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Personal Solar UV Exposure Measurements Employing Modified Polysulphone with an Extended Dynamic Range^{+¶}

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ABSTRACT

Polysulphone dosimeters using a simple to use filter have been developed and tested to provide an extended dynamic measurement range of personal solar UV exposures over an extended period (3 to 6 days). At a Southern Hemisphere subtropical site (27.6°S, 151.9°E), the dynamic range of the filtered polysulphone allowed measurements of erythemal exposures to approximately 100 minimum erythemal dose (MED) for a change in optical absorbance at 330 nm (ΔA_{330}) of 0.35. In comparison, unfiltered polysulphone dosimeters were exposed to approximately 8 MED for the same ΔA_{330} . The error associated with the use of the filtered polysulphone dosimeters is of the order of $\pm 15\%$, compared with $\pm 10\%$ of the unfiltered variety. The developed filtered polysulphone dosimeter system allowed the measurement of erythemal UV exposures over 3 to 6 days at a subtropical site without the need to replace the dosimeters because of saturation. The results show that longer-term measurement programs of personal solar UV have been made more feasible with the use of these polysulphone dosimeters with an extended dynamic range compared with unfiltered polysulphone dosimeters.

INTRODUCTION

Minimization of the UV exposure of humans is necessary to reduce the risk of the induction of skin cancers, skin damage, premature skin aging and wrinkling, and sun-related eye disorders (1). On the beneficial side, exposures to UV are required for the production of vitamin D (2). Consequently, an understanding of the solar UV environment for humans is essential to optimize the solar UV exposures to the population. An essential component of this is the monitoring of personal UV exposures during normal daily activities with dosimeters. This can be achieved through the use of biological and chemical dosimeters with the general characteristic that a measurable property changes in a reproducible manner upon exposure to solar UV radiation (3–7). One category of UV dosimeters undergo UV-induced photodegradation, for example, poly-sulphone that responds to wavelengths shorter than approximately 340 nm (8,9), allyl diglycol carbonate (CR-39) (10), nalidixic acid (11), 8-methoxypsoralen (12), poly(phenylene oxide) (13,14) and iodouracil (15). Other types of UV dosimeters are based on the photodamage of DNA in spores, bacteria or bacteriophages (16–18) or the conversion of 7-dehydrocholesterol to previtamin D (19).

The use of polysulphone as a dosimeter material is a straightforward process by measuring the UV-induced change in optical absorbance at 330 nm (ΔA_{330}). The spectral response (R[λ]) of polysulphone to solar UV radiation approximates the erythemal action spectrum (20) and has a good cosine response to UV with incidence angles up to 70° to the normal (21). Recent research has reported that the $R(\lambda)$ of polysulphone is closer to the erythemal action spectrum than reported previously (22). In summary, polysulphone is a valuable tool for the assessment of personal solar erythemal UV exposures to humans during normal daily activities over a wide range of latitudes (for example, see 23-34). Polysulphone dosimeters have been used in the investigation of the effectiveness of UV protection provided by the different UV minimization strategies of tree shade, hats, clothing, shade cloth and the timing of outdoor activities (35-45). Other applications have been the measurements of biologically damaging UV underwater (46), the measurements of the UV exposures to the surface of the eye with polysulphone fabricated into contact lenses (47) and in the measurement of personal UV exposures in a welding environment (48).

For ΔA_{330} above 0.3, the coefficient of variation increases and the error associated with the use of polysulphone increases as the response of polysulphone approaches saturation (8). Consequently, for high ambient UV environments, the dynamic range of polysulphone for UV exposures allows the use of the polysulphone to measure solar UV over periods of approximately 3 to 6 h. Measurement periods longer than this require the replacing of the dosimeters. Previously, the use of mesh as a filter over the polysulphone has been reported to extend the dynamic range of polysulphone (9). In this article, the use of an inexpensive, simple and readily available filter that is incorporated as part of the dosimeter to extend the dynamic range is used in personal solar UV measurements.

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Abbreviations: ΔA_{330} , change in optical absorbance at 330 nm; EST, Australian Eastern Standard Time; MED, minimum erythemal dose; $R(\lambda)$, spectral response; SZA, solar zenith angle; $T(\lambda)$, spectral transmission; UV_{ery}, erythemally weighted UV.

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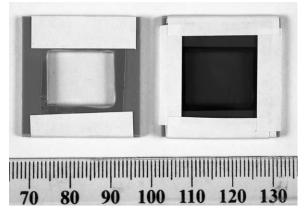


Figure 1. A sample of the unfiltered and filtered dosimeters.

