

CHAPTER 22

The Effect on Quench Curve Shape of the Solvent and Quencher in a Liquid Scintillation Counter

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ABSTRACT

When preparing quench calibration curves, commercial sealed standards are often used, although it is advisable to use the same composition, scintillation liquid, and sample as the unknowns. Commercial sealed standards usually contain a toluene or xylene based cocktail and carbon tetrachloride or nitromethane as quencher. However, the unknown samples may contain another solvent and other chemical quenchers. The solvent has become more significant with the introduction of new "safe" solvents that behave differently from the traditional toluene solvent.

As reported in earlier literature, different solvents and chemical quenchers lead to different quench curves, but no physical explanation has been given. In this work, quench curves for several commercial cocktails with chemical quenchers and one color quencher have been measured. The counting efficiency and the mean pulse height of the isotope (^3H) were recorded for different amounts of quencher and with varying coincidence resolving time of the counter. The differences in quenching characteristics can be explained as differences in the scintillation pulse shapes. The shape of the scintillation pulse is primarily dependent on the way the excitation energy is deposited in the solvent and on how the chemical quenchers act on the excited solvent molecules. The data indicate that there are mainly two different chemical quenching mechanisms: quenching of the higher excited states, which are precursors of the triplet states, and quenching of the lower singlet states.

INTRODUCTION

As liquid scintillation counting is frequently used for quantitative analytical measurements of low energy isotopes, such as tritium and ^{14}C , it is extremely important to know the counting efficiency of the samples. For that purpose, most counters today have automatic methods for determining the quench level and the counting efficiency. Generally, an empirical relationship between the counting efficiency and the quench index must be established at first, e.g., by measuring a set of quenched standards. A question that often arises is how to prepare this set of quenched standards; which scintillation cocktail and which

quencher substance should be used in the standards? The usual advice to users who want to suppress the risk of systematic errors is to use the same composition in the standards as in the unknowns. This means using the same vials, same scintillation cocktail (same volume), and same quencher. Using the same vials is mostly not a problem, but the two other factors are worth some consideration.

During the last few years the number of new solvents used in liquid scintillation cocktails has increased remarkably through the introduction of high flashpoint solvents. Typically these solvents have a flashpoint above 60°C. The purpose of these solvents is to make scintillation counting less hazardous. The most common scintillation liquids today are still based on toluene or xylene, both of which are rendered as toxic and hazardous chemicals. The new solvents not only have a low vapor pressure, they are generally considered less toxic than toluene. In a laboratory, cocktails based on both traditional solvents and on the new safe solvents may be in use at the same time. Commercial sealed calibration standards usually contain a traditional solvent. Because of this, a natural question that arises is whether or not quench curves based on traditional cocktails may be used together with these new safe cocktails. In current literature, there is very little or no information available on the quenching behavior of these new solvents as compared to the traditional ones. There are also remarkably few reports in current literature comparing quench curves from different quenchers. Wunderly¹ has investigated a number of substances in relation to the sample channels ratio (SCR) and the H-number used in Beckman Instruments counters as quench level index. The H-number is equal to the shift of the ¹³⁷Cs Compton edge as compared to the unquenched position. Wunderly found differences between the assessed quenchers in terms of counting efficiency vs. SCR or H-number. He could not explain this nor could he propose any solution on how to avoid it. It is also well known at Wallac Oy that users of the Wallac Rackbeta LS counters have encountered this problem without being able to explain it or reduce the errors involved. Furthermore, the new safe cocktails introduce one more source of uncertainty. The present work has been undertaken in order to cast some light on these problems and show how the errors can be minimized by improving the LS counter. The aim of this work has also been to increase the general knowledge of the physics behind liquid scintillation and quenching.

EXPERIMENTAL

Two different measurements were performed. At first, quench curves for five commercial cocktails were recorded. The cocktails were: xylene based Lipoluma from Lumac AG, Netherlands, toluene based OptiScint 'T', pseudo cumene based OptiScint Safe, di-isopropyl-naphthalene based OptiScint HiSafe, and OptiPhase HiSafe II (containing emulsifiers, but no added water). The last four are trademarks of Wallac Oy. The isotope spectra were

recorded at three coincidence resolving times (15, 72, and 800 nsec). The isotope mean pulse height of the isotope spectrum, SQP(I), was used as the quench index. The quenching agent was carbon tetrachloride.

