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## Fluorescence efficiencies of thin scintillating films in the extreme ultraviolet spectral region

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### Abstract

Fluorescence efficiencies of the organic scintillators tetraphenyl butadiene (TPB), p-terphenyl (TPH), and diphenyl stilbene (DPS) are measured relative to sodium salicylate at incident wavelengths of 58.4 and 74.0 nm. Optimum thickness and dopant concentration are determined for maximum fluorescence yield in evaporated, sprayed, and doped plastic films. Measurements made with alpha ( $\alpha$ ) particle induced scintillations in gaseous argon (a broad band vacuum ultraviolet light source) were in good agreement with those made using the line source. Transparent scintillator doped plastic films have been developed which yield fluorescence efficiencies comparable to that of sodium salicylate. Evaporated films show the highest fluorescent yields, reaching almost four times the efficiency of sprayed sodium salicylate. On the other hand, doped plastic films offer some advantages. © 1997 Elsevier Science B.V.

### 1. Introduction

Fluorescent materials are often used in the detection of extreme ultraviolet (XUV) radiation. These materials emit visible light upon the absorption of XUV radiation. Direct XUV detection, although possible with high efficiency, can be problematic due to the inability to transmit or guide XUV radiation to a detector; use of frequency down-converters alleviates this problem. In addition, frequency down-conversion can significantly

increase the number of photons available for detection.

A typical XUV detection system consists of a photosensitive device coated with a translucent layer of fluorescent material. Certain experiments, however, prohibit the close proximity of source and detector and cannot make use of this technique. Two such experimental examples are the recently proposed magnetic trapping of ultra-cold neutrons [1] and the measurement of the neutron electric dipole moment using ultra-cold neutrons and polarized <sup>3</sup>He [2]. There the XUV photons emanate from an inaccessible reservoir of liquid helium, and scintillation light must be transported some distance external to the cryostat.

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The XUV scintillators tetraphenyl butadiene (TPB), p-terphenyl (TPH), and diphenyl stilbene (DPS) have emission spectra with peaks at 440, 335, and 409 nm, respectively, and widths of about 50 nm. They are all well suited for energy down-conversion because of their high fluorescence efficiencies [3-7], and can be evaporated into thin films, yielding adherent, durable coatings. In contrast to these evaporated films, fluor doped plastic films have the advantages of less light scattering, better abrasion resistance, ease of preparation, and index matching to plastic light guides [8]. These qualities have led to the consideration of using doped plastic films in several applications, including detection of Cerenkov radiation [9], ultraviolet imaging [10], and detection of dark matter [3]. However, fluorescence efficiencies of doped plastic films have been measured to be lower than their evaporated film counterparts at short wavelengths [3,10].

We report here studies of evaporated, sprayed, and doped plastic films under excitation by XUV light created in a radio frequency (RF) gas discharge. Optimum thicknesses and dopant concentrations for maximum fluorescence are determined. Fluorescence efficiencies of these films are measured relative to sodium salicylate. A reference standard of known absolute fluorescence efficiency [11], sodium salicylate has an emission spectrum peaked at 420 nm [12], with a width of about 80 nm.

Relative fluorescence efficiencies have also been studied making use of alpha ( $\alpha$ ) particle induced scintillations in gaseous argon at 1 bar. Although the wavelengths of XUV radiation created in the discharge source more closely approximate the wavelengths (60-100 nm) [13] emitted in liquid helium scintillations, we have found the flexibility of the argon technique to be an advantage in some cases. Thus it is interesting to compare the results of measurements carried out with the different techniques.

## 2. Sample preparation

Fluorescent materials are deposited onto 25 mm  $\times$  10 mm  $\times$  0.81 mm nylon substrates

[14]. Three methods of deposition are used: evaporation, spraying, and doping of plastic thin films.

