

Chapter 1

Impurity Quenching of Organic Liquid Scintillators

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INTRODUCTION

For the English-speaking world 1975 is the silver jubilee of liquid scintillation counting, although the Italians could have celebrated the event last year. The 1950 issues of *Physical Review* included three papers, by Reynolds *et al.*¹ from Princeton, Kallmann² from New York and Ageno *et al.*³ from Italy, each claiming the first discovery of scintillations from organic liquid solutions. These were the first reports of liquid scintillators published in English, but priority belongs to Ageno *et al.*⁴ who also published their results in a small Italian journal in 1949.

Organic scintillation counting originated in 1947 when Kallmann⁵ discovered that crystalline naphthalene, grown from moth-balls garnered from the chemists' shops of war-ravaged Berlin, and irradiated with β -particles or γ -rays, emitted scintillations which could be detected and converted into electrical pulses with a photomultiplier. In 1948, Bell⁶ found crystalline anthracene to have a much higher scintillation efficiency than crystalline naphthalene, and Collins⁷ measured its scintillation lifetime to be about 10 ns. This is much less than that of impurity-activated zinc sulphide, the visual scintillator which dominated the first 25 years of experimental nuclear physics, or of thallium-activated sodium iodide, introduced by Hofstadter⁸ in 1948 and since used extensively for γ -ray detection and spectroscopy. It was thus shown that organic scintillators offer major advantages in time resolution and counting rates compared with inorganic scintillators.

As mentioned previously, organic liquid solution scintillators were discovered in Italy in 1949^{3,4} and in the United States in 1950.^{1,2} Two other types of organic solution scintillator were also discovered in 1950. Schorr and Torney⁹ introduced plastic solution scintillators, destined to have a major impact in high-energy physics. Birks¹⁰ discovered organic crystal solution scintillators (mixed crystals), but these have found little practical application compared with their liquid and plastic solution counterparts. The first paper on the organic scintillation process was also published in 1950, in which Birks¹¹ proposed a relation between the specific scintillation efficiency of an anthracene crystal and the specific energy loss of an ionising particle, a relation which later proved applicable to all types of organic scintillator. Nineteen seventy-five is thus a personal silver

jubilee. My interest in the subject started in 1948, however, so that the Sydney symposium in 1973 was chosen as the occasion for personal argento-jubilation.¹² Participation in the early stages of any new branch of science offers several subsequent advantages. One is strategically placed to write books on the subject to inform newcomers to the field.^{13,14} One is invited to participate in meetings in many interesting places.

At the 1973 Sydney symposium¹⁵ I drew an analogy between a liquid scintillation counting symposium and a theological assembly: so the choice of topic here is between two opposing themes: good or evil, virtue or vice, purity or impurity. Those interested in the fundamental physical processes in liquid scintillators usually study them under conditions of extreme purity, even excluding the oxygen dissolved in the solvent.

Those concerned with the utilisation of internal liquid scintillation counting for radioassay do not usually operate under such high-purity conditions. The addition of the radioactive specimen and any associated incorporating agents to the scintillator introduces impurity quenching which reduces the scintillation efficiency of the system. Since most of the present audience are concerned with the practical world of the impure scintillator, and not with the monastic world of the pure scintillator, the present talk will deal with the physics of impurity quenching, commonly but incorrectly known as chemical quenching.

The theme will thus be impurity rather than purity, pollution rather than perfection. The theological overtone is thus to consider how one can reduce the harmful effects of impurity in order to see more clearly the inner light.

THE SCINTILLATION PROCESS

The following sequence of processes in a liquid scintillator solution leads to the prompt scintillation emission.¹⁴ Processes involving thermal dissipation of the excitation energy by internal quenching, or the formation and internal conversion of excited triplet states leading to delayed scintillation emission via triplet-triplet interaction, are omitted to simplify the discussion.

