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Review Article

In vitro testing of zinc oxide sunscreens

P. G. McCormick* and T. Tsuzuki†

*Faculty of Engineering, Computing and Mathematics University of Western Australia, 35 Stirling Highway, Crawley, WA 6009 and †Institute for Technology Research and Innovation, Deakin University, Geelong, Vic., Australia

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Synopsis

The UVA performances of two all-mineral zinc oxide sunscreens are measured following Colipa and ISO procedures and compared to a sunscreen containing only organic actives. It is found that the two sunscreen types yield very different *in vitro* SPF and UVA results. It shown that the results can be rationalized in terms of the differences in the monochromatic extinction spectra of the two types of sunscreens.

Introduction

The increase in understanding of the harmful effects of UVA of sunlight in recent years is leading to the development of *in vitro* procedures for characterizing UVA protection levels in suncare products. Colipa [1] and ISO [2] have recently published guidelines for determining an *in vitro* UVA protection factor, UVAPF, to provide a common test methodology for measuring UVA protection levels that takes into account product photoinstability.

The Colipa and draft ISO procedures involve measuring the monochromatic transmittance of a thin layer of sunscreen applied to a roughened substrate over the wavelength range of 290–400 nm and converting the transmittance measurements to an absorbance spectrum. A coefficient of adjustment parameter ('C' parameter) is used to adjust the absorbance spectrum so that the calculated *in vitro* SPF value equals the *in vivo* value for the sunscreen. The adjusted absorbance spectrum is used to calculate the level of pre-irradiation that the sample is exposed to using a solar simulator. Following pre-irradiation, a second transmittance measurement is taken, and the resulting absorbance spectrum is adjusted using the previously measured value of C and used to calculate UVAPF and critical wavelength values.

It is claimed [1] that the Colipa procedures provide *in vitro* UVAPF parameters that correlate well with *in vivo* UVA protection factors derived from the PPD method. However, it appears that the validation of the guidelines was carried out on a limited range of product types and did not include measurements on the new generation of photostable all-mineral UV absorbers that are becoming increasingly important in the suncare market.

This paper reports measurements of UVAPF and other UVA parameters taken using Colipa [1] procedures on two commercial all-mineral sunscreens. The results are compared with tests carried out on a commercial sunscreen containing organic UV actives.

Materials and methods

Details of the sunscreens tested are shown in Table I. Sunscreens A and B are water-in-oil sunscreens containing zinc oxide as the sole UV active. Sunscreen C is an oil-in-water emulsion sunscreen containing several chemical UV actives. All sunscreens are labelled SPF 30+.

The sunscreens were applied to PMMA substrates following the prescribed Colipa and ISO procedures [1,2]. The recommended substrate is a PMMA plate, roughened to simulate the application of a thin layer of sunscreen product to skin topography. Substrates [3] with 2- and 6-μm roughness values as specified by Colipa were used. The prescribed film loadings of 0.75 ± 0.1 and 1.3 ± 0.1 mg cm^{-2} were applied to the 2- and 6-μm substrates, respectively. The procedures for applying the film, film stabilization and area and number of measurements were in accord with that prescribed [1].

Following rub-in and stabilization, the spectral transmittances of the samples were measured using a Cary 3E spectrophotometer for the 2-μm substrates and a Jasco V-670 spectrophotometer for the 6-μm substrates. Both instruments were fitted with integrating spheres for the measurement of total transmittance. Transmittance measurements were taken at four locations on each substrate and converted to monochromatic absorbance values using eqn (1).

Table I Details of sunscreens tested

Sunscreen	UV actives	Concentration (%w/w)	Type	% water
A	Zinc oxide	20	w/o	45
B	Zinc oxide	22	w/o	45
C	Octyl methoxycinnamate	10	o/w	70
	4-Methylbenzylidene camphor	3		
	Butyl methoxydibenzoylmethane	3		
	Octocrylene	2		

Correspondence: P. G. McCormick, Faculty of Engineering, Computing and Mathematics, University of Western Australia, 35 Stirling Highway, Crawley, WA 6009, Australia. Tel.: 61864885539; fax: 61864881024; e-mail: paulm@mech.uwa.edu.au