Standard film deposition techniques are used to produce evaporated films of TPB, DPS, and TPH [15]. Evaporation is performed in a vacuum chamber evacuated using a diffusion pump with a liquid nitrogen cooled baffle to less than  $10^{-5}$  mbar. Film thickness is controlled by varying the distance from the molybdenum evaporation boat to the film substrate. Sample thickness is measured by weight, and ranges from  $49 \pm 6$  to  $2650 \pm 100$   $\mu\text{g cm}^{-2}$ , with uncertainties in thickness determined by the uncertainty in the weighing technique.

Sprayed phosphor coatings of sodium salicylate and TPB are prepared by airbrushing the scintillator solution onto nylon substrates [16]. The scintillator solution consists of either sodium salicylate dissolved in methyl alcohol or TPB dissolved in ethyl ether. Although easier to prepare, films made using this technique are less uniform than evaporated films. Film thickness is measured by weight, and ranges from  $80 \pm 40$  to  $3040 \pm 40$   $\mu\text{g cm}^{-2}$ .

Doped plastic films used in XUV discharge source measurements are prepared by either (a) controlled dipping of the substrate into a solution of the plastic and dopant, (b) dripping the solution directly onto the substrate, or (c) spinning plastic-dopant solution onto the substrate using a commercial spinner. In cases (a) and (b) the solutions consist of 30 ml toluene per gram of plastic, with a varying concentration of fluor. Film thickness is measured using a micrometer. Dipped films are  $12 \pm 2$   $\mu\text{m}$  thick, while the films formed by dripping are  $31 \pm 2$   $\mu\text{m}$  thick. Chloroform is used as a solvent in the making of the spun films. Thicknesses of spun films (case c) range from  $1.6 \pm 0.1$  to  $40.1 \pm 0.1$   $\mu\text{m}$ , as measured with a profilometer. The plastic used for most applications is pure polystyrene, with an average molecular weight of 280,000. Also tested are polyvinyltoluene (PVT), poly(2,4-dimethylstyrene) (PDMS) [17], polymethylmethacrylate (PMMA), nitrocellulose [18], long chain polystyrene (MW=1,880,000), short chain polystyrene (MW=2727), and dicarboxy terminated polystyrene [19].

Thin plastic films for the argon scintillation experiments are prepared by dripping the solution

directly onto the nylon substrates. In these experiments, TPB [20] and polystyrene are dissolved in UVASOL grade toluene. No attempt is made to measure the layer thickness of the samples used for the argon measurements.

### 3. Apparatus and measurement technique

#### 3.1. Measurements with an XUV discharge source

Fluorescence efficiency measurements are performed by illuminating thin film samples with XUV light and measuring the intensity of the emitted fluorescent light with a photomultiplier tube (see Fig. 1). The XUV source is a 66 MHz RF discharge in 99.999% pure helium (58.4 nm) or 99.995% pure neon (74.0 nm) gas. A continuous flow of gas through the system is required to maintain cleanliness. We found this to be important for maintaining a high XUV intensity. Visible and near-UV light is filtered from the excitation spectrum by a 200 nm thick aluminum window [12]. The filtered spectrum consists solely of the desired XUV line. This was verified by measuring the output spectrum of the XUV system with a vacuum ultraviolet spectrometer.

Twenty-one samples can be loaded into the apparatus at one time and can be interchanged and tested in situ. The XUV light emitted from the RF discharge illuminates a central area of 5 mm<sup>2</sup> on an individual sample. Scintillation light that enters into the diffusing nylon substrate has its direction randomized. This ensures that for a constant geometry, a fixed portion of light is collected by the bi-alkali cathode photomultiplier tube (PMT)

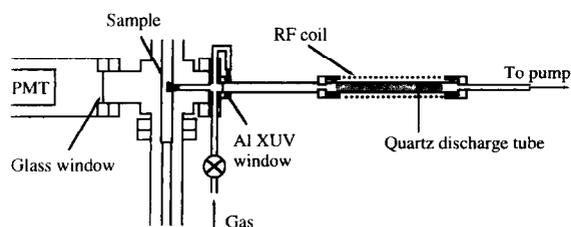


Fig. 1. Apparatus used to measure fluorescence efficiencies of thin film samples.

positioned directly behind the sample. The PMT is biased within the linear range of its voltage divider circuit. Comparison of the recorded anode currents, corrected for the wavelength dependent photocathode sensitivity, determines the relative fluorescence efficiencies of the samples. No fluorescence is observed for nylon substrates without scintillator coatings. Light attenuation through nylon is taken to be independent of the emission wavelengths of the tested samples.

