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Determination of Sun Protection Factor by UV-Vis Spectrophotometry

Fonseca AP* and Rafaela N

Instituto Politécnico de Coimbra, ESTESC, D Farm, GIAF, Rua 5 de Outubro S. Martinho do Bispo Apartado 7006, 3040-854 Coimbra, Portugal

Abstract

Background: Sunscreen products contain active ingredients that can absorb, reflect or scatter the sunlight, depending on their nature. We can evaluate the effectiveness of a sunscreen by determining the sun protection factor (SPF). This SPF should be specific for each phototype, so as to the protection against the damaging effects of UV rays may be the best. Besides the choice of the adequate sunscreen, care must be taken with the application method and the amount of product that is applied. In most cases, the real SPF did not correspond to the labeled SPF.

Aim: The aim of this study was to determine the real SPF values of ten chemical or physical sunscreens through UV-Visible Spectroscopy, as well as the degradation by direct solar radiation and temperature at 37°C.

Methods: UV-Vis spectrophotometry was used to measure the UV absorption of each sample and the Mansur equation was applied to obtain the final SPF.

Results: The majority of the studied sunscreens have much lower SPF when compared to the labeled value.

Conclusion: To avoid the damaging effects of UV radiation, we have to encourage the correct use of sunscreen, reapplication and double-application to reach a desirable effect of the sunscreen, promote the use of other physical protection (clothes, hats) and avoid the hours of peak radiation. We also concluded that it is important to have constant monitoring of SPF on sunscreens marketed in World, in order to allow their use with complete quality assurance.

Keywords: Sun protection factor; Sunscreens; UV-visible spectroscopy; Degradation

Introduction

The skin is part of the integumentary system, which also includes accessory structures such as hair, nails and glands. The skin has two major tissue layers, the dermis and the epidermis, and rests on the hypodermis, also known as subcutaneous tissue, which consists of loose connective tissue with collagen and elastin fibers [1].

The function of the dermis is to provide structural strength to the skin. It consists of connective tissue with fibroblasts, a few adipose cells and macrophages, and has two layers: the deeper reticular layer and the more superficial papillary layer [1].

The most superficial layer of the skin is the epidermis and it is separated from the papillary layer of the dermis by a basement membrane. The epidermis has no blood vessels and is nourished by diffusion from the capillaries of the papillary layer, consists of a stratified squamous epithelium and most cells are keratinocytes, being responsible for the structural strength and the permeability characteristic of this layer. On the epidermis, there are also melanocytes (which contribute to the skin color), Langerhans cells (part of the immune system) and Merkel's cells (detection of light touch and superficial pressure) [1].

The spectrum of the sun's solar radiation has a range of 100 nm to 1 mm that may be divided into five regions: Ultraviolet C or UVC (from 100 nm to 290 nm), which is absorbed by the atmosphere; Ultraviolet B or UVB (from 290 nm to 320 nm); Ultraviolet A or UVA (from 320 nm to 400 nm); visible range or light (from 380 nm to 780 nm) that is visible to the naked eye; and Infrared (from 780 nm to 106 nm) [2].

In Western culture, a darker skin color (sun tan) is considered beautiful and healthy, so most people achieve sun tanning by exposing the body to ultraviolet radiation from the sun or from artificial sun lamps [3]. This process will increase the amount of melanin (dark pigment) inside skin cells. However, this exposure to UV radiation has damaging effects [1].

UVA radiation damages skin cells and DNA, being responsible for photo aging and photo carcinogenesis. The effects of UVA only manifest after a long period of exposure, even if the doses are low. UVA contribute for reduction of skin elasticity, increase of wrinkling and production of reactive oxygen that leads to acute and chronic changes on the skin. Moreover, they cause exacerbation of cutaneous lupus erythematoses and also cause immunosuppression that contributes to the growth of skin cancer [4].

UVB radiation causes some changes, such as pigmentation and sunburn, as well as chronic changes, such as immune-suppression and photo carcinogenesis. Both UVA and UVB can cause sunburn, photo ageing, erythema and inflammation. To protect the skin from the sun, we apply sunscreen products to avoid all of the aforementioned damaging effects [4].

Sunscreens have an individual sun protection factor (SPF), value that is defined as the ratio of the minimal erythemal dose on sunscreen protected skin (MEDp) to the minimal erythemal dose on unprotected skin (MEDu), as showed on Equation 1 [2,5,6].

$$SPF = \frac{Minimal\ erythemal\ dose\ in\ sunscreen\ protected\ skin\ (MEDp)}{Minimal\ erythemal\ dose\ in\ unprotected\ skin\ (MEDu)} \quad (1)$$

Sunscreening agents used on preparations applied topically on the

***Corresponding author:** Paula Ana Fonesca, Instituto Politécnico de Coimbra, ESTESC, D Farm, GIAF, Rua 5 de Outubro S. Martinho do Bispo Apartado 7006, 3040-854 Coimbra, Portugal, Tel: +351 239802430; Fax: +351 239813395; E-mail: paula_fonseca@estescoimbra.pt

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skin can be divided into organic and inorganic agents, has shown in Figure 1.

