The Mechanisms of the Liquid Scintillation Process

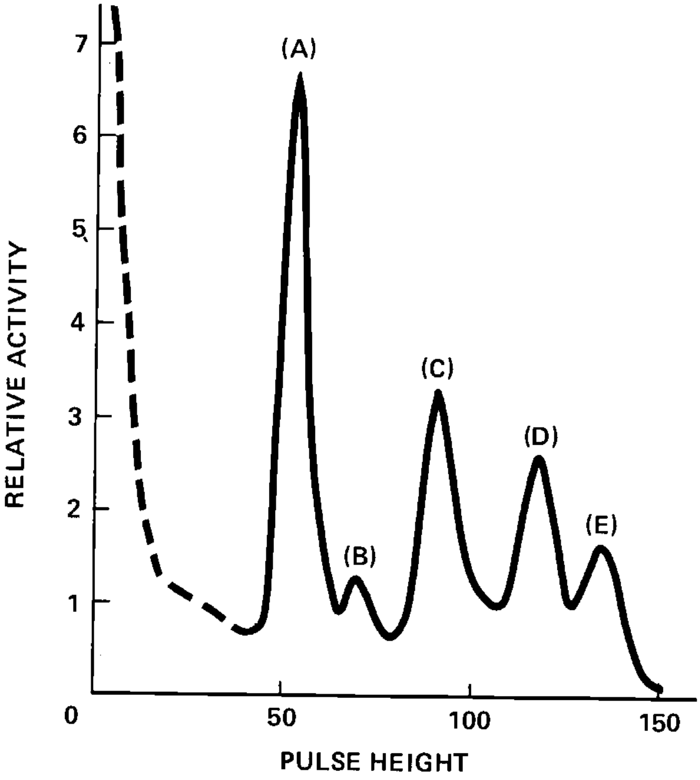
by

Donald L. Horrocks
Scientific Instruments Division
Beckman Instruments Inc.
Irvine, California 92713

The liquid scintillation process is based upon the conversion of part of the kinetic energy of an ionizing particle (usually from the decay of a radionuclide) into photons. These photons are collected and measured by multiplier phototubes (MPTs) and subsequently, the pulses from the MPTs are summed, sorted, and counted. Initially, the liquid scintillation process was used only as a means of detecting and quantitating the amount of radionuclide present in a sample. However, in recent years, there have been more and more applications involving not only the detection and quantitating, but also the measure of the distribution of the amplitudes of pulses produced by the interaction of the radiations with the liquid scintillators. Since the pulse amplitude can be calibrated with the energy of the radiations, it is possible to measure more than one radionuclide in a sample by selection of the pulse amplitudes emanating from the different radionuclides. Figure 1 shows a pulse height spectrum of a sample of thorium showing the presence of several radionuclides which can be identified by the different pulse amplitudes produced in the liquid scintillator.

In the history of liquid scintillation, it seems as though the number of "users" of liquid scintillators has increased at a tremendous rate. However, as is the case with many analytical methods, many "users" do not totally appreciate the complexity of the liquid scintillation process and as a result, often misinterpret results or attempt experiments which are beyond the capability of the method.

In this paper, it will be attempted to discuss the many mechanisms which comprise the "liquid scintillation process". It is hoped that an understanding of the mechanisms will help the many "users" to obtain more meaningful and accurate data from their experiments.



DIFFERENTIAL PULSE HEIGHT SPECTRUM FOR Th^{232}, Th^{228}, AND DAUGHTERS PLUS A SMALL AMOUNT OF Th^{230}.

Figure 1. Pulse height spectrum of Thorium sample dissolved in a liquid scintillation solution.