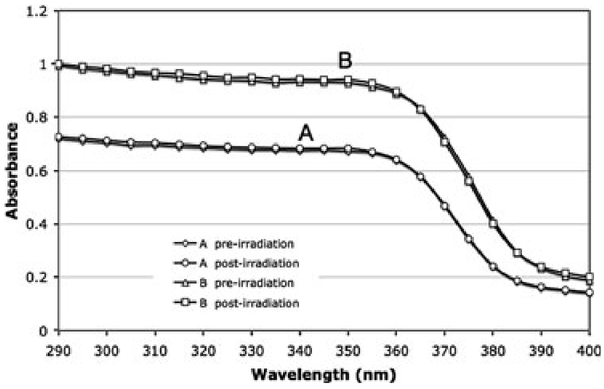

Figure 1 Measured absorbance curves for sunscreens A and B pre and post irradiation.

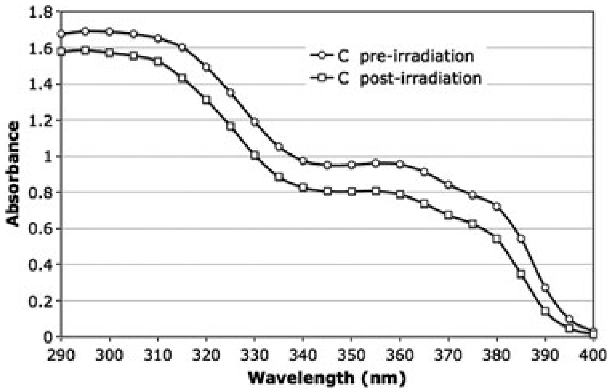

Figure 2 Measured absorbance curves for sunscreens C pre and post irradiation.

$$A(\lambda) = -\log(T(\lambda)/100) \qquad (1)$$

where $T(\lambda)$ is the measured % transmittance measured at wavelength λ.

A minimum of three substrates were used for each sample. Following the initial transmittance measurement and determination of the irradiation dose, the samples were pre-irradiated in an Atlas Suntest XLS+ and retested to obtain values of UVAPF and critical wavelength, λ_c.

Results

Absorbance measurements

Figure 1 shows absorbance curves before and after irradiation for sunscreens A and B, respectively. Each curve is the average of four measurements taken on different locations on the substrate. In all cases, the coefficient of variation for the four measurements was less than the maximum of 20% required by the Colipa procedure. Both samples exhibit a relatively flat absorbance spectrum typical of zinc oxide. The pre- and post-irradiation curves are nearly identical because of the photostability of zinc oxide.

The absorbance curves for sunscreen C are shown in Fig. 2. The curves reflect the combined absorbances of the four organic UV actives contained in the sunscreen, of which only avobenzone is classified as a UVA absorber. Comparison of the absorbance curves before and after irradiation shows photodegradation occurred during the pre-irradiation step.

The values of $\mathrm{SPF}_{in\ vitro}$, adjustment parameter C, UVAPF_0, UVAPF, critical wavelength and UVA/UVB were calculated from the monochromatic absorbance curve as prescribed in references [1] and [2].

Table II Sunscreen parameters measured following Colipa and ISO procedures

Sample	SPF_0	C	UVAPF_0	λ_c (nm)	UVAPF	SPF/ UVAPF	UVA/ UVB
2-μm substrate							
A	5.0	2.14	11.6	371.6	11.7	2.6	0.71
B	9.9	1.49	13.2	372.4	12.5	2.4	0.72
C	39.6	0.93	6.7	370.0	4.8	6.3	0.48
6-μm substrate							
B	11.3	1.42	13.4	372.4	13.4	2.2	0.72

The results of the *in vitro* tests are shown in Table II. Although all three sunscreens exhibited label *in vivo* SPF values of 30+, *in vitro* evaluation of the products yielded significantly differing values of the test parameters for the inorganic sunscreen as compared to the organic sunscreen. In particular, using 2-μm roughness PMM substrates and 0.75 mg cm^{-2} application rate, the *values* of $\mathrm{SPF}_{in\ vitro}$ for sunscreens A and B were only 5.0 and 9.9, respectively, as compared with the value of 39.6 measured for sunscreen C. Sunscreen B was also tested using the ISO-recommended conditions of 1.3 mg cm^{-2} applied to a PMMA plate having a surface roughness of 6 μm. A slightly higher value of SPF_0, 11.3 as compared to 9.9, was obtained.

