A STOCHASTIC MODEL OF THE LIQUID SCINTILLATION COUNTING PROCESS

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ABSTRACT

A stochastic multidimensional model for colour and chemical quenching is being developed for a coincidence liquid scintillation spectrometer. The programme, written in FORTRAN, is run on a CDC 6400 computer and requires a modest amount of memory but a considerable amount of central processor time.

The model produces a pulse height spectrum appropriate to the degree and type of quenching. The simulation is initiated within the computer by generating a β-event of random energy (following the energy probability spectrum of that radioisotope) in a random position within the vial. An appropriate number of photons of random wavelength (following the fluorescence spectrum of the phosphor solution) are emitted in random directions. The model also incorporates chemical and/or colour quenching, total internal reflection of light at the vial-air interface, quantum efficiency of the photomultipliers at the wavelengths of the photons, and the coincidence gate. Currently pulse height spectra are produced for a few thousand scintillations.

INTRODUCTION

Although mathematical modelling is well known to many scientists, it is worthwhile to restate briefly the basic concepts involved. The technique abstracts an observable closed system from the real world and describes, analyses and predicts its behaviour by developing and analysing a mathematical model of the system. In simulating the behaviour of the liquid scintillation counting (LSC) process on the computer, a 'pseudo-vial' containing a 'pseudo-sample' is counted by a 'pseudo-liquid scintillation counter'.

This work has evolved from an earlier attempt to produce a more comprehensive program package for LSC data reduction and processing. It became apparent that a deeper appreciation of the dynamics of the LSC process was needed, and the model has been developed with this aim in view.

The known appearance of the β-spectrum and the pulse height spectrum of an unquenched sample are compared with each other, and also with the pulse height spectra of chemical- (or impurity-) quenched and colour-quenched samples. For the case of ^{14}C it is known that the spectrum is compressed towards the left, or low-pulse-height end, as chemical quenching increases (see Fig. 1). An increase in colour quenching causes a similar compression towards the low-pulse-height end of the spectrum, but with the accompaniment of a greater spread in the spectrum than with chemical quenching. These two transformations of the pulse height spectrum are described *quantitatively* rather than *qualitatively*, and thus the dynamics of colour or chemical quenching can be considered.

A deeper understanding of the transformation of pulse height spectra for combined colour and chemical quenching can be applied in the following way. LSC measurements can be standardized for both colour and chemical quenching, and thus each type of quenching can be corrected for individually in DPM calculations; hopefully, more accurate and reliable results will be obtained.

Ways of improving the efficiency of the optics of the LSC process are also under investigation. Preliminary results indicate that transmitted light losses can be reduced as much as 50% when using counting vials of square rather than circular cross-section. This should improve counting efficiency, especially when counting heavily quenched or low-energy samples.

Several workers have proposed fairly complete models of the LSC process, but none appear to have developed a comprehensive stochastic model. ten Haaf (1) has presented a one-dimensional model which, although very simple, shows broader energy distributions and larger coincidence losses for colour-quenched samples compared with equivalent chemical-quenched samples. These results were in accordance with the earlier ones of Neary and Budd (2), who suggested that the wide divergence in behaviour between heavily colour- and chemical-quenched samples was due to the more probabilistic nature of colour quenching. Kaczmarczyk (3) has presented a detailed model of chemical quenching but has not extended it to include colour quenching, optical considerations, or details of photomultiplier response.

The work presented here is an attempt to combine the generality of ten Haaf's approach with the detail of Kaczmarczyk's work.

MATERIALS AND METHODS

Experimental. Counting was performed in a Packard Liquid Scintillation Spectrometer Model 3390-544. The instrument was fitted with RCA 4501 V4 bialkali photomultipliers which were operated at $20^\circ \pm 0.5^\circ$. Pulse height spectra were obtained with a 200-channel Packard Spectrazoom Multichannel Analyzer (MCA) which was connected to the test point at the rear of the RED pulse height analyzer. Here the pulses have been amplified according to the setting on the front panel. Discriminators were set at 3-1000. Coincidence was established by a gating pulse from the RED channel rate-meter output.

The phosphor solution contained 8g PPO (2,5-diphenyloxazole) in 1 litre toluene. PPO was obtained from Ajax Chemicals Ltd., Sydney, Australia. Its absorption spectrum was similar in toluene to that published (4). Toluene was "Proalys" grade of May and Baker (Aust.) Pty. Ltd. 15 ml samples of this phosphor were used in Packard Low Background vials, the glass of which had a refractive index close to 1.50. Vials were closed with Polyseal cones to minimize evaporation.