Interaction of Ionizing Radiation

The energy or distribution of energies of the radiations from a radionuclide are always the same. They are, with only a few exceptions, unaltered by the nature of the sample. However, the response that they produce in a liquid scintillator will depend upon many factors. The first factor to keep in mind is that only that energy or part of the energy which is released to the liquid scintillator can contribute to the response that will be produced. Any energy which is carried out of the liquid scintillator solution will be lost. This fact is often overlooked when measuring radionuclides which emit particles with high energies or when using small volumes of the liquid scintillator. In all liquid scintillation counting with homogeneous distribution of the radionuclide, there is always a fraction of radionuclides near the walls of the container. Part of these radiations can reach the wall before losing all of their energy. Thus, the response produced will be less than that produced by a particle of the same energy which releases all of its energy to the liquid scintillation medium. This is often called the "wall effect". The wall effect will have only a slight effect on counting in a wide open counting channel (accepting all pulse heights), but can markedly alter the relative counts in narrow counting channels (accepting only a fraction of the pulse heights).

If the sample is not homogeneously distributed within the liquid scintillator, the energy released to the scintillation-producing medium can also be reduced. This effect is most commonly encountered when the radionuclide is in a second phase such as deposited on a filter paper, a gel slice, a precipitate, etc. In these cases, part of the energy is released in the solid matrix before it reaches the liquid scintillator system. Thus, the radiations interact as if they originate with less energy. This effect is often referred to as "self-absorption". If the radiation energy is totally released within the second phase, there will be no response produced within the liquid scintillator.

When the scintillating solvent system is diluted by sample or secondary solvents, part of the energy may be released in the non-scintillation producing diluents. For a given energy, less excited solvent molecules will be produced with a smaller number of photons being emitted from the liquid scintillator. Thus, the response produced will be only equivalent to the response produced by a less energetic event in the undiluted liquid scintillator. This effect is referred to as "dilution absorption". (As will be explained later, dilution can also effect the energy migration and energy transfer processes.)

Another type of process which leads to decreased excited solvent molecules can be referred to as "annihilation". This effect is experienced when the total energy is removed in one catastrophic event. This effect can be noted in samples which contain heavy atoms (high atomic number atoms) which, when the ionizing particle strikes the heavy atom, absorb all of the kinetic energy without producing excited solvent molecules. Depending upon how far the particle has traveled in the liquid scintillator before it encounters such an "annihilation", the response will be proportionally decreased.

In liquid scintillator solutions, the primary excitations occur in the solvent part of the solution. The final response is directly proportional to the number of excited solvent molecules produced in this initial step. Of course, as already discussed, many processes can inhibit the production of excited solvent molecules. Also, it should be pointed out that different types of ionizing particles have different efficiencies for producing excited solvent molecules. And further, it should be remembered that only a small fraction of the total particle energy goes into the production of excited solvent molecules; only about 4-6% of electron kinetic energy, about 0.5-0.7% of alpha particle kinetic energy, and about 1.0% of proton kinetic energy.

Primary Excitation Process

The ionizing particles interact with molecules (mainly solvent molecules) as they are slowed down and finally stopped in the scintillator solution. The kinetic energy is released in many forms. The bulk is converted into thermal energy (kinetic) of the molecules. Other interaction products include:

S^*	excited molecules
$S^+ + e^-$	ions and electrons
$A^\bullet$	free radicals
B^+, C^-	ion fragments
D, E, F	molecular fragments

The concentration of these species can be great along the primary track of the particle. The specific ionization of the particle will determine the concentration. The high specific ionization of alpha particles leads to high concentrations of the various products. Because of the high concentration, many of the excited molecules and ions interact with the other products leading to a reduction of excited solvent molecules and the subsequently lower photon yield. This type of quenching is often referred to as "track" quenching. Track quenching is less for the lower specific ionization electrons (i.e., beta particles). In some cases, secondary electrons produce excited solvent molecules.(1)

