> In the case of both density and refractive index the material of the vial will also affect results since some of the Cerenkov emission is due to electrons travelling through the walls. Variations between samples may cause significant errors.

**c. Other characteristics of solvent.** Certain organic solvents exhibit weak scintillator effects which may not be reproducible due to variable degrees of impurity quenching. The effect of a number of different solvents has been studied by Haviland and Bieber.<sup>25</sup>

Absorption bands in the solvent will considerably reduce the number of photons reaching the phototubes, and may occur in both the visible and near ultraviolet parts of the spectrum. Colour quenching of this type can be very important and is considered in detail below.

**d. Wavelength shifters.** Certain substances have the property of absorbing light of short wavelength (e.g. in the near ultraviolet) and re-emitting it isotropically in the visible region. Thus the effects of both ultraviolet absorption and the direction of Cerenkov light are reduced.

Heiberg and Marshall,<sup>26</sup> who examined a number of possible substances, suggested the use of 2-amino-6, 8-naphthalene-disulphonic acid, disodium salt. Other workers recommend 2-naphthylamine-6, 8-disulphonic acid, sodium potassium salt<sup>21, 22, 24</sup> and 7-amino-1, 3 naphthalene-disulphonic acid.<sup>27</sup> Ross<sup>23</sup> studied a number of compounds and favours 4-methylumbelliferone at a concentration of about 100–200 mg/litre since it is stable and relatively independent of pH over a wide range. Some idea of the improvement obtained can be seen from Table 1.

Table 1. Detection efficiency in water.

Nuclide	$\beta_{\max}$ (MeV)	Counting efficiency % of disintegrations			
		S-11 cathode	S-11 with wavelength shifter	RCA 4501 -Ve photomultiplier	Max. theoretical value
<sup>36</sup> Cl	0.71( 98%)	2.3	4.7	5.3	58
<sup>40</sup> K	1.32( 89%)	13	31	35	82
<sup>32</sup> P	1.71(100%)	25	50	43	86
<sup>144</sup> Pr	2.98( 98%)	54	75	59	95
<sup>42</sup> K	2.0 ( 19%)	61	85	76	95
	3.6 ( 82%)				

**e. Volume of sample.** The sample volume will affect light collection and hence counting efficiency. Again the effect is more pronounced at low  $\beta$ -energies.<sup>15</sup> Counters using high sensitivity photomultipliers do not exhibit such marked dependence.<sup>21</sup> Note that the whole volume can contain sample, not just 20–30% as in liquid scintillation counting.

## EXPERIMENTAL VALUES OF COUNTING EFFICIENCY

A literature search<sup>7,8,14,21,22,28-30</sup> reveals considerable agreement in experimental values for different radionuclides, indicating that the make of counter has little effect. Parker and Elrick<sup>14</sup> report substantially higher values when high sensitivity photomultipliers are used. Typical values are given in Table 1, together with results using S-11 photocathodes with the wavelength shifter 2-naphthylamine-6, 8-disulphonic acid<sup>24</sup> and the maximum theoretical efficiency<sup>16</sup> which is based on the number of  $\beta$ -particles exceeding the Cerenkov threshold.

It is interesting to note that at low energies it is more important to detect the small numbers of photons (i. e. use a high quantum efficiency phototube) than re-emit them isotropically. At high energies there is no problem in actually detecting the majority of the photons, so redirection is more important. A combination of the two would presumably give an even greater effect.

An additional improvement is given by using polyethylene vials.<sup>9,14,20,21</sup>

## BACKGROUND COUNT RATE

One of the advantages of the Cerenkov technique is that the background counting rate is lower than when a scintillator is used. Furthermore, a number of workers<sup>8,9,14,27</sup> have reported that plastic vials (notably polyethylene) have lower backgrounds than glass. Table 2<sup>15</sup> lists the background count-rates obtained for various types of vial in the pre-set counting channels using Intertechnique SL-40 equipment. The total count-rate is not too dependent on the volume of water, the addition of which causes a widening rather than an increase in the background pulse-height spectrum. It is clear that the radioactive content of the vial material is an important component of the background and some correlation with potassium content is apparent. Care must be taken with some materials (such as quartz and polystyrene) which can exhibit long-term phosphorescence.<sup>24,31</sup>

Table 2. Background count-rates obtained in the various pre-set counting channels using Intertechnique SL-40 equipment.<sup>15</sup>

Type of vial	Background (c. p. m.)					
	<sup>3</sup> H channel		<sup>14</sup> C channel above <sup>3</sup> H channel		<sup>14</sup> C channel	
	empty	20 ml water	empty	20 ml water	empty	20 ml water
Polyethylene	11.2	12.4	5.6	12.2	24.1	30.2
Wheaton	19.2	19.4	5.2	12.0	31.9	37.8
Low K glass	36.2	36.4	4.6	11.3	48.4	55.2
Soda glass	100.2	93.0	6.2	11.9	123.1	118.3

Other causes of background include thermal and electronic noise, and Laney<sup>32</sup> has described an electronic method by which cross-talk may be reduced. Cerenkov emission in the photomultiplier, counting vial and sample due to environmental  $\gamma$ -radiation, cosmic rays and nearby  $\gamma$ -emitting samples contribute to the remaining background, as mentioned elsewhere in these Proceedings.

