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UV quantum efficiencies of organic fluors

C.H. Lally, G.J. Davies *, W.G. Jones, N.J.T. Smith

Blackett Laboratory, Imperial College, Prince Consort Road, London, SW7 2BZ, UK

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Abstract

The need for, and benefits of using, wavelength shifters with certain dark matter scintillator detectors is discussed. The dependence of conversion efficiency on thickness and incident wavelength is extensively investigated for evaporated coatings of *p*-terphenyl and tetraphenyl butadiene, and for plastic waveshifters based upon *p*-terphenyl. For the latter the effect of varying the *p*-terphenyl concentration is studied and some factors which must be considered when developing them for use in the UV are also discussed.

1. Introduction

Whereas dark matter detectors based on ionization in semiconductors and low temperature bolometric techniques have been under study since 1985 [1], only recently has the use of scintillators become widespread [2]. They are suitable for scale-up (and hence annual modulation experiments) and may offer significant discrimination of the nuclear recoil signal from the background electron/gamma events via differences in the pulse shape of the scintillation light [3]. As the expected energy deposit for a recoiling nucleus from a dark matter event is small, scintillators with high light output, such as liquid xenon (LXe) and sodium iodide (NaI) are required. Thus the most important parameter limiting sensitivity in these detectors becomes the light collection efficiency, as this determines the achievable energy threshold and the discriminatory power. However, because all or some of the scintillation light is in the UV region for both detectors (175 nm for LXe and 300 nm for pure NaI) several problems can arise in achieving a good collection efficiency:

(1) UV sensitive photomultiplier tubes (PMTs) are required which are more radioactive necessitating a long (~ 30 cm) lightguide.

(2) The lightguides needed to separate the PMTs from the target lose light through high UV attenuation and poor UV reflectance.

(3) Light will not emerge from the target vessel due to the poor UV reflectance of the walls.

These problems can be avoided and substantial gains in light collection made if the light is shifted to the visible region via a wavelength shifter (WLS). These fluors absorb light in the UV and re-emit at longer wavelengths.

Some aromatic organic compounds fluoresce when their Π-orbital electrons are excited, either by ionizing particles or UV radiation [4]. Electrons excited to the vibrational states of the first excited state (S_1) relax within picoseconds to the lowest lying level of S_1 before decaying to the ground state with the radiation of a photon at the compound's characteristic emission wavelength, see Fig. 1. In plastic scintillators, the binder in which the WLS is dissolved, must also have a Π-electron structure, and absorbs the incident energy. If the concentration of the wavelength shifting solute is high enough this energy is transferred by non-radiative dipole–dipole interactions to its excited levels producing fluorescence [5]. The transfer is efficient if there is good overlap between the binder's emission spectrum and the absorption spectrum of the solute. Energy transfer to further solutes is possible, allowing the final light to be shifted to even longer wavelengths.

Traditionally these fluors have been applied by vacuum evaporation from powder form and so can be applied directly to crystal faces, target vessel walls or the front face of lightguides or photomultipliers [6]. It is possible to tune the final emission wavelength of the shifter to a detector's optimum sensitivity (~ 400 nm for a conventional photomultiplier) either directly by selecting a single suitable compound or by adding a secondary shifter to further increase the final wavelength of the light (a ternary system). More recently they have been dissolved in plastic binders offering greater rigidity, higher wavelength shifter concentrations and making the production of ternary systems easier.

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* Corresponding author. Fax: (44) 171 823 8830, E-mail: g.j.davies@ic.ac.uk.