The values of the adjustment parameter C for sunscreens A and B were 2.14 and 1.49, respectively, failing to meet the Colipa requirement of C = 1 ± 0.2, whereas for sunscreen C, the value of C was well in the required range. It is also noted that sunscreen B just met the ISO specification of $0.8 \le C \le 1.6$ [2]. Evidently, sunscreen A would fail to be classified as a sunscreen where regulations are based on the Colipa or ISO protocols.

For sunscreen C, the pre-irradiation caused the *in vitro* SPF to decrease from 39.6 to 26.5, a ~25% reduction. If this sunscreen had been photostable, the resulting UVAPF would have equalled 6.7 as compared with its final value of 4.8. For either case, this sunscreen did not meet broad-spectrum classification of SPF/UVAPF<3.

Sunscreens A and B both meet the broad-spectrum requirement based on their SPF/UVAPF values. The values of the UVA/UVB ratios for the inorganic sunscreens were also significantly greater than for the organic sunscreen. On the other hand, the values of λ_c calculated from the absorbance curves of the three sunscreens are all ≥370 nm, generally taken to be a measure of broad-spectrum protection [4].

Effect of application rate on SPF

Measurements of the effect of sample application rate to the substrate on *in vitro* SPF were taken. The sunscreens were applied onto

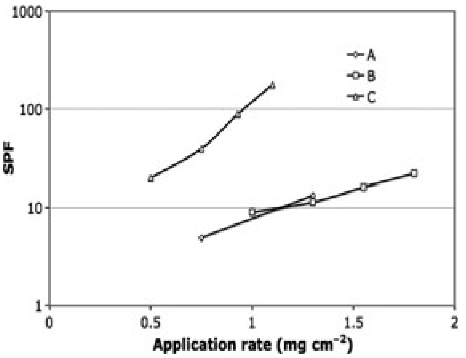

Figure 3 Effect of application rate on *in vitro* SPF.

PMMA substrates following the Colipa procedures except that the samples were not irradiated. Sunscreens A and C were tested using 2-μm roughness PMMA substrates and sunscreen B using 6-μm substrates.

Figure 3 shows the effect of application rate on *in vitro* SPF. With all sunscreens, the in *vitro* SPF increased approximately exponentially with increasing loading rate. Sunscreen C exhibited the highest dependence on application rate because of its significantly higher UVB absorbance.

Extinction coefficients

The monochromatic absorbance is determined by the monochromatic extinction coefficient, concentration of UV actives and the film thickness as

$$A = \varepsilon c d \qquad (2)$$

where ε is the extinction coefficient (L mol cm^{-1}), c equals the molar concentration (M), and d is the film thickness (cm).

Extinction coefficients for the three sunscreens were determined from absorbance measurements taken on samples of uniform film thickness prepared in flat quartz optical cells. De-emulsification and dewatering of the samples were carried out prior to testing, and the sunscreens were then diluted by an appropriate amount to keep the absorbance measurements within the linear region of the spectrophotometer.

Figure 4 compares the monochromatic extinction curves for the three sunscreens. The curves for the two zinc oxide sunscreens were very similar, showing relative constant values throughout the UVB and UVA up to 360 nm. The values of extinction coefficient for sunscreen C in the UVA were greater than for the zinc oxide sunscreens and showed significant variation over the UV range. The measured curve for sunscreen C was in good agreement with that calculated using extinction data for the individual actives [5].

Discussion

The measurements show significant differences in the *in vitro* properties of the organic and inorganic sunscreens having the same label values of *in vivo* SPF. The *in vitro* SPFs of the inorganic sunscreens A and B seem remarkably low, given the value of the *in vitro* SPF for the organic sunscreen and their label *in vivo* SPFs. It is shown that the difference in the *in vitro* SPF values of the organic and inorganic sunscreens may be a consequence of several factors including differences in film thickness, film topography and spectral variation of extinction coefficients, as well as differences between label SPF and measured *in vivo* SPF.

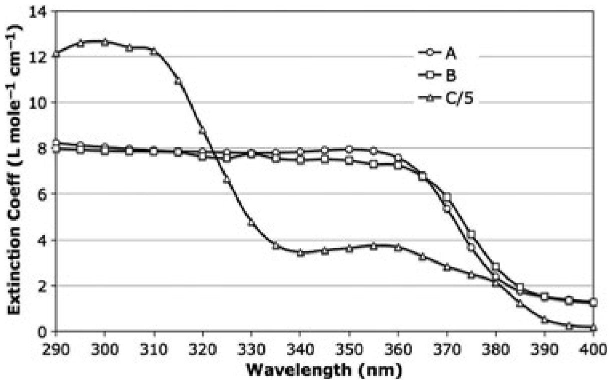

Figure 4 Extinction coefficient measurements.

