Dosimeter Based on 8-Methoxypsoralen for UVA Exposures over Extended Periods

L. Wainwright1*, A.V. Parisi1 and N. Downs1

1Faculty of Health, Engineering and Sciences, University of Southern Queensland, Toowoomba. 4350. Australia

*Corresponding author
Abstract

A miniaturized UVA dosimeter based on 8-methoxypsoralen (8-MOP) has been developed and characterized for the evaluation of UVA (320 - 400 nm) exposures over extended periods longer than one day. Current research indicates that UVA is a contributing factor in non-melanoma skin cancers and the associated financial cost of damage caused by UVA is significant. Dosimetry is a technique that is commonly employed to measure UV exposures to an object or subject. Miniaturized dosimeters using polyphenylene oxide (PPO) have previously been used to measure received erythemal UV (UV_{ery}) exposures. A new miniaturized dosimeter using 8-MOP as the photoactive material has been characterized and a technique developed for the calibration of UVA exposures. Using Mylar as a UVB filter the spectral response showed 8-MOP to react only to wavelengths between 320 - 400 nm. The measured cosine response has an error of less than 13.8% for angles between 0° and 60°. Seasonal dose response tests conducted, indicate that these UVA dosimeters are able to measure exposures < 4.6 kJ/m^2. These results have shown that a dosimeter constructed from 8-MOP in conjunction with a Mylar filter can measure UVA exposures over extended periods longer than one day.

Keywords

Dosimeter; UVA; UV; 8-MOP; 8-methoxypsoralen
1. Introduction

In light of the changing composition of the Earth's atmosphere and the consequences of ultraviolet (UV) radiation for the biological environment, it is important to be able to determine the specific UV levels that reach humans on the Earth's surface. Current research indicates that the financial and social cost of damage such as melanoma, caused by UVB (280-320 nm) is extensive and that UVA (320-400 nm) is a contributing factor in skin cancers [1]. The longer wavelength of UVA means that it is not affected by atmospheric (Rayleigh) scattering to the same degree as UVB. Additionally, ozone absorption is minimal in the UVA waveband, with absorption falling significantly from 315 to 320 nm [2]. There has been less research in the area of UVA damage to humans than that caused by UVB although it has been established that UVA contributes to biological damage [3, 4], the damage caused by UVA is produced differently to that caused by UVB. UVA penetrates further into the human skin, with the impacts being less acute but taking longer to show [5]. Given that there is greater than six times more measurable UVA than UVB [5] in terrestrial surface spectra, it is possible that a larger dose of UVA compared to UVB may be received, thereby enhancing the potential biological effect.

Dosimetry is a technique that is commonly employed to measure UV exposures to an object or subject. Dosimeters have been employed in a number of studies [6, 7, 8] that have successfully measured UVB radiation exposures. Dosimeters have also been used to measure UVA exposures for specified wavelengths and limited times [9, 10]. There are other dosimetric systems capable of measuring the full UV spectrum and also ionising radiation [11 12].
Dosimeters utilizing polyphenylene oxide (PPO) or polysulphone (PS) that have a response to the UVB wavelengths have previously been used to measure received erythemal UV \( (U_{\text{ery}}) \) exposures by humans for exposure periods of half a day up to seven days depending on the season and latitude \([13, 14]\). PS dosimeters allow the measurement of \( U_{\text{ery}} \) exposures over shorter time periods of up to one day. A PPO dosimeter with its larger dynamic range can record longer exposures of five or seven days subject to seasonal and atmospheric conditions \([15]\). An extension of this type of dosimeter is the PVC based dosimeter \([16, 17]\) that allows \( U_{\text{ery}} \) measurements over periods of up to three weeks before requiring replacement. A dosimeter based on phenothiazine has been reported for the measurement of UVA exposures. The phenothiazine dosimeter is useable for periods up to approximately half a day at subtropical southern latitudes \([9]\). Further UVA dosimeters employ the use of radiochromic film for measurement over shorter periods \([18, 19]\) however these require frequent changes over extended measurement periods making them impractical for some applications. A short wavelength UVA dosimeter has also been employed in measuring the shorter UVA2 wavelengths of 320 to 340 nm \([10]\). There is however, a research need for a dosimeter sensitive to the UVA1 (340 to 400 nm) and UVA2 (320 to 340 nm) wavebands that allows for measurement over longer time frames. This research reports on the characterization and evaluation of a UVA dosimeter sensitive to wavelengths between 320 to 400 nm, and which is capable of longer periods of measured exposure than is possible with the dosimeters currently in use.

