

Extending the dynamic range of polysulphone for measuring UV exposures

Alfio V. Parisi^{a,*} and Michael G. Kimlin^b

^aCentre for Astronomy, Solar Radiation and Climate, Faculty of Sciences, University of Southern Queensland, Toowoomba, AUSTRALIA. 4350

^bNational Ultraviolet Monitoring Centre, Department of Physics and Astronomy, University of Georgia, Athens, GA, USA 30606

ABSTRACT

Polysulphone has been widely used as a dosimeter to quantify personal solar UV exposures to humans during normal daily activities. In summer at sub-tropical and tropical latitudes, the dynamic range for UV exposures allows the use of the polysulphone to measure solar UV over periods of approximately three to six hours. The use of mesh as a filter over the polysulphone has been previously reported to extend the dynamic range. In this paper the use of a simple filter that is incorporated as part of the dosimeter is reported. The dynamic range of the polysulphone was significantly extended with the incorporation of the filter by a factor of approximately four to five.

Keywords: Polysulphone; erythema; UV; solar; dosimeter

1. INTRODUCTION

Human exposure to solar ultraviolet (UV) radiation have been linked to an increased risk for the induction of skin cancers, skin damage, premature skin ageing and wrinkling, and sun related eye disorders¹. In order to minimize the UV exposure of humans and reduce the risk of these disorders, a complete understanding of the solar UV environment is necessary. The World Health Organization² has recommended research to monitor personal UV exposures in order to establish the percentage of the ambient solar UV received by the population. In order to monitor solar UV exposures, biological and chemical dosimeters have been developed for the measurement of UV exposures³⁻⁷. A general characteristic of these dosimeters is that a measurable property of these dosimeters changes in a reproducible manner upon exposure to solar UV radiation. This change is calibrated to a UV instrument to allow the use of the dosimeter for measuring UV exposures. Examples of UV dosimeters are polysulphone dosimeters that undergo a photochemical alteration due to UV exposures with wavelengths shorter than approximately 340 nm^{8,9}, dosimeters based on the conversion of 7-dehydrocholesterol to previtamin D¹⁰ and dosimeters based on the photodamage of DNA in spores, bacteria or bacteriophages¹¹.

Polysulphone has been widely used as a UV dosimeter to quantify personal solar UV exposures to humans during normal daily activities¹²⁻¹⁶. The spectral response of polysulphone to solar UV radiation approximates the erythral action spectrum¹⁷, hence it is a valuable tool for the assessment of erythral UV exposures. Polysulphone dosimeters have also been employed in the investigation of the UV protection provided by different UV minimisation strategies, for example tree shade¹⁸, hats¹⁹⁻²¹, cotton clothing²² and shade cloth²³ and measurements of biologically damaging UV underwater have been undertaken with polysulphone²⁴. Measurements of the UV exposures to the surface of the eye have been undertaken with polysulphone fabricated into contact lenses²⁵. The advantage of measurements with polysulphone

* Correspondence to: Alfio Parisi, Faculty of Sciences, University of Southern Queensland, Toowoomba, 4350, Australia.
parisi@usq.edu.au Ph: 61 7 4631 2226; FAX: 61 7 4631 2721.

dosimeters is that it is straight forward to process for the evaluation of the UV exposures and allows the measurement of UV exposures simultaneously at multiple sites over the object of interest.

In summer at sub-tropical and tropical latitudes, the dynamic range of polysulphone for UV exposures allows the use of the polysulphone to measure solar UV over periods of approximately three to six hours. This is due to the saturation of the response of polysulphone as a result of the protective filtering effect of the products of the photodegradation⁸. As a result, this has required the replacing of the dosimeters for the measurement of UV exposures over any longer periods. The use of mesh as a filter over the polysulphone has been previously reported to extend the dynamic range⁹. In this paper the use of an inexpensive, simple and readily available filter that is incorporated as part of the dosimeter is investigated and tested for the extension of the dynamic range of polysulphone.

