

ORIGINAL ARTICLE

Metal oxide sunscreens protect skin by absorption, not by reflection or scattering

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Key words:

absorption; anatase; band gap;
barium sulfate; protection;
reflection; rutile; scattering;
sunscreen; titanium dioxide;
ultraviolet radiation; zinc oxide

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Accepted for publication:

27 September 2015

Conflicts of interest:

None declared.

SUMMARY

Background/Purpose

The inorganic metal oxide sunscreens titanium dioxide and zinc oxide have been considered to protect against sunburning ultraviolet radiation by physically reflecting/scattering the incident photons and thus protecting the skin. Earlier publications suggested, however, that the primary action of UV protection by these sunscreen agents is through absorption and not by reflection. The purpose of this work was to quantitate the contributions of each of these modes of action to the protection provided by inorganic UV sunscreen filters.

Methods

An optical integrating sphere was used to measure the transmission and the reflectance of titanium dioxide and zinc oxide.

Results

The average range of reflection for zinc oxide and titanium dioxide throughout the UV range was only 4–5% (less than SPF 2), providing minimal UV protection via this mechanism. The remainder of the UV protection is provided by semiconductor band gap mediated absorbance of the UV photons. At wavelengths above the semiconductor band gap absorption energy levels (in the long UVA and visible wavelengths), they are predominantly reflectors of light (up to 60% reflection) and non-absorbing.

Conclusion

Titanium dioxide and zinc oxide provide UV protection primarily via absorption of UV radiation and not through significant reflection or scattering.

Photodermatol Photoimmunol Photomed 2016; 32: 5–10

Sunscreen products to protect the skin against sunburn were first developed in the 1940s and have evolved from simple 'glacier creams' to a wide variety of delivery forms with 16 to over 30 different UV filter 'actives' approved globally to provide protection against

incidental as well as prolonged intense sun exposure. These UV sun protection filter actives have been described by two classifications, 'chemical/organic' filters, that are typically either in liquid form, or readily dissolved into a liquid oil- or water-based medium, and

'physical/inorganic' filters that are insoluble particulates such as zinc oxide and titanium dioxide. The FDA 1978 Proposed Rule for Sunscreen Products describes titanium dioxide as 'a physical sunscreen'. *'It reflects and scatters UV and visible rays providing a barrier for sun-sensitive individuals... Titanium dioxide scatters both UV and visible light radiation (290–700 nm) rather than absorbing the rays... Titanium dioxide is recognized as an effective opaque chemical for use as a physical sunscreen because it scatters UV rays thereby preventing sunburn'* (1). Within that initial Proposed Rule was a specification (§352.3c) for a sunscreen with only titanium dioxide as the UV filtering active to be described as '*sunscreen opaque sunblock – an opaque sunscreen active that reflects or scatters all light in the UV and visible range at wavelengths from 290 to 777 nm and thereby prevents or minimizes suntan and sunburn*' (2). This definition for 'sunblock' was subsequently dropped in the 1999 Final Rule for Sunscreen Products primarily to recognize that the term 'sunblock' suggested total protection which was not appropriate for any sunscreen and also noting that micronized inorganic sunscreen filters did not function in this same way and also functioned via absorption based on a reference from Sayre *et al.* (3, 4). The concept that inorganic sunscreens function strictly via reflectance and scattering continues to persist in virtually every public descriptor of sunscreen actives.

Kollias (5) was first to recognize the absorptive properties of the inorganic filters noting the pronounced change in absorption properties just below 400 nm similar to those of semiconductor materials. This work was further expanded into the subsequent publication by Sayre and Kollias (4) showing the difference between absorptive semiconductor materials including TiO_2 and ZnO and non-absorptive scattering materials such as barium sulfate and talc. Kollias followed with a letter to the editor in Archives of Dermatology (6) recommending the use of 'non-soluble' and 'soluble' sunscreen filters instead of the misnomers 'physical' and 'chemical' categories so commonly used by medical professionals and industry scientists. The article shows clear evidence of the absorptive nature of these physical UV filters, but do not provide a full quantitative description on the magnitude of the absorptive versus the scattering and reflecting properties of the insoluble UV filters. The present study was conducted to provide these data and to emphasize yet again that the true function of these insoluble 'physical' or 'mineral' UV filters is in fact identical to that of the soluble 'chemical' UV filters.

