Dosimeter for measurement of UVA exposures

Alfio V. Parisi[a,*] and Michael G. Kimlin[b]

[a]Centre for Astronomy, Solar Radiation and Climate, Faculty of Sciences, University of Southern Queensland, Toowoomba, AUSTRALIA. 4350
[b]National Ultraviolet Monitoring Centre, Department of Physics and Astronomy, University of Georgia, Athens, GA, USA 30606

ABSTRACT

A prototype UVA dosimeter that is responsive to the UVA wavelengths only has been developed for measurement of personal exposures. The chemical phenothiazine, cast in thin film form and which is responsive to both the UVA (320-400 nm) and UVB (280-320 nm) part of the spectrum was used and filtered with mylar. This combined system responded to the UVA wavelengths only and underwent a change in optical absorbance as a result of UVA exposure. The wavelength of 370 nm was employed for quantifying the change in optical absorbance of the combined mylar/phenothiazine dosimeter and a calibration curve determined for measuring the UVA exposures. UVA exposures to approximately 50 J cm^{-2} may be measured prior to saturation of the response.

Keywords: UVA; phenothiazine; UV; solar; dosimeter

1. INTRODUCTION

Recent research has shown that there is a predominance of UVA mutations in the basal cell layer of human skin[1]. This research has implicated the longer UVA wavelengths (320 to 400 nm) of the solar spectrum as a potential carcinogen in human skin. Previous research has also indicated the cumulative damage and premature photoageing of human skin due to UVA wavelengths[2-4]. The irradiances in the solar UVA waveband are higher than the UVB irradiances by approximately a factor of 100 and as a result highlight the biologically damaging effectiveness of the UVA waveband. Additionally, they have a greater depth penetration into human skin when compared to the UVB wavebands. These research results have highlighted the necessity to understand the solar UVA environment. It has been found that the ratios of the UVA to erythemal UV irradiances are higher in the winter months than the summer months[5]. Similarly, on a relatively cloud free day, the ratio of UVA to erythemal UV is lowest at solar noon with higher ratios in early morning and late evening. This is due to the longer path of the radiation through the atmosphere at the higher solar zenith angles results in more scattering and absorption of the shorter wavelengths. At a sub-tropical latitude, the peak daily UVA exposure in summer (December to February) was 205 J cm^{-2} and in winter (June to August), the minimum daily value was 19 J cm^{-2} on a cloudy day[5].

Transparent materials such as glass found in office and home windows and in other structures and glass in vehicle window glass and windscreens act as a filter to some of the shorter solar UV wavelengths[6], but still allow the transmission of the UVA wavelengths. Due to the filtering properties of glass, the UVA and the visible (400 to 700 nm) wavebands of solar radiation are transmitted with no significant UVB wavelengths transmitted. The effectiveness of the erythemal action spectrum[7] is highest for the UVB wavelengths, however the effectiveness extends into the UVA wavelengths with the effectiveness reduced by a factor of approximately 1000. Previous research has found that for a clear spring day an erythemal exposure of 0.85 MED (minimum erythemal dose) to a horizontal plane and 0.38 to a vertical plane over a six hour period was measured within a glass enclosure[8]. On a partially cloudy day six weeks later,

[*] 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.

these were 0.89 MED and 0.44 MED for the horizontal and the vertical planes respectively. These erythemal exposures would have been predominantly due to the effectiveness of the erythemal action spectrum in the UVA waveband. For the different environment of a glass greenhouse, the erythemal exposures have been evaluated in late spring and late summer at three sites and five orientations at each site[9]. The maximum in the erythemal irradiance in the glass enclosed environment was not necessarily at noon, the maximum erythemal exposure occurring on the eastern side of the greenhouse in the morning and on the western side in the afternoon. The erythemal irradiance on the eastern side in the morning was higher by 26% and 50% for horizontal and vertical surfaces respectively compared to the same site at noon. On the western side, the irradiance was higher by 45% and 78% for the horizontal and vertical surfaces respectively compared to the same site at noon. For vehicles, preliminary research[10] has found the UVA irradiances within the vehicle were not reduced significantly by the untinted window glass. Further research[11] measured the UVA irradiances inside vehicles at different periods over a year and found significant UVA irradiances inside the vehicle during the year. The solar ultraviolet spectrum measured in two common Australian vehicles with the windows closed using a UV spectroradiometer inside the vehicle found that all of the shorter UVB wavelengths were completely removed, however the UVA radiation from 340 nm to 400 nm were still recorded in the vehicles[12].