In the second set of measurements, the quench behavior of eight quenchers was recorded using the toluene based cocktail (OptiScint 'T', Wallac Oy). The uncolored substances were: nitromethane, carbon tetrachloride, methanol, acetone, acetophenone, dibutylamine, and methyl benzoate. One colored substance, the commercial yellow dye Sudan 1, was also used. All quenchers were of *pro analysi* quality. A dilution series was also made by diluting the OptiScint 'T' with pure toluene, resulting in a decreased concentration of the fluors.

Normal 20 mL glass vials were used, with 10 mL of scintillation liquid. All samples were in equilibrium with air; thus containing the same amount of oxygen-quench. Wallac Internal Standard Capsules 1210-1220, containing tritium labeled cholesterol, were used for dispensing the activity. All measurements were done on a prototype of the new 1410 LS counter from Wallac Oy, which has an adjustable coincidence resolving time.

RESULTS

The results of the solvent measurement are shown in Figures 1-3. Figure 1a shows the quench curves for all the cocktails at normal coincidence resolving time (15 nsec), and Figure 1b shows the relative error in DPM when the toluene based calibration curve was used as a reference for all cocktails. The DPM error is defined according to the equation

$$DPM_{Err} = 100 \% \cdot (DPM_0 - DPM_1) / DPM_1$$

wherein DPM_1 is the activity predicted by the toluene calibration curve and DPM_0 is the true activity. Figures 2 and 3 show the DPM errors at longer coincidence resolving times.

A quencher other than CCl_4 may lead to quench curve behavior different than that described above. The next figures show the influence of quencher on the quench curve shape in a toluene based cocktail. Figure 4a shows a plot of all nine quench curves for tritium in the case of normal coincidence resolving time, while Figure 4b shows the same data plotted as relative error in DPM when a CCl_4 -based calibration curve is used as a reference. The curves in Figures 4a and 4b show that at normal coincidence resolving time, and in the case of tritium, the nine quenchers can be divided into two groups. One group comprises methanol, carbon tetrachloride, nitromethane, and dibutylamine situated above, and another group, comprises the toluene dilution, acetone, methyl benzoate, acetophenone, and Sudan 1 situated below. The toluene dilution shows the greatest deviation. From these curves one can see that nitromethane or carbon tetrachloride, which are often used for preparing quenched standards, may not be the correct choice when the unknown samples contain ketones like acetone or acetophenone.