2. **Materials and Methods**

Diffey and Davis \([20]\) identified, but only partially characterized and evaluated a potential UVA dosimeter using 8-methoxypsoralen (8-MOP). The following tests have been undertaken in order to assess the capability of 8-MOP for use as a long term UVA dosimeter: the dark
reaction, repeatability of measurement, seasonal dose response, cosine response, spectral response, temperature independence and dose rate independence [14, 21, 22].

2.1 Dosimeter Fabrication

The 8-MOP film for the UVA dosimeter was cast using a solution of 8-MOP (Sigma, Saint Louis, USA) and polyvinyl chloride (PVC) (catalogue no. 34,657-6, Sigma Aldrich) dissolved in tetrahydrofuran (THF) [20] on a specifically constructed casting table employing a glass slab smooth to one micron. The spectral response of the PVC dosimeter determined there was no reaction of this dosimeter in the UVA area [17]. These sheets have an average thickness of 26 μm as measured using a thickness gauge (Logitech, UK). The cast film was attached to dosimeter holders made with a thin flexible plastic frame measuring 1.0 cm x 3.0 cm, with a 0.7 cm diameter aperture at one end. This miniaturized size provides a dosimeter that is smaller and less obtrusive than the 3 cm x 3 cm size dosimeter used with previous long-term film dosimeters [23, 16]. The sheets of film were cut into 1.0 cm x 0.9 cm sections and attached to the frame using waterproof tape (Figure 1). To ensure that 8-MOP only reacts to the UVA waveband the dosimeter film was covered with a piece of 120 μm thick Mylar (Cadillac Plastics, Australia) that does not transmit the majority of the UVB wavelengths [24, 25].

Figure 1 – Photograph of a fabricated miniaturized UVA dosimeter.
To provide information on the degree of photodegradation of the film, the dosimeters were measured for optical absorbance both before and after exposure. Using a spectrophotometer (UV-1601, Shimadzu & Co, Kyoto, Japan) with a rotating mount specifically constructed to hold the miniaturized dosimeters, each dosimeter was measured at four different sites over the dosimeter film surface by rotating the dosimeter and mount in increments of 90° and measuring the absorbance at each increment. The testing of the dosimeters was carried out by measuring the variation in absorbance at a specific wavelength of 305 nm. This wavelength corresponds to the maximum change in optical absorbance for 8-MOP [20].

The mean of the four measured absorbances was used for all calculations in the characterization and evaluation of the dosimeter. Using the measured absorbance at four separate sites over the dosimeter improves the accuracy of the individual measurements as it takes into account any variations in thickness of the photoactive material or disturbances that may have occurred on the surface during deployment. During absorbance measurements with the spectrophotometer, each dosimeter was visually inspected to ensure the film was free of aberrations and breakages.

2.2 Reproducibility

It is essential that dosimeters react in a reproducible and consistent way when exposed to the same UV source under exactly the same conditions. In order to ensure that the dosimeters yielded consistent results, the reproducibility of the UV induced change of the measured mean dosimeter absorbance was assessed. Thirty 8-MOP dosimeters were exposed concurrently to five hours of solar UV in the same location and under identical conditions. The solar zenith angle range (SZA) was 71.4° - 41.8°. The dosimeters for this and the research in the following sections were exposed on a horizontal plane in an unshaded site at the Southern Hemisphere subtropical location of Toowoomba Australia (27° 33’ S 151° 55’ E, elevation of 691m) unless
otherwise stated. Absorbance measurements were taken immediately before and immediately following exposure to evaluate the consistency of the change in the absorbance of the dosimeters.

2.3 Dark Reaction

Chemical film dosimeters such as PS and PPO continue to change in optical absorbance when stored after exposure [7]. This post exposure behaviour of the dosimeters is known as the dark reaction. In this research, thirty dosimeters were exposed to five hours solar UV simultaneously under the same conditions. This was done on a relatively cloud free day with the solar disc unobscured by cloud. The SZA range was 71.4° - 41.8°. The absorbance of the dosimeters was measured immediately after removal from the source and the dosimeters were then placed in a light free box. The dark reaction was quantified by measuring the pre exposure absorbance of each dosimeter and measuring the post exposure absorbance immediately following exposure to give the change in absorbance at nil storage time ($\Delta A_0$). The dosimeters were removed from storage at different time intervals to determine subsequent absorbance changes ($\Delta A_t$). In this way any change in absorbance from $\Delta A_0$ can be attributed to a dark reaction. For each time (t), $\Delta A_t$ was calculated as:

$$\Delta A_t = A_t - A_i.$$  \hspace{1cm} (1)

