Influence of the absorption behavior of sunscreens in the short-wavelength UV range (UVB) and the long-wavelength UV range (UVA) on the relation of the UVB absorption to sun protection factor

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Abstract. The absorption of filter substances in sunscreens, reducing the incident ultraviolet (UV) radiation, is the basis for the protecting ability of such formulations. The erythema-correlated sun protection factor (SPF), depending mainly on the intensity of the UVB radiation, is the common value to quantify the efficacy of the formulations avoiding sunburn. An *ex vivo* method combining tape stripping and optical spectroscopy is applied to measure the absorption of sunscreens in the entire UV spectral range. The obtained relations between the short-wavelength UV (UVB) absorption and the SPF confirm a clear influence of the long-wavelength UV (UVA) absorption on the SPF values. The data reflect the historical development of the relation of the concentration of UVB and UVA filters in sunscreens and points to the influence of additional ingredients, e.g., antioxidants and cell-protecting agents on the efficacy of the products. [DOI: 10.1117/1.3497047]

Keywords: sunscreen; tape stripping; short-wavelength ultraviolet spectroscopy; long-wavelength ultraviolet spectroscopy; sun protection factor; universal sun protection factor.

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1 Introduction

Ultraviolet active filters are the decisive components in sunscreens, reducing the intensity of the sun radiation reaching the living cells of the human body.[1] Therefore, it seems worthwhile to use a recently proposed *ex vivo* spectroscopic method[2] to investigate the relation between the UV filter absorption to the classical sun protection factor (SPF). This SPF value has been used for a number of years to quantify the sunscreen protection. It is strongly correlated to the well-investigated sun-induced injury to the human body—the formation of an erythema, well-known as sunburn.[3]

The erythema action spectrum[4] shows a strong efficacy of the short-wavelength UV (UVB) part of the sun radiation. Influences of an additional radiation in the long-wavelength UV (UVA) range are outlined by the terms photoaugmentation and/or photoaddition.[5]

Photoaugmentation describing the potentiation of UVB induced effects by long-wave radiation is confirmed, e.g., for the erythemal component of the sunburn reaction but not for the sunburn cell production.[6] Photoaddition was found to be the main process determining the erythemally effective irradiance, taking into account the additional influence of UVA radiation on the UVB efficacy.[7]

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In this paper the influence of the absorption behavior of sunscreens in the UVB and UVA ranges on the UVB absorption/SPF relation is determined. To obtain a broad overview, sunscreens that have been developed during recent years are taken into account.

2 Methods

2.1 *Volunteers*

The sunscreen was applied on the flexor forearms of six healthy volunteers (in total one-third males and two-thirds females), aged between 23 and 45 years (skin phototypes I to III).[8] The volunteers stayed in an inner room without sun exposure (room temperature about 21 °C) from half an hour before the examination started until the end of the examination. The ethical approval for these experiments was obtained from the Ethics Committee of the Charité Universitaets-medizin Berlin, Department of Dermatology, Berlin, Germany. All volunteers gave their written informed consent.

2.2 *Sunscreen Application*

The investigated sunscreens were bought directly before the measurements were carried out (commercial samples) or were freshly prepared [COLIPA (European Cosmetics Toiletry and Perfumery Association) emulsions and model formulations], thus guaranteeing that all products were used within their date

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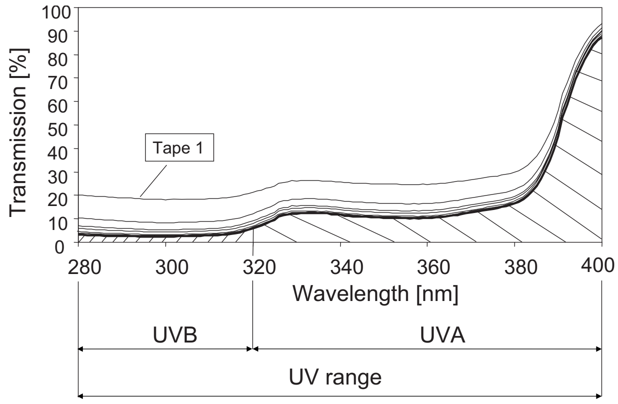

Fig. 1 Determination of the sum transmission spectrum and the corresponding areas beneath the sum spectrum used to determine the average UVA und UVB sum transmissions (sunscreen sample 7 with SPF 16).

labeling. Samples with the following SPF values were investigated: 4, 6, 8, 12, 13, 16, 20, 25, 26, 30, 50, 55, and 60.