Product application rate and the effect of density on film thickness

The Colipa and ISO guidelines specify that the sunscreen be applied to the textured PMMA substrate according to a mass application rate and not a prescribed film thickness. As previously stated, an application rate of 0.75 mg cm^{-2} is specified for substrates having 2-μm roughness and 1.3 mg cm^{-2} for substrates with 6-μm roughness. If the densities of all sunscreens are the same, the specification of a mass application rate is equivalent to specifying a constant average film thickness. For example, if the density of the sunscreen is 1 g cm^{-3}, then 0.75 mg cm^{-2} corresponds to a uniform film thickness of 7.5 μm. However, if sunscreens of differing density are tested, the film thickness will vary according to the specific gravity of the sunscreen. Given that the monochromatic absorbance varies linearly with film thickness and the monochromatic SPF varies exponentially with absorbance, it is clear from eqn (2) that the use of a mass application rate instead of specifying film thickness via a volumetric application rate is fundamentally incorrect for both *in vivo* and *in vitro* testing of sunscreens [6].

For the case of sunscreens containing zinc oxide as the UV active, the density of zinc oxide is 5.61 g cm^{-3}, as compared to $\sim$1 g cm^{-3} for sunscreens containing only organic actives. As a consequence, the density of a zinc oxide sunscreen increases significantly with increasing active concentration.

Figure 5 shows the effect of zinc oxide content on film thickness for applied application rates of 0.75 and 1.3 mg cm^{-2}. The film thickness decreases linearly with increasing zinc oxide concentration. The density of a sunscreen containing 25% zinc oxide as the UV active is 1.26 g cm^{-3} as compared to the density of $\sim$1 g cm^{-3} for a sunscreen containing all organic UV actives. The resulting film thickness of the zinc oxide sunscreen is 5.96 μm for the application rate of 0.75 mg cm^{-2}, and 10.33 μm for 1.3 mg cm^{-2} as compared to the respective values of 7.5 and 13 μm for a sunscreen containing organic actives with an assumed density of 1 g cm^{-3}.

The measurements of the effect of application rate on *in vitro* SPF in Fig. 3 have been used to determine the SPF of sunscreens A and B when measured at the same film thickness as the organic

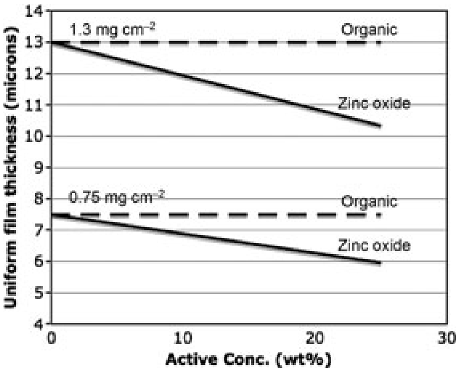

Figure 5 Effect of density on the average thickness of sunscreen layers applied at loadings of 1.3 and 0.75 mg cm^{-2}, respectively.

Table III Increase in *in vitro* SPF owing to testing at constant film thickness instead of constant application rate

Sunscreen	Application rate (mg cm^{-2})	Film thickness (μm)	SPF
A	0.75	6.4	5.0
	0.88	7.5	7.2
B	1.3	10.9	11.4
	1.5	13.0	16.1

sunscreen C. In Table III, the values of SPF are shown. The measurements show that testing at the same film thickness as used for the organic sunscreen increases the SPF of sunscreen A by 44% and sunscreen B by 41%. However, it is clear that the increase in film thickness cannot fully explain the significant difference in *in vitro* SPF between the organic and inorganic sunscreens.

Film uniformity

To properly evaluate the effect of film thickness (or application rate) on sunscreen performance, it is necessary to take into account the effect of film uniformity on SPF. Although sunscreen testing procedures can prescribe the application rate or average thickness of a sunscreen being tested, it is well established that the measured SPF for a given average film thickness is highly dependent on the uniformity of the applied film. To maintain a level of consistency in uniformity, testing procedures prescribe in some detail the method for applying samples to the substrate [1]. The prescribed application rate for *in vitro* SPF testing is based on the fact that the *in vitro* film is more uniform, and therefore a thinner layer is used in comparison with *in vivo* testing, where the film thickness is more non-uniform due in part to the topography of the skin.

