

# A novel fluorescence technique for measurements of additive migration from polymers

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Diffusion coefficients for two antioxidants *N,N'*-diphenyl-*p*-phenylene-diamine (DPPD) and 2,5-di(5-*tert*-butyl-2-benzoxazolyl)thiophene (Uvitex OB) have been measured by extraction from a low density polyethylene film into 1-propanol at 22°C. Extraction was carried out in a special cuvet-equipped vessel which excludes oxygen during extraction and permits direct fluorescence monitoring of the extraction solvent. Oxygen exclusion eliminates errors due to fluorescence quenching and antioxidant oxidation and allows precise measurement of the diffusion coefficient.

(Keywords: antioxidant; diffusion coefficient; *N,N'*-diphenyl-*p*-phenylenediamine; extraction; low density polyethylene; migration; 1-propanol; Uvitex OB)

## INTRODUCTION

The durability of most commercial polymers depends mainly on the presence of additives which maintain useful properties. However, the additives can be lost by exudation, volatilization, and solvent extraction during fabrication, and also by processes occurring under end-use conditions since the loss of the additives is followed by the failure of polymers, it is important to measure additive migration from polymers.

A number of techniques have been used to measure additive migration. For example, Johnson and coworkers<sup>1-3</sup> measured the migration of benzophenone u.v. stabilizers by radioactively labelling their compounds. Similarly, Smith and coworkers<sup>4</sup> used radioactively-labelled  $n\text{-C}_{18}\text{H}_{38}$ ,  $n\text{-C}_{32}\text{H}_{66}$  and BHT[2,6-bis(1,1-dimethylethyl)-4-methylphenol] to measure the migration of their compounds from both linear and branched polyethylenes into ethanol and into *n*-octanol. In addition, Klein and Briscoe<sup>5-7</sup> used infra-red micro-densitometry to measure the diffusion of deuterium-labelled long-chain amides in polyethylene.

Although the fluorescence technique has been used to determine additive concentrations in polymers<sup>8,9</sup>, to our knowledge, there has been no report on the use of this technique to measure the diffusion of an additive from a polymer matrix into an extracting solvent. To carry out successfully a diffusion measurement by the fluorescence technique, one must take precautions to exclude oxygen from the extracting solvent since oxygen quenches the fluorescence of the additive and, in some cases, contributes to its photodegradation. In this paper, we describe how oxygen exclusion was incorporated into a procedure to measure the diffusion of an additive from a polymer matrix into an extracting solvent. We also give values for the diffusion coefficients of DPPD (*N,N'*-diphenyl-*p*-phenylene-diamine) and Uvitex OB [2,5-di(5-*tert*-butyl-2-benzoxazolyl) thiophene] in low-density polyethylene (LDPE) under the experimental conditions described below.

## EXPERIMENTAL\*

### Antioxidant

DPPD was purified by recrystallization from toluene according to the following procedure: A mixture consisting of 20.0 g of DPPD and 950 ml of toluene was slowly heated with stirring in a nitrogen-filled glove-bag until the temperature of the mixture reached 43°C, whereupon DPPD solids completely dissolved. The solution thus obtained was filtered by gravity inside the glove bag. After slow cooling to 22°C, crystals of DPPD formed. The filtrate containing the crystals was removed from the glove bag and placed overnight in a refrigerator at 0.5°C; subsequently, the crystals were collected on a Buchner funnel, washed with toluene chilled to 0.5°C, and vacuum-dried at room temperature.

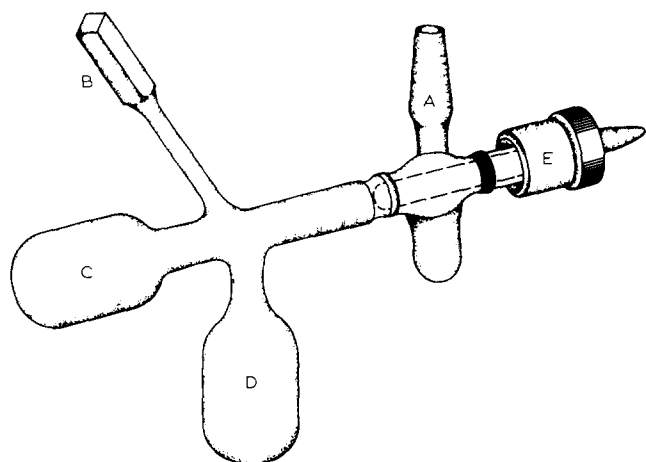
Uvitex OB, obtained from Ciba-Geigy Corp., was used without further purification when it was found that the material entirely melted within 1°C at 203°C as it was slowly heated.

