

# New Red-Emitting Liquid Scintillators with Decay Times Near One Nanosecond\*

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### ABSTRACT

Several fast liquid scintillators with peak emission wavelengths in the 600 to 750 nm range are described, which are useful for transmitting fast plasma diagnostic information through long fiber optic cables. These fluors all use styryl laser dyes as the final emitters: DCM in the 650 nm fluors, and LDS-722 in the 735 nm fluors. The solvents are either straight benzyl alcohol (BA) or BA mixed with 1-methylnaphthalene. Coumarin-480 is the intermediate wavelength shifter for the DCM fluors and rhodamine-610 perchlorate (Rh-610P) for the LDS-722 fluors. Some systems also contain added tetramethyltin for enhanced X-ray sensitivity. It was found that very high rhodamine concentrations cause a large increase in the solubility of LDS-722 in BA, which leads to a decrease in scintillation decay time. The fastest 735 nm fluor has a WHM of 370 psec and a decay time of about 320 psec. The fastest 600 nm emitter has a FWHM of 1.1 nsec and a decay time of 0.87 nsec.

### INTRODUCTION

Several fast, red-emitting liquid scintillator formulations have been described previously.<sup>1,2</sup> They all consist of relatively polar laser dyes dissolved in polar solvents, either benzyl alcohol or benzonitrile. Intermediate wavelength shifters are used in all cases to bridge the gap between the solvent emission spectrum and the absorption spectrum of the final emitter. The new, faster fluors are the result of changes in the solvent and/or the intermediate shifter.

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The efficiencies of all the red-emitting fluors are relatively low, only about 3% or 4% of that of anthracene.<sup>2</sup> However, that is the price one pays for very fast time response, which is usually a result of quenching of the excited states and/or nonradiative internal molecular deactivation processes, both of which reduce the fraction of the excited molecules that actually emit light. It should be noted, though, that the peak efficiencies are affected less than the integral efficiencies when the scintillator is quenched. This comes about because the area of a scintillation pulse can be approximated by the product of the FWHM and the peak height. Thus, when the decay time and the integral light output both become smaller, the peak intensity tends to remain more constant. The extent to which the peak height remains constant depends on the pulse rise time; the faster the rise time, the less quenching affects the peak efficiency. The peak efficiency that is most important when the time response of the fluor is slower than the overall time response of the measurement system. On the other hand, it is actually disadvantageous to employ a fluor whose response time is significantly faster than the overall response of the measurement system, because the peak intensity will be integrated to a lower value by the slower system. It would, therefore, be better to employ a slower but brighter fluor whose time response is appropriate for the bandwidth of the detection system.

The terms "scintillator" and "fluor" are used interchangeably in this paper. For the sake of brevity, abbreviations are used for most of the individual fluor ingredients and some formulations, as shown in the Appendix.

## EXPERIMENTAL

All the materials were used as received from the manufacturer, except for 1-methylnaphthalene (AMN), which was purified on a spinning-tape column to remove a distinct yellow color. The fluorescence emission spectra were taken with a SPEX Fluorolog 2 spectrofluorimeter. The exciting wavelength was either 300 or 350 nm. Emission spectra were observed from the same face as the incident excitation light, as well as through a 1 cm thick solution. The latter measurement gives an indication of the extent of self-absorption of the emitted light. Absorption spectra were taken with a Beckman Model UV 5270 absorption spectrophotometer. The dye concentrations are too high to easily determine the complete absorption spectra of the actual fluors, although spectra of the individual ingredients could be taken in dilute solution. As a rough criterion for estimating solutions transparency to their own emission, we have chosen to tabulate the wavelength beyond which the transmittance of a 1-cm thick fluor is greater than 50%.