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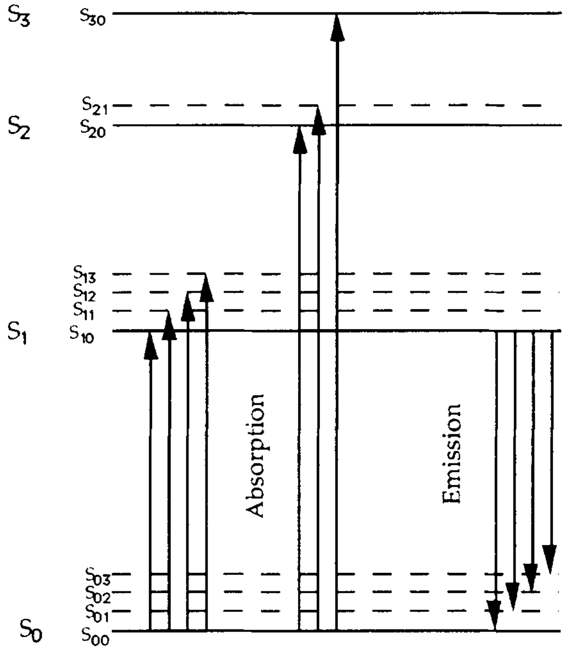

Fig. 1. Energy levels of an organic molecule with Π-electron structure.

We have produced evaporated samples of *p*-terphenyl (TPH) and tetraphenyl butadiene (TPB) and obtained plastic samples, based upon TPH, of varying thickness from NE Technologies [7] and BICRON [8]. For each we have measured its conversion efficiency as a function of incident wavelength and its emission spectrum.

2. Method

Coatings of a range of thicknesses were produced using the evaporation chamber shown in Fig. 2. The wavelength shifting powder is heated in a nickel foil boat and the evaporated fluor is deposited on a glass slide near the top of the evacuated chamber. The thickness of the coating is controlled by interposing a mechanical shutter in front of the glass slide when the attenuation of a light beam by the coated slide has reached a pre-set level. Samples whose thicknesses have been measured directly by weighing are used to obtain the light attenuation coefficient from a plot of light attenuation against thickness. The evaporations were made at a pressure of $1-1.5 \times 10^{-1}$ Torr; improving the vacuum to 1×10^{-2} Torr did not improve the conversion efficiency of the fluors. TPB goes through a liquid

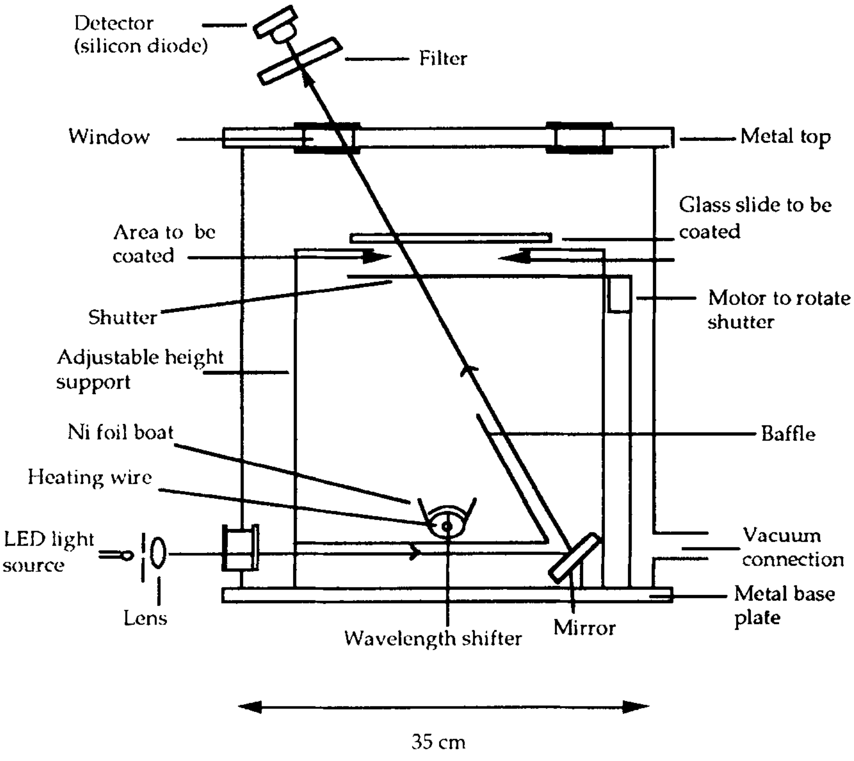

Fig. 2. Evaporation chamber.

phase when heated whereas TPH sublimes; the bubbling which occurs during this liquid phase can lead to poor quality coatings unless controlled. Thus the heating profile for TPB must be adjusted according to the amount of powder to be evaporated making it a more difficult compound to evaporate uniformly.