## QUENCHING

In normal liquid scintillation counting, chemical quenching, in which molecules are de-excited without the emission of visible radiation, is often serious. It does not

exist with Cerenkov counting due to the nature of the effect. Many workers have substantiated Cerenkov's original observation<sup>2</sup> in this respect. Thus there is considerable freedom with regard to sample preparation, which is normally limited only by chemiluminescence<sup>33</sup> and colouration.

Colour quenching can be serious, particularly if the absorption bands lie in the ultraviolet or blue parts of the spectrum, thus yellow or red colouration is worse than blue. Figure 2 shows the pulse-height spectrum of quenched and unquenched Iodine-131 and Phosphorus-32. In the case of the higher-energy nuclide the pulse-height spectrum shifts to lower energies, together with a reduction in intensity; for the lower-energy nuclide there is little energy shift but considerable intensity reduction. S-11 photocathodes were used.

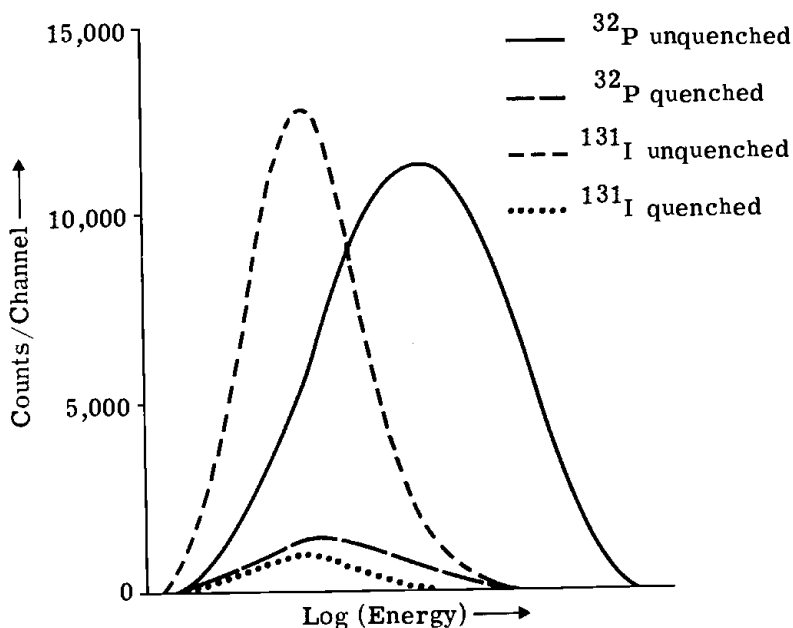


Fig. 2. Cerenkov spectra of unquenched and heavily quenched Phosphorus-32 and Iodine-131.

During the past 3 years there have been a number of references in the literature to quench correction methods for Cerenkov counting, together with some disagreement as to the best one to choose. The following are the methods considered:

### 1 Decolouration of sample

This is the most direct method, and has been used extensively for urine samples by Gomm.<sup>34</sup> If the counting rate is adequate it is often useful to dilute the samples in order to decrease the colouration.

### 2 Internal standardisation<sup>35</sup>

The disadvantages are similar to those encountered in liquid scintillation counting, namely the recounting necessary, the difficulty in sample recovery and the extra labour involved. It does not appear to have been widely used in Cerenkov counting.

### 3 Internal channels ratio<sup>36,37</sup>

Since this is based on the degree of shift in the pulse-height spectrum, Fig. 2 indicates that it will be more suitable for Phosphorus-32 and higher-energy  $\beta$ -emitters than for those of about 1 MeV  $\beta_{\max}$  and below. High quantum efficiency photocathodes should improve the situation. For this reason it was not favoured in the earlier report by Elrick and Parker,<sup>24</sup> although Stubbs and Jackson<sup>38</sup> reported favourably in the case of Phosphorus-32 and Moir<sup>39</sup> has shown it to be successful for Potassium-42. Wiebe *et al.*<sup>40</sup> carried out a comprehensive study in the case of Phosphorus-32 and showed that the nature of the shift of the pulse-height spectrum is the same for all colours, but the degree of shift at a given absorbancy is dependent upon the colour involved. The errors involved were estimated to be up to 5%.

Figure 3 shows the calibration curves we have obtained for S-11 photocathode equipment using blue and yellow dyes for three different energy radioisotopes. The greater accuracy at high energies is clearly demonstrated and with modern apparatus the method should be satisfactory for Phosphorus-32 and above, but must be used with caution for lower-energy  $\beta$ -emitters. The results are also, of course, dependent on the counting statistics obtained.

### 4 External standardisation

An external  $\gamma$ -ray source will produce a Compton electron distribution in the sample and vial; if the electrons are of sufficient energy, Cerenkov light will be emitted which will be subject to quenching in a similar way to the sample, provided the spectra are not too different.

Figure 4 illustrates the pulse-height spectra obtained for water using both Radium-226 (10  $\mu\text{Ci}$ ) and Caesium-137 (20  $\mu\text{Ci}$ ) external standards. It is clear that only the Radium-226 is suitable. Both Elrick and Parker<sup>24</sup> and Brownell and Lauchli<sup>41</sup> suggest that the change in total count-rate from the Radium-226 source is a reliable indicator of the amount of quenching. A typical calibration curve for the low-energy  $\beta$ -emitter Iodine-131 is shown in Fig. 5. One curve is sufficient for all colours, but the total count-rate can vary from one vial to the next due to differences in wall thickness.