The phosphor was labelled with [Me-^{14}C]toluene obtained from the Radiochemical Centre, Amersham, U.K. It was diluted with unlabelled toluene so that 300 µl at 20° contained about 5×10^5 d.p.m. It was then calibrated against a standard [^{14}C]toluene sample. Each vial contained 300 µl of the diluted [^{14}C]toluene and this was checked by weighing. Two similar samples were quenched incrementally with either carbon tetrachloride as a chemical quencher, or a

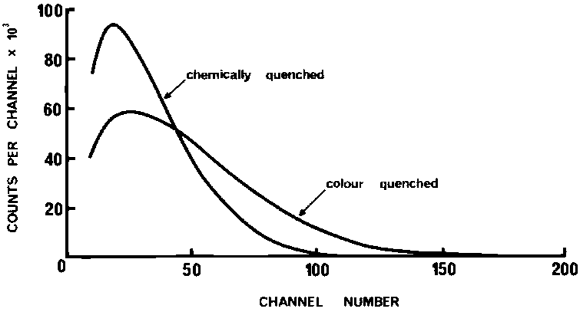

Fig. 1. OBSERVED PULSE HEIGHT SPECTRA OF COLOUR AND CHEMICALLY QUENCHED ^{14}C. Counting efficiency is 65%.

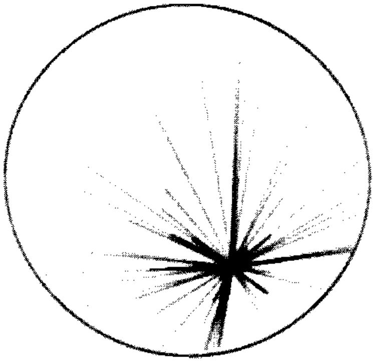

Fig. 2. A PHOTOGRAPH OF A SIMULATED SCINTILLATION OBTAINED AS SHOWN IN FIG. 4. Note the random positions of the 'scintillation' and the escape angles of the 'photons' and also the shorter distances travelled by the 'colour-quenched photons'.

saturated solution of methyl orange in ethanol as a colour quencher. Each sample was measured at 5% decrements in efficiency. Counting efficiencies of the two sets of samples were determined using spectrometer settings of 3-∞ at 100% amplification. For multichannel analysis the amplification was set so that the spectrum fitted easily into 200 channels. Counting time on the spectrometer was 2 min or 5×10^5 counts. A period of 600 seconds live time was used on the MCA.

The Stochastic Model. In this section the modelling process and the term 'stochastic' will be discussed, and then the model will be outlined in non-mathematical terms.

In developing a simulation of the behaviour of the LSC process an attempt has been made to isolate the fundamental components of this process, which have been described quantitatively rather than qualitatively. Programs following these quantitative descriptions have been prepared and have been assembled to produce a stochastic model of the LSC process.

A *stochastic* model is one in which the components are described (or modelled) probabilistically. The β-spectrum of the particular radioisotope is treated as a probability distribution, and 'β-events' with random energies are generated following that distribution. This means that, while the energies of any two 'β-events' are mutually independent, the spectrum produced mimics the β-spectrum.

The technique of stochastic modelling is particularly applicable to the LSC process because many of its components are random events. Energies of real β-particles, for example, are mutually independent, yet follow the β-spectrum of the emitter.

Fig. 2 is a photograph of the computer output showing the random trajectories of the simulated photons; the circle represents the vial surface and a trajectory ending short of it indicates that the 'photon' was colour quenched. The model is very simple; a point is chosen at random in a circle representing a cross-section of the counting vial. From a β-event at this point it is assumed that a fixed number, say 50, 'photons' would be emitted at random angles. Any consideration of energy forms, energy spectra, or energy transformations is ignored.

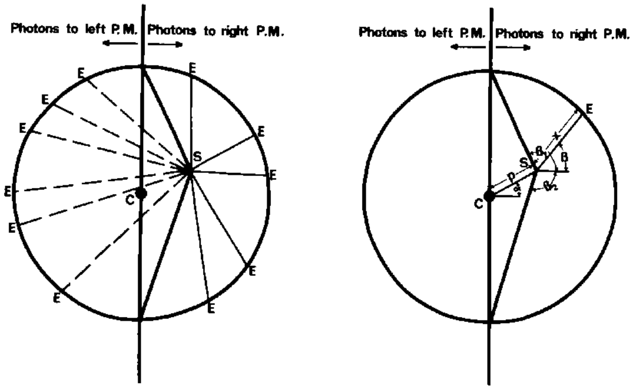

Fig. 3. THE GEOMETRY OF THE SIMPLE MODEL

C is the centre of the vial.
S is a random position of a 'scintillation' with polar coordinates (p, α) relative to C.

