A new development for determining the ultraviolet protection factor

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1.- INTRODUCTION

In recent years concern about ultraviolet radiation (UV) has increased dramatically. It is one of the types of radiation emitted by the sun that is not visible nor can it be felt. Ultraviolet radiation is an electromagnetic radiation with a wavelength shorter than visible light and greater than weak X rays. The range of ultraviolet radiation is also subdivided into UVA (400-315nm), UVB (315-280nm) and UVC (<280nm). The effects of ultraviolet radiation on human health depend on the wavelength of the UV radiation. [1-3] UVA radiation contributes to the premature aging of the skin, and some recent studies have concluded that prolonged exposure can also cause skin cancer. UVB radiation causes most cancers, cataracts and sunburn. UVC radiation is extremely harmful but it is completely absorbed in the atmosphere by the ozone layer before it reaches the earth's surface.

UVB radiation is more harmful that UVA due to its shorter wavelength, which is more energetic .The intensity of UVB radiation on earth surface is 5W/m2, whilst UVA radiation on earth surface is 27W/m2. [4]

In fact, 99% of the ultraviolet radiation that reaches the earth's surface is UVA radiation. However, in areas where the ozone layer is thinning this is not the case. One of the most troubling environmental problems faced by humans is the overall thinning of the ozone layer. This decrease in the thickness of the ozone layer is causing an increase of the amount of UVB radiation that reaches the Earth's surface. A 1% decrease in the ozone layer will cause an increase in solar radiation at the earth's surface that could increase the number of cases of skin cancer by up to 2.3%. [5]

The demand for information about ultraviolet radiation is increasing and a number of studies have been carried out to determine appropriate protection measures, including recommendations on use, behaviour and personal protection. [1] The World Health Organization (WHO) recently recommended the use of textiles with high protection factors. [6]

Textiles provide protection against UV radiation but in many cases the protection they provide is not sufficient. The Ultraviolet Protection Factor (UPF) is used to assign a textile's degree of protection. Recent studies have provided

information regarding the characteristics that textiles must have in order to offer good UV protection. [7, 8]

In engineering woven fabric with good UV radiation (UVR) protection, the following factors must be considered [9-14]: Composition of the fibers (most natural fibers transmit UV radiation more than synthetic ones); Tightness of the weave (the more closely woven the fabric, the less UV radiation is transmitted); Color (light pastel shades of the same fabric type will transmit UV radiation more strongly than dark colors and will consequently have lower UPFs); Stretch (the greater the stretch, the lower the UPF rating); and Finishing (UV absorbing chemicals improve UPF). [11] The more the transmittance of the textile, the less UPF value it will have.

It is also known that worn and faded fabrics may have reduced UPF ratings, while washed cotton and polycotton fabrics, because of fabric shrinkage, slightly improve UPF.

Some studies on different ways to determine the UPF value of fabrics have been published [15-20]. The first system used was the in vivo methodology. This methodology consisted of applying a textile sample to an area of an individual's back. This area and an unprotected adjacent area of skin were then irradiated with a standardized light that had a spectrum similar to sunlight. The spectrophotometric method is internationally accepted and is the most widely used due to its objectivity and reproducibility. The measurement device consists on the following items: UV source providing UV radiation throughout the wavelength range from 290 to 400 nm, integrating sphere, monochromator suited for measurements with a spectral bandwidth of 5 nm or less in the wavelength region 290–400 nm, UV transmitting filter, which transmits significantly only at wavelength less than approximately 400 nm and which does not fluoresce [15]. Other authors have also recently published a methodology that works outdoors. UVB radiation is detected by dosimeters. This method is based on the known absorbance variation of dosimeters at a determinate wavelength after exposure to sunlight. Dosimeters are placed both above and below the fabric of a garment that is placed on a mannequin. The amount of UVB radiation blocked by the textile is determined from the difference in absorbance between the dosimeters. There are a lot of materials under study as detectors. Wilson et al. [16] use polysulphone dosimeters, R. Shweikani et al. [17] and F. Abu-Jarad et al. [18] use in their studies CR-39 plastic] and M. Kozicki et al. [19, 20] use nitro blue tetrazolium chloride as an active compound.