The time-response data were obtained with a time-correlated single photon counting system that has been described elsewhere,<sup>3</sup> but some of the data were obtained with excitation by a <sup>90</sup>Sr beta source, which gave a much faster data rate than the <sup>60</sup>Co source mentioned in Reference 3. The time response FWHM of the system was determined by the beta particles response to flashes of

Cerenkov light generated in a piece of high-purity quartz or by Compton electrons produced by the  $^{60}\text{Co}$  gamma rays. The system FWHM was less than 200 psec; therefore, the scintillation pulses were not significantly broadened by the instrument response. Start-timing signals were obtained from a disc of the bright, commercial (Bicron) scintillator, BC-422.

Relative scintillation efficiencies of the various fluors were determined from the relative single-photon count rates for  $^{60}\text{Co}$  gamma ray excitation. The comparisons were made through a 570-nm long-pass filter, because the emission peaks were not the same. The observed count rates were corrected for background dark counts and for Cerenkov light produced by 1 cm of pure solvent, observed through the same filter. The relative peak efficiencies were estimated by dividing the integral efficiencies by the respective FWHM values.

## RESULTS

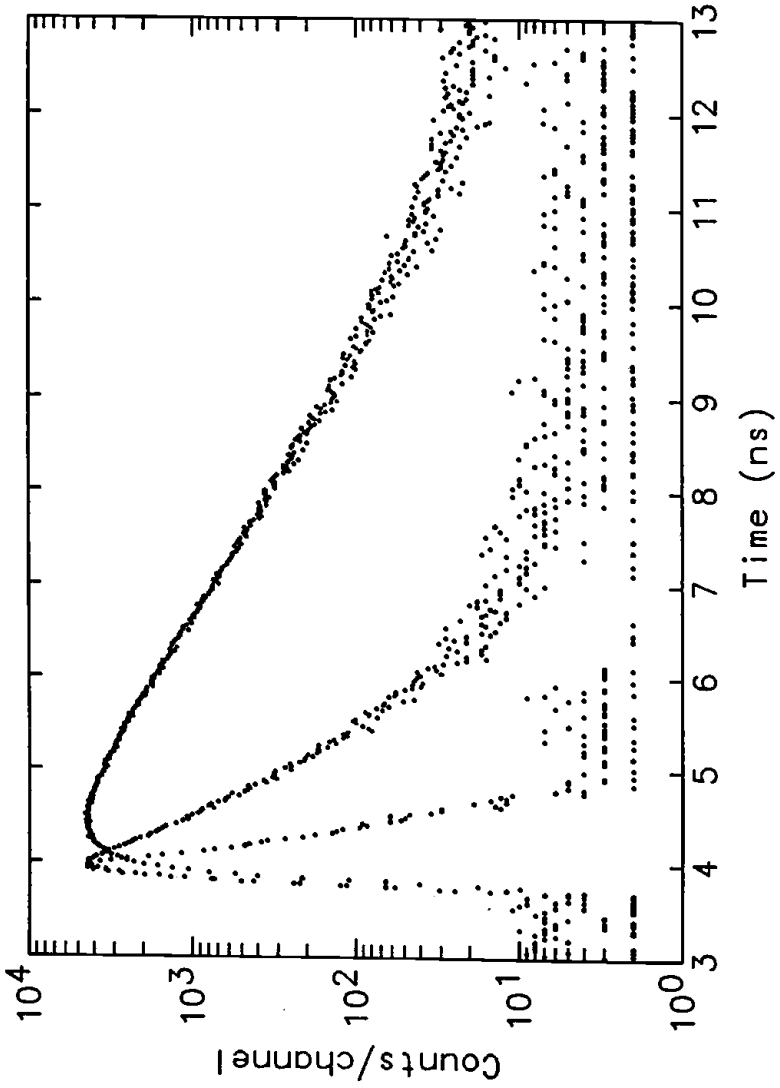
### 735-nm Fluors

A fast, 735 nm liquid scintillator, consisting of 0.02 *M* LDS-722 and 0.10 *M* C-540A in benzonitrile (BN), has been described previously.<sup>2</sup> This fluor has an impulse response FWHM of about 1.7 nsec, and has been named L-735. When 10% by volume of tetramethyltin (TMSN) was added to improve the absorption cross section for soft X-rays, the solubility of the LDS-722 decreased to just over 0.01 *M*. A fluor with 10% TMSN, 0.01 *M* LDS-722, and 0.10 *M* C-540A is called L-735A-10T, and its pulse parameters appear at the bottom of Table 1. The methyl groups in the TMSN effectively shield the tin atoms from quenching the excited singlet states,<sup>4</sup> as can be seen from the relative efficiencies and decay times of L-735A (without TMSN) and L-735A-10T.

A number of experiments with changes in solvent and intermediate wavelength shifters have now been carried out, partly in an effort to reduce the slight photochemical degradation that was observed with L-735 under ultraviolet illumination. One such combination, benzyl alcohol (BA) as the solvent and rhodamine 610 perchlorate (Rh-610P) as the shifter,\* actually decreased the photochemical stability somewhat but resulted in a series of fluors with exceptionally fast time response.