Fluorescence of each film is compared to sprayed sodium salicylate, a standard with relatively constant response to ultraviolet radiation over a wide wavelength range. The absolute fluorescence efficiency of sprayed sodium salicylate, expressed in units of blue photons per XUV photon, was measured by Bruner [11] to be 0.42 for 58.4 nm excitation and 0.37 for 74.0 nm excitation. We normalize the fluorescence of each tested film to the average of at least five sodium salicylate samples. Based on the observed spread of the fluorescence yields of sodium salicylate and our samples, we estimate that relative fluorescence efficiency measurements of individual films are accurate to within 10%. No attempts are made to directly measure absolute fluorescence efficiencies.

#### 3.2. Measurements using scintillations in gaseous argon

The fact that argon scintillates at around 120 nm when excited by ionizing radiation has been known for some considerable time [21]. For our measurements, we use an  $\alpha$ -source to excite the scintillations. Given the availability of an alpha source, this technique is rather easy to set up and is extremely flexible. It allows rapid measurements and can be used to measure the emission from either side of a sample. In addition it can be used for preliminary room temperature measurements and selection of the actual liquid helium containers before they are inserted into the cryostat. The <sup>210</sup>Po source employed was produced by electroplating a pure copper wire with bismuth [22] and irradiating the samples in the neutron irradiation facility at the research reactor BER-II at the Hahn-Meitner Institute. A typical source has a strength of 4000 Bq.

Measurements are carried out in a cell made by sealing one end of a 50 mm PMMA tube with a PMMA window (see Fig. 2). The other end of the tube is glued to a metal flange which is connected to a gas handling system, which maintains an absolute argon pressure of 1 bar within the cell. Because small impurities in the argon gas can cause significant changes in the intensity of the scintillation light, the sample cell is fed continuously with flowing argon gas (99.998% pure). The gas is further purified by passing through a cold trap. In this way stable fluorescence levels are achieved.

The  $\alpha$ -source is located on the axis of the cell, 2 cm above the converting film to be investigated. The samples are mounted at a distance of 4 cm from the end window. Aluminium foil on the walls of the cell reflects the light through the end window which is directly mounted over a 5.1 cm diameter bialkali photomultiplier (8850 Burle). The PMT signal is fed into a pulse height analyzer. Pulse height spectra can be calibrated with the single electron peak, which is well separated in this PMT. The pulse height spectrum of the scintilla-

tions shows an asymmetric peak which is well separated from the single electron peak. The position of the maximum of these pulse height spectra gives a measure of relative fluorescence efficiencies accurate to within 10%. The signal yield of the 30 mm  $\times$  25 mm samples used is typically 25 photoelectrons per event. Measurements in a cell devoid of wavelength shifter gave no detectable signal showing that the argon scintillations produce no light in the sensitive region of the PMT, centered around 400 nm.

The light diffusing and transmitting properties of the nylon were tested by comparing the efficiencies for  $\alpha$ -particle excitation from above the sample and below the sample with an inverted geometry, preserving the source–film and film–window distances (see Fig. 2). No difference in the efficiencies could be detected for the two different excitation geometries where the light is detected after being transmitted through the substrate in one case and directly in the other.