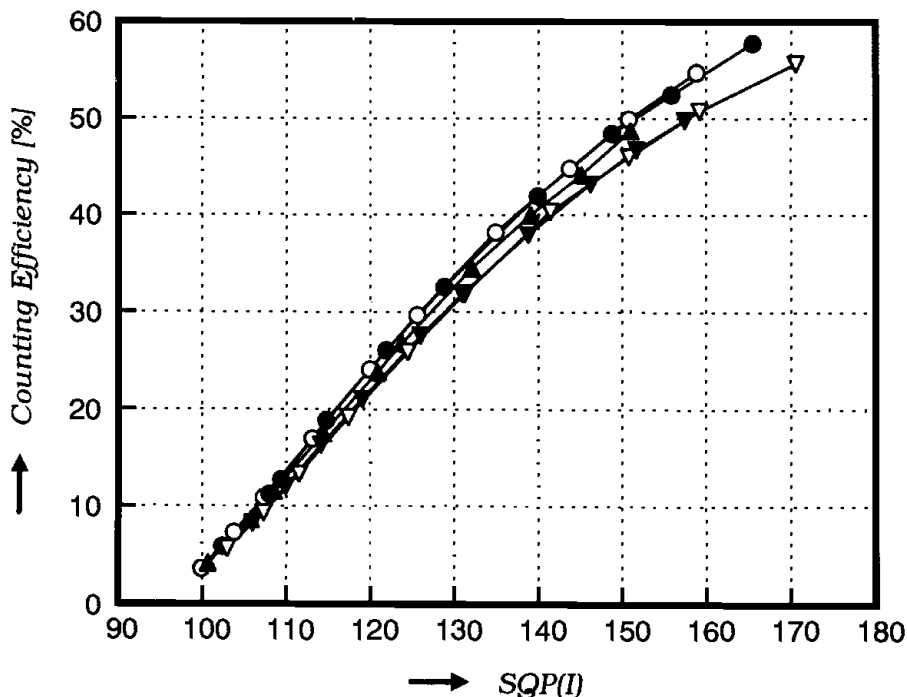


Figure 1a. Tritium quench curves (counting efficiency as a function of quench index) for the 5 different cocktails and a coincidence resolving time of 15 nsec.

The relative error for some of the quenchers depends very much on the coincidence resolving time. Figures 5 and 6 show the relative DPM error as a function of SQP(I) for two more resolving times, 40 and 72 nsec. At 72 nsec all of the curves join except the color curve and the toluene dilution. The color curve does not in fact depend very much on the coincidence resolving time.

In normal commercial instruments the coincidence resolving time has to be quite short (≈ 15 nsec) in order to decrease the number of random coincidences from, e.g., chemiluminescence. As can be seen from Figure 1b, in single label counting, the relative error in the DPM will be a constant value independent of quench level when measuring unknown samples containing other solvents than toluene against a toluene based calibration curve in a normal instrument using SQP(I) as the quench index. This can be satisfactory if the *absolute* activity is of minor interest and the results are used for comparison only. With different quenchers this is not so as the error varies with the quench level from 0 to -40% for a sample quenched with a ketone measured against a CCl_4 calibration curve. When measuring dual labeled samples, the errors in both cases will be even bigger, as the shape of the isotopic spectra differ and the spill over curves look completely different. Figures 7a and 7b

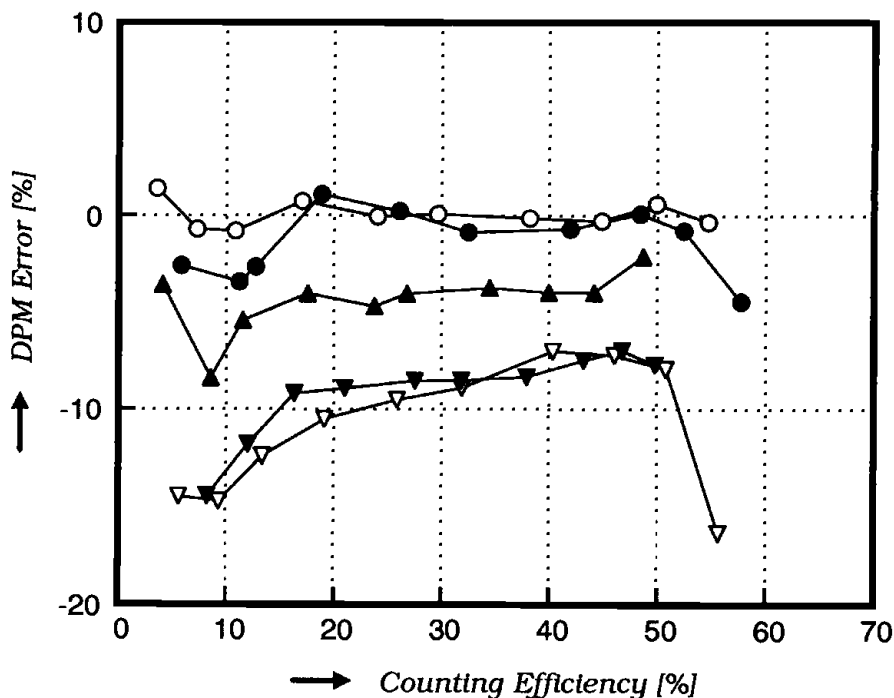


Figure 1b. The DPM error as a function of the tritium counting efficiency when using the toluene based quench curve (OptiScint 'T') for computing DPM values. The symbols are: \circ = OptiScint 'T', \bullet = Lipoluma, \blacktriangle = OptiScint Safe, ∇ = OptiScint HiSafe, \blacktriangledown = OptiPhase HiSafe II.

shows the influence of coincidence resolving time on spectral shape for 1. an OptiScint 'T' sample and 2. an OptiScint HiSafe sample.

