

# Evaluating sunscreen ultraviolet protection using a polychromatic diffuse reflectance device

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## Abstract

**Background:** Sun protection factor (SPF) and UVA protection factor (UVA-PF) are determined using in vivo tests, with high exposures of subjects to ultraviolet (UV) radiation. Hybrid diffuse reflectance spectroscopy (HDRS) enables estimation of both indices using only trace amounts UVB. However, the equipment requires two expensive monochromators that must synchronously scan the spectrum.

**Methods:** An alternate approach was developed using a polychromatic source that illuminates the skin via a custom light guide array, and the diffuse reflected light is measured with a photomultiplier. The ratio of the diffuse reflectance with and without the sunscreen on the skin determines the polychromatic diffuse reflectance UVA-PF (PDRS UVA-PF<sub>0</sub>). This factor was used to adjust in vitro UV spectroscopy scans of the sunscreen (with and without UV exposure to assess photostability), to calculate SPF and UVA protection factors. Ten sunscreens were evaluated and compared to in vivo SPF and UVA-PF values.

**Results:** The data show an excellent correlation with known in vivo determinations.

**Conclusion:** This polychromatic HDRS approach uses simpler, faster, and less expensive equipment to determine both UVA-PF and SPFs without high doses of UV radiation to the test subjects.

## KEYWORDS

diffuse reflectance spectroscopy, polychromatic, sun protection factor (SPF), sunscreens, ultraviolet, UV-A protection factor (UVA-PF)

## 1 | INTRODUCTION

It has been established that efficacy of a topical sunscreen product<sup>1-3</sup> is dependent on both the ultraviolet absorbing filters formulated into a product and the nature and components of the vehicle of the product. Sunscreen protection is also dependent on establishing a continuous and uniform optical barrier across the surface of the skin. The more uniform the barrier is, the higher the protection provided by the filters. For this reason, regulators globally have required in vivo testing of sunscreen products on human subjects

to substantiate the protection claims made by sunscreen manufacturers. These tests, SPF for sunburn prevention and UVA-PF (PPA+ in Japan), rely on testing of sunscreen products on human subjects and exposing them to high doses of full-spectrum UV radiation (UVA+UVB for erythema) and UVA (only) for pigment darkening assessment of UVA protection. These tests are designed to elicit minimal and supra-minimal erythema and/or pigmentation responses from the skin with high doses from an ultraviolet solar simulator.

Sunscreen industry scientists and academicians have worked extensively over the past 40 + years to establish reliable in vitro test

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methods, with yet no clear solution to the inherent technical difficulties.<sup>4</sup> The *in vitro* spectroscopic absorbance scan of the products yields a consistent spectral shape independent of the substrate; however, the absolute magnitude of the absorbance (height) is highly variable depending on the sunscreen composition, its interaction with the substrate surface, and application and spreading techniques. The ISO24443 *in vitro* method<sup>5</sup> was developed to estimate UVA-PF of sunscreens; however, this method requires prior knowledge of *in vivo* SPF value of the sunscreen being tested in order to accurately scale the magnitude of the *in vitro* absorbance scan. The primary difficulty obtaining absolute absorbance measurements of thin films of sunscreens lies in the differences in how the sunscreens interact and set up a film on the surface of the plastic (polymethylmethacrylate—PMMA) plates used for the spectroscopy. The infinite variety of sunscreen vehicle components (with the many UV filters and combinations possible) often react differently on human skin than on these plastic plates, leading to unpredictable over- and under-estimations of the magnitude of the absorbance. Automated robotic spreading of the sunscreens on the plates has helped reduce variability, but has not addressed the primary issue of film/sunscreen interaction differences between PMMA plates and human skin.<sup>6</sup> The most relevant and critical element of the absorbance measurements appears to require actual human skin.

Nikoforos Kollias and his colleagues pioneered the use of diffuse reflectance spectroscopy on skin to evaluate skin chromophores and changes upon UV exposure, and then applied it to evaluate sunscreens.<sup>7</sup> DRS was first used to assess UVA-PFs of sunscreens<sup>8</sup> by testing the dose response of the system with oxybenzone and avobenzone. Later, DRS was used to evaluate a variety of products to establish the clear correlation of this technique with *in vivo* UVA-PF measurements.<sup>9</sup> By this time, the COLIPA-UVA test<sup>10</sup> was the primary testing being utilized for UVA protection assessment, and the DRS technique was seen mostly as an “interesting other method,” but somewhat unneeded as the *in vitro* test method provided the answer for determining a UVA-PF value and critical wavelength (CW). However, the COLIPA-UVA-PF test, as well as the ensuing ISO 24443 test method, requires knowledge of the actual *in vivo* SPF of the product being tested, and not just the SPF claimed on the product label. Thus, *in vivo* SPF measurements are essential to evaluate the UVA protectiveness with this technique.