The numbers of solvent ions and excited solvent molecules are both important in the determination of the scintillation yield. Ion recombination can lend to an appreciable fraction of the number of excited solvent molecules which lead to the production of photons. Previous studies (2-4) showed that in some solvent systems, 60% of the observed fluorescence was the result of ion recombination. Essentially, all of the excited solvent molecules produced by the ionizing particle are excited to upper excited energy levels ($n\geq2$). These upper excited energy levels undergo an internal conversion process (non-radiative) to produce the first excited singlet state. It is the yield of the first excited singlet state of the solvent molecules which determined the maximum scintillation yield.(5) Some studies have shown that energy transfer involving upper excited energy levels can occur when the energy acceptors (solutes) are present in high concentrations.(3) One reason for the different efficiencies of solvents is the fact that the internal conversion efficiency from upper excited states to the first excited state are different. Table 1 summarizes the known data on the calculated and measured relative efficiencies of some aromatic solvents.

Energy Migration

The excitation energy migrates from one solvent molecule to its neighbor solvent molecule. In this manner, the energy moves from one area to another until the solvent gives its excitation energy to other molecules in the liquid scintillator system. (These other molecules can be scintillator solutes or quencher molecules.) Two theories have been presented to describe the energy migration processes.

TABLE I. Comparison of calculated excitation yield from ion recombination and direct excitation with experimentally measured values for common liquid scintillation solvents.

Solvent	Internal Conversion (I.C.) Efficiency (a)	Direct Excited Solvent Yield	Excited S* Yield From I.C.	From Ion Recombination	Total Yield	Normalized Yield (%)	Measured (b) Sx (%)
Benzene	0.44	0.9	0.4	1.2	1.6	84	85
Toluene	0.76	0.9	0.7	1.2	1.9	100	100
p-Xylene	1.00	0.9	0.9	1.2	2.1	111	110
1,2,4-Trimethyl Benzene	1.00	0.9	0.9	1.2	2.1	111	112

(a) C. W. Lawson, F. Hirayama and S. Lipsky, J. Chem. Phys. 51, 1590 (1969).

(b) At 5 g/l of PPO

Birles(16) described the transfer as being due to the formation and disassociation of two solvent molecules to form excited dimers (excimers). In this process, the energy may be transferred to the previously unexcited solvent molecule when the excimer breaks apart. Voltz(7) stated that the energy actually jumps from the excited solvent molecule to its neighbor by a non-radiative process. Energy migration can lead to transfer between many solvent molecules before actual transfer to solute molecules.

Energy Transfer

Because most scintillator solvents have properties which reduce the yield of photons, often molecules are added which efficiently accept the solvent excitation energy and emit that energy as photons. The efficiency of scintillator solutions is dependent upon how efficiently the energy is scavanged by these added molecules (solutes). Some of the properties of solvents which make them poor scintillators by themselves are:

a. Solvent molecules have low probabilities for photon emission.

b. The energy (wavelength) distribution of emitted photons is in the range where common detectors (multiplier phototubes) have reduced sensitivity.

c. The emission lifetimes are long (∿30 nanoseconds) which means a greater probability of quenching before emission.

d. Due to the high solvent concentration, the probability of reabsorption of emitted photons is high.

The properties of the solute molecules are such as to minimize these drawbacks. The solute molecules have:

a. High fluorescence probabilities, ∿90%.

b. Wavelength distributions which match favorably with peak sensitivity of MPTs.

c. Very prompt photon emission, lifetimes between 1-2 nanoseconds.

d. Very low reabsorption probability because solutes are present in low concentration.

The transfer of energy from excited solvent molecules to acceptor molecule (solute or quencher) is considered to be basically a long range interaction and is not diffusion-controlled.(8) At fairly low solute concentrations (∿10^{-2} M), the energy transfer process is quantitative(9) with many solutes. This means that every excited solvent molecule leads to an excited solute molecule. At lower concentrations, the energy transfer efficiency decreases with a corresponding decrease in photon yield. The energy transfer from solvent to solute is not reversible because of a vibrational de-excitation in the solute molecule, leaving it with insufficient energy to re-excite a solvent molecule. Thus, the excitation energy is trapped by the solute molecules.