where $A_t$ is the absorbance following storage for a given time and $A_i$ is the absorbance prior to exposure. The dark reaction (D) after a given time was expressed as a percentage and calculated as:

$$D = \frac{(\Delta A_t - \Delta A_0)}{\Delta A_0} \times 100$$  \hspace{1cm} (2)
2.4 Spectral Response
In order to ensure that the 8-MOP dosimeter was only reacting to the UVA part of the spectrum, a spectral response was determined for the dosimeter. Sets of two dosimeters were simultaneously exposed to a specific wavelength from 300 to 400 nm in 10 nm increments. The discrete irradiances were produced using an irradiation monochromator (model 66870, Oriel Instruments, USA) producing a beam with a full width at half maximum (FWHM) of 6.1 nm for an exposure at each wavelength of 39 kJ/m². This exposure was used as it produced a measurable change in absorbance (ΔA) within a reasonable time frame. For each wavelength, one of the dosimeters in the exposed set of two had a Mylar filter and the other was unfiltered. Spectral irradiance measurements of the irradiation monochromator beam were taken at each discrete wavelength both before and after exposure using a calibrated spectroradiometer, traceable to the NPL UK standard (model DMc150, Bentham Instruments Ltd., Reading, UK). Spectral irradiance measurements were performed to include 10 nm either side of the specified discrete wavelength in 0.1 nm intervals to ensure there was no unexpected exposure outside the required monochromator wavelength. All the following exposure tests were performed with a Mylar filter in place.

2.5 Cosine Response
The cosine response of the 8-MOP dosimeters was determined in a controlled environment using a UV source (UV solar simulator, 19160-1000, Newport Co., California, USA). This source provides a collimated beam of 5 cm × 5 cm. Batches of four 8-MOP (Mylar filtered) dosimeters were irradiated sequentially at incidence angles ranging from 0° to 80° in intervals of 10°. The ambient temperature was maintained at 21° during exposure and the laboratory lights were filtered and tested to eliminate stray UV emissions. Various positions within the beam area were tested with the calibrated Bentham spectroradiometer measuring from 320 to 400 nm in 0.5 nm increments to confirm that the simulated UV irradiance was uniform to within
5%. This uniformity of the beam allowed for up to four dosimeters to be tested simultaneously at each of the angles. The (ΔA) was found by measuring each dosimeter both before and immediately after exposure to the simulated UV source.

The exposure time required was ascertained using an incidence angle of 0°, exposing the dosimeters for a total of 90 minutes and measuring the dosimeters after each 10 minute exposure in the 90 minute interval before replacing them beneath the source. This test showed that 60 minutes exposure was required at each of the angles in order for a measurable photochemical change to take place. Plotting the cumulative exposure versus time at 0° allowed a dose response equation for the film to be determined for the solar simulator.

2.6 Dose Rate Independence

Groups of five dosimeters were placed at different distances from a fluorescent lamp UV source (Philips 40/12, supplier Lawrence and Hansen, Toowoomba). Three distances 5, 10 and 15 cm from the source were employed. In order to ensure the total exposure received was the same for all dosimeters the irradiance was measured for each distance before the exposure and after one hour of exposure. The UVA irradiances measured were 1.6, 2.19 and 3.7 W/m² for the three distances. The average pre exposure absorbance for all groups of dosimeters was 1.185. Using this information and knowing the dose required to affect a measurable change in the absorbance (from the cosine zero test) the calculated UVA exposure required for all three groups was 40 kJ/m². This UV exposure was reached for the closest dosimeters in 3 hours, for the next group in 5 hours and for the group with the largest distance after 7.1 hours. The post exposure absorbance of the dosimeters was measured straight after removal from the source for each group.
2.7 Temperature Independence

Two separate tests relating to temperature were performed on the 8-MOP dosimeters. The first investigated the temperature used during the drying phase of the film manufacture. The second test investigated the reaction of the film when exposed to a UV source at different temperatures. After the dosimeter film was cast and removed from the glass further drying time was required before use to ensure all the remaining THF was removed from the film. Diffey and Davis [20] recommend drying at 55° for 24 hours under vacuum even though their testing showed no change in reactivity when the film was dried at different temperatures. In order to test the drying temperature a sheet of freshly cast 8-MOP was cut into sections and placed in separate drying ovens set at different temperatures for 24 hours. The oven temperatures employed were 25 °C, 35 °C, 45 °C and 55 °C. A separate section of film was allowed to dry in a light free cupboard at room temperature which was between 19° to 21 °C.