- (i) The ionising particle excites solvent molecules (1X) into higher excited singlet ($^1X^{**}$) states.
- (ii) The particle also ionises solvent molecules yielding molecular ions ($^2X^+$) and electrons ($^2e^-$).
- (iii) $^2X^+$ and $^2e^-$ recombine to yield $^1X^{**}$.
- (iv) $^1X^{**}$ undergoes internal conversion to the lowest excited singlet ($^1X^*$) state of the solvent molecule.
- (v) $^1X^*$ transfers its energy radiationlessly, by a process involving molecular diffusion, excimer ($^1D^*$) formation and dissociation, and excitation migration, to a primary solute molecule (1Y), thereby exciting it into its lowest excited singlet ($^1Y^*$) state.
- (vi) The $^1Y^*$ excitation energy is either transferred radiationlessly to a secondary solute molecule (1Z), thereby exciting it into its lowest excited singlet ($^1Z^*$) state, or it is emitted as a fluorescence photon, which may be absorbed by 1Z , so that the $^1Y^*$ energy is transferred radiatively to 1Z yielding $^1Z^*$.
- (vii) The $^1Z^*$ fluorescence (and any unabsorbed fluorescence of $^1Y^*$) constitutes the scintillation emission of the solution.

The introduction of an impurity molecular species Q into the pure scintillator solution (1X , 1Y , 1Z) reduces the scintillation efficiency by interfering, through competitive processes, at various stages in the above sequence. Very fast processes are unaffected by Q. Thus the excitation and ionisation processes (i) and (ii) which occur in about 10^{-15} s, and the internal conversion process (iv) which occurs in about 10^{-12} s, are immune to impurity quenching. The processes which are susceptible to impurity quenching are those that occur on the 10^{-10} - 10^{-9} s time scale, namely (iii) solvent ion recombination, (v) solvent ($^1X^*$) excitation, (vi) primary solute ($^1Y^*$) excitation, and (vii) secondary solute ($^1Z^*$) excitation.

ELECTRON CAPTURE QUENCHING

Because of its high mobility, an electron ($^2e^-$) produced by the primary ionisation process (ii), is susceptible to capture by an impurity species Q, particularly if it has sufficient energy to be removed from the Coulombic field of the associated molecular ion ($^2X^+$). Such electron capture competes with ion recombination (iii) and thus reduces the yield of $^1X^{**}$ (and hence the subsequent yields of $^1X^*$, $^1Y^*$ and $^1Z^*$).

The electron capture cross-section of Q increases with its electron affinity A . Molecules with relatively high values of A include chlorine, bromine, iodine, iodine chloride, *p*-chloranil, *p*-bromanil, *p*-iodanil, *p*-benzoquinone, trinitrobenzene and tetracyanoethylene.¹⁶ Oxygen, which is a very efficient excitation quencher, has a relatively low value of A . Blaunstein and Christophorou¹⁷ have compiled a list of the electron affinities of 198 molecules which may be used to assess the probability of electron capture quenching by a particular molecular species Q.

In most liquid scintillator solutions, excitation ($^1X^*$, $^1Y^*$, $^1Z^*$) quenching appears to be more important than electron capture quenching.

EXCITATION QUENCHING

The fluorescence quantum yield q_{FM} of an excited molecule $^1M^*$ in a 'pure' solution, i.e. in the absence of Q, is

$$q_{FM} = \frac{k_{FM}}{k_{FM} + k_{NM}} = \frac{k_{FM}}{k_M} \quad (1)$$

where k_{FM} is the radiative (fluorescence) rate parameter and k_{NM} is the total radiationless rate parameter. k_{NM} is the sum of the rates of all radiationless processes operating on $^1M^*$, including internal quenching (rate k_{IM}) due to intersystem crossing and internal conversion,¹⁶ oxygen quenching (rate $k_{OM} [O_2]$, where $[O_2]$ is the molar concentration of dissolved oxygen), and radiationless energy transfer (rate $k_{BM} [^1B]$) to another molecular species, molar concentration $[^1B]$, in the solution. k_M is the total $^1M^*$ decay rate and $\tau_M (= 1/k_M)$ is the $^1M^*$ fluorescence (excitation) lifetime.