In the course of these studies, it was found that Rh-610P is much more soluble in BA than had been realized: to approximately 0.45 *M/L*. This amounts to about 25 wt% of the rhodamine salt, so the medium can no longer be expected to have the same solvent properties as benzyl alcohol. One unexpected consequence of this is that the solubility of LDS-722 in BA increases

\*It might be mentioned that rhodamine 610 (rhodamine "B") has an exceptionally small Stokes' shift, and therefore would not be expected to be useful as an intermediate shifter. We attribute its efficiency in this application to excitation into S2 or S3 by energy transfer from the solvent, since these bands occur near 300 nm.



**Figure 1.** Time-correlated photon counting data for L-735 and L-735XF, along with the system response function. The slowest decay time shown, 1.27 nsec, is for L-735.

dramatically as the rhodamine concentration is increased, from just over 0.005 *M* LDS-722 in pure BA to at least 0.02 *M* in BA containing 0.40 *M* Rh-610P. The combined effects of increasing the concentration of the LDS-722 and the Rh-610P result in the fastest red-emitting scintillators we have observed to date. Figure 1 contains semilogarithmic plots of data for the fastest of these, L-735XF, as well as for the original L-735 and the pertinent system response function.

Table 1 contains pulse parameters, relative brightness with gamma excitation, and fluorescence emission maxima for a series of these BA-based fluors. The fluorescence emission maxima were determined with an excitation wavelength of 300 nm, and the fluorescence was observed from the opposite face of the 1 cm spectrophotometer cells. The 50% absorption edges for the 1 cm optical path appear in the last column of the table.

The results in Table 1 are presented in order of increasing rhodamine concentration. The fluors described in the last two lines have FWHM values near 500 psec and peak emission wavelengths near 740 nm. The 50% absorption edges for these scintillators increase rather smoothly from 675 nm for the 0.01 *M* to 0.03 *M* solutions to 698 nm for 0.20 *M* Rh-610P. The solution with no rhodamine is the only one out of line. The 1/e self-absorption lengths are estimated to be in the range of 30 to 50 cm at 740 nm, which is of considerable interest for possible use in systems involving fluor-filled capillaries.

Incidentally, the decay time of Rh-610P itself in BA was found to decrease from almost 9.0 nsec in very dilute solution ( $5.0 \times 10^{-6}$  *M*) to 2.1 nsec at 0.10 *M* and about 1.35 nsec at 0.20 *M*. This may be either an energy-transfer effect or possible evidence of concentration quenching.

