Manual for Polysulphone Dosimeters Characterisation, Handling and Application as Personal UV Exposure Devices

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Physical and Chemical Exposure (PCE)

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Introduction

What is Ultraviolet Radiation ?

There are natural and artificial sources of the ultraviolet radiation. The artificial sources inculde sunlamps, mercury vapor lamps etc. The sun is a natural source of ultraviolet radiation. UV radiation consists of three main components namely UV-A, UV-B and UV-C.

UV-C : [100 nm-280 nm]

This part of radiation is destructive and causes most damage to the biosphere but it is completely absorbed by ozone and oxygene molecules in the upper atmosphere, so this of little importance.

UV-B : [280 nm – 315 nm]

This part of radiation is strongly absorbed by ozone levels in the stratosphere and only small amounts reaches the earth's surface, but with the thinning of the stratospheric ozone more UV-B can reach the earth's surface, thus becoming the environmental problem.

UV-A : [315 nm – 400 nm]

This part of radiation is only slightly affected by ozone levels, so the earth's surface is composed of large amounts of this radiation.

On what does the amount of UV-Radiation reaching the earth's surface depend on ?

Stratospheric Ozone

Since ozone absorbs most of the sun's UV-B radiation, the intensity of the UV-B that reaches the surface strongly depends on the total amount of ozone in the atmosphere.

Time of the day / Solar Elevation

The sun is at its highest position in the sky around noon. At this time the sun's rays have the least distance to travel through the atmosphere and the levels of UV are at their highest, and the ground received most direct radiation. In the early morning and late afternoon, the sun's rays pass through the atmosphere at an angle an their intensity is greatly reduced.



Typical radiation distribution during a clear day in March (Ispra 2002)

Time of the Year

The sun's angle varies with the seasons causing the intensity of UV rays to change. UV intensity is high during summer, less in spring and autumn and least in winter months.



Typical radiation course during one year (Ispra – Italy)

Altitude

UV intensity increases with altitude because there is less atmosphere to absorb the damaging rays. Thus, the higher the altitude, the higher the risk of overexposure. Measurements indicate a 16-18 % increase of UVR with each 1000 m.

Latitude

At higher latitudes the sun is lower in the sky, so UV rays must travel a greater distance through ozone-rich portions of atmosphere and in turn exposes those latitudes to less UVR.

Haze and Clouds

Cloud cover normally reduces UV levels, but not completely, depending on the thickness of the cloud cover. A thick, heavy layer of clouds blocks UV whereas thin fairy-weather

clouds can be easily penetrated by UV rays. At certain conditions and for short times a small amount of clouds could enhance UV irradiance.

Ground Reflection

Some surfaces reflect much of UV radiation. For example snow may reflect up to 80% of the UVR.

Which are the Effects of UV-B Exposure ?

All living organisms are UV-B sensitive. Since UV-C is completely absorbed in the upper atmosphere it does not impose environmental problems.

UV-B causes sunburn, it damages the skin. This damage can lead to skin cancer, delayed skin pigmentation, premature aging of the skin, immune system suppression, and reduces vitamin D synthesis. It can also cause eye cataracts by burning the surface of the eye and lead to retinal aging.

Although UV-A is less in energy compared to UV-B, it still has long term effects such as aging, and causes the skin to be fragile and break easily.

Measuring-Units and Action Spectra

The total irradiance $[J/m^2]$ provides information about the total photon energy (Joules) in the UV waveband falling on a unit area (m²) of the surface of the body in consideration. Because the response of the biological body to UVR varies with the wavelength of the radiation, this quantity is not a good index of biological effects.



Solar spectral global irradiance at Ispra for two solar zenith angles (SZA) on September 25, 2003. The upper curve (green) was measured at a SZA of 46° and the lower curve (blue) at a SZA of 83°.

To assess the biologically affective exposure to a selected biological tissue, it is necessary to know the sensitivity of the tissue to UVR. This method requires rescaling the spectral irradiance by the relative sensitivity of the biological tissue.

Both the passive sampler and the broadband sensor should have a spectral response suitable for the assessment of the effect of UVR on the biological body in consideration.

In our case we are looking for erythemal weighted action spectra sensors.

The CIE (1987) erythmal action spectrum for humans has been employed widely for assessing the UV effect on human skin.



The spectral sensitivities of the broad band radiometer used in this stud (red curve), the polysuphone film (blue curve), and the Erythema action spectrum (green doted curve)

The Measuring Units

$$1 W = 1 J/s$$

What we are measuring with the broadband radiometer is [$W / m^2 * min$]. So we have to multiply the amount of [W/m^2] with 60 to get Joules per square meter.

The Unit MED

The amount of UVR may be expressed in terms of physical or biological units, depending upon which aspects of radiation are under consideration.

The physical units are Joules per square meter or Watt per square meter.

MED units (Minimal Erythemal Dose) is described as the amount of UV radiation, which causes the reddening of the skin, commonly known as sunburn.

The MED (1 MED) is defined as the effective UV dose that causes a perceptible reddening/tanning of previously unexposed human skin persisting over 24h.