If a 'photon' is emitted from S at a random escape angle β, it will travel a distance x before reaching the vial surface at point E.

β_1 and β_2 are the maximum and minimum escape angles at which a 'photon' can be emitted and still leave the right-hand side of the vial.

For a vial of unit radius -

$$x = \sqrt{1-p^2\sin^2(\beta-\alpha)} - p\cos(\beta-\alpha)$$

$$\beta_1 = \tan^{-1}\left(\frac{p\sin\alpha-1}{p\cos\alpha}\right) \qquad \beta_2 = \tan^{-1}\left(\frac{-p\sin\alpha-1}{p\cos\alpha}\right)$$

Thus, 50 'photons' are emitted at random angles from a random point within a circle. Chemical quenching is simulated by discarding a proportion of these 'photons' immediately; for each 'photon', the computer generates a random number r between 0 and 1 and compares it with the expected proportion p of 'photons' lost by chemical quenching, p being set as a model parameter. If r is greater than p, then the 'photon' is not chemically quenched; if r is less than p, then it is.

For each 'photon' that avoids chemical quenching, the computer calculates the escape distance x (see Fig. 3) that it must travel to reach the vial surface, and also whether it would leave the vial on the right- or left-hand side (i.e. which photomultiplier). Colour quenching is simulated by calculating a probability of escape to the vial surface. The escape distance x and another model parameter q (to calibrate the amount of colour quenching) are used to calculated $u = 1\text{-}\exp(-x \cdot q)$. u therefore gives the probability that the 'photon' is unquenched; as either i) the excape distance x, or ii) the optical density modelling parameter q, increase, then $\exp(-x \cdot q)$ decreases and therefore u increases exponentially. The computer now generates a random probability v and compares it with u. If v exceeds u, then the 'photon' is unquenched, and when v is less than u, the 'photon' is colour quenched. Whereas the unquenched 'photon' has now reached the vial surface, a colour-quenched 'photon' was absorbed somewhere between the point of scintillation and the surface. The computer simulates the actual distance travelled by a quenched 'photon' by taking a random proportion of the escape distance x; thus, the unquenched 'photon' would travel a distance x to reach the vial surface and, if it is quenched, it travels some random smaller distance before being absorbed.

A short ciné film* showing the behaviour of this very simple model was prepared as follows (see Fig. 4): The program for the model was written in FORTRAN and run on a CDC 6400 computer, which then punched data on a paper tape; this was read into a PDP 8 computer; displays of successive time slices of a 'photon burst' (or scintillation) were drawn on a Tektronix 611 storage oscilloscope under the control of a FOCAL program in the PDP 8. As the display of

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*The film was viewed at the Symposium and each scintillation lasted about 5 seconds.

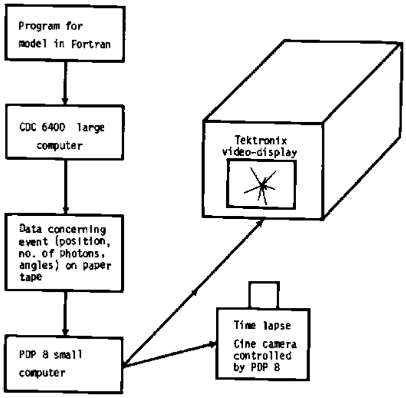

Fig. 4. STAGES IN PREPARING THE FILM

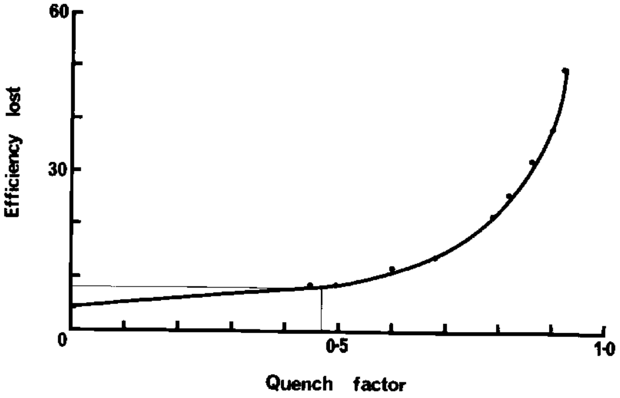

Fig. 5. A CHEMICAL QUENCH CALIBRATION CURVE

each time slice for each 'photon burst' was completed, the PDP 8 triggered a single half-second exposure by a ciné camera. The PDP 8 thus drew a picture, then photographed it, and then drew the next picture and so on.