## 4. Results and discussion

### 4.1. Measurements with an XUV discharge source

The fluorescence efficiency ( $F(\lambda)$ ) measurements of optimized evaporated, sprayed, and plastic-doped films are summarized in Tables 1 and 2. As discussed earlier, these measurements are relative to sodium salicylate. Variation of fluorescence efficiency with coating thickness in evaporated films is shown in Fig. 3. TPB yields the highest fluorescence efficiency, measured to be  $3.9 \pm 0.1$  for 58.4 nm down-conversion and  $3.7 \pm 0.1$  for 74.0 nm down-conversion, with an optimum coat-

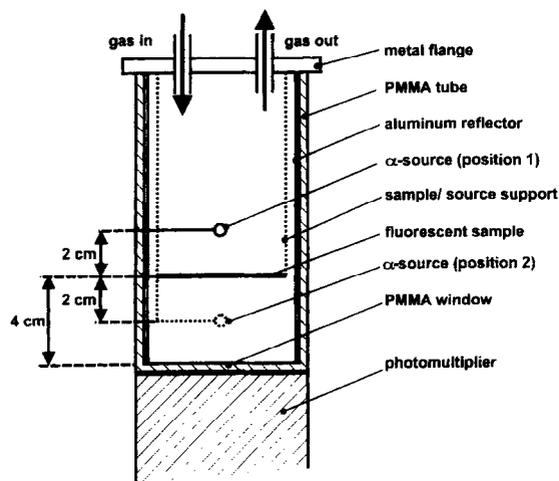


Fig. 2. Cell for measurements using scintillations in gaseous argon (not drawn to scale). The configuration with the alpha source in position 1 is for measuring the emission transmitted through the sample. Changing the alpha source to position 2 allows the measurement of the direct emission from the fluorescent coating. In both configurations the coated side of the sample faces the alpha source.

Table 1

Values of the fluorescent efficiencies of optimized evaporated films relative to that of sodium salicylate

Scintillator	Thickness ( $\text{mg cm}^{-2}$ )	$F(58.4 \text{ nm})$	$F(74.0 \text{ nm})$
TPB	0.2	3.9	3.7
TPH	0.1	3.4	3.0
DPS	0.2	3.4	3.3

Table 2

Maximum values for the relative fluorescent efficiencies of doped plastic films relative to that of sodium salicylate

Scintillator	Matrix	Cons. (%)	$F$ (58.4 nm)	$F$ (74.0 nm)
TPB	Polystyrene	$\geq 2.0$	1.00	0.76
TPB	Polyvinyltoluene	$\geq 2.0$	0.81	–
TPB	Poly(2,4-dimethylstyrene)	$\geq 2.0$	0.85	0.69
TPB	Polymethylmethacrylate	10.0	0.35	–
TPB	Nitrocellulose	13.3	0.40	–
TPH, POPOP	Polystyrene	$\geq 1.2$	0.77	0.66

ing thickness of  $0.2 \text{ mg cm}^{-2}$  (measured separately for each wavelength).

The fluorescence efficiencies for sprayed films are shown in Fig. 4. No variation with coating thickness is observed in sprayed sodium salicylate samples with thicknesses greater than  $0.08 \text{ mg cm}^{-2}$  (the thinnest tested in these experiments). Fluorescence efficiencies of sprayed TPB films are roughly two and a half times greater than those of the sodium salicylate films. The scatter of points is attributed to the nonuniformity of the sprayed films. The evaporated films show less spread and therefore appear to yield a more uniform coating.

Fig. 5 illustrates the effect of dopant concentration on the fluorescence yield of TPB doped polystyrene. XUV fluorescence efficiency depends strongly on TPB concentration at low concentration values, but begins to level off as the TPB concentration reaches 1% by weight. Furthermore, by

measuring the fluorescence yield of spun films as a function of film thickness, we find that the relationship between fluorescence efficiency and TPB con-

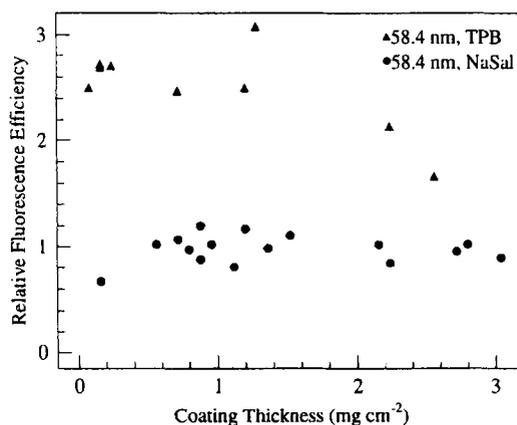


Fig. 4. Relative fluorescence efficiencies of sprayed films excited by 58.4 nm radiation.