A second solute is sometimes used in liquid scintillation counting. In early times, the second solute was used to shift the spectral distribution of photons to more closely match the most sensative response range of the MPTs. In more recent times, with the new bi-alkali MPTs, the secondary solute is used more to reduce the effect of certain "color" quenchers which may be present in the scintillator-sample system. The concentration of the second solute can be adjusted to provide quantitative energy transfer from the first solute to the second solute.(10) Again, the molecular internal de-excitation of the second solute renders the energy transfer irreversible. Usually, the concentration of the second solute is only a few percent of the concentration of the first solute.

The energy transfer processes are all non-radiative, i.e., no photons are emitted and then reabsorbed by other molecules. This has been most dramatically demonstrated by measurements of the fluorescence decay times of liquid scintillator solutions. Excitation of the solvent molecules alone showed no change in the decay time of solute fluorescence compared to direct excitation of the solute molecules. Thus, the energy transfer processes must be many times faster than the decay times of the solutes.(10) Energy transfer processes are of the order of 10^2 to 10^3 times faster than the fluorescence decay time of the fastest known solute (∿10^{-9} seconds).

A recent experiment(10) using the pulsed Van de Graaff showed the energy transfer from primary solute (PPO) to secondary solute (M_2-POPOP) had an energy transfer rate constant of about 2.5 x 10^{13} l/mol-sec., which is about 10^3 times greater than the diffusion-controlled rate constant. It was possible to measure the relative emission of PPO and M_2-POPOP with constant PPO concentration and increasing M_2-POPOP concentration because of the high intensity of scintillation produced by the Van de Graaff pulses. Figure 2 shows the fluorescence spectra obtained.

Quenching Mechanisms

Quenching is a term commonly used to denote some process which causes a decrease in the photon yield of a liquid scintillator solution relative to no quenching (i.e., ideal). These quenching mechanisms can be divided into four main categories:

a. Energy absorption.

b. Dilution - concentration.

c. Impurity (sometimes called chemical).

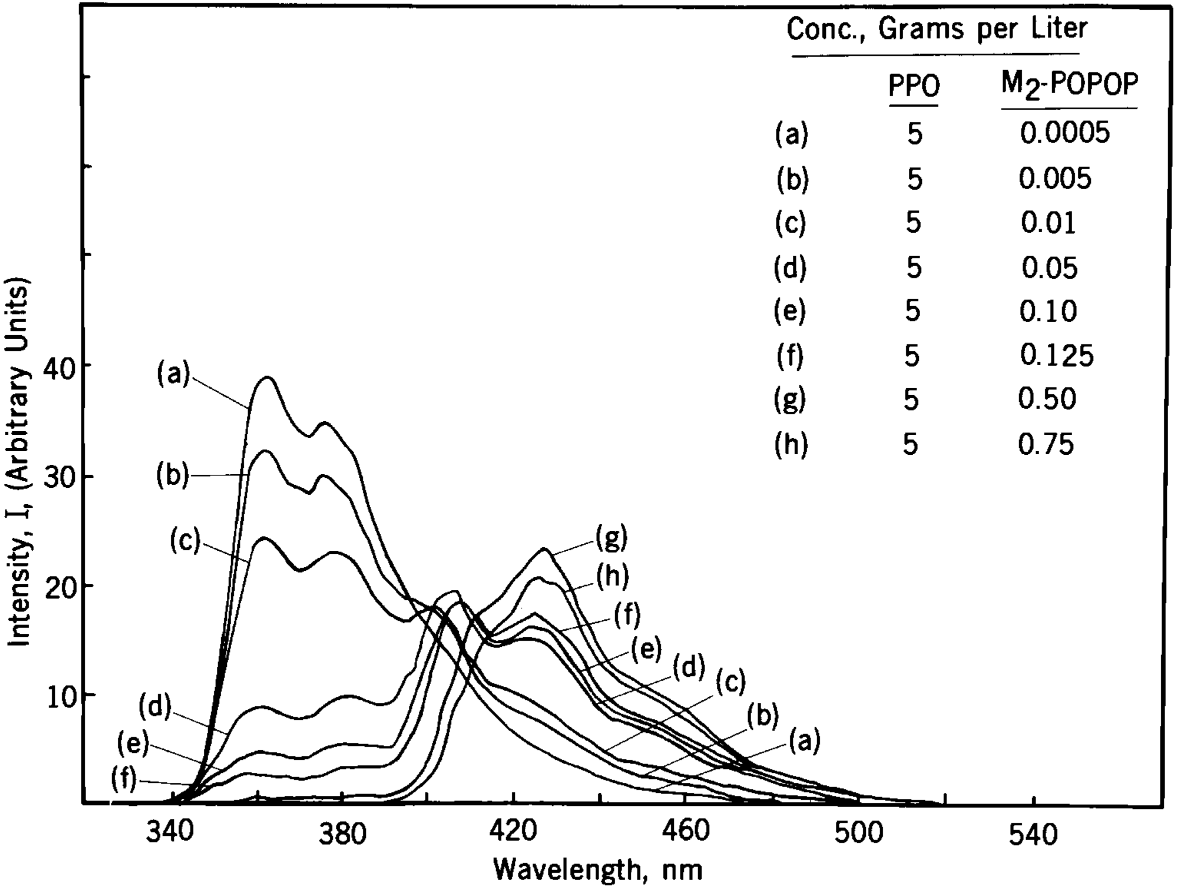
d. Color.