Dosimeters based on polysulphone[13] have been widely employed for the measurement of UV exposures for wavelengths shorter than 330 nm. However, this material is not sensitive to wavelengths longer than 330 nm[14]. Previous research has reported a method to extend the exposure time of polysulphone before saturation of the response occurs[15]. There have been some UVA dosimeter materials proposed[16-21]. However, there is no dosimeter sensitive to the UVA that is as convenient to use and process as the polysulphone dosimeters. The most promising UVA dosimeter material to date has been that based on the chemical or chromophore thiodiphenylamine. However, this chemical is sensitive to both the UVA and UVB wavelengths[22] and the material is too sensitive with saturation of the response within several hours of solar UV exposure, even at higher latitudes, whereas, it is necessary to measure the exposures over a period of at least a day. Similarly, another material based on the chemical 8-methoxypsoralen that has been employed as a dosimeter is sensitive to both the UVA and UVB wavebands[23]. This paper reports on the use of phenothiazine, that is normally responsive to all UV wavelengths, cast in thin film form and filtered to restrict the wavelengths transmitted to the dosimeter material to the UVA wavelengths only.

2. MATERIALS AND METHODS

2.1 UVA Dosimeter

A novel technique for the development of a prototype UVA dosimeter that is responsive to the UVA wavelengths only and does not respond to the UVB wavelengths was used. The chemical phenothiazine cast in thin sheet form of approximately 40 microns thickness was employed as the active detector[22]. This polymer material responds to both the UVA and UVB wavebands of the UV spectrum. In order to be employed as a dosimeter, the thin film was mounted in a 3 cm x 3 cm holder constructed from thin PVC of several mm thickness and with an opening of approximately 1.2 cm x 1.6 cm (Figure 1). As shown in previous research[22], the phenothiazine film is also responsive to the UVB waveband and easily saturates with exposure to UV and as a result becomes unsuitable for use after 15 to 30 minutes exposure in the midday sun.

To overcome this problem of quick saturation and eliminate the response to the UVB wavelengths, the incoming UV radiation available to the phenothiazine dosimeter was filtered with a filter material, namely mylar film (Cadillac Plastics, Australia). The mylar film has been previously employed in UV irradiation research to remove the UVB wavelengths from UVB lamps[24-26]. The transmission of the mylar filter as measured in a spectrophotometer (model 1601, Shimadzu Co., Kyoto, Japan) is provided in Figure 2. For this measurement, the mylar was placed normal to the spectrophotometer beam. The treansmission drops quickly to zero for wavelengths shorter than approximately 320 nm. Although, the transmission of the filter is not flat, this is taken into account in the calibration of the combined dosimeter. In this application, the UVA transmission of the mylar is known to reduce as a result of exposure to UV. Over a period of a week, the UV transmission is approximately halved due to degradation of the mylar[24]. In the current application, the exposure period will be less than this and of the order of half a day to one day. Any deterioration of the filter over this period will be incorporated into the calibration of the combined phenothiazine/mylar dosimeter. In order to fabricate the dosimeter, a piece of mylar of size 25 mm x 25 mm was taped over the phenothiazine to form the combined mylar/phenothiazine dosimeter ensuring that no gaps were presented between the two film materials. In the remainder of the text, the combined mylar/phenothiazine dosimeter will be referred to as the UVA dosimeter

