Broad-spectrum solar protection (UV-Vis-IR) with non-nanometric zinc oxide filters

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Abstract (Maximum of 200 words)

Sunlight may have not only beneficial but also detrimental effects on our health (erythema, photo-ageing, pigmentation or serious disorders). Skin protection from ultraviolet (UVB, UVA), visible (VIS) and infrared (IR) radiation is recommended. Sunscreens and daily care cosmetic products may combine UV filters and other actives or antioxidants to protect and prevent from solar radiation effects. Mineral sunscreens are preferred for environmental protection and recognized as safe and effective. In this scenario, we present new zinc oxide filters which provide high protection against UVB (SPF) and UVA radiation. In addition, they can absorb Vis and IR radiation when including iron oxides in their composition. Antioxidant properties have been demonstrated for these zinc oxide filters and improved thanks to the combination with niacinamide or argan extract. These filters are manufactured with a patented technology that achieves non-nanometric filters and superior performance. An optimized combination of technology, ingredients selection and particles size are the key. As far as we know, this is the first time that this combination of properties has been presented in a single ingredient.

Keywords: Solar protection Zinc oxide UV filter color antioxidant

Introduction.

The harmful solar radiation effects on health depends on its components' wavelength and energy: The UVB radiation (290-320nm) acts mainly on the epidermis where it causes erythema (it is the most energetic radiation). The UVA radiation (320-400nm) passes through the dermis and is responsible for photo-ageing and pigment darkening. Both UV radiations induce delayed tanning and are associated with cellular damage, through direct or indirect DNA damage, and thus with potential risk of skin cancer. Visible light, Vis (380-700nm) and IR radiation (700nm-1mm) reach the hypodermis (the subcutaneous tissue). Visible light can induce pigmentation, especially in skin types IV–VI [1], darker and more sustained than pigmentation induced by UVA light. [2] The severity of photo-induced pigmentary disorders, such as melasma or post inflammatory hyperpigmentation may be related to the exposure to Vis radiation that also can induce reactive oxygen species (ROS) generation. Blue light, BL, or High Energy Visible, HEV (380-500nm) has been related to DNA damage, cell and tissue injury, eye and skin barrier damage, and photoaging.[3] IR-A radiation (700-1400nm) may damage skin collagen by ROS radicals' generation and by increasing the Matrix Metalloproteinases MMP-1 and MMP-9 activity that results in cleavage of fibrillar collagen and impairs the structural integrity of the dermis thus inducing premature skin aging. [4] UV, Vis and IR have all been reported to generate ROS, through different mechanisms, while in combination, an increased ROS generation in primary fibroblasts has been observed. [5] Multiple studies demonstrate the need to protect the skin from all the components of the sun's spectrum. In a context of growing concern for environmental protection, mineral sunscreens are recommended. Zinc oxide and titanium dioxide are UV filters globally-approved and generally recognized as safe and effective (GRASE I) by the FDA. They are typically used in the form of TiO2 nanoparticles for UVB protection or ZnO for UVA protection.

Iron oxides can be incorporated to get tinted sunscreen that may suppress Vis light induced pigmentation and better prevent relapses of melasma patients [6,7] We have previously

reported that the combination of titanium dioxide and iron oxides allow for non-nanometric mineral filters and pigments with unusual protective properties from UV-Vis-IR radiation [8]

Moreover, other ingredients can be added to formulations to minimize UV-induced oxidative damage and mitigate skin photoaging through mechanisms such as reduction in erythema, sunburn cell development, and immunosuppression.[9] Polyphenols, niacinamide, ascorbic acid, ferulic acid or tocopherol are antioxidant that can be found in sunscreens due to these properties.

It is a well-known challenge in the state of the art to select an appropriate combination of mineral filters to obtain high protection and pleasant sensory characteristics. In this scenario, we would like to present new zinc oxide filters that provide high protection against UVB (SPF) and UVA radiation. In addition, Vis and IR radiation blocking properties or even antioxidant action have been demonstrated.

Materials and Methods.

The samples studied were zinc oxide mineral filters (composition or INCI in brackets): UZ (Zinc Oxide), UZL/UZM/UZW (Zinc Oxide, CI-77492, CI-77491, CI-77499), UZnia (Zinc Oxide, niacinamide), Uzar (Zinc Oxide, Argania Spinosa Leaf Extract)

Proprietary technology has been used for zinc oxide filters fabrication.

Inductively Coupled Plasma Optical Emission spectroscopy (ICP-OES) was used to determine samples composition, expressed as oxides content.

