

A Study of the Fluorescence Response of Tetraphenyl-butadiene

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Abstract

Tetraphenyl-butadiene (TPB) is a widely used fluorescent wavelength-shifter. A common application is in liquid-argon-based particle detectors, where scintillation light is produced in the UV at 128 nm. In liquid argon experiments, TPB is often employed to shift the scintillation light to the visible range in order to allow detection via standard photomultiplier tubes. This paper presents studies on the stability of TPB with time under exposure to light. We also examine batch-to-batch variations. We compare scintillation-grade TPB to 99% pure TPB response. In the 99% pure samples, we report a yellowing effect, and full degradation of the TPB emission-peak, upon extended exposure to light.

1. Introduction

1,1,4,4-Tetraphenyl-1,3-butadiene (TPB) is used as a wavelength shifter in many experiments. For example, TPB is used in numerous liquid argon (LAr) experiments including ICARUS [1], WARP [2], MiniCLEAN [3, 4], DEAP [4, 5] and MicroBooNE [6] to shift scintillation light, which is produced at 128 nm in LAr, to the visible, where it can be detected by photomultiplier tubes (PMTs). TPB absorbs light across a broad range from the high UV to its emission peak, which lies at approximately 425 ± 50 nm.

TPB has the chemical formula $(C_6H_5)_2C=CHCH=C(C_6H_5)_2$. Scintillation-grade TPB, which is used in LAr experiments, has an assay of $> 99\%$ purity. TPB dissolves in toluene, and this mixture is often used when coating surfaces such as PMTs. One can spray or paint the TPB-toluene mixture onto the surface and allow the toluene to evaporate, leaving only a layer of TPB behind. Alternatively, one can dissolve polystyrene into the mix to produce a thin plastic skin with embedded TPB when the toluene evaporates.

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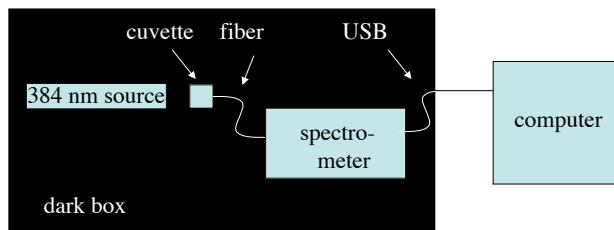


Figure 1: A diagram of the setup for the measurements. The light source illuminates the cuvette. The light may be transmitted or absorbed and re-emitted at a longer wavelength. The spectrometer measures the wavelength of light which exits the back of the cuvette.

In this paper, we investigate whether the TPB fluorescence response degrades over time when the chemical is exposed to light. This is relevant to the handling of the TPB-coated materials as experiments are assembled.

2. Methods

All studies used samples of 0.25 g of TPB dissolved in 100 ml of toluene. We found that tests using dissolved mixtures in a cuvette, as opposed to tests of TPB powder in a cuvette, gave a more repeatable measured response when the sample was removed and replaced in the test-stand spectrometer

We studied two grades of TPB: scintillation grade TPB (SG-TPB) and 99% pure TPB. For consistency in the studies over time, all samples of a given grade were taken from the same batch of TPB powder purchased from Sigma-Aldrich [7]. In our studies of freshly mixed samples, we also report on results of TPB powder purchased from ACROS [8]. All TPB powder batches were kept in opaque brown bottles in a dark cabinet throughout the study.

For studies of exposure to light, TPB-toluene mixtures were stored in clear glass bottles. These were illuminated by a SOLUX solar spectrum lamp [9] for periods of three months and one month. The samples were maintained at room temperature during the exposure to the SOLUX light.

The experimental setup used to measure the fluorescence of the TPB-toluene samples is shown in Fig. 1. The samples were held in a cuvette with $(1\text{ cm})^2$ cross section, which was illuminated by a 384-nm light source. This particular wavelength transmits through toluene, which absorbs UV light with $<315\text{ nm}$ wavelength[10]. On the other hand, 384 nm is within the absorption range of TPB. The fluorescence spectrum from the samples is piped to a spectrometer via a fiber coupled to the back of the cuvette. We use a StellarNet Black Comet

