

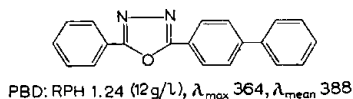
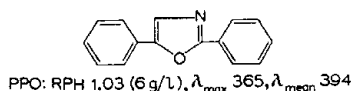
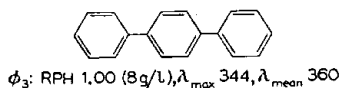
# ROUND-TABLE ON 'CHEMISTRY OF THE COUNTING SAMPLE' SCINTILLATION SOLUTES

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*p*-TERPHENYL was the first solute to be used extensively in liquid scintillators. It remains unsurpassed today for many applications. Many other chemical compounds have been screened—particularly those which are commercially available. A characteristic property of those which have emerged as *good* solutes is that they are compounds containing several conjugated aromatic rings combined in a linear, as opposed to an extensively fused, manner.

Below are shown the structures of compounds which are receiving the most use as primary solutes in liquid scintillators. *p*-Terphenyl ( $\phi_3$ ) has been assigned to this figure a relative pulse height value of 1.00; the central compound, 2, 5-diphenyloxazole or PPO, a relative pulse height of 1.03; and the



bottom compound on the Figure, 2-(4-biphenyl)-5-phenyl-1,3,4-oxadiazole (PBD), a relative pulse height of 1.24. PBD appears to be the most efficient scintillation solute which has been tested.

The concentration at which the pulse height is a maximum follows the pulse height value. The wavelengths (in  $m\mu$ ) at which the maximum of the emission spectrum occurs is also given for each compound, as well as the mean wavelength, which may be defined as that wavelength which divides the emission spectrum into two portions, each having an equal number of photons.

Many derivatives of these compounds have been investigated. Since the

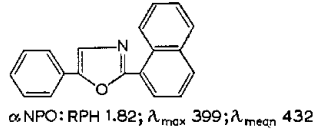
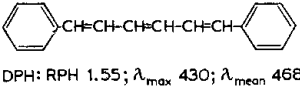
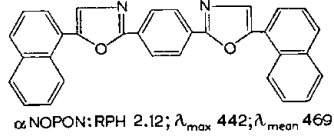
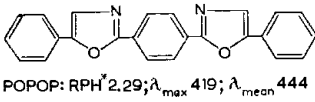
relative pulse height vs. concentration curve for  $\phi_3$  is still rising when the solubility limit is reached at around 8 g/l., this nucleus has been variously substituted in attempts to increase solubility. Similar substitutions have been made with *p*-quaterphenyl. Further  $\phi_3$ -analogs have been tested, e.g. diphenyl- or biphenyl-naphthalenes and anthracenes. At least one secondary solute now receiving some attention, 9,10-diphenylanthracene, is such a compound, although it is not likely that terphenyl, itself, will be replaced by one of its derivatives as a generally useful primary solute. The same is true of the parent member in the oxazole series, PPO. Many oxazoles bearing various substituents on aromatic groups attached at the 2- and 5-positions have been tested, but only for very specialized purposes could they be more practical than PPO as a primary solute. The oxadiazoles were also quite thoroughly investigated, but did not result in the discovery of compounds of practical importance with the exception of PBD.

The requirements that a compound must meet in order for it to be a practical scintillation solute are quite simple: First, it must scintillate well (this includes satisfactory spectral properties). Second, it must be relatively economical; and third, its solubility must be satisfactory for the purpose. *p*-Terphenyl, for example, is a very efficient primary solute and it is economical and readily available. For some purposes, however, its solubility is not satisfactory, such as when it is desired to load the solution with water, or to cool the solution to a low temperature. PPO has much better solubility characteristics under these conditions and this is one of the chief reasons for its use. Any advantage PPO may have, owing to its longer wavelength of emission, may be readily offset by using a secondary solute with  $\phi_3$ . With at least one type of solvent system—that employing naphthalene as secondary solvent as devised by Kallmann— $\phi_3$  fails to perform efficiently because of poor energy transfer from naphthalene, so PPO is used. Another factor must occasionally be considered—the oxazoles will react under anhydrous conditions with such materials as strong acids or acid halides.

The choice of optimum concentration of primary solute to use is generally an arbitrary balance of the same three factors: performance, cost, and solubility requirements.

Primary solutes are frequently used with secondary solutes in order to shift the spectrum of the emitted light to longer wavelengths—a factor desirable because of photomultiplier sensitivity, longer mean-free-path of the emitted light, or reflector considerations. In small-volume detectors using a non-discriminatory reflector such as aluminum, there is little to be gained by adding a wavelength shifter to a PPO solution. However, with a reflector such as  $\text{TiO}_2$  or a solution which absorbs in the shorter wavelength region, such an addition is beneficial. With large detectors, the addition is essential—both because of the longer mean-free-path of the light through the solution, and because of discriminatory reflectors which are used.

