Multicenter comparison of sunscreens by *in vitro* determination of relative parameters

H. Gers-Barlag[1], R. Bimczok[2], H. Driller[3], P. Finkel[4], H.U. Gonzenbach[8], U. Heinrich[5], W. Johncock[6], K. Juhkason[7], E. Klette[1], D. Kockott[8], R. Langner[6], F. Pflücker[3], T. Rudolph[4], P. Schneider[9], C. Springob[2], H. Tronnier[5]

[1]Beiersdorf AG, Hamburg; [2] Wella AG, Darmstadt; [3] Merck KG, Darmstadt; [4] Sara Lee Deutschland GmbH, Düsseldorf; [5] Institut für Experimentelle Dermatologie, Witten; [6] Haarmann & Reimer, Holzminden; [7] BASF AG, Ludwigshafen; [8] Dr. Kockott UV Technik, Hanau, Germany; [9] Roche Vitamins, Basel, Switzerland

Introduction

Sunscreens should deliver an efficient protection of human skin from harmful UV radiation. Today the efficacy of sun products is described by the sun protection factor (SPF). The SPF value determines the potency of the inhibition of an erythema which is mainly induced by the short wavelength UVB light (290 – 320 nm). Therefore most recently it has been proposed to use the term "SPF" as sunburn protection factor.

The demand to measure and to label the efficacy of the sunscreens in order to protect against longer wavelength UV radiation (320–400 nm) reflects the increasing scientific knowledge about UVA induced skin damage such as premature skin ageing or photodermatoses.

A number of methods is discussed with regard to the UVA protection. In Australia an in vitro determination is officially accepted which is based on a transmission measurement through a layer or a solution of the sunscreen [Lit. 1]. In comparison Japanese authorities accept the PPD method (persistent pigment darkening), an in vivo method which takes the darkening/tanning reaction following to UVA exposure as an endpoint [Lit. 2]. In Europe as well as in US the debate about the right or relevant method is still ongoing.

The task force "sun protection" of the DGK (German Society for Scientific and Applied Cosmetics) designed an in vitro determination of relative parameters such as the critical wavelength or the UVA/B ratio [Lit. 3]. The main aim of this initiative is the application of the resulting protocol to a number of marketed sunscreens and also the investigation of the reproducibility of the chosen relative parameters measured in different laboratories. The tested products should represent a variety of commonly used vehicles in this segment (o/w-, w/o-emulsions, oils and sticks) and different UV filter systems.

Method

In this study seven laboratories participated and their individual technical devices are given in [Lit. 3]. Following to the results of previous ring studies the substrate was identified as a probable source of variation. Therefore we used in the present

investigation roughened quartz plates with the same quality as substrates.
As described by several authors [Lit. 4, 5, 6] the principle of the analysis is a transmission measurement. A sample amount of 0.75 mg/cm² was spotted evenly across the plate surface using an appropriate device (e.g. self-displacing pipette). Afterwards these spots were homogeneously distributed with a saturated (latex-) gloved finger. Then the plates were equilibrated in the dark for about 15 minutes before they were measured. Quartz plates covered with a film of glycerin across the surface were taken as a reference.

Calculation

Three different parameters were calculated from the transmission curves. On the one hand we followed the absolute in vitro sun protection factor (SPF) and on the other hand the two relative parameters, the critical wavelength and the UVA/B ratio. The detailed description of the calculation of these factors is given elsewhere [Lit. 3, 1].

Products

In order to cover a) different UVA protection levels, b) different UVA filter systems and c) a broad variety of product forms and vehicles ten different commercially available products were selected for this investigation. A detailed description (product type, UV filtersystem etc.) of all chosen sunscreens is given in Table 1.

Code	Product	SPF	Type	Filtersystem
A	Ambre Solaire Oil gel	8	O	OC-BMDBM
B	Ambre Solaire Sun lotion	5	OW	OC-TDSA-TiO2-BMDBM
C	Coppertone Kids Colorblock	30	OW	EHMC-OXY-OS-HS
D	Delial Lip protection stick	16	O	MBC-BMDBM-EHT-OC
E	Delial Sun lotion for children	15	WO	MBC-OS-BMDBM-OC
F	Hawaiian Tropic Sunblock	30	WO	OS-EHMC-TiO2
G	Nivea Sun Sensitiv Balm	24	BA	MBC-EHT-BMDBM-TiO2
H	Ombra Sun cream	12	OW	EHMC-BMDBM
I	Ombra Sun lotion for children	30	WO	OC-ZnO-EHMC-PBSA
K	Penaten Baby Sunblock	30	OW	ZnO-EHMC-MC-PBSA-IMC-BMDBM

Table 1 Test products

Results and Discussion

Spectra

Fig. 1a and 1b show the inverse transmission spectra (monochromatic protection factor) of two products which differ significantly with regard to their UV protection profile. Product B (SPF 5) provides a broad protection with a flat decrease from the UVB to the UVA region and product C (SPF 30) starts with an enormous peak in the UVB but drops steeply down in the UVA region. At wavelengths higher than 350 nm no protection has been determined due to the use of Benzophenone-3 as single UVA filter.