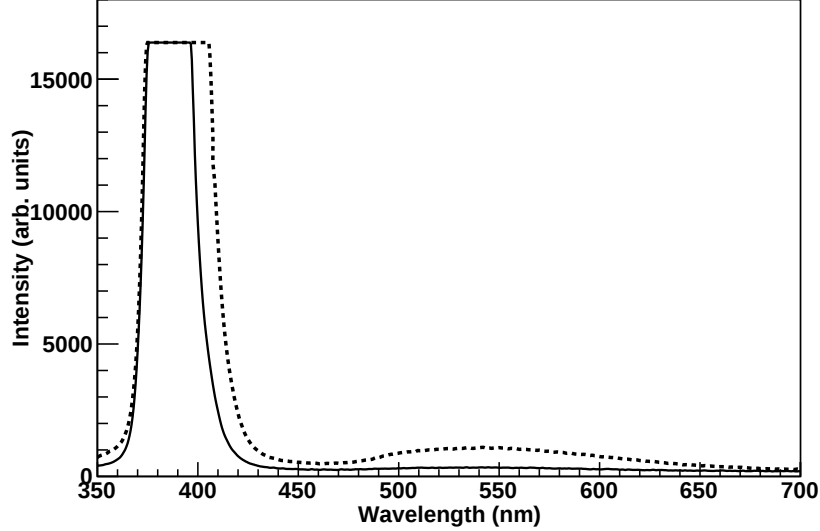


Figure 2: Solid: The light source as observed through the empty cuvette. Dashed: The light source observed through a cuvette filled with toluene. The broad toluene peak, centered at about 550 nm can be seen. The peak from the light source, which is at 384 nm, is truncated so that the toluene peak is visible.

(model C) spectrometer [11]. This is a concave grating spectrometer with a range from 190 to 850 nm.

Fig. 2 (solid) shows the peak of the 384 nm light source as observed through the empty spectrometer cuvette, while Fig. 2 (dashed) shows the spectrometer measurement when the cuvette is filled with pure toluene. One can see that the toluene produces a broad peak centered at about 550 nm. The stability of the height of the toluene peak provides a useful benchmark for our study. We do not expect the toluene fluorescence peak to substantially change with exposure to light, and so this peak provides a method to normalize the absolute light measurements, which can vary with minor changes of the alignment of the light source to the spectrometer.

Fig. 3 shows the resulting spectrum from a cuvette filled with freshly-mixed SG-TPB-toluene solution. The light from the source is absorbed by the TPB, and so there is no visible peak at 384 nm. One can see a strong peak at 425 nm from the TPB and the broad peak from the toluene. This curve provides a basis of comparison for other samples in this study.

When normalizing to the toluene peak at 550 nm, we observed that the peaks of freshly-mixed samples of the same TPB batch vary from lowest to highest counts by 10%. We present this below as a $\pm 5\%$ systematic error on the measurement. We believe this is consistent with the expected combined error

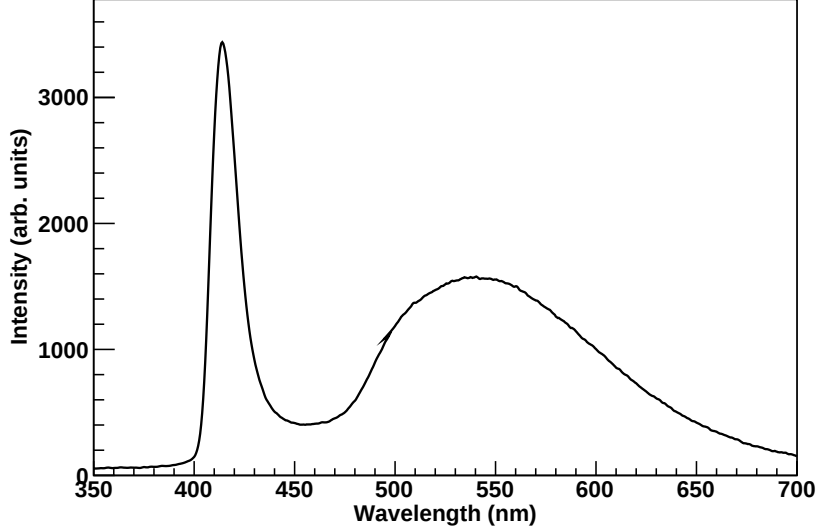


Figure 3: Spectrum from freshly-mixed TPB and toluene. The TPB peak and toluene peak are visible, while the peak from the light source is fully absorbed.

of the measurement of the mass of TPB powder and the toluene volume during mixing.

As noted above, we also provide a comparison of the SG-TPB response to 99% pure TPB, which is generally considered poor for use as a wavelength shifter, but which is also less expensive. During this phase of the study, we observed a striking effect. When a sample of 99% pure TPB was mixed with toluene and exposed to ambient room light, within the time-scale of a few days, the originally clear mixture became yellow-green, as shown in Fig. 4 (left). We also noticed yellowing when the 99% pure TPB powder was left exposed to ambient room light for three days, as shown in Fig. 4 (right). This effect can be reproduced with the SOLUX full-spectrum light source. We report on this further below.

