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Photoprotective Ability of Colored Iron Oxides in Tinted Sunscreens against Ultraviolet, Visible Light and Near-Infrared Radiation

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Abstract

Solar-induced skin damage continues to pose a problem to human health worldwide, despite the widespread recommendation and use of sunscreens. We have previously reported that solar visible light and near-infrared also contribute to skin damage and photoageing. Most commonly recommended sunscreens are only effective throughout the UV spectrum, offering no protection from visible light and near-infrared. To evaluate the enhanced solar-spectrum blocking ability of iron oxides, a double-beam spectrophotometer was used to optically measure the transmission spectra. The spectrophotometer deploys a unique, single monochromatic design to detect wavelength penetration in the range of 240 to 2600 nm. The sample without iron oxide (control) blocked over 80% of ultraviolet-C and ultraviolet-B but did not block ultraviolet-A, visible light, or near-infrared wavelengths. The samples with yellow, and red iron oxide blocked over 90% ultraviolet, but did not block visible light and near-infrared effectively. The sample with black iron oxide blocked visible light, and near-infrared effectively compared with other samples with yellow, blue, and red iron oxide. The sample with red and black iron oxides, and the sample with yellow, blue, red, and black iron oxides blocked ultraviolet through to near-infrared. It can be concluded that dark colored iron oxide combinations are effective at blocking from ultraviolet through to visible light and near-infrared radiation. The results of this study may also suggest that biological colour of human skin and subcutaneous tissues are conserved for comprehensive photoprotection.

Keywords

Anti-Photoageing, Photoimmunosuppression, Photoprotection, Sunscreen, Ultraviolet, Visible Light, Near-Infrared

1. Introduction

Despite the considerable and growing evidence that visible light (VL) and near-infrared (NIR) are harmful to human skin, these wavelengths are not effectively blocked by photoprotective materials including sunscreens, eyewear, glass film treatments, umbrellas and wearable fibers [1]-[15]. VL has many documented deleterious effects on human skin and deeper tissues including hyperpigmentation, photodermatoses (solar urticaria, porphyrias, polymorphic light eruption etc.), erythema and inflammation [16].

NIR radiation is capable of penetrating skin and sclera, affecting deeper tissues that include muscles, lens and retina, resulting in varied and considerable biological effects [3] [4] [6]. Photoageing [1]-[7] [11], chronic vasodilation [9], skin sagging and ptosis [1] [2] [3] [4], photoimmunosuppression and photocarcinogenesis are all undesirable sequela related to VL and NIR exposure long term where innate biological photoprotection is inadequate [1]-[13] [17] [18].

In consideration of the facts that human skin is exposed to biologically active doses of electromagnetic spectral radiation [1]-[13] daily, and that most solar filtering materials do not attenuate VL and NIR, developing and deploying photoprotective materials against VL and NIR should be considered a high priority [1] [11] [14] [15] [19]. Sunscreens containing titanium dioxide (TiO_2) and zinc oxide (ZnO) help provide UV protection but provide limited protection against VL and NIR [20]. Topical formulations containing metallic oxides can provide additional photoprotection beyond UV to include VL and NIR [15]. For example, a recent study involving broad-spectrum sunscreens containing iron oxides improved melasma lesions and relapses [21] [22]. Iron oxides including red iron oxide (Fe_2O_3), yellow iron oxide ($Fe(OH)_3$/FeOOH), and black iron oxide (Fe_3O_4) effectively block high energy VL and NIR [23].

To clarify the complete solar-spectrum blocking ability of colored iron oxides contained in tinted sunscreens, a double-beam spectrophotometer was used to optically measure the transmission spectra from 240 to 2600 nm.

2. Materials and Methods

2.1. Sunscreen Evaluated

Seven variations of colored iron oxides contained in tinted sunscreens and control sample with no iron oxide were used in this study (**Table 1** and **Figure 1**).

2.2. Optical Evaluation of Sunscreens Using Transmission Spectra

Seven variations of colored iron oxides contained in tinted sunscreens and control sample wit A double-beam spectrophotometer covering wavelengths from 240 to 2600 nm was used to optically measure the transmission spectra. Each sunscreen sample was embedded in sapphire cuvette with a thickness of 0.1 mm and 0.2 mm, simulating practical use of human skin. The light emitted was detected by a photomultiplier tube.