The secondary solutes shown below are not the only ones which have been used. POPOP is probably the most popular.  $\alpha$ -NPO was used for some time and still is to some extent in established systems. 1,6-Diphenyl-1,3,5-hexatriene (arbitrarily abbreviated to DPH) is also still used. The pulse height



\*At 0.1 g/l with 4 g/l  $\phi_3$  in  $\phi\text{CH}_3$  with respect to 4 g/l  $\phi_3$  in  $\phi\text{CH}_3$  "S-9" photomultiplier,  $\text{TiO}_2$  reflector, Kimble glass cell

values given are those for the compound as a secondary solute at a concentration of 0.5 g/l. in a solution of 4 g/l.  $\phi_3$  in toluene. They were taken under conditions which favor the long wavelength of emission. The compound in the upper right has not actually been used as yet in a scintillation detector. It is believed that  $\alpha$ -NOPON will find use in the large detectors, particularly with solutions which have impaired transmission in the 400 m $\mu$  region.

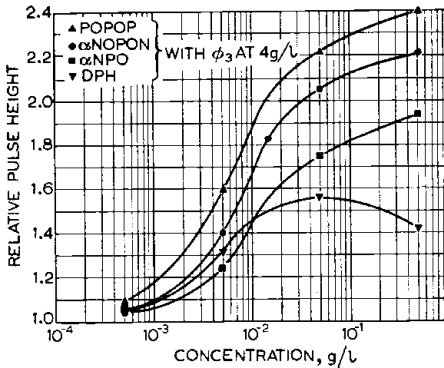


Fig. 1. Relative pulse height vs. concentration of secondary solute

The concentration of secondary solute to be used is again somewhat an arbitrary balance of the three factors: performance, economics, and solubility, but generally lies in the 0.05–0.5 g/l. region. The pulse heights were taken from the curves presented in Fig. 1. We have tried to synthesize or find compounds which were better than POPOP, but it always comes out on top, as shown here. DPH is the only compound in this series which exhibits a maximum at these concentrations—in this case,  $\sim$ 0.05 g/l. is the peak.

The relative merits one assigns to a series of scintillators depends greatly on the testing method. This is the primary reason why discrepancies exist among data from various laboratories. The testing methods are dependent on the spectral distribution of the emitted light.

Figure 2 shows three representative fluorescence spectra. They were obtained by adaptation of a Beckman DK recording spectrophotometer, followed by correction for instrument sensitivity and dispersion. Fluorescence

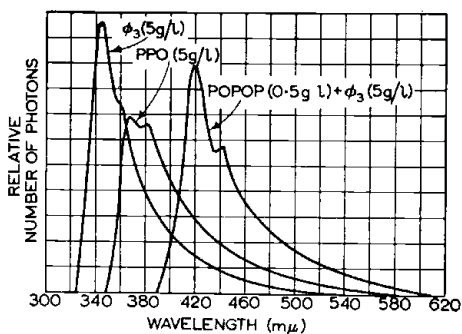


Fig. 2. Fluorescence spectra

was excited by the 314  $m\mu$  mercury lines at the face of the cell opposite to that from which the fluorescent light was analyzed. They are quite comparable to spectra obtained by radioactive source excitation.

The spectrum of the emitted light enters into the relative pulse height or relative current obtained in evaluation procedures through the modifying effects of the sample container and reflector as well as through the spectral sensitivity of the particular photomultiplier employed.

Table 1 illustrates values which may be obtained owing to different spectral responses of the components. The spectral ratio is the relative pulse height of the two solutions given at the bottom of the slide— $\phi_3$ , it will be noted, has a spectrum to considerably shorter wavelength than the POPOP solution.

The central column indicates that a  $TiO_2$  reflector and glass cell favor the longer wavelength solution. In the left-hand column illustration is provided for the varying spectral response within a group of tubes of the same type—the top tube is more sensitive to longer wavelengths. The column on the right is as unbiased as possible—the aluminum reflects light equally well from both solutions, and the quartz cell does not discriminate against the shorter wavelength portion of the terphenyl spectrum.

It can thus be seen that it is possible to obtain one result which says that the addition of 0.5 g/l. POPOP to a terphenyl-toluene solution increases the pulse height by a factor of 2.19; whereas another result may say that an increase of only 5% was observed. Apparently some standardization is

necessary if results from different laboratories are to be comparable. Swank and Hayes are co-operating at the present time on working out such methods.