The absorbance curves of powders we obtained with Shimadzu UV-2600i UV-Vis spectrophotometer (200-1200nm: UV, Vis and IR). Particle size distribution is analyzed by Laser Diffraction technique with a Malvern Mastersizer 2000 Instrument, equipped with the solids measurement accessory (Scirocco). The intensity of light scattered is measured as a laser beam passes through a dispersed particulate sample.

The effectiveness of the products in sun protection has been evaluated through the manufacture of sun creams with the filters and subsequent in vitro and in vivo analyses. Results of in vitro SPF, UVA or UVA/ UVB ratio and critical wavelength were obtained with the SPF 290-AS from Solar Light (290-400nm region). 1.3 mg/cm2 of sunscreen were spread on PMMA plate of controlled roughness (Schönberg). In vivo SPF was determined according to ISO 24444:2019/Amd.1:2022 standard (3-6 volunteers).

Antioxidant activity was determined by anti-inflammatory efficacy study in irradiated human skin explants. Human organotypic skin explant cultures (hOSEC) were used. Distress mimicking skin inflammation was induced by daily solar-like irradiation (5 J/cm2) of skin explants for 2 days. Prior to irradiation hOSEC are topically treated with sunscreens containing 17wt% of filter concentration (2 mg/cm2). The photo-protective efficacy of the test items applied topically on hOSEC was determined by measuring pro-inflammatory cytokines (IL-6 and IL-8) by ELISA essay.

Results.

ICP showed the UZ sample is only composed by zinc oxide. Samples UZL, UZM and UZW are composed by zinc oxide and iron oxides, being UZL the sample with lower iron oxides content and UZW the sample with higher iron oxides content. UZnia contains more important antioxidant concentration than UZar.

TABLE I. Composition determined by ICP-OES.

Sample	UZ	UZL	UZM	UZW	UZnia	UZar
ZnO%	98-100	95-99	93-97	88-92	72-77	95-99
Fe_2O_3 %	0	1-5	3-7	8-12	0	0

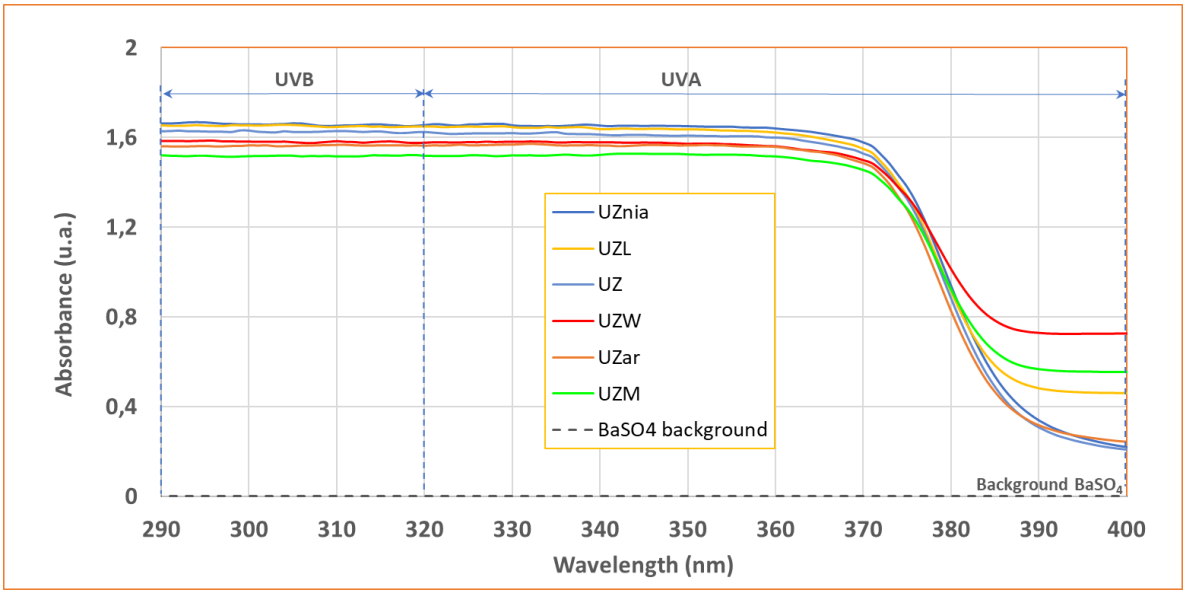
Similar particle size was observed for all the samples, at around 1-3 µm, thanks to the accessory that maximize the agglomerates breakage.

