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Photoacoustic study of the photostability of sunscreens

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Abstract