The conundrum of how to assess SPF without having to expose human skin to doses of UVB and UVA sufficient to cause sunburn and pigmentation responses was solved using a hybrid method (HDRS) combining DRS with *in vitro* thin-film sunscreen spectroscopy (on plastic plates), as reported by Ruvolo et al in 2014.<sup>11</sup> DRS works very well in assessing the absorbance of sunscreens on the skin throughout the UVA range (320–340 nm) as there is sufficient remitted light signal from the skin for measurement purposes. However, when entering the wavelength range below 320 nm, the remitted light signal drops precipitously as the energy is strongly absorbed by proteins and DNA in the stratum corneum and epidermis, leaving insufficient remitted signal for measurement purposes.

The spectrum and the absolute magnitude of the sunscreen absorbance in the UVA can be determined by comparing the skin's remitted light before and after sunscreen has been applied (at 2 mg/cm<sup>2</sup>). To be able to determine the SPF, the shape of the UVB absorbance spectrum is required, which can be separately measured *in vitro* on plastic plates and appended to the *in vivo* DRS measurement of the sunscreen absorbance by scaling it to match the DRS UVA curve in a range of overlap of the two measurements (330–340 nm). With the now completed and accurately scaled absorbance spectrum of the sunscreen, the standard SPF calculations can be completed to project the *in vivo* SPF values, as well as the UVA-PF and the critical wavelength. Thus, with one technique, both UVA-PF, SPF and critical wavelength values of a test sunscreen product can be estimated from human skin, without having to expose the skin to biologically damaging doses of ultraviolet radiation.

Recent HDRS testing reported by Mathias. Rohr<sup>12</sup> used pre-exposure of the *in vitro* sunscreen-treated plates to incorporate consideration of photostability into the calculations in a manner similar to the pre-exposure step utilized in ISO24443. Testing was conducted on over 100 sunscreens over the full SPF range, and a high degree of correlation with *in vivo* SPF values was reported.

To date, all DRS spectroscopy has been conducted using two monochromators, one illuminating the skin through a bifurcated fiber optic and the second monochromator synched to the same wavelength to filter the remitted light from the skin before entering a photomultiplier detector system. Thus, the spectral shape of the absorbance of the sunscreen can be determined in the UVA range and used to scale the separate *in vitro* thin-film spectroscopy scan on a PMMA plate. These monochromators have typically been double monochromators, to yield a highly filtered/purified bandpass of the energy at a given wavelength. With this level of filtration, there is added loss of signal and inefficiencies from each reflective surface encountered in the beam's path. The complexity of controllers to couple and synch the scanning monochromators adds to the non-insignificant cost of the monochromators used in this system, resulting in a large, complex, and bulky test system.

We report herein a new and simplified approach to assessing the SPF and UVA-PF of sunscreens using a polychromatic light source and light sensor system that eliminates the need for monochromators altogether, with a simple two-point measurement to provide the information needed for the sunscreen protective indices. By constructing an optical measurement system that has a response spectrum similar to the human pigment darkening response (used for *in vivo* UVA-PF determinations as well as for *in vitro* UVA-PF calculations), coupled with the same UV spectral source input used in clinical testing for sunscreen UVA-PF values, we replicate the clinical test system with instantaneous reading of the UVA-PF values of the test product. This UVA-PF value can then be used to scale an *in vitro* spectral absorbance scan to calculate the SPF. A proof-of-concept trial was performed with 10 widely varying sunscreen compositions to evaluate this polychromatic approach to diffuse reflection measurements of sunscreen products.