TABLE 2 Particle size determined by Laser Diffraction, expressed as D50.

Sample	UZ	UZL	UZM	UZW	UZnia	UZar
D50 (µm)	1.9	1.8	2.1	2.2	1.2	1.1

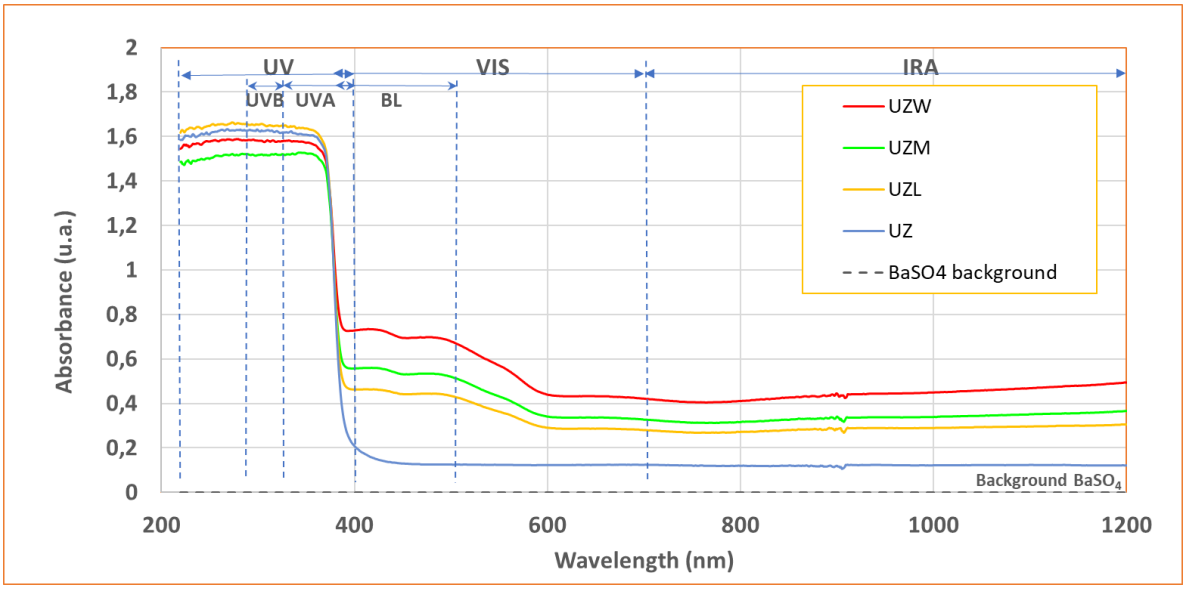
The absorbance curves at increasing wavelength (graph 1) confirm important UVB and UVA radiation protection (wavelength 290-320 and 320-400nm respectively) for all the filters.

GRAPH 1 Absorbance curves of Zinc oxide filters.



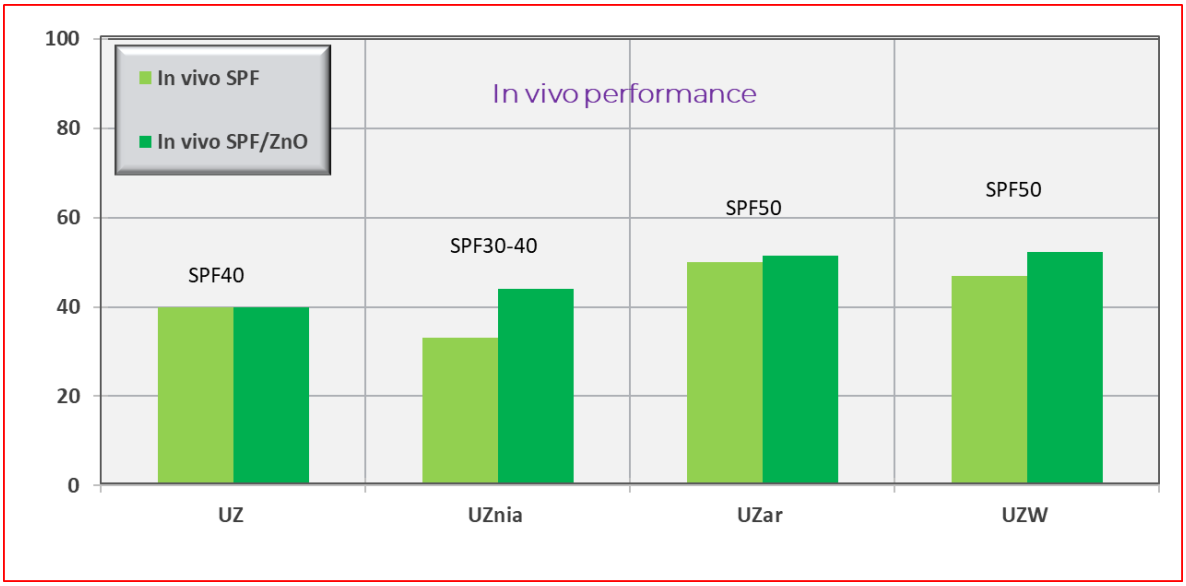
Differences are mainly observed from 400nm to 1200nm, the Vis and IR areas (graph 1): Filters containing iron oxide showed important absorbance of Vis radiation (380-700nm) mainly BL radiation (380-500nm) and also remarkable IR-A absorbance (from 700nm).