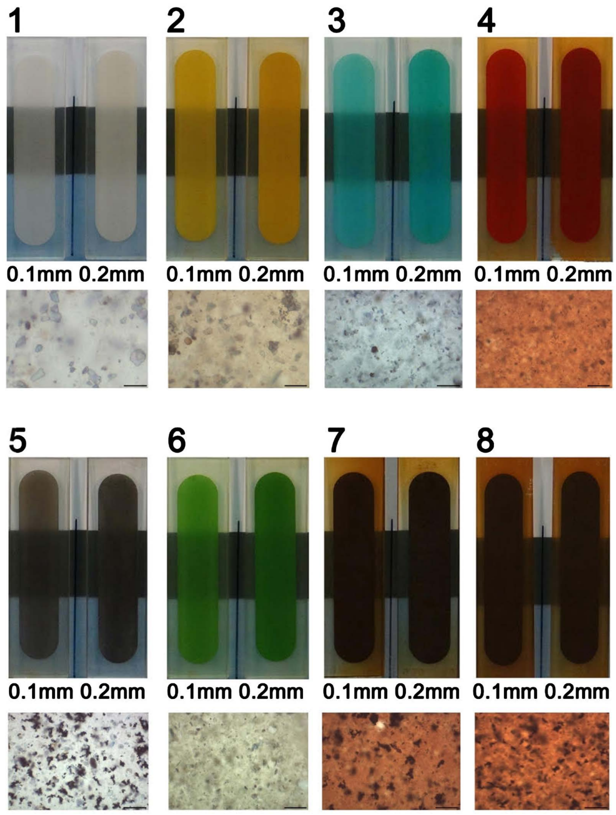

Figure 1. Sunscreen sample in sapphire cuvette with a thickness of 0.1 mm and 0.2 mm. Microscopic photos shown below each sample, scale bars = 1000 μm (magnification: ×40).

Table 1. Characteristics of colored iron oxides.

1) A control sample with no iron oxide
2) Modified sample with only yellow iron oxide
3) Modified sample with only blue iron oxide
4) Modified sample with only red iron oxide
5) Modified sample with only black iron oxide
6) Modified sample with yellow and blue iron oxides
7) Modified sample with red and black iron oxides
8) Modified sample with yellow, blue, red, and black, iron oxides

3. Results

Blocking abilities against UV-C (100 - 280 nm), UV-B (280 - 315 nm), UV-A (315 - 400 nm), VL (400 - 760 nm), and NIR of each sunscreen sample are shown in Table 2 (0.1 mm width) and Table 3 (0.2 mm width). The results of the transmission spectra of sunscreens are shown in Figure 2.

Samples containing iron oxide with a thickness of 0.1 mm and 0.2 mm blocked 82.5% - 99.1% of UV-C, 90.1% - 99.1% of UV-B, 67.0% - 99.9% of UV-A, 39.5% - 99.9% of VL, and 18.1% - 98.4% of NIR (Table 2 and Table 3).

The sample without iron oxide blocked UV-C and UV-B over 80%, but did not block UV-A, VL, and NIR sufficiently (Table 2 and Table 3). The samples with yellow, and red iron oxide blocked UV over 90%, but did not block VL and NIR sufficiently (Table 2 and Table 3). The sample with black iron oxide blocked VL, and NIR effectively, compared with other samples with yellow, blue, and red iron oxide (Table 2 and Table 3). The sample with red and black iron oxides, and the sample with yellow, blue, red, and black iron oxides (0.1 mm width) blocked almost over 80% of UV through to NIR (Table 2). The sample with red and black iron oxides (0.2 mm width) blocked almost over 90% of UV through to NIR (Table 3). The sample with yellow, blue, red, and black iron oxides (0.2 mm width) blocked almost over 95% of UV through to NIR effectively (Table 3).

Transmission spectra showed that yellow, blue, red, black colored iron oxide characteristically blocked 280 - 500 nm, 550 - 600 nm, 280 - 650 nm, 650 - 2600 nm, respectively (Figure 2).

Table 2. Blocking abilities of colored iron oxides (0.1 mm width).