The formulations that are commercially available include a combination of these agents to cover a wide spectrum of UV radiation. This sunscreen agent's action may vary from blocking, reflecting and scattering sunlight. Chemical sunscreens absorb UV rays, whereas physical sunscreens reflect or scatter light [4].

An ideal sunscreen agent has to be safe, chemically inert, nonirritating, nontoxic, photo stable, and should provide complete protection to the skin [4,7]. The choice of the adequate sunscreen is influenced by the phototype of the individual. There are different types of categorization of phototypes. For example, one is based on Individual Typology Angle (ITA°) which is obtained by measuring the skin color in the L*a*b* system as defined by the "ComissionInternationale de l'Eclairage". After the L*a*b* colorimetric measurements, the ITA° were calculated using one formula (Equation 2), being, then, classified according the person's skin, as presented on Table 1 [8].

$$ITA° = [Arctg((L^* - 50)/b^*)]\ 180/3.14159 \quad (2)$$

The most used classification of phototypes is the Fitzpatrick's, which is based on the first 30-45 minutes of sun exposure after a winter season of no sun exposure, as presented on Table 2 [9]. To help with the choice of a sunscreen that is suitable to each phototype, the indications exhibited on Table 3 were followed.

The aim of this work was to determine the SPF values of ten different sunscreen formulas containing organic or inorganic sunscreen agents through UV-Vis spectrophotometry and the application of the Mansur mathematical equation (Equation 3) [10]. Also was to evaluate the effect of direct solar radiation and temperature (37°C) under dark conditions.

$$SPF\ spectrophotometric = CF \times \sum_{290}^{320} EE(\lambda) \times I(\lambda) \times Abs((\lambda) \quad (3)$$

Where:

EE (λ): Erythemal effect spectrum; I (λ): Solar intensity spectrum; Abs (λ): Absorbance of sunscreen product; CF: Correction factor (=10) [10].

Material and Methods

Reagents and samples

Analytical grade ethanol was purchased from Fluka (98%). Commercially available sunscreen formulas from different trademarks were purchased from pharmacies and other stores that sell these products.

Instrumentation

The UV measurements were performed using the Shimadzu UV-

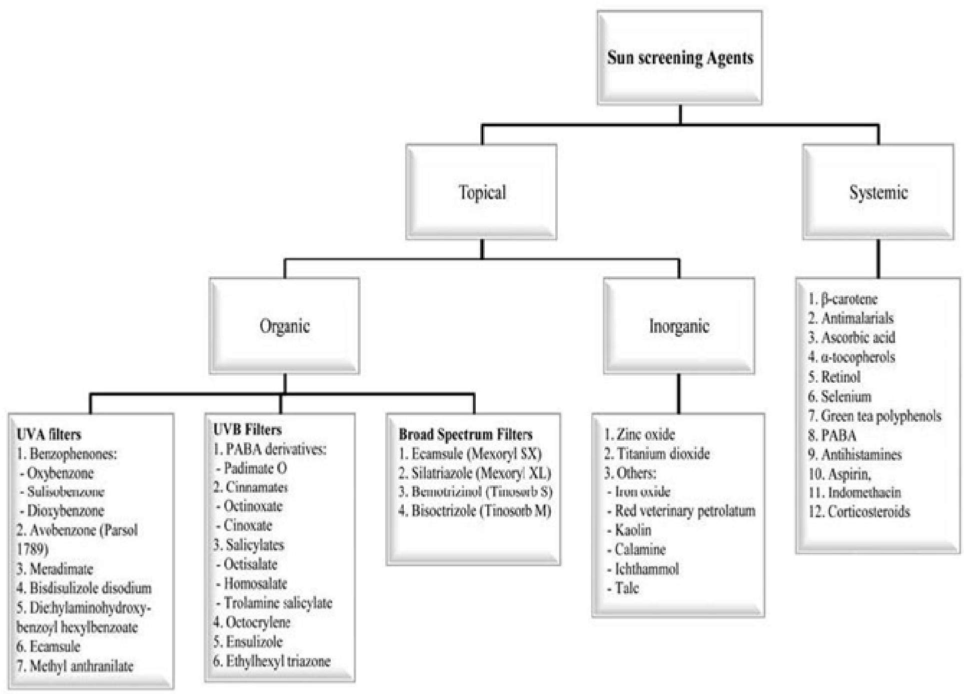

Figure 1: Classification of sunscreening agents (Latha et al. [4]).