GRAPH 2 Absorbance curves of Zinc oxide-color filters (UZL, UZM, UZW) compared to UZ.



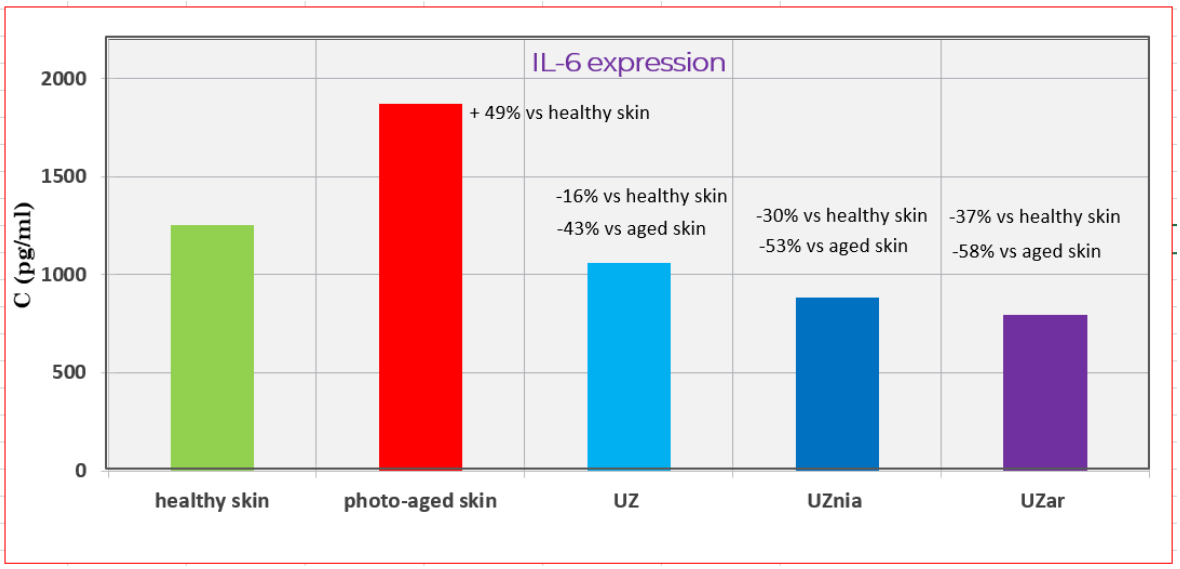
The zinc oxides filters incorporated in standard O/W or W/O sunscreen formulations (UZ, UZnia, UZar 17wt% or UZW or 15wt%, respectively) showed in vivo SPF30-50 results.

GRAPH 3 Zinc oxide filters in vivo performance and results related to ZnO concentration.