The first category, energy absorption, has been discussed in the section on "Interaction of Ionizing Radiation", and includes wall effect, self-absorption, dilution-absorption, and annihilation. All of these processes involve the release of part or all of the particle energy to non-scintillation-producing media.

Dilution-concentration refers to the reduced efficiency of energy migration and energy transfer processes. A second solvent can dilute the scintillation solvent to a degree that interferes with the normal energy migration process. Thus, the excitation energy does not have the ability to migrate to the regions of the solute molecules. If the concentration of the solute(s) is reduced below the ideal concentration, there will be insufficient solute molecules to efficiently scavange the excitation energy from the excited solvent molecules.

Impurity quenching refers to the competition of other non-fluorescent molecules for the solvent excitation energy. These non-fluorescent molecules will prevent the energy from being transferred to the solute molecules.

Figure 2.
Scintillation spectra for toluene solution with 5 g/l PPO and designated concentration of M_2-POPOP for excitation with 3 nanosecond pulses of 3 meV electrons from a pulsed Van de Graaff accelerator.



These three processes all decrease the number of excited solute molecules formed and thus the number of photons released. The latter process, color quenching, refers to molecules present in the scintillator solution which absorb the photons after they have been produced.

There are three other factors which can lend to a reduced response by reducing detection of photons from the scintillator solution:

a. Photon trapping in scintillation vial.

b. Photon loss in optical light collection system.

c. Quantum efficiency of the MPTs.

Glass counting vials prevent a small fraction of the produced photons from escaping from the scintillation solution by reflecting the photons at the outside of the glass wall, at the air-glass interface, due to the difference in the index of refraction of glass and air. Since the index of refraction of toluene and glass are nearly the same, no light is lost at the inside of the glass vial wall. Gordon and Curtis (11) showed that the introduction of rough areas on the outside wall of a glass vial increased the photon escape from a liquid scintillation vial by disrupting the internal reflection process. This effect is more pronounced for the measurement of events which produce photon yields near the threshold of detection. Roughing the outside of a glass counting vial can increase the tritium counting efficiency up to 2%.

