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Atmospheric Chemistry and Physics

Utilising polyphenylene oxide for high exposure solar UVA dosimetry

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Abstract. A personal UV dosimeter that can quantitatively assess high exposure solar UVA exposures has been developed. The chemical polyphenylene oxide has been previously reported on its ability to measure high UVB exposures. This current research has found that polyphenylene oxide, cast in thin film form, is responsive to both the UVA and UVB parts of the solar spectrum. Further to this, the UVB wavelengths were filtered out with the use of mylar. This combined system responded to the UVA wavelengths only and underwent a change in optical absorbance as a result of UVA exposure. Preliminary results indicate that this UVA dosimeter saturates steadily when exposed to sunlight and can measure exposures of more than 20 MJ/m^2 of solar UVA radiation with an uncertainty level of no more than ±5%.

1 Introduction

Exposure to UV radiation is known to be a causative factor in the induction of skin cancers and other sun-related disorders. Most acute responses of humans to UV exposure occur as a result of UVB (280 to 315 nm) exposures, as these wavelengths are highly effective in creating a human biological response. However, this does not mean that UVA radiation has no impact on human UV exposures and health. UVA can cause erythema in human skin, yet, the exposures required to create such a response is much larger than UVB radiation. UVA radiation penetrates much deeper into human skin tissue than UVB, resulting in impacts that are not as acute, taking many years to manifest. Past research has shown that UVA (315 to 400 nm) plays a significant role in human skin carcinogenesis, immune suppression, DNA damage, photoageing and wrinkling (Agar et al., 2004; Moan et al., 1999; Garland et al., 2003). Skin cancer is considered the most common malignant neoplasm in Australia and the USA (Kricker and Armstrong, 1996; Glanz and Mayer, 2005; NCI, 2006). Over 1600 Australians die from skin cancer each year and a further 380 000 Australians are treated for skin cancer each year (NCCI, 2003; AIHW, 2004; AIHW, 2005). Skin cancer is Australia's most expensive cancer with estimated amounts of $264 million and $30 million spent in Australia during 2001 on NMSC and melanoma respectively (AIHW, 2005). As a result, it is essential to decrease the amount of exposure to damaging solar UV radiation that the population experiences. This requires methods to understand the solar UV radiation environment that humans live in. Spectroradiometers, broadband meters and dosimeters are often utilised for the measurement of incident solar UV radiation. Quantification of the individual level of solar UV radiation exposure requires personal dosimetry due to changes in the position of people compared to the radiation source. Dosimetry is very useful as researchers can leave the dosimeters in situ for extended periods of time to monitor long term UV trends. However, dosimeters need to be calibrated against a spectroradiometer or broadband meter. On the other hand, spectroradiometers and broadband meters are more useful for analysing the effect of changing atmospheric variables (e.g. clouds, aerosols and ozone) upon UV dosages.

Commonly used UV chemical dosimeters are polysulphone and phenothiazine. Phenothiazine has been used for measuring UVA wavelengths in various environments (Parisi et al., 2005). However, phenothiazine only has the capability to record a cumulative exposure over a small time period, usually three to four hours. This small dynamic range greatly reduces the amount of time over which a UVA exposure can be measured in the field. Therefore, a chemical dosimeter that is capable of measuring large amounts of UVA radiation over a long time period would be very useful. Research conducted by Davis et al. (1976) showed that Poly (2,6-dimethyl-1, 4-phenylene oxide) (PPO) film could

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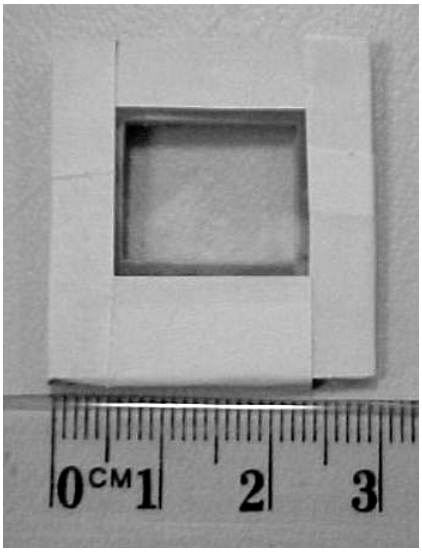

Fig. 1. A sample PPO dosimeter with the mylar film attachment.

be employed to measure high levels of UV exposure. Further research found PPO to be ideal for this purpose as it would allow for unattended UVB measurements to be made at various locations over a time period of at least one week with high levels of accuracy when compared against radiometric measurements (Davis et al., 1981; Berre and Lala, 1989; Lester et al., 2003). Schouten et al. (2007) found that PPO has a progressively increasing response to UVA wavelengths over time. PPO dosimeters have been utilised in the measurement of global UVB and erythemal exposures, however, they have not been used to measure solar UVA exposures. The aim of this paper was to extend the previous research that has employed PPO dosimeters for the measurement of solar UVB and erythemal exposures to investigate the suitability of PPO for the measurement of high exposure solar UVA irradiances.