The introduction of a molar concentration $[Q]$ of a quenching species Q reduces the fluorescence quantum yield to

$$\begin{aligned}\phi_{\text{FM}} &= \frac{\tau_{\text{FM}}}{k_{\text{M}} + k_{\text{QM}} [\text{Q}]} \\ &= \frac{q_{\text{FM}}}{1 + \tau_{\text{M}} k_{\text{QM}} [\text{Q}]} = \frac{q_{\text{FM}}}{1 + K_{\text{QM}} [\text{Q}]}\end{aligned}\quad (2)$$

where k_{QM} (units $\text{M}^{-1} \text{s}^{-1}$) is the bimolecular rate parameter of impurity quenching of $^1\text{M}^*$ by Q. The parameter K_{QM} (units M^{-1}) is the Stern-Volmer coefficient of impurity quenching. Its reciprocal $[\text{Q}]_{0.5}$ ($= 1/K_{\text{QM}}$) is the half-value quencher concentration at which $\phi_{\text{FM}} = 0.5q_{\text{FM}}$.

The impurity quenching rate parameter k_{QM} is given by the relation

$$k_{\text{QM}} = \frac{4\pi N p D R'}{10^3} \left(1 + \frac{p R'}{(\pi D t)^{1/2}} \right)\quad (3)$$

obtained from Einstein-Smolochowski diffusion theory,¹⁶ where N is Avogadro's number, D ($= D_{\text{M}} + D_{\text{Q}}$) is the sum of the diffusion coefficients of the reactant species, R' ($= R_{\text{M}} + R'_{\text{Q}}$) is the sum of their interaction radii, t is time and p (≤ 1) is the quenching probability per molecular collision. The term in parentheses is the so-called transient term. Except at very short times, it is of the order of unity and it can usually be disregarded, so that Eqn. (3) simplifies to

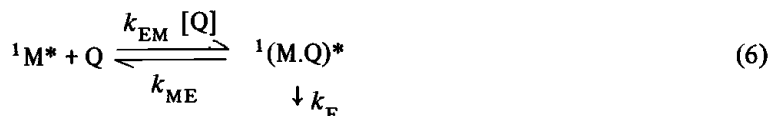
$$k_{\text{QM}} = \frac{4\pi N p D R'}{10^3}\quad (4)$$

The Stern-Volmer coefficient of impurity quenching of $^1\text{M}^*$ by Q may be written as

$$K_{\text{QM}} = \tau_{\text{M}} k_{\text{QM}} = a \tau_{\text{M}} D R p\quad (5)$$

where a ($= 4\pi N \times 10^{-3}$) is constant.

The factors determining τ_{M} , D and R' are known. We shall now discuss the factors determining p , the probability of quenching during a molecular collision between $^1\text{M}^*$ and Q. Such a collision usually results in the formation (rate $k_{\text{EM}} [\text{Q}]$) of an excited complex or *exciplex* $^1(\text{M.Q})^*$,¹⁶ which undergoes internal quenching (rate k_{E}) or dissociation (rate k_{ME}) into $^1\text{M}^*$ and Q as follows:



The quenching rate parameter k_{QM} is given by

$$k_{QM} = k_{EM} \frac{k_E}{k_E + k_{ME}} = p k_{EM} \quad (7)$$

where k_{EM} is the diffusion-controlled rate parameter, given by Eqn. (4) with $p = 1$,

$$k_{EM} = \frac{4\pi NDR'}{10^3} \quad (4a)$$

Thus p is given by

$$p = \frac{k_E}{k_E + k_{ME}} \quad (8)$$

p is large when k_E is large, i.e. strong internal quenching of $^1(M.Q)^*$, or when k_{ME} is small, i.e. low $^1(M.Q)^*$ dissociation rate.

k_E is large when Q contains heavy atoms of high atomic number. These increase the spin-orbit coupling in the complex (the heavy-atom effect) and thus enhance the rate of intersystem crossing from the singlet exciplex $^1(M.Q)^*$ to the triplet exciplex $^3(M.Q)^*$.¹⁶ This explains the strong fluorescence quenching ($p = 1$) of scintillator solvents and solutes by carbon tetrabromide.¹⁸

