

Chapter 1

Liquid Scintillators

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INTRODUCTION

Liquid scintillation counting is widely used for the radioassay of biological and other materials labelled with carbon-14, tritium or other radioisotopes. Since the discovery¹ of liquid organic solution scintillators in 1949, many combinations of solvents and solutes have been tested, and a great variety of scintillator 'cocktail' recipes have been prescribed and used. Many of these liquid scintillator solutions do not have optimum performance, although they may be adequate and economical for some applications.

The main criterion (apart from price) used in the comparison of different scintillator solutions is the *relative pulse height* (RPH) which depends on the following factors:

1. *the nature and purity of the solvent.* (These determine the solvent fluorescence lifetime and spectrum and its scintillation yield (G-value) of excited solvent molecules/100 eV of energy expended by the ionizing particle);
2. *the nature of the primary solute.* (This determines its fluorescence quantum efficiency, lifetime and spectrum);
3. *the absorption spectrum and concentration of the primary solute.* (These determine the quantum efficiency of solvent-solute energy transfer);
4. *the nature and concentration of any secondary solute.* (These determine the secondary solute absorption and fluorescence spectra and its fluorescence quantum efficiency and lifetime);
5. *the nature and energy of the ionizing radiation.* (For β -particles or Compton electrons of energy $E > 100$ keV, the RPH is proportional to E , but for lower energy electrons and for protons, α -particles and other heavy ionizing particles, the scintillation efficiency is reduced);
6. *the concentration of dissolved oxygen in the solution, which depends on the temperature and the external atmospheric pressure.* (This determines the degree of oxygen quenching of the solvent and solute molecules at a given temperature);
7. *the form and concentration in which the radioactive specimen is introduced into the solution.* (These determine the magnitude of the impurity (chemical) quenching and of any colour quenching);
8. *the size and shape of the scintillator vial.* (This determines the optical path length for

- radiative transfer from the primary to the secondary solute and for any colour quenching attenuation of the RPH);
9. *the material of the vial.* (This determines its transmission spectrum for the scintillation emission);
 10. *the nature of the reflector and light collection system.* (This determines the fraction of the scintillation emission incident on the photomultiplier cathode, which is a function of the scintillator emission spectrum); and
 11. *the spectral response of the photomultiplier cathode.* (This converts the scintillation photons into electrons, which are accelerated and multiplied in the dynode system, yielding anode pulses which are fed to amplifiers, discriminators, channel analysers, scalars, etc. and are ultimately recorded as counts).

PREVIOUS STUDIES

The original studies of liquid scintillators, which led to the adoption of *p*-terphenyl (TP), the oxazoles (e.g. PPO), the oxadiazoles (e.g. PBD) and the substituted *p*-quaterphenyls (e.g. BIBUQ) as primary solutes, and the choice of toluene, *p*-xylene and *p*-dioxan containing 100 g/l naphthalene as standard solvents, have been described by Birks.²

The Los Alamos group, who were responsible for many of these developments, adopted a standard technique for comparing the RPH of different scintillator solutions.³ The 1 ml solution specimen was contained in a quartz cell, the base of which was optically coupled to the photomultiplier window, and it was excited externally by 624 keV internal conversion electrons from caesium-137. The light was collected by a hemispherical aluminium reflector (aluminium has a higher reflectivity than titanium dioxide paint in the near ultraviolet), and it was observed by a DuMont 6292 photomultiplier, chosen to have an 'average' S11 spectral response, with peak sensitivity at about 440 nm wavelength. Air-equilibrated toluene was used as the standard solvent. Due to the high altitude (6000 ft = 1830 m) and consequent reduced atmospheric pressure, the average Los Alamos oxygen quenching factor of 18% is less than the corresponding factor at sea level and normal atmospheric pressure. The RPH of an 8 g/l TP solution in toluene (= the RPH of a 3 g/l PPO solution in toluene = 100) was adopted as a reference standard. The RPH of each solution was measured as a function of concentration, and the maximum RPH recorded at the optimum solute concentration c_0 , or at the maximum solubility c_s , if $c_s < c_0$.

In 1955 the Los Alamos group⁴ reported the RPH, c_0 (or c_s) and mean emission wavelength $\bar{\lambda}$ for 102 compounds in toluene solution. They found 60 primary solutes, all except six of which are oxazole or oxadiazole derivatives, with RPH ≥ 75 and 27 with RPH ≥ 100 . The best primary solutes included PBD, PBO, PPO and TP.

The Los Alamos group³ also compared the RPH of 49 carefully purified, but air-equilibrated, solvents each containing 3 g/l PPO. The best solvents were *p*-xylene, isopropyl biphenyl, *m*-xylene, phenylcyclohexane and toluene. *p*-Dioxan is a further useful solvent for internal liquid scintillation counting, since it has a high solubility for many materials and it is completely miscible with water. Its efficiency as a scintillator is considerably enhanced by adding up to 100 g/l naphthalene, which functions as a secondary solvent, and increases the solvent-solute energy transfer efficiency.

The Los Alamos group⁵ also compared a number of secondary solutes, using the standard conditions described above, except that a titanium dioxide reflector was used as an alternative to the aluminium reflector, to provide a better indication of large volume scintillator performance. The best secondary solutes included POPOP, BBO, PBO and

α -NPO.

The energy transfer from the primary to the secondary solute is primarily radiative,⁶ unlike the solvent-solute transfer which is due to solvent excitation migration and diffusion and which is non-radiative. The increase (or decrease) in RPH on adding a secondary solute to a binary solution depends critically on the following spectral factors:

1. the primary solute emission spectrum;
2. the solution volume (the radiative transfer efficiency increases with optical path length);
3. the secondary solute absorption spectrum and concentration (at higher concentrations non-radiative transfer may become significant);
4. the transmission spectrum of the vial (which limits the fraction of primary solute emission detected);
5. the reflection spectrum of the reflector and light collection system; and
6. the spectral response of the photomultiplier.

The function of a secondary solute is to optimize the match between the scintillator emission and the photomultiplier spectral response. Due to the several factors involved, the RPH values for solutions containing secondary solutes are sensitive to the experimental conditions.

THE NEED FOR A NEW LIQUID SCINTILLATOR SURVEY

The pioneer studies described above have provided a reasonable basis for the choice of liquid scintillator solutions, although later recipes have sometimes been introduced on the basis of RPH measurements made under less precise experimental conditions. Nevertheless, the measurements suffer from several defects when they are applied to modern liquid scintillation counting practice:

1. the current quartz-windowed alkali photocathode tubes have a spectral response (peak at about 380 nm) which differs markedly from that of the earlier tubes (peak at about 440 nm);
2. the early measurements were made with external radiation sources, while in the internal counting technique the source is incorporated into the scintillator;
3. the light collection geometries used in the early studies differ markedly from those used in modern instruments;
4. the extensive Los Alamos data were obtained in high altitude conditions of reduced oxygen concentration. The solute oxygen quenching factor depends on the solvent viscosity, the solute fluorescence lifetime, and the oxygen concentration, and it is not independent of the solvent and solute as assumed by the Los Alamos group. Hence, the order of merit of air-equilibrated specimens at sea level is not necessarily the same as at higher altitudes;
5. several new compounds have come into use, usually backed by commercial claims of superiority over existing materials;
6. the early measurements were made with single photomultipliers, while current liquid counting instruments usually employ two photomultipliers operating in coincidence to reduce background noise.
7. many of the early measurements involved integration of the scintillation intensity or pulse, so that both the prompt and delayed scintillation components contributed to the RPH. In the Philips instrument the coincidence resolving time is 10 ns, so that only the prompt component contributes to the RPH. In other instruments, which employ slower

photomultipliers, the coincidence resolving time is considerably increased, so that the delayed scintillation component may then contribute to the RPH.