### Polyethylene

NBS-SRM 1476, a low-density polyethylene whole polymer (LDPE), was washed under a nitrogen atmosphere, first with toluene at 110°C, and then with heptane at 22°C in order to remove the antioxidant that would interfere with fluorescent measurements. The LDPE powder, obtained by vacuum drying the precipitate at room temperature, was checked for fluorescent interference with antioxidant. Additional washing with 1-propanol was carried out if interference was found.

\* In this report, to describe procedures adequately, we have occasionally identified commercial products and equipment. In no case does such identification imply NBS recommendation or endorsement, nor does it imply that the item identified is necessarily the best available for the purpose.

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**Figure 1** Extraction vessel: A, ground glass joint for connection to vacuum line; B, fluorescence cuvet; C, chamber into which films are introduced prior to extraction; D, chamber in which solvent is degassed; E, outer part of removable stopcock

#### Blending of additive and polyethylene

The washed LDPE powder was dissolved in high purity solvent grade toluene at 110°C under a nitrogen atmosphere. To this solution we added sufficient DPPD to produce a mixture containing 0.05 wt% of this component on a dry basis. Alternatively enough Uvitex OB was added to toluene LDPE solutions to provide dried mixtures containing 0.08 to 0.21% antioxidant for Uvitex OB studies. For both additives toluene was removed at reduced pressure by means of a rotary evaporator. The additive-LDPE mixtures were stored in vacuum desiccators under nitrogen in the dark until use.

#### Fusion of additive-LDPE powder

The DPPD-LDPE powder used for extraction studies was pressed in air into pellets with an IR pellet press. These pellets were placed in teflon moulds, fused under a nitrogen atmosphere, and then quenched with dry ice. The films thus obtained were approximately 0.355 mm thick; they were trimmed with an arch punch to form discs 0.95 cm in diameter. Two films with a combined mass of  $0.49 \pm 0.006$  g extracted during each diffusion coefficient determination made for DPPD. For studies with Uvitex OB a single film was used.

#### Fluorescence measurements

Uncorrected fluorescence spectra were taken on a SPEX spectrofluorimeter equipped with a thermostatically controlled sample holder kept at 22°C, and a reference detector which was used to correct for variation in the lamp intensity. Each fluorescence reading was referenced to a quinine sulphate standard (NBS SRM 936) excited at 350 nm and emitting at 450 nm. All the spectra were taken with frontal illumination. The excitation wavelength  $\lambda_{ex}$  was 305 nm and the emission wavelength  $\lambda_{em}$  was 400 nm for DPPD. The bandpasses were 10 nm and 5 nm for the excitation monochromator and the emission monochromator, respectively. For Uvitex OB, 366 and 390 nm were used for  $\lambda_{ex}$  and  $\lambda_{em}$ , respectively.

#### Extraction procedure

10 ml of 1-propanol were added to a weighed, specially constructed extraction vessel (Figure 1). A side arm of the vessel (A in Figure 1) was attached with wax to a high

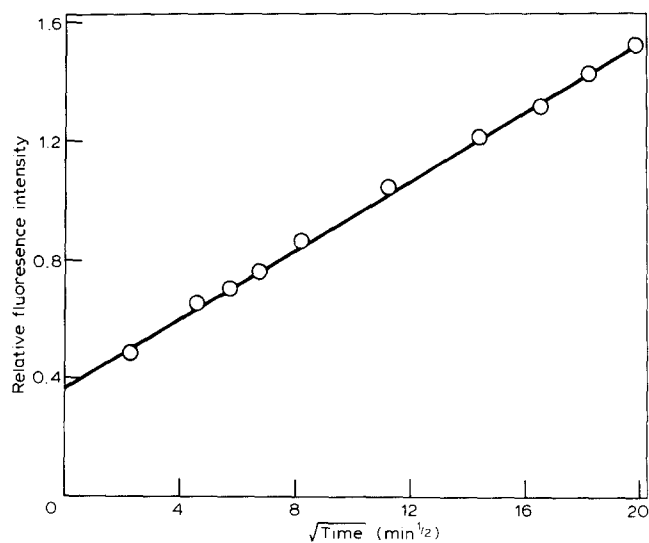
vacuum line. Solvent in chamber D was degassed inside the vessel by repeated freezing, evacuation and thawing. Partial loosening of the stopcock (E in Figure 1) opened the vessel to the vacuum line while sealing it from the atmosphere. By means of the vacuum line, oxygen-free, purified nitrogen, at a pressure slightly greater than one atmosphere, was introduced into the vessel. Then, the vessel stopcock was removed. Nitrogen gas flowed through the vessel and out the opening while a plastic tube was first inserted; then additive-LDPE films were introduced into the vessel through the tube. The plastic tube was designed to prevent transfer of stopcock grease into the vessel, and to guide the films into the empty vessel chamber (C in Figure 1). After film introduction, the stopcock was quickly replaced, and the 1-propanol allowed to thaw. The nitrogen-filled vessel was removed from the vacuum line with the stopcock closed, and the system equilibrated to 22°C.