The structure of a more refined model which includes the energetics of the LSC process is shown in Table I. Individual 'β-events' are modelled in a 3-dimensional 'vial' and, by repeating the simulation for a large number of these 'events', a pulse height spectrum is generated. The model simulates the behaviour of the LSC process using the probabilistic approach; a 'β-event' of a radioisotope is generated at some random position (3-dimensionally) within the 'vial' giving the emission of a 'β-particle' whose energy is randomly selected from a Fermi probability distribution following the β-spectrum of that isotope. About 4% of the energy is transferred to the fluor (PPO) *via* the solvent (toluene), and any losses due to chemical quenching are simulated randomly. Emission of 'photons' by the fluor [about 11 photons/keV of β-particle energy (4,5)] is the next step in the simulation; the random wavelengths of the emitted 'photons' are constrained to follow a probability distribution given by the fluorescence spectrum of PPO (4,6).

Colour quenching is simulated using an experimentally determined absorption spectrum for the vial and its contents. The computer calculates the absorbance of the solution for each 'photon' according to its wavelength and escape distance. The probability of transmittance is then calculated using the Beer-Bouguer Law, and transmittance or absorption of the photon is then simulated using an algorithm similar to the chemical-quenching one.

Any 'photons' left have by now reached the outer wall of the vial and are therefore susceptible to total internal reflection at the vial-air interface. This is simulated by calculating the angle of incidence of the 'photon' in a 3-dimensional vial; any 'photons' with an incident angle greater than the critical angle are lost.

Currently it is assumed that once a 'photon' leaves the vial it reaches the appropriate photomultiplier either directly or *via* a perfectly reflecting surface, and thus the next step in the simulation is to model the photocathodes of the photomultipliers. This is done using the quantum efficiency spectrum (7) of the photocathodes, and

TABLE I. THE LIQUID SCINTILLATION PROCESS AND ITS MODEL

Energy form	Stage in LSC process	Energy loss		Included in model of LSC process
		Type	% Loss from previous stage	
β-particle	β-disintegration	heat	95	Yes. Random β-energies following β-spectrum are produced. Yes. This loss is varied to calibrate counting efficiency.
excited molecules	solvent (toluene)	chemical quenching	40-95	Yes. Losses depend on sample.
photons	fluor (PPO)	colour quenching	38-85	Yes. Losses depend on sample.
	outer vial wall	total internal reflection	50-60	Yes. Partial internal reflection not modelled yet.
	detection chamber	reflection losses	?5-10	No. Second-order effect.
photo electrons	photocathode	quantum efficiency of photomultiplier is < 100%	75-90	Yes.
voltage pulse	dynode chain	pulse spread and losses	?	No. Lack of information.
voltage pulse	photomultiplier anode	assume zero losses		
summed voltage pulse	coincidence gate	coincidence losses (pulse from either anode below coincidence threshold)	various	Yes. Important with small numbers of photons.
	pulse height analyser and the remainder of the system			

randomly producing (or failing to produce) photoelectrons according to that spectrum.

The next stage in the model is to simulate coincidence by considering the pulses from each photomultiplier. Coincidence is enabled only when there is a pulse from each photomultiplier; the pulses are then summed as in a summation amplifier.

Many such β-events produce a pulse height spectrum. This spectrum is the main output of the model.

RESULTS

One particularly striking feature of the model is its requirement for computer time, since at least 5 hours per day are essential for work to proceed at a reasonable pace on the CDC 6400 (each event taking up to 1 second to simulate). This means that calculations equivalent to 10 man-years of work are required daily of the computer.

General trends in the behaviour of the model which are now apparent are presented here. Thus, the first-order effects (see Table I) modelled to date show close agreement with the experimental data. The current full-scale model was first calibrated for chemical quenching by plotting a graph of counting efficiency against the chemical quench factor p (see Fig. 5). A counting efficiency of 96-97% was found in the absence of chemical quenching (i.e. p=0), and as p increased, counting efficiency decreased according to an exponential-type relationship.

The accelerating rate of efficiency lost when p exceeds 0.7 corresponds to a moderately quenched sample. Note that for large p, even a small change in p will cause a marked change in counting efficiency. However, when p is small, there is only a small change in efficiency for a small change in p. An increase in p caused a compression of the pulse height spectrum towards the low-pulse-height end. These results are in accordance with experimental evidence.