To take into account the effect of the inherent non-uniformity of a sunscreen layer on the SPF, O'Neil [7] modelled a sunscreen film as having a profile consisting of steps of equal depth and spacing. As shown in Fig. 6 for a single step, in the O'Neil step film model a film of average thickness, d, is characterized by two parameters, g, which gives the spatial fraction of thin and thick regions of the film, and f, which gives the relative thicknesses of the two regions.

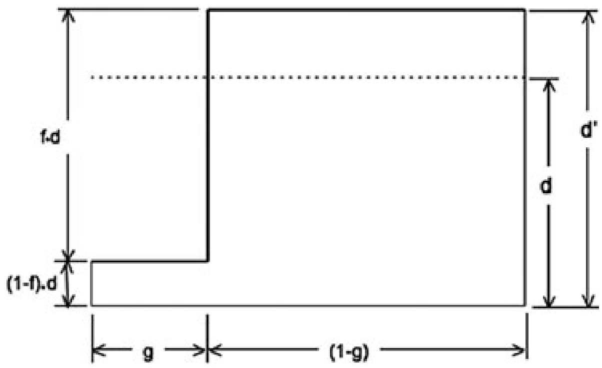

Figure 6 Step film model geometry.

The monochromatic transmittance through the film is expressed as

$$\tau(\lambda) = g * 10^{-\varepsilon(\lambda)*c*d*(1-f)} + (1-g) * 10^{-\varepsilon(\lambda)*c*d*[g*f/(1-g)+1]} \qquad (3)$$

where ε, c and d are defined in eqn (2).

The SPF of the non-uniform film is then calculated using the transmittance given by eqn (3).

On the basis of the step film model, the values of g and f define the film geometry associated with the reduction in SPF from its value for a uniform film to its *in vitro* or *in vivo* value.

Herzog [5,8,9] determined values of g and f that gave the best collective fit of the calculated *in vivo* SPF with the measured *in vivo* values for three Colipa standard sunscreens.

Using the obtained values of g and f, $g = 0.269$ and $f = 0.935$, Herzog then calculated the '*in vivo*' SPFs of a wide range of sunscreens from the values of average molar extinction coefficients of the mixtures of UV actives in each sunscreen, and the values of the step film parameters g and f. The calculated SPF values were correlated with the *in vivo* SPF values of the sunscreens. This procedure has formed the basis of well-known predictive software [10] for estimating the SPF of sunscreen formulations.

Ferrero *et al.* [10–12] extended the step film analysis of O'Neil by using continuous distribution functions to model variations in film thickness. Ferrero *et al.* appear to be the first to note that the shape of the absorbance curve is dependent on film uniformity. Ferrero *et al.* showed that not only the SPF but also all parameters used to characterize relative UVB/UVA performance, such as SPF/UVAPF, UVA/UVB and λ_c, are dependent on film uniformity. Ferrero *et al.* measured the effect of substrate roughness on *in vitro* SPF and showed that the SPF decreased with increasing surface roughness. In addition, Ferrero *et al.* showed that the UVA/UVB increases with increasing substrate roughness.

Modelling

In spite of its inherent simplicity, the step film model provides a useful, intuitive tool to evaluate the effects of film uniformity (film step height and breadth) on the *in vivo* and *in vitro* performance of sunscreens. In this section, the experimental results are modelled using the step film model.

Starting with the extinction coefficients measured at constant film thickness, the values of *g* and *f* corresponding to the *in vitro* SPF, measured prior to UV pre-irradiation, were determined for the three sunscreens.

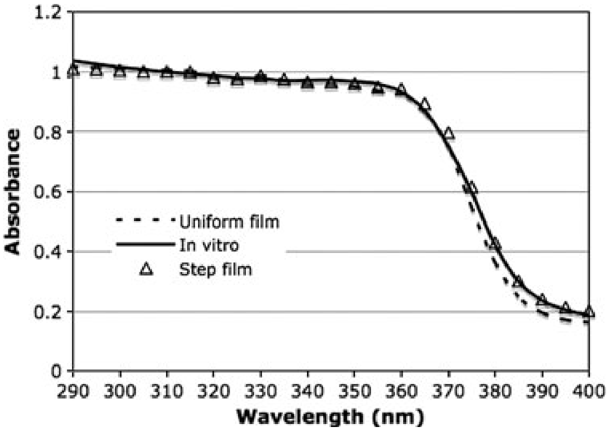

Figure 7 Comparison of measured and calculated absorbance curves with absorbance curves for constant film thickness – sunscreen B.