### 600 to 650 nm Fluors

A fast, 650 nm liquid scintillator consisting of 0.03 *M* DCM and 0.10 *M* C-480 in BA has also been described previously.<sup>2</sup> Its impulse response FWHM is 1.8 nsec, and it has been named L-650A. The original motivation for trying AMN as a solvent for DCM-based fluors was twofold: to enhance the efficiency, since BA is not a particularly efficient scintillator solvent, and to take advantage of the high refractive index of AMN, 1.60, for possible use in scintillating capillaries. A number of DCM-containing fluor formulations in BA, AMN, and mixtures of the two have been examined, and the principal results are shown in Table 2, in order of increasing proportion of AMN. It can be seen that the addition of AMN generally causes the integral efficiency to increase, as had been hoped. What was not anticipated was that the AMN-rich fluors were also faster. As a result, the peak efficiencies increase even more than the integral efficiencies as the solvent is changed from BA to AMN.

The effect of coumarin-480 as an intermediate wavelength shifter can be seen in the first two lines and the last two lines of Table 2. When the solvent is BA, there is only fair spectral overlap between the solvent emission and the DCM absorption, resulting in the fairly slow pulse rise time of about 1.05 nsec.

Table 1. Pulse Parameters for  $^{60}\text{Co}$  Gamma-excited LDS-722 in BA with and without 10% Tetramethyltin (TMSN), using Rhodamine 610 Perchlorate (Rh-610P) as the Intermediate Wavelength Shifter. A 670-nm Long-pass Filter was used in all the Runs. The Peak and Integral Values are Referenced to L-735-A-10T. RT is the 10% to 90% Pulse Rise Times, TAU is the  $1/e$  Decay Time (taken from 0.7 to 0.7/e of the peak height), and IRT is the 10% to 90% Rise Time of the Integral of the Pulse

Rh-610P (M/l)	LDS-722 (M/l)	RT (nsec)	FWHM (nsec)	TAU (nsec)	IRT (nsec)	Peak (est.)	Integral	Wavelength (nm)	
								Emission maximum	Absorption edge (50%)
0.00	0.010 <sup>a,b</sup>	(1.0)	6.44	6.11	16.1	0.2	0.69	720	685
0.00	0.020 <sup>a</sup>	—	(6.6)	5.25	12.1	—	0.60	—	—
0.02	0.010 <sup>b</sup>	1.18	3.26	2.03	4.6	0.55	0.98	720	675
0.05	0.010 <sup>a,b</sup>	0.73	2.08	1.37	3.3	0.75	0.81	722	678
0.10	0.010 <sup>b</sup>	0.47	1.39	0.99	2.4	0.6	0.45	730	690
0.20	0.005	0.33	1.52	1.25	2.85	—	—	—	—
0.20	0.010 <sup>b</sup>	0.37	0.97	0.63	1.75	0.5	0.25	736	698
0.30	0.005 <sup>b</sup>	0.25	0.55	0.58	2.1	0.45	0.14	—	—
0.40	0.020	0.15	0.37	0.32	0.91	0.3	0.06	740	—
L-735	0.020 <sup>c</sup>	0.35	1.67	1.27	2.25	1.1	1.0	735	711
L-735A	0.010 <sup>c</sup>	0.54	2.12	1.48	3.4	1.2	1.1	735	—
L-735A-10T	0.010 <sup>b,c</sup>	0.60	1.89	1.42	3.4	[1.00]	[1.00]	732	698
System response <sup>d</sup>		0.134	0.193	0.085	0.36	—	—	—	—

<sup>a</sup>LDS-722 was supersaturated; some crystallized out over several days.

<sup>b</sup>Contains 10 volume percent tetramethyltin.

<sup>c</sup>Shifter is 0.10 M C-540A; solvent is benzonitrile. See Appendix for composition.

<sup>d</sup>Response to Cerenkov light flashed from Compton electrons generated by the  $^{60}\text{Co}$  gamma rays (see Reference 4).