The plastic samples were based upon a primary WLS of TPH of varying concentration, with POPOP as the usual secondary shifter, in a polyvinyltoluene (PVT) binder. Thicknesses of 40 μm to 5 mm were tested.

We have measured the output spectrum of the WLS using a specially adapted monochromator (Fig. 3a): The light from a deuterium lamp (D_2) passes through a 185 nm interference filter (25 nm FWHM bandwidth) onto the WLS. The emitted (isotropic) light is then focused by a lens, via the grating, onto a calibrated photomultiplier tube. We needed to use a PMT instead of a diode as the amount of shifted light reaching the exit was very low.

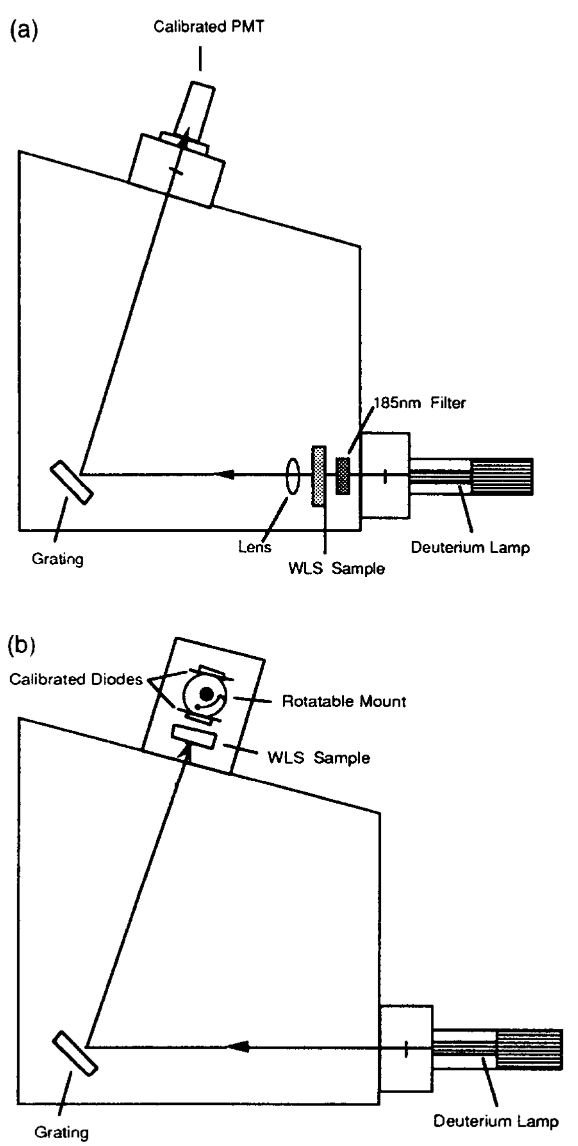

Fig. 3. (a) Schematic of monochromator set-up for measuring emission spectra. (b) Schematic of monochromator set-up for measuring conversion efficiency.

The conversion efficiency of the WLS is measured using the monochromator but in a different configuration (Fig. 3b): This time the light from the D_2 lamp passes directly to the grating which is set to reflect a particular wavelength of light onto the monochromator exit. This light is then first measured by a calibrated, UV sensitive diode (to calculate the flux of UV photons at the exit) and then, after rotating the diode mount, is shone onto the WLS sample which is fixed directly in front of a second calibrated diode (from which we can estimate the flux of wavelength shifted photons). The external quantum efficiency (defined as the number of photons emitted divided by the number of incident photons) can then be calculated by correcting for the different active areas of the two diodes, the quantum efficiencies of the diodes at the relevant wavelengths, the solid angle of the isotropic shifted light that the second diode 'sees', and the various reflective and refractive processes that the shifted light undergoes before reaching the diode surface. Values of 1.3 and 1.5 were taken for the refractive indices of the evaporated coatings and plastics, respectively. Although these correction factors can carry significant systematic errors, they are the same for each type of shifter (evaporated or plastic) and hence a comparison of different evaporated or plastic shifters is insensitive to them.