Skin Type	Tanning	Sun Burn	Hair Colour	Eye Colour	1 MED
					[J/m ²]
1	Never	Always	Red	Blue	200
2	Sometimes	Sometimes	Blond	Blue/green	250
3	Always	Never	Brown	Grey/brown	350
4	Always	Never	Black	brown	450

$1 \text{ MED / h} = 58.333 \text{ mW/m}^2$ $1 \text{ MED} = 210 \text{ J/m}^2$

Defined for Skin Type 1.

Advantages of Polysulphone Dosimeters

• The film dosimeter provides a simple means of integrating UVR exposure continously

- It allows numerous sites, inaccessible to bulky and expensive instrumentation, to be compared simoultaniously
- Spectral response similar to that of human skin
- Cheap
- No or very small temperature and relative humidity effects
- Easy to handle

Characterization and Properties of Polysulphone

Chemical Structure of Polysulphone



IR - Spectrum of Exposed and un-Exposed Polysulphone Film



Optical Properties of Polysulphone

The absorption spectrum of 40 μ m polysulphone film before and after exposure to UVR is shown in the figures below. During exposition a deterioration of the polymer takes place.



Changes in the absorbance spectrum due to different amounts of radiation At which wavelength does the increase in absorbance reach the highest value ?

Basically two methods can be applied to find out the wavelength at which the ΔA is highest:

Subtraction of unexposed from exposed spectrum

The result is an <u>absolute</u> value.

Divison (Ratio) of the exposed and the unexposed spectrum

What we become here is the <u>relative</u> (percentage) increase in absorbance. This is what we are looking for.



The film may be used as a dosimeter for UVR by relating the incident radiant exposure (or dose) to the increase in absorbance measured at a wavelength of 330 nm.

Absorbance Maximum of Polysulphone : 330 nm





Which film-thickness is best to use ?

The choice of film thickness is a compromise between minimizing the absorption of wavelengths greater than 330 nm and achieving mechanical strength to facilitate handling.

One of the most commonly used thicknesses is 40 µm.

Handling of the Dosimeters

How do the following parameters influence the polysulphone films ?

Temperature during exposition

The response remains stable inbetween –4 C and 53 C.

Storage before exposition

The film can be stored at room-temperature in a dark, UV-less place.

Relative Humidity

Relative humidity has no effect on the film.

Pratical Section

Calibrating the Dosimeters by broadband radiometry

The method we use to determine the biologically effective irradiance is the calibration by broadband radiometry.

The sensor of the broadband radiometer has a spectral sensitivity closely approximating erythmal action spectrum for human skin.



Spectral response of Yankee-broadband radiometer and human skin

This type of calibration is useful when the polysulphone films are intended to be used as monitors for personal exposure to UVR.

What has to be done, is to expose the badges near the broadband radiometer (see foto below) for defined periods of time.



After the exposition and the measuring of the difference in absorbance before and after exposition, the ΔA can be put into relation with the amount of radiation measured by the broadband radiometer in the defined period of time.

The following calibration curve is obtained.



The equation of this calibration curve is

Radiation amount $[J/m^2] = 8025 (_{\Delta}A)^2 + 1980.8 * _{\Delta}A$

Erythmically weighted radiation amount

 $_{\Delta}A$ = Absorbance at 330 nm after exposure – Absorbance at 330 nm before exposure

Measuring UVR

The procedure is the following:

- Measure absorbance before exposure (A1). The value should be inbetween 0.105 Abs and 0.133 Abs for 40 μm film.
- Expose
- Measure absorbance after exposure (A2) after 24 h (see dark reaction section)
- put $_{\Delta}A$ into the equation and calculate radiation amount

Errors associated with Polysulphone Film Dosimetry

There are two types of error associated with the calibration of any dosimetric system: systematic uncertainties in calibration and random uncertainties due to the reproducibility of the dosimeter.

In this section only those factors which affect the reproducibility of response (random errors) of polysulphone film will be considered.

Within batch variation

Ten polysulphone film badges were exposed simultaneously for 30 min in an artificial weathering chamber (Davis and Gardiner, 1982). Exposing a number of films manufactured from the same batch under these controlled conditions yields a coefficient of variation of 1,4 %.

Film ID	Abs before Exposure	Abs after Exposure	ΔA_{330}
1	0.170	0.465	0.295
2	0.169	0.459	0.290
3	0.166	0.461	0.295
4	0.170	0.159	0.289
5	0.168	0.455	0.287
6	0.170	0.461	0.291
7	0.171	0.461	0.290
8	0.172	0.460	0.288
9	0.169	0.453	0.284
10	0.175	0.474	0.299
		Variation	1.4 %

Dark Reaction

It was found (Davis et al., 1976) that when stored, a previously exposed polysulphone film undergoes a "dark reaction"

The graph illustrates that the $\Delta A330$ measured immediately after exposure is about 8% less than that measured 24h later and 10% less than that measured one week later.

If exposed film are kept for several months their $\Delta A330$ is about 5% higher than values obtained after 24h after exposure.



Effect of surface contamination

Tate (1979) has studied the effects of surface contamination on the performance of polysulphone films. A summary of these results is given in the following figure.