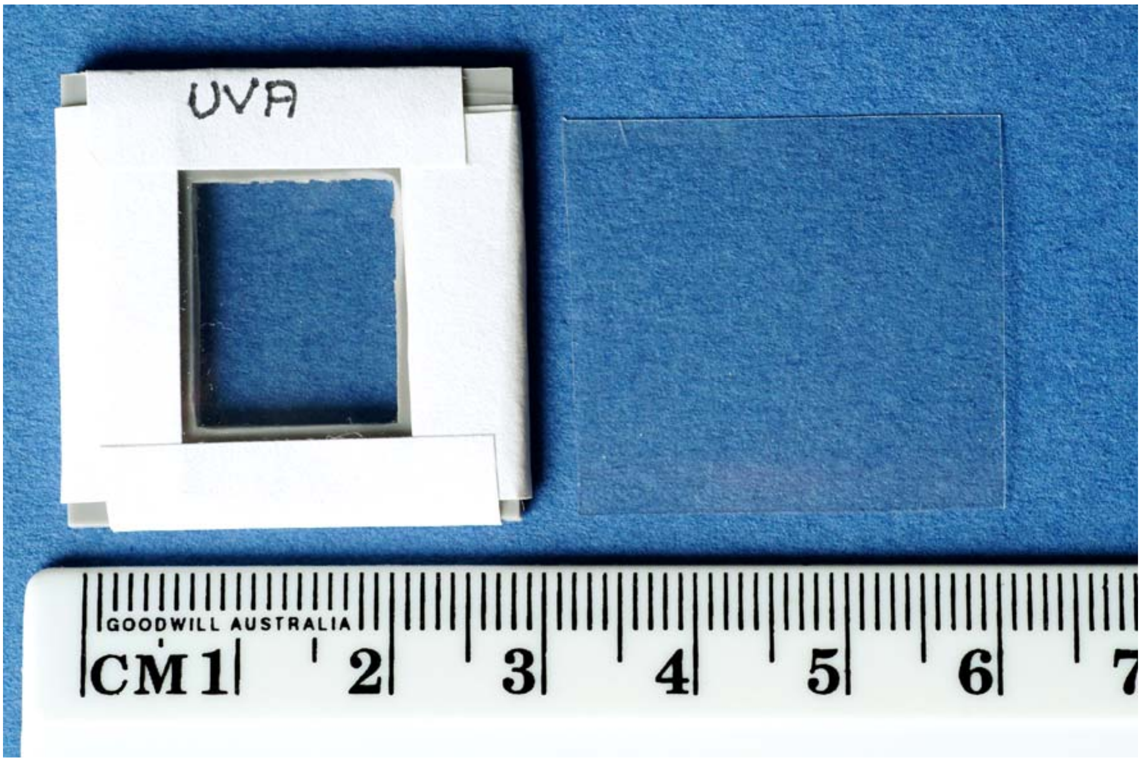

Figure 1: A sample of the UVA dosimeter on the left and on the right is a piece of mylar used as a filter.

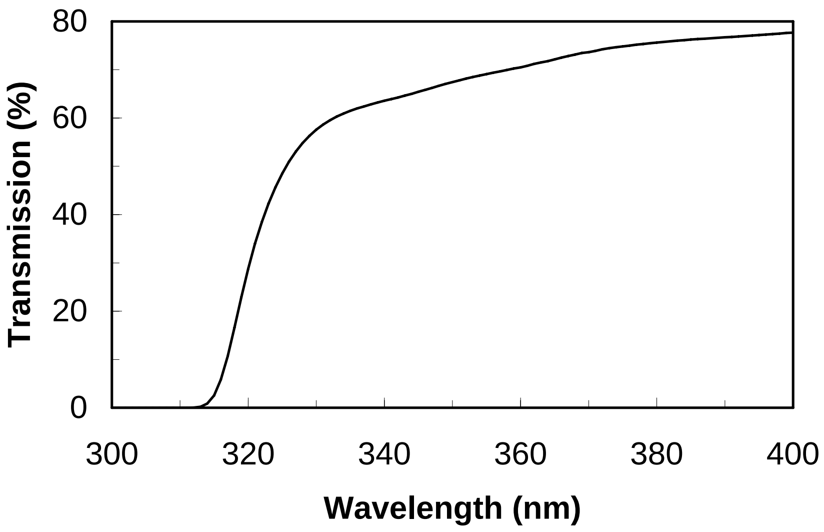

Figure 2: Transmission spectrum of the mylar filter measured in a spectrophotometer.

