Original Article

Sunscreen protection against visible light: a new proposal for evaluation

Proteção oferecida por fotoprotetores contra luz visível – uma proposta de avaliação

ABSTRACT

Introduction: In order to protect against visible light, pigmented sunscreens have been developed by combining organic non-particulate sunscreens and opaque pigments. No reliable method has yet been proposed to measure the protection offered by these pigments.

Objective: To evaluate the effectiveness of white and colored sunscreens in the protection against visible light.

Methods: Twenty sunscreens marketed in Brazil were evaluated (13 colored and 7 white). Colorimetric measurements were used to classify the brightness and translucency of the products, which were applied to polymethylmethacrylate sheets. Spectrophotometric measurements were taken to evaluate the product's absorbance within the visible light spectrum between 400 and 450 nm, using the Absorptive Efficacy in the visible light range as a parameter.

Results: Colored products presented a higher Evis than white products. Statistical analysis demonstrated that there is strong correlation between absorptive effectiveness and the product's brightness and translucency. No correlation was verified between absorptive effectiveness and the products' sun protection factor.

Conclusions: Absorptive efficacy in the visible light range was a useful parameter in the assessment of sunscreens' effectiveness in protecting against visible light. Pigmented products provide more effective photoprotection within that band.

Keywords: sunscreening agents; photobiology; sunlight.

RESUMO

Introdução: *Têm sido desenvolvidos fotoprotetores pigmentados, com a combinação de filtros inorgânicos não particulados e pigmentos opacos, para a proteção contra a luz visível. Ainda não foi apresentado, entretanto, método confiável para a medida dessa proteção.*

Objetivo: *O objetivo do estudo foi avaliar a eficácia de fotoprotetores brancos e coloridos na proteção contra a luz visível.*

Métodos: *Foram avaliados 20 fotoprotetores comercializados no mercado brasileiro, sendo 13 produtos classificados como coloridos, e sete como brancos. Medidas colorimétricas foram realizadas para classificação da luminosidade e da translucidez dos produtos quando aplicados em placas de polimetilmetacrilato, e medidas espectrofotométricas foram calculadas para avaliação da absorbância na faixa de luz visível, entre 400 e 450nm, utilizando-se como parâmetro a eficácia absortiva na faixa de luz visível (Evis).*

Resultados: *Produtos coloridos apresentaram Evis superior à dos produtos brancos. A análise estatística mostrou que há forte correlação entre a eficácia absortiva e a luminosidade e translucidez do produto, e não houve correlação entre a eficácia absortiva e o valor de FPS dos produtos.*

Conclusões: *O uso da Evis mostrou-se parâmetro útil na avaliação de eficácia de fotoprotetores na proteção contra a luz visível. A presença de pigmentos nos produtos coloridos confere maior eficácia fotoprotetora dentro dessa faixa.*

Palavras-chave: *protetores de raios solares; fotobiologia; luz solar.*

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INTRODUCTION

A clear understanding of the destructive effects of solar radiation, in particular its chronic consequences such as skin cancer and photoaging, only came about in the last two decades of the 20th century[1].

Within the solar radiation spectrum, ultraviolet radiation (UVR) promotes the main photobiological phenomena in cutaneous tissue, particularly solar erythema and pigmentation (acute cutaneous effects) and photocarcinogenesis and photoaging (chronic actinic damage) [2].

Visible radiation, also called visible light, is a component of the solar spectrum within the 400-700 nm band [3]. Its main biological effect is the stimulation of the human retina, and it is mainly perceived in the form of colors ranging from red to violet. Although it represents about 40% of the total solar energy that reaches the Earth's surface, until recently, visible light was never thought to have any significant effect on the skin.

It was only in the 21st century that the first studies linked the effects of visible light with some pathophysiological mechanisms in the skin, particularly those related to pigmentary phenomena and oxidative damage [4]. A 2008 study by Mahmoud BH and colleagues [5] demonstrated that both long UVA radiation (340-400 nm) and visible light (400-700 nm) are capable of – in different ways – promoting pigmentation of the skin, since not only melanin but also oxyhemoglobin acts as a chromophore.