MATERIALS AND METHODS

Optical measurements

A 6" diameter integrating sphere (Labsphere, Inc., Sutton, NH, USA) was used for measuring the reflectance and the transmittance of inorganic sunscreen actives. The integrating sphere had four-one-inch ports which were covered with a cap coated with the BaSO_4 inside the integrating sphere. The entrance ports, sample port, and detector ports were at $+/- 20^\circ$, 180° , and 270° . One entrance port ($+20^\circ$) was always closed with the coated cap. A xenon lamp light source guided by fiber optic was inserted into the other entrance port to illuminate the sample at the sample port. The distance between the fiber optic end and the sample port was optimized to reduce the influence of the presence of the light guide within the spherical integrator blocking reflected light. Optimal fiber position was determined to be the position of the fiber with the greatest signal-to-noise ratio, which was about 1 inch from the sample port. At this position, minimal light from the light source was reflected from the integrating sphere wall, and reflected light blocked by the light guide was minimized. A schematic of the measurement setup is shown in Fig. 1.

Reflectance and transmission spectra were measured using Model OL754 spectroradiometer (Optronics Laboratories, Inc., Orlando, Florida, FL, USA) fitted with an integrating sphere. Transmittance was measured by placing the spectroradiometer directly behind the sample port, and reflectance was measured by placing the spectroradiometer at the detector port of the integrating sphere, 90 degrees to the side and behind the test sample and sample port. The OL754 spectroradiometer was set to scan wavelength range of 250–800 nm with 1 nm increments. The scan setting was set at 0.5 s integration time and 0.5 s settling time per wavelength.

This optical measure design captures the total transmitted radiation, which includes forward scattered radiation. This forward scattered radiation would also enter the skin to cause sunburn and skin damage as if it had no interaction with the sunscreen filters. Only when the incident energy is reflected or 'back-scattered' by at least $90-180^\circ$, and thus does not enter the skin, is there protection provided by these inorganic filters in the sunscreen via this mechanism. We have chosen to directly measure the magnitude of this reflected or 'back-scattered' portion of the incident radiation as only this portion of radiation measures protection via 'reflecting and scattering'.

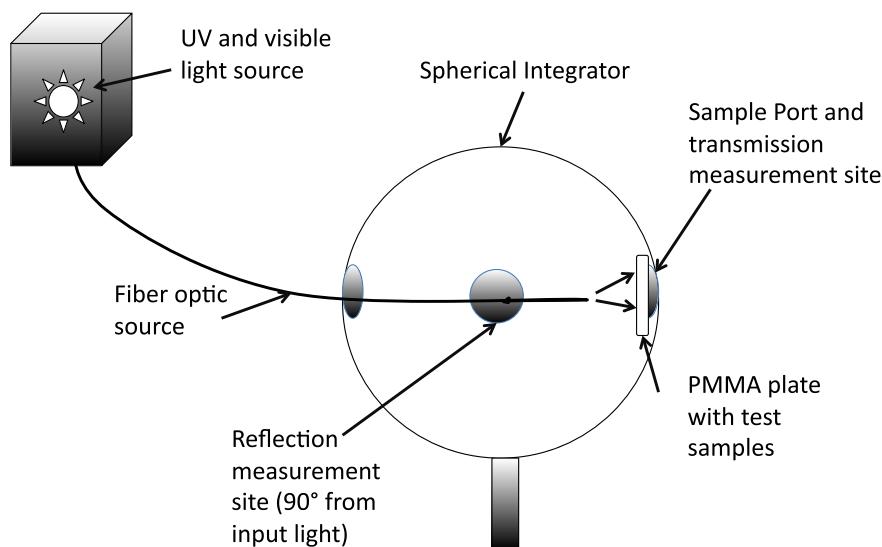


Fig. 1. Schematic of the optical sampling equipment for the measurement of reflection and transmission properties of the test samples.

Six Labsphere diffuse reflectance standards (Labsphere, Inc.) with reflectance of 2%, 5%, 10%, 20%, 60%, and 80% were placed on the sample port and measured. The values obtained closely matched the standard reflectance validating the optical layout for the integrating sphere measurements. Transmission and absorption measurements were also conducted using a Labsphere UV2000 Spectrophotometer instrument (Labsphere) which was designed specifically for thin film UV spectroscopic evaluation of sunscreen samples.

Test materials

Seven different ingredients were tested at 10% and 20% concentration suspended in petrolatum (Table 1) by heating the petrolatum until it melted, and dispersing the test materials in the liquid with light agitation, and cooling at room temperature as it solidified. These included two forms of pigmentary size titanium dioxide and a surface-treated nano-size titanium dioxide, a USP zinc oxide and a nano-sized zinc oxide, as well as barium sulfate.