The optical light collector is that part of the counting system which guides the emitted photons onto the face of the MPTs. Highly efficient diffuse reflector material gives the most efficient means of collecting and guiding the photons. This property is usually fixed by the instrument, but can sometimes change if for any reason the diffuse reflector has been contaminated or has gotten dirty. This is important for systems which are very old or have had spillage in the counting chamber.

The quantum efficiency of the MPTs is also an instrument-fixed factor. Most commercial instruments use MPTs with bialkali photo cathodes which have quantum efficiencies of

TABLE 2. Summation of scintillation effiency parameters as function of electron energy

Electron Energy keV	Sx	$\bar{N}_{ph}$	Photons per keV	keV/photon	keV/photoelectron
1000	0.062	19,375	19.4	.052	.186
500	.062	9,688	19.4	.052	.186
300	.062	5,813	19.4	.052	.186
158	.058	2,864	18.1	.055	.196
50	.052	813	16.3	.061	.218
18.6	.047	273	14.7	.068	.243
5	.040	63	12.6	.079	.283
1	.031	9.7	9.7	.103	.368
0.5	.024	3.8	7.5	0.133	.475

about 28% for photons of 380-400 nm wavelength. The MPTs are usually operated under conditions such that a single electron produced at the photocathode which undergoes the full amplification will, on the average, produce a measurable pulse.

Scintillation Efficiency

Scintillation efficiency is defined as the energy released as photons divided by the energy of the ionizing particle.(12) The scintillation efficiency varies with energy of the particle. Figure 3 shows a plot of scintillation efficiency (Sx) as a function of the energy of electron. Above 300 keV energy, the scintillation efficiency of this liquid scintillator solution (5 g PPO and 0.1 g M_2-POPOP per liter of toluene) was independent of electron energy. Below 300 keV, the scintillation efficiency decreased with decreasing electron energy. Thus, 1 keV electrons produced only one-half as many photons per unit energy as 300 keV electrons. Table 2 summarizes the values of scintillation efficiency (Sx), average number of photons ($\bar{N}_{ph}$), photons per keV, and keV per photon of a scintillator solution (5 g PPO and 0.1 g M_2-POPOP in one liter of toluene) excited by different energy electrons. The last column is based upon a MPT which has an average quantum efficiency of 28% for photons from the liquid scintillator solution.

Table 3 and Figure 4 give the same information for excitation of the same liquid scintillator solution with alpha particles of different energy. The scintillation efficiencies for alpha particles is about one-tenth the scintillation efficiency for electrons.

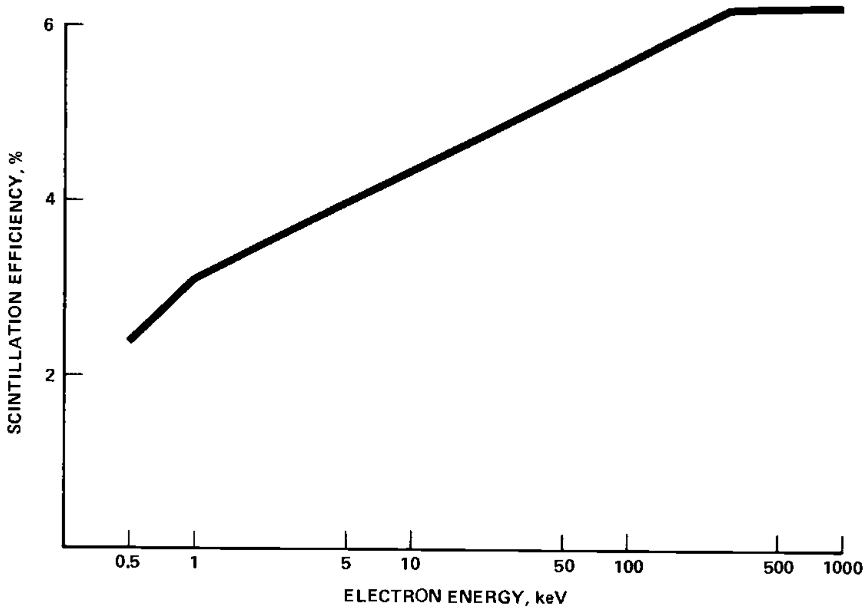


Figure 3. Scintillation efficiency as a function of electron excitation energy.