The production of free radicals, which cause oxidative damage, is an important photobiologic phenomenon that has been correlated to solar radiation [6]. Oxidative phenomena are the main factors that cause photoaging, they cause elastosis and common pigmentary changes in photoexposed skin [6].

UVA radiation was already known to cause oxidative damage, since it is the major producer of free radicals and its lipid peroxidation capacity is 10 times greater than that of UVB radiation [6]. More recently however, visible light has been reported to also participate in the generation of free radicals. According to Mahmoud BH and colleagues [4], UVA radiation is responsible for approximately 67% of the production of free radicals in the stratum corneum, whereas visible light participates in the production of the remaining 33%.

The development of topical sunscreens has always been based on the concept of protection against the effects of UVR on the skin, such as sunburn and, more recently, skin cancer and photoaging [1]. As a result, sunscreens used to offer basic protection against UVB and, more recently, against UVA radiation.

The organic filters that are currently available offer very limited protection against visible light [7]. On the other hand, since inorganic sunscreens have reflective particles, they can protect against visible light, depending primarily on the size of the particles, as seen in Graph 1. Only large – and therefore visible (pigmentary) – particles can provide good protection in the visible light bandwidth[8].

The effectiveness of such colored sunscreens within the visible light bandwidth is correlated to their capacity to reflect light, which is linked to diffused reflection, which makes them look white when they are applied to a surface [9,10].

Since inorganic pigment-based sunscreens have low cosmetic acceptance due to the whitish coloration they leave on the skin, pigment particles, such as iron oxide, can be alternatively added to the formulation to provide a foundation effect in the product (colored or pigmented sunscreen), which has great acceptance among female users. Adding absorption pigments to white sunscreens considerably increases their protective capacity because the amount of light they reflect is significantly increased by lengthening the light's path through the protective sunscreen [10]. Formulations containing opaque filters and absorption pigments provide effective photoprotection and better cosmetic acceptability for individuals sensitive to visible light [10].

The literature describes validated and internationally recognized methods – such as sun protection factor (SPF) and the persistent pigment darkening method (PPD) – [11] that are used to evaluate sunscreens' photoprotective efficacy within the UVB and UVA bands.

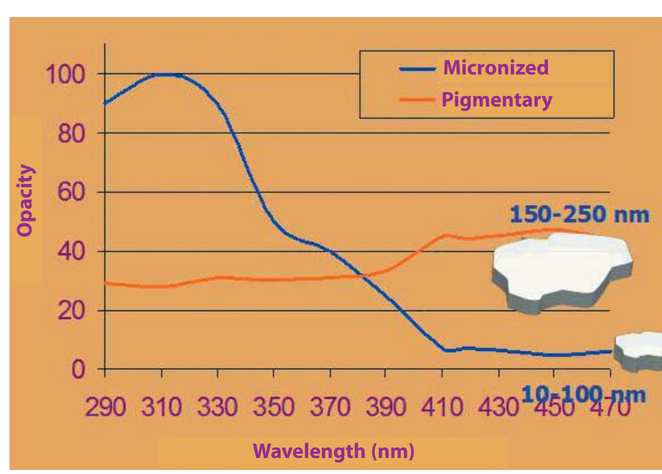
In contrast, the quantification of sunscreens' protection in the visible light bandwidth has not been the subject of publication, despite the growing importance of this radiation spectrum for cutaneous pathophysiology.

This study compares the protection provided by transparent and colored sunscreens against visible light through the spectrophotometric evaluation of the products' absorption curve and their SPF values and colorimetric characteristics, and proposes alternative measurements for quantifying protection within that radiation band.

METHODS

This study performed a comparative evaluation of 20 different sunscreens marketed in Brazil, regarding their spectrophotometric features within the 290-450 nm band, particularly within the 400-450 nm band.

The study was carried out at the Medcin Instituto da Pele's photoprotection laboratory between April and June 2011. Medcin is a private clinic that conducts dermatology and clinical research in the city of Osasco in Greater São Paulo, Brazil.