The self-attenuation of the evaporated coatings was tested by illuminating them with light whose wavelength equalled that at their peak emission.

3. Results

Fig. 4a, b gives the emission spectra for TPH and TPB and is in fairly good agreement with earlier measurements quoted in the literature [7,9]. We have observed that, as would be expected, this emission spectrum does not vary with WLS thickness or wavelength of incident light (even for light incident with a higher energy than the fluors primary absorption band).

Fig. 5a, b shows their external quantum efficiency for incident light of 175 nm versus thickness. The errors here, as for all other graphs, are dominated by the systematic uncertainty (~ 15%) in the quantum efficiencies of the diodes arising from the uncertainties in the intensity of the light source with which they were calibrated. We took advantage of TPH's more gentle decrease in efficiency with thickness to make a crude evaporation onto the cylindrical walls of a small LXe test cell (a protective transparent layer of magnesium fluoride was placed over the shifter to prevent contamination of the LXe). Scintillation light was observed but some of the TPH migrated to unprotected surfaces. Whilst this problem is solvable it illustrates an advantage of plastic shifters over evaporated coatings.

Fig. 6a, b shows the transmittance of TPH and TPB coatings at their emission wavelengths (335 nm and 440 nm, respectively) as a function of thickness. Clearly the attenuation of the longer light by the TPB is far greater than the attenuation of the shorter light by the TPH.

Fig. 7a, b shows the external quantum efficiency as a function of wavelength for two samples of approximately optimum thickness. We believe the peak in the efficiency of TPH at about 260 nm corresponds to this fluor's S_1 absorption peak (i.e. transitions from the ground state to the first excited state) which occurs at this wavelength [4]. The absorption of light by TPB is far more rapid than by TPH, as supported by Fig. 5 and 6, and all the incident light at all wavelengths is fully absorbed by the sample. Thus, in contrast to TPH, we believe we cannot directly see the fluor's absorption peaks; the S_1 absorption peak for TPB occurs at about 340 nm [4]. Mechanisms (M_1) exist [4] whereby a molecule which absorbs an incident photon of energy greater than that required to excite a single electron to the lowest S_1 level can excite a further electron in a neighboring molecule. These processes can be qualitatively represented by

$$S^{**} + S \rightarrow S^{*} + S^{*},$$

where S signifies a WLS molecule. For M_1 to be significant, the molecular density must be high and the time taken for the usual thermal dissipation of this excess energy relatively long. We suggest that, as one approaches the energy required for excitation to S_2 (the second excited energy level) the likelihood of M_1 increases. However, the higher energy S_2 vibrational states will be shorter lived and fall more rapidly to the lowest S_1 level. Therefore, for a given molecular density, there will be an optimum energy at which these further excitations can occur. Thus we conjecture that the greater than 100% external quantum efficiency peaks at 175 nm and ~ 275 nm for TPH and TPB in Figs. 5a and 7b respectively are explained by the above processes.