Calibration for colour quenching in the model was achieved using an absorption spectrum determined for that sample. Colour quenching was found to occur even in the pure PPO-toluene phosphor, as the fluorescence and absorption spectra for PPO in toluene overlap. This is shown in Fig. 6.

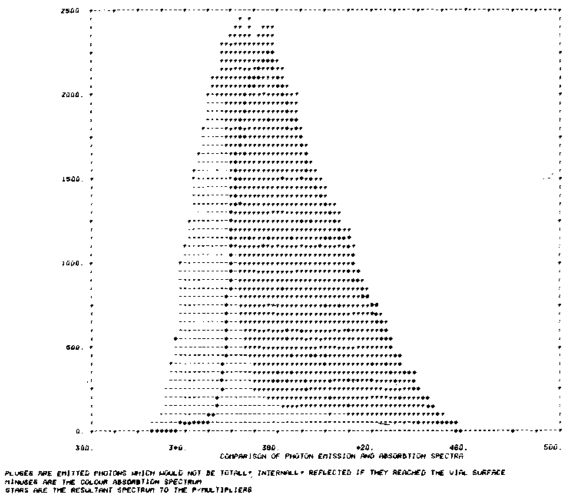

Fig. 6. A COMPUTER OUTPUT SHOWING COMPARISON OF THE PPO FLUORESCENCE (+ histogram) AND ABSORPTION (- histogram) SPECTRA INCLUDING THE RESULTANT SPECTRUM (* plot) LEAVING THE VIAL.

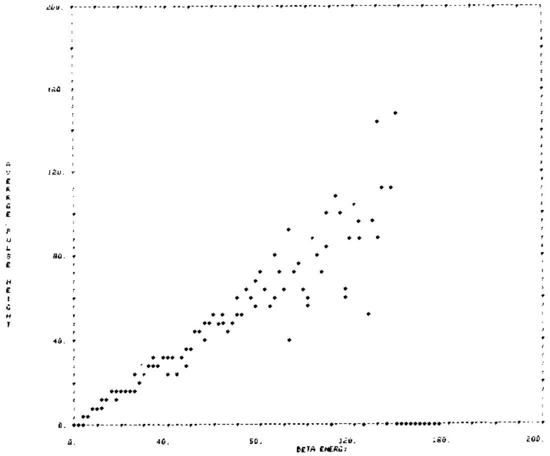

Fig. 7. A COMPUTER OUTPUT SHOWING PLOT OF THE AVERAGE PULSE HEIGHT AGAINST BETA ENERGY. Note the linear relationship and the greater scatter at higher energies.

An increase in colour quenching was simulated using absorption spectra determined for individual colour-quenched samples. Again the expected movement of the pulse height spectrum was found; as colour quenching increased, there was a compression of the spectrum toward the low-pulse-height end. As predicted, there was a greater spectral spread than found in the corresponding chemical-quenched sample. When quenching was due to the overlap of the PPO absorption and fluorescence spectra, then the model gave a counting efficiency of 96-97%. In practice, however, the nominally unquenched sample had a counting efficiency of only 92% and the difference can be ascribed to oxygen quenching. Purging the 'unquenched sample' with argon caused the counting efficiency to rise to 96%.

Another output of the model is a plot of mean pulse height against β-energy (see Fig. 7), which was expected to follow a linear relationship. Most (80%) β-events produced by ^{14}C fall in the energy range of 0-80 keV, and in this range the linear relationship between mean pulse height and β-energy is evident since there is little spread in the data points. At higher energies, however, there are relatively few β-events, and thus there are fewer recordings in each mean pulse height. This is reflected as an increased spread in the values of the mean pulse height, which also explains why the high end of a pulse height spectrum falls off more slowly than the corresponding β-spectrum. The few β-particles of such high energy are subject to a series of probabilistic processes, thus producing marked fluctuations in the resultant pulse height.

One weakness in the model is the energy transformation from the β-event to the fluor. Published values (5,8) indicate that 10 or 12.5 photons are produced for each keV ←* of β-energy. The model is relatively insensitive to changes in this value for ^{14}C. In the case of an unquenched ^{3}H sample it is found that 13.5 photons/keV were needed to obtain a 67% counting efficiency, whereas an efficiency of only 63% was obtained with 12.5 photons/keV.

While relatively complete results are to hand for samples subjected to either colour or chemical quenching, it is clear that more experience with the model is required before reliable results can be obtained for their combined effects.

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