Graph 1: Correlation between opacity (reflective capacity) at different wavelengths between micronized and pigmentary TiO2 (adapted from 8)

I – Studied Products

Twenty sunscreens, formulated and compounded as UV filters, available in the Brazilian market were studied (Table 1).

II – Equipment

II A – Spectrophotometry Equipment

The UV Transmittance Analyzer UV-1000 UV (Labsphere®, New Hampshire, USA) emits radiation through a 10W xenon lamp in the 250-450 nm band at intervals of 1 nm wavelength (as detected by spectrograph).

The spectrophotometer's optical component consists of two chambers (upper and lower). The upper chamber is comprised of the integrating sphere, the beaming light a fiber optic cable. This This group is responsible for the incidence of the rays that reach the sample. The lower chamber is composed of lenses, mirrors, and an additional fiber optic cable that together are responsible for capturing the transmitted light.

II B – Colorimetry equipment

The equipment Chroma Meter CR-400 (Minolta®, Osaka, Japan) evaluates the color of surfaces using three parameters (L*, a*, b*) [12], using the CIE (*Commission International de l'Eclairage*, International Commission on Illumination) color system.

The L* value is defined as the brightness of a surface, which is expressed on a scale of 0 (black) to 100 (white).

Table 1: Sunscreens evaluated by color and composition of SPF filters

	Color	SPF	Sunscreens (INCI name)
1	Colored	100	Bis-Ethylhexyloxyphenol Methoxyphenyl Triazine / Titanium Dioxide / Bis-Benzotriazolyl Tetramethylbutylphenol / Butylmethoxydibenzoylmethane / Octocrylene
2	Colored	100	Bis-Ethylhexyloxyphenol Methoxyphenyl Triazine / Titanium Dioxide / Bis-Benzotriazolyl Tetramethylbutylphenol / Butylmethoxydibenzoylmethane / Octocrylene
3	Colored	60	2-Ethylhexyl Salicylate / Bis-Ethylhexyloxyphenol Methoxyphenyl Triazine / Titanium Dioxide / Butylmethoxydibenzoylmethane / Octocrylene / Drometrizole Trisiloxane / Terephtalylidene Dicamphor Sulfonic Acid
4	Colored	60	Ehtylhexyl Triazone / Bis-Ethylhexyloxyphenol Methoxyphenyl Triazine / Titanium Dioxide / Butylmethoxydibenzoylmethane / Drometrizole Trisiloxane
5	Colored	60	Ethylhexyl Methoxycinnamate / Bis-Ethylhexyloxyphenol Methoxyphenyl Triazine / Titanium Dioxide / Bis-Benzotriazolyl Tetramethylbutylphenol / Zinc Oxides
6	Colored	35	Homosalate / Ethylhexyl Methoxycinnamate / Ehtylhexyl Triazone / Bis-Ethylhexyloxyphenol Methoxyphenyl Triazine / Titanium Dioxide
7	Colored	35	Homosalate / Ethylhexyl Methoxycinnamate / Ehtylhexyl Triazone / Bis-Ethylhexyloxyphenol Methoxyphenyl Triazine / Titanium Dioxide
8	Colored	30	Homosalate / Ethylhexyl Methoxycinnamate / Bis-Ethylhexyloxyphenol Methoxyphenyl Triazine / Titanium Dioxide / 2-Ethylhexyl Salicylate / Benzophenone-3
9	Colored	30	Homosalate / Ethylhexyl Methoxycinnamate / Bis-Ethylhexyloxyphenol Methoxyphenyl Triazine / Titanium Dioxide / 2-Ethylhexyl Salicylate / Benzophenone-3
10	Colored	40	Bis-Ethylhexyloxyphenol Methoxyphenyl Triazine / Titanium Dioxide / Butylmethoxydibenzoylmethane / Octocrylene / 2-Ethylhexyl Salicylate
11	Colored	65	Ethylhexyl Methoxycinnamate / Bis-Ethylhexyloxyphenol Methoxyphenyl Triazine / Titanium Dioxide / Bis-Benzotriazolyl Tetramethylbutylphenol / 4-Methylbenzylidene Camphor / FeO / Phenylbenzimidazole Sulfonic Acid
12	Colored	50	Titanium Dioxide / Zinc Oxides
13	Colored	25	Ethylhexyl Methoxycinnamate / 4-Methylbenzylidene Camphor
14	White	100	Bis-Ethylhexyloxyphenol Methoxyphenyl Triazine / Bis-Benzotriazolyl Tetramethylbutylphenol / Butylmethoxydibenzoylmethane / Octocrylene
15	White	30	Ethylhexyl Methoxycinnamate / Bis-Benzotriazolyl Tetramethylbutylphenol
16	White	60	Ehtylhexyl Triazone / Bis-Ethylhexyloxyphenol Methoxyphenyl Triazine / Titanium Dioxide / Butylmethoxydibenzoylmethane / Octocrylene / Drometrizole Trisiloxane / Terephtalylidene Dicamphor Sulfonic Acid
17	White	70	Ehtylhexyl Triazone / Bis-Ethylhexyloxyphenol Methoxyphenyl Triazine / Titanium Dioxide / Bis-Benzotriazolyl Tetramethylbutylphenol /Butylmethoxydibenzoylmethane / Octocrylene / 2-Ethylhexyl Salicylate
18	White	50	Zinc Oxides
19	White	30	Homosalate / Ethylhexyl Methoxycinnamate / Bis-Ethylhexyloxyphenol Methoxyphenyl Triazine / Titanium Dioxide / 2-Ethylhexyl Salicylate / Benzophenone-3
20	White	60	Ethylhexyl Methoxycinnamate / Bis-Ethylhexyloxyphenol Methoxyphenyl Triazine /Titanium Dioxide, Bis-Benzotriazolyl Tetramethylbutylphenol / Zinc Oxides