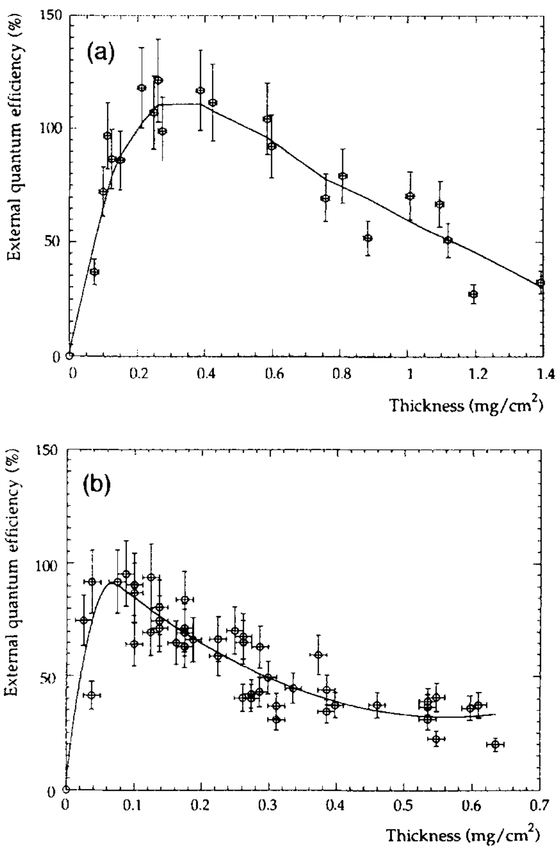

Fig. 5. External quantum efficiency versus thickness of TPH and TPB for 175 nm incident light.

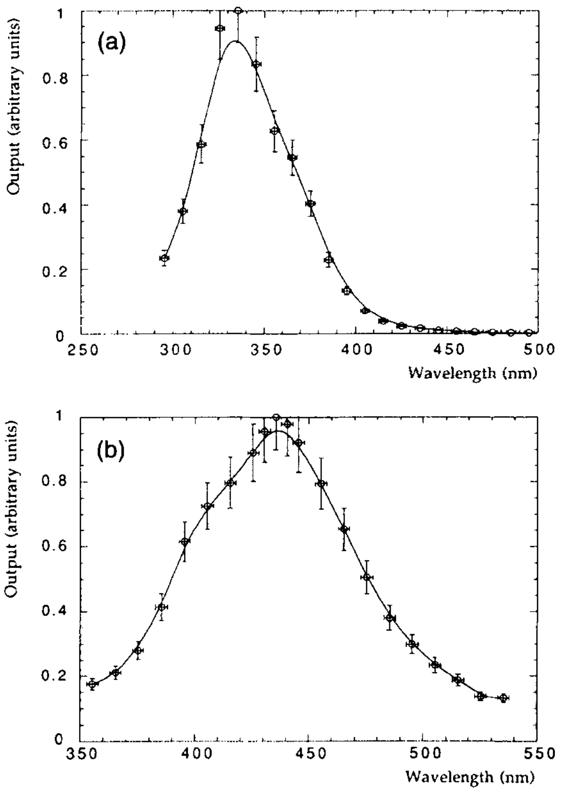

Fig. 4. Emission spectra for TPH and TPB with 185 nm wavelength incident light.

A number of the TPH and TPB samples were repeatedly retested over a six month period. During this time they were sealed in petri dishes and kept in a dark cupboard (to avoid the large degradation which would result from a continuous exposure to sunlight). Fig. 8a, b shows the ageing effects at the end of this period due to oxidation and hydration for the two fluors, random errors are shown only. The deterioration occurred steadily and is worse at the optimum thickness of the WLS and corresponds to a decrease in efficiency of 10–15%. It should be noted that, in contrast to some previous published results [6], the ageing of TPB appears to be no worse than that of TPH.

Fig. 9 shows the external quantum efficiency versus wavelength for three of the plastic shifters. The random error alone is plotted on the lower graph to illustrate the significance of the differences between the samples. The most efficient plastic, denoted by '0.2 mm, 30% enriched TPH', contained 30% more *p*-terphenyl than usual and was 0.2 mm thick. The conversion efficiency decreases as either the concentration of TPH is decreased, see the curve '0.2 mm', or as the thickness of the sample is increased, see curve '2 mm 30% enriched TPH'. As mentioned previously, for a plastic wavelength shifter, the energy is absorbed by the binder and transferred non-radiatively to the primary shifter, TPH in our case. As this process is of a finite range, and the concentration of TPH limited, one is sensitive to the structure of its absorption spectrum. We believe that the resulting external quantum efficiency versus wavelength curve can be explained as follows:

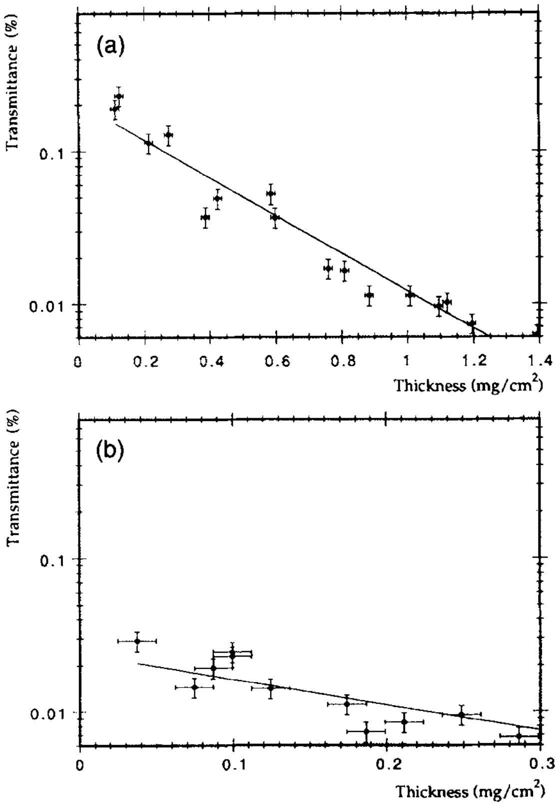

Fig. 6. Transmittance of TPH and TPB versus thickness at their respective emission wavelengths.

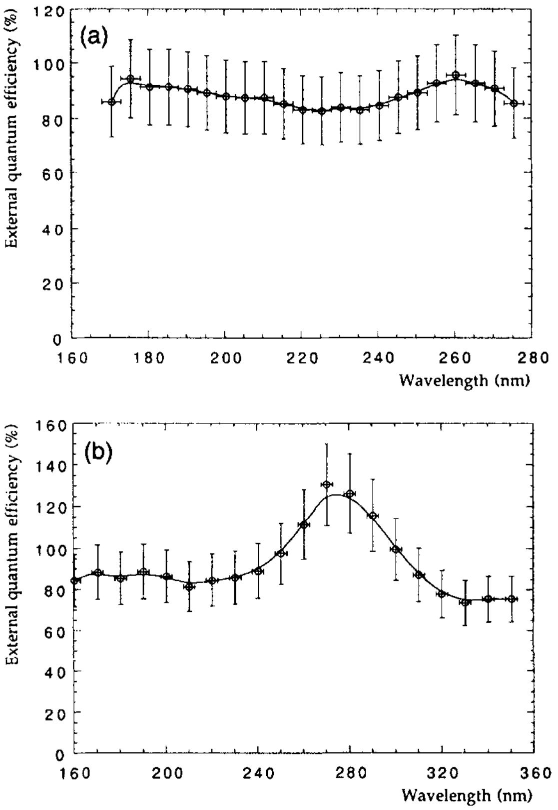

Fig. 7. External quantum efficiency versus incident wavelength for TPH and TPB for two samples of approximately optimum thickness.

For incident wavelengths around 280 nm the energy is absorbed by the S_1 vibrational states of the PVT, and with little energy loss falls to the S_1 ground state from where it is efficiently transferred to the broad S_1 absorption peak of the TPH at 280 nm.

For incident wavelengths around 210 nm, the energy is absorbed by the S_2 vibrational states of the PVT, and with more significant loss falls to the S_2 ground state which is at a lower energy than the very narrow S_2 absorption peak in the TPH at 210 nm. Indeed, as the TPH has a minimum in absorption at 230 nm, the energy transfer to the TPH is inefficient and the resulting conversion efficiency low in this wavelength region.

However, for incident wavelengths around 170 nm, the energy absorption proceeds via the S_3 states in the PVT, which lie at slightly higher energy than the TPH S_2 states, allowing efficient energy transfer to the TPH S_2 energy level. Thus we see an increase in the conversion efficiency in this region.