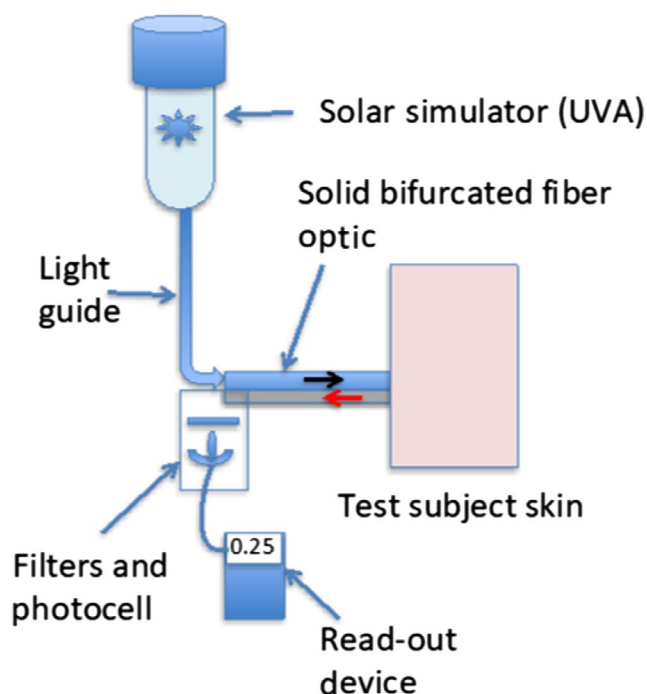
## 2 | MATERIALS AND METHODS

The schematic of the optical system used for the skin remittance measurements is shown in Figure 1.

The light source is similar to the standard UVA solar simulator utilized in clinical testing for determining sunscreen UVA-PF and meets the specifications identified in the ISO 24442 test method with only radiation between 320 and 400 nm. The UVA radiation passes through the light guide into an optical light guide array and onto the test subject's skin. The incident light passes through the sunscreen layer on the surface of the skin, is scattered within the upper layers of the stratum corneum and epidermis, and a portion is remitted back through the sunscreen layer again, and enters the custom (Solar Light Company, Inc.) optical "pickup" path of the optical light guide that brings the signal to a photomultiplier (PMT) detector for measurement.

### 2.1 | Test products

Ten products were chosen based on their previous use in test method development and the availability of in vivo SPF values from a minimum of two laboratories each. They ranged from SPF of 4 to 85 and a UVA-PF value from 1.25 to 22. The filters were selected to represent the variety of possible sunscreen filter type (organic, inorganic, and combinations) spectral absorption combinations, and



**FIGURE 1** Schematic of equipment for polychromatic HDRS (PHDRS) measurements of sunscreen protection. The black arrow represents polychromatic UVA radiation from the solar simulator illuminating the test site on the subject's back. The red arrow represents the light remitted from the subject's back after passing twice through the sunscreen film on the test site. The remitted light passes through the shaping filters and is measured by the photocell [Colour figure can be viewed at [wileyonlinelibrary.com](http://wileyonlinelibrary.com)]

to cover the range of SPFs from 8 to 85. UVA-PF values of the sunscreens with known values are listed in Table 1. The spectra of these sunscreens are shown in Figure 2.

### 2.2 | PDRS UVA-PF<sub>0</sub> determination procedure

Test subjects were recruited based on FDA sunscreen monograph testing criteria, having skin phototypes I, II, or III, with no disqualifying skin conditions or markings. The test protocol and test materials were reviewed and approved by an independent Investigational Review Board, and written statements of informed consent were obtained from all test subjects. Eight to 10 subjects were tested for each test sample.

Two measurements were required to calculate the PDRS UVA-PF<sub>0</sub> of the sunscreen being tested. This value is used to scale the pre-irradiation in vitro absorbance scan measurements. Skin without blemishes or nevi on the test subject's backs were chosen and marked as the test sites. After obtaining four measurements of remittance intensity for unprotected skin at each test site, sunscreen was applied at the same application density (2 mg/cm<sup>2</sup>) and application procedures used in all human SPF testing, and allowed to dry for 15 minutes. The sites were randomly assigned to the test sunscreens prior to initiating the measurements. After drying, the remitted light was again measured with the device to determine the ratio of intensity, with and without the sunscreen. There were no visual skin changes during or after the remittance measurements. Since the remitted light passes through the sunscreen layer twice, the calculation for the UVA-PF of the sunscreen is as follows:

$$PDRS\ UVA-PF_0 = \sqrt{\left(\frac{I_u}{I_p}\right)}$$

where  $I_u$  represents the intensity of the remitted light of unprotected skin and  $I_p$  represents the intensity of the remitted light of protected skin.

Since the response spectrum of the photocell unit was shaped with UG11 black glass filters to correspond to the shape of the persistent pigment darkening action spectrum, and the light source is identical to the sources used for DRS UVA-PF testing, the ratio of the remitted signals represents the level of protection provided by the sunscreen in the same way as human skin during the in vivo UVA-PF test.