Table 1. Sample ingredient information

	Active ingredient	Primary particle size	Coating	Target active concentration	Average specular reflection SCI-SCE 360–770 nm (%)
1	Anatase TiO ₂	<25 nm [†]	No	10%	2.88
				20%	3.49
3	Anatase TiO ₂	45 nm [†]	No	10%	3.91
				20%	4.26
5	Rutile TiO ₂	50 microns*	No	10%	3.39
				20%	3.08
7	USP ZnO	100–150 nm*	No	10%	4.05
				20%	2.84
9	Barium Sulfate	300 nm*	No	10%	4.11
				20%	3.26
11	TiO ₂ – MT-100TV	15 nm [†]	Al, Stearic Acid	10%	4.02
				20%	3.74
13	ZnO – Z-cote	67 nm [†]	No	10%	3.95
				20%	3.79

*Denotes particle size of the raw material based on scanning electron microscope measurements.

†Denotes particle size of the raw material based on vendor information. Specular reflectance of sample on the PMMA plate was measured using Minolta Spectrophotometer.

The sample plates were prepared by evenly applying 1.3 mg/cm² of the prepared petrolatum samples on 5 by 5 cm PMMA plates. This is the application density typically used in UV transmission spectroscopy for sunscreen absorption evaluations on the 'rough' surface of the PMMA plates and which approximates the optical properties of application of 2 mg/cm² on human skin (based on correlation of *in vitro* and *in vivo* sunscreen evaluations). The blank reference plate was prepared by applying 1.3 mg/cm² of the petrolatum vehicle on PMMA plate. The plates were allowed to equilibrate for at least 15 min before testing. The plates were then taped to the sample port within the integrating sphere for reflectance and transmittance measurement. Spectra were corrected for spectral non-uniformity of the integrating sphere surface reflection (Ba₂SO₄ coating).

RESULTS AND DISCUSSION

The transmission spectra for the various test materials confirmed the dramatic change in mode of action of the inorganic sunscreen materials that occur around the 400 nm region of the spectrum. The titanium dioxide samples showed a sharp transition from blocking transmission below 400 nm to significant transmission in the visible range (see Fig. 2). Transmission measurements have been transformed mathematically to an absorbance scale familiar to those working with sunscreen samples by the equation $A = -\log(I_s/I_o)$, where

I_s = (Intensity of input source through sunscreen treated plate), and I_o = (Intensity of the input source through placebo treated plate).

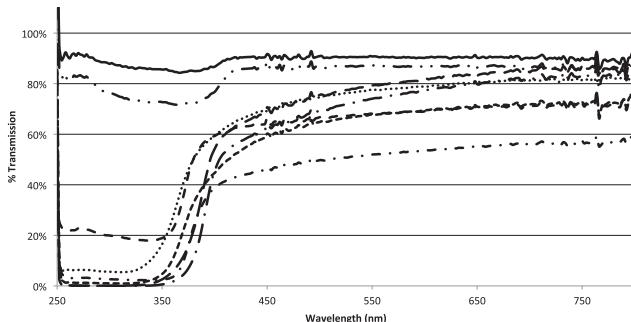


Fig. 2. Absorbance of titanium dioxide samples in thin film on PMMA plates as measured at the sample port. Anatase TiO₂ < 25 nm at 10%, ---- anatase TiO₂ < 25 nm at 20%, --- anatase TiO₂ 45 nm at 10%, - - - anatase TiO₂ 45 nm at 20%, — (solid) rutile TiO₂ 50 μ m at 10%, — - - rutile TiO₂ 50 μ m at 20%, — rutile TiO₂ 15 nm at 10%, — · rutile TiO₂ 15 nm at 20%. All titanium dioxide samples show little transmission below 350 nm range except for the large particle size Rutile TiO₂ samples.

The large particle size (50 micron) rutile titanium dioxide samples show the lowest efficiency in blocking UV radiation and highest transmission in the visible range. Titanium dioxide materials used in sunscreens have been optimized through the years to provide maximum UV absorption per unit of material by increasing the absorption cross section of the TiO₂ crystals by decreasing their particle size. These examples here show the dramatic difference between pigmentary size TiO₂ and the 'nano-' sized samples. The second purpose for micronization of the titanium dioxide samples is to minimize the reflectance and scattering function of these materials in the visible range that would otherwise make them appear colored or white on the skin.

Similarly, the zinc oxide samples show marked absorbance (Fig. 4) at wavelengths below 370 and very high transmissivity above these wavelengths (Fig. 5) with an even sharper transition point compared with the titanium dioxide samples (Figs 2 and 3). In contrast, the barium sulfate samples show only a monotonic change in transmission across the entire UV and visible spectrum, with no abrupt changes in these properties, and acting as a simple scatterer of incoming radiation (Figs 4 and 5).