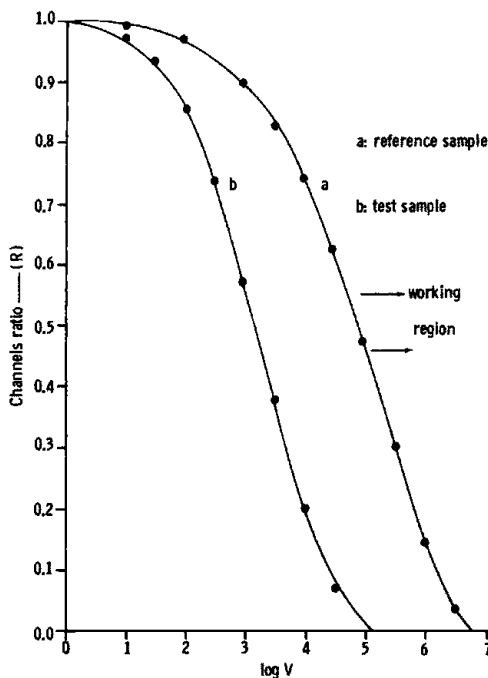


Fig. 1. Ratio R of count rates in channels 1 and 2 as a function of $\log V$.

EXPERIMENTAL METHOD

For all these reasons it was considered desirable to measure the RPH of a wide range of scintillator solutions under conditions which correspond closely to those used for current internal liquid scintillation counting. The measurements were made with a Philips automatic liquid scintillation analyser, which utilizes two 56 DUVP photomultipliers (quartz window, bialkali cathode) operating in coincidence (resolving time 10 ns). The measurements were made on air-equilibrated solutions at ambient temperature (about 20°C) and normal atmospheric pressure (about 760 torr). The specimens were contained in standard 20 ml vials, made of low potassium content glass, which give a low background of < 20 c.p.m. A small quantity of ¹⁴C-labelled hexadecane (which is a non-quencher) was added to each solvent to provide an internal source of carbon-14 β-rays of about 20000 d.p.m.

The RPH was determined from the integral pulse height spectrum, using a channels ratio method to determine the latter. This method has the advantage of being independent of the carbon-14 activity. Channels 1 and 2 were initially set to accept all counts above noise and background, and gave equal count rates. A variable discriminator was used to set the minimum height V of pulses recorded in channel 2, and the ratio R of the count rates in channels 2 and 1 was measured as a function of $\log V$ (Fig. 1). The RPH was taken to be proportional to the value of V ($= V_{0.5}$) at which $R = 0.5$. The curve of R against $\log V$ is

linear in the region of $R = 0.5$, so that $V_{0.5}$ can be evaluated by interpolation between observations of $\log V$ at R above and below 0.5. The logarithmic discriminator error was $< 2\%$, and the probable statistical error was about 1%. The RPH is expressed relative to that of a 3 g/l solution of PPO in toluene (= 100), the same reference standard as the Los Alamos group.

MATERIALS

The solvents were:

- (i) benzene
- (ii) toluene
- (iii) xylene
- (iv) *p*-xylene
- (v) mesitylene, and
- (vi) *p*-dioxan containing 100 g/l naphthalene,

and were supplied by Koch-Light Laboratories Ltd. The mesitylene was passed through an alumina chromatographic column and fractionally distilled and the middle fraction was collected. The other solvents were used without further purification.

The primary solutes were:

- (i) TP (*p*-terphenyl)
- (ii) PPO (2,5-diphenyloxazole)
- (iii) BBOT (2,5-bis(5'-*tert*-butyl-2'-benzoxazolyl)-thiophene)
- (iv) PBO (5-phenyl, 2-(4-biphenyl)-oxazole)
- (v) butyl-PBD (2(4'-*tert*-butylphenyl),5-(4''-biphenyl)-1,3,4-oxadiazole)
- (vi) PBD (2-phenyl, 5-(4-biphenyl)-1,3,4-oxadiazole)
- (vii) BIBUQ (4,4-bis(2-butyloctyloxy-*p*-quaterphenyl)),

and were supplied by Koch-Light Laboratories Ltd. and used without further purification.

The secondary solutes were:

- (i) PBBO (2-(4-biphenyl)-6-phenylbenzoxazole)
- (ii) POPOP (1,4-bis-[2-(5-phenyloxazolyl)]-benzene)
- (iii) dimethyl POPOP (1,4-bis-[2-(4-methyl-5-phenyloxazolyl)]-benzene)
- (iv) BBO (2,5-di-(4-biphenyl)-oxazole)
- (v) bis-MSB (*p*-bis-(*o*-methylstyryl)-benzene),

supplied by Koch-Light Laboratories Ltd., and

- (vi) α -NPO (2-(1-naphthyl), 5-phenyl-oxazole)
- (vii) DPH (1,6-diphenylhexa-1,3,5-triene)

supplied by Nuclear Enterprises Ltd., and they were used without further purification.

For the quenching studies carbon tetrachloride supplied by Eastman-Kodak Co. was used without further purification.

BINARY SOLUTIONS

Measurements of RPH against primary solute concentration (g/l), were made for binary solutions in benzene, toluene, xylene, *p*-xylene, mesitylene and *p*-dioxan containing 100 g/l naphthalene, of the following primary solutes: TP (this solute gives negligible RPH in the *p*-dioxan/naphthalene solvent because of the absence of solvent-solute energy

transfer) (Fig. 2), PPO (Fig. 3), BBOT (Fig. 4), PBO (Fig. 5), butyl-PBD (Fig. 6), PBD (Fig. 7), and BIBUQ (Fig. 8).

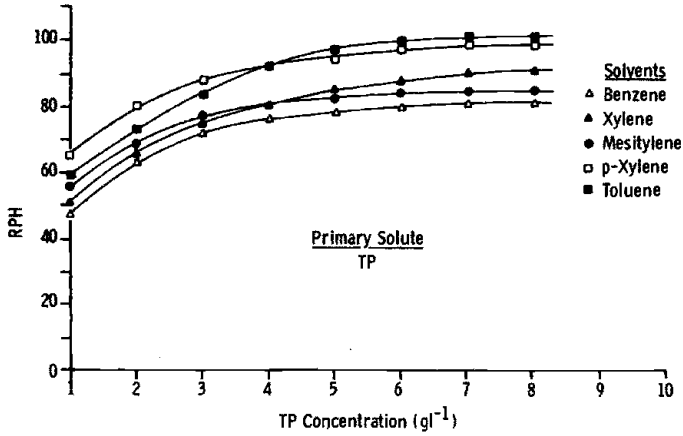


Fig. 2.

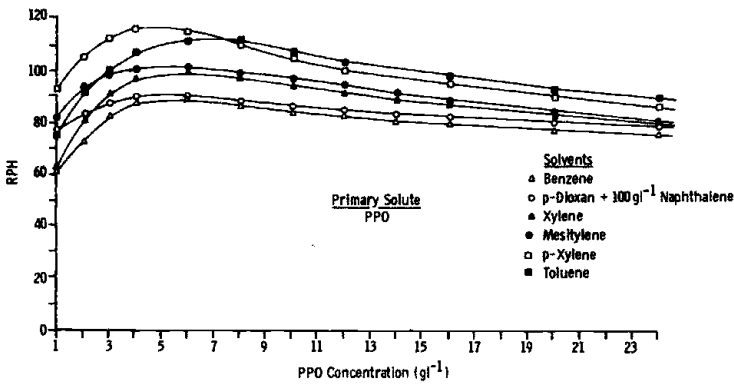


Fig. 3.