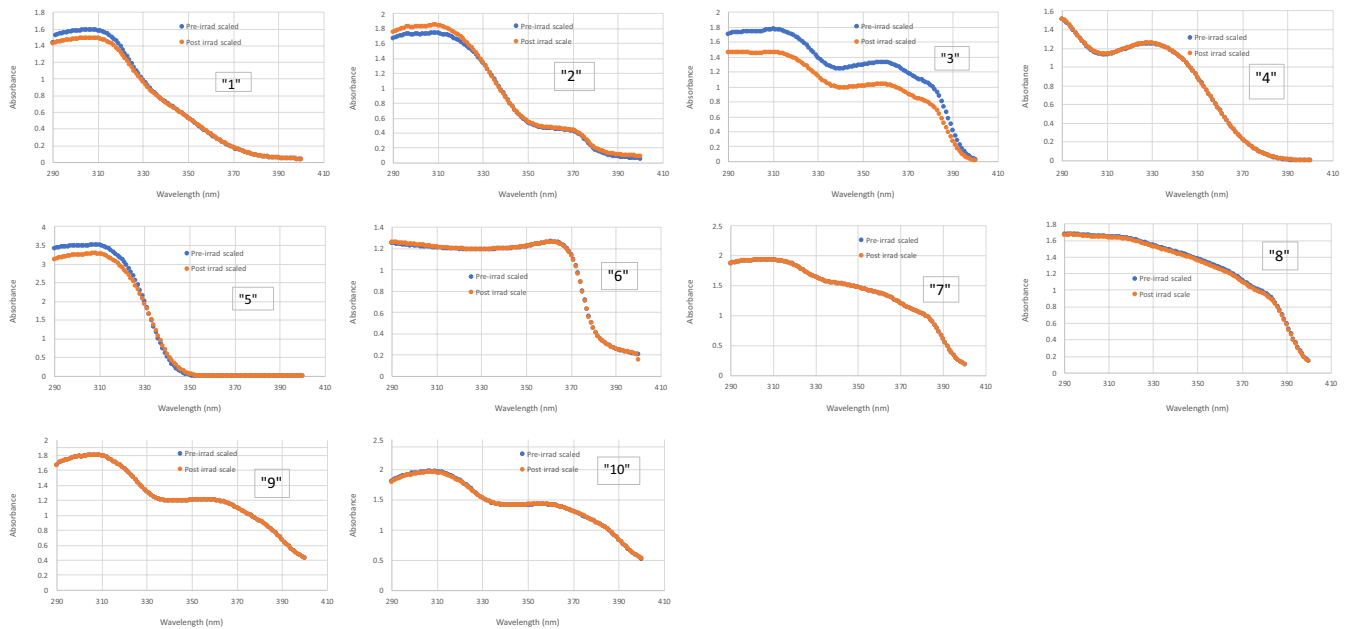
### 2.3 | Calculation of the absorbance spectrum pre-UV

Thin-film spectroscopic measurements were conducted on the test sunscreens using a single-grating spectrophotometer. Sunscreens were applied to PMMA HD6 plates at 1.3 mg/cm<sup>2</sup> (the standard application rate for in vitro testing per ISO24443) and allowed to dry in a dark area for at least 15 minutes before absorbance measurements. Four plates were prepared for each test sunscreen, and absorbance measurements were conducted for each plate with the spectrophotometer. Sunscreen absorption measurements from the in vitro PMMA plate scans, pre- and post-UV exposure, were

**TABLE 1** Test Sunscreens and Results

Treatment code	UV filter composition	In vivo SPF (avg. 2 labs)	Device estimated SPF (SE)	In vivo UVA-PF (avg. 2 labs)	Device estimated UVA-PF (SE)
1	Organic only, UVB, UVAIL	16.2	13.9 (0.9)	3.2	2.2 (0.14)
2	Organic + Inorganic, UVB, UVAIL, UVAI	11.1	13.1 (0.4)	2.2	3.0 (0.1)
3	Organic, UVB, UVAIL, UVAI Not photostable	12	12.5 (1.9)	4.3	5.8 (0.9)
4	Organic, UVB, UVAIL	9	11.7 (1.0)	3.1	2.9 (0.25)
5	Organic, UVB	8	10.8 (0.3)	1.7	1.2 (0.03)
6	Inorganic, UVB, UVAIL, UVAI	17.7	15.9 (1.5)	10.6 <sup>a</sup>	9.6 (0.9)
7	Organic, UVB, UVAIL, UVAI	85	74.9 (10.6)	18.9 <sup>a</sup>	19.6 (2.8)
8	Organic, UVB, UVAIL, UVAI	30	33.8 (2.9)	12.5	14.9 (1.28)
9	Organic + Inorganic UVB, UVAIL, UVAI	42.0	47.3 (4.0)	13.3 <sup>a</sup>	13.3 (1.11)
10	Organic + Inorganic UVB, UVAIL, UVAI	67.7	71.5 (7.4)	22.3 <sup>a</sup>	24.5 (2.7)