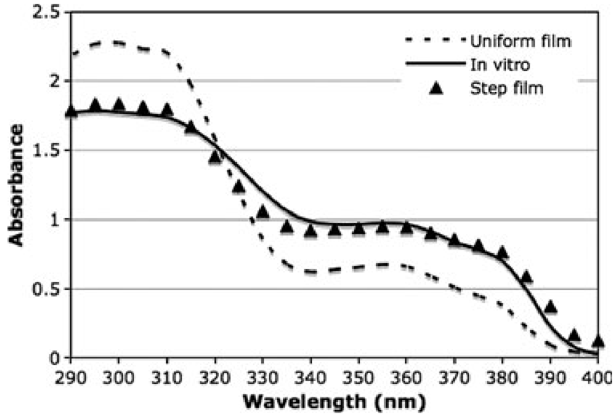

Figure 8 Comparison of measured and calculated absorbance curves with absorbance curve for constant film thickness – sunscreen C.

In Figs 7 and 8, the measured absorbance curves for sunscreens B and C, respectively, are compared with the absorbance curves calculated using the step film model, with *g* and *f* used as fitting parameters. Also plotted in the each figure is the absorbance curve for a uniform film of thickness equal to that required for the SPF to equal the measured value. For both sunscreens, the calculated absorbance curves are in good agreement with the measured curves as shown in Figs 6 and 7.

With sunscreen B, the calculated absorbance curve for the uniform film is almost identical to the measured and calculated *in vitro* curves. On the other hand, with sunscreen C, the shape of the absorbance curve for uniform thickness differs markedly from the *in vitro* curves. The absorbance curves in Figs 7 and 8 illustrate an often overlooked outcome of the current methodology of characterizing sunscreen performance, that the relative balance of UVA and UVB protection is dependent on film uniformity. As demonstrated by Ferrero *et al.* [10–12], the large difference in the *in vitro* and uniform film absorbance curves for sunscreen C is attributed to the spectrally non-uniform extinction coefficient combined with the non-uniform film thickness and causes the relative UVA and UVB absorbances to vary with film uniformity.

Values of *g* and *f* determined from the curve fitting are given in Table IV. Also shown are the values of *f* for each sunscreen to achieve an *in vitro* SPF of 30 and an '*in vivo* SPF' of 30 (application rate of 2 mg cm^{-2}), using the same value of *g* as determined for the measured *in vitro* curves.

Comparison of the values of *f* for the *in vitro* SPF shows that the value of *f* for sunscreen B is significantly smaller than for sunscreens A and C (0.57 for B as compared to 0.85 for C). The lower value of *f* for sunscreen B indicates that this film had a more uniform film thickness in comparison with sunscreens A and C.

It is noted that the values of *g* and *f* calculated for sunscreen C for *in vivo* conditions are similar to that obtained by Herzog for similar oil-in-water formulations not containing inorganic actives. Herzog [5] noted that a particular SPF is not unique to a particular set of *g* and *f* values. However, in the present analysis, it is clear that the best fit to the measured curves, and, hence, UVA properties, can only be obtained with a single combination of *g* and *f* values.

To estimate the effect of increasing film non-uniformity, the values of UVA/UVB, λ_c and SPF/UVAPF calculated for a uniform film of thickness corresponding to SPF 30 are compared to the corresponding values determined from the *in vitro* absorbance curves and values calculated using the step film model for a hypothetical *in vivo* SPF equal to 30 (application rate equal to 2 mg cm^{-2}).