### 5 External standard channels ratio

This employs changes in the channels ratio due to the external standard, and a calibration curve obtained with Iodine-131 and Radium-226 external standards is shown in Fig. 6. One curve is again sufficient for all colours except at very high pigmentations. It has the advantage over the straightforward external standard techniques in that the results are relatively volume-independent, but it should be noted that the optimum channel settings are very different from those used with a scintillator.

### 6 Spectrophotometric methods

Here the counting efficiency is correlated with the optical transmission at a fixed wavelength. They have been used for Cerenkov counting<sup>24,40</sup> but are more time-consuming than the above methods, which can be made automatic.

### 7 Cerenkov inserts

A novel method of avoiding colour quenching effects is to contain the sample in an opaque, thin-walled cylinder which is immersed in a colourless liquid contained in a standard counting vial.<sup>42</sup> Whilst the  $\beta$ -rays penetrating the central tube can be detected by Cerenkov emission it is more effective to surround the tube with a

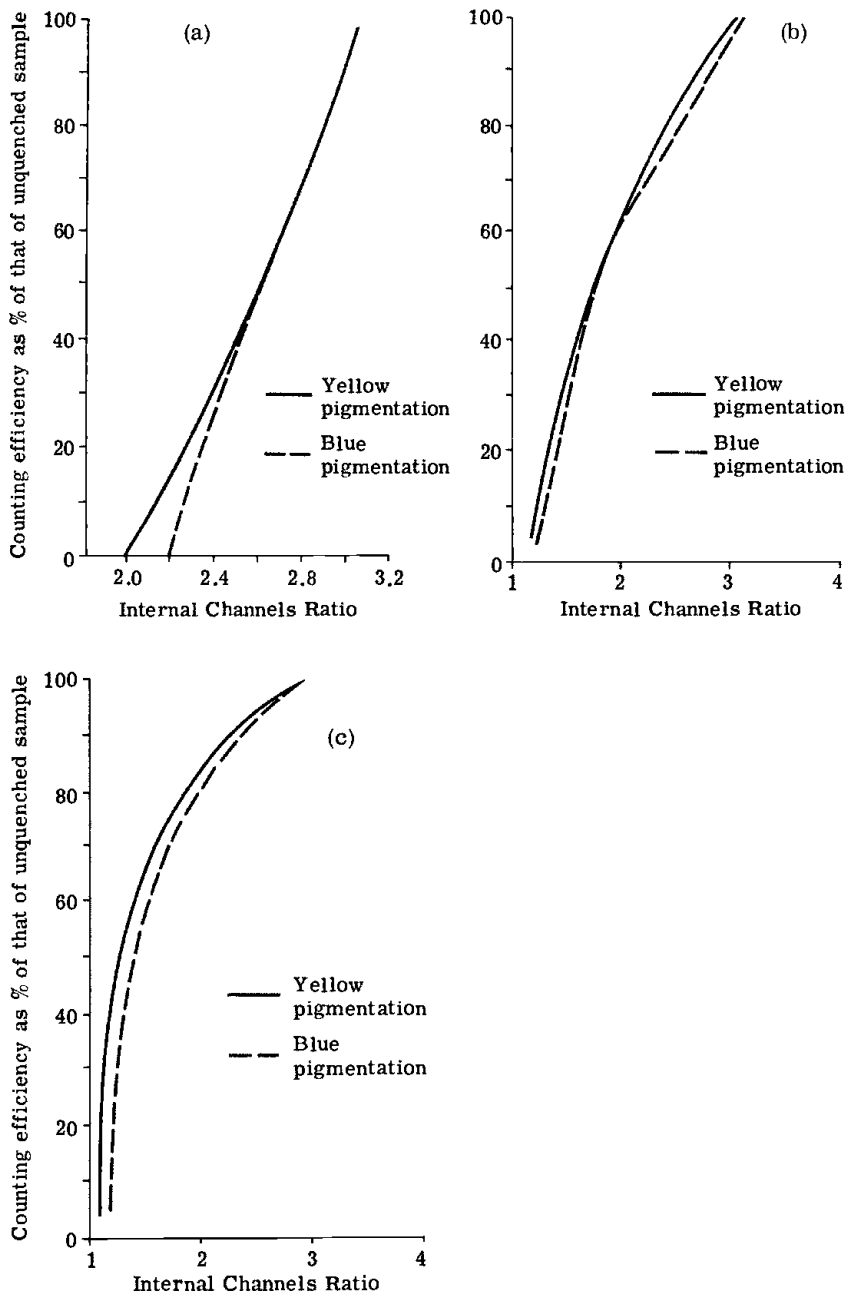


Fig. 3. Internal channels ratio calibration curves for (a) Chlorine-36, (b) Phosphorus-32 and (c) Ruthenium-106-Rhodium-106.