3. Results

3.1. Scintillation Grade TPB Exposed to Light and Over Time

Fig. 5 (top) compares the results of SG-TPB–toluene mixtures exposed to the light as a function of time. For reference, the solid line is the freshly-mixed SG-TPB–toluene. The dashed curve shows the response of the mixture exposed for one month, while the dot-dashed line shows the mixture exposed for three months. The height of the toluene peak at 550 nm was used for relative

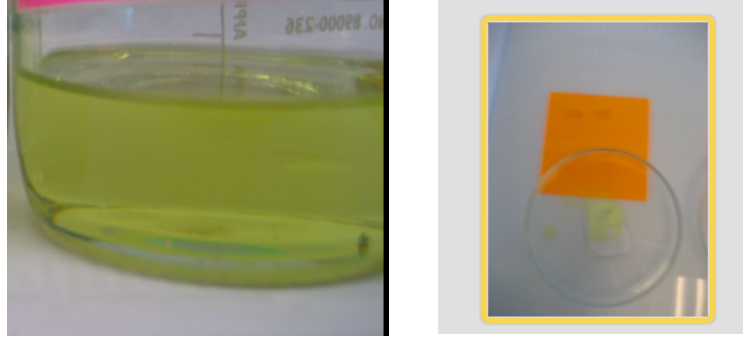


Figure 4: Left: Toluene and 99% TPB mixture exposed to light for three days. The initially clear mixture became yellow-green. Right: Powdered 99% pure TPB exposed to the SOLUX lamp for five days. The initially white powder became yellow.

normalization of the curves. Within the $\pm 5\%$ systematic error, the TPB peak responses are in agreement.

We kept one SG-TPB–toluene mixed sample for a period of three months in a dark cabinet. In Fig. 5 (bottom), we compare the transmitted light from this sample (dashed line) to the freshly-mixed (solid line) and the mixture with three month exposure to the SOLUX light source (dotted line). Again, the TPB peaks are in agreement.

3.2. Comparison of Three Batches of Scintillation Grade TPB

The initial batch of TPB from Sigma-Aldrich was compared to a batch from Sigma-Aldrich purchased six months later and to a batch purchased from ACROS [8]. The results of this cross comparison is shown in Fig. 6. One can see that the samples agree well within the $\pm 5\%$ systematic error.

3.3. Comparison of Scintillation Grade and 99% Pure TPB Response

Next, we compare the response of SG-TPB and 99% pure TPB mixtures in Fig. 7 (top) solid and dashed lines, respectively. From this, we conclude that the light output from 99% pure TPB is reduced compared to SG-TPB, as expected.

We observed that the 99% pure TPB–toluene mixture suffered yellowing with exposure to sunlight, ambient room light, and also to the SOLUX lamp light. This effect was observed in three separately acquired batches of 99% pure TPB ordered months apart. We did not see this effect with any batch of SG-TPB. Recently, we learned that the WARP experiment has seen a similar yellowing of one batch of SG-TPB mixed in toluene [12].

In our studies, the yellowing was visible after about three days of exposure to light and did not visibly change after this, over a period of one month. The spectrum from the yellowed mixture is compared to the one-month exposure of