	Blocking abilities				
	UV-C	UV-B	UV-A	VL	NIR
Sample without iron oxide	83.8% - 91.7%	91.3% - 91.8%	62.6% - 97.6%	37.2% - 60.4%	19.5% - 46.4%
Sample with yellow iron oxide	91.7% - 95.8%	95.4% - 96.0%	95.4% - 99.7%	50.2% - 99.6%	21.8% - 50.1%
Sample with blue iron oxide	82.5% - 90.5%	90.1% - 91.0%	67.0% - 96.9%	39.5% - 79.6%	21.3% - 48.4%
Sample with red iron oxide	94.4% - 97.2%	97.1% - 97.5%	97.1% - 99.8%	65.5% - 99.9%	27.7% - 65.4%
Sample with black iron oxide	88.2% - 94.6%	94.0% - 94.6%	81.9% - 98.3%	70.5% - 81.0%	64.1% - 76.8%
Sample with yellow and blue iron oxides	89.0% - 94.4%	93.8% - 94.4%	93.9% - 99.1%	44.9% - 99.1%	18.1% - 44.8%
Sample with red and black iron oxides	97.9% - 99.1%	98.9% - 99.1%	98.9% - 99.9%	90.6% - 99.9%	78.2% - 90.6%
Sample with yellow, blue, red, black iron oxides	93.6% - 96.9%	96.3% - 96.9%	96.4% - 99.7%	91.0% - 99.8%	79.9% - 91.0%

Table 3. Blocking abilities of colored iron oxides (0.2 mm width).

	Blocking abilities				
	UV-C	UV-B	UV-A	VL	NIR
Sample without iron oxide	80.9% - 90.3%	89.4% - 90.3%	81.6% - 98.3%	49.5% - 79.5%	28.0% - 66.6%
Sample with yellow iron oxide	90.6% - 95.5%	95.1% - 95.7%	95.1% - 99.7%	62.6% - 99.8%	31.6% - 67.1%
Sample with blue iron oxide	86.9% - 93.0%	92.6% - 93.4%	85.8% - 98.5%	51.1% - 93.7%	29.9% - 67.4%
Sample with red iron oxide	92.7% - 96.6%	96.5% - 96.9%	96.6% - 99.8%	77.2% - 99.9%	36.9% - 77.1%
Sample with black iron oxide	87.5% - 93.5%	93.6% - 93.9%	93.7% - 98.9%	86.1% - 94.0%	80.1% - 90.7%
Sample with yellow and blue iron oxides	93.2% - 96.6%	96.3% - 96.7%	96.5% - 99.5%	61.3% - 99.5%	34.2% - 68.5%
Sample with red and black iron oxides	92.9% - 96.8%	96.6% - 96.9%	96.5% - 99.8%	97.1% - 99.9%	91.1% - 97.1%
Sample with yellow, blue, red, black iron oxides	95.3% - 97.7%	97.3% - 97.8%	97.5% - 99.9%	98.4% - 99.9%	94.5% - 98.4%