DISCUSSION

From the curves in Figures 1-6 one general conclusion can be drawn: the shorter the coincidence resolving time, the bigger the difference between the various solvents and quenchers. Why then is the coincidence resolving time critical to the quench curve behavior? The lowest excited singlet state of the aromatic solvent and most fluors have quite short lifetimes and will result in prompt light emission, a few nanoseconds after the disintegration. Triplet states, superexcited states, and ionized states have, in comparison to the singlet states, long lifetimes. These states may either relaxate, through internal conversion, to the ground singlet state and liberate energy in the form of heat, or they may end up in an excited singlet state which can lead to light emission several hundreds of nanoseconds after the disintegration. The first light burst is usually called the prompt pulse, and the second emission is called the

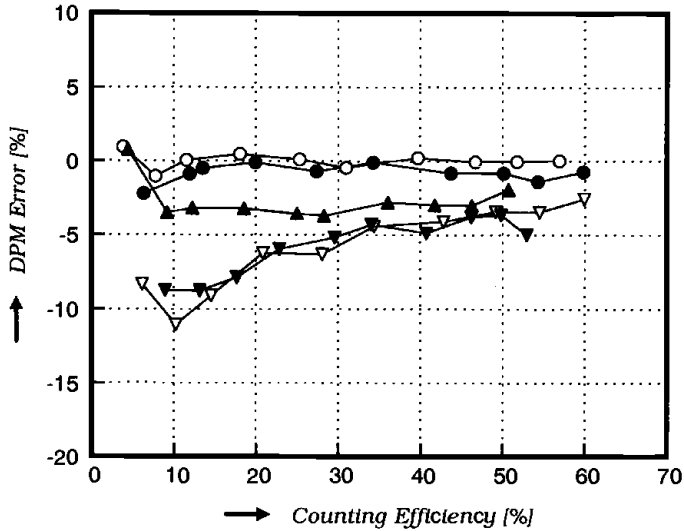


Figure 2. The DPM error as a function of the tritium counting efficiency when using the toluene based quench curve and a coincidence resolving time of 72 nsec. The symbols are the same as in Figure 1.

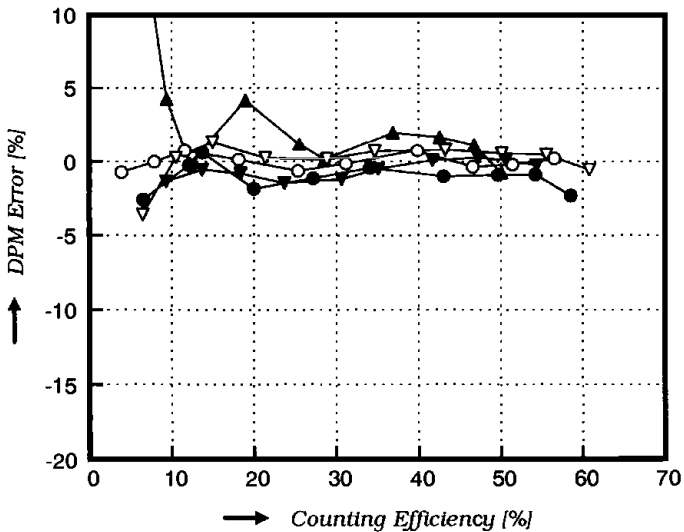


Figure 3. The DPM error as a function of the tritium counting efficiency when using the toluene based quench curve and a coincidence resolving time of 800 nsec. The symbols are the same as in Figure 1.