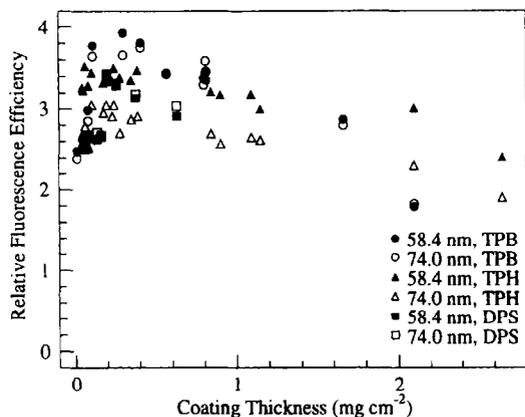


Fig. 3. Relative fluorescence efficiencies of evaporated films excited by 58.4 and 74.0 nm radiation. All fluorescence efficiencies are specified relative to sodium salicylate.

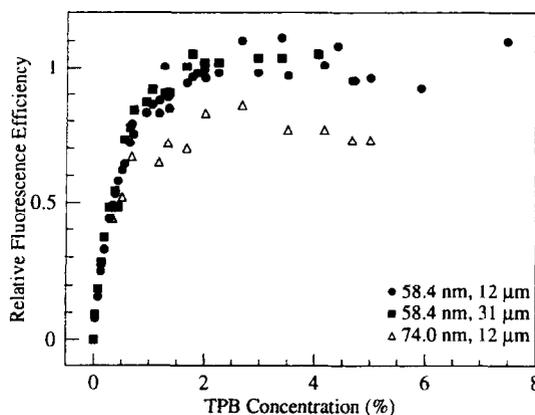


Fig. 5. Fluorescence efficiencies of thin TPB doped polystyrene films relative to sodium salicylate.

centration does not depend on film thickness. Evidently, the absorption length of XUV light in TPB doped polystyrene is much shorter than the film thicknesses used in this experiment. At low concentrations of TPB, fluorescence efficiencies are limited by XUV absorption by the polystyrene matrix, while the maximum fluorescent yield at higher concentrations is limited by a second process, presumably excitation quenching of the TPB by the plastic matrix. PMMA and nitrocellulose based plastic films were found to yield lower fluorescence efficiencies than polystyrene based films.

Polystyrenes of varying molecular weight and chain termination were tested as matrix materials, showing no noticeable increase in fluorescence efficiency. Matrix materials similar to polystyrene were also tested, including PVT and PDMS, yielding similar results. This stands in contrast to the case of electron scintillators, where it is found that adding methyl groups to polystyrene can increase fluorescence as much as 59% [23,24]. We attribute the lower fluorescence efficiencies of these materials to the difference in excitation mechanisms; electron scintillators are excited largely by energy transfer from the matrix to the fluor, while XUV light excites the fluors directly.

p-Terphenyl was also tested in a polystyrene matrix. In order to shift all emitted light to the visi-

ble spectrum, a small (1500 ppm) amount of POPOP [25] was added. The relatively high fluorescent yield of TPH doped polystyrene suggests that widely used electron scintillators, usually doped with TPH and POPOP, could be used to efficiently detect XUV radiation. TPB is however the superior fluor for this application because of its high fluorescence efficiency and because it is less likely to crystallize in the film than TPH or DPS, allowing greater optical clarity.

#### 4.2. Measurements using scintillations in gaseous argon

Relative fluorescence efficiencies as a function of TPB concentration are shown in Fig. 6. TPB concentrations up to 50% have been found to show no visible crystallization of TPB in the polystyrene matrix while with higher concentrations the TPB tends to crystallize within the matrix. Thus the measurements have been limited to concentrations up to 50% TPB in polystyrene. Different molecular weight polystyrene (range MW = 10,000–700,000) has been used with a TPB concentration of 50% showing no change in efficiency.