Grease as a consequence of holding the film between the fingers, and dust shaken onto the film, both serve to increase the $\Delta A330$ over "control" films.



The uncertainty in the measured dose



In the next figure the percentage difference in-between effective radiation (measured with broadband radiometer) and the radiation calculated by applying the formula is shown.

Reasons for measuring errors

- Differences in response (action spectra) of skin and the dosimeter film
- Differences in response (action spectra) of polysulphone film and broadband radiometer
- Saturation of polysulphone film at $\Delta A > 0.3$

Applications of Polysulphone Film Dosimetry

Polysulphone films have been used principally as personal dosimeters for evaluating human exposure to both natural and artificial UVR in a variety of situations.

They have also been used as an alternative to physical detectors in monitoring radiation exposure in photochemical processes.



Dosimeter with clip

Polysulphon film dosimeter (UV dosimeter) handeled in the before described way were used for the evaluation of the personal UV exposure of participants at a measuring campaign in South France. The measurement period during that campaign lasted from the 8^{th} to the 14^{th} of April 2003. The personal UV dosimeters, 2 per person, one horizontal (on top of a hat) and one at 90°, were changed each day during that period and the participating people used a simple micro-environment (see below) protocol for documenting their personal activities. In comparsion all days a set of UV dosimeter was exposed on three fixed positions (horizontal, 90°).

Material Used:

Polysulphone Film (40 um thickness) purchased from Dr.Parisi (Australia).Calibration curve used: 7 darkness reaction after expositionCalculated Value: Erythemally weighted UV-B Radiation [J/m²]

Name								
			Init Time	End Time of		Remarks		
			of exposure	exposure				
Date	Weather							
	Sunny							
	Cloudy							
	Mixed							
	Rain							
1 Time w is taken o	hen Dosimeter off	is wo	orn ₂ Time w	/hen dosimeter				

Microenvironment Protocol used during the measurement campaign:



The graph shows the results achieved during that measurement campaign. The results show clear the differences between the personal exposure and the "exposure" measured at the fixed places. That makes sense because it depends always on the daily behaviour of the people, which was stated in the microenvironment protocol. This underlines the necessity of a detailed micro-environment protocol because only these data together with the exposure data are useful as input data for personal exposure and risk assessment models.

Instruments used for characterisation and calibration of the Polysulphone films

Spectrophotometer:

JASCO V-750 UV/	VIS/NI	R Spectrophotometer
UV/VIS-Region	:	1200 lines/mm plane grating
NIR-Region	:	300 lines/mm plane grating
Double beam Type		
Resolution	:	0.1 nm (UV/VIS)
		0.5 nm (NIR)
Wayalangth ranga		100 nm to 2500 nm

Wavelength range

190 nm to 2500 nm



In order to reduce scattering during the measurement to a minimum, we measured the absorbance inside an integrating sphere.



Integrating Sphere

Spectral bandwidth	:	UV 5 nm NIR 20 nm
Inside diameter of Integrating Sphere	:	60 mm
Detector	:	PbS photoconductive cell

Measuring Parameters (Single Measurement)

Wavelength	:	330 n	m		
Mode	:	Absor	Absorbance		
Spectral bandwidth	:	UV	5 nm		

Measuring Parameters (Spectrum)

Wavelength	:	500 nm - 240	nm
Mode	:	Absorbance	
Bandwidth	:	UV/VIS	5nm
Data Pitch	:	2 nm	
Scanning Speed	:	400 nm/min	

Broadband Radiometer

Manufacturer Model Spectral Response Cosine Response Sensitivity Sensor Active Area Response Time Ambient Temp. Range Yankee Enivornmental Systems, Inc. UVB-1 Ultraviolet Pyranometer 280 nm to 320 nm +/- 5% for 0-60 Degree solar zenith angle 1.97 Volt/ (Watt/m2) of effective UV-B irradiance ca. 2,54 cm diameter 0.1 s -40 C to +40 C



Broadband Radiometer





References

Diffey, B.L. (1986). Possible Errors Involved in the Dosimetry of Solar UB-B Radiation. NATO ASI Series, Vol. G8. Springer Verlag Berlin Heidelberg 1986

Herlihy, E., Gies, P.H., Roy, R.C. & Jones, M. (1994). Personal Dosimetry of Solar UV Radiation For Different Outdoor Activities. Photochemistry and Photobiology, Vol. 60, No.3, pp.288-294

Parisi, A.V., Wong, C.F. (1994). A Dosimetric Technique For The Measurement Of Ultraviolet Radiation Exposure To Plants. Photochemistry and Photobiology, Vol.60, No.5, pp.470-474

Parisi, A.V., Meldrum, L.R., Kimlin, M.G. Photobiology. www.photobiology.com/UVR98/parisi/

Diggey, B.L. (1987). A Comparison Of Dosimeters Used For Solar Ultraviolet Radiometry. Photochemistry and Photobiology, Vol.46, No.1, pp. 55-60

Diffey, B.L. (1989). Radiation Measurement in Photobiology. Academic Press Limited, 24-28 Oval Road, London NW1 7DX. ISBN 0-12-215840-7

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