A precleaning of the skin was realized by rinsing the flexor forearm with cold water and drying it with a paper towel afterward. We applied 2 mg/cm^2 of the commercial sunscreens or model formulations to an area of 8×10 cm^2 corresponding to the COLIPA standard.[3]

2.3 *Tape-Stripping*

The tape-stripping procedure; as described previously,[9,10] started 1 h after sunscreen application, transferring the stratum corneum layer by layer to the tape strips together with the UV filters. After pressing the adhesive tapes (tesa film, 5529, Beiersdorf, Hamburg, Germany, width: 19 mm) onto the human skin with a stamp (pressure: 15 kP/cm^2) the strips were quickly removed. Ten tapes were taken from the treated and untreated skin areas.

2.4 *Spectroscopic Measurements*

The absorption spectra were recorded immediately after removal — within 15 s — to avoid disturbances by diffusion processes inside the adhesive layer, which result in a homogeneous distribution of the UV filters.[11,12]

The spectra of the tape strips together with an empty tape as a reference were recorded in the range 240 to 500 nm using the UV/VIS spectrometer Lambda 5 (PerkinElmer, Frankfurt/Main, Germany) with an integrating sphere and a rectangular beam diameter of 8×10 mm^2.

The software UV Winlab Version 2.70.01 (PerkinElmer, Frankfurt/Main, Germany) was used to correct the corneocyte-correlated influences and to calculate the sum of the transmission spectra.

2.5 *Sum Transmission Spectra and Average Sum Transmission Values*

The sum transmission spectra in the complete UV range (see Fig. 1 in the following section) were calculated by adding the spectra of all tape strips with a detectable amount of UV filters on the basis of the absorbance values. The obtained sum spectrum was subsequently changed to the transmission values.

The areas beneath the last curve (sum transmission spectrum) are the basis on which we calculated the average sum transmission values, representing the remaining intensity after sunscreen application in the corresponding spectral ranges:

1. average UV sum transmission, dividing the area measured in the range of 280 to 400 nm by the spectral interval 120
2. average UVB transmission, dividing the area measured in the range of 280 to 320 nm by the spectral interval 40
3. average UVA transmission, dividing the area measured in the range of 320 to 400 nm by the spectral interval 80.

All spectroscopic data discussed hereafter are mean values balancing out the interindividual differences found for different volunteers as a result of a varying skin profile determined by furrows and wrinkles.[11]

3 Results and Discussion

The applied protocol resulted in the sum transmission spectra describing the absorption behavior of the filter substances applied with sunscreens under *ex vivo* conditions which were taken as the basis to calculate average sum transmission values.

3.1 *Average Sum Transmission Spectrum*

The protocol determining the sum transmission spectra was described previously[2] and in the previous section. Figure 1 illustrates the development of a sum transmission curve taking into account the individual spectra of the tape strips removed one by one.

The area beneath the sum transmission curve and the calculated average UV sum transmission values reflect the influence of the applied UV filters on the incident UV radiation. In the given example, the average UV sum transmission resulted in 12% transmission, the average UVB sum transmission resulted in 2% transmission, and the average UVA sum transmission resulted in 18% transmission.

The corresponding data determined for all investigated sunscreens are taken to discuss the relationship between the characteristic values of the UVB filter — described by the average UVB sum transmission — and the SPF. To understand the influence of the variable UVB/UVA intensity ratio, the average UVA sum transmission was also taken into account.