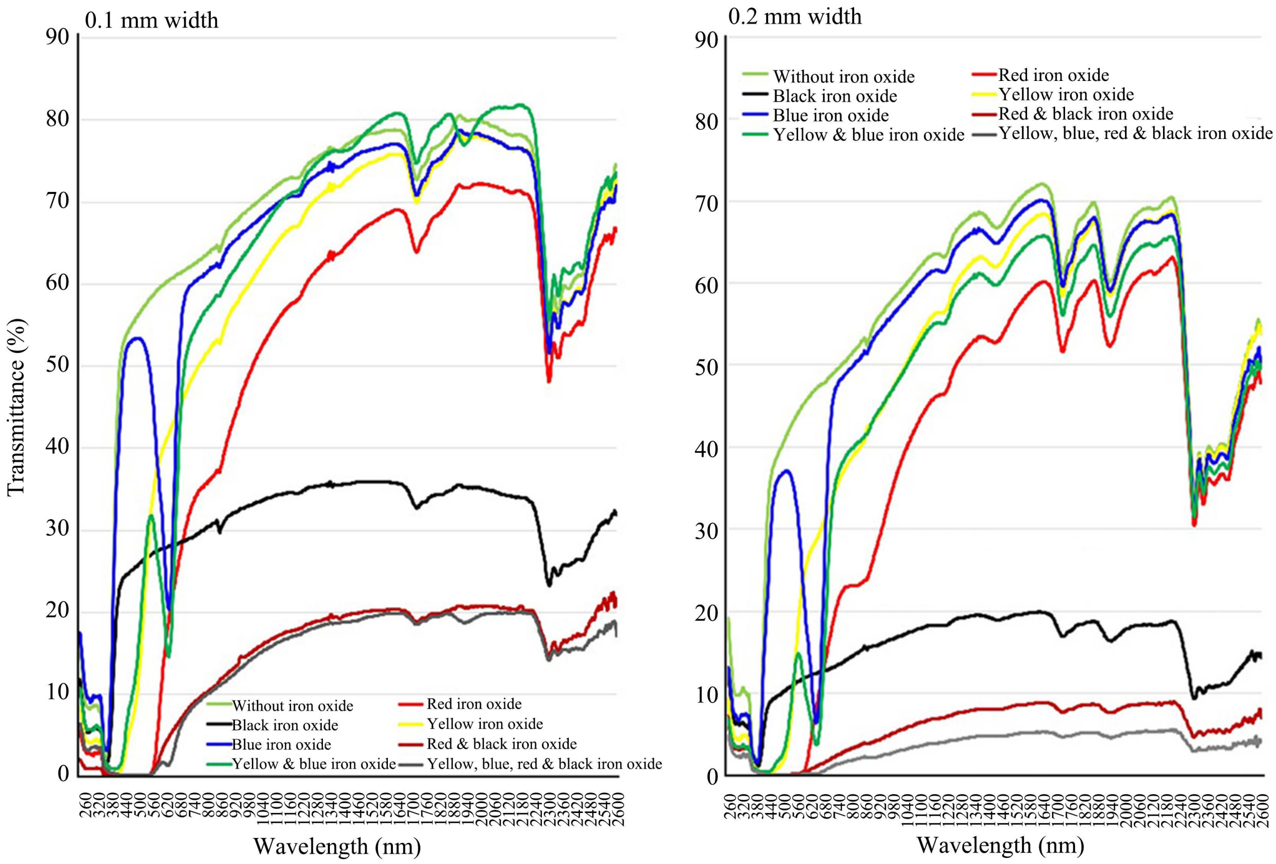

Figure 2. Optical evaluation of colored iron oxides using transmission spectra. The results of the samples with a thickness of 0.1 mm (left), and the samples with a thickness of 0.2 mm (right).

4. Discussion

Over 90% of incident solar radiation affecting the Earth consists of VL and NIR, and intensive or ongoing exposure to VL and NIR, when combined with UV, also contributes to photoageing, skin diseases, and skin cancers [11]. VL alone or in combination with NIR generates reactive oxygen species, increases collagen degradation, and leads to DNA damage [14] [24]. It must be noted that the global sunscreen industry has not embraced effective formulation technologies designed to filter VL and NIR [11] [13] [15]. As the biological effects of incident solar energy (UV, VL and NIR) are significant and due to the lack of sunscreens offering protection beyond UV, novel photoprotection from UV through to NIR is essential for preventing photoageing [11] [13] [15] [19].

Iron oxide, titanium oxide and various pigments provide protection against VL-induced pigmentaiton [25], for example, in one study, yellow iron oxide reduced VL-induced pigmentaiton [26]. Daily application of tinted sunscreens reduced the appearance of cutaneous hyperchromias [19], and tinted mineral sunscreens were proven more beneficial than nontinted sunscreens, since they protect against UV and VL [23].

In our prior study, we demonstrated that commercially available sunscreens blocked UV-C and UV-B sufficiently (approximately 99%). However, 8 out of 9 samples were not able to block over 99% of UVA, and did not effectively block VL and NIR, and this could potentially explain increasing levels solar-induced skin damage being reported despite the widespread prevalence of sunscreen usage [13].

In this study, to investigate the photoprotective ability of colored iron oxides contained in tinted sunscreens, a double-beam spectrophotometer was used to optically measure the transmission spectra.

All of samples containing iron oxide blocked over approximately 80% of UV-C and over 90% of UV-B. Regarding UV-A, all of samples containing iron oxide except blue iron oxide blocked over approximately 80% of UV-A. None of the single iron oxide color samples, with the exception of iron oxide red, effectively blocked VL. Similarly, none of the single iron oxide color samples, with the exception of iron oxide black effectively blocked NIR.

Combination color iron oxides samples containing red and black, and also yellow, blue, red, and black (0.1 mm, 0.2 mm width) blocked almost over 80%, 90% of UV through to NIR, respectively. Interestingly, with a thickness of 0.1 mm significant difference was not observed between combinations with red and black, and with yellow, blue, red, and black. In thicker layer samples (0.2 mm), significant differences were observed between these dark color combinations.