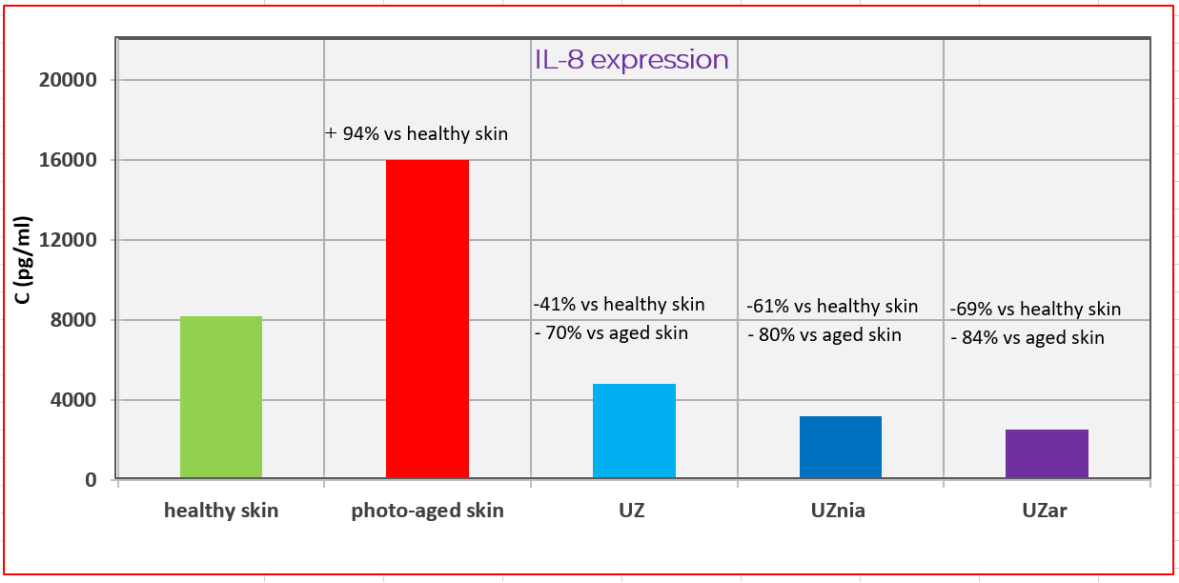


Anti-inflammatory activity of the zinc oxides filters (incorporated in standard O/W formulation) was determined by the study of IL- 6 and IL-8 expression. Both IL-6 (graph 4) and IL-8 (graph 5) are reduced with respect to the photo-aged skin by UZ filters.

GRAPH 4 IL-6 secretion of healthy skin, photo-aged skin or irradiated and treated with UZ, UZnia or UZar filters.



GRAPH 5 IL-8 secretion of healthy skin, photo-aged skin or irradiated and treated with UZ, UZnia or UZar filters.



Discussion.

Non-nanometric sized powder products have been developed with a proprietary technology that allows obtaining non-nanometric particle size composites. These products are mainly

composed by zinc oxide and may contain iron oxides (CI-77492, CI-77491, CI-77499) that confer color or antioxidants (niacinamide or argania spinosa extract).

The absorbance curves showed important UVB and UVA protection potential for all zinc oxide filters. Besides, visible light (from 380 to 700nm) and IR radiation protection (from 700nm) may be achieved when iron oxides are included in the composition, increasing with its concentration. The absorption of blue light, BL (380-500nm), is especially remarkable and proportionally increases with the iron oxides content of the filter (graph 1). It is though that the absorbance will continue to rise for the filter UZW that contain the highest iron oxide concentration in their composition thus protecting from IR radiation with higher wavelength.

In vitro and in vivo SPF results up to 30-50 were achieved with standard W/O and O/W sunscreens compositions, with all the combinations: zinc oxide, iron oxides and niacinamide or argan. It is well known that increasing the filter concentration higher protection can be achieved. In vivo SPF results are thus related to ZnO concentration in formula and ZnO content in the filter as seen in graph 3 for UZnia, UZar and UZW.

Anti-inflammatory activity was demonstrated with the filters containing zinc oxide, zinc oxide-niacinamide, zinc oxide-argania spinosa extract by reducing IL-6 and IL-8 expression (44-58% and 69-84%, respectively, *vs.* photo-aged skin). Interesting results were also observed in comparison with non-irradiated (healthy) skin because all the filters showed lower secretion of pro-inflammatory cytokines.

Conclusion.

Non-nanometric sized zinc oxide filters have been developed with a proprietary technology that allows remarkable performance in sun protection. These filters may contain iron oxides (CI-77492, CI-77491, CI-77499) that confer color or antioxidants (niacinamide or argania spinosa extract). In vitro and in vivo SPF results up to 30-50 were achieved with several sunscreens compositions, depending of filter composition and concentration in formula. UVA radiation

protection was also confirmed for all of them and Vis-IR radiation absorbance may be achieved with the filters containing iron oxides. Anti-inflammatory activity demonstrated vs. photo-aged skin with the filters containing zinc oxide, zinc oxide- niacinamide, zinc oxide-argania spinosa extract lead to conclude that the filters have a preventive action on solar-induced inflammation. Anti-inflammatory activity demonstrated vs. non irradiated skin showed these products may be also used to skin. As far as we know, zinc oxide-based filters with such complete protection properties have not been reported before.

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Conflict of Interest Statement.

NONE.

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