Potential dosemeter for quantifying biologically effective blue light exposures

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Short title: Dosimeter for damaging blue light exposures

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ABSTRACT

This paper reports on the development of a blue light (VIS\textsubscript{BL}) dosimeter. The VIS\textsubscript{BL} dosimeter is based on the combination of polysulfone and phenothiazine as a potential VIS\textsubscript{BL} dosimeter for population studies of exposures related to the blue light hazard. This research found that this combination of photosensitive chromophores reacts to both ultraviolet and visible wavelengths of the solar spectrum. Further to this, the majority of the ultraviolet wavelengths below 380 nm can be filtered out with the use of a low pass filter. It was found that a large change in optical absorbance at 437 nm occurred when the dosimeter was employed to quantify the solar blue light hazard exposures. Preliminary results indicate that this dosimeter saturates relatively slowly and is able to measure exposures equivalent to more than 1200 kJ/m\textsuperscript{2} of blue light hazard weighted solar radiation.

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INTRODUCTION
A range of eye disorders including cataract, macular degeneration, pterygium and photokeratitis have been shown to be sun-related (1). The adverse effects to ocular health caused by exposure to high levels of optical radiation are of great concern and can result in the severe degradation of vision capabilities (2). For example, when optical radiation with wavelengths between 380 and 1400 nm of sufficient intensity reaches the retina it can cause photochemical injury (2). Blue light is found to trigger a reaction in the eye and has been characterized by the International Commission on Non-Ionising Radiation Protection as the blue light hazard (2). Blue light has been shown to affect photoreceptor and retinal pigment epithelium cell function, as well as inducing photochemical damage and apoptotic cell death (3). This blue light photochemical injury to the human retina is termed photoretinitis (4,5). Photoretinitis can result from either viewing an extremely bright light source for a short amount of time or a less bright source for a longer period of time (2). The blue light hazard action spectrum is applicable for broad-band non-laser light sources. The review by Margrain et al (6) reported that there is sufficient evidence to support the long held belief that blue light plays a significant role in the pathogenesis of macular degeneration.

Macular degeneration is a major cause of visual impairment in Australia and the USA. In Australia, two out of three people will develop age-related macular degeneration and one in four will suffer significant loss of vision from it (7). Age-related macular degeneration is estimated to affect more than 8 million people in the United States alone and is expected to increase by more than 50% by 2020 (8). The number of cases of age-related macular degeneration are estimated at 130 000 in Australia and 3.35 million in Western Europe (8).

Protecting the public against non-ionising radiation has profound implications on public health worldwide (9). In order to achieve this, quantitative scientific data on the non-ionising radiation environment that humans are exposed to during various activities is required. This necessitates the need to assess the different environments that humans use. This is not only limited to the high UV exposure environments but to those environments that significantly reduce UVB radiation but still allow the majority of UVA and visible radiation to be incident on the human skin and eyes (for example, glasses, office windows and car windows/windcreens) and also those settings where blue light is a major component of the lighting environment (for example, the office environment). Office buildings are important as the lighting most commonly used is from fluorescent bulbs (fluorescent bulbs produce radiation with a significant output at approximately 405 and 436 nm (10) that coincides with the greatest biological response of the blue light hazard).

Dosimetry is an effective and less costly (than other radiometric devices) means of quantifying the individual level of non-ionising radiation exposure. Numerous photoactive chemical dosimeters have been developed for use in the measurement of UV radiation exposures, such as: polyphenylene oxide (11); polysulphone (12); phenothiazine (13); 8-methoxypsoralen (14); and nalidixic acid (15). However, no dosimeter exists that can be used for the measurement of radiation exposures related to the blue light hazard. Information on the non-ionising radiation environment that can be gained from future experiments utilizing these dosimeters is essential to allow for a better understanding of modifiable risk factors and to identify and change at-risk behaviours, and implement preventative strategies (16).
MATERIALS AND METHODS

Thin Film Casting

The chromophores of polysulfone and phenothiazine were chosen for this research. Polysulfone has been shown to have a spectral sensitivity that is high in the UVB region but is lacking in response above approximately 340 nm; whereas phenothiazine has been shown to respond to both UVB and UVA wavelengths (12). Phenothiazine cannot be cast into a thin sheet by itself as its tensile properties cause any casting to produce an unusable thin film sheet that disintegrates when handled. Therefore, in order to create a useable polymer sheet with appropriate flexibility and tensile strength, polysulfone was added to act as a substrate. The polysulfone and phenothiazine solution was cast into thin film form of 40 μm thickness. The solution was cast on a glass slab that is optically flat to 1 micron. A motor driven blade sweeps across the glass slab to spread the solution evenly and the solvent is allowed to evaporate and to leave a thin film. The thickness of 40 μm was employed as the starting point based on this being the optimum thickness found from previous dosimeter studies (e.g. 13,17).