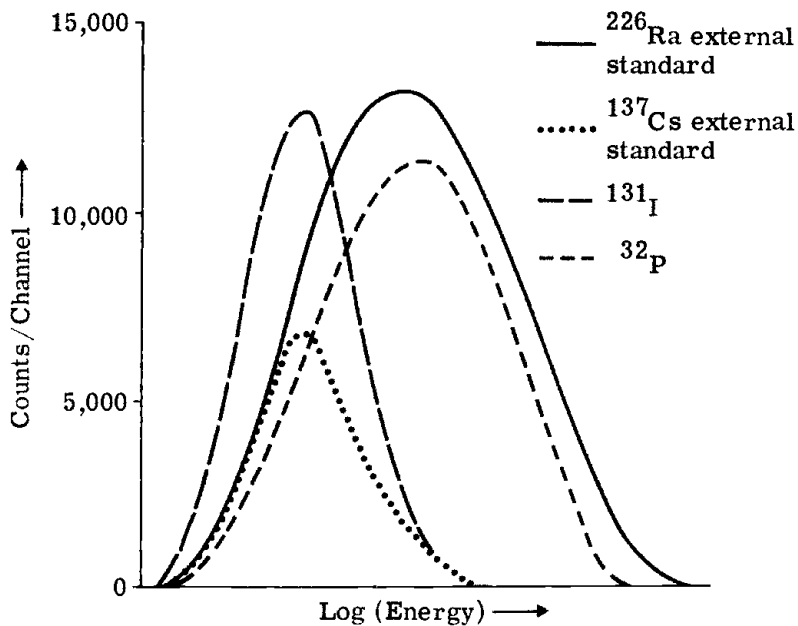


Fig. 4. Cerenkov spectra of unquenched Iodine-131 and Phosphorus-32 compared with the Cerenkov spectra due to external sources of Radium-226 and Caesium-137.

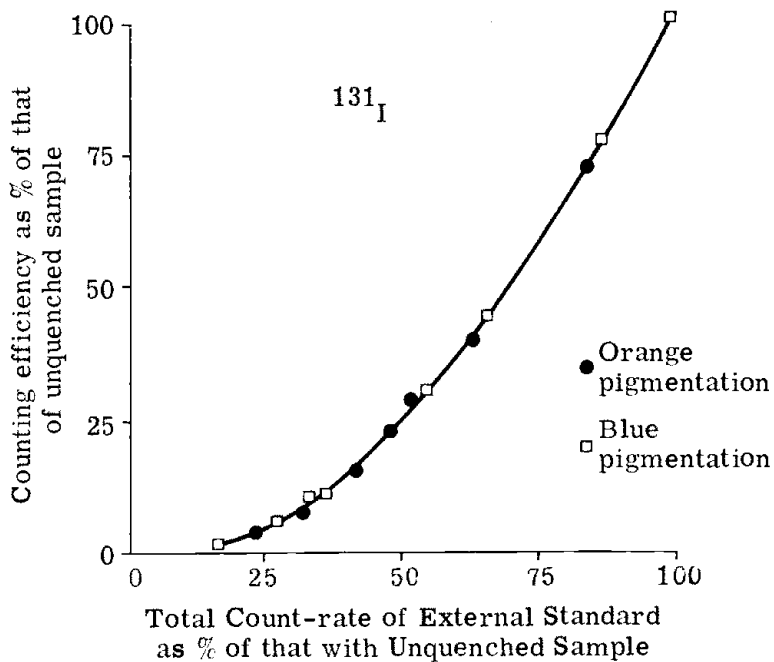


Fig. 5. Variation in total count-rate due to an external Radium-226 source with counting efficiency for quenched samples of Iodine-131.

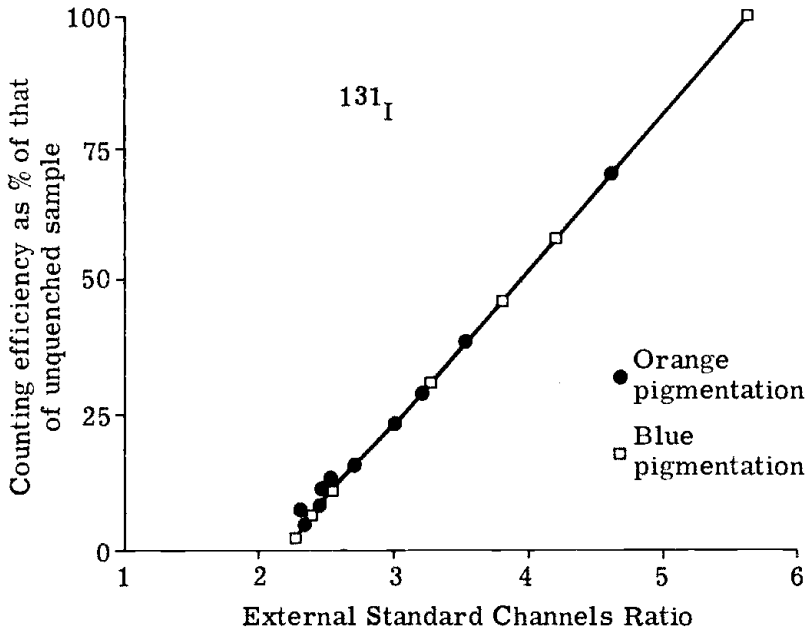


Fig. 6. Quench calibration curve for Iodine-131 using the external channels ratio technique with Radium-226.

liquid scintillator, a method also reported by Braunsberg and Guyver.<sup>6</sup> Colour quenching problems are thus avoided, but at the expense of efficiency.