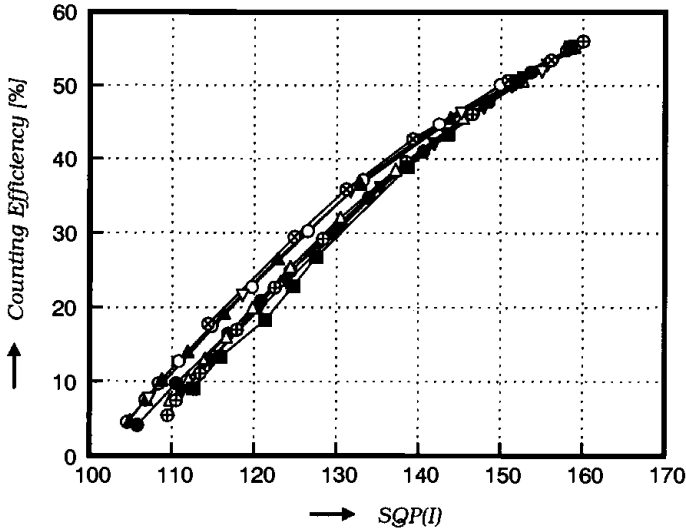


Figure 4a. Tritium quench curves for OptiScint 'T' and 9 different quenchers and a coincidence resolving time of 15 nsec.

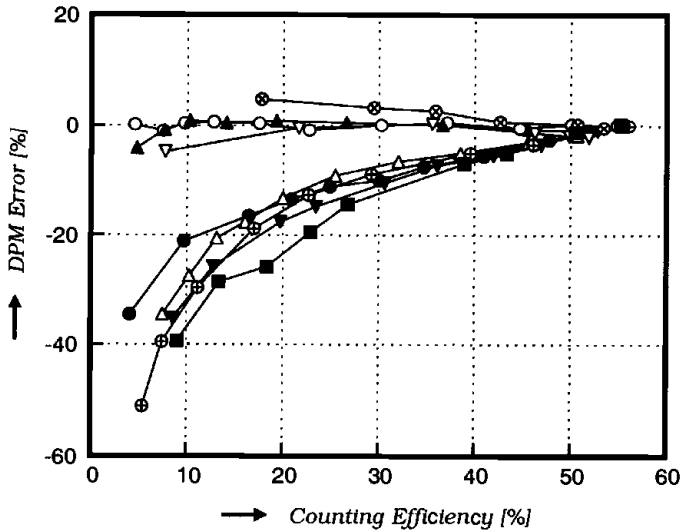


Figure 4b. The DPM error as a function of the tritium counting efficiency when using the carbon tetrachloride quench curve for computing DPM values. The symbols are: \circ = methanol, \circ = carbon tetrachloride, \blacktriangle = nitromethane, ∇ = dibutylamine, \blacksquare = toluene dilution, \bullet = acetone, \blacktriangledown = methyl benzoate, \triangle = acetophenone and \circ = Sudan 1 (a yellow dye).

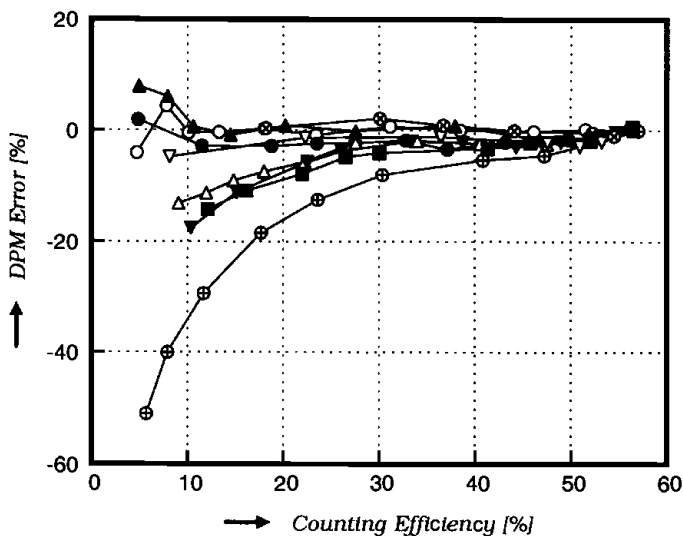


Figure 5. The DPM error as a function of the tritium counting efficiency when using the carbon tetrachloride quench curve and a coincidence resolving time of 40 nsec. Symbols as in Figure 4.