In addition to the scintillation solutes, mention may be made of other solutes added for special purposes, e.g. neutron-capture solutes or gamma-conversion solutes. Neutron-capture solutes provide a means for neutrons

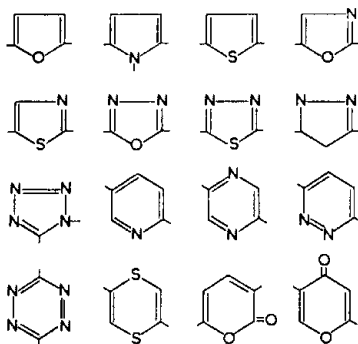
TABLE 1  
*Effect of Spectral Response on Relative Pulse Height*

DuMont 6292 tube number	Spectral ratio	
	Reflector TiO <sub>2</sub> cell: Kimble glass	Al quartz
3185-Y	2.19	1.46
2214-EA	1.81	1.20
4291-EA	1.60	1.05

Solution	$\lambda_{\max}$	$\lambda_{\text{mean}}$
$\phi_3(5) + \text{POPOP}(0.5)$ in $\phi\text{CH}_3$	419	444
$\phi_3(5)$ in $\phi\text{CH}_3$	344	360

to produce ionizing events which are readily detected in the scintillator. The cadmium salt of 2-ethylhexanoic acid—sometimes referred to as cadmium octoate—appears to be the most popular. Gamma-conversion solutes are intended to increase the efficiency of gamma detection by increasing the electron density of the solution. The addition of such special-purpose materials may influence the choice of scintillation solutes.

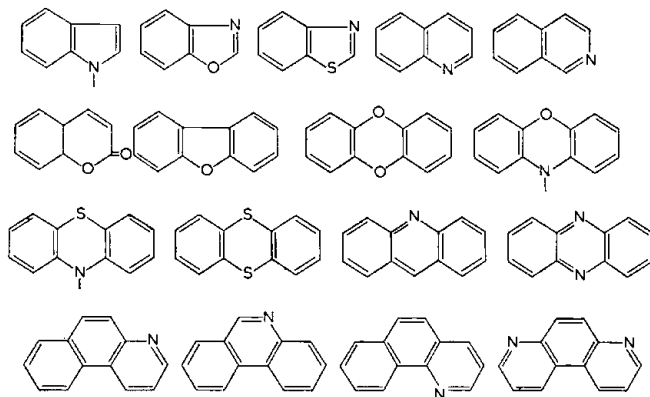


At Los Alamos, an extensive program of screening numerous types of compounds as scintillation solutes has been pursued.<sup>1, 2, 3</sup>

Above are shown various heterocyclic nuclei which have been tested.

Substitution of these with two phenyl groups give what are considered parent members of the series.

Further heterocyclic nuclei which have been screened are illustrated below.



A large amount of interesting information regarding the effects of molecular structure on scintillation ability has been obtained. It appears that none of these compounds, however, is destined to replace the oxazole nucleus as a building block.

Table 2 compares the 'best' of the organic scintillators. These pulse heights are as unbiased as possible with respect to the testing method. Anthracene

TABLE 2  
Comparison of the 'Best' Organic Scintillation

Solvent	Primary solute (conc., g/l.)	Secondary solute (conc., g/l.)	Relative pulse height*
Anthracene	—	—	2.00
<i>trans</i> -Stilbene	—	—	1.64
Polyvinyltoluene	<i>p</i> -terphenyl (36)	4, 4'-diphenylstilbene (0.9)	1.07
Polyvinyltoluene	<i>p</i> -terphenyl (36)	POPOP (1)	1.05
<i>p</i> -Xylene	PBD (10)	—	1.18, 1.47†
Toluene	<i>p</i> -terphenyl (5)	POPOP (0.5)	1.00, 1.25†

\* Volume, 1 ml (cylinder: 0.3 in. ht. × 0.5 in. diam.)

Reflector, aluminum

Photomultiplier, DuMont 6292 with 'average spectral characteristics'

Cell for liquids, quartz

† Dissolved air replaced with argon

and stilbene crystals are the first two entries, plastic scintillators are the next two. PBD at 10 g/l. in xylene is the most efficient liquid scintillator—at least for small volumes. The last entry is for a  $\phi_3$ -POPOP solution.

In conclusion, many organic compounds have been tested as liquid scintillation solutes. The choice of which of the better solutes to use and at what concentration, either for primary or secondary solutes, is governed by a compromise among performance, economics, and solubility considerations.

#### REFERENCES

- <sup>1</sup> F. N. HAYES, D. G. OTT, V. N. KERR and B. S. ROGERS. *Nucleonics* **13**(12), 38 (1955).
- <sup>2</sup> F. N. HAYES, D. G. OTT and V. N. KERR. *Nucleonics* **14**(1), 42 (1956).
- <sup>3</sup> D. G. OTT, F. N. HAYES, E. HANSBURY and V. N. KERR. *J. Amer. Chem. Soc.* **79**, 5448. (1957).