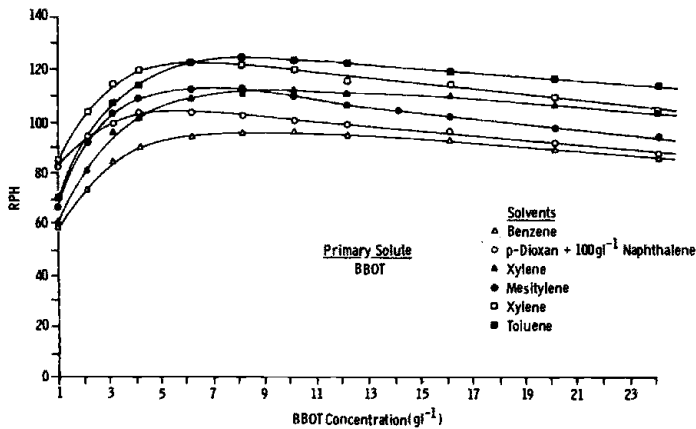


Fig. 4.

Liquid Scintillators

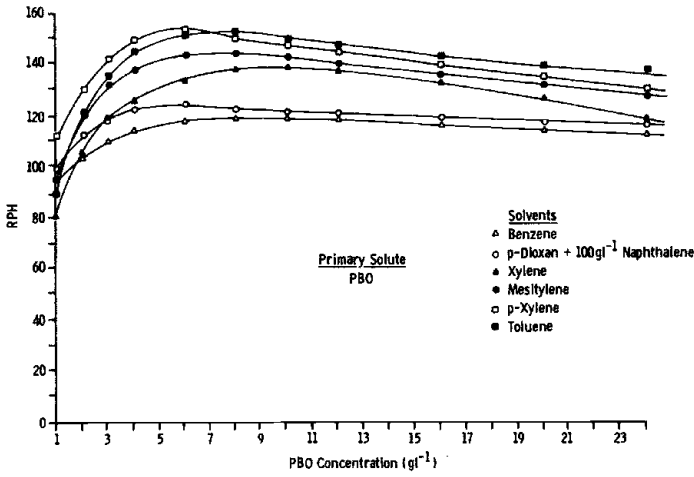


Fig. 5.

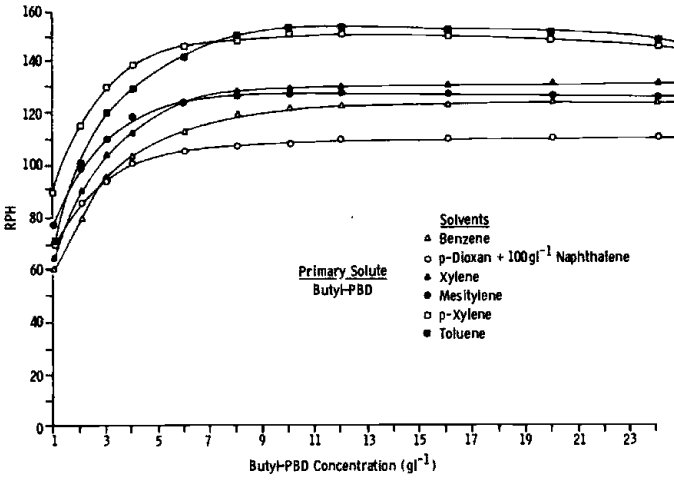


Fig. 6.

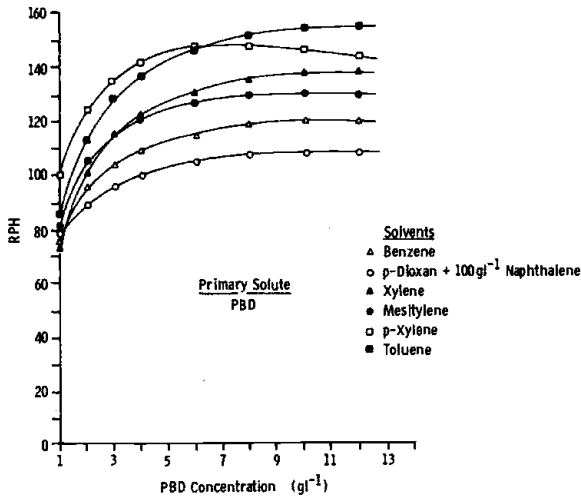


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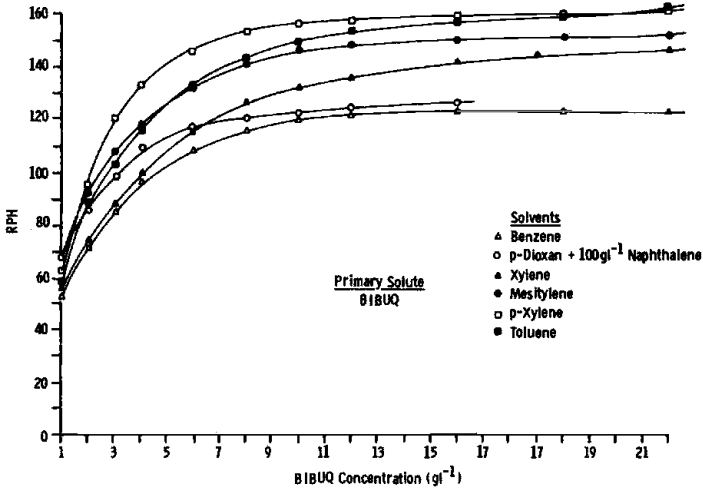


Fig. 8.

Table 1. Binary solutions – maximum RPH and optimum concentration c_0 (g/l).

Solute	Solvent											
	Benzene		Toluene		Xylene		<i>p</i> -Xylene		Mesitylene		<i>p</i> -Dioxan + 100 g/l naphthalene	
	RPH	c_0	RPH	c_0	RPH	c_0	RPH	c_0	RPH	c_0	RPH	c_0
TP	81	8	101	7	91	8	99	8	86	8	—	—
PPO	90	5.5	112	7	100	6	117	5	102	5.5	91	5
BBOT	95	8	123	8	111	10	122	6	112	6	104	6
PBO	120	9	152	7.5	139	10	153	6	144	8	124	6
Butyl-PBD	124	20	153	12	131	20	150	12	128	12	111	24
PBD	120	11	155	12	139	12	148	7	130	11	108	10
BIBUQ	123	16	160	24	147	24	160	20	152	20	127	16

The values of the maximum RPH and optimum concentration c_0 (g/l) for each of the binary solution systems are listed in Table 1.