3.2 *Relation of the Absorption Behavior in the UVB Range to SPF*

In a first step, the originally determined average UVB sum transmission values obtained after tape stripping and spectroscopic measurements are compared with the corresponding SPF values declared by the sunscreen producers (Table 1).

It is obvious that the UVB sum absorption obtained for sunscreens with identical SPF values varies to a high extent.

In a previous publication,[13] the UVB sum transmission as a measure of the active UVB radiation intensity was correlated to the SPF demonstrating the principal relation of the spectroscopic data and the SPF. The connection of the data was described by an exponential trend line.

Table 1 Summary of the average UVB sum transmission values in relation to the SPF values.

Filter Substances	Sample	SPF	Average UVB Sum Transmission (%*T*)
A	1	4	4.3
Model emulsion	2	6	2.8
F, A, G	3	8	4.1
G, D, F	4	8	2.9
Model emulsion	5	11	0.7
G, A, I	6	12	3.1
B, C	7	13	0.4
A, D, E	8	16	2.3
H, D, J, A	9	16	1.9
H, D, J	10	20	2.1
D, H, J, G, I	11	20	2.6
G, A, I	12	20	1.2
F, D, N, G, I	13	25	3.9
H, D, J, I	14	26	1.5
D, M, A, G, I	15	30	2.1
I, E, H, J, D	16	50	0.6
Model emulsion	17	55	1.4
A, K, I, L	18	60	0.4

Model emulsions: the filter substances contained in the model emulsions are not available for publication.
Filter substances: A, ethylhexyl methoxycinnamate; B, octyl dimethyl PABA; C, benzophenone-3; D, butyl methoxy dibenzoylmethane; E, phenylbenzimidazole sulfonic acid; F, bis ethylhexyloxyphenol methoxyphenol methoxyphenyl triazine; G, octocrylene H, 4-methylbenzylidene camphor; I, titanium dioxide; J, octyl triazone; K, methylene bis-benzotriazolyl tetramethylbutylphenol; L, zinc oxide; M, diethylhexyl butamido triazone; N, butyl methylpropianate citronellolphenyl.

Enlarging the number of sunscreens by taking into account formulations with a broader variation of the UVB/UVA ratio, including the “historical” formulations with an extremely low UVA protection, give new insights.

In the graph presented in Fig. 2, the reciprocal UVB transmissions are used to obtain linear trend lines of these data to the SPF values. In the graph, three trend lines can be recognized with a higher variation of the individual points around the middle rank. The existence of the different trend lines becomes understandable when we take into account the interaction of the UVB and the UVA radiation producing the erythema.

The available spectroscopic data enabled the calculation of the sample specific UVB/UVA relation factors $F_{\mathrm{UVB/UVA}}$ dividing the average UVB sum transmission by the average UVA sum transmission.

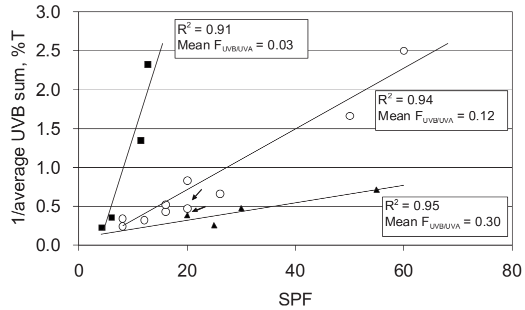

Fig. 2 Relation of the reciprocal values of the average UVB sum transmissions to SPF.

Two samples belonging to the upper and the lower trend lines are both shown in Fig. 3 to illustrate the differences in the UVB/UVA relation.

The calculated factors given in Table 2 quantify the absorption behavior of the investigated sunscreens in the UVB and the UVA range, thus describing the possible influence of photoaugmentation and/or photoaddition. The given mean values of the UVB/UVA relation (row 2 of the table) clearly describe the affiliation of the UVB transmissions to one of the three trend lines with a stronger variation for the samples collected in the middle trend line. This underlines a clear influence of the accompanying radiation intensity in the UVA range on the UVB/SPF correlation. Without an absorption in the UVA range, the UVB filter concentration must be much higher to obtain the same SPF value.