Reflectance measurements made within the integrating sphere demonstrate the low level of total of reflectance and back scattering of the titanium dioxide and zinc oxide samples in the UV range, but with high levels of reflection in the visible wavelength ranges (Figs 6 and 7). Barium sulfate, however, shows low levels of reflectance due to its lower refractive index compared to titanium dioxide or zinc oxide and relatively larger particle size.

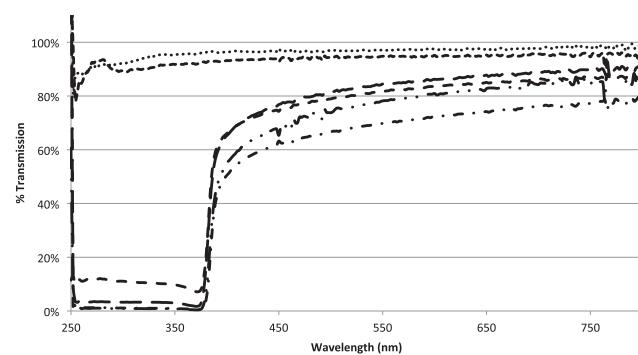


Fig. 3. Absorbance of titanium dioxide samples in thin film on PMMA plates as measured at the sample port. Anatase TiO₂ < 25 nm at 10%, ---- anatase TiO₂ < 25 nm at 20%, --- anatase TiO₂ 45 nm at 10%, - - - anatase TiO₂ 45 nm at 20%, — (solid) rutile TiO₂ 50 μ m at 10%, — - - rutile TiO₂ 50 μ m at 20%, — rutile TiO₂ 15 nm at 10%, — · rutile TiO₂ 15 nm at 20%. All titanium dioxide samples show high absorbance below 350 nm range except for the large particle size Rutile TiO₂ samples.

Similar observations have been reported (7) for titanium dioxide and zinc oxide in which the back-scattered radiation was calculated as a constant proportion of the forward scattered radiation, which in turn was measured by the difference of the spectral attenuation of incident radiation with, and without, a collecting spherical integrator after the test sample. Estimates of back-scattered radiation from TiO_2 were calculated to be 10%, and from ZnO were 15% of incident radiation in this study. Our direct measurements of this back-scattered radiation show a much lower proportion in the range of less than 5% in the UV range.

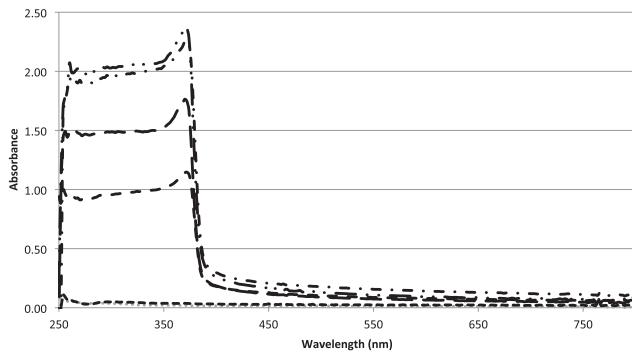


Fig. 4. % Transmission of zinc oxide and barium sulfate samples in thin film on PMMA plates as measured at the sample port. — — USP ZnO 150 nm at 10%, — · · · USP ZnO 150 nm at 20%, — — nano- ZnO 67 nm at 10%, — · · · nano- ZnO 67 nm at 20%, · · · · · barium sulfate at 10%, - - - - barium sulfate at 20%. All the ZnO samples show little transmission in the UV range with a sudden transition to transmission at wavelengths above 370 nm. In contrast, the barium sulfate shows consistent transmission across both the UV and visible ranges.

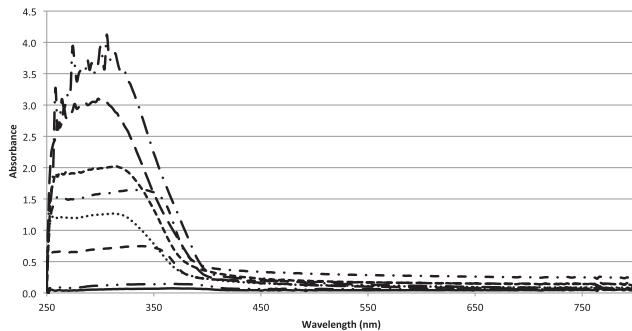


Fig. 5. % Absorbance of zinc oxide and barium sulfate samples in thin film on PMMA plates as measured at the sample port. — — USP ZnO 150 nm at 10%, — · · · USP ZnO 150 nm at 20%, — — nano- ZnO 67 nm at 10%, — · · · nano- ZnO 67 nm at 20%, · · · · · barium sulfate at 10%, - - - - barium sulfate at 20%. All the ZnO samples show significant absorbance below 370 nm, while barium sulfate shows little absorbance across the entire range.