The susceptibility of the various binary solutions to impurity quenching was compared using carbon tetrachloride as quencher. The addition of a molar concentration [M] of quencher reduces the RPH from V_0 (when [M] = 0) to V , where V is given by the Stern–Volmer relation:

$$V_0/V = 1 + [M]/[M]_{0.5} \tag{1}$$

and $[M]_{0.5}$ is the half-value quencher molar concentration at which $V = 0.5V_0$. Graphs of V_0/V against the carbon tetrachloride molar concentration [M] are presented for binary solutions in benzene, toluene, xylene, *p*-xylene, mesitylene and *p*-dioxan containing 100 g/l naphthalene, of the following primary solutes: 5 g/l TP (excluding the *p*-dioxan/naphthalene solvent) (Fig. 9), 6 g/l PPO (Fig. 10), 8 g/l BBOT (Fig. 11), 8 g/l PBO (Fig. 12), 10 g/l butyl-PBD (Fig. 13), 10 g/l PBD (Fig. 14) and 15 g/l BIBUQ (Fig. 15).

Liquid Scintillators

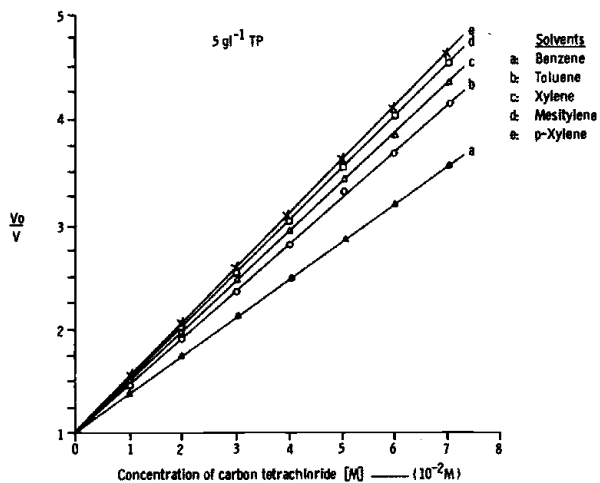


Fig. 9.

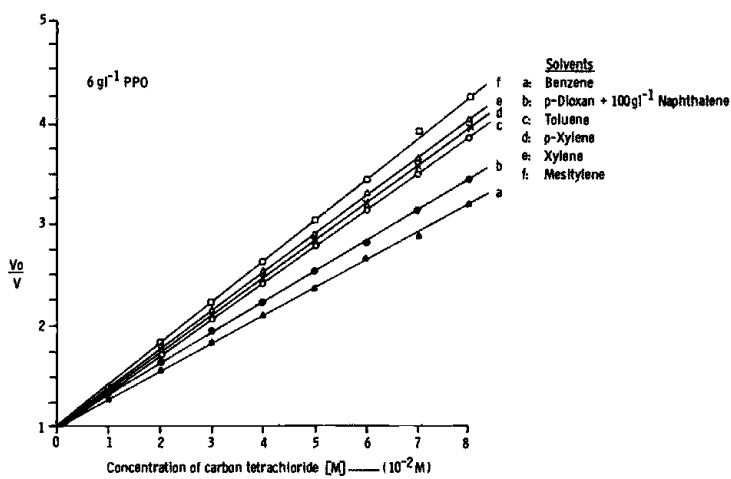


Fig. 10.

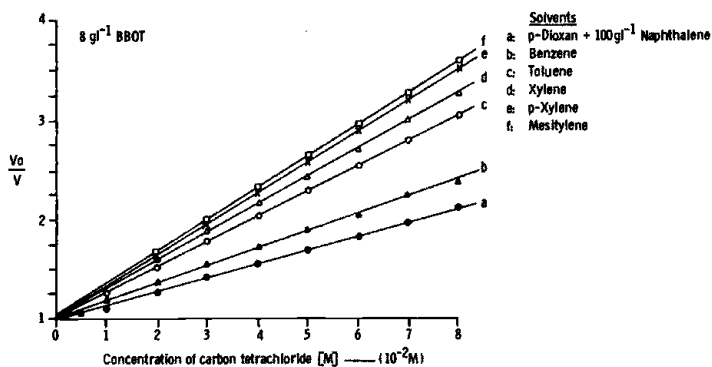


Fig. 11.

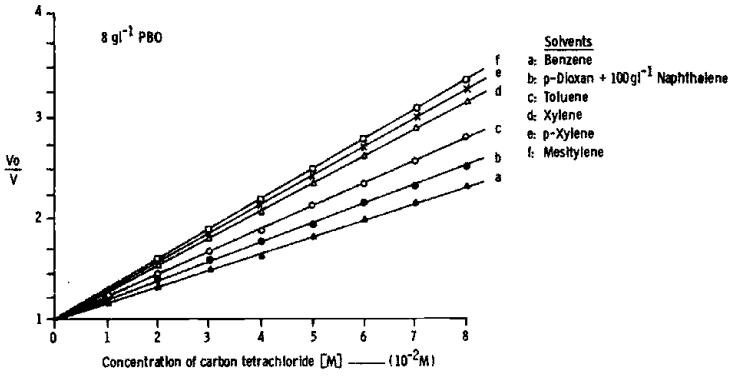


Fig. 12.

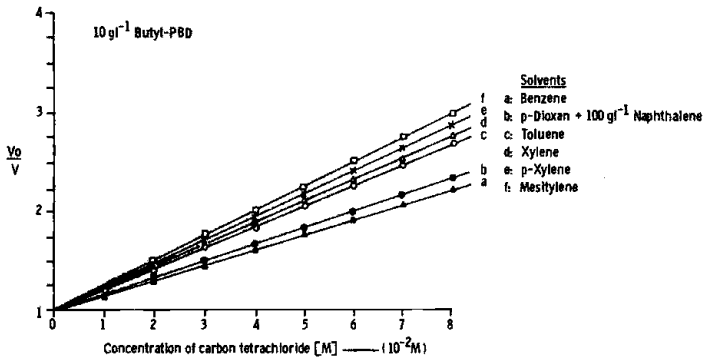


Fig. 13.

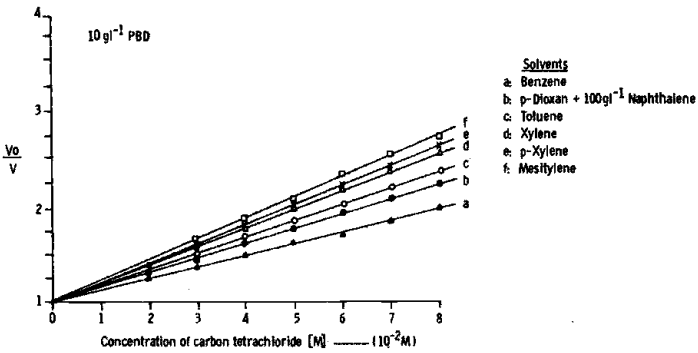


Fig. 14.

Liquid Scintillators

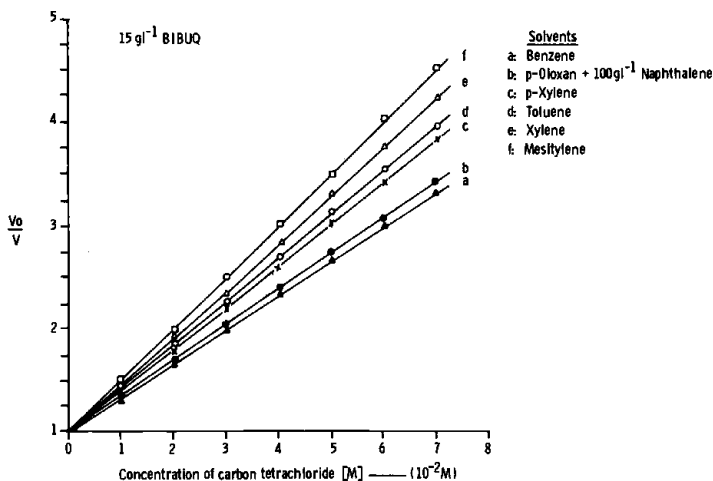


Fig. 15.