The magnitude of k_{ME} depends on the exciplex thermodynamics.¹⁶ The molar equilibrium constant of Eqn. (6) is given by

$$\frac{k_{EM}}{k_{ME}} = \exp(\Delta S/R) \exp(-\Delta H/RT) \quad (9)$$

so that

$$k_{ME} = k_{EM} \exp(-\Delta S/R) \exp(\Delta H/RT) \quad (9a)$$

where ΔH and ΔS are the enthalpy and entropy of the exciplex, R is the gas constant and T is the absolute temperature. The parameter $B (= -\Delta H/N)$ is the exciplex binding energy. k_{ME} is proportional to k_{EM} (Eqn. (4a)), so that it increases with the diffusion coefficient D . k_{ME} also increases with increase in temperature T , and with decrease in the exciplex binding energy B . k_{ME} is large, and hence p tends to be small (Eqn. (8)), in a system of high diffusion coefficient D (i.e. low viscosity), high temperature T and low exciplex binding energy B . The magnitude of B is determined mainly by the ionisation potential I and electron affinity A of the exciplex constituents. The theory of exciplexes has been developed to an advanced state,¹⁹ but no simple rules have been formulated for the evaluation of B or p for a given pair of molecules. Two empirical approaches^{21,22} to the problem will be considered later.

PRACTICAL ASPECTS OF QUENCHING

The magnitude of the quenching of a singlet-excited molecule $^1M^*$ by Q is, from Eqn. (2),

$$\frac{q_{FM}}{\phi_{FM}} = 1 + K_{QM} [Q] \quad (10)$$

where

$$K_{QM} = a\tau_M DR'p \quad (5)$$

Thus the quenching depends on $[Q]$, τ_M , D , R' and p .

There are several alternative methods by which the quenching of a liquid scintillator can be reduced.

Oxygen removal

The dissolved oxygen in a liquid scintillator, which introduces up to 20% quenching, can be eliminated by nitrogen bubbling or otherwise. Operation at a lower temperature, where the oxygen solubility in the solvent is reduced, is an alternative method of reducing oxygen quenching.

Decreased specimen concentration

The specimen concentration which determines $[Q]$ can sometimes be reduced. The disadvantage of an increased counting time is offset by the smaller quench correction required.

Reduced diffusion coefficient

The diffusion coefficient D can be reduced by operating at low temperatures or by using a viscous solvent (e.g. methylnaphthalene) or a viscous emulsion. The associated decrease in k_{QM} may be offset by an increase in p .

Increased primary solute concentration

The solvent ($^1X^*$) lifetime is given by

$$\tau_X = \left(k_{FX} + k_{IX} + k_{YX} [^1Y] \right)^{-1} \quad (11)$$

$$= \left(k_{FX} + k_{IX} \right) \text{ for } [^1Y] = 0 \quad (12)$$

$$\cong 1/k_{YX} [^1Y] \text{ for } [^1Y] \text{ large} \quad (13)$$

In the absence of the primary solute (Eqn. (12)) $\tau_X \cong 30$ ns, but in the scintillator solution this is reduced considerably due to radiationless energy transfer (rate parameter k_{YX}) to the primary solute, molar concentration $[^1Y]$. For toluene solutions at room temperature, $k_{YX} = 5.6 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$,¹⁶ so that for $[^1Y] = 5 \times 10^{-2} \text{ M}$, $\tau_X = 0.36$ ns. An increase in the primary solute concentration $[^1Y]$ thus provides a simple method of reducing τ_X (Eqn. (13)) and hence reducing the $^1X^*$ Stern-Volmer quenching coefficient K_{QX} (cf. Eqn. (5)).

Choice of primary solute

The primary solute ($^1Y^*$) lifetime is

$$\tau_Y = \left(k_{FY} + k_{IY} + k_{ZY} [^1Z] \right)^{-1} \quad (14)$$

where k_{ZY} is the rate parameter of radiationless energy transfer to the secondary solute, molar concentration [1Z]. In the absence of [1Z], the experimental values of τ_Y for various primary solutes, mainly in toluene solution, are as follows:¹⁶

diphenylstilbene	1.1 ns
BBOT	1.1 ns
<i>p</i> -terphenyl	1.2 ns
BBO	1.2 ns
PBD	1.3 ns
butyl PBD	1.3 ns
PPO	1.8 ns
α -NPO	2.0 ns
α -NPD	2.0 ns

The $^1Y^*$ quenching coefficient K_{QY} (Eqn. (5)) can be minimised by the choice of a primary solute with a low fluorescence lifetime τ_Y .

Increased secondary solute concentration

In a typical scintillator, τ_Y is reduced to about 0.5–0.75 of its initial value $(k_{FY} + k_{IY})^{-1}$ by radiationless energy transfer to 1Z . τ_Y and the $^1Y^*$ quenching coefficient K_{QY} can be further reduced by increasing the secondary solute molar concentration [1Z].