## 8 Conclusion

For most applications the internal channels ratio method would appear satisfactory, provided the pigmentation is not too intense or the  $\beta$ -energy too low. In these cases a Radium-226 external standard method is preferable. A useful comparison of quench correction methods for liquid scintillation counting has been given by Noujaim *et al.*<sup>4,3</sup>

## APPLICATIONS

Cerenkov counting has found widespread application primarily due to the simplicity of sample preparation, the fact that the sample can be recovered for further treatment and the saving in cost compared with scintillator methods. Since the whole of the sample is the test solution the figure of merit — (efficiency)  $\times$  (sample volume) — may well be greater than if the liquid scintillation method were used.

There are now well over 40 publications specifically describing applications of Cerenkov counting in radioassay and a number of these will be summarised in order to show the diversity of uses. The divisions used below are somewhat arbitrary, and are chosen primarily for convenience.

### 1 Reaction effluent and protection problems

Following Belcher's early work, Yamada<sup>1,2</sup> developed an 8-litre detector for the estimation of  $^{90}\text{Sr}$ – $^{90}\text{Y}$ , the sensitivity being adequate for the determination of an  $8 \times 10^{-4}$  Ci/cm<sup>3</sup> sample in a counting time of 5 min. A large volume can be used because the path length of the Cerenkov radiation is large. De Volpi and Porges<sup>7</sup>

also measured reactor effluents using a specially designed counter, this time with only 12-ml samples, and determined Manganese-56 and Sodium-24 as well as  $^{90}\text{Sr}$ - $^{90}\text{Y}$ . Iwakura<sup>21</sup> used a standard liquid scintillation counter for measuring low-level aqueous waste with a detection limit of  $5 \times 10^{-13}$  Ci/ml for 1 MeV  $\beta$ -emitters. The general problem of Cerenkov light-monitoring for evaluating fission-product contamination in reactor effluent streams is considered by Rippon.<sup>44</sup> Recently a continuous flow measuring system has been developed<sup>73</sup> in which the higher-energy  $\beta$ -emitters are measured by Cerenkov counting after the continuous separation of the individual radionuclides. An interesting variation is that of Vaninbrouck<sup>45</sup> who used the Cerenkov effect for the accurate determination of the activity of extended reactor probes, such as the fast neutron monitors based on the Phosphorus-31 (n, p) Silicon-31 and Sulphur-32 (n, p) Phosphorus-32 reactions. An accuracy better than 1% is claimed. This is primarily due to the simple sample preparation and the absence of errors in correcting for chemical quenching.

## 2 Animal and human studies

The majority of these applications concern the determination of Phosphorus-32. Media include ashed biological materials,<sup>11</sup> supernatants from soft tissues,<sup>47</sup> phospholipids from rats,<sup>48,49</sup> labelled RNA<sup>50</sup> and DF-Phosphorus-32 platelets.<sup>51</sup> Palmer<sup>52</sup> and Schneider<sup>75</sup> describe the measurement of Phosphorus-32 following colorimetric phosphorus analysis, the blue reduced phosphomolybdate complex being decolourised before counting. In this way the specific activity may be determined, and the method is especially recommended for the analysis of samples separated by thin-layer chromatography. The Phosphorus-32 effluents from a column chromatogram have also been counted using a modified fraction collector.<sup>53</sup> In plasma proteins Potassium-42 may be determined.<sup>28</sup> The Cerenkov method is attractive for those applications because of the ease of sample preparation and availability for subsequent analyses; even inhomogeneous samples such as Sodium-24 labelled tissue slices can be counted directly in buffer solution.<sup>6</sup>

## 3 Plant studies

These are interesting since many workers have counted dry material and reported satisfactory results. In a series of papers Lauchli<sup>27,54</sup> describes the determination of Rubidium-86 and Chlorine-36 in plant roots and similar samples, using a sophisticated technique employing a wavelength shifter and correcting for colour quenching using a Radium-226 external standard. Efficiencies of 60% for Rubidium-86 and 13% for Chlorine-36 are reported. A similar quench correction method was used by White and Ellis<sup>55</sup> for Phosphorus-32 in dry ashed plant tissues. Algae may be counted directly on glass fibre filters with an efficiency for Phosphorus-32 of 12% in glass vials and 24% in polyethylene vials.<sup>56</sup> An alternative method<sup>57</sup> is to place the plant tissues in a vial containing water or hexane, the latter providing a greater counting efficiency due to scintillator action, particularly if leakage of the Phosphorus-32 is possible. In agrochemical studies, low specific activities are often encountered, but wet ashing with decolouration using activated charcoal can be satisfactory.<sup>58,59</sup> The use of Cerenkov inserts containing plant material on glass fibre filters is another technique used,<sup>42</sup> but is really a variation on liquid scintillation counting.