2. MATERIALS AND METHODS

2.1 Dosimeters

Dosimeters were fabricated by attaching a piece of polysulphone film of approximately 40 microns thick with adhesive tape to a holder constructed from thin PVC. The polysulphone film was manufactured by the first author of this paper on a specifically constructed casting table at the University of Southern Queensland, Toowoomba, Australia. The size of the dosimeter holder is 3 cm x 3 cm with an aperture of approximately 1.2 cm x 1.6 cm. The filter utilized was black and white photographic film (Kodak Plus-X Pan, ISO 125) that had been previously exposed and developed. The average thickness of the filter was 0.15 mm. This film was exposed evenly across the entire length to ensure a uniform optical density. A single piece of this pre-exposed and processed film was employed as a filter for the polysulphone dosimeter. The filter was placed (using adhesive tape) over the polysulphone ensuring that no UV radiation could penetrate beneath the filter. During the fabrication of the filtered dosimeters it was ensured that the tape did not cover the aperture of the dosimeter holder. The dosimeter fabrication was undertaken in an environment where the ambient lighting did not have a UV component below 340 nm in order to prevent pre-exposure of the polysulphone (a darkened room with incandescent lighting). Additionally, the polysulphone film and filter were not handled on the active 1.2 cm x 1.6 cm sensor area of the dosimeter in order to avoid fingerprints or other forms of contamination of the film and filter. The fabricated dosimeters were stored in a light proof container prior to use to prevent accidental exposure to UV.

2.2 Optical absorbance/transmission

The optical transmission spectrum of the filter employed in this research was measured with a UV/visible spectrophotometer (Shimadzu Co., Kyoto, Japan). This was measured from 300 to 400 nm in 1 nm increments. In order to investigate if there is any deterioration of the filter due to solar UV, the transmission of the filter was measured pre and post-exposure to solar UV. The optical absorbance of the filtered dosimeter system was also measured in this spectrophotometer. A specifically fabricated holder was employed in the sample holder of the spectrophotometer to allow positioning of the filtered dosimeters in a reproducible orientation with respect to the spectrophotometer beam. This is important to ensure that the absorbances pre and post-exposure for each of the dosimeters are measured at a reproducible orientation. For the dosimeter holders employed in this research, this was achieved by employing a dosimeter holder containing a 3 cm x 3 cm slot for the dosimeter with the holder screwed into place in the spectrophotometer sample compartment.

The spectrum of the pre and post-exposure optical absorbency of the filtered dosimeters was measured in the spectrophotometer in order to determine the wavelength dependent change in the filtered dosimeter as a result of solar UV exposures. In order to quantify the change in optical absorbance (ΔA), the pre and post-exposure optical absorbency of the filtered dosimeters was measured at 330 nm in the spectrophotometer. This wavelength was employed based on the use of this wavelength for measuring the optical absorbances of unfiltered polysulphone dosimeters by previous research⁸. The spectrophotometer beam passes through only a small portion of the active part of the dosimeter. As a result, the reliability of the dosimetric measurement of UV exposures was improved by the measurement of the optical absorbance at four locations over the dosimeter for both the pre and post-exposure measurements²⁶. The dosimeter holder in the spectrophotometer permits the measurement of the pre and post-exposure absorbances at four reproducible points over the dosimeter.

2.3 Use of the filtered dosimeters

The reproducibility of the filtered polysulphone dosimeters was investigated by exposing nine dosimeters to solar UV over consecutive days on a horizontal plane at a sub-tropical Southern Hemisphere site at the University of Southern Queensland, Toowoomba, Australia (27.6 °S, 151.9 °E, altitude 693 m). The exposures were on an unshaded roof in winter and were brought indoors each evening at sunset and exposed again at dawn.

The calibration of the filtered dosimeters was undertaken in both summer and winter by exposing a series of dosimeters on a horizontal plane to a range of solar UV exposures on each day from approximately 8:30 to 16:00 Australian Eastern Standard Time (EST) for the range of solar zenith angles (SZA) encountered in these seasons. Concurrently, the erythral UV exposures were measured with an erythral UV meter (model 501, Solar Light Co., Philadelphia, USA) permanently mounted outdoors on an unshaded roof and whose spectral response approximates the erythral action spectrum. The UV meter was calibrated against a calibrated spectroradiometer. The number of days exposure for the filtered polysulphone calibration was 4 days and 6 days in summer and winter respectively and the exposure times on each day were from approximately 8:00 to 16:00 EST (Australian Eastern Standard Time).

Following exposure to UV radiation, the polysulphone film undergoes a “dark reaction” that produces a change in optical absorbance of about 4% in 24 hours after the polysulphone has been removed from the UV source⁸. The consequence of this is that there is a change in the optical absorbance of the dosimeters during each overnight period of the exposure period. However, this change in absorbance is taken into account in the calibration of the dosimeters as the calibration dosimeters have also undergone this “dark reaction”.