Omission of secondary solute

The secondary solute ($^1Z^*$) lifetime is

$$\tau_Z = \left(k_{FZ} + k_{IZ} \right)^{-1} \quad (15)$$

and it is unaffected by energy transfer. τ_Z (POPOP 1.3 ns, dimethyl POPOP 1.5 ns, α -NPO 2.0 ns¹⁶) is longer than τ_X (~ 0.4 ns) or τ_Y (~ 0.7 ns) in a typical liquid scintillator solution. This makes $^1Z^*$ particularly susceptible to impurity quenching. The omission of the secondary solute is the simplest method to eliminate this quenching. This can usually be done without loss in scintillation efficiency, provided there is no appreciable colour quenching present in the solution. Although the omission of 1Z makes the primary solute excitation $^1Y^*$ more vulnerable to quenching because of its increased lifetime in the absence of [1Z] (Eqn. (14)), the elimination of one step in the scintillation process reduces the overall quenching. As noted previously,²⁰ in the absence of colour quenching, secondary solutes are redundant with modern bi-alkali cathode photomultiplier tubes with maximum spectral response at 380 nm wavelength, provided primary solutes like PBD and butyl PBD whose fluorescence emission matches this response are used in association with vials which do not attenuate the scintillation emission.

Chemical treatment of specimen

Kerr *et al*²¹ investigated the quenching of three standard solutions (4 g l⁻¹ PPO and 0.1 g l⁻¹ POPOP in toluene; 7 g l⁻¹ PPO, 0.05 g l⁻¹ POPOP and 50 g l⁻¹ naphthalene in *p*-dioxan; and 8 g l⁻¹ *p*-terphenyl in toluene) by the addition of seventy different organic compounds. They found that aliphatic compounds, as a group, quench less than aromatic compounds. They classified the degree of quenching by aliphatic compounds in terms of functional groups as follows:

Diluters (weak quenchers): R - H, R - F, R - O - R, (RO)₃ PO, R - CN, R - OH, R - COO - R, R - Cl

Mild quenchers: R - COOH, R - NH₂, R - CH = CH - R, R - Br, R - S - R

Strong quenchers: R - SH, R - OCOCO - R, R - CO - R, R - COX, R - NH - R, R - CHO, R₂N - R, R - I, R - NO₂

In the light of subsequent experience,¹⁸ the bromides (R - Br) should be reclassified as strong, rather than mild, quenchers.

Chemical treatment of the specimen prior to its incorporation into the scintillator, aimed at the elimination of functional groups which act as strong quenchers, represents a further approach to the reduction of impurity quenching.

Choice of scintillator solution

Extensive tables¹⁴ and graphs²² have been published comparing the relative scintillation efficiencies of numerous liquid scintillator solutions, under oxygen-free or air-equilibrated conditions. These data are commonly used in the selection of a liquid scintillator. This can be misleading, since liquid scintillators differ in their susceptibility to impurity quenching.

Birks and Poullis²² have studied the quenching of a series of air-equilibrated binary liquid solution scintillators by carbon tetrachloride. Table 1 lists the values of the half-value quencher concentration $[Q]_{0.5}$, the reciprocal of the Stern-Volmer quenching coefficient. A low value of $[Q]_{0.5}$ corresponds to strong quenching and a high value to weak quenching. The solvents and solutes are arranged in horizontal and vertical columns in order of decreasing $[Q]_{0.5}$, i. e. of increasing quenching susceptibility, in Table 1 and there are only minor deviations from the general pattern. The quenching susceptibility of the alkyl benzene solvents increases with increasing molecular weight and with decreasing ionisation potential, a result to be expected theoretically. *p*-Dioxan containing 100 g l⁻¹ naphthalene is more resistant to quenching than any of the solvents except benzene. In all solvents, PBD is the solute most resistant to quenching. Butyl PBD, PBO and BBOT have a reasonable quenching resistance, but PPO, BIBUQ and *p*-terphenyl are rather strongly quenched.