Considerable ageing of the wavelength-shifter doped plastic layers has been noted when these

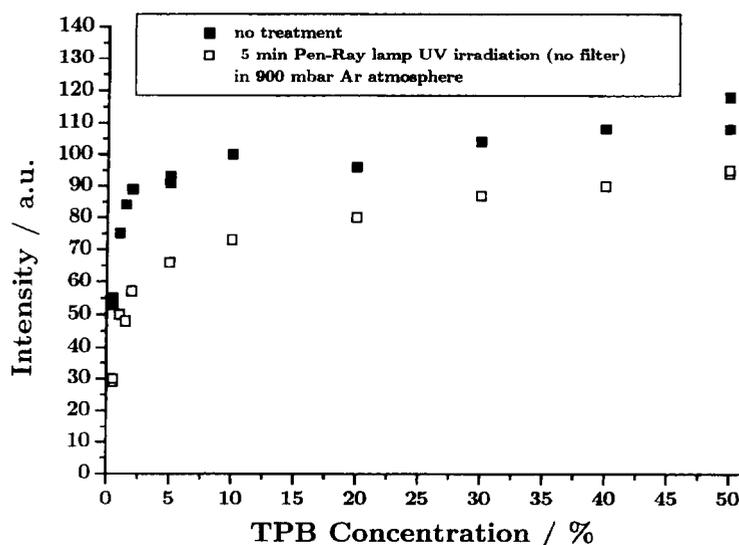


Fig. 6. Relative fluorescence quantum efficiency of TPB doped polystyrene films as a function of TPB concentration.

came into contact with the atmosphere and were illuminated with a source of soft UV at 254 nm. The samples used for these experiments have been measured directly after the application of the wavelength shifting layers. By pumping the samples in a vacuum oven it could be shown that there is no significant effect on the fluorescence efficiency due to long term residual solvent in the plastic. The results in Fig. 6 were taken with a 5 min exposure to a xenon (Pen-Ray) [26] lamp in a 900 mbar argon atmosphere. Deterioration due to exposure to UV in the laboratory atmosphere is significantly worse; exposure to the same UV illumination in the atmosphere resulted in a deterioration by a factor of four. Exposure to the ordinary fluorescent lighting in laboratory air for 24 h resulted in a factor of two reduction in pulse height.

In measurements using argon scintillations where the wavelength shifter was coated on the walls of the cylindrical cell (work in progress) we have found that the attenuation of the signal as a function of distance of the  $\alpha$  source from the end window was much greater in cells coated with evaporated films. For distances larger than 8 cm (cell i.d. 44 mm) the clear films were superior, in spite of their smaller intrinsic efficiency.

## 5. Conclusion

Fluorescence efficiencies of evaporated, sprayed, and doped plastic films at incident wavelengths of 58.4 and 74.0 nm were measured. Measurements made with the argon technique are in good agreement with those made with the discharge source. Optimum coating thicknesses and dopant concentrations have been found for these films. We have found that the thick evaporated films necessary for efficient soft UV detection can be replaced by thinner, less opaque films when detecting XUV radiation. Evaporated films of TPB, PTP, and DPS have been found to yield especially high fluorescence efficiencies.

Doped plastic films are a useful alternative to evaporated films. Although they have lower fluorescence efficiencies than comparable evaporated films, they can be index matched to plastic light guides, avoiding the need for a secondary wave-

shifter for light guide coupling. In addition, tubes coated with transparent plastic films show significantly better transmission than tubes coated by evaporation, which can be an advantage. These clear films could also find use as sensitive coatings for XUV imaging systems, where low scattering and high transmission of the fluorescent light are important.

Both evaporated films and doped plastic films show great potential in the construction of detection systems for measuring scintillations in liquid helium. Design and optimization of such systems is currently in progress.

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