The second test examined the temperature independence of the film exposure. Temperature independence requires that dosimeters return similar responses despite the exposure being undertaken at different temperatures. Using the UV fluorescent lamp as the exposure source, three sets of dosimeters were exposed at different temperatures. The temperatures were controlled using an ice bath and a heated water bath, with additional dosimeters placed at room temperature. The temperatures tested ranged from 10°- 40°C. Dosimeters received the same exposure time of four hours with the irradiance at the dosimeter surface being measured by the spectroradiometer before and after exposure. Distances between the UV source and the dosimeters were measured prior to exposure to the source to ensure they were the same.

2.8 Dose Response

A UVA Biometer (model 501A UV-Biometer, Solar Light Co., PA, USA) sensitive to the UVA wavelengths between 320 and 400 nm located on a rooftop at the University of Southern Queensland, Toowoomba campus was employed for the calibration of the dosimeters in winter.
and spring. This instrument was calibrated on a cloud free day in each season to a scanning double grating spectroradiometer (Model DM300, Bentham Instruments, Ltd., Reading, UK) measuring the terrestrial solar spectrum in each of the relevant seasons. This spectroradiometer scans the global UV in 0.5 nm wavelength increments every 10 minutes from 5:00 am until 7:00 pm daily and is wavelength calibrated to the UV mercury spectral lines and irradiance calibrated to a quartz tungsten halogen lamp with calibration traceable to the primary standard located at the National Physical Laboratory (United Kingdom).

The dosimeter dose response was carried out by exposing a series of dosimeters to solar UV on a horizontal plane in close proximity to the rooftop UVA Biometer for a specific range of time intervals, with all of the dosimeters having a Mylar filter in place. These time intervals were 4, 8, 12, 16, 24, 32 and 40 hours. The same time intervals were used for spring and winter. A minimum of five dosimeters were exposed concurrently for each time interval. Following exposure, the dosimeters were placed in an envelope and stored away from any ambient light. After the final dosimeters were removed all were stored for eight more days before the average change in absorbance and the standard deviation was determined for each time interval.

3. Results and Discussion

3.1 Reproducibility

The results of twenty eight of the dosimeters were used due to two being damaged during the absorbance reading. The mean change in absorbance for the five hour Solar UV exposure interval was 0.362. Sixty seven percent of the dosimeters were within one standard deviation of the mean, with 89% within 1.5 standard deviations. The variance of these dosimeters was ± 4.6%. This variance is in line with the reproducibility of other dosimeters. PPO has a variance of up to 6.5% dependent on exposure levels [22] and PVC has a variance of 5% [26].
Reproducibility was also assessed in other non-specific tests such as the seasonal dose response. These tests showed that the dosimeters had a variance of ± 2.6% when exposed under the same conditions. Some variation in dosimeter measurements is to be expected due to the very small differences in dosimeter thickness.

3.2 Dark Reaction

The dark reaction of the 8-MOP dosimeters is shown in Figure 2 for the periods of storage of one hour and one, two, four, eight and thirty nine days following exposure. The majority of the dark reaction (87%) as calculated with equation 2 occurred within the first two days. The change between four and thirty nine days represents 2% of the total observed change. In order to avoid delays that may arise from an eight day wait period; a researcher can choose to read the dosimeters immediately after exposure or at another time selected by the researcher as long as the selected time remains consistent. To minimize dark reaction impact all dosimeters in this project were measured eight days after exposure unless otherwise stated.

![Figure 2 – Post exposure change in absorbance showing the dark reaction of the UVA dosimeter.](image-url)
3.3 Spectral Response

Figure 3 shows the results when two dosimeters are exposed simultaneously to the same wavelength, one dosimeter being uncovered and one using Mylar as a UVB filter. The dosimeters using the filter showed no response until a wavelength of 320 nm was reached. This was the boundary used in this research to define the UVA waveband although the wavelength boundary between the UVB and UVA is defined at both 315 nm and 320 nm. The CIE [27] defines the boundary as 315 nm; however 320 nm is employed in a significant number of publications, due largely to the biological significance of wavelengths between 315 and 320 nm [28, 29].

Figure 3 shows that the dosimeters with the Mylar filter respond predominantly to wavelengths within the UVA range. The error bars show the average standard deviation of the dosimeters. With Mylar the standard deviation was 0.012 the standard deviation for unfiltered dosimeters was 0.019.

![Figure 3 – Spectral response of the UVA dosimeter covered with the Mylar filter and with no Mylar filter.](image-url)
3.4 Cosine Response

The equation employed for the calibration to the solar simulator source, with an $R^2$ of 0.9997 was:

$$UVA = -563799\Delta A^3 - 196622\Delta A^2 - 101344\Delta A \ [J/m^2]$$  \hspace{1cm} (3)

where UVA is the UV exposure from 320 nm to 400 nm.