The data are presented in a different form in Table 2, which lists the relative scintillation pulse heights of the solutions in the absence (V_0) and presence (V_Q , V'_Q) of 0.1 M carbon tetrachloride. V_0 and V_Q are expressed relative to $V_0 = 100$ for 10 g l⁻¹ PBD in toluene. V'_Q is the value of V_Q normalised to $V'_Q = 100$ for 10 g l⁻¹ PBD in toluene. The relative orders of merit of the values of V_0 and V'_Q are shown in parentheses in the V_0 and V'_Q columns, respectively, in Table 2.

The addition of the quencher produces some dramatic changes in the order of merit. The BIBUQ solutions in *p*-xylene and toluene drop from (1)= to (16) and (17), respectively. The BIBUQ solutions in *p*-dioxan and benzene slip from (9) and (12)=, respectively, to (19)=. Clearly BIBUQ is very susceptible to CCl₄ quenching. On

Table 1. Binary solutions. Quenching by carbon tetrachloride. Half-value quencher concentration $[Q]_{0.5}$ in units of 10^{-2} M.²²

Solute conc (g l ⁻¹)	Solute	Solvent					
		Benzene	<i>p</i> -Dioxan ^a	Toluene	Xylene	<i>p</i> -Xylene	Mesitylene
10	PBD	8.17	6.44	5.79	5.06	4.83	4.50
10	butyl PBD	6.31	6.03	4.66	4.60	4.22	3.98
8	PBO	6.12	5.25	4.50	3.71	3.51	3.42
8	BBOT	5.64	7.23	3.82	3.56	3.17	3.09
6	PPO	3.96	3.25	2.78	2.64	2.72	2.44
15	BIBUQ	2.98	2.85	2.24	2.19	2.46	1.93
5	TP	2.74	—	2.22	2.12	1.91	1.97

^aPlus 100 g l⁻¹ naphthalene.

the other hand, the benzene solutions of PBD, butyl PBD and PBO climb from (15)=, (10)=, and (15)= to (2), (4)= and (7), respectively. Benzene is relatively immune to CCl₄ quenching. All the *p*-dioxan/100 g l⁻¹ naphthalene solutions, except that containing BIBUQ, improve their relative positions, showing the quench resistance of this solvent. The toluene solution of PBD, which improves from (3) to (1), is the most efficient scintillator in the presence of 0.1 M carbon tetrachloride.

The results show that impurity quenching can be minimised by the proper choice of scintillator solution. Although the numerical data refer only to carbon tetrachloride (Table 1) and to a particular quencher concentration (Table 2), the results are of more general application. The quenching susceptibility of an excited solvent or solute molecule to *any quencher* depends on its inherent molecular properties (singlet excitation energy and lifetime, ionisation potential, electron affinity). It is therefore proposed that the *order* of decreasing quench resistance to CCl₄ quenching of the solvents and solutes listed in Table 1 applies also to other quenchers. Table 1, together with the data on V_0 ,²² the relative scintillation efficiency of the unquenched solution, thus provides a general guide to the choice of quench-resistant scintillator solutions. Benzene, *p*-dioxan/100 g l⁻¹ naphthalene, and toluene are the best quench-resistant solvents, and PBD, butyl PBD, and PBO are the best quench-resistant solutes, of the materials considered. Similar studies using other quenchers are required to test the general validity of the order of quench resistance shown in Table 1, and provide further numerical data on impurity quenching.

Micellar scintillators

A further method of reducing impurity quenching is to separate the radioactive specimen and its associated quenching component Q from the liquid scintillator solution (¹X, ¹Y, ¹Z) by the use of a micellar scintillator. Ewer and Harding²³ have developed such a micellar scintillator (available as NE 260 from Nuclear Enterprises, Ltd.) which segregates proteins, nucleotides, salts and sugars from the xylene-based liquid scintillator solution. If there is complete segregation of Q from the liquid

scintillator, the impurity quenching should be eliminated, although the micelle walls absorb some of the β -particle energy and thus reduce the scintillation efficiency to some extent.

CONCLUSION

Impurity quenching in liquid scintillators can be minimised by (i) removal of dissolved oxygen, (ii) reduction of the specimen concentration, (iii) reduction of the diffusion coefficient by the use of a viscous solvent or emulsion, (iv) increase in the primary solute concentration, (v) choice of the primary solute, (vi) increase in the secondary solute concentration, (vii) omission of the secondary solute, (viii) chemical treatment of the specimen, (ix) choice of the scintillator solution (solvent and solute) and (x) the use of miscellar scintillators.