The a* values vary on a scale from red (+100) to green (-100), and the b* values are measured on a scale from yellow (+100) to blue (-100).

III - Other Materials

III A Helioplate HD6 plates (HelioScreen Labs®, Marseille, France)

The plates are made of polymethylmethacrylate (PMMA) with 6 μm standardized coarseness on one of its surfaces.

IV – Procedures

IV A – Spectrophotometric Evaluation

The sunscreens were applied on a PMMA plate in the amount of 0.75 mg/cm2 onto the coarse surface. The amount and manner in which the product is applied on the substrate are critical for the fidelity and reproducibility of the test, therefore all procedures were performed by the same researcher, who had expertise in the application process.

After the application of the sunscreens, the PMMA plate was placed in the dark, at room temperature, for 15 minutes, in order for the products to dry and form a thin and homogeneous film. The plates were then inserted into the spectrophotometer, and five different points were analyzed on each plate.

The data collected by the equipment were compiled in order to determine the spectrophotometric curves. The integral of the area of the different curves within the visible light bandwidth ($Ivis_{400\ -\ 450\ nm}$) was determined using the following equation:

$$Ivis = \int_{400}^{450} A(\lambda)d(\lambda)$$

IV B Colorimetric Ratings

The L*parameter, which defines the brightness of a surface, was one of the studied variables. A higher L* value indicates a brighter or whiter plate where the sunscreen has been applied. To enhance the precision of the comparison of the measured L*, the difference between the values found on the plate – with and without the sunscreens – was calculated.

ΔL was calculated using the following equation:

$$\Delta L^* \ (DL^*) = L^*sp - L^*p$$

Where:

L*sp = L value of the empty plate

L*p = L value of the plate after the application of the product

The variation in opacity was measured using the translucency parameter (TP) [13]. The TP equation correlates a surface's opacity parameters by contrasting it against a white background (L* = 90.22; a* = 2.99; b* = -3.13) and a black background (L* = 21.48; a* = 0.70; b* = 0.22).

Completely opaque surfaces do not allow any transmission of light. In contrast, fully transparent surfaces allow the total transmission of light. A lower TP indicates that is surface is closer to complete opacity.