Spectral Response

To determine the wavelength at which the largest change in optical absorbance occurs due to radiation exposure, the optical absorbance spectrum for the UV and visible wavelengths was measured in a spectrophotometer (model UV1601, Shimadzu Co., Kyoto, Japan). The error of the spectrophotometer is ± 0.004%. The spectral response was measured by irradiating the dosimeters with a known monochromatic exposure of UVA and visible radiation followed by measurement of the change in absorbance of the material. The 1600 W xenon mercury system (model 66870) with digital exposure controller (model 68951) from Oriel Instruments (Stratford, CT, USA) was utilised. The exposures applied to the polymer ranged from 100 to 1000 kJm$^{-2}$ with a fluence rate of approximately 15 W/m$^2$. The exposures were applied in 10 nm steps in the appropriate wavebands. The input and output slit widths were adjusted to provide an output beam with a FWHM of approximately 5 nm. The irradiance output of the irradiation monochromator at each setting was measured with a spectrometer system (model USB4000, Ocean Optics, Dunedin, FL, USA) to determine the period of exposure necessary to produce the required irradiance. The spectrometer is based on a CCD array and has a slit width of 25 μm to give a resolution of less than 1 nm. Further details of the system are described elsewhere (18). The spectrometer was also calibrated against a scanning spectroradiometer (Bentham Instruments, Ltd, Reading, UK). The spectroradiometer is based on a double grating monochromator, a UV/VIS sensitive detector and amplifier with software variable gain provided by a programmable high voltage power supply. Further details of the system are described in Parisi and Downs (19).

To block unwanted wavelengths interfering with the response of the dosimeter, a low pass filter (ST70A, Bekeart Specialty Films Australia Pty Ltd, NSW, Australia) was used. The optical transmission characteristics of the ST70A filter is provided in Figure 3. The ST70A film was used as it was found that the transmission of wavelengths below 380 nm drops quickly to zero.

Exposure Response

The dosimeters were fabricated by mounting the polysulfone and phenothiazine film in a 3 cm x 3 cm holder constructed from PVC sheeting with a thickness of several mm. This holder has an opening of approximately 1.2 cm x 1.6 cm. A low pass filter (ST70A, Bekeart Specialty Films Australia Pty Ltd, NSW, Australia) was then placed on top of the dosimeter to block unwanted wavelengths. The dosimeters were calibrated for the blue light hazard (2),
that is provided in Figure 1a, by exposing a series of dosimeters on a horizontal plane to clear sky solar radiation from approximately 0800 to 1400 h Australian Eastern Standard Time (EST) on August 22, 2005. This calibration was at a subtropical Southern Hemisphere site at the University of Southern Queensland, Toowoomba, Australia (27.6°S, 151.9°E, altitude 693 m). The solar zenith angle (SZA) ranged from 35° to 65°. The dosimeters were calibrated by comparing the change in optical absorbance of the dosimeter with exposures calculated with the data from the spectral measurements obtained with the scanning spectroradiometer described above.

Reproducibility
To test the reproducibility or the variation of the response of the dosimeters for the measurement of VISBL exposures, ten dosimeters were exposed simultaneously to solar radiation over a three hour period on a horizontal plane. These exposures were conducted for clear sky conditions.

Dark Reaction
The optical density of chemical film dosimeters is known to continue to change during storage after an exposure to solar radiation, which is referred to as the dark reaction. A set of ten dosimeters were exposed on a cloud free day during summer to solar radiation for three hours around noon on a clear day and the optical absorbance for each dosimeter was measured before and immediately after exposure. The dosimeters were then stored in a light free environment for twenty-four hours and then measured again for absorbance. This was followed by storage in the same light free environment for a week after exposure and the absorbance measured again. The differences between the absorbances measured immediately after exposure, twenty-four hours after exposure and a week after exposure provided the dark reaction of the VISBL dosimeter.