MATERIALS AND METHODS

Filtered polysulphone. The filter used was black and white photographic film (Kodak Plus-X Pan, ISO 125, Brisbane, Australia) that had been developed with a standard processing technique of developer (7 min at 20°C), stop bath (30 s), fixer (2 min), water rinse (30 s), water rinse (120 s), water rinse (5 min) and photoflo (1 min). A higher neutral density filter can be obtained by exposing the film evenly across its entire length, to ensure a uniform optical density, to visible light. The reproducibility of the transmission of the filter was tested by developing two films and comparing the transmission below 340 nm. The difference in the transmission below 340 nm was minimal, with the average of the transmission difference at 0.14%. The average thickness of the filter was 0.15 mm, and a single piece of this processed photographic film was used as a filter for the polysulphone dosimeter. The holders for the dosimeters were 3×3 cm in size and fabricated from thin polyvinylchloride with an aperture of approximately 1.2×1.6 cm. Polysulphone film of approximately 40 μ m thickness, manufactured by the first author of this article at the University of Southern Queensland, Toowoomba, Australia, was attached with adhesive tape to the holder and the filter attached over the polysulphone so that no UV radiation could penetrate beneath the filter. A sample of the filtered and unfiltered dosimeters is shown in Fig. 1.

A UV/visible spectrophotometer (model 1601, Shimadzu Co., Kyoto, Japan) was used to measure the pre- and postexposure absorbances of the filtered dosimeter. The reliability of the ΔA_{330} was improved by the measurement of the pre- and postexposure optical absorbances at four locations over the dosimeter (49). In addition, the pre- and postexposure optical transmission spectrum of the filter and the absorption spectrum of the filtered dosimeters were measured in the spectrophotometer from 300 to 400 nm in 1 nm increments. The transmission spectrum of the filter was measured to quantify the transmission of the filter in the UV waveband and to investigate the error associated with any possible deterioration of the filter due to solar UV exposure. The spectrum of the pre- and postexposure optical absorbency of the filtered dosimeters was measured in the spectrophotometer to determine the wavelength-dependent change in the filtered dosimeter as a result of solar UV exposures.

 $R(\lambda)$ and reproducibility. The $R(\lambda)$ of the filtered polysulphone to UV, $SRF(\lambda)$, was calculated as follows:

$$SRF(\lambda) = \mathbf{R}(\lambda) \times \mathbf{T}(\lambda)$$
 (1)

where $R(\lambda)$ is the spectral response of unfiltered polysulphone available in the literature (9) and $T(\lambda)$ is the spectral transmission of the filter. The results were divided by the highest value (at 315 nm) to normalize the data.

To test the reproducibility, nine filtered dosimeters were exposed simultaneously to solar UV over consecutive days on a horizontal plane at a subtropical Southern Hemisphere site at the University of Southern Queensland, Toowoomba, Australia (27.6°S, 151.9°E, altitude 693 m). These exposures were on an unshaded roof in winter, and the dosimeters were brought indoors each evening at sunset and exposed again at dawn.

Calibration. The dosimeters were calibrated for erythemally weighted UV (UV_{ery}) exposures (20) in both summer and winter by exposing a series of dosimeters on a horizontal plane, to solar UV on each day from approximately 0830 to 1600 h Australian Eastern Standard Time (EST) for the range of solar zenith angles (SZA) encountered in these seasons. The

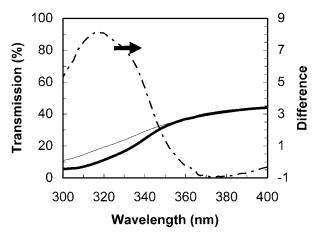


Figure 2. $T(\lambda)$ of the filter before (thick line) and after (thin line) solar UV exposure and the difference (right axis) between the post- and preexposure transmission (dashed line).