## 4 Multi-nuclide studies

A combination of Cerenkov counting (to measure high-energy  $\beta$ -emitters such as Phosphorus-32, Iodine-131 and Potassium-42) and liquid scintillation counting (to measure low-energy  $\beta$ -emitters as well, including Hydrogen-3, Carbon-14 and

Phosphorus-33) permits rapid determinations of suitable isotope mixtures.<sup>60-62</sup> It has been extended<sup>63</sup> to a true two-channel Cerenkov technique for Strontium-89-Strontium-90 using a ratios technique modified from Hydrogen-3/Carbon-14 mixture analysis. The build-up of the Yttrium-90 daughter permits estimation of Strontium-90 even in the presence of long-lived high-energy  $\beta$ -activity. Giubileo and Camera<sup>64</sup> report a quick method for the measurement of  $\beta$ - $\gamma$ -activity in biological samples, using liquid scintillation counting for  $\beta$ -emitters below 1 MeV, Cerenkov counting for those above and gamma spectrometry where applicable. A combination of Cerenkov counting and decay studies has been used to determine radon and thoron in environmental samples.<sup>8,21</sup> Bromine-80g and Bromine-80m (via its Bromine-80g daughter) were measured with high efficiency in organic solutions by the Cerenkov radiation from the high-energy  $\beta$ -rays emitted in the Bromine-80g decay.<sup>76</sup> The efficiency for the contaminating Bromine-82 activity was less than 1%.

## 5 Activation analysis

Although Cerenkov counting has not found great use in this field, three papers are of interest. In the first<sup>65</sup> the phosphorus content of micro samples of nucleic acids is determined quantitatively by neutron activation, separation of the phosphorus on a chromatographic column and subsequent Cerenkov counting. Hoch *et al.*<sup>66</sup> have utilised the Cerenkov technique to count Iodine-128, formed by neutron activation of Iodine-127 used as a biological tracer. Nanogram quantities of iodine may be measured. Lithium has been determined in the 3-400  $\mu$ g range by detecting the 13 MeV (max)  $\beta$ -particles from the 0.84 s Lithium-8 produced by the reaction Lithium-7 (n,  $\gamma$ ) Lithium-8.

## 6 Special applications

There have been some novel applications in unrelated fields which are worthy of mention. Wilson *et al.*<sup>67</sup> have used Cerenkov light to detect radioactive sources beneath the sea: the main problem was apparently bioluminescence. Cerenkov light emitted by Phosphorus-32 incorporated in the eye has been detected by a photo-multiplier as a test for ocular lesions.<sup>68</sup> Sealed Cerenkov sources may be used as standard light sources for testing equipment<sup>69</sup> and as a sensitive spectrophotometer when incorporated with a narrow-band optical filter in a liquid scintillation counter.<sup>70</sup> The substance under investigation is placed around the rod-like light source, and the absorption measured. Liquid scintillation counters have also been used for the determination of particle concentration (for example 0.5  $\mu$ m polystyrene spheres or suspensions of *E. coli*) by the extinction of the Cerenkov emission from a solution of Chlorine-36. It should be of value when the particle concentration is too high for normal turbidimetry or manipulation is hazardous, as in the case of pathogenic bacteria.

Finally, mention should be made of a flow counter developed by Eyre<sup>72</sup> in which a scintillation fluid is automatically mixed with the column effluent of an automatic amino acid analyser. Counting efficiencies of 60-65% for Carbon-14 and 7-10% for Hydrogen-3 were obtained. By omitting the scintillator it should be possible to use it for high-energy  $\beta$ -emitters by the Cerenkov technique, as in the work on fission products described by Colomer *et al.*<sup>73</sup> This has also been successfully carried out for Krypton-85 in a water stream. The Krypton-85 can be separated from the water for Cerenkov counting by diffusion into polyethylene.<sup>20</sup>

## CONCLUSIONS

The large and varied number of applications is clear evidence that Cerenkov counting is now receiving widespread application in the assay of high-energy  $\beta$ -emitting

radioisotopes, primarily due to the simplicity and cheapness of sample preparation and the absence of chemical quenching. Workers have experimented with solid and inhomogeneous samples with considerable success and have thus exploited the simplicity of sample preparation. Quench corrections are now being applied with confidence, avoiding the need for decolouration. There have been only a few attempts at routinely measuring  $\beta$ -emitters of less than 1 MeV, but the use of wave-length shifters and high quantum efficiency phototubes should improve the situation.

It is hoped that this trend will be encouraged by the manufacturers, who could usefully provide pre-set Cerenkov counting channels similar to those already supplied for Hydrogen-3 and Carbon-14. Correct settings should be available for use with Radium-226 external standardisation techniques, and there is little doubt that counting efficiencies would be considerably increased using more sensitive photomultipliers, or if more than two photomultipliers were used in order to minimise the direction effect of the Cerenkov emissions. Whilst increasing the complexity, it should add relatively little to the cost of the sophisticated equipment now being marketed. Certainly the design of the reflecting chamber of a liquid scintillation counter should be examined in order to optimise it for Cerenkov techniques.