Table 2. Binary solutions – quenching by carbon tetrachloride. Half-value quencher concentration $[M]_{0.5}$ (units: 10^{-2} M).

Solute concentration	Solute	Solvent					<i>p</i> -Dioxan + 100 g/l naphthalene
		Benzene	Toluene	Xylene	<i>p</i> -Xylene	Mesitylene	
5 g/l	TP	2.74	2.22	2.12	1.91	1.97	—
6 g/l	PPO	3.96	2.78	2.64	2.72	2.44	3.25
8 g/l	BBOT	5.64	3.82	3.56	3.17	3.09	7.23
8 g/l	PBO	6.12	4.50	3.71	3.51	3.42	5.25
10 g/l	Butyl-PBD	6.31	4.66	4.60	4.22	3.98	6.03
10 g/l	PBD	8.17	5.79	5.06	4.83	4.50	6.44
15 g/l	BIBUQ	2.98	2.24	2.19	2.46	1.93	2.85

Linear Stern–Volmer plots of V_0/V against $[M]$, consistent with Eqn. (1), are observed in all cases. The values of $[M]_{0.5}$, the half-value quencher molar concentration, are listed in Table 2.

TERNARY SOLUTIONS

The influence of secondary solutes on representative binary solutions was studied. Measurements of RPH against secondary solute concentration (g/l, plotted on a logarithmic scale) were made for the addition of DPH, α -NPO, dimethyl POPOP, BBO, POPOP, bis-MSB, and (in some cases) PBBO, to the following binary solutions: 4 g/l TP in benzene (Fig. 16), 4 g/l TP in toluene (Fig. 17), 4 g/l TP in xylene (Fig. 18), 4 g/l TP in *p*-xylene (Fig. 19), 4 g/l PPO in benzene (Fig. 20), 4 g/l PPO in toluene (Fig. 21), 4 g/l PPO in xylene (Fig. 22), 4 g/l PPO in *p*-xylene (Fig. 23), 5 g/l butyl-PBD in benzene (Fig. 24), 5 g/l butyl-PBD in toluene (Fig. 25), 5 g/l butyl-PBD in xylene (Fig. 26), 5 g/l butyl-PBD in *p*-xylene (Fig. 27).

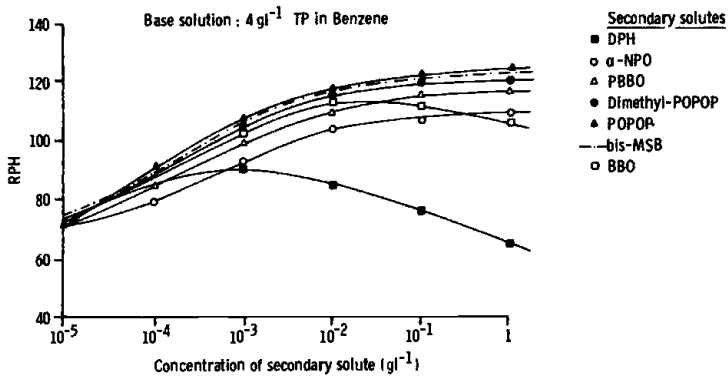


Fig. 16.

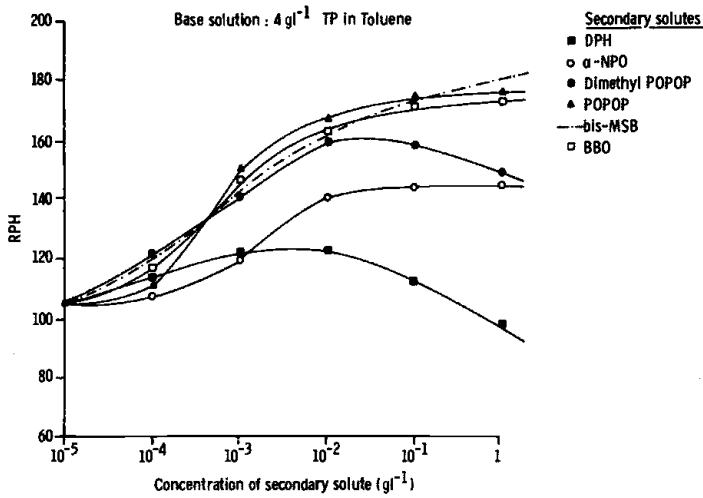


Fig. 17.

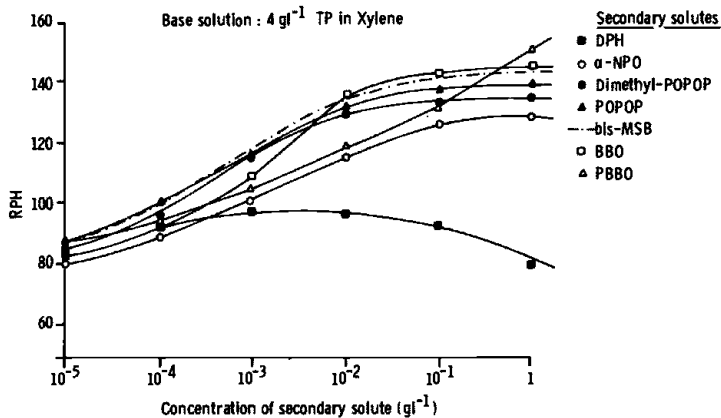


Fig. 18.

Liquid Scintillators

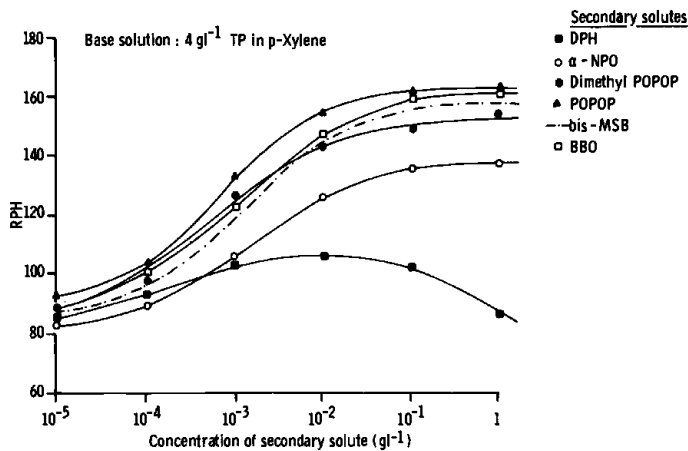


Fig. 19.

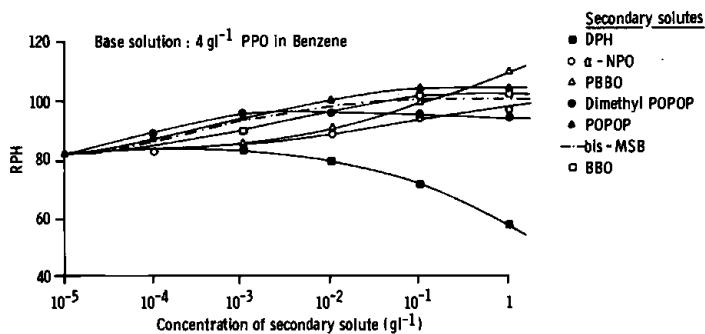


Fig. 20.