As the concentration of TPH is increased so is the efficiency of the energy transfer from the PVT to it; thus higher TPH concentrations yield higher conversion efficiencies. Some of the light emitted by the POPOP i.e. light

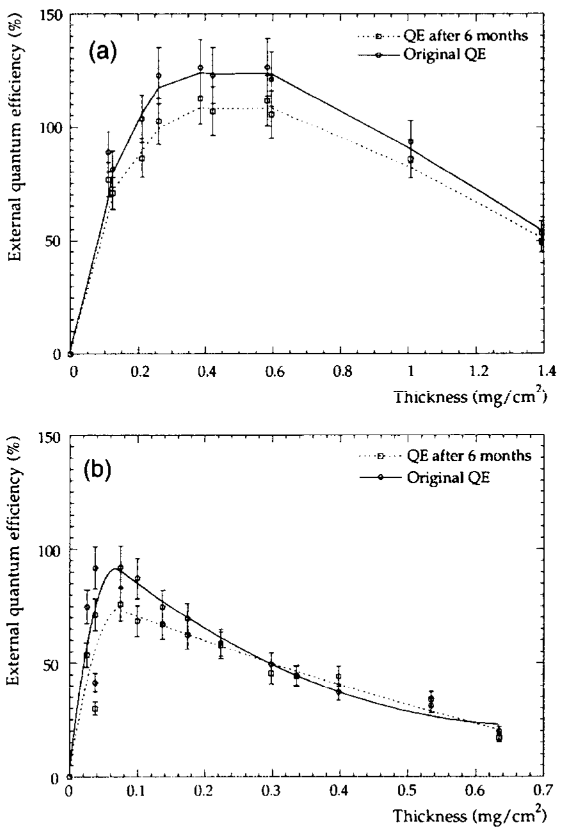

Fig. 8. Deterioration in efficiency of TPH and TPB after a six month period (175 nm incident light).

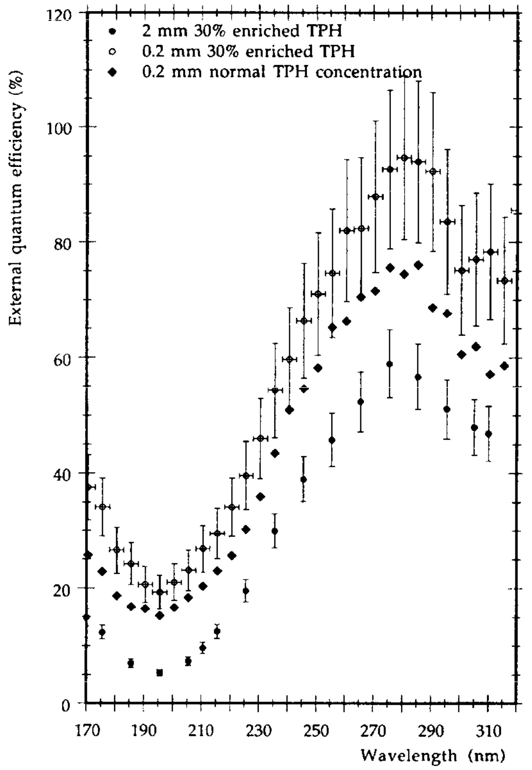

Fig. 9. External quantum efficiency versus wavelength for TPH + POPOP of varying concentration in PVT binders of different thicknesses.

at the final, detected wavelength (~ 400 nm) will be absorbed by the PVT. Hence, as all wavelengths of incident light are absorbed within the first few tens of microns, the '0.2 mm 30% enriched TPH' sample is more efficient than the corresponding 2 mm one due to reduced absorption of the 400 nm light by the PVT. The absorption of light in the PVT was confirmed by measuring the transmittance of a pure PVT sample, see Fig. 10. The transmittance below 295 nm is consistent with zero.

To further investigate the possible improvement with thinner plastic binders, enriched 100 μm samples and 40 μm samples with the usual TPH concentrations were tested. Fig. 11 shows the result for one of the 100 μm thick samples. The attenuation length (~ 20 mm at ~ 400 nm) calculated from Fig. 10 would suggest that there should be little difference between the enriched 200 and 100 μm samples as is indeed observed at wavelengths above ~ 240 nm. There is however a significant improvement at the shortest wavelengths. The efficiency of the 40 μm thick samples was considerably less, especially at the shortest wavelengths, than that of the 0.2 mm sample with the equivalent TPH concentration. These two effects can be explained in terms of depletion regions which contain little or no TPH. These have been observed by the manufacturer to form at the faces of the plastic binder when either very thin samples with the usual TPH concentrations are produced directly (i.e. the 40 μm samples) or when samples with very high TPH concentrations of any thickness are produced.