SZA ranged from 51° to 70° and 48° to 6° in winter and summer, respectively. Concurrently, the erythemal UV exposures on a horizontal plane were measured for every 5 min period in units of minimum erythemal dose (MED) with an erythemal UV meter (model 501, Solar Light Co., Philadelphia, PA) permanently mounted outdoors on an unshaded roof and whose R(λ) approximates the erythemal action spectrum. The UV meter was calibrated against a wavelength- and irradiance-calibrated spectrorradiometer that measured the solar UV spectrum S(λ) and the spectrum was weighted with the CIE (International Commission on Illumination) erythemal action spectrum A(λ) to calculate the UV_{ery} as follows:

$$UV_{ery} = \sum_{280}^{400} S(\lambda) A(\lambda) \Delta \lambda$$
 (2)

where $\Delta\lambda$ is the wavelength increment. The spectroradiometer is based on a dual holographic grating (1200 lines/mm) monochromator (model DH10, Jobin Yvon Co., Longjumeau, France) and a UV sensitive photomultiplier tube detector (model R212, Hamamatsu Co., Hamamatsu City, Japan), temperature stabilized to $15.0 \pm 0.5^{\circ}$ C and measures the spectral irradiances in 1 nm steps. The input optics of the spectroradiometer are based on a 15 cm diameter integrating sphere (model OL IS 640, Optronics Laboratories, Orlando, FL).

The filtered polysulphone calibration was over 4 days and 6 days in summer and winter, respectively, between approximately 0800 and 1600 h EST on each day, and the dosimeters were brought indoors each evening and exposed again the next day. For the solar UV exposure measurements, the postexposure "dark reaction" of polysulphone produces a change in optical absorbance of about 4% in 24 h (8). This is taken into account in the calibration of the dosimeters because both the calibration dosimeters and the dosimeters used for personal solar UV measurements have also undergone this dark reaction.

Personal solar UV exposure measurements. The use of the filtered dosimeters for personal solar UV measurements was tested in the field on a manikin headform on a motor-driven rotating platform in a similar manner to that used in previous research (36). The filtered dosimeters were attached to the vertex of the head, forehead, nose and chin and exposed for 3 days in winter from 11 June to 13 June between approximately 0900 and 1600 h EST with the SZA range of 51° to 70°. The measurement area was surrounded by buildings with partial shading each afternoon after approximately 1500 h EST. The filtered dosimeters were tested on humans for personal solar UV measurements on two subjects who wore the dosimeters on the shoulder and chest, respectively, during normal daily activities. The dosimeters were for periods of 5 and 6 days for a SZA range of 18° to 56°.

RESULTS

Filtered polysulphone

The pre- and postexposure filter $T(\lambda)$ (Fig. 2) changes from 40% to 5–10% over the 400–300 nm range. The difference between the

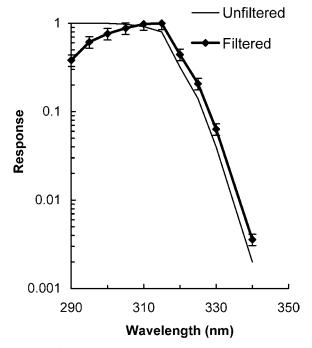


Figure 3. $R(\lambda)$ of the unfiltered polysulphone (9) and the filtered polysulphone.

post- and preexposure transmission is on the right-hand axis. The postexposure transmission of the filter increases for wavelengths shorter than 350 nm compared with the preexposure transmission. The maximum increase is at 317 nm from approximately 9.7% to 17.9%. The change in the spectral absorbance pre- and post-exposure of the filtered polysulphone from 300 to 400 nm was largest at 320 nm compared with unfiltered polysulphone that has a maximum change at approximately 330 nm (8). For the filtered dosimeter, there is a shift in the wavelength at which the maximum change occurs by approximately 10 nm because of the change in the transmission of the filtered dosimeter, and as a result, 330 nm was used in the quantification of the UV exposures.

The nine dosimeters receiving the same exposure of solar UV produced a mean ΔA_{330} of 0.172 with a standard deviation of 0.010. This standard deviation is of the order of $\pm 6\%$ and is higher than that in the literature for the reproducibility of unfiltered polysulphone ($\pm 1.4\%$) (49). The extra variation is expected to have been introduced by any possible variability over the surface of the filter. For unfiltered polysulphone, the coefficient of variation is approximately $\pm 10\%$ for a ΔA_{330} up to 0.3 (49). On the basis of this, the error associated with the use of the filtered polysulphone dosimeters to measure solar UV exposures for a ΔA_{330} up to 0.3 is expected to be of the order of $\pm 15\%$. The R(λ) of the unfiltered (9) and filtered polysulphone is shown in Fig. 3. Error bars of $\pm 15\%$ on the basis of the reproducibility of the filtered polysulphone are plotted.