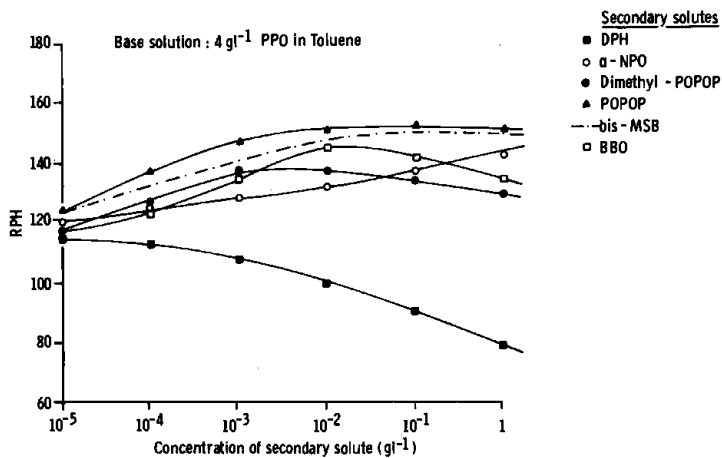


Fig. 21.

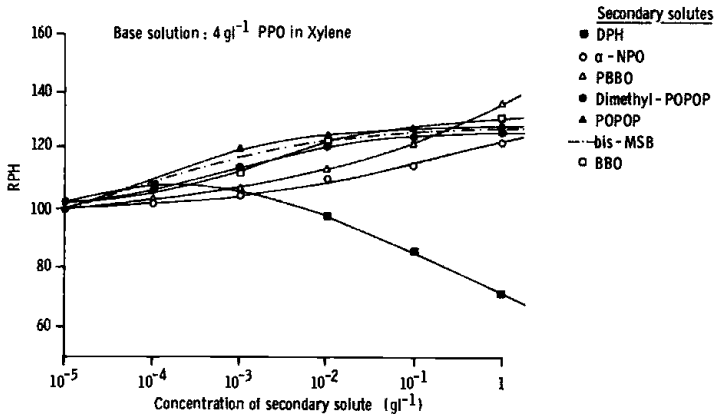


Fig. 22.

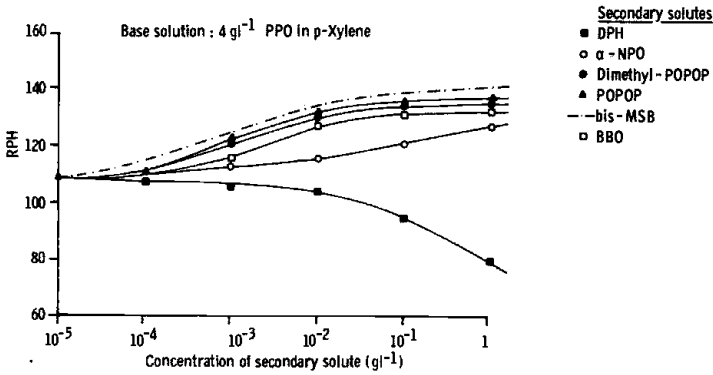


Fig. 23.

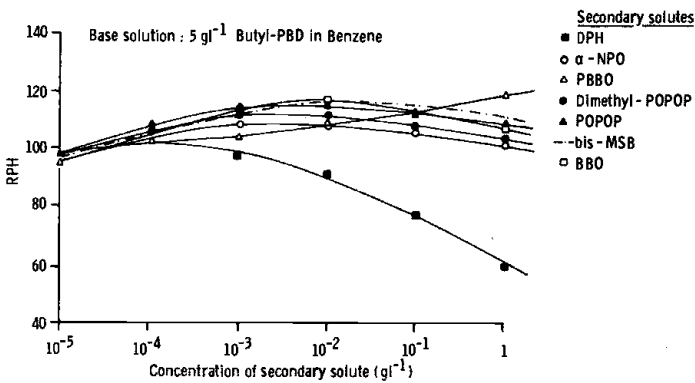


Fig. 24.

Liquid Scintillators

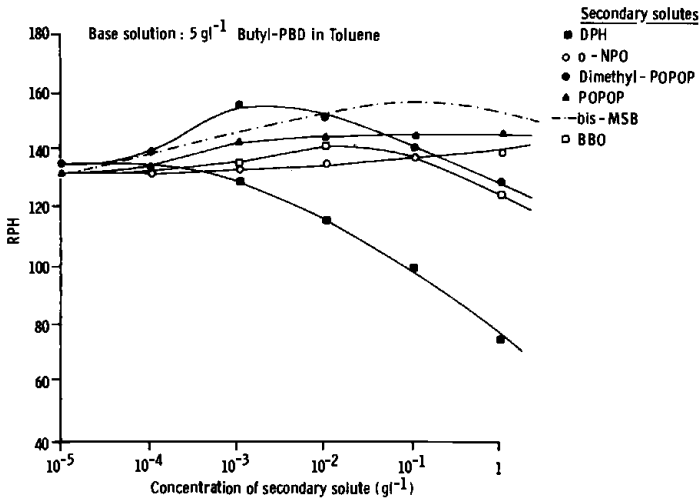


Fig. 25.

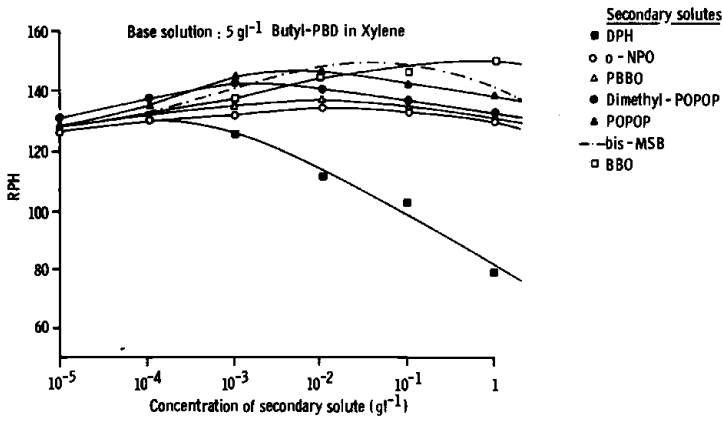


Fig. 26.

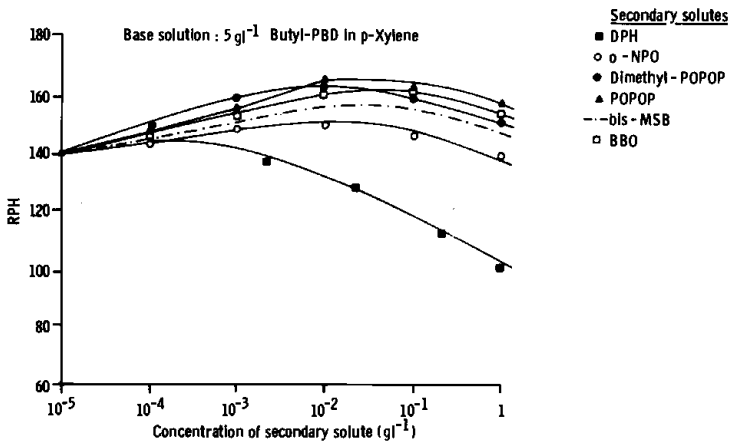


Fig. 27.

Table 3. Ternary solutions containing 4 g/l TP – maximum RPH and optimum secondary solute concentration c_0 (g/l).