Interestingly, all laboratories found a similar shape of the spectra but with an extremely different level of absorption.

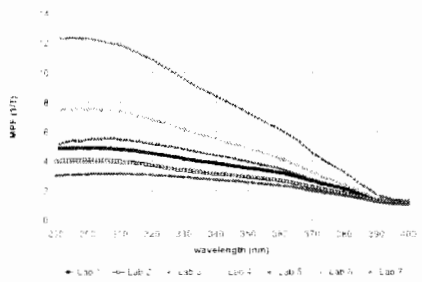

Fig. 1 a Monochromatic protection factor / spectrum of Product B

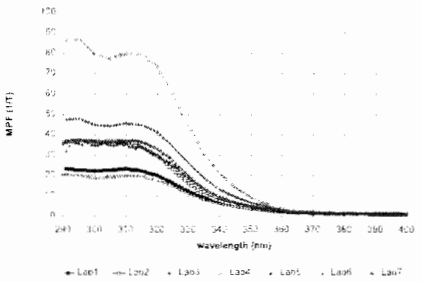

Fig. 1 b Monochromatic protection factor / spectrum of Product C

Sun protection factor (in vitro)

The SPF data of the ten products are given in Table 2. Again these results reflect the observation described above. The in vitro SPF represents the absolute altitude of the transmission curve and it differs dramatically between various laboratories. A standard deviation for each of the ten sunscreens is found between 20 and 64%. Consequently, in almost all cases the highest value is more than doubled compared to the lowest value for the same product.

It was obvious that the oily formulation (product B = oil SPF 8 and product E = stick SPF 16) leads to extraordinarily high values. Any determination of the in vitro SPF depends on the product type.

All described investigations indicate that the reproducibility of the absolute protection parameter, the in vitro SPF, is currently not sufficient enough.

Critical wavelength and UVA/B ratio

The relative determination of the UVA protection can be achieved in a more reproducible manner. As listed in Table 3 we found the values for the critical wavelength in very small ranges. For most of the samples the standard deviation is significant lower than 10%. Only the data for product F, which provide the lowest UVA

Lab / Product	A	B	C	D	E	F	G	H	I	K
Lab 1	15.2	4.5	13.2	24.9	12.6	6.5	9.0	8.8	18.8	19.0
Lab 2	11.5	4.0	17.0	18.2	8.9	6.3	10.0	8.8	13.9	18.0
Lab 3	18.0	10.4	21.4	36.0	13.0	10.6	20.7	7.8	27.2	28.1
Lab 4	18.5	6.7	27.5	21.6	14.1	11.6	22.8	8.6	30.8	27.6
Lab 5	-	5.1	19.5	-	-	13.5	10.1	8.8	-	-
Lab 6	9.6	3.7	12.0	36.1	6.8	4.9	9.9	5.1	13.9	13.1
Lab 7	19.9	2.8	15.7	41.7	12.2	7.6	12.4	8.0	14.7	17.8
Mean	15.4	5.4	17.8	29.8	11.3	7.9	14.2	7.8	19.9	20.6
+ - SD	4.12	2.79	5.79	9.43	2.79	2.63	6.04	1.43	7.39	5.98
+ - SD*	28.5	64.1	34.4	32.8	27.2	38.0	45.9	20.9	39.1	30.5

* 100% = (mean - 1)

Table 2 in vitro SPF

Lab / Product	A	B	C	D	E	F	G	H	I	K
Lab 1	372.0	373.0	353.7	371.0	374.0	340.0	376.7	353.0	359.0	374.0
Lab 2	371.0	371.0	350.2	370.0	373.0	335.0	373.4	351.2	355.0	373.2
Lab 3	373.3	373.0	355.0	372.0	375.3	349.7	377.7	360.3	361.7	373.7
Lab 4	371.0	371.7	353.2	369.2	373.4	337.9	375.4	354.3	358.2	371.9
Lab 5	-	371.5	350.0	-	-	337.5	367.0	350.5	-	-
Lab 6	372.0	373.0	353.0	370.7	374.0	347.3	376.7	356.3	361.7	373.0
Lab 7	373.0	370.7	351.2	371.1	374.1	340.4	374.8	353.5	356.8	373.7
Mean	372.1	372.1	352.7	370.7	374.0	341.1	375.8	354.8	358.7	373.2
+ - SD	0.98	1.06	1.71	0.95	0.79	5.39	1.54	3.18	2.65	0.74
+ - %SD*	1.9	2.0	5.2	1.9	1.5	25.5	2.8	9.1	6.8	1.4