2 Materials and methods

2.1 PPO

PPO film of approximately 40 μm thickness was attached with adhesive tape to a plastic holder. The holders for the dosimeters were 3×3 cm in area and fabricated from thin polyvinylchloride with an aperture of approximately 1.2×1.6 cm (Fig. 1). A UV/visible spectrophotometer (model 1601, Shimadzu Co., Kyoto, Japan) was used to measure the pre and post exposure absorbance of the dosimeter. The uncertainty range for optical absorbance measurements in the spectrophotometer has been stated as ±0.002 by the manufacturer. PPO is responsive to both the UVA and UVB part of the solar spectrum, therefore the UVB wavelengths were filtered by placing 120 μm thick mylar film (Cadillac Plastics, Australia) on top of the PPO film. For each dosimeter, the change in optical absorbance (ΔA_{320}) due to UV exposure was measured at 320 nm (with mylar removed) at four different sites over the dosimeter in order to minimise any errors due to any possible minor variations in the PPO film over the size of the dosimeter. The change in optical absorbance was measured at 320 nm as previous studies have shown that this is the wavelength where the greatest overall UV energy induced change occurs (Lester et al., 2003; Schouten et al., 2007). The post exposure absorbance was measured at a standardized time following exposure to minimize any error associated with the post exposure "dark reaction" of the PPO (Lester et al., 2003; Schouten et al., 2007). Lester et al. (2003) has shown previously that the PPO dosimeter is not a temperature dependent system, so fluctuations in temperature over the exposure time period will not have any influence upon the subsequent measurement error.

2.2 Calibration

The dosimeters were calibrated for UVA exposures by exposing a series of dosimeters on a horizontal plane, to relatively clear sky solar UV from approximately 08:00 to 16:00 h Australian Eastern Standard Time (EST) for a total of 22 days. One dosimeter was removed from solar exposure at regular periods of time ranging from one to two days with the last dosimeter being removed after 22 days. The dosimeters were brought in at the end of each day to ensure that they did not receive any overnight damage. These calibrations ran over the months of April and May 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 30° to 75°. The PPO dosimeters were calibrated on a horizontal plane with a UVA meter (501 UVA Biometer, Solar Light Co., Philadelphia, USA). The UVA meter was calibrated against a scanning spectroradiometer (Bentham Instruments, Ltd, Reading, UK). The spectroradiometer is based on a double grating monochromator, a UV sensitive detector and amplifier with software variable gain provided by a programmable high voltage power supply. The container in which the spectroradiometer is housed is temperature stabilised with a Peltier system and the temperature set to 25°C. The temperature inside the container at each scan is recorded by the software. For the times that the temperature inside the container housing the spectroradiometer varied by more than 1°C from the set temperature due to hot ambient temperatures, the manufacturer supplied temperature correction factor of −0.4%/°C was applied in the post processing to the spectral irradiance data collected at each 0.5 nm increment. This correction was the same at all wavelengths. The wavelength shift of the instrument due to temperature as provided by the manufacturer is 0.005 nm/°C. Consequently, any wavelength shift was minimal and no correction for wavelength shift has been applied. The input optics of the spectroradiometer are provided by a PTFE (polytetrafluoro ethylene)

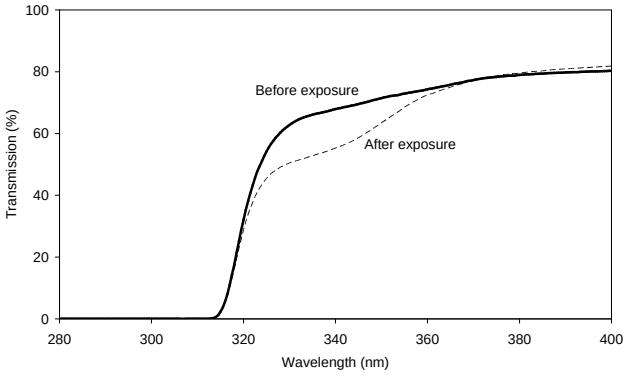

Fig. 2. The spectral transmission of mylar film before and after a total solar UVA exposure of 20 MJ/m^2.

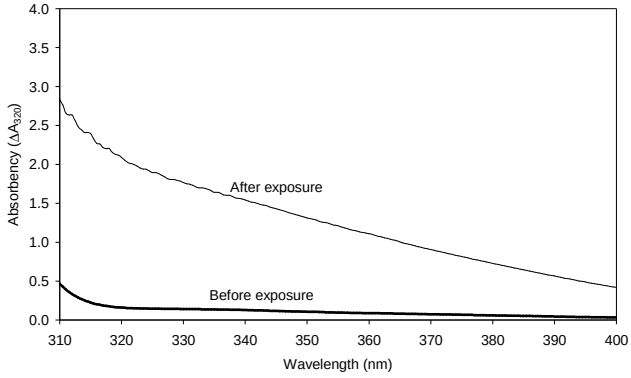

Fig. 3. The absorption spectrum of PPO before and after a total solar UVA exposure of 20 MJ/m^2.

diffuser and connected by an optical fibre to the input slit of the monochromator. The spectroradiometer is programmed to start scanning the global UV spectrum from 280 to 400 nm in 0.5 nm increments from dawn, and thereafter every 10 min till dusk. The instrument is wavelength calibrated to the UV spectral lines of a mercury lamp and irradiance calibrated to a 150 Watt quartz tungsten halogen lamp with calibration traceable to the National Physical Laboratory, UK standard.