<sup>a</sup>UVA-PF values for samples H, K, S, and T are estimated by ISO24443 computations using in vivo SPF results.



**FIGURE 2** Spectral absorbance characteristics of the sunscreens tested [Colour figure can be viewed at wileyonlinelibrary.com]

imported into an Excel spreadsheet. Averages were computed at each wavelength for each sunscreen across the four plates.

To determine the properly scaled absorbance spectrum of the sunscreen, the in vitro absorbance scan is multiplied by a scalar factor such that the calculated UVA-PF<sub>in vitro</sub> matches the PDRS-UVA-PF<sub>0</sub>.  $A_{\lambda,preUV} = A_{\lambda,postUV} \times S$ .

### 2.4 | Calculation of absorbance spectrum post-UV

The PDRS UVA-PF<sub>0</sub> measured on the skin represents the initial non-exposed UVA-PF for a sunscreen. For a non-photostable sunscreen, this value is too high when compared to the clinical UVA-PF values determined using the JCIA PPD or ISO24442 tests where the sunscreen is irradiated extensively during those test procedures,

significantly degrading the sunscreen absorbance during the exposures on human skin. To account for this change in absorbance with photodegradation and to initiate the procedure to estimate the SPF value with the PHDRS system, the extent of photostability of the test product must be evaluated using in vitro techniques on PMMA plates.

The in vitro sunscreen-treated plates (previously prepared and measured) were exposed to broad-spectrum UV radiation (UVB + UVA) where the exposure dose for each sunscreen was calculated as 1.2 J/cm<sup>2</sup> UVA times the PDRS UVA-PF<sub>0</sub> calculated from the unirradiated absorbance scan (as per ISO 24443 UVA testing methodology). Sunscreen absorbance on the plates was then measured after the prescribed UV dose had been delivered, and the calculated UVA-PF factors (pre-/post-UV) give a photostability factor

(PSF) that was used to scale the absorbance measurements at each wavelength 320–400.

$$A_{\lambda_{\text{postUV}}} = A_{\lambda_{\text{preUV}}} \times S \times \text{PSF}$$

## 2.5 | Spectrum hybridization and final calculations

Using the procedure described by Ruvolo<sup>9</sup>, the *in vitro* post-UV absorbance values from 290 to 340 are “concatenated” to the “post-UV” *in vitro* spectrum ( $A_{\lambda_{\text{postUV}}}$ ) (340–400 nm) to provide a final full spectrum of absorbance from 290 to 400 nm. This final resulting spectrum is then used to calculate the sunscreen SPF and UVA-PF using standard clinical solar simulator spectra with the CIE erythema action spectrum and the persistent pigment darkening (PPD) action spectrum (as per ISO 24443). These values were then compared against the *in vivo* clinical results for these sunscreens and correlations determined.