The purpose of internal liquid scintillation counting is to obtain an accurate radioassay of the specimen. The raw data available for this purpose are the photomultiplier pulses generated by the scintillator photons. The subsequent stages of data processing,

Table 2. Liquid scintillators. Relative pulse heights in the absence (V_0) and presence (V_Q , V'_Q) of 0.1 M carbon tetrachloride.^{12,22}

Solute	Solvent	V_0	V_Q	V'_Q
10 g l ⁻¹ PBD	toluene	100 (3)	37	100 (1)
10 g l ⁻¹ PBD	benzene	77 (15)=	35	95 (2)
10 g l ⁻¹ butyl PBD	toluene	99 (4)=	31.5	86 (3)
10 g l ⁻¹ PBD	<i>p</i> -xylene	96 (8)	31	84 (4)=
10 g l ⁻¹ butyl PBD	benzene	80 (10)=	31	84 (4)=
8 g l ⁻¹ PBO	toluene	98 (6)	30	82 (6)
8 g l ⁻¹ PBO	benzene	77 (15)=	29.5	81 (7)
10 g l ⁻¹ butyl PBD	<i>p</i> -xylene	97 (7)	29	79 (8)
8 g l ⁻¹ BBOT	<i>p</i> -dioxan ^a	67 (21)	28	77 (9)
8 g l ⁻¹ PBO	<i>p</i> -dioxan ^a	80 (10)=	27.5	75 (10)
10 g l ⁻¹ butyl PBD	<i>p</i> -dioxan ^a	72 (18)=	27	74 (11)=
10 g l ⁻¹ PBD	<i>p</i> -dioxan ^a	70 (20)	27	74 (11)=
8 g l ⁻¹ PBO	<i>p</i> -xylene	99 (4)=	25.5	70 (13)
8 g l ⁻¹ BBOT	toluene	79 (12)=	22	60 (14)=
8 g l ⁻¹ BBOT	benzene	61 (24)	22	60 (14)=
15 g l ⁻¹ BIBUQ	<i>p</i> -xylene	103 (1)=	20.5	56 (16)
8 g l ⁻¹ BBOT	<i>p</i> -xylene	79 (12)=	18.5	51 (17)=
15 g l ⁻¹ BIBUQ	toluene	103 (1)=	18.5	51 (17)=
15 g l ⁻¹ BIBUQ	benzene	79 (12)=	18	49 (19)=
15 g l ⁻¹ BIBUQ	<i>p</i> -dioxan ^a	82 (9)	18	49 (19)=
6 g l ⁻¹ PPO	benzene	58 (26)	16	44 (21)=
6 g l ⁻¹ PPO	<i>p</i> -xylene	76 (17)	16	44 (21)=
6 g l ⁻¹ PPO	toluene	72 (18)=	16	44 (21)=
6 g l ⁻¹ PPO	<i>p</i> -dioxan ^a	59 (25)	13	35 (24)
5 g l ⁻¹ TP	toluene	65 (22)	11.5	32 (25)
5 g l ⁻¹ TP	benzene	52 (27)	11	30 (26)
5 g l ⁻¹ TP	<i>p</i> -xylene	64 (23)	10	28 (27)

^aPlus 100 g l⁻¹ naphthalene.

however sophisticated, cannot improve, they may even degrade, these data. The source of the data, the scintillator, is the most critical component of the system and it is the only one under the full control of the experimenter.

Quench reduction is always preferable to quench correction. Quench reduction improves the quality of the data. Quench correction accepts inferior data and attempts by various approximate methods to normalise them to unquenched conditions. The methods proposed in this paper should enable impurity quenching to be reduced to a sufficiently low level that quench correction methods can be applied more reliably to obtain an accurate radio-assay.

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DISCUSSION

A. Dyer: You have drawn our attention to the effective choice of quenched and unquenched cocktails. The quenching agent you have used is carbon tetrachloride. Have you continued this work to determine the relative effect of quenchers of a different chemical type – such as acetone, for example?

J. B. Birks: No — but I am sure that a different quencher would produce the same order of ranking as that seen for carbon tetrachloride.