Table IV Values of *g* and *f* for measured *in vitro* SPF, *in vitro* SPF = 30 and *in vivo* SPF = 30

	Measured *in vitro* SPF (0.75 mg cm^{-2})			***In vitro* SPF = 30 (0.75 mg cm^{-2})**		***In vivo* SPF = 30 (2 mg cm^{-2})**	
Sample	**SPF**	***g***	***f***	***g***	***f***	***g***	***f***
A	4.8	0.3	0.81			0.3	0.69
B	9.9	0.3	0.57	Not possible		0.3	0.72
C	33.7	0.25	0.85	0.25	0.87	0.25	0.953
	Measured *in vitro* SPF 1.3 mg cm^{-2} 6 μm PMMA			*In vitro* SPF = 30 (1.3 mg cm^{-2})			
B	11.3	0.3	0.75	0.3	0.57		

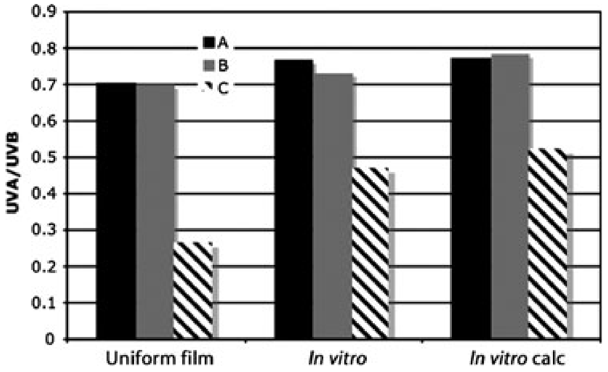

Figure 9 Effect on decreasing film uniformity on UVA/UVB.

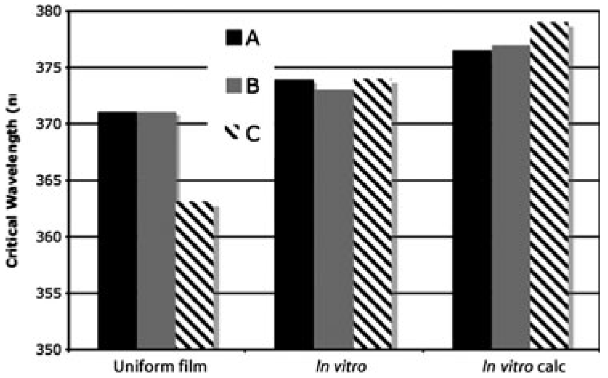

Figure 10 Effect on decreasing film uniformity on λ_c.

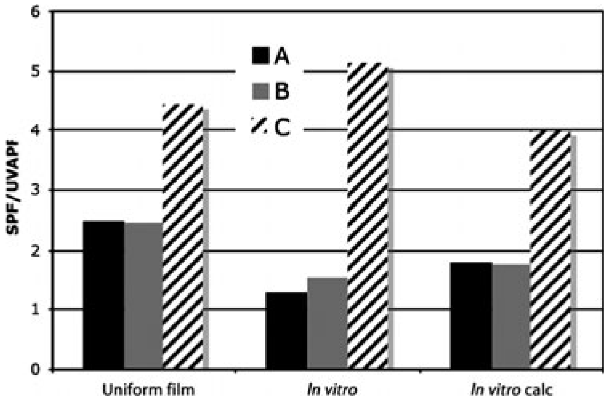

Figure 11 Effect on decreasing film uniformity on SPF/UVAPF.

As shown in Fig. 9, the values of UVA/UVB for all three sunscreens increase on going from the uniform film to the *in vivo* film. With sunscreens A and B, the increase is small; however, with sunscreen C, the UVA/UVB ratio doubles in value. In Fig. 10, the values of λ_c also increase with increasing film non-uniformity, with sunscreen C showing a much larger variation than sunscreens A or B. There appears to be no systematic variation of SPF/UVAPF with film uniformity (Fig. 11). The lower effect of film uniformity for sunscreens A and B is attributed to the relatively more uniform monochromatic extinction coefficient of zinc oxide. As noted previously, the values of SPF/UVAPF for sunscreens A and B easily met the broad-spectrum requirement of SPF/UVAPF<3, whereas sunscreen C failed.

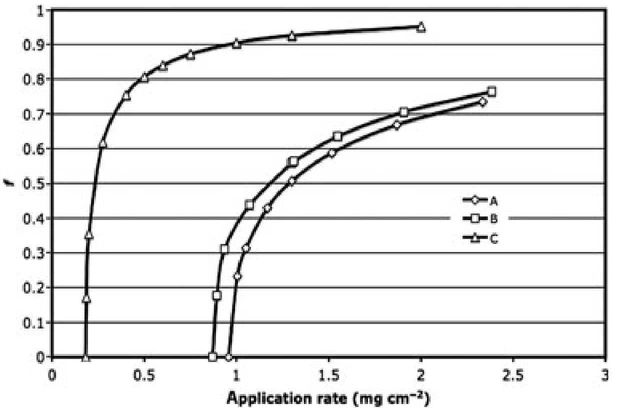

Figure 12 Effect of product application rate on value of *f* for *in vitro* SPF = 30.