Secondary solute	Solvent							
	Benzene		Toluene		Xylene		<i>p</i> -Xylene	
	RPH	c_0	RPH	c_0	RPH	c_0	RPH	c_0
DPH	91	10^{-3}	124	3×10^{-3}	101	3×10^{-3}	106	10^{-2}
α -NPO	110	1	145	1	130	1	137	1
BBO	115	2×10^{-2}	173	1	143	1	161	1
bis-MSB	120	0.2	184	1	141	0.1	155	1
dimethyl POPOP	121	1	161	2×10^{-2}	134	1	154	1
POPOP	125	1	175	1	140	1	163	1
PBBO	117	1	–	–	153	1	–	–

Table 4. Ternary solutions containing 4 g/l PPO – maximum RPH and optimum secondary solute concentration c_0 (g/l).

Secondary solute	Solvent							
	Benzene		Toluene		Xylene		<i>p</i> -Xylene	
	RPH	c_0	RPH	c_0	RPH	c_0	RPH	c_0
DPH	84	10^{-4}	115	10^{-5}	108	10^{-5}	108	10^{-5}
α -NPO	97	1	142	1	123	1	128	1
BBO	102	1	147	2×10^{-2}	128	1	132	1
bis-MSB	101	1	150	0.2	130	1	141	1
dimethyl POPOP	97	3×10^{-3}	138	10^{-3}	124	1	135	1
POPOP	105	0.2	153	0.1	129	1	138	1
PBBO	110	1	–	–	137	1	–	–

Table 5. Ternary solutions containing 5 g/l butyl-PBD – maximum RPH and optimum secondary solute concentration c_0 (g/l).

Secondary solute	Solvent							
	Benzene		Toluene		Xylene		<i>p</i> -Xylene	
	RPH	c_0	RPH	c_0	RPH	c_0	RPH	c_0
DPH	102	10^{-4}	134	5×10^{-5}	130	10^{-5}	144	10^{-4}
α -NPO	108	2×10^{-3}	139	1	134	2×10^{-2}	149	10^{-2}
BBO	118	10^{-2}	142	10^{-2}	150	1	161	7×10^{-2}
bis-MSB	117	0.1	156	0.1	147	5×10^{-2}	156	2×10^{-2}
dimethyl POPOP	111	5×10^{-3}	155	10^{-3}	142	2×10^{-3}	163	10^{-2}
POPOP	115	10^{-2}	146	1	146	5×10^{-3}	165	10^{-2}
PBBO	119	1	–	–	136	2×10^{-2}	–	–

The values of maximum RPH and optimum secondary solute concentration c_0 for each of the ternary solution systems are listed in Tables 3, 4 and 5.

DISCUSSION

The RPH depends on the *solvent* (Table 1). For all the solutes, the lowest values of RPH are for solutions in benzene and in *p*-dioxan + 100 g/l naphthalene, intermediate values of RPH are obtained for solutions in mesitylene and in xylene, and the highest values of RPH are for solutions in toluene and in *p*-xylene. The preferred solvents, in the absence of quenching, are thus toluene and *p*-xylene.

The RPH depends on the *primary solute* (Table 1). In all the solvents the TP solutions have the lowest RPH. (This is due to the low transmission coefficient of the glass vial for the TP emission. The RPH of the TP solutions is increased considerably if a polyethylene or quartz vial is used). The PPO solutions have the next lowest RPH, followed by the BBOT solutions. The PBO, PBD and butyl-PBD solutions have similar high RPH values in all the solvents, but the optimum concentration c_0 is higher for butyl-PBD than for the other solutes. Under the conditions of measurement BIBUQ is the best primary solute. The preferred binary solutions with the maximum RPH, in the absence of quenching, are:

- (A) 24 g/l BIBUQ in toluene (RPH = 160)
- (B) 20 g/l BIBUQ in *p*-xylene (RPH = 160)

The susceptibility to impurity quenching, which is proportional to $1/[M]_{0.5}$ (Table 2), depends on the *solvent*. The least susceptible solvents are benzene and *p*-dioxan + 100 g/l naphthalene; those of intermediate susceptibility are toluene and xylene; and those most liable to quenching are *p*-xylene and mesitylene. *Toluene* is therefore to be preferred to *p*-xylene under quenching conditions. Under such conditions the relative insensitivity of benzene and *p*-dioxan/naphthalene solutions to quenching may be sufficient to compensate for their lower 'unquenched' RPH.

The susceptibility to impurity quenching depends on the *primary solute* (Table 2). In each of the alkyl benzene solvents the susceptibility to quenching increases in the order PBD, butyl-PBD, PBO, BBOT, PPO, BIBUQ and TP. BIBUQ and TP are 2 to 3 times more prone to quenching than PBD, butyl-PBD and PBO. Hence, in the presence of quenching, the preferred binary solutions with maximum RPH are:

- (C) 12 g/l PBD in toluene (RPH = 155)
- (D) 12 g/l butyl-PBD in toluene (RPH = 153)
- (E) 7.5 g/l PBO in toluene (RPH = 152)

It is difficult to compare the relative merits of *secondary solutes*, since the RPH of a ternary solution depends on several factors as discussed above. A mean order of increasing merit can, however, be derived from the data of Tables 3 to 5, as follows: DPH (1); α -NPO (2.1); dimethyl POPOP (3.7); BBO (4.5); bis-MSB (5.1); POPOP (5.3) and PBBO (5.9), where the number in parentheses is the average order of increasing RPH from among six or seven secondary solutes. The preferred secondary solutes are therefore PBBO, POPOP, bis-MSB and BBO.

The addition of a secondary solute to a 5 g/l butyl-PBD solution produces only a marginal increase in RPH (Table 5). This is to be expected, since the butyl-PBD emission is already well matched to the photomultiplier spectral response. The addition of a secondary solute to a 4 g/l PPO solution produces a useful increment in RPH (Table 4) due to the improved spectral matching. Three of the ternary solutions:

- (F) 4 g/l PPO + 0.1 g/l POPOP in toluene (RPH = 153)
- (G) 4 g/l PPO + 0.2 g/l bis-MSB in toluene (RPH = 150)
- (H) 4 g/l PPO + 2×10^{-2} g/l BBO in toluene (RPH = 147)

have RPH values comparable with the preferred binary solutions (C), (D) and (E).

The addition of a secondary solute to a 4 g/l TP solution produces a dramatic increase in RPH (Table 3), and yields RPH values exceeding those of the best binary solutions (A) and (B). The best of these ternary solutions are:

- (I) 4 g/l TP + 1 g/l bis-MSB in toluene (RPH = 184)
- (J) 4 g/l TP + 1 g/l POPOP in toluene (RPH = 175)
- (K) 4 g/l TP + 1 g/l BBO in toluene (RPH = 173)

It should be noted, however, that the ternary solutions (F)–(H) and (I)–(K) will be subject to impurity quenching, similar to that of the binary PPO toluene solutions and binary TP toluene solutions, respectively. The order of merit of solutions (A)–(K) which, in the absence of quenching is (I), (J), (K), (A), (B), (C), (D), (F), (E), (G), (H), will thus be modified when impurity quenching is present. The 'quenched' RPH values can be determined from the 'unquenched' RPH values and the values of $[M]_{0.5}$ (Table 2) using Eqn. (1).

In the present studies only one impurity quencher, carbon tetrachloride, has been used. Different quenching behaviour is to be expected with other impurities. It is hoped to extend the studies to other quenchers, including amines, carboxylic acids and other molecules which have groups characteristic of biological molecules.