As defined in the literature, translucency can be calculated based on the correlation between the color of a surface against a white background (ΔE *ab) and the color of the same surface against a black background, [13] using the following equation:

$$\sqrt{}\ (L^*b-L^*p^2 + (b^*b-b^*p)^2$$

Where:

L*b and L*p = L* value against a white and a black background, respectively

a*b and a*p = a* value against a white and a black background, respectively

b*b and b*p = b* value against a white and a black background, respectively

Therefore, ΔTP can be determined using the following equation:

$$\Delta TP = TPsp - TPp$$

Where:

TPsp = translucency parameter of the plate without the product

TPp = translucency parameter of the plate with the product

A product or surface with a higher ΔTP has a greater translucency variation than an empty plate and, therefore, a higher opacity. The evaluated sunscreens were divided into two groups: white products (no presence of colored pigments) and colored products (presence of colored pigments).

V - Statistical Analysis

The correlation between the variables was assessed using dispersion plots, Pearson's linear correlation coefficient and the hypothesis test for the correlation coefficient.

RESULTS

The 20 products underwent spectrophotometric curve determination and subsequent colorimetric determination of bands according to the procedures described above.

I - Absorptive Effectiveness

Absorptive effectiveness in the visible light bandwidth ($Evis_{400-450\ nm}$) was determined by calculating the integral of the area in that spectrophotometric band. Therefore, the values refer to the sum of the absorption rates in all wavelengths between 400 and 450 nm (Evis). Table 2 describes the calculated values for the evaluated products.

As seen in Table 2, the colored products presented higher absorptive effectiveness values than the white products, suggesting that the presence of pigment in the formulation increases protection within the visible light bandwidth (400-450 nm). We observed no relationship between SPF values and absorptive effectiveness within the visible light bandwidth. In order to verify this relationship, the values were statistically compared.

Graph 2 shows the scatter plot of the correlation between nominal SPF and absorptive effectiveness within the visible light bandwidth.

The relationship between the variables was assessed using the linear correlation coefficient and Pearson's hypothesis test for the correlation coefficient. Graph 2 - Relationship between absorptive effectiveness in visible light (Evis) and SPF

Integral (400-450 nm) = Integral (400-450 nm)

Delta L = ΔL

The result is shown in Table 3 below. We found no significant correlation between nominal SPF and the integral of 400-450 nm.

II - Colorimetric **E**valuation **of the** Plates

The degree of opacity of the products applied on the PMMA plates is an important parameter to be evaluate, since it can show that higher opacity is related to absorptive effectiveness within the visible light bandwidth. The colorimetric evaluation of the plates was conducted to identify the intensity of their opaqueness through the ΔL* and ΔTP indices, as described above.

The higher a product's ΔL value, the greater the difference in brightness between the plates with and without the product, and thus a greater degree of pigmentation. The higher the ΔTP value, the greater the difference in translucency between the plates with and without the product, and thus a greater degree of opacity (Table 4).

Table 2: List of evaluated sunscreens and respective color classifications, SPF and integral of the absorption rate in the visible light bandwidth (400-450 nm)

	Color	SPF	Integral (400-450nm)
1	Colored	100	14,70
2	Colored	100	26,54
3	Colored	60	14,05
4	Colored	60	14,12
5	Colored	60	16,78
6	Colored	35	22,62
7	Colored	35	26,01
8	Colored	30	30,61
9	Colored	30	27,39
10	Colored	40	32,76
11	Colored	65	15,08
12	Colored	50	30,81
13	Colored	25	28,33
14	White	100	7,15
15	White	30	7,38
16	White	60	9,68
17	White	70	4,26
18	White	50	3,33
19	White	30	2,39
20	White	60	8,39

As seen in Table 4, the ΔL and ΔTP values of the colored sunscreens are greater than those of the white products. To determine whether there was any correlation between the ΔL and ΔTP values and the absorptive effectiveness values in the visible light bandwidth, the data were statistically evaluated. Graph 3 shows the correlation between the absorptive effectiveness in the visible light bandwidth and ΔL.

The graph shows that the higher the ΔL, the higher the value of the integral of 400-450 nm (absorptive effectiveness). In Table 5, we verify whether this correlation is significant using the Pearson's linear correlation coefficient.