2.2 Calibration

In order to employ these polymer materials as a UVA dosimeter, it was necessary to determine the wavelengths at which there was a maximum change in absorbance as a result of UV exposure. In order to determine the wavelength at which there is a reasonable change in optical absorbance (ΔA) due to UVA exposure, the absorption spectrum was measured in the spectrophotometer. From the results (Figure 3), the wavelengths of 330 nm and 370 nm were selected for further investigation as a suitable wavelength for the measurement of ΔA due to UVA exposure. The wavelength of 370 nm was selected as this is a wavelength at which a larger ΔA occurs. The wavelength of 330 nm was selected for comparison as this is the wavelength used for polysulphone. Following the methodology for the measurement of ΔA, the dosimeters were placed in a holder in the spectrophotometer that allowed the pre and post-exposure optical absorbances to be measured at four reproducible locations over the dosimeter. This measurement of the absorbances over four sites has been previously employed in the use of polysulphone as a dosimeter. In order to calibrate the UVA dosimeter, dosimeters were exposed for different periods of time between 7.55 EST (Eastern Standard Time) and 13.50 EST on a horizontal plane while concurrently measuring the UVA exposures with a UV radiometer (model 501, Solar Light Co., Philadelphia, USA) permanently mounted outdoors on an unshaded roof. The calibration was undertaken on a relatively clear day in summer (17 January, 2003) at a sub-tropical latitude (27.6 °S, 151.9 °E, altitude 693 m) on the grounds of the University of Southern Queensland, Toowoomba, Australia. The ΔA's were related to the measured UVA exposures in order to determine a calibration curve.

3. RESULTS

3.1 UVA Dosimeter

The pre- and post- exposure absorption spectrum of the UVA dosimeter is provided in Figure 3. There is an increase in optical absorbance due to UVA exposure and the largest ΔA occurs for wavelengths larger than 360 nm. The transmission spectrum of the UVA dosimeter measured prior to solar UV exposure is shown in Figure 4. This shows that the mylar filter is effectively filtering the solar UVB and the phenothiazine/mylar combination is sensitive only to the UVA wavelengths of the solar UV spectrum.

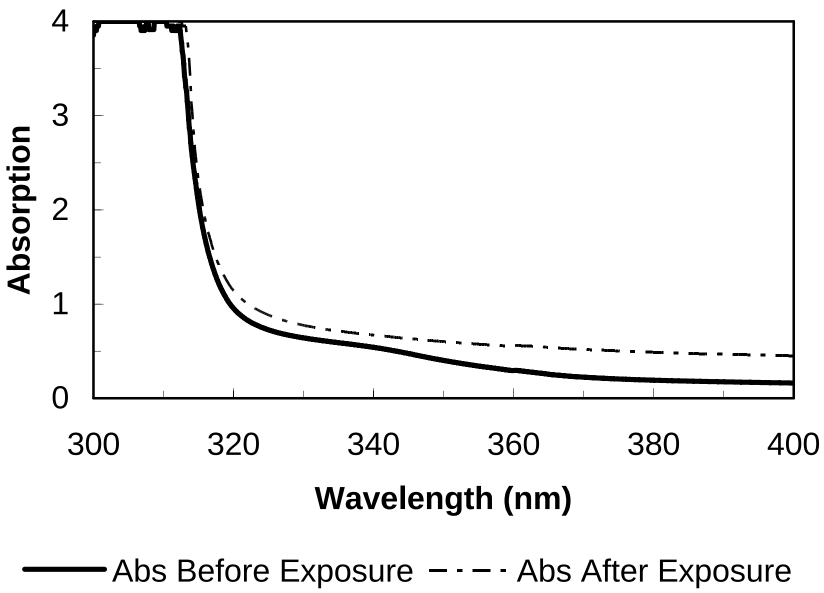

Figure 3: The pre-exposure and post-exposure optical absorbance from 300 to 400 nm for the UVA dosimeter. The exposure was to solar UV radiation.