Cosine Response
The cosine response of the dosimeter was tested by utilizing a solar simulator (model 15S solar UV simulator, Solar Light Co., Philadelphia, USA). Using a stand and a rotating dosimeter clamp, the dosimeter was positioned in front of the solar simulator aperture. One dosimeter was exposed on a plane normal to the incident radiation (0°) and then used as a comparison for the measurements at the other angles of incidence. The mount holding the dosimeter was then rotated 10° from the normal plane and another dosimeter was exposed for the same period of time as the initial dosimeter at 0°. This was carried out for the following angles from the plane normal to the incident irradiance: 10°, 20°, 30°, 40°, 50°, 60°, and 70°. All dosimeters were exposed to the same amount of radiation. The change in absorbance of the dosimeter at a given angle was normalized and then compared to the cosine curve.

RESULTS
An example of a global UV/VIS spectrum is shown in Figure 1b for a cloud free period during winter of 2005 at approximately noon (SZA of 40°). For comparison, the global solar spectrum has been weighted with the blue light hazard action spectrum (2). This shows the negligible effect that wavelengths below approximately 380 nm and above 560 nm have in relation to the blue light hazard.

The spectral response (normalized at 380 nm) of the polysulfone and phenothiazine film is shown in Figure 2. The polysulfone and phenothiazine film has a response well into the shorter UV wavelengths but also extends well into the visible waveband. The spectral
response testing showed that the film continued to respond to wavelengths up to at least 560 nm. However, much larger exposures were necessary to produce a response at these longer wavelengths. The response in the visible waveband is due to the phenothiazine, as polysulfone has been shown to have a negligible response above approximately 340 nm. The error associated with the spectral response is of the order of approximately 10.8% (20).

The spectral transmission of the blue light (VIS\textsubscript{BL}) dosimeter was measured pre-exposure and post-exposure to solar radiation. The change in spectral transmission of the VIS\textsubscript{BL} dosimeter is provided in Figure 4. The maximum change in optical transmission after an exposure of nearly 1200 kJ/m\textsuperscript{2} was approximately 24% at 437 nm. Consequently, 437 nm was chosen as the read out wavelength for the determination of the calibration of the VIS\textsubscript{BL} dosimeter. Although the agreement between the spectral response of the dosimeter and the action spectrum for the blue light hazard is not exact, calibration of the dosimeter for the different situations and seasons that it is to be used for makes it possible to allow for this.

The dark reaction of the VIS\textsubscript{BL} dosimeter measured at 437 nm for the periods of 24 hours and 1 week after exposure is provided in Table 1. From Table 1 it can be seen that the VIS\textsubscript{BL} dosimeter changed on average by -7.0% after 24 hours and -11.3% after 1 week. In comparison, polysulfone has been shown to have a dark reaction of approximately 4% and 5% after 24 hours and 1 week, respectively (12). No data is known with respect to the dark reaction of phenothiazine.

The calibration of the VIS\textsubscript{BL} dosimeters for solar exposure in winter for a SZA range of 40\textdegree{} to 65\textdegree{} is shown in Figure 5. The data points are the averages of the measured changes in absorbency ($\Delta A\textsubscript{437}$) measured at 437 nm across four points on each dosimeter and the error bars denote the standard deviation of the four measurements. A power law function was fitted to the data with the form of:

$$VIS\textsubscript{BL} = 13256 \Delta A\textsubscript{437}^{1.191} \text{ kJ/m}^2$$

where $\Delta A\textsubscript{437}$ is the change in absorbency. The resulting $R^2$ for the calibration was 0.96.

For reproducibility tests, ten dosimeters were placed on a horizontal plane and exposed to solar radiation. All dosimeters received the same exposure of solar radiation producing a mean $\Delta A\textsubscript{437}$ of 0.13 with a maximum standard deviation of 11%. This variation is most likely due to minor variations over the surface of the sheet of the film from which the dosimeters were fabricated and possibly the influence of dust particles that accumulated on the surface of the dosimeters during the exposure period.

The cosine response of the VIS\textsubscript{BL} dosimeter compared to the cosine curve for the range of 0\textdegree{} to 70\textdegree{} is provided in Figure 6. The error bars represent ± 8% variance for post-exposure absorbance measurements. The cosine response of the VIS\textsubscript{BL} dosimeter is within 17% of the cosine curve for the range up to 70\textdegree{}.