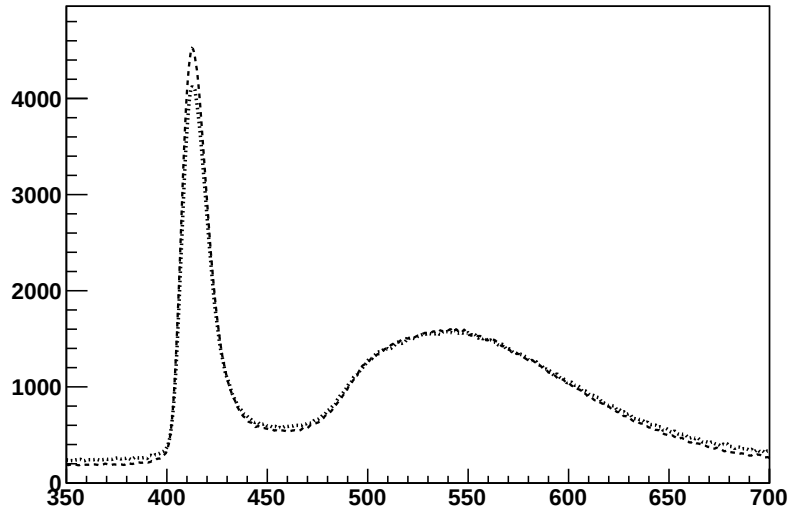
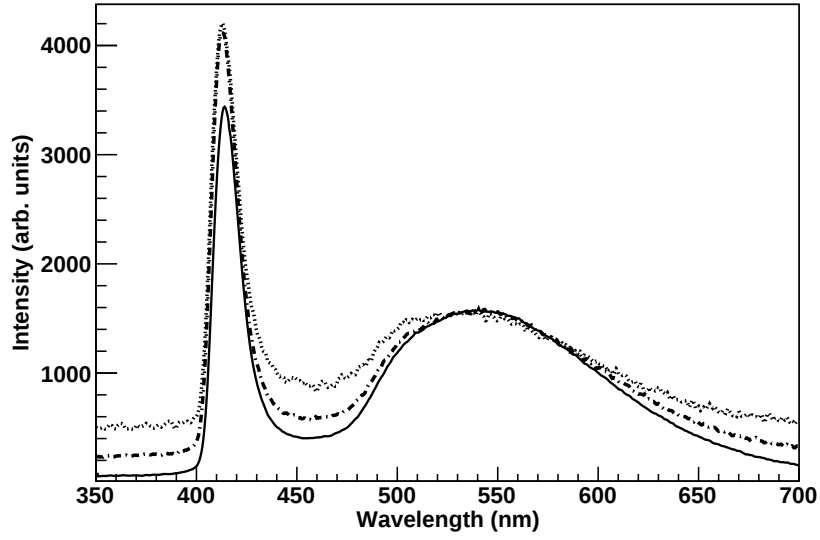


Figure 5: Top: Spectra for scintillation grade TPB dissolved in toluene for samples exposed to SOLUX light source for three months (dot-dashed) and one month (dotted) compared to the spectrum from a freshly mixed sample (solid). Bottom: Spectrum for scintillation grade TPB dissolved in toluene exposed to SOLUX lamp for three months (dotted) compared to a sample stored in the dark for three months (dashed). In both sets of plots, there is agreement within the systematic error of this study.

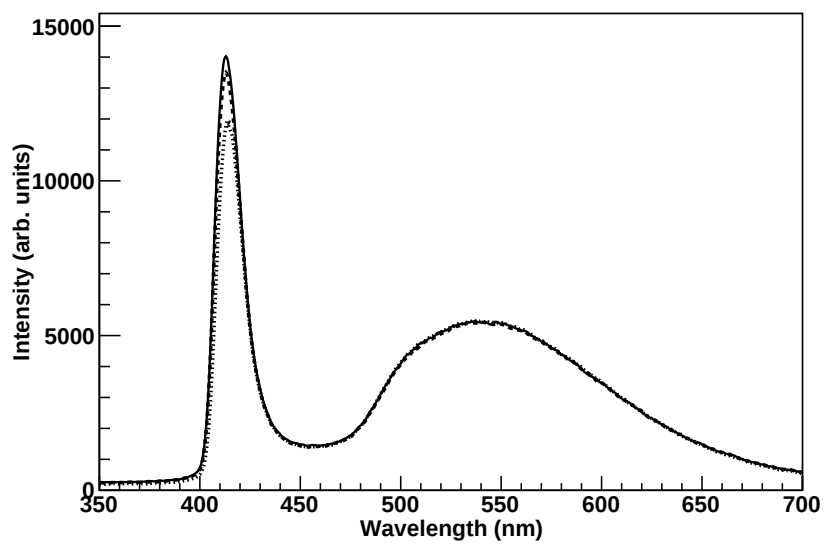


Figure 6: Spectra for scintillation grade TPB dissolved in toluene, freshly mixed. Results from three separate batches are compared. Solid: batch recently purchased from Sigma Aldrich; Dotted: batch purchased from Sigma-Aldrich six months earlier; Dashed: batch purchased recently from ACROS. All results are in good agreement within the $\pm 5\%$ systematic error.