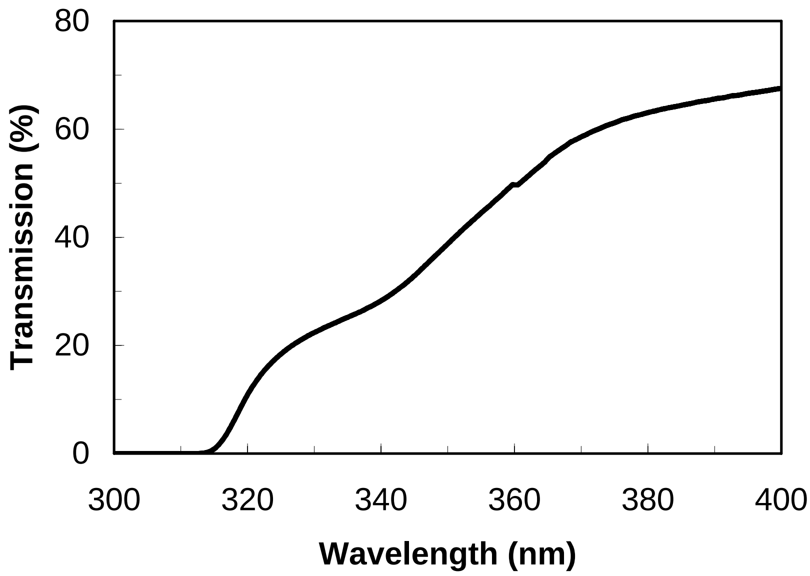

Figure 4: The spectral percentage transmission of the UVA dosimeter before solar UV exposure.

3.2 Calibration

The calibration curve for the UVA dosimeter that has been measured at the two wavelengths of 330 nm and 370 nm is provided in Figure 5. This relates the change in absorbance to the UVA exposure. From these results the better read-out wavelength is 370 nm due to the larger change in optical absorbance (hence a reduced error in the measurements). The UVA dosimeter response starts to saturate for exposures of 40 to 60 J cm^{-2} of UVA radiation. However, it should be reliably used for exposures up to 60 J cm^{-2} when using a read out wavelength of 370 nm. For this calibration, this exposure corresponds to four hours from 7.55 EST to 11.55 EST. It is necessary to note that the solar UVA exposures for this calibration were during summer at a sub-tropical southern hemisphere site, which is some of the highest UVA exposures that can be received. At higher latitudes and other seasons, the exposure time before saturation of the dosimeter occurs will be longer.

A calibration curve was been fitted to the data where the ΔA is measured at 370 nm. The equation was of the form:

$$UVA = 0.569e^{17.56\Delta A} \quad \text{J cm}^{-2} \qquad (1)$$

where UVA is the UVA exposure in J cm^{-2}. The R^2 value for this equation was 0.98. The form of the calibration equation for polysulphone is cubic. In this case, the exponential function provided a better fit compared to a cubic function.