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DISCUSSION

B. E. Gordon: Are you planning to study quenchers which interact with the solvent? This would alter the diffusion coefficients of the solvents and so change the order of the effectiveness of the solvent in preventing quenching.

J. B. Birks: Carbon tetrachloride interacts with excited solvent (or solute) molecules to

form excited complexes (exciplexes). The competition between the radiationless dissipation of the excitation energy of the exciplex and the dissociation of the exciplex determines the magnitude of the quenching. The exciplex dissociation rate depends on its enthalpy, which is determined by the ionization potential and electron affinity of the solvent (or solute) and quencher molecules. The magnitude of the solvent quenching increases with decrease in ionization potential I of the solvent, e.g. benzene ($I = 9.25$ eV), toluene ($I = 8.8$ eV), *p*-xylene ($I = 8.4$ eV), mesitylene ($I = 8.4$ eV). It is probable that the susceptibility of the solute to quenching similarly increases with decrease in its ionization potential.

As mentioned in the paper it is proposed to extend the studies to other quenchers which have groups characteristic of biological molecules. These quenchers act in a similar manner to carbon tetrachloride, i.e. they form exciplexes with excited solvent or solute molecules. They do not form donor-acceptor complexes with unexcited solvent or solute molecules, which would be undesirable since it would lead to immediate (static) quenching rather than to diffusion-controlled (dynamic) quenching. The distinction between these different types of quenching has been discussed elsewhere.⁷

The diffusion coefficients of benzene and its alkyl derivatives are similar, so that diffusion is not the determining factor in the present studies. It is difficult to envisage any quencher which would appreciably alter the diffusion coefficient of a solvent without altering the nature of the solvent.

F. Battig: According to your figures in a system containing toluene, butyl-PBD and oxygen or quencher there was some positive but small effect of bis-MSB and dimethyl POPOP on pulse height of carbon-14. Would you therefore suggest the general use of secondary solutes together with butyl-PBD in practical measurements?

J. B. Birks: The results referred to are shown in Fig. 25. They show that the addition of 0.1 g/l bis-MSB or 10^{-3} g/l dimethyl POPOP to a 5 g/l butyl-PBD in toluene solution increases the RPH from 135 to 155 or 156. However, reference to Fig. 6 shows that a 12 g/l butyl-PBD solution in toluene has an RPH of 153, which is about the same as that obtained with the solutions containing secondary solutes. Providing the optimum concentration of butyl-PBD is used, there appears to be no advantage in using a secondary solute under our particular experimental conditions.

I would hesitate to lay down any general prescriptions. We have indicated the solutions with the maximum RPH, but we have also presented all the experimental data so that users can estimate the influence of the solvent and the nature and concentration of the primary solute and secondary solute and the effect of quenching for themselves. The ultimate test of any scintillator solution is its performance under the particular operational conditions.

A. R. Ware: You commenced your lecture by confining your remarks to aromatic solvents. In view of some recent success I have had using a long chain hydrocarbon solvent, I would like to hear your comments on the possible use of solvents other than aromatic solvents in scintillation solutions. Would these solutions offer any beneficial properties from the quenching viewpoint?

J. B. Birks: This is a most interesting question. *p*-Dioxan, which is an aliphatic compound, is an efficient scintillator solvent when used in conjunction with 100 g/l naphthalene. Recent work by Hirayama and Lipsky, described elsewhere,⁷ has shown that a large number of aliphatic hydrocarbons are fluorescent, with a fluorescence spectrum peaking between 207 and 230 nm. The quantum yields for excitation at 147 nm wavelength increase with molecular size, e.g. hexane (0.0002), decane (0.002), hexadecane (0.0045), cyclo-

hexane (0.0035), methylcyclohexane (0.0055), bicyclohexyl (0.02) and decalin (0.021). The latter values are of similar magnitude to those for liquid benzene excited at 147 nm. It is thus to be expected that the larger aliphatic hydrocarbons should function satisfactorily as scintillator solvents. The choice of scintillator solute may differ, because the solvent fluorescence spectrum differs from that of an alkyl benzene, and the use of a secondary solvent, like the 100 g/l naphthalene added to *p*-dioxan, might prove advantageous. The ionization potential of the aliphatic hydrocarbons is considerably higher than that of benzene, so that the quenching of the solvent excitation should be even less than for benzene. Provided no snags are encountered with solubility or viscosity, liquid scintillators based on aliphatic solvents appear promising alternatives to the existing scintillator solutions.

A. Dyer: Further to the possible use of other solvent systems in liquid scintillation counting, there is a recent publication by Gomez (E. Gomez *et al.*, *Intern. J. Appl. Radiation Isotopes* 22, 243 (1971)) citing the use of various nitriles with apparent success.

J. B. Birks: No comment.

A. Dyer: Would you care to comment on the excitation of scintillator systems by processes other than β -particles, i.e. α -particles, γ -rays, etc.?

J. B. Birks: I have discussed this topic at length elsewhere² and will therefore confine myself to a few remarks. Internal liquid scintillation counting of α -particles has been brought to a fine art by McDowell and Henley⁸ who have resolved the 4.0, 5.4, 5.7, 6.3 and 6.8 MeV peaks of thorium-232, thorium-228, radium-224, radium-220 and polonium-216 and 4.19 and 4.79 MeV peaks of uranium-238 and uranium-234 in a solution of 5 g/l PPO and 200 g/l naphthalene in toluene using a single photomultiplier and a multichannel analyser. They used organic phase-soluble solvent-extraction reagents to incorporate the radionuclides in the scintillator with minimal quenching. This is a remarkable achievement since quenching increases rapidly with the atomic number of the impurity.

γ -rays interact with matter in a different manner from charged particles: by the photoelectric effect, by the Compton effect, and by pair production. Pair production does not occur at energies below 1.02 MeV, and can usually be neglected. The photoelectric effect is negligible in normal liquid scintillators above 30 keV, but it extends to higher energies in the walls of the vial and in scintillators loaded with heavy elements. Ignoring these points, the principal γ -ray absorption is due to the Compton effect, which yields electrons ranging in energy from zero to about 0.75 of the γ -ray energy. These Compton electrons interact with the scintillator in the same manner as β -particles. If the Compton electron energy exceeds the Cerenkov threshold (electron velocity > velocity of light in scintillator), Cerenkov emission occurs in addition to the scintillation. The detection efficiency for γ -rays is generally much less than for β -rays because of the reduced stopping power of the detection element.

B. W. Fox: Is it ever possible to use the 95% of energy lost in the initial fluorescence process?

J. B. Birks: Not in present liquid scintillation counters. Possibly in the future, the development of solid state systems may enable this lost energy to be utilized.

The 95% energy loss to which you refer is that of the overall scintillation process. The solute fluorescence, which is the final step, has an efficiency of 80 to 90%. The major loss occurs at the first step of the process. Only 14% of the electrons in benzene are π -electrons

Liquid Scintillators

(even less in the case of the alkyl benzenes), so that only one in seven of the initial solvent ionizations and excitations can lead to a scintillation. The manner in which the 14% gets reduced to 5% has been discussed previously.² Possible methods of increasing the 5% are being explored, but the 14% appears to be inherent to liquid scintillators based on aromatic solvents. The 95% energy loss appears as heat. It could be detected by calorimetry. Calorimetry was used to measure radioactivity over 60 years ago.