**Table 2. Pulse Parameters for DCM Fluors in BA, AMN, and Mixtures of the Two. A 650-nm Band-pass Filter was used in all the Runs. The Peak and Integral Values are Referenced to L-650A. RT is the 10% to 90% Pulse Rise Times, TAU is the 1/e Decay Time (taken from 0.7 to 0.7/e of the peak height), and IRT is the 10% to 90% Rise Time of the Integral of the Pulse.**

C-480 (M/l)	DCM (M/l)	AMN %	RT (nsec)	FWHM (nsec)	TAU (nsec)	IRT (nsec)	Peak (est.)	Integral	Wavelength (nm)		
									Emission maximum	Absorption edge (50%)	
0.0	0.03	0.0	1.06	3.58	2.93	6.03	0.9	1.77	—	—	
0.10	0.03	0.0	0.69	1.79	1.58	4.05	[1.00]	[1.00]	648	629	
(L-650-A reference)											
0.10	0.05	50%	0.59	1.62	1.49	3.90	1.4	1.26	640	624	
0.20	0.05	67%	0.49	1.37	1.13	3.22	1.25	0.96	632	622	
0.10	0.05	100%	0.49	1.11	0.87	2.85	1.7	1.06	600	605	
0.0	0.05	100%	0.57	1.61	1.34	4.11	1.55	1.38	600	600	

When 0.10 *M* C-480 is added, the pulse rise time decreases to about 0.7 nsec, due to improved energy transfer. On the other hand, the pulse rise time of DCM in AMN, without C-480, is nearly as short as that of L-650A, because there is much better spectral overlap between the broad emission spectrum of AMN and the absorption band of DCM than there is between BA and DCM. This is why the addition of C-480 to DCM in AMN has less effect on the pulse rise time than it does in BA.

In addition, there is quenching of DCM by C-480 in either solvent, as shown by the decreases in decay time and integral brightness when C-480 is added. Quenching by C-480 accounts for the lower integral efficiency of the fluor with 67% AMN than the fluor with only 50% AMN, since there is twice as much C-480 in the 67% fluor. The fact that there is quenching by C-480 was confirmed by laser-excitation experiments with DCM in BA, in which a similar effect was observed.

Unfortunately, the fluors with AMN show such strong self-absorption that their use in capillaries seems unlikely. This is due to the fact that the emission spectra shift faster towards the blue than do the absorption spectra as the proportion of AMN is increased. When the solvent is changed from pure BA to pure AMN, the emission peak wavelength for DCM moves from 650 to 600 nm, but the absorption peak moves only from 490 to 470 nm. The 50% absorption edge through a 1 cm path of 0.05 *M* DCM moves from about 630 to about 600 nm, while the peak emission moves from 648 to about 600 nm.

## CONCLUSIONS

The time response of scintillator formulations can be strongly dependent on the nature of the solvent, as well as any intermediate wavelength shifter. In each of the systems described above, there is quenching of the final emitter by the intermediate shifter, which was completely unanticipated, and which is largely responsible for the faster time response of the modified formulations. These results also demonstrate that a considerable fraction of the peak efficiency can be retained in the quenched scintillator, provided the pulse rise time is fast enough.

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## APPENDIX

AMN	alpha-methylnaphthalene, or 1-methylnaphthalene
BA	benzyl alcohol (alpha-hydroxy toluene)
BN	benzointrile (phenyl cyanide, cyanobenzene)
C-480	Coumarin 480 (or Coumarin 102)
C-540A	Coumarin 540A (or Coumarin 153)
DCM	red-emitting styryl laser dye, also Kodak dye No. 14567
L-650A	BA with 0.1 M C-480 and 0.03 M DCM
L-735	BN with 0.10 M C-540A and 0.02 M LDS-722
L-735A	BN with 0.10 M C-540A and 0.01M LDS-722
L-735A-10T	BN with 0.10 M C-540A, 0.01 M LDS-722, and 10% TMSN
L-735XF	BA with 0.40 M Rh-610P and 0.02 M LDS-722
LDS-722	far-red-emitting styryl laser dye (Exciton)
Rh-610P	Rhodamine 610 (or Rhodamine B) perchlorate salt
TMSN	tetramethyltin