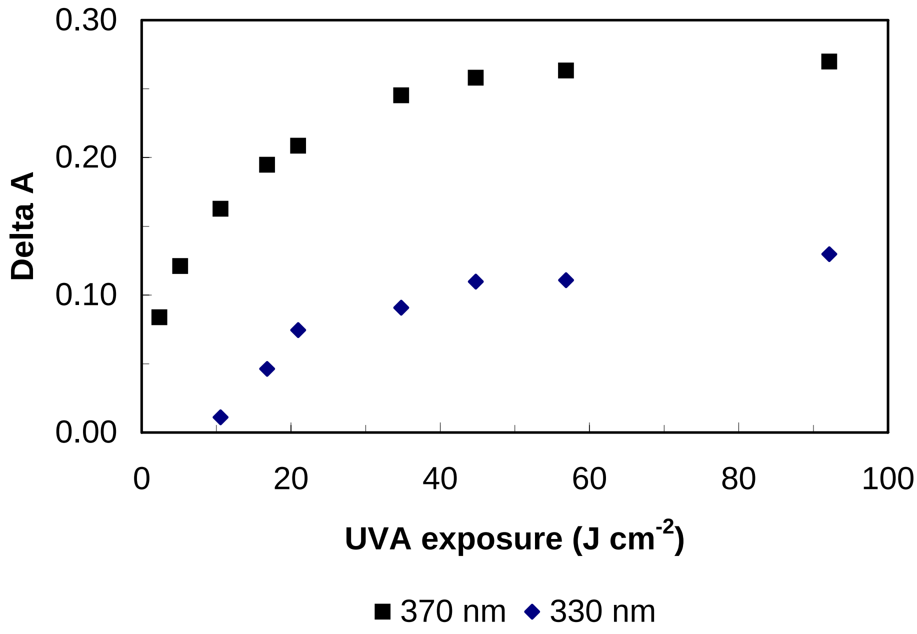

Figure 5: The calibration curve for the UVA dosimeter relating the change in optical absorbance at 330 nm and 370 nm to the solar UVA exposure.

4. DISCUSSION

This paper presents a new and novel method for the measurement of UVA exposures using a dosimetric material. Data presented in this paper indicates that the UVA dosimeter presented may be used as a reliable material for personal solar UVA exposure measurements. Such data on personal UVA exposures of the population do not currently exist, and when combined with the new research suggesting that UVA is a greater contributor to skin cancer than previously thought, this newly developed UVA dosimeter should be of great use to the UV research community. However, although the prototype UVA dosimeter saturates reasonably quickly, it is not an insurmountable problem to extend the dynamic range of the dosimeter. This may be done using a similar technique to that employed to extend the dynamic range of polysulphone as a UVB dosimeter by a factor of approximately four to five[15]. This was achieved by utilizing a carefully selected and charaterised filter material.

ACKNOWLEDGMENTS

The first author (AP) thanks the Ian Potter Foundation for a travel grant that funded part of the travel costs to attend this conference. The authors would also like to acknowledge the technical staff in Physics and the Sciences workshop, USQ for their technical assistance in this project.