In order to test the use of the filtered dosimeters in the field, four dosimeters were attached to a manikin headform on a motor driven rotating platform (Figure 1) in a similar manner to that employed in previous research¹⁹. The filtered dosimeters were attached to the vertex of the head, forehead, nose and chin and exposed for three days in winter from 11 June to 13 June. On each day, the exposures were between approximately 9:00 and 16:00 EST and the headforms and dosimeters were brought in overnight. The site of the exposures was surrounded by buildings with partial shading each afternoon after approximately 15:00 EST.

3. RESULTS

3.1 Optical absorbance/transmission

The spectral transmission of the filter pre and post-exposure is shown in Figure 2 and the transmission changes from 40% to 5-10% over the 400 nm to 300 nm range. From the shape of the transmission curve, it is inferred that the visible irradiances at the wavelengths longer than 400 nm are also attenuated by the filter. However, the attenuation in the visible does not influence the use of the dosimeter for measuring UV wavelengths as the polysulphone is not responsive to wavelengths longer than approximately 340 nm⁹. As a result of exposure to solar UV, the transmission of the filter increases for wavelengths shorter than 350 nm by approximately 5%. There is negligible change in the filter transmission for wavelengths between 350 and 400 nm. This change in the percentage transmission of the filter at the shorter wavelengths will be incorporated with the change in optical absorbance of the combined filter/dosimeter system. As a result, it will be taken into account in the calibration of the filtered dosimeters as the filters on the calibration dosimeters will also undergo this change.

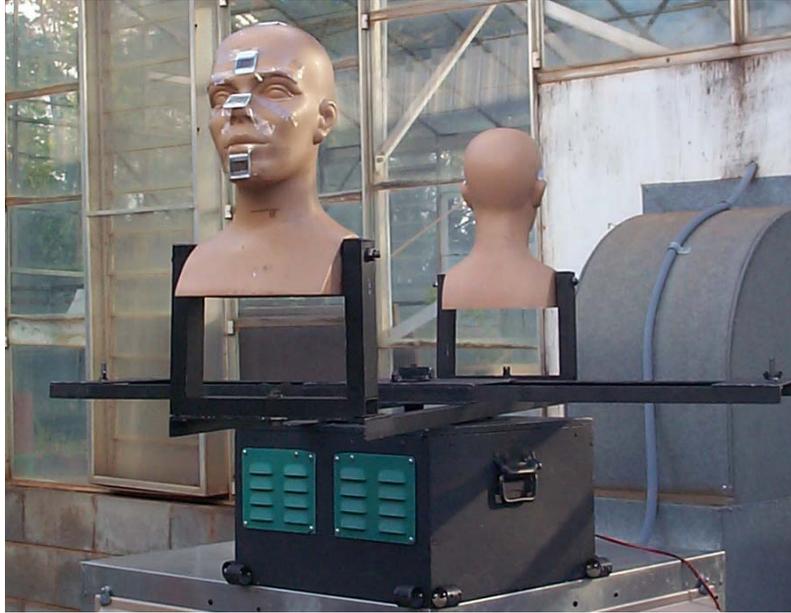


Figure 1: The filtered dosimeters exposed on a manikin headform mounted on a motor driven rotating platform.

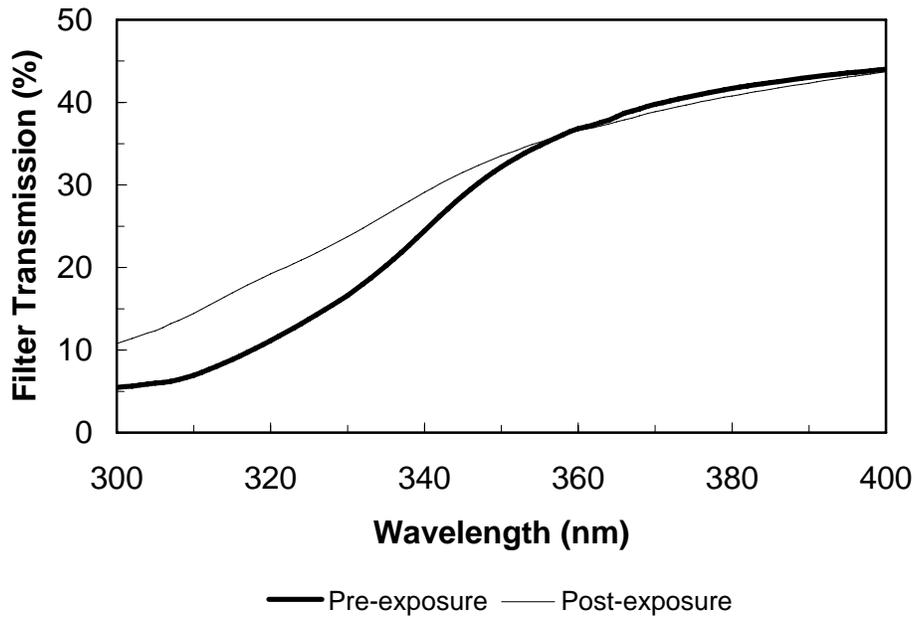


Figure 2: Percentage transmission of the filter used in the filtered dosimeter, pre and post-exposure to solar UV radiation.