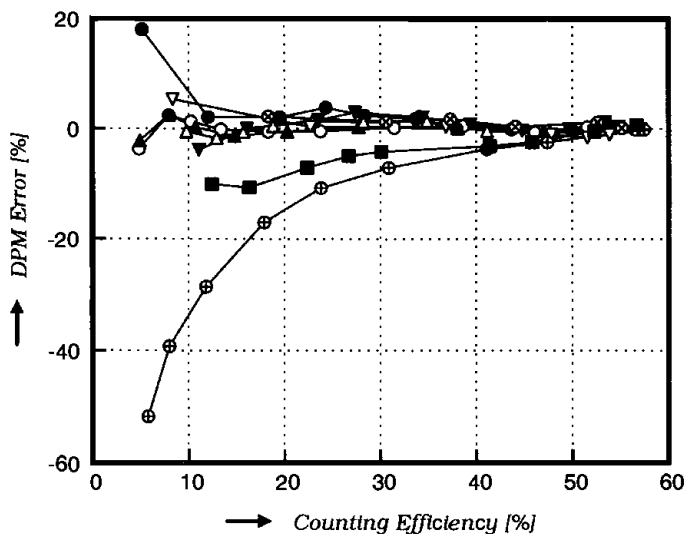


Figure 6. The DPM error as a function of the tritium counting efficiency when using the carbon tetrachloride quench curve and a coincidence resolving time of 72 nsec. Symbols as in Figure 4.

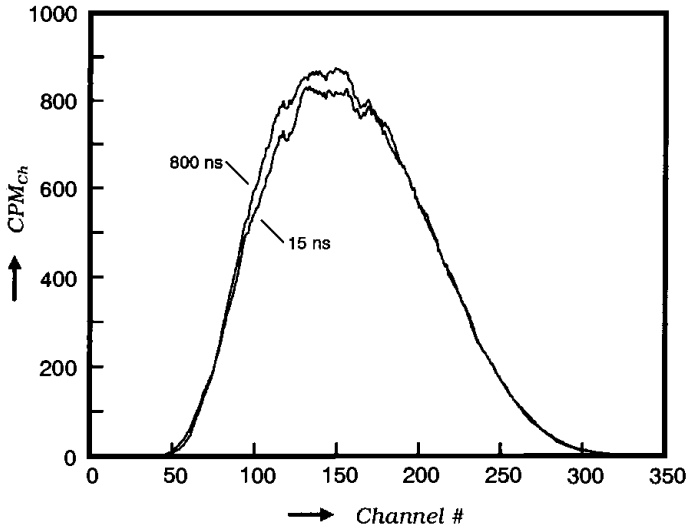


Figure 7a. The tritium spectrum of an air-quenched OptiScint 'T' sample at two different coincidence resolving times.

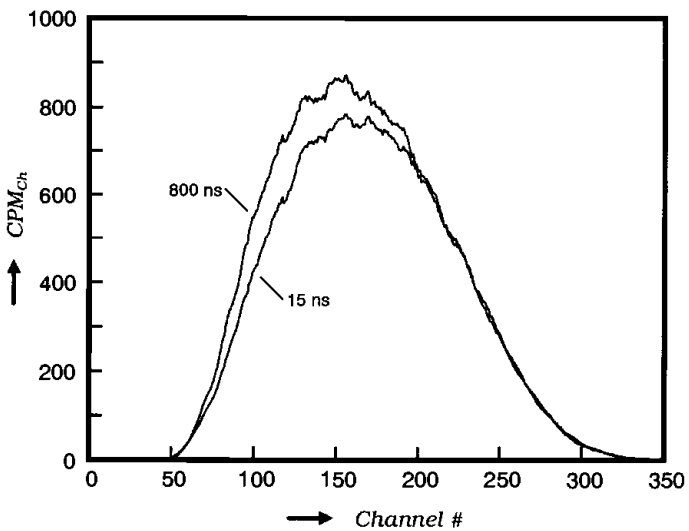


Figure 7b. The tritium spectrum of an air quenched OptiScint HiSafe sample at two different coincidence resolving times.

delayed pulse (see, e.g., Fuchs, et al.^{2,3}). When the coincidence resolving time is so short that a noticeable part of the delayed component is situated after the coincidence analyzer closes, one would expect to find mainly a reduced number of small pulses comprising only a few photoelectrons. The reason for this is as follows: when the number of photoelectrons produced decreases, the spacing in time between the photoelectrons increases if the overall pulse length remains constant (compare randomly dividing a distance into ten parts or two parts). Thus the chance increases that the time delay between the first electron, starting the coincidence analyzer, and the second electron, causing a valid coincidence pulse, will be longer than the coincidence resolving time. Hence, for a sample at fixed quench level, as the number of small pulses is decreased, the mean pulse height is shifted upwards and the counting efficiency downwards. This behavior can be observed in all the data presented here and especially in Figure 7.