The AS/NZ 4399: 1996 standard is used to classify the textiles. This standard was created in Australia and is a pioneer in the classification of tissues according to their UPF. This standard is intended to provide information to the consumer on the relative capability of textiles and articles of personal apparel to provide protection against solar ultraviolet radiation.

The aim of this study is to develop a new method for determining the UPF with less measurement error than the existing methods commits. It consisted of an UV lamp which has a known wavelength and a UV radiation detector wich was placed below the fabric. Results were statistically studied in order to validate the method's usefulness.

2.- MATERIALS AND METHODS

2.1. Materials

A total of 72 samples have been evaluated. These samples were chosen systematically by varying the parameters in order to obtain a wide sample range. The parameters varied were the weave, the colour, the weft material, the weft density and the fabric weight (g/m^2). A standardized warp thread (150den) and warp density (60h/cm) was used for all samples.

The colours of the woven samples are yellow (according to CIELAB L*:67,21, a*:5,24, b*:24,78) and brown (according to CIELAB L*:30,62, a*:5,43, b*:3,29).

Insert table 1 about here.

2.2. Methods

The new system consists of three basic elements as shown in Figure 1. An UV radiation lamp, a photodetector connected to a computer, and an opaque box that encompasses the entire system to avoid lighting interferences. The photodetector consists on a photoelectric sensor that absorbs all the radiation emitted by the UV-lamp.

Insert figure 1 about here

The operating procedure used in the laboratory is fairly simple. Firstly, the samples are prepared and conditioned according to the ISO 139:2005 standard. All samples were extracted from the centre of the fabric at an exact distance of 1250mm from the selvage. The second sample of the same reference was extracted from a distance of 1cm from the first sample. All samples were conditioning for a time of 120 minutes at a temperature of 22ºC and 62% of relative humidity. The standardized size of each sample is 10x10cm because covers the photodetector completely. Once the samples have been prepared the measuring process can begin. The fabric sample covers the detector so that all radiation that reaches the probe must first pass through the sample. A total

of 60 measurements of each sample were taken, because the photodetector takes a measurement in a 5 seconds interval in a total measurement time of 300 seconds.

The measuring conditions are always identical and the detector is always placed in the same position on the base lamp. The detector has unique measurement characteristics as the measurement area is about 1cm^2. This means that the detector measures an area of fabric and not an individual point.

The ultraviolet lamp is then turned on with the required bulb and it takes some time to reach the correct radiation values. Once the test piece is in place the opaque cover is fitted.

UPF determination is based on measuring the ultraviolet radiation transmission through the textile compared with the radiation without fabric. The emission source emits ultraviolet radiation at two specific wavelengths, 312nm and 365nm, which correspond to UVB radiation and UVA radiation respectively. These two emission sources were chosen because they represent the ultraviolet radiation and are available in the market easily.

Thus the sample is perpendicularly irradiated and the UV transmittance of the sample is obtained.

In according with European Standard EN 13758-1, the UPF of fabric is determined from the total spectral transmittance as follows:

$$UPF = \frac{\sum_{\lambda=290}^{400} E(\lambda) \cdot \varepsilon(\lambda) \cdot \Delta(\lambda)}{\sum_{\lambda=290}^{400} E(\lambda) \cdot T(\lambda) \cdot \varepsilon(\lambda) \cdot \Delta(\lambda)} \qquad (1)$$

Where $E(\lambda)$ is the solar irradiance expressed in $\text{Wm}^{-2}\text{nm}^{-1}$, $\varepsilon(\lambda)$ is the erythema action spectrum, λ is the wavelength interval and $T(\lambda)$ is the spectral transmittance at wavelength λ.

The UPF is actually the measure of UV radiation (UVA and UVB) blocked by the fabric. Higher UPF value means more blocked UV radiation. UPF is measured by a spectrophotometer [15].

The UPF value represents the mean value of UPF calculated for a set of fabric specimens, rounded down to the nearest 5. Regarding UV protection, fabrics are classified as shown in Table 2 [21].