As well as these clear dependencies, two exceptions exist in the group of the investigated sunscreens. First, a small amount of overlap between the ranges found for the $F_{\mathrm{UVB/UVA}}$ factors collected in the upper and the middle trend lines (lines 2 and 3 in the third row of Table 2). Second, the two samples marked by arrows in Fig. 2, both with an SPF of 20, vary considerably in the UVB/UVA factor (upper point $F_{\mathrm{UVB/UVA}}=0.13$, lower point $F_{\mathrm{UVB/UVA}}=0.36$). These exceptions hint to the influences of parameters affecting the formation of the erythema in addition to the changes in the UVB/UVA relation, e.g., ingredients with antioxidizing or cell-protecting qualities, etc.[14–18]

Generally, the different trend lines reflect, illustratively, the historical development of the filter types used in sunscreens. Originally, sunscreens were restricted to contain only a UVB

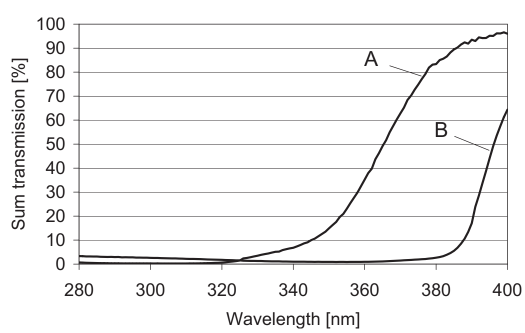

Fig. 3 Sum transmission spectra of sunscreens belonging to the upper and the lower trend lines in Fig. 2: line A, sample 7, SPF=13; line B, sample 11, SPF=20.

Table 2 Correlation of the position of the reciprocal values of the average UVB sum transmission and the SPF values (Fig. 2) to the UVB/UVA factors.

	Mean Value	Range of Measured Values
Upper trend line	0.03	0.01–0.06
Middle trend line	0.12	0.05–0.22
Lower trend line	0.28	0.22–0.35

filter, resulting in the four points on the upper curve measured for historical formulations not now on the market, These historical sunscreens contained high amounts of UVB filter to obtain reasonable SPF values, because of the missing UVA absorption.

Later in sunscreen development, UVA filters were added, resulting in a higher UVB/UVA relation. This situation is reflected by the sunscreens found in the middle trend line. In this group of formulations, a relatively broad variation around the trend line occurs.

The lowest trend lines summarize three highly effective modern sunscreens with a high absorption in the UVA range, lowering the absorption necessary in the UVB range to realize the measured SPF. This underlines the fact that spectroscopic data are suited to estimate, in an orientated manner, the size of the SPF values taking into account the absorption behavior in the UVB and the UVA ranges. The application of this method is of special interest for the investigation of filter substances not yet approved, not using human but porcine skin.[19,20]

The discussion concerning the SPF is limited to one biological response to the formation of erythema with an individual dependence on the intensity of the incident radiation. It is to be expected that corresponding investigations considering other described sun-induced injuries will provide additional and possibly quite different insights. Therefore, it is important to characterize the efficacy of sunscreens not by different effects of biological responses in the human organism, but by noninvasive spectroscopic measurements, as described in this paper.

4 Conclusion

The results presented in this paper demonstrate that the described noninvasive method of sum transmission measurements, based on tape stripping, is well suited to characterize the UV absorption of sunscreens under *ex vivo* conditions. It can be used to distinguish between the absorption properties of sunscreens in the UVB and UVA spectral ranges. Therefore, the results are well suited to develop a universal spectral sun protection factor (USPF), which describes the protection efficiency of sunscreens in relation to the absorption in the whole spectral range of sun radiation.

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