Solvents

As all investigated cocktails may be expected to contain principally the same fluors, like PPO and bis-MSB, the reason for the difference in quench curve shape lies in the behavior of the solvents. It is known that naphthalene crystals have very long scintillation pulses⁴ and that solvents based on naphthalene derivatives have longer pulses than mono-aromatics.⁵ There may be three reasons for the longer pulse:

1. The electron may cause more extensive ionization in the naphthalene based solvent than in xylene. Ionization leads to formation of triplets through ion and electron recombination. The triplet states may eventually form singlet states through the triplet-triplet annihilation process.
2. Longer lifetimes of the excited singlet states may cause longer pulse decay times.
3. The bulkier molecule may slow the diffusion rates of the excited molecules.

Even at the longest coincidence resolving time (800 nsec), there is still some difference between the curves. But this difference may be due to other factors than the pulse shape. In general, with "infinitely" long coincidence resolving time, both the counting efficiency (E) and the mean pulse height (F) may be considered as functions of three parameters:⁶

$$E = E(a,b,X) \text{ and } F = F(a,b,X)$$

The parameter *a* is equal to the scintillation efficiency of the liquid, and thus depends on both the solvent and the concentration of quenching agent, while the parameters *b* and *X* are dependent on solvent only. The parameter *b* reflects the degree excited states are quenched by ionized states in the vicinity, while *X*, the mean excitation potential, has a direct effect on the stopping power of the solvent, and thus also on the density of ionized and excited states.

Variations in the mean excitation potential X and the ionization quenching parameter b result in variations of the quench curve shape.

Quenchers

What then is the explanation for the behaviors depicted in Figures 4–6? The answer might lie in the relation between the energy levels of a certain quencher and the solvent (toluene). This phenomenon has been extensively studied by, e.g., Fuchs, et. al.,^{2,3} who have proposed the theory that certain quenchers, which can be classified as “electron scavengers” (like oxygen and carbon tetrachloride) and have their excited levels above the energy levels of the solvent, may interact with the higher energy states of the solvent, and thus cause a reduced relative contribution of the delayed component. Compounds having their singlet energy levels just below the corresponding energy levels of the solvent may interact by accepting the excitation energy from the singlet states of the solvent and decrease the intensity of both the prompt component and the delayed component. The different forms of “impurity” or chemical quenching has also been discussed extensively by Birks.⁷

The fact that the color quench curve deviates from all the others, at all coincidence resolving times, is related to the special characteristics of color quench.⁸ Apart from the other quench modes, color quench depends on the spatial coordinates of the disintegrations. Sudan 1 also has a small amount of chemical quench, otherwise it would behave exactly like the toluene dilution, but the main amount of quenching comes from the color. The results show that color quench can not be handled the same as other forms, just by prolonging the coincidence resolving time.

CONCLUSION

Different quench curves are produced by different solvents and quenchers, when using a quench index reflecting the position of the pulse height spectrum of the dissolved isotope (as the mean pulse height or samples channels ratio), this can be explained on the basis of the shape of the scintillation pulse. The pulse shape is mainly dependent on two factors: 1. the distribution of different excited states of the solvent molecules when a β -electron traverses the solution and 2. the probability of quenching certain excited states in the solution. If the probability of forming higher excited states (e.g., Rydberg states) or ionized states is large, then the scintillation pulse will be stretched out in time. Quenchers capable of quenching the triplet and higher excited states, combining with ionized states, or acting as electron scavengers very effectively quench the delayed component of the pulse. Substances capable of quenching only the lowest singlet levels however, quench both the prompt and the delayed component to an equal degree. The differences in the quench curves caused by this effect can be reduced by increasing the coincidence resolving time of the counter to above 40 nsec.

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