To produce the calibration curve, the UVA exposure (MJ/m^2) was measured over specific intervals with the UVA meter. This measurement was then calibrated to the scanning spectroradiometer by employing a transfer equation with a calculated R^2 value of no less than 0.99. After each interval, the ΔA_{320} for a single PPO dosimeter was measured by the spectrophotometer to provide a single data point, where ΔA_{320} was calculated by the following

$$\Delta A_{320} = A_{320}^{\mathrm{FINAL}} - A_{320}^{\mathrm{INITIAL}} \quad (1)$$

where A_{320}^{FINAL} is the final optical absorbance measurement after exposure taken at 320 nm and $A_{320}^{\mathrm{INITIAL}}$ is the initial absorbance measurement before exposure taken at 320 nm. After the absorbency was measured, the dosimeter was then removed from the batch.

2.3 Reproducibility

To test the reproducibility of the dosimeters for the measurement of solar UVA, ten dosimeters (with mylar filter) were exposed simultaneously to solar UV over a three hour period on a horizontal plane. These exposures were conducted on an unshaded sports oval in autumn under clear sky conditions to ensure that the dosimeters were exposed to all of the incident solar UV radiation, both direct and diffuse radiation from the sky.

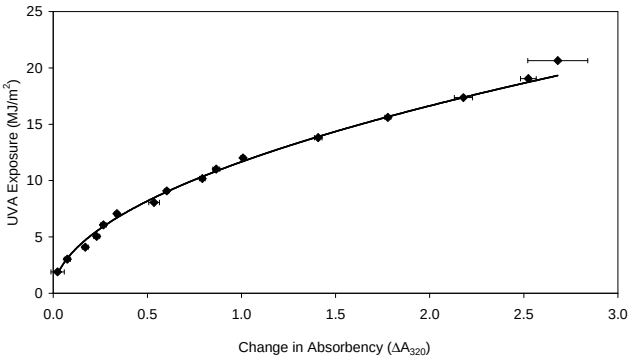

Fig. 4. Calibration curve of PPO for UVA exposures. The error bars represent the standard deviation in each series of absorbency measurements.

3 Results

3.1 Filtered exposures

The spectral transmission of the mylar film was measured pre-exposure and post-exposure to solar UV to test for any significant changes. The change in spectral transmission of the mylar film is provided in Fig. 2. The maximum change was approximately 13% from 331 to 337 nm. The change in absorbency of the PPO film pre- and post-exposure is provided in Fig. 3.

3.2 Calibration

The calibration of the PPO dosimeters for solar UVA exposure is shown in Fig. 4. The data points are the averages of the four ΔA's measured for each dosimeter and the error bars on the x-axis values are the standard deviation of the four measurements. A power law was fitted to the calibration data with the form of:

$$\mathrm{UVA}=11.7(x^{0.51})\ \mathrm{MJ/m^2} \quad (2)$$

where x is the change in absorbency. The resulting R^2 for the calibration was greater than 0.99.

3.3 Reproducibility

For the reproducibility tests, all dosimeters received the same exposure of solar UV producing a mean ΔA_{320} of 0.598 with a standard deviation of no more than 3% and a coefficient of variation equal to approximately 5%. This variation may be due to minor variations over the surface of the sheet of PPO film, from which the dosimeters were fabricated, that are inherent in the casting process and are difficult to eliminate. Variation can also be influenced by dust particles that may have accumulated on the surface of the dosimeters during the exposure period.

4 Discussion

PPO film has never before been used to measure solar UVA exposures, however, preliminary results indicate that this UVA dosimeter saturates reasonably slowly when exposed to sunlight and can measure exposures of more than 20 MJ/m^2 of solar UVA radiation with an uncertainty level of no more than ±5%. For the Toowoomba measurement site, this equates to approximately two weeks of full day UVA exposures under clear sky conditions. This exposure period will be extended for higher latitude sites and also for varying atmospheric conditions.

The size and lightweight properties of the dosimeter means that it can be attached to any anatomical site on the human body in different environments such as underneath shade or in a vehicle in order to measure the solar UVA exposures with a level of ease, simplicity and cost-effectiveness not associated with counterpart radiometric measurements. The usage of the dosimeter requires the calibration against a calibrated UVA meter. The profile of the calibration curve will vary with the season and this can be overcome by calibrating the dosimeter in the season that it will be employed to measure the solar UVA exposures. Schouten et al. (2008) found that when the PPO dosimeter is calibrated to UVB wavelengths over different seasons there was a slight but definite variation between calibration profiles. However, when PPO is calibrated to UVA wavelengths this variation will be significantly reduced due to the fact that UVA wavelengths are not affected by atmospheric parameters to the extent that UVB wavelengths are.

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