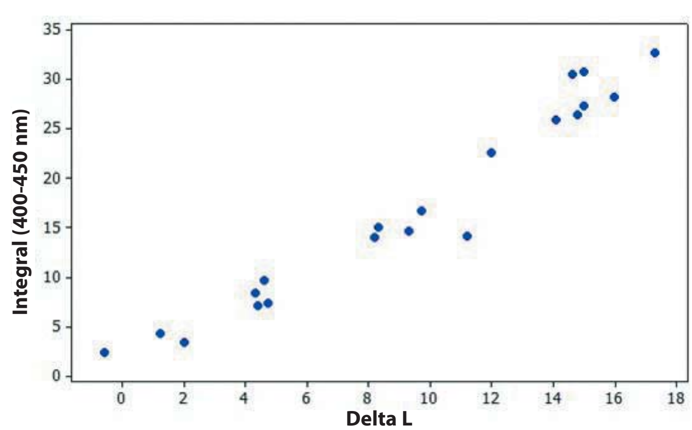
As seen in Table 5, there is a strong positive correlation between ΔL and the absorptive effectiveness in visible light bandwidth (Evis). Graph 4 represents the correlation between absorptive effectiveness in the visible light bandwidth and ΔTP.

The graph shows that the higher the ΔTP, the larger the integral of 400-450 nm. The significance of this correlation is assessed using the Pearson's linear correlation coefficient (Table 6).

As observed in Table 6, there is a strong positive correlation between ΔTP and absorptive effectiveness in the visible light bandwidth.

DISCUSSION

Recent studies that demonstrate visible light's ability to stimulate pigmentation in melanocompetent patients – and potentially interfere with hyperpigmentary dermatoses such as melasma and post inflammatory hyperpigmentation – raised awareness of the importance of protecting against light in this spectrum 5.



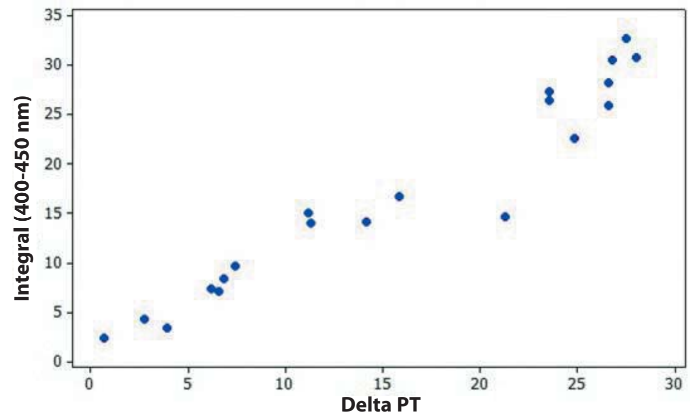
Graph 2: Relação entre eficácia absortiva na luz visível (Evis) e FPS

Table 3: Pearson's correlation coefficient between SPF and E(vis)

Variables	Correlation coefficient	P-value	Conclusion*
SPF vs Integral 400-450nm	-0,279	0,233	Does not reject the hypothesis **

Table 4: Color classification of evaluated sunscreens and integral of the absorption rate in the visible light bandwidth (400-450 nm), Delta L and Delta TP

	Color	Integral (400-450nm)	ΔL	ΔPT
1	Colored	14,70	9,3	21,27
2	Colored	26,54	14,8	23,56
3	Colored	14,05	8,2	11,31
4	Colored	14,12	11,2	14,13
5	Colored	16,78	9,7	15,84
6	Colored	22,62	12	24,82
7	Colored	26,01	14,1	26,57
8	Colored	30,61	14,6	26,77
9	Colored	27,39	15	23,57
10	Colored	32,76	17,3	27,47
11	Colored	15,08	8,3	11,15
12	Colored	30,81	15	28
13	Colored	28,33	16	26,60
14	White	7,15	4,4	6,57
15	White	7,38	4,7	6,18
16	White	9,68	4,6	7,41
17	White	4,26	1,2	2,74
18	White	3,33	2	3,91
19	White	2,39	-0,6	0,69
20	White	8,39	4,3	6,81