		ITA°	>	55°	Very light
55°	≥	ITA°	>	41°	Light
41°	≥	ITA°	>	28°	Intermediate
28°	≥	ITA°	>	10°	Tan/Matt
10°	≥	ITA°	>	-30°	Brown
		ITA°	≤	-30°	Black

Table 1: Classification of the skin phototype based on Individual Typology Angle (ITA) (COLIPA, [8]).

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Phototype I	Always burn easily: never tans
Phototype II	Always burns easily: tans minimally
Phototype III	Burns moderately: tans gradually
Phototype IV	Burns minimally: always tans well
Phototype V	Rarely burns: tans profusely
Phototype VI	Never burns, deeply pigmented

Table 2: Fitzpatrick's Classification of Skin Phototypes (Fitzpatrick, [9]).

Phototype	Recommend SPF
I	>40
II	20-40
III	7-20
IV	6-15
V	5-10
VI	4

Table 3: Recommended SPF based on Fitzpatrick's Phototypes (Fitzpatrick, [9]).

1603 Spectrophotometer UV-Visible System, and all the samples were measured in a 1 cm quartz cell.

Methods

Sample preparation: 1 g of each sample was diluted with ethanol and degassed in ultrasonic bath for 5 min and filtered through filter paper.

All the solutions were closed in quartz vials. Samples A, B and H were kept under direct solar radiation. Samples C, D, E, F, G, I and J were kept under dark conditions at 37°C. All the solutions measurements were made after 7, 14 and 21 days.

The study was accomplished at the city of Coimbra (Portugal) and with an average irradiance value of 5.2 KWh/m^2 [11].

Measurement of UV absorption: After preparation, all the samples were scanned at wavelength between 290 and 320 nm, in the range of UVB, every 5 nm, and three replicates were made at each point. In the end of all measurements, the Mansur equation was applied to calculate SPF values.

To study the effects of UV radiation and temperature, all absorbance values were measured every seven days during twenty one days.

Results and Discussion

SPF values determination

The determination of SPF values for all ten samples was made through the UV spectrophotometric method and the Mansur equation was applied. The results are shown in Table 4.

Among the samples analyzed, sample H exhibits the highest absorbance value, considering the corresponding SPF labeled. This sample's found SPF corresponds to 86.7% when compared to the labeled SPF. Contrariwise sample I exhibit the lower SPF value, 38.7%, when compared to labeled value.

We also determinate the difference between values of SPF labeled and SPF founded on ten samples as seen is Figure 2.

Samples A, B, C and H have a difference of 4,46; 6,67; 5,89 and 2,66 respectively, when compared do SPF 20 labeled. Samples D and G have a difference of 9,91 and 13,68 respectively, when compared do SPF 30 labeled. Samples E, F, I and J have a difference of 30,54; 28,62; 30,77 and 21,77 respectively, when compared do SPF 50 labeled.

Sample	Sunscreen agent	Labeled SPF	Found SPF Mean (± SD*)	(FoundSPF/ Labeled SPF)*100
A	Avobenzone Octocrylene Tinosorb M Tinosorb S	20	15.54 (± 0.003)	77.72%
B	Avobenzone Octocrylene Tinosorb S Titaniumdioxide	20	13.33 (± 0.052)	66.67%
C	Diethylaminohydroxybenzoyl hexylbenzoate Tinosorb S	20	14.11 (± 0.013)	70.56%
D	Octocrylene Ethylhexylsalicylate Avobenzone Titaniumdioxide	30	20.09 (± 0.016)	66.98%
E	Avobenzone Ethylhexyltriazone Tinosorb M	50+	19.46 (± 0.026)	38.91%
F	Octocrylene Tinosorb M Tinosorb S	50+	21.38 (± 0.025)	42.75%
G	AvobenzoneOctocrylene Tinosorb M	30	16.32 (± 0.008)	54.41%
H	Octocrylene Ethylhexylmethoxycinnamate Tinosorb M	20	17.34 (± 0.006)	86.70%
I	Avobenzone Octocrylene Tinosorb S	50+	19.23 (± 0.012)	38.47%
J	Avobenzone Octocrylene Tinosorb S	50+	28.26 (± 0.042)	56.51%

*standard deviation

Table 4: Values of SPF labeled and SPF founded on ten samples (n=3).

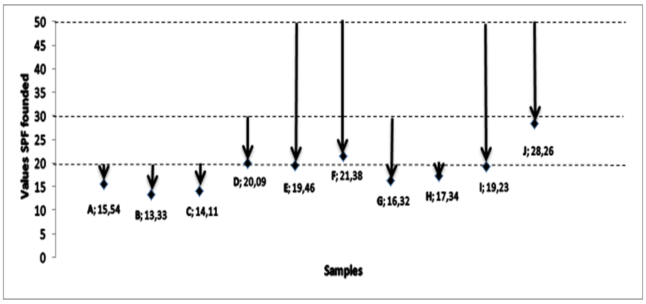

Figure 2: Representation of observed (founded) and expected (labeled) values of SPF labeled on ten samples; (–) SPF difference; (-----) labeled/ expected SPF; (•) founded SPF.