Importantly, each iron oxide has a different electromagnetic spectral attenuation profile. Transmission spectra showed that yellow, blue, red, black colored iron oxide characteristically blocked 280 - 500 nm, 550 - 600 nm, 280 - 650 nm, 650 - 2600 nm, respectively.

The combination of UV filters and pigments can protect the skin from solar radiation and reduce skin hyperpigmentation [19]. In our prior study, we demonstrated slight UV attenuation by saline imitating perspiration and by oil imitating sebum on the skin and almost complete impedance by human blood and skin structures [4]. Epidermal thickness and melanization are important protective mechanisms for UV-C and UV-B, whereas the attenuation of UV-A is primarily via melanin [27]. These results suggest that perspiration and/or sebum on the skin alone cannot sufficiently block most wavelengths of UV. However, human skin itself can mitigate UV as demonstrated in our study demonstrating that very thin skin (with a thicknesses of 0.25 mm) blocked over 99% of all UV wavelengths tested [4]. This is notable since the thinnest location of human skin regularly exposed to the sun is the eyelid (thickness, ≥0.5 mm).

VL was almost completely blocked by human skin, blood, adipose tissue, and muscle [4]. Wavelengths below 650 nm are absorbed by hemoglobin in the skin, which is analogous to the results seen with red iron oxide in this study, while wavelengths below 1100 nm are absorbed by melanin [28].

NIR was also only slightly attenuated by saline and lipids, and blocked (>70%) by skin, blood, adipose tissue, and muscle. NIR wavelengths between 1400 and 1500 nm are absorbed by hemoglobin and water in the skin, while wavelengths above 1850 nm are absorbed by water therein [28]. Absorption peaks in water transmission spectra are related to the O-H bond in water molecules [29], with the NIR spectrum of biological materials basically attributable to overtones and combinations of O-H, C-H, and N-H bond stretching [30]. The various bonds that form a bioplastic matrix, O-H, C-O absorb infrared radiation [31]. Since water and fatty acids are the major components of skin and consist of O-H and C-H intramolecular bonds, these molecules are the major NIR-absorbing materials in soft tissues [29]. Thin skin likely allows deeper penetration of UV, VL, and NIR, allowing deeper tissue damage as opposed to thicker skin [4].

UV, VL, and NIR will induce vasodilation to protect subcutaneous tissues, and for fair skin blood also acts an effective sunscreen. Rosacea can be induced by NIR exposure and is more common in Caucasians and fair-skinned populations [32]. Degeneration of myoglobin and apoptosis of vascular smooth muscle cells induced by NIR results in sustained vasodilation [9], which protects against NIR exposure by increasing water and hemoglobin retention [9]. The blocking ability of adipose tissue was much higher than those of lipids, even though both contain fatty acids. However, adipose tissue also contains blood vessels, which may play an important role in enhancing the blocking ability of this tissue [4].

Fair skin tends to wrinkle and sag earlier in life [33] [34], and characteristic age-related skin changes occur at a more accelerated rate in fair skin people [35]. Dark skin individuals will photoage slower compared to fair skinned people. These results reinforce that our biological skin colour and colour of subcutaneous tissues are conserved for comprehensive photoprotection.

It is theorized that these photoprotective effects of these endogenous biological pigments can be approximated by red, yellow, blue and black iron oxides. Since samples evaluated in this study with a thickness of 0.1 mm and 0.2 mm appear to be quite thick compared with consumer application dosage of sunscreens, and to be very dark for consumer with fair skin, further investigation and invention are required to achieve comprehensive and cosmetically elegant photoprotection.

It should be noted that this was a preliminary study based on a relatively small number of colored iron oxide combinations. Further studies are needed in larger numbers, including various types and concentrations of metals and ingredients for sunscreens and in investigation of biological effects of VL and NIR.

5. Conclusion

Dark colored iron oxide combinations are effective at blocking UV, VL and NIR radiation. The results of this study reinforce that our biological colour of the skin and subcutaneous tissues are conserved for comprehensive photoprotection, and that while current sunscreens provide adequate UV protection, further development should continue to extend sunscreen photoprotection to include VL and NIR for comprehensive skin protection from solar damage.

Disclosure

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Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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