#### REFERENCES

- 1 L. Mallett, C.R. Acad. Sci. (Paris) 188, 445 (1929).
- 2 P.A. Cerenkov, C.R. Acad. Sci. (U.S.S.R.) 2, 451 (1934).
- 3 I. Frank and Ig Tamm, C.R. Acad. Sci. (U.S.S.R.) 14, 109 (1937).
- 4 E.H. Belcher, Brit. J. Radiol Suppl. No. 2, p.282 (1950).
- 5 E.H. Belcher, Proc. Royal Soc. A216, 90 (1953).
- 6 H. Braunsberg and A. Guyver, Anal. Biochem. 10, 86 (1965).
- 7 A. De Volpi and K.G.A. Porges, Intern. J. Applied Radiation and Isotopes 16, 496 (1965).
- 8 K. von Haberer, Atomwirtschaft 10, 36 (1965).
- 9 V.W. Hoffman, Radiochim. Acta. 4, 117 (1965).
- 10 J. Narrog, Atompraxis 11, 373 (1965).
- 11 V.H. Vemmer and J.O. Gutte, Atompraxis, 10, 475 (1964).
- 12 S. Yamada, J. Phys. Soc. (Japan) 17, 865 (1962).
- 13 H.H. Ross, Analyt. Chem. 41, 1260 (1969).
- 14 R.P. Parker and R.H. Elrick, in The Current Status of Liquid Scintillation Counting (Ed. E.D. Bransome) Grune and Stratton, New York, 1970, p.110.
- 15 R.P. Parker, Cerenkov Counting, Digitechniques Tech. Rev. No.4, Inter-technique, Paris, 1970.
- 16 D. Santoso, Ph.D. Thesis, Univ. of Maryland (Univ. Microfilms 72-21, 131), 1972.
- 17 H.H. Ross in The Current Status of Liquid Scintillation Counting (Ed. E.D. Bransome) Grune and Stratton, New York, 1970, p.123.
- 18 J.V. Jelley, Cerenkov Radiation and its Applications Pergamon, London, 1958.
- 19 J. Marshall, Phys. Rev. 86, 685 (1952).
- 20 J.D. Buchanan, Radiochim. Acta 9, 218 (1968).
- 21 T. Iwakura, Radioisotopes (Tokyo) 18, 500 (1969).
- 22 R.P. Parker and R.H. Elrick, Intern. J. Applied Radiation and Isotopes 17, 361 (1966).
- 23 H.H. Ross, in Organic Scintillators and Liquid Scintillation Counting (Ed. D.L. Horrocks and Chin-Tzu Peng), Academic Press, New York, 1971, p.757.

- 24 R.H. Elrick and R.P. Parker, Intern. J. Applied Radiation and Isotopes 19, 263 (1968).
- 25 R.T. Haviland and L.L. Bieber, Anal. Biochem. 33, 323 (1970).
- 26 E. Heiberg and J. Marshall, Rev. Sci. Instr. 27, 618 (1956).
- 27 A. Lauchli, Intern. J. Applied Radiation and Isotopes 20, 265 (1969).
- 28 J.E. Johnson and J.M. Hartsuck, Hlth Phys. 16, 755 (1969).
- 29 B. Francois, Intern. J. Applied Radiation and Isotopes 18, 525 (1967).
- 30 P.J. Garrahan and I.M. Glynn, J. Physiol. 186, 55P (1966).
- 31 E.H. Belcher, Nature, 170, 571 (1952).
- 32 B.H. Laney in Organic Scintillators and Liquid Scintillation Counting (Ed. D.L. Horrocks and Chin-Tze Peng), Academic Press, New York, 1971.
- 33 D.S. Kearns, Intern. J. Applied Radiation and Isotopes 23, 73 (1972).
- 34 P.J. Gomm, AERE-PR/HPM 11, 47 (1967).
- 35 F.M. Hayes, Intern. J. Applied Radiation and Isotopes 1, 46 (1956).
- 36 L.A. Baillie, Intern. J. Applied Radiation and Isotopes 8, 1 (1960).
- 37 E.T. Bush, Analyt. Chem. 35, 1024 (1963).
- 38 R.D. Stubbs and A. Jackson, Intern. J. Applied Radiation and Isotopes 18, 857 (1967).
- 39 A.T.B. Moir, Intern. J. Applied Radiation and Isotopes 22, 213 (1971).
- 40 L.I. Wiebe, A.A. Noujaim and C. Ediss, Intern. J. Applied Radiation and Isotopes 22, 463 (1971).
- 41 J.R. Brownell and A. Lauchli, Intern. J. Applied Radiation and Isotopes 20, 797 (1969).
- 42 P.E. Ballance and S. Johnson, Intern. J. Applied Radiation and Isotopes 20, 447 (1971).
- 43 A. Noujaim, C. Ediss and L. Wiebe, in Organic Scintillators and Liquid Scintillation Counting (Ed. D.L. Horrocks and Chin-Tze Peng), Academic Press, New York, 1971, p. 705.
- 44 S.E.H. Rippon and Nuc. Instr. Meth. 21, 185 (1963).
- 45 R.L. Vaninbroukx, Proc. Symp. Standardization of Radionuclides, Vienna: IAEA, 1967, p. 443.
- 46 V. Camera and H. Tanguy, EUR-4084, 1 (1968).
- 47 M.K. Johnson, Anal. Biochem. 29, 348 (1969).
- 48 J. Plesums and W.H. Bunch, Anal. Biochem. 42, 360 (1971).
- 49 G. Threlfall, D.M. Taylor and A.T. Buck, Am. J. Pathology, 50, 1 (1967).
- 50 S. Mizuno, H. Eguehi, K. Yano and H. Yamaguchi, Radioisotopes (Tokyo) 18, 19 (1969).
- 51 R.D. Smith, J.J.B. Anderson and Ristic Miodrag, Intern. J. Applied Radiation and Isotopes 23, 513 (1972).
- 52 F.B. St. C. Palmer, Anal. Biochem. 31, 493 (1969).
- 53 H.R. Matthews, J. Chromatogr. 36, 302 (1968).
- 54 A. Lauchli, in Organic Scintillators and Liquid Scintillation Counting (Ed. D.L. Horrocks and Chin-Tzu Peng), Academic Press, New York, 1971, p. 771.
- 55 R.P. White and B.G. Ellis, Soil Science Am. Proc. 32, 740 (1968).
- 56 W. Hülsen and U. Prenzel, Anal. Biochem. 26, 483 (1968).
- 57 T. Awerbuch and Y. Avnimelech, Plant Soil 33, 260 (1970).
- 58 F.J. Haasbroek and E. Lotz, S. Afr. J. Agr. Sci. 10, 285 (1967).
- 59 D. Sipos and L. Koch, Atomtech. Tajek 12, 313 (1969).
- 60 W.E. Kisieleski, A.N.L. - 7635, 152 (1969).
- 61 J.R. Robinson, Intern. J. Applied Radiation and Isotopes 20, 531 (1969).
- 62 L.C. Brown, Analyt. Chem. 43, 1326 (1971).