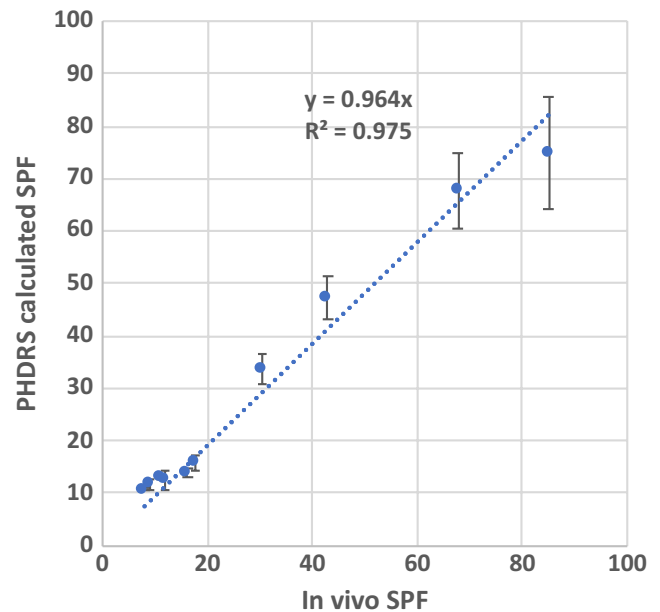
## 3 | RESULTS

SPF values and UVA-PF values, with standard errors (SE), were calculated for each of the sunscreen samples used in the test and are shown in Table 1 and Figures 3 and 4. The regression plot comparing the *in vivo* UVA-PF values (for the sunscreens with known *in vivo* UVA values) with the polychromatic HDRS device UVA-PF estimates is shown in Figure 4. Both graphs show high correlation of the PHDRS estimates with the *in vivo* clinically determined values of SPF and UVA-PF.

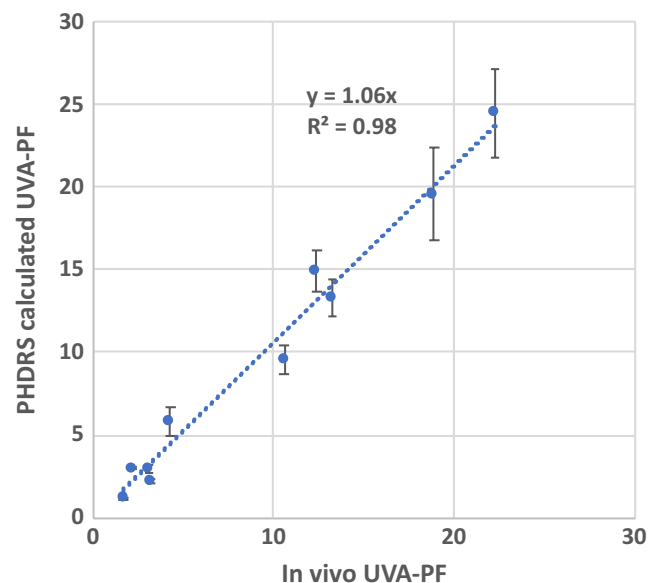
Both correlations have coefficient of determination of  $R^2 > 0.97$ , showing highly correlated values as predicted by the PDRS device.

## 4 | DISCUSSION

These data support the concept that a polychromatic spectral diffuse reflectance device can be a useful tool to evaluate sunscreen protectiveness throughout the UV spectrum when combined with a full-spectrum *in vitro* scan. With a much simpler optical and mechanical design compared with devices utilizing two monochromators, the device can be constructed at a significantly lower cost, and tests conducted in a shorter time frame versus a monochromatic device that has to scan the spectrum one wavelength at a time. By replicating the skin's *in vivo* spectral response spectrum with the filtered photocell, it can accurately estimate the UVA protectiveness of the applied sunscreen. Once a UVA-PF value is determined, it can be combined with the *in vitro* full-spectrum absorbance curve to scale it appropriately and estimate the SPF of the sunscreen. The high-end range of UVA-PF values the device design is currently capable of measuring is approximately 50, as a result of having a signal range of 2500 (approximately 3.5 OD) as the beam must traverse the sunscreen film twice. The variance appears to be similar to variability



**FIGURE 3** Correlation of SPF values determined clinically versus projected SPF values determined using polychromatic HDRS device [Colour figure can be viewed at [wileyonlinelibrary.com](http://wileyonlinelibrary.com)]



**FIGURE 4** Correlation of UVA-PF values determined clinically (or via ISO24443) versus projected UVA-PF value determined using polychromatic HDRS device [Colour figure can be viewed at [wileyonlinelibrary.com](http://wileyonlinelibrary.com)]

from standard SPF test and both may be inherently limited to the capabilities of evenness of sunscreen spreading on human skin.

## 5 | CONCLUSIONS

This device can provide a low cost and simple tool to rapidly assess sunscreen efficacy without having long and laborious, high dose *in*

vivo exposures to human subjects and provides a tool for evaluating sunscreen performance in a number of situations and conditions that were previously impossible to test. Best of all, no damaging UVB exposures are necessary to determine the SPF and the exposure to UVA is equivalent to less than a few seconds of sunlight exposure. The test can be conducted on all forms of sunscreen products, and the measurements are conducted on human skin, as the product is actually used.

## ACKNOWLEDGEMENTS

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