DISCUSSION
Exposure to intense light sources can cause serious adverse health effects. Theoretically, wavelengths across the entire optical spectrum can cause damage (2). The risk of eye injury due to radiation in the visible and near-infrared is of particular concern. Exposure limits vary enormously across the optical spectrum due to variations in the different structures of the eye and the possible biological effects (2). Epidemiological studies have indicated a positive
correlation between the incidence of age-related macular degeneration and accumulated exposure to the visible component of solar radiation (21-23). Sliney and Wolbarsht (24) found that gazing at the midday sun for about 1000 s could result in threshold retinal damage solely from the blue part of the solar spectrum. However, the natural aversion response of the eye to bright light and thermal discomfort sensed by the skin and cornea will considerably reduce potentially hazardous exposures (2). Nevertheless, certain exposures to the visible waveband of the solar spectrum remain potentially hazardous (2). Assessment of these damaging exposures can be achieved through the use of the dosimeter developed in this research.

Preliminary results indicate that the VIS$_{BL}$ dosimeter saturates reasonably slowly when exposed to sunlight. It was found that the VIS$_{BL}$ dosimeter can measure exposures to more than 1200 kJ/m$^2$ of blue light hazard weighted solar radiation. This covers the blue light effective exposure limit range of $\leq$ 1.0 MJ m$^{-2}$ sr$^{-1}$ (effective) (2). The response of the dosimeter showed a spectral response up to approximately 560 nm. The dark reaction of the VIS$_{BL}$ dosimeter is very dissimilar to that for polysulfone and is most likely due to the addition of the phenothiazine. Past research has shown polysulfone to have a dark reaction of approximately 4 to 5% (12); however, there is no known data for phenothiazine. Although the agreement between the spectral response of the dosimeter and the blue light hazard action spectrum is not exact, it is possible to allow for this, if the relative spectral distribution of the incident irradiance is quantified (12) or by calibrating the VIS$_{BL}$ dosimeter to the light spectrum (natural or artificial) that will be encountered in the measurements.

Dosimeters used for exposure measurements of more than one day will undergo a dark reaction after each period of exposure. However, the nature of the dark reaction over alternating periods of exposure is currently unclear (25). It has been implicitly assumed that the dark reaction is independent of exposure (12,26) and inconsistencies due to the dark reaction can be minimised by establishing a regular post-exposure measurement routine (15,27).

The unexposed VIS$_{BL}$ dosimeter can be stored for many years after manufacture. Research showed that unexposed VIS$_{BL}$ dosimeters stored in a light proof environment for five years showed no change in optical characteristics. The VIS$_{BL}$ dosimeter is also robust enough to be worn on the human body during normal daily activities.

The usage of the VIS$_{BL}$ dosimeter requires the calibration against a calibrated spectroradiometer or broadband meter. The size and lightweight properties of this dosimeter means that it can be attached to any site in different environments such as office buildings, sunglasses or in vehicles in order to measure the exposures effective for possible damage to the human eyes. The level of accuracy of the dosimeter and the profile of the calibration curve will vary with the season and environment. This can be overcome by calibrating the dosimeter in the season and for the environment that it will be employed to measure the exposures. The period of exposure before saturation occurs, inter-batch variability and the use of alternate filters will be investigated further in future research.
REFERENCES

2. ICNIRP (International Commission on Non-Ionising Radiation Protection) Guidelines on limits of exposure to broad-band incoherent optical radiation (0.38 to 3µm). Health Phys. 73, 539-554 (1997).
Table 1. Average dark reaction of the VIS\textsubscript{BL} dosimeter.

<table>
<thead>
<tr>
<th>Period of time</th>
<th>Change in absorbance</th>
<th>Change (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>24 hours</td>
<td>-0.010</td>
<td>-7.0</td>
</tr>
<tr>
<td>1 week</td>
<td>-0.016</td>
<td>-11.3</td>
</tr>
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**Figure legends**

**Figure 1.** The blue light hazard action spectrum (2) (a); and the unweighted solar irradiance spectrum (thick) and the solar irradiance weighted with the blue light hazard action spectrum (thin) (b).

**Figure 2.** Spectral response of the polysulfone and phenothiazine film (normalized at 380 nm).

**Figure 3.** Transmission characteristics of the ST70A filter.

**Figure 4.** The spectral transmission of the dosimeter before and after exposure to nearly 1200 kJ/m$^2$ of blue light hazard weighted solar radiation.

**Figure 5.** The calibration curve for the VIS\textsubscript{BL} dosimeter for a southern hemisphere winter during 2005. The error bars represent the standard deviation of the data.

**Figure 6.** Comparison of the cosine response of the VIS\textsubscript{BL} dosimeter to the cosine curve. The error bars represent ±8% variance for post-exposure absorbance measurements.
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