At the beginning of an extraction experiment, 1-propanol was introduced into the chamber containing the films by tipping the vessel. The fluorescence intensity of the propanol solution was monitored in cell B and was observed to increase with time. The intensity was measured at suitable time intervals until no further increase was noted, usually after a week. Between measurements, the vessel was placed in a constant temperature bath at 22°C, and the alcohol solution covering the films was stirred with a magnetic stirrer. To guard against stopcock oxygen leakage, nitrogen was passed through needles piercing a serum cap which covered the open arm (A in Figure 1) above the stopcock.

After completion of the 22°C experiments, control experiments were performed, which established that no additional DPPD was extracted when the system temperature was increased to 60°C.

## RESULTS AND CONCLUSION

To determine the diffusion coefficient  $D$  from fluorescence measurements made on the 1-propanol solution at suitable time intervals, fluorescence intensity was plotted as a function of square root of extraction time. For these plots,



**Figure 2** Plot of measured relative fluorescence intensity,  $F_t$ , as a function of square root of time for solutions of DPPD in 1-propanol

**Table 1** Diffusion coefficients for extraction from LDPE into 1-Propanol at 22°C

Additive	$\lambda_{ex}$ (nm)	$\lambda_{em}$ (nm)	% Additive in LDPE	No. Trials	$D \times 10^{10}$ (cm <sup>2</sup> s <sup>-1</sup> )	Standard Deviation (%)
DPPD	300	405	0.05	7	8.67	4.97
Uvitex OB	366	390	0.08–0.21	4	2.04	2.2

there was an initial linear increase in fluorescence intensity followed by approach to a horizontal asymptote (at times longer than those shown in *Figure 2*) from which we obtained the initial slope, and the asymptotic fluorescence intensity,  $F_{\infty}$ . Use of the relation<sup>10</sup>

$$M_t/M_{\infty} = (4/\pi^{1/2})(Dt/l^2)^{1/2}$$

(for which  $l$  is the thickness of polymer film undergoing extraction,  $t$  is the time in seconds, and  $M_t$  and  $M_{\infty}$  are the amounts of diffusing substance present in the extracting solvent at times  $t$  and at equilibrium respectively) allowed calculation of  $D$  if the ratio  $M_t/M_{\infty}$  was replaced by the ratio of sample fluorescence intensity at time  $t$ ,  $F_t$ , to sample fluorescence intensity after extraction was complete,  $F_{\infty}$ . We verified that in the concentration range of these experiments, fluorescence intensity is linearly related to concentration. Values for  $D$  found from our measurements appear in *Table 1*.

Advantages of this method are that once the films are added, the vessel need not be reopened, thus eliminating errors produced by oxygen fluorescence quenching or solvent loss. Because of the careful control of other experimental sources of error, the accuracy with which  $D$  can be found is limited principally by the accuracy of the final fluorescence value ( $F_{\infty}$ ), and accuracy of the  $F_{\infty}$  value is dependent upon a reliable fluorescence standard. Use of the uranyl oxide-containing glass block ( $\lambda_{ex} = 365$  nm,  $\lambda_{em} = 530$  nm) for this purpose did not prove as satisfactory as did use of a solution of quinine sulphate. The quinine sulphate standard was superior because it has a small fluorescence intensity change with temperature, is conveniently prepared at the desired fluorescence

intensity, and absorbs and emits at wavelengths close to those for the compounds being studied. Fresh solutions can be made which provide reproducible values with time.

To summarize, we have described a convenient and accurate method for determining the migration rates of fluorescent additives from polymer matrices into solvents. Since many additives are fluorescent, the method should have wide applications. The method can also be used to determine the diffusion coefficients of additives in polymer matrices, if the extracting solvents do not swell the polymers and Fickian diffusion prevails.

#### ACKNOWLEDGEMENT

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