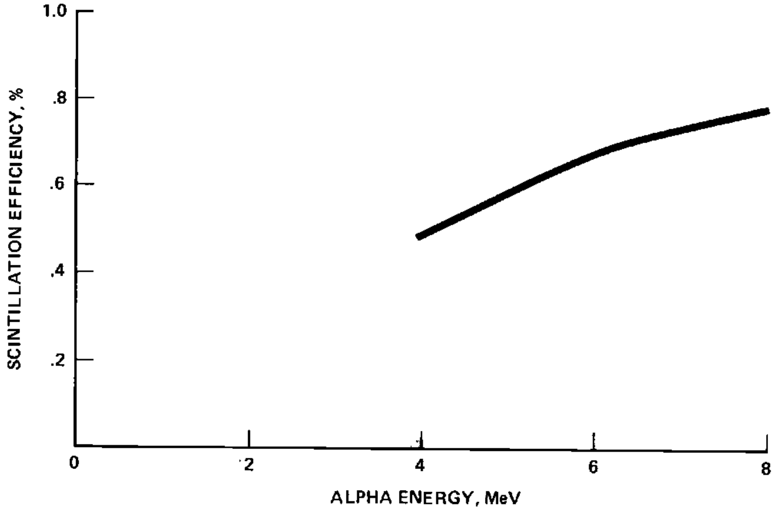


Figure 4 Scintillation efficiency as a function of alpha particle excitation energy.

TABLE 3. Summation of scintillation efficiency parameters as function of alpha particle energy

Alpha Particle Energy MeV	Sx	$\bar{N}ph$	Photons per keV	keV per Photon	keV per Photoelectron
8.0	0.0078	19569	2.45	0.41	1.46
7.5	.0076	17922	2.39	.42	1.50
7.0	.0074	16178	2.31	.43	1.54
6.5	.0071	14338	2.21	.45	1.61
6.0	.0068	12788	2.13	.47	1.68
5.5	.0064	10947	1.99	.50	1.79
5.0	.0058	9106	1.82	.55	1.96
4.5	.0054	7556	1.68	.59	2.11
4.0	.0049	6103	1.53	.65	2.32

References

1. G. Laustriat, in "Organic Scintillators", D. L. Horrocks, ed. (Gordon and Breach, New York, 1968) pp. 127-145.

2. R. Cooper and J. K. Thomas, J. Chem. Phys. 48, 5097 (1968).

3. D. L. Horrocks, J. Chem. Phys. 52, 1566 (1970).

4. J. B. Birks, in "Organic Scintillators and Liquid Scintillation Counting", D. L. Horrocks and C. T. Peng, eds. (Academic Press, New York, 1971) pp. 3-23.

5. C. W. Lawson, F. Hirayama and S. Lipsky, J. Chem. Phys. 51, 1590 (1969).

6. J. B. Birks, J. C. Conte and G. Walker, IEEE Trans. Nucl. Sci. NS-13, No. 3, 148 (1966).

7. R. Voltz, G. Laustriat and A. Coche, C. R. Acad. Sci., Paris 257, 1473 (1963).

8. Th. Forster, Discuss. Faraday Soc. 27, 7 (1959).

9. I. B. Berlman, J. Chem. Phys. 33, 1124 (1960).

10. D. L. Horrocks, Nucl. Instr. Meth. 128, 573 (1975).

11. B. E. Gordon and R. M. Curtis, Anal. Chem. 40, 1486 (1968).

12. D. L. Horrocks, "Applications of Liquid Scintillation Counting" (Academic Press, New York, 1974) pp. 27-30.