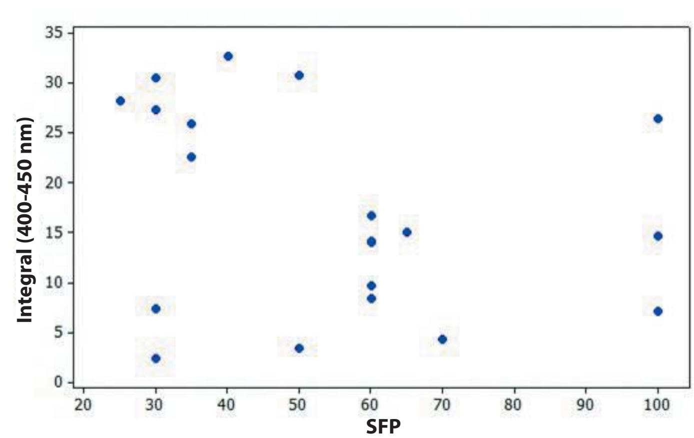


Graph 3: Scatter plot of the integral between 400-450 nm XDelta L

Table 5: Pearson's linear correlation coefficient between Delta L and E(vis)

Variables	Correlation coefficient	P-value	Conclusion*
Delta L vs Integral 400-450nm	0,975	<0,001	Rejects the hypothesis. **

* Significance level: 5%
** Hypothesis: there is no correlation between the variables



Graph 4: Scatter plot of the integral of 400-450 nm X Delta L

According to the literature, within the visible light bandwidth, shorter wavelengths (the most energetic) present the greatest photobiologic action [14]. This band, also called blue light, comprises wavelengths from 400-450 nm.

Although pigmented sunscreens are effective in treating and preventing pigmentary dermatoses, there is no description in the literature of a suitable method for quantifying their photoprotective effect. Among the quantitative methods available, the spectrophotometric evaluation of the absorption curve in the visible light bandwidth is the most feasible thus far; the development and pathophysiological mechanisms of pigmentation due to visible light are not yet clearly understood.

This study evaluated 20 different sunscreen formulations – white and colored – available on the Brazilian market. By taking spectrophotometric and colorimetric measurements, the study attempted to identify a reliable method for quantifying the protection provided by these products against visible light, in particular within the blue light range (400-450 nm).

The study's results demonstrate that calculating the absorptive effectiveness in the visible light bandwidth (Evis) – which can be defined as the integral of the index of absorption in the 400-450 nm band – is a reliable method of quantifying the protective effect within this band.

This measurement succeeded in distinguishing the effects of the white and pigmented products: all 13 colored products presented higher measurements than the 7 white products. Furthermore, absorptive effectiveness in the visible light bandwidth (Evis) was strongly correlated to the color and opacity levels calculated using the colorimetric indices ΔL and ΔTP. This data reinforce the hypothesis that opaque products are more effective in protecting against visible light than more lightly colored ones.

Finally, this study has shown that a sunscreen's SPF value

Table 6: Pearson's linear correlation coefficient between Delta TP and E(vis)

Variables	Correlation coefficient	P-value	Conclusion*
Delta PT vs Integral 400-450nm	0,967	<0,001	Rejects the hypothesis**

* Significance level: 5%

** Hypothesis: there is no correlation between the variables

has no direct correlation to its protection against visible light, which means that choosing a sunscreen based solely on its SPF does not yield adequate protection against the effects of visible light.

CONCLUSIONS

This study demonstrated that the use of spectrophotometry can be an important parameter for evaluating the photoprotective effectiveness of sunscreens in the visible light bandwidth. The results showed that products classified as colored have better absorptive efficacy in the visible light bandwidth compared to white products.

The data also suggest that measuring absorptive effectiveness in the visible light spectrum (Evis) is the most appropriate method to determine photoprotectiveness because it can distinguish the effectiveness of colored and white products, and can rate the photoprotective effects of colored sunscreens according to an efficacy scale.

Furthermore, the data indicate that the SPF value is not related to absorptive effectiveness in the visible light bandwidth. Therefore, when prescribing colored sunscreens to protect against this band of solar radiation, physicians should not only consider SPF, but should also consider their photoprotective efficacy within the light visible band and, in particular, the absorptive efficacy (Evis) measurement. ●

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