The spectral absorbance pre- and post-exposure of the filtered polysulphone from 300 to 400 nm is shown in Figure 3. This change in absorbance is the combined result of the change in absorbance of the polysulphone and the filter. For unfiltered polysulphone the maximum ΔA is at approximately 330 nm⁸. The ratio of the post to pre-exposure absorbances is plotted on the right hand axis of Figure 3. For the filtered dosimeter, there is a minor shift in the wavelength at which the maximum ΔA occurs to a wavelength shorter than 330 nm. This is due to the change in the transmission of the filter (Figure 2). However, there is still an appreciable ΔA at 330 nm for the filtered dosimeter and as a result, this wavelength will to be employed in the quantification of the ΔA and the UV exposures.

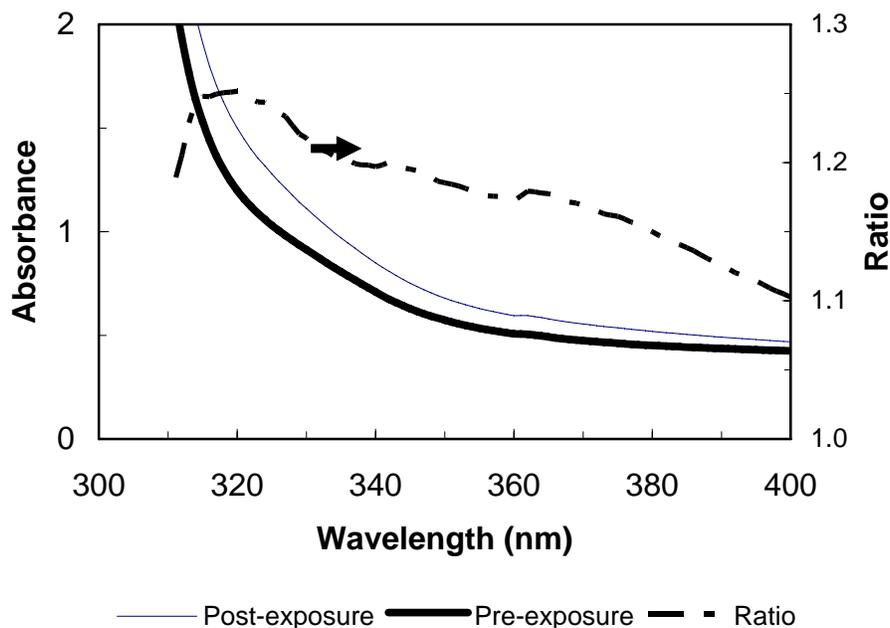


Figure 3: Spectral absorbance of the filtered dosimeter system pre and post-exposure to solar UV and the ratio of the post to pre-exposure absorbances (right axis scale).

3.2 Spectral response

The spectral response of the filtered polysulphone to UV (Figure 4) was calculated as follows:

$$R(\lambda) * T(\lambda)$$

where $R(\lambda)$ is the spectral response of unfiltered polysulphone as determined previously⁹ and $T(\lambda)$ is the spectral transmission of the filter prior to UV exposure as shown in Figure 2. This can introduce an error of approximately 5% as the transmission of the filter changes by up to approximately 5% as a result of UV exposure. However, error bars of $\pm 5\%$ on the data points in Figure 4 are smaller than the size of the symbols. The calculation was performed at each of the data points in Figure 4. Dividing the results by the highest value (at 315 nm) provides a normalisation of the data and produces the data in Figure 4. Following normalisation, the largest difference between the response of the unfiltered and filtered polysulphone occurs at 290-295 nm. The solar UV irradiance is small to negligible at these wavelengths and this deviation of the response of the filtered polysulphone compared to polysulphone will not introduce any significant error as the filtered polysulphone dosimeters will be calibrated to the source spectrum that they will be measuring.