The findings of this investigation in no way alter the usefulness of, nor require modifications to, approaches to formulating these ingredients in suncare products. Raw material manufacturers of the inorganic UV filters have modified these ingredients to provide optimal absorbance properties with minimal visual appearance (8). This has been performed primarily by changing particle size distributions (increasing the total absorption cross section) and diminishing large particle sizes that are more efficient in reflection. Surfaces of titanium dioxide and zinc oxide used in sunscreen preparations

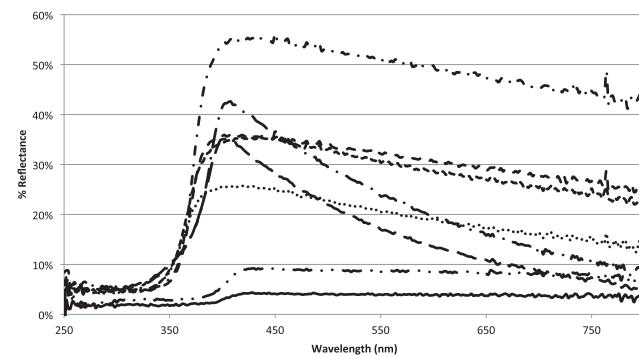


Fig. 6. Reflection spectra of titanium dioxide samples (as measured 90° from sample surface). Anatase TiO_2 <25 nm at 10%, ---- anatase TiO_2 <25 nm at 20%, -- - anatase TiO_2 45 nm at 10%, - - - anatase TiO_2 45 nm at 20%, — (solid) rutile TiO_2 50 μm at 10%, — · · · rutile TiO_2 50 μm at 20%, — — rutile TiO_2 15 nm at 10%, — · · · rutile TiO_2 15 nm at 20%. All the titanium samples show little reflected light from the surface of the sample in the low UV ranges, with high levels of reflectance above 350 nm.

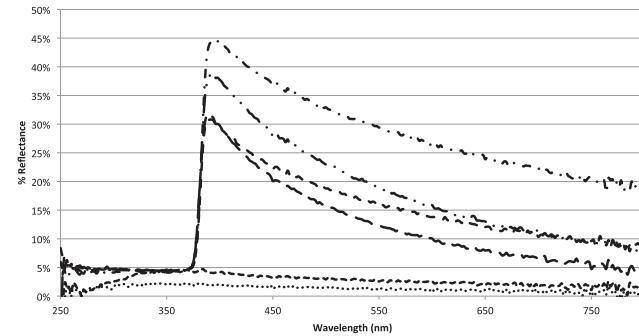


Fig. 7. Reflection spectra of zinc oxide and barium sulfate samples (as measured 90° from the sample surface. — — USP ZnO 150 nm at 10%, — · · · USP ZnO 150 nm at 20%, — — nano- ZnO 67 nm at 10%, — · · · nano- ZnO 67 nm at 20%, · · · · · barium sulfate at 10%, - - - - barium sulfate at 20%. The ZnO samples showed high reflectance above 370 nm and across the visible range, but virtually no reflectance of incident light below 370 nm. Barium sulfate reference material showed consistent (low) reflectivity across both UV and visible regions with no transition points.

are also coated with inert materials to eliminate surface reactivity and oxidation (9). These surface coatings also provide more pleasant tactile properties to the formulated products making them more likely to be applied properly and in sufficient quantity. Smijl and Pavel (9) have a thorough discussion of the semiconductor energy band gap behavior of titanium dioxide and zinc oxide showing the absorbance transitions are in complete agreement with transition wavelengths associated with the 3.1–3.3 eV band gap of these materials and also caution that prediction of the Mie scattering functions is limited for these materials as they are not spherical and are always agglomerated in use.

This study confirms and provides quantitative data relating to the mechanism of action of the inorganic sun-

screen filters. These data indicate clearly that these filters act primarily as UV-absorbing materials, and not as UV-scattering or UV-reflecting materials. The relative amount of UV reflection of titanium dioxide and zinc oxide in sunscreen preparations as measured in thin film is on the order of less than 5%, while reflecting much more efficiently in the visible portion of the spectrum on the order of 30–50% of incoming radiation. These materials reflect very little UV radiation as their energy is being almost completely absorbed by these materials in the UV wavelength range, and there is little remaining to be reflected. Independent of how these inorganic UV filters function, they provide an effective and alternate category of UV filters available for manufacturers and consumers to choose based on their personal choice.

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