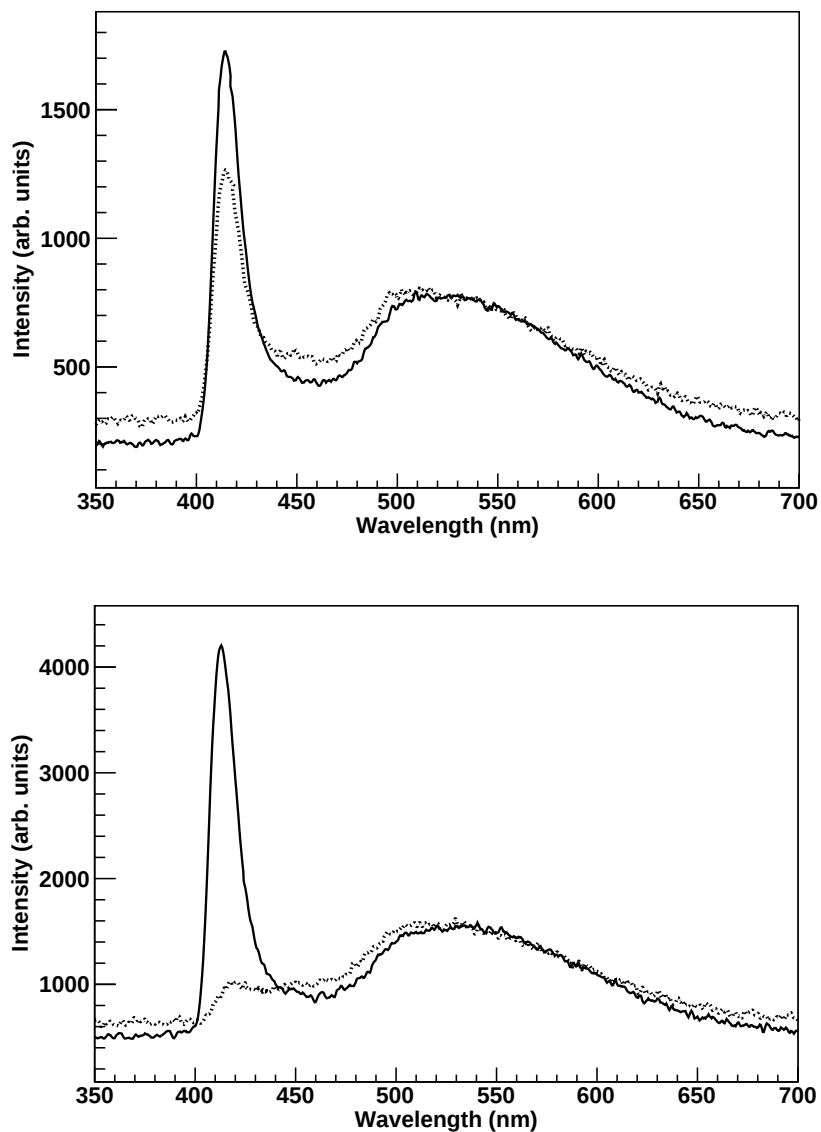


Figure 7: Spectra for scintillation grade TPB dissolved in toluene (solid) compared to 99% pure TPB dissolved in toluene (dotted). Top: Freshly mixed samples. The 99% pure TPB response is about two thirds of the level of the scintillation grade. Bottom: After exposure to light where the 99% pure TPB mixture has shown yellowing. The TPB peak is substantially reduced in the yellowed mixture.

SG-TPB in Fig. 7 (bottom). The TPB peak of the yellowed mixture is nearly entirely absorbed.

In order to demonstrate that the yellowing is due to exposure to light, a 99% pure TPB-toluene mixture was produced and divided. Half half exposed to light immediately and half was stored in a dark cabinet. After a period of about three days, the mixture in the light showed clear yellowing while the mixture stored in the dark looked clear. The latter mixture was removed from the cupboard and set into the light. After about three days of exposure, yellowing appeared.

4. Conclusions

We have investigated the fluorescence response of TPB dissolved in toluene. We studied the effect of exposure to light for extended periods and conclude that within the level of $\pm 5\%$ systematic variations, the scintillation grade TPB is stable to exposure to light. This would indicate that TPB-coated equipment does not require special protection from light.

We compared three batches of scintillation-grade TPB and found that the relative response agreed within the systematic error. We also showed that scintillation-grade TPB has superior response compared to 99% pure TPB.

The 99% pure TPB showed yellowing upon exposure to light over a period of several days. At this point, we do not know the cause of the yellowing. It appears to be an impurity in the TPB which reacts when exposed to light. While we have not observed yellowing in the three scintillation-grade batches we studied, there was a report from WARP of one scintillation-grade batch which showed yellowing which may be the same effect. Because the initial mixture appears clear, with yellowing occurring over several days, we recommend that all batches of TPB, even those which are scintillation grade, be tested for this effect before use. A simple test is to place a small amount of the TPB powder from each batch into a petri dish and expose it to light for one week before use. Batches which show yellowing should be rejected.

Acknowledgments

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