Normalization of the response of the dosimeters at each angle of incidence to the solar source was calculated using:

$$R_N = \frac{UVA(\theta)}{UVA(0)}$$  \hspace{1cm} (4)

where $UVA(0)$ is the exposure measured at an angle of 0° and $UVA(\theta)$ is the exposure measured for the respective incidence angle.

Figure 4 – Cosine response of the UVA dosimeter.

Figure 4 shows a normalized cosine response of the 8-MOP UVA dosimeters. The error bars reflect the standard deviation of each of the absorbance measurements. The dosimeters showed
a very uniform change in absorbance when exposed under the same conditions, hence the small range in the error calculations. The cosine response of the 8-MOP dosimeter is within 14% of the cosine curve up to 60°. At angles of 70° and 80° there was a noticeable reflection from the Mylar which may have contributed to the larger deviation from the cosine curve at these angles.

3.5 Dose Rate Independence

The dose rate independence test was designed to show that for dosages derived from an irradiating UV source there is an equal response in change of dosimeter absorbance that is unrelated to the exposure time taken or dose rate used. Figure 5 shows the normalized change in dosimeter absorbance against irradiance for each of the distances tested. The post exposure measurement was expressed as a percentage of the initial absorbance due to the range of initial absorbance values of the dosimeters. The error bars show the standard deviation of the measured post exposure absorbance which was between 0.019 - 0.028. The results show that for UVA irradiances between 1.6 and 3.8 W/m² the response of the 8-MOP dosimeters is dose rate independent.

![Figure 5 - Dose rate independence of the UVA dosimeters for each irradiance, with the error bars representing one standard deviation of the change in absorbance measurements.](image-url)
3.6 Temperature Independence

The absorbance was measured for the various drying temperatures and the result expressed as a percentage of the absorbance measured for the section of film dried at room temperature. Both 25° and 35° are within 5% of the air dried absorbance however with the higher temperatures the difference was 30%. Based on these results, all films produced for calibration to the solar UVA exposure were air dried in a light secure cupboard at temperatures between 18° - 22° C.

In the second test for temperature independence, absorbance readings were taken before and immediately after exposure. The post exposure measurements were calculated as a percentage of the initial measurements. For the low (10 - 20°) and medium (20 - 30°) temperature ranges the variation was less than 2% in the initial absorbance. For the higher (30 - 40°) temperature range the difference in absorbance was less than 6%. The variance within the dosimeter measurements in each instance was < ± 2%. These results show that the dosimeter response is independent of temperature in the 10 - 40° temperature range ±6%.

3.7 Dose Response

Figures 6 and 7 provide the dose response calibration for each of winter and spring respectively with the y axis providing the UVA exposure in kJ/m². In winter the overall exposures were lower and there was less change in absorbance for the same exposure time. Correspondingly, the higher exposures in spring mean that the change in absorbance occurred at a faster rate than the dosimeters received in winter. The significant difference in the dose response of the dosimeters that occurs between seasons can be taken into account by doing a calibration in the season and under the atmospheric conditions in which the dosimeters will be used. The threshold exposure of the UVA dosimeter was found to be between 45 and 70 J/m² with an exposure time of 30 to 45 minutes.
Figure 6 - Winter dose response of the UVA dosimeter.

Figure 7 - Spring dose response of the UVA dosimeter.

4. Conclusion

To date no photochemical dosimeter has successfully measured UVA radiation in isolation for a period of several days. In this research the properties of a dosimeter using 8-MOP as the photoactive chemical in conjunction with a Mylar filter were investigated specifically for measuring UVA over periods longer than a day. The dark reaction showed no ongoing change
within the dosimeters after eight days post exposure. The spectral response did not record UVB at 300 nm or 310 nm indicating that Mylar is an effective UVB filter. The cosine response showed an error of less than 13.8% for angles between 0° and 60°. Dose rate independence had a difference of 0.013 in the normalized response for the irradiances tested indicating the 8-MOP/Mylar dosimeter is suitable for extended UVA measurement provided the film is seasonally calibrated. Temperature testing showed that the cast sheets could be air dried at room temperature and that the dosimeters were temperature independent in the range 10° - 40° ± 6%. Seasonal dose response tests conducted over spring and winter at subtropical latitude show the UVA dosimeters were able to measure exposures < 4.6 kJ/m². The successful outcome of this range of testing has established that 8-MOP coupled with a Mylar filter is suitable for use as a long term UVA dosimeter.
References