Thus we suggest the effect of the depletion regions in the 40 μm samples is more strongly felt by the shorter

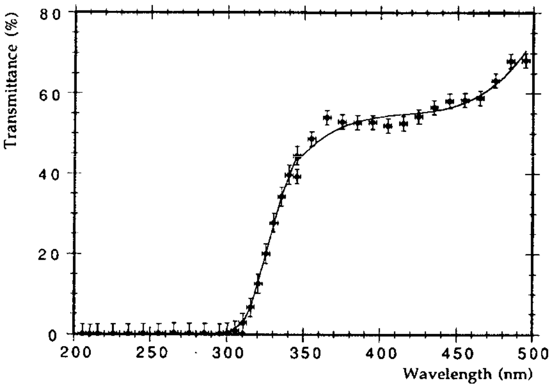

Fig. 10. Transmittance versus wavelength of a 10 mm pure PVT sample.

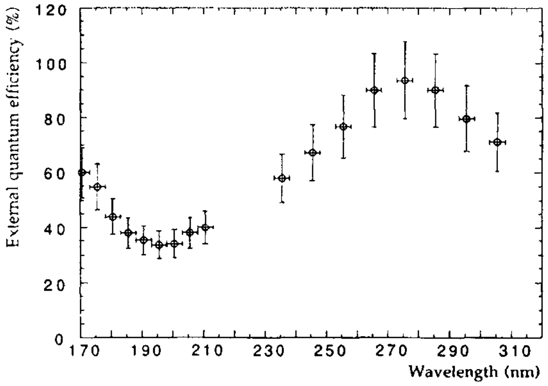

Fig. 11. External quantum efficiency versus wavelength for an enriched TPH + POPOP sample in a 100 μm PVT binder.

wavelengths because, as they are absorbed more rapidly in the PVT, they are unable to reach the undepleted region. The 100 μm enriched samples were produced by compressing thicker samples. As a result of this thinning process, the depth of the depletion regions in the 100 μm samples was reduced such that short wavelengths are able to traverse it.

We have recently successfully operated plastic wavelength shifter disks in the cooled (160 K), pure NaI (scintillation at 300 and 420 nm) detector as used underground. The disks were placed between the crystal and the lightguides. The discrimination achieved with non-UV sensitive tubes was equal to that with UV sensitive ones, indicating that the latter can be replaced with lower background tubes in conjunction with a WLS. Furthermore, their lower radioactivity means that the lightguides can be shortened, improving the light collection and hence both the experiments sensitivity and discriminatory power.

4. Conclusions

As expected, the conversion efficiency of both TPB and TPH is high at very short wavelengths [6,10,11]. Thus both fluors should allow the construction of a detector without needing a UV reflector, although TPH would require a secondary shifter for use with a low activity borosilicate PMT this is most easily achieved with a plastic shifter.

The optimum thicknesses are 0.3 mg/cm^2 for TPH and 0.07 mg/cm^2 for TPB, similar to previous measurements although there is variation in the literature [6,11]. The thinner optimum thickness and faster fall-off of TPB are easily explained by its greater self-attenuation as seen from Fig. 6.

The efficiency of the plastic shifters is maximised by using the highest possible TPH concentration. Although it is better to reduce the binder thickness as much as possible care must be taken as to how this is done; it would appear that the best method is simply to compress thicker samples to minimise the depth of any depletion regions.

An interesting possibility currently under investigation is a plastic shifter based upon TPB alone. Such a shifter would not need a secondary fluor as the TPB emits directly at 440 nm, thus avoiding the loss of efficiency in the transfer from primary to secondary shifter and perhaps benefiting from the greater overlap of the TPB and PVT energy levels. An extension of this, as suggested in [12], would be a mixture of shifters with overlapping absorption bands to minimise the poor overlap between PVT and a single fluor at certain wavelengths.

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