- 63 M. Goldman and E. Beckman, *U.C.D.* — 472 — 116, 100 (1969).  
64 M. Giubileo and V. Camera, *EUR* — 4066, 1 (1968).  
65 F. Giradi, V. Camera and E. Sabbioni, *Radiochem. radioanalyt., Lett.* 2, 195 (1969).  
66 F.L. Hoch, R.A. Kuras and J.D. Jones, *Anal. Biochem.* 40, 86 (1971).  
67 A.E. Wilson, J.F. Timney and J.J. Koch, *UCRL* — 50007 — 68 — 2, 8 (1966).  
68 W.M. Burch, *Nature* 234, 358 (1971).  
69 W. Anderson and E.H. Belcher, *Brit. J. Appl. Phys.* 5, 53 (1954).  
70 P. Jordan and P. Koberle, *Experientia* 25, 335 (1969).  
71 J. Ashcroft, *Intern. J. Applied Radiation and Isotopes* 20, 555 (1969).  
72 D.R. Eyre, *Anal. Biochem.* (in the press).  
73 J. Colomer, M. Cousigne and G. Metzger, in *Liquid Scintillation Counting* Vol.2. (Ed. M.A. Crook, P. Johnson and B. Scales), Heyden, London, 1972, p.181.  
74 E. Rapkin, *Intern. J. Applied Radiation and Isotopes* 15, 69 (1964).  
75 P.B. Schneider, *J. Nuc. Med.* 12, 14 (1971).  
76 G.P. Gemaro and K.E. Collins, *J. Radioanalytic Chem.* 5, 387 (1970).

## DISCUSSION

E. Gunther: What can you say about the uncertainties of Cerenkov counting in comparison with LSC (toluene scintillator)? Are measurements with the same reproducibility of, for example 0.1% in the case of Phosphorus-32, possible?

R. P. Parker: Yes.

J.F. Stoutjesdijk: The count-rate of a  $^{32}\text{P}$ -solution in 30–70%  $\text{H}_2\text{SO}_4$  is about 5% higher than in  $\text{H}_2\text{O}$ ; in 90%  $\text{H}_2\text{SO}_4$  it is about 5% lower. Can you explain this? (The refractive index of  $\text{H}_2\text{SO}_4$  is about the same as that of  $\text{H}_2\text{O}$ : the density of pure  $\text{H}_2\text{SO}_4$  is 1.8.)

R. P. Parker: In fact the refractive index of  $\text{H}_2\text{SO}_4$  varies from 1.339 at a density of 1.028 to 1.437 at a density of 1.811. There are two competitive processes: as the density increases the count-rate relative to  $\text{H}_2\text{O}$  will decrease, whilst as the refractive index increases the count-rate relative to  $\text{H}_2\text{O}$  will increase. The photon yield relative to water is not directly proportional to the refractive index at a given density, and careful calculation shows that experimental results are borne out by the theory. It is not a chemical quenching effect.

D. L. Horrocks: Chemical quench may not be as important in Cerenkov counting using wavelength shifters as in ordinary liquid scintillation counting since the transfer to the wave-shifter is by a radiative process and the process of chemical quenching occurs by a non-radiative competition with the excited molecule. There is a possibility of molecular competition for the excitation energy once it is associated with the wavelength shifter.

Also the use of quartz-faced, high efficiency MPT's will provide a higher detection efficiency but these advantages may be negated if a glass bottle is used for the sample vial. It is necessary to use a plastic vial or a quartz vial to see the maximum effect.

R. P. Parker: Chemical quenching occurs in Cerenkov counting, but I agree it is possible (although somewhat unlikely) when wavelength shifters are used. I fully agree with your point concerning choice of sample vial, which is very important and which can alter the amount of colour quenching observed, if, for example, there is an absorption band in the near ultra-violet.

**J.F. Stoutjesdijk:** When wavelength shifters are added, chemical quenching may influence the counting efficiency and so the composition of the sample may become important. This possible source of error is not stressed sufficiently when the use of wavelength shifters is advocated.

**R.P. Parker:** This is true, but it is not normally an important effect. The efficiency of a wavelength shifter will depend on the concentration and on the pH of the solution. Also the addition of a wavelength shifter is likely to affect the degree of colour quenching. All these possible effects must be taken into account, and the user may feel that the added complexity and need for additional sample preparation is not justified. My own view is that it is only really worthwhile when low count-rates are encountered and there are many samples of the same type to be measured.