Insert table 2 about here

3. RESULTS AND DISCUSSION

To determine the UPF factor of the new method the equation in EN 13758-1 is slightly amended. This is because in the UPF determination of the new method

does not scan radiation from 290 to 400nm. In the new method there are only two point measurements, 312nm and 365nm. The equation of the ultraviolet protection factor of the new method is as follows:

$$UPF = \frac{E(312)\cdot\mathcal{E}(312)\cdot\Delta(\lambda)+E(365)\cdot\mathcal{E}(365)\cdot\Delta(\lambda)}{E(312)\cdot\mathcal{E}(312)\cdot T(312)\cdot\Delta(\lambda)+E(365)\cdot\mathcal{E}(365)\cdot T(365)\cdot\Delta(\lambda)} \qquad (2)$$

Both solar irradiance (E), and the erythemal action spectrum with CIE (ε) are taken from EN 13758-1 where values are tabulated for each wavelength. The increase in wavelength is 53 because that is the difference between both measurements.

The transmittance is determined from the relationship between the irradiance measured by the detector and the initial irradiance at each wavelength:

$$\mathrm{T} = \frac{I}{Io} \qquad (3)$$

Initial irradiance corresponds to the measured irradiance in summer in Albuquerque and is termed solar irradiance, being tabulated in EN 13758-1. The relative erythemal effectiveness (ε) is also tabulated in EN 13758-1.

Insert table 3 about here

3.1. Regression model

The samples have been tested with both the spectrophotometric method and the new method to get two UPF values. The whole range of samples has been tested with the new method, and 34 of them have been tested also with the spectrophotometric method to get the UPF values. Those 34 samples were chosen because in a previous work "*Influencia de los parámetros estructurales de los tejidos de calada en la protección frente a radiación ultravioleta*" [22] it was showed the weak influence of the colour of the sample and materials used. According to Diaz et. Al. the parameters with the greatest influence on UV protection factor are the structural parameters such as weave of the sample or the fabric weight (g/m^2). These results are shown in Table 4.

Insert table 4 about here

In order to model the new method and obtain a correlation with the actual UPF statistical modelling has been performed as shown in Figure 2.

Insert figure 2 about here

The equation fit for the regression lineal model and describes the relationship between both methods:

$$UPF = 31.7936 + 2.04437 \cdot UPFn \qquad (4)$$

Where UPFn is the value of the UPF obtained with the aternative method.

In Table 5, the ANOVA table shows that the p-value is less than 0.01, so there is a statistically significant relationship between the spectrophotometric UPF measurements and the new UPF measurements using the new method with a confidence level of 99%.

Insert table 5 about here

The R-squared statistic analysis indicates that the model explains 97.61% of UPF variability. The correlation coefficient is 0.9527, denoting a strong relationship between the variables.

3.2. Residuals analysis

Strength and robustness were tested to describe the behaviour of the statistical model more precisely. Additional statistical tests were also carried out including the distribution of residuals, residual expectation, homoscedastic behaviour, and the covariance of residuals.

Figure 3 shows the density traces and residuals histogram adjustment to normal distribution. That figure shows the estimated parameters of the fitted distribution.

Insert figure 3 about here

3.2.1. Analysis of the normality of the residuals

First the normality of residuals is checked by the Shapiro-Wilks W test. This test is considered one of the most potent tests for normality contrast, especially for small sample sizes (n <30). [23] It was postulated that a sample came from a normally distributed population.

H_0: Residuals are distributed normally.

H_1: Residuals are not distributed normally.

The p-value of the Shapiro-Wilks test is 0.5714, higher than 0.05, and therefore it is not possible to reject the hypothesis that the residuals come from a normal distribution with a confidence level of 95%. That statistical analysis indicates that the model is meaningful.