It is also noted that the values of λ_c showed no correlation with the other indicators of UVA performance. For example, with sunscreen C, λ_c for the *in vitro* test is 374 nm, whereas the UVA/UVB equals only 0.47 and SPF/UVAPF = 5. In comparison, λ_c for sunscreen B is slightly smaller ($\lambda_c = 373$) than for C; however, both the values of UVA/UVB and SPF/UVAPF reflect much higher levels UVA protection.

In Fig. 12, values of *f* required to achieve *in vitro* SPF equal to 30 using the step film model are plotted as a function of the application rate. For all three products, the values of *f* corresponding to $\text{SPF}_{in\ vitro}$ equal to 30 decrease with decreasing application rate, indicating that an increase in the uniformity of film thickness is required for the film to exhibit a SPF of 30 as the average film thickness or application rate is decreased.

The calculations show that, to achieve the same *in vitro* SPF value as the labelled *in vivo* SPF using the Colipa method, the zinc oxide sunscreens require more uniform film thicknesses (smaller values of *f*) than organic sunscreen C for all application rates. The film thickness at which *f* falls to zero is equal to the uniform film thickness for SPF = 30, t_{30}. It is seen that t_{30} for the zinc oxide sunscreens is greater than for the organic sunscreen. With the two zinc oxide sunscreens tested in this study, the calculations show that it is not possible to achieve the same *in vitro* SPF value of 30 as the labelled *in vivo* SPF for the application rate of 0.75 mg cm^{-2} recommended by the Colipa procedure, in agreement with the experimental findings. For this application rate, the *in vitro* SPF for a uniform film is only 14.5 for sunscreen A and 18.8 for sunscreen B.

According to Fig. 12, while using an application rate of 1.3 mg cm^{-2} as recommended by ISO [2], both zinc oxide sunscreens A and B can achieve an *in vitro* SPF of 30, but only when a much more uniform film (lower values of *f*) than for a film tested under the *in vivo* conditions. As a consequence, the values of the adjustment parameter will be much >1, causing the product to fail the test, even though its *in vivo* SPF is 30 and the product has excellent UVA properties.

Thus, the intent of having test conditions that provide *in vitro* SPF values near 30 is not achievable in sunscreens containing high levels of zinc oxide, due to the fact that the Colipa and ISO test conditions, in particular the application rate and substrate roughness, have not been validated for sunscreens with high concentrations of inorganic actives.

Conclusions

The use of high-density mineral UV actives such as zinc oxide cause a significant increase in the density of the sunscreen in comparison with sunscreens with organic actives where the density does not increase with active concentration. This results in a decrease in the average film thickness of the zinc oxide sunscreens relative to the organic sunscreen. Measurements of the effect of film thickness on *in vitro* SPF showed that the *in vitro* SPF of the zinc oxide sunscreens containing 20–22% zinc oxide should increase by 41–44% when tested at the same film thickness as organic sunscreens with organic actives.

The *in vitro* SPF values of the zinc oxide sunscreens are significantly less than that measured for the sunscreen containing organic UV actives. The low *in vitro* SPFs of the zinc oxide sunscreens resulted in the adjustment parameter C being outside the acceptable range for the Colipa test conditions and at the limit of the range for ISO test conditions. The SPF for the organic sunscreen was well with the accepted range.

The measurements and calculations show that the Colipa and ISO test conditions of application rate and substrate roughness, although valid for organic sunscreens, are not suitable for zinc oxide sunscreens. Using the Colipa or ISO conditions, it is not possible to obtain *in vitro* SPF values near the *in vivo* value.

Comparison of absorbance curves measured at constant film thickness with the *in vitro* absorbance curves confirmed the effect of deceasing film uniformity in improving UVA properties, including UVA/UVB, λ_c and SPF/UVAPF. The measurements showed that the UVA properties of zinc oxide sunscreens are less affected by film uniformity than organic sunscreens.

Using the step film model to describe film non-uniformity gives excellent agreement between theory and experiment. It is shown that it is possible to accurately model both SPF and UVA properties with a unique combination of step height and spatial distribution of steps.

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