As can be seen the higher differences observed between labeled and founded values were in sunscreens with labeled SPF 50. This should be an alert since sunscreens SPF 50 are greatly used in Phototype I that includes babies, children, persons with clear skin, persons who can´t be exposed directly to the sunlight and also professionals of outdoor exposure like fishermen, building workers, street sellers, policeman and lifeguards.

SPF values degradation

The study under direct solar conditions was made after 7, 14 and 21 days (3 weeks) and was observed that the exposition of the samples A, B and H to direct solar radiation decreases their SPF values, revealing

Sample	Labeled SPF	Found SPF After UV exposition 1st week	(Found SPF/ Labeled SPF)*100	Found SPF After UV exposition 2nd week	(Found SPF/ Labeled SPF)*100	Found SPF After UV exposition 3rd week	(Found SPF/ Labeled SPF)*100
A	20	10.25	51.25%	9.36	46.78%	9.21	46.05%
B	20	9.25	66.26%	8.53	42.64%	8.30	41.48%
H	20	12.30	61.52%	10.34	51.70%	9.99	49.98%

Table 5: SPF found after direct solar radiation exposure (n=3).

Sample	Labeled SPF	Found SPF After Temp exposition 1st week	(Found SPF/ LabeledSPF)*100	Found SPF After Temp exposition 2nd week	(Found SPF/ LabeledSPF)*100	Found SPF After Temp exposition 3rd week	(Found SPF/ LabeledSPF)*100
C	20	14.74	73.71%	17.02	85.05%	18.08	90.41%
D	30	21.65	72.16%	23.91	79.70%	24.69	82.29%
E	50	20.55	41.09%	22.39	44.77%	23.22	46.44%
F	50	25.81	51.62%	28.98	57.95%	29.58	59.15%
G	30	18.46	61.52%	19.68	65.61%	19.84	66.12%
I	50	23.02	46.03%	24.99	49.98%	25.60	51.21%
J	50	31.20	62.40%	32.81	65.61%	33.20	66.40%

Table 6: SPF found after temperature (37ºC) exposure under dark conditions (n=3).

that sunscreen products are photosensitive in range between 290 and 320 nm (Table 5), as expected.

The study under temperature at 37ºC (98.6°F) at dark conditions was made after 7, 14, 21 and 30 days. These specifically temperature was chosen because is commonly accepted average core body temperature (taken internally), however normal body temperature varies by person, age, activity, and time of day, beyond some studies suggest there is a wider range of "normal" body temperatures [12].

The tested samples increased their SPF values as seen in Table 6. This is a huge advantage for persons, who can´t be exposed directly to the sunlight, e.g. skin diseases, photosensitizing medicines or other pathologies.

Conclusion

The SPF represents the effectiveness of a sunscreen formulation. These products should absorb the majority of UV radiation (290 to 400 nm) so as to be effective in preventing skin cancer, wrinkle formation, photo ageing, sunburn and other skin damages.

This study allowed us to conclude that all of the tested samples had a lower real SPF when compared with labeled SPF values, especially for SPF 50 with much higher difference. Also it was proven the photo degradation of sunscreens exposed to directly solar radiation and the increase of SPF values under dark condition at a temperature of 37°C.

The method used in this work is simple, fast, not expensive and easy-to-use. Therefore, it is our belief that it could be used more often to monitorise and evaluate the SPF value on sunscreens and other cosmetic products.

Many questions may be raised as a warning to the population like: why does skin cancer increase?; is the available information enough?; do people use sunscreen products?; is the application of sunscreen the correct one?; are the sunscreens effective?; is the mode of application or the amount of applied sunscreen the correct ones and is the amount of sunscreening agents on formulations enough?.

Every year, statistical data indicates an increase of skin cancer incidence; this is contradictory when we think of many products available on the market with useful information and high performance sunscreens. On the other hand, it is important that the chosen SPF be correct for each individual's Phototype. The application of sunscreens should be done correctly (over the entire body, before sun exposure and reapplied regularly) and in the correct amount, around 2 g/cm^2 [6].

We are sure about only one thing: we have an obligation to alert the population for the correct use of sunscreens, to provide correct and precise advice to prevent skin damages caused by UV radiation. With this study we want to address the attention of the scientific community about this problem and also legal authorities that should control the sunscreens industry in order to supervise and prevent this kind of incorrections, maybe creating legal limits for SPF labeled and the correct amount to apply.

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