Calibration

A comparison of the calibration of the unfiltered and filtered polysulphone dosimeters is shown in Fig. 4 for summer, along with a calibration of the filtered dosimeter for winter. The difference in the calibration curve between summer and winter is due to the change in the relative shape of the solar spectrum in summer

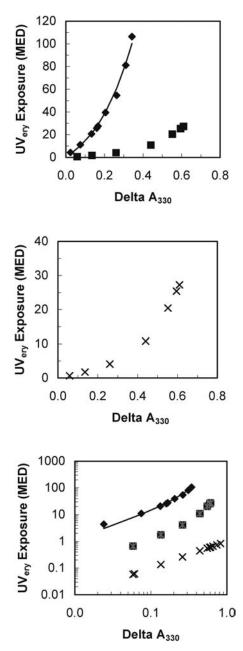


Figure 4. Comparison of the calibration in summer of the filtered dosimeters (\blacklozenge), unfiltered dosimeters (\blacksquare) and fitted curve (—) and the calibration of the filtered dosimeters in winter (x) plotted on a linear scale and a log-log scale.

compared with winter. The ΔA_{330} for the unfiltered dosimeters was approximately 0.6 due to 1 day of solar UV exposure in summer corresponding to a UV_{ery} exposure of approximately 24 MED. In comparison for a ΔA_{330} of approximately 0.35, the filtered dosimeter allowed the measurement of UV exposure over a period of 4 days, corresponding to an erythemal UV exposure of 106 MED. A trendline was fitted to the summer calibration data with the general form that has been previously used (49):

$$UV_{ery} = K[9(\Delta A)^3 + (\Delta A)^2 + \Delta A]$$
(3)

where K is a constant determined in the calibration. For the filtered dosimeter, the value of K was determined as 122.2. In comparison,

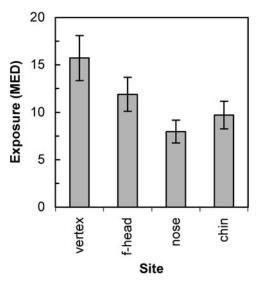


Figure 5. Personal solar UV exposures measured with the filtered dosimeters to the anatomical sites of the manikin headform.

the value of K for the unfiltered dosimeter summer calibration data was 8.8.

Personal solar UV exposure measurements

Figure 5 shows the solar UV exposures to the different facial sites on the manikin over 3 winter days measured using the filtered dosimeters, and the error is represented as $\pm 15\%$. In this case, the chin received a higher exposure than the nose because of the larger SZA in the winter and also the close proximity of the surrounding buildings increasing the relative amount of diffuse UV resulting from scattering from the walls of the buildings. The personal erythemal UV exposures to the two subjects over 6 days (subject 1) and 5 days (subject 2) are provided in Table 1. In this case, the ΔA_{330} ranged from 0.046 to 0.185.

DISCUSSION

The dynamic range of polysulphone has been extended and applied for personal solar UV exposure measurements by the use of a simple to use filter. The wavelength of 330 nm was used for the measurement of optical absorbances on the basis of the use of this wavelength for unfiltered polysulphone dosimeters by previous research (8). However, on the basis of the results from the research in this article, 320 nm appears to be a better wavelength to use in future research using filtered polysulphone dosimeters as the change in the spectral absorbance pre- and postexposure of the filtered polysulphone from 300 to 400 nm is a maximum at approximately 320 nm compared with unfiltered polysulphone that has a maximum change at approximately 330 nm. The filter material transmission after UV exposure compared with before UV exposure increases for wavelengths shorter than 350 nm as a result of UV exposure. This change is incorporated with the change in optical absorbance of the combined filter-dosimeter system and is taken into account in the calibration of the filtered dosimeters because the filters on the calibration dosimeters will also undergo this change. The difference in the normalized $R(\lambda)$ of the filtered dosimeters compared with that of the unfiltered dosimeters is largest at 290-295 nm, where the solar UV irradiance is small to negligible. This deviation of the response of the filtered

 Table 1. Personal erythemal UV exposures measured with the filtered polysulphone over 6 days (subject 1) and 5 days (subject 2)

| | UV _{ery} (MED) | |
|----------|-------------------------|-------------|
| | Subject 1 | Subject 2 |
| Shoulder | 34 ± 5 | 26 ± 4 |
| Chest | 9.8 ± 1.5 | 5.9 ± 0.9 |

polysulphone compared with polysulphone will not introduce any significant error because the filtered polysulphone dosimeters will be calibrated to the source spectrum that they will be measuring.

Filtered polysulphone extends the capability for the use of polysulphone in the measurement of the UV exposures to different anatomical sites during normal daily activities over a number of days. Results gained from this study indicate that longer-term measurement programs, using the filtered polysulphone dosimeter system will aid in the insight into human exposures over a series of days, rather than individual days.

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