3.2.2. Analysis of the residual's homoscedastic behaviour

Secondly, residual's homoscedasticity is studied. The homoscedasticity is presented in a statistical model when occur errors with the same variance in all observations of the endogenous variable. The statistical model relates the spectrophotometric UPF value to the predicted alternative UPF value. If the model is unbiased, the predicted value is the average of the variable being

measured. Homoscedasticity is said to exist when the variance of stochastic errors of the regression is the same for each observation. This quality is necessary, according to the Gauss-Markov theorem, in order that the estimated coefficients in a model are the most efficient, linear and unbiased. When the variance of each error term is not a constant number, heteroscedasticity is said to exist.

The following equation is established to perform the analysis:

$$e^2 = \beta_0 + \beta_1 x + U \qquad\qquad (5)$$

And the following hypothesis test:

H_0: β1=0

H_1: β1≠0

As shown in Table 6, the p-value in the ANOVA table is greater than 0.05, therefore there is no statistically significant relationship between the variables for a confidence level of 95%. This result denotes that there is no heteroscedasticity, so residuals can be said to have homoscedastic behaviour. As the model has homoscedastic behaviour it is available to determine the UPF value of the fabrics.

Insert table 6 about here

3.2.3. Autocorrelation analysis of residuals

Finally the residuals autocorrelation analysis is carried out using autocorrelation and partial autocorrelation plots analysis. These two tests check that there is no residuals autocorrelation. As shown in Figure 4, there is no autocorrelation or partial autocorrelation, as the autocorrelation limits are not exceeded in either case. There is no autocorrelation between the model and the residuals so the model can be used to determine the real UPF value.

Insert figure 4 about here

3.3. Measurement error

The most important aspect of this paper is the reduction of measurement error when using the alternative system as compared to the spectrophotometric method. To evaluate the measurement error that both methods possess, a comparison of the measurement UPF standard deviation has been carried out. Analysing a comparison of the standard deviation with the following test hypothesis corroborates this:

H_0: $\sigma_1 = \sigma_2$

H_1: $\sigma_1 < \sigma_2$

The p-value obtained by the F-test is 0.00004 so the null hypothesis can be rejected. The standard deviations are not similar. Therefore, the typical deviation of the new methodology is less than the spectrophotometric method.

Insert figure 5 about here

While in the spectrophotometric method the measuring area is the size of a light beam [15], which irradiates the sample, the measurement area is 1cm^2 in the new method proposed in this paper.

As Figure 5 shows, in some samples the measurement error is equal in the two methods, but the difference of the measurement error in other samples is considerably. The measurement error by the new methodology is lower than the spectrophotometric method.

It is also worth noting that the new method works better with textiles whose UPF values are low, because in this range of UPF values, is where the measurement error is minimized to levels that do not reach the unit. At higher UPF values, the error obviously increases, but remains lower in the new method than the spectrophotometric method.

To complete the study of the measurement error the variation coefficient is studied. To obtain the variation coefficient is according to the following equation:

$$COV = \frac{\sigma}{Mean} \qquad\qquad (6)$$

The variation coefficient enables the statistical error to be studied in greater detail. The variation coefficient is defined as the deviation of each sample related to its mean.

The variation coefficient obtained by the new method is also lower than the values obtained spectrophotometrically, but in this case three samples have a greater error with the new method than the spectrophotometric method, as can be seen in Figure 6.

Insert figure 6 about here

Samples with an excessive error committed by the new method are 8.1, 31.1, 30 and 34. Both the 8.1 and 30 samples have errors slightly above those obtained spectrophotometrically, while sample 34 and 31.1 have an error about 75% greater. For UPF values lower than 5, the new method gets UPF values below that of the spectrophotometric method. This last point is very important because according to EN 13758-2, Classification and marking of apparel, above a UPF value of 40, the textiles are categorized as providing excellent protection

(UPF 40 +). Below this value it is important to distinguish between factors eg 20 or 25 because the classification varies from "good" to "very good" [24].

That is, the new method provides lower measurement errors than spectrophotometrically in almost any measurement range of UPF. The new method is especially sensitive in UPF values lower than 5, where the sample is much lighter and the holes generated in textiles are higher. In that UPF measuring range the new method makes a measurement error less than a UPF point. As noted, the new method measurement error is lower than the spectrophotometric method, and this is because the new method measurement area is approximately 100 times bigger.