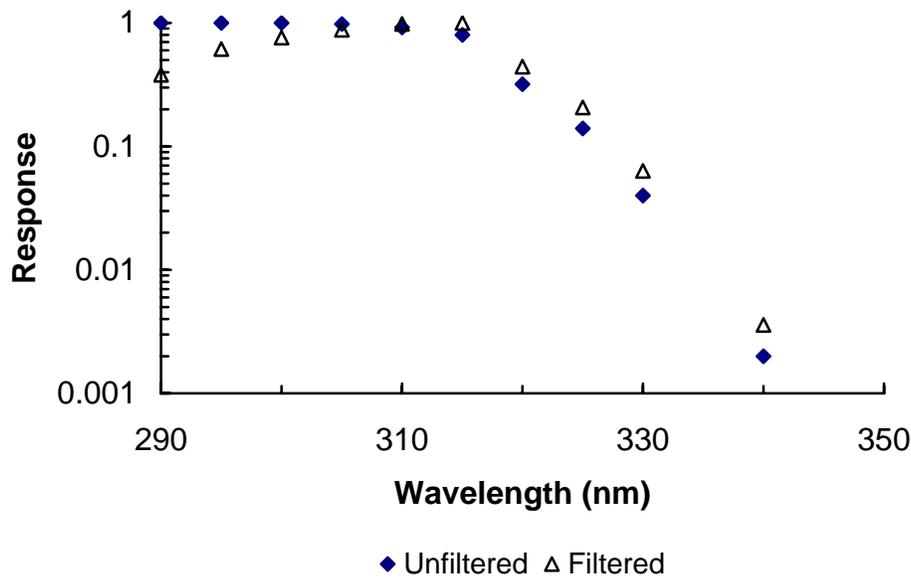


Figure 4: Spectral response of unfiltered polysulphone⁹ and the normalized spectral response multiplied by the transmission of the filter.

3.3 Calibration

The calibration of the unfiltered and filtered polysulphone dosimeters at a Southern Hemisphere sub-tropical site during summer 2003 are shown in Figure 5. Both the filtered and unfiltered dosimeter calibrations were started on the same day (14 Jan 2003). The unfiltered dosimeters underwent a change in absorbance (ΔA) at 330 nm of approximately 0.6 as a result of one day of solar UV exposure in summer. This corresponded to approximately 24 MED (minimum erythemal dose) of erythemal UV exposure. An MED is defined as the amount of erythemal UV required to produce barely perceptible erythema in people with skin type I after an interval of 8 to 24 h following UV exposure²⁷. Calibration of the broad band meter used for the calibration of the filtered dosimeters against a calibrated spectroradiometer provided a conversion factor in this case of 218 J m⁻² as equivalent to 1 MED. In comparison the filtered UV allowed the measurement of UV exposure over a period of 4 days, corresponding to an erythemal UV exposure of 106 MED. The resulting ΔA at 330 nm is approximately 0.35.

The calibration equation of the filtered dosimeters at the sub-tropical Southern Hemisphere site in summer is:

$$UV_{ery} = 3305.7(\Delta A)^3 - 861.35(\Delta A)^2 + 214.06(\Delta A) \quad \text{MED}$$

with an R squared value of 0.998. A different calibration curve was found for the filtered dosimeters in winter (Figure 6) with the expression:

$$UV_{ery} = 4 \times 10^{-7}(\Delta A)^3 - 0.0002(\Delta A)^2 + 0.0125(\Delta A) \quad \text{MED}$$

with an R squared value of 0.996. The difference in the calibration curve is due to the change in the relative shape of the solar spectrum in winter compared to summer.