REFERENCES

1. Agar, N.S., Halliday, G.M., Barnetson, R., Ananthaswamy, H.N., Wheeler, M. & Jones, A.M. 2004, "The basal layer in human squamous tumors harbours more UVA than UVB fingerprint mutations: A role for UVA in human skin carcinogenesis," *Proc. Nat. Acad. Sci*. vol.101, pp.4954-4959.
2. Lavker, R.M., Gerberick, G.F., Veres, D., Irwin, C.J. & Kaidbey, K.H. 1995, "Cumulative effects from repeated exposures to suberythemal doses of UVB and UVA in human skin," *J. Am. Acd. Derm*. vol.32(1), pp.53-62.
3. Lavker, R.M., Veries, D.A., Irwin, C.J. & Kaidbey, K.H. 1995, "Quantitive assessment of cumulative damage from repetitive exposures to suberythemogenic doses of UVA in human skin," *Photochem. Photobiol.* vol.62, pp.348-352.
4. Bissett, D.L., Hannon, D.P., McBride, J.F. & Patrick, L.F. 1992, "Photoaging of skin by UVA," in *Biological Responses to Ultraviolet A Radiation*, ed. F. Urbach, pp.181-188, Valdenmar Publishing Co., Kansas.
5. Kimlin, M.G., Parisi, A.V., Sabburg, J.S. & Downs, N.J. 2002, "Understanding the UVA environment at a sub-tropical location and its consequent impact on human UVA exposure," *Photobiol. Photochem. Sci.* vol.1, pp.478-482.
6. Parisi, A.V., Sabburg, J. & Kimlin, M.G. 2004, "Scattered and Filtered Solar UV Measurements," Kluwer Academic Publishers, Dordrecht.
7. CIE (International Commission on Illumination) 1987, "A reference action spectrum for ultraviolet induced erythema in human skin," *CIE J*. vol.6, pp.17-22.
8. Parisi, A.V. & Wong, C.F. 1997, "Erythemal irradiances of filtered ultraviolet radiation," *Phys. Med. Biol.* vol.42, pp.1263-1275.
9. Parisi, A.V. & Wong, C.F. 1997, "The erythemal ultraviolet exposure for humans in greenhouses," *Phys. Med. Biol.* vol.42, pp.2331-2339.
10. Kimlin, M.G. & Parisi, A.V. 1998, "Ultraviolet radiation penetrating vehicle glass: A field based comparative study," *Phys. Med. Biol.* vol.44, pp.917-926.
11. Parisi, A.V. & Kimlin, M. 2000, "Estimate of annual ultraviolet-A exposures in cars in Australia," *Rad. Prot. Dos.* vol.90(4), pp.409-416.
12. Kimlin, M.G., Parisi, A.V., Carter, B.D. & Turnbull, D. 2001, "Comparison of the solar spectral ultraviolet irradiance in motor vehicles with windows in an open and closed position," *Int. J. Biometerol.* vol.46, pp.150-156.
13. Davis, A., Deane, G.H.W. & Diffey, B.L. 1976, "Possible dosimeter for ultraviolet radiation," *Nature*, vol.261, pp.169-170.
14. CIE (International Commission on Illumination) 1992, "Personal dosimetry of UV radiation," Publication No. CIE 98.
15. Parisi, A.V. & Kimlin, M.G, 2004, "Personal solar UV exposure measurements employing polysulphone with an extended dynamic range," *Photochem. Photobiol.* vol.79(5), pp.411-416.
16. Fanselow, D.L., Pathak, M.A., Crone, M.A., Ersfeld, D.A., Raber, P.B., Trancik, R.J. & Dahl, M.V. 1983, "Reusable ultraviolet monitors: Design, characteristics, and efficacy," *J. Am. Acad. Dermatol*. vol.9, pp.714-723.
17. Butson, M.J., Cheung, T., Yu, P., Abbati, D. & Greenoak, G.E. 2000, "Ultraviolet radiation dosimetry with radiochromic film," *Phys. Med. Biol*. vol.45, pp.1863-1868.
18. Jankowski, J.J., Kieber, D.J., Mopper, K. & Neale, P.J. 2000, "Development and intercalibration of ultraviolet solar actinometers," *Photochem. Photobiol.* vol.71, pp.431-440.

19. Wong, C.F. & Parisi, A.V. 1996, "Measurement of UVA exposure to solar radiation," *Photochem. Photobiol*. vol.63(6), pp.807-810.
20. Jackson, S.A. 1980, "A film badge dosimeter for UVA radiation," *J. Biomed. Engng*. vol.2, pp.63-64.
21. Quintern, L.E., Furusawa, Y., Fukutsu, K. & Holtschmidt, H. 1997, "Characterization and application of UV detector spore films: the sensitivity curve of a new detector system provides good similarity to the action spectrum for UV-induced erythema in human skin," *J. Photochem. Photobiol. B: Biol.* vol.37, pp.158-166.
22. Diffey, B.L., Davis, A., Johnson, M. & Harrington, T.R. 1977, "A dosimeter for long wave ultraviolet radiation," *Br. J. Dermatol*. vol.97, pp.127-130.
23. Diffey, B.L. & Davis, A. 1978, "A new dosemeter for the measurement of natural ultraviolet radiation in the study of photodermatoses and drug photosensitivity," *Phys. Med. Biol.* vol.23, pp.318-323.
24. Parisi, A.V., Wong, C.F. & Galea, V. 1996, "A method for evaluation of UV and biologically effective exposures to plants," *Photochem. Photobiol.* vol.64, pp.326-333.
25. Parisi, A.V., Wong, C.F. & Galea, V. 1998, "A study of the total ultraviolet exposure to all the leaves for small plant growth," *J. Photochem. Photobiol. B: Biol.* vol.45, pp.36-42.
26. Parisi, A.V., Galea, V.J. & Randall, C. 2003, "Dosimetric measurements of the visible and UV exposures on field grown soybean plants," *Agric. For. Meteorol.* vol.120, pp.153-160.