Based on spectrophotometric measurements and mathematical calculations, the ultraviolet protection factor of a textile is determined in vitro. This technique is the most established test method for the determination of UV protection of a garment. However, the validity and practicality of the in vitro UV protection factor (UPF) determined in the laboratory has been a controversial issue with regard to its significance in the field. Several studies have verified the in vitro UPF by comparing it with various in vivo test protocols using solar-simulated radiation for the determination of the minimal erythema dose. The spectrophotometric method also has a very high measurement error so that the variation in the measurements is important. This is because the beam measurement is very precise and depending on the irradiation area of the sample the mean can vary in excess. The new method has the main advantage of the methodology and minimizes spectrophotometric measurement errors. Gambichler et al. in their study comparing in vivo and in vitro methodologies conclude that the results using both techniques are very similar [25]. However, the in vivo method has some drawbacks. The main drawbacks are that in order to obtain a reliable measure of in vivo protection factor requires a sufficiently representative number of individuals subjected to the test; specialized personnel can visually determine the time that has reddened skin without inducing a considerable error. Therefore it can be considered that this method lacks speed, reproducibility and objectivity. It is also an invasive method so it can cause irreversible damage in patients. Furthermore, UV dosimetry is a suitable method for quantifying UV transmission through a garment. Chemical dosimeters and biological UV detector films have been used in in vivo-simulated studies in the form of small portable badges monitoring solar UV transmittance through garments on manikins and mobile subjects. As sunlight consists to a considerable extent of diffuse radiation, which is more scattered and absorbed by the fabric than direct radiation, UPF values obtained by measurements in real exposure situations are usually higher than those obtained by conventional in vitro and in vivo testing with collimated radiation beams. Wilson et al. describe a methodology based on polysulfone films. The main drawback of this method is that only measures UVB radiation absorbed at a given wavelength,

being UVA radiation outside the measuring area. The measuring system of the ultraviolet radiation is not suitable to obtain the UPF value. [16] Thus the discrepancy between laboratory-based testing and field-based measurements may be due to different radiation geometry of UV sources. Taken together, the in vitro method is the most practicable and inexpensive method for routine measurements of UPF, but dosimetry seems to be a highly useful method for determining the UPF in real exposure situations. [26]

The new method, therefore, has the advantages of spectrophotometric method being fast, reproducible and objective. The new method also minimizes the measurement error getting considerably more accurate results. Faced with the impossibility of making measurements in the field of the spectrophotometric method, the new method is similar in this aspect to polysulfonic dosimeters. Polysulfonic systems allow making measurements in the field but is impossible determine the UPF. The new system allows measurements in the field and also determines the UPF with high precision. Therefore the new method for determining the UPF combines the advantages of existing methods and minimizes inconvenience.

4.- CONCLUSIONS

The new method is totally reproducible because it is according the European standards. The samples are prepared and conditioned according to the ISO 139:2005 standard, and the UPF values are obtained according the spectrophotometric method standards. The new method uses as parameters of erythemal effectiveness and solar irradiance the values of EN 13758-1 norm, so the new method proposed is completely reproducible and extrapolated.

The main conclusion is that there is a statistical correlation of 95.27% between the data obtained by the new method and the spectrophotometric method, therefore the real UPF can be obtained from the alternative method due to the strong correlation between the two methods. Is notable that the statistical correlation is stronger at lower UPF values than at higher values.

The UPF is obtained by the new method and using the following equation: $UPF = 31.1591 + 2.0443705774 \cdot UPFn$.

The measurement error in the samples studied is less than the measurement error committed by spectrophotometric technique, and the deviation of the samples of the new method is lower than the spectrophotometric method.

Table 1. Protection categories of fabrics according to AS/NZ 4399: 1996.

UPF range	Protección category	Effective UVR transmission (%)	Rating
15 - 24	Good protection	6,7 a 4,2	15, 20
25 - 39	Very good protection	4,1 a 2,6	25, 30, 35
40 - 50, 50+	Excelent protection	≤ 2,5	40, 45, 50, 50+