Table 3 Critical Wavelength

protection over all, exceed this value. When the critical wavelength is higher than 370 nm then the standard deviation levels down to 2% or less. The reproducibility of all the data for the UVA/B ratio is very high between all the different institutes. The calculated standard deviation is slightly higher compared to the critical wavelength.
In contrast to the in vitro SPF determination there is no evidence that the measured relative UVA parameters are dependent on the product type or formulation.
The UVA protection efficacy of the sunscreens was differentiated according to their critical wavelength. Six out of ten products reached values higher than 370 nm indicating a broad UV protection. All ten products contain the UVA filter Butylmethoxydibenzoylmethane (BM-DBM) which at the moment is known as the most efficient UVA filter, especially with its activity in the long wavelength region around 360 nm. Three out of ten sunscreens exhibit a critical wavelength between 350 and 370 nm. Here the UVA protection is provided by low amounts of BM-DBM, by zinc oxide or oxybenzone. Product F contains only titanium dioxide as a UVA screening agent. The critical wavelength is lower than 350 nm and indicates a very weak UVA protection. There is a good correlation between the UVA/B ratio and the data of the critical wavelength determination (cf. Table 4).

Lab Product	A	B	C	D	E	F	G	H	I	K
Lab 1	0.65	0.64	0.36	0.48	0.53	0.19	0.55	0.27	0.32	0.45
Lab 2	0.62	0.60	0.33	0.43	0.50	0.16	0.51	0.25	0.31	0.42
Lab 3	0.67	0.64	0.40	0.48	0.58	0.23	0.60	0.34	0.35	0.42
Lab 4	0.63	0.63	0.39	0.43	0.55	0.18	0.52	0.30	0.33	0.37
Lab 5	-	0.64	0.33	-	-	0.17	0.30	0.27	-	-
Lab 6	0.63	0.64	0.36	0.47	0.54	0.21	0.53	0.29	0.32	0.39
Lab 7	0.66	0.64	0.36	0.46	0.55	0.20	0.51	0.29	0.36	0.40
Mean	0.64	0.63	0.36	0.46	0.54	0.19	0.50	0.29	0.33	0.41
+- SD	0.020	0.015	0.028	0.023	0.026	0.024	0.094	0.028	0.020	0.027
+-%SD	3.1	2.4	7.6	5.1	4.8	12.2	18.8	9.7	6.0	6.6

Table 4 UVA/B-Ratio

Critical wavelength and SPF
The general concept of the relative UVA parameters such as the critical wavelength or the UVA/B ratio is that the UVA protection provided by a sunscreen should be appropriately adjusted to its protection against sunburn. For products with a different SPF value reaching or exceeding a wavelength of e.g. 370 nm, this means

that the UVA protection is appropriately adopted. Only products with the same or very similar SPF numbers can be compared directly by using the critical wavelength criteria. Within such a comparison, the relative parameter represents the absolute UVA protection. This is illustrated in Figure 2 where the UVA protection of the four sunscreens with SPF 30 are depicted.
In the described study the highest UVA protection is found for product J whereas product F provides the lowest UVA protection.

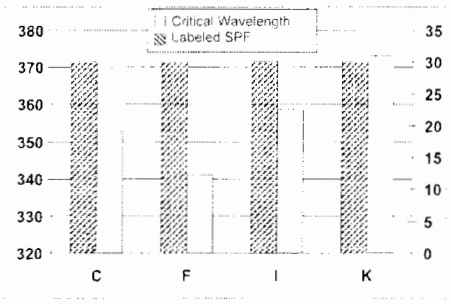

Fig. 2 Different Levels of UVA-Protection, equal UVB-Protection

Conclusion

The results of our investigations with ten different commercial sunscreens give evidence that the protocol of the UVA measurement developed by the DGK task force "sun protection" can be applied to a broad variety of sun products from the European and US market. The test results of the seven participating laboratories for the two relative parameters, the critical wavelength as well as the UVA/B ratio, are reproducible and comparable. There is still a contradiction between these results and the ones obtained by a measurement of the in vitro SPF, an absolute parameter.
The method allows to judge the UVA protection of sunscreens for which an in vivo SPF is known and to compare the efficacy of sunscreens with similar SPF values.

References

1. Australian Standard, AS-2604:93
2. JCIA, "Measurement Standards for UVA Protection Efficacy"; 1995
3. H. Gers-Barlag, E. Klette, R. Bimczok, C. Springob, P. Finkel, T. Rudolph, H.U. Gonzenbach, P. Schneider, D. Kockott, U. Heinrich, H. Tronnier, R. Bernklau, W. Johncock, R. Langner, H. Driller, H. Westenfelder: "In vitro determination to assess the UVA protection performance of sun care products": Int. J. Cos. Sci. 22, in press (2000)
4. B.L. Diffey: "A method for broad spectrum classification of sunscreens": Int. J. Cos. Sci. **16,** 47-52 (1994)
5. L.H. Kligman, F.J. Akin, A.M. Kligman: "The contribution of UVA and UVB to connective tissue damage in hairless mice": J. Invest. Dermatol. **84,** 272-276 (1985)
6. L.H. Kligman: "The protective effect of a broad-spectrum sunscreen against chronic UVA radiation in hairless mice: a histologic and ultrastructural assessment": J.Soc. Cosmet. Chem. **45,** 21-33 (1994)