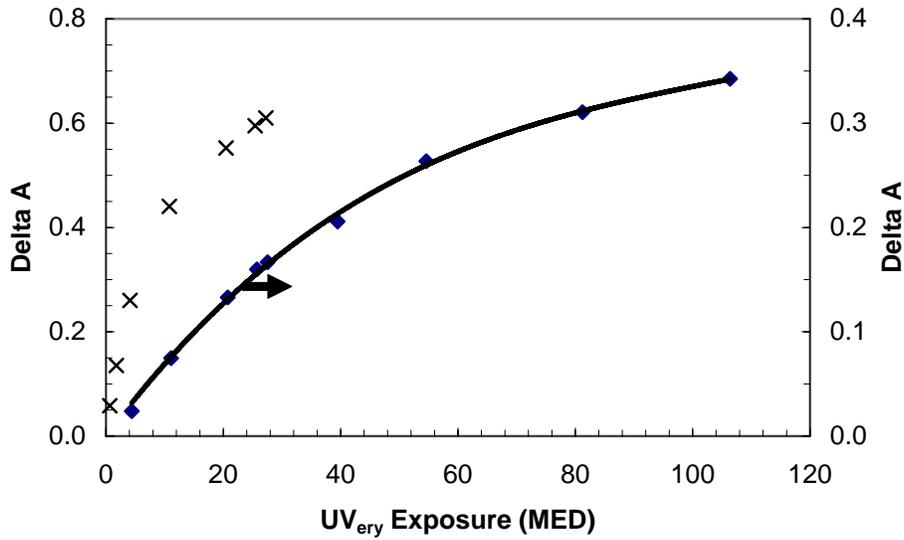


Figure 5: Comparison of the calibration of the unfiltered polysulphone (x) (left axis scale) and the filtered polysulphone (♦) (right axis scale) at a sub-tropical Southern Hemisphere site in summer.

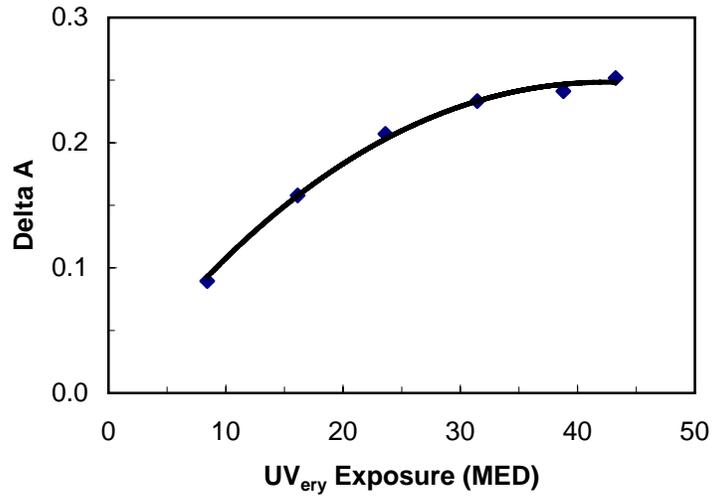


Figure 6: Calibration of the filtered polysulphone to winter solar UV at a sub-tropical Southern Hemisphere site.

3.4 Reproducibility

The result of exposing the nine dosimeters to the same exposure of solar UV produced a mean ΔA of 0.172 with a standard deviation of 0.010. This is of the order of $\pm 6\%$ and is higher than that found previously for unfiltered polysulphone ($\pm 1.4\%$)²⁶. The extra variation is expected to have been introduced by any possible radiation transmission variability within the filter. For unfiltered polysulphone, previous research has found a coefficient of variation of

approximately $\pm 10\%$ for a ΔA up to 0.3²⁶. Based on this, the error associated with the use of the filtered polysulphone dosimeters to measure solar UV exposures as described in this paper is expected to be of the order of $\pm 15\%$.

3.5 Solar UV exposures

The solar UV exposures to the different facial sites over three winter days measured using the filtered dosimeters are shown in Table 1 and the error is represented as $\pm 15\%$. Generally, for small solar zenith angles (SZA) in an open environment, the bridge of the nose is expected to receive higher exposures than a more vertical surface such as the chin¹⁹ due to the angle of the nose with respect to the sun. In this case, the opposite is found and it is expected that it is due to the larger SZA at the time of this research and also the close proximity of the surrounding buildings increasing the relative amount of diffuse UV due to scattering from the walls of the buildings.

Table 1: Cumulative erythemal UV exposures over three winter days to different facial sites measured using the filtered dosimeters.

Site	UV _{ery} (MED)
Vertex	16 \pm 2
Forehead	12 \pm 2
Nose	8.0 \pm 1.2
Chin	9.7 \pm 1.2

4. DISCUSSION

The dynamic range of polysulphone has been extended by the use of a simple to use and readily available filter. Previous to this work, the usefulness of polysulphone film at tropical and sub-tropical latitudes was limited to single day exposure measurement only, requiring high fabrication costs and personnel requirements. This filtered polysulphone dosimeter system has extended the possibilities for the use of polysulphone in the quantification of the erythemal UV exposures to humans during normal daily activities. The use of the filter for polysulphone extends the capability for the use in the measurement of the UV exposures to different anatomical sites during normal daily activities. The developed filtered polysulphone dosimeter system will facilitate the measurement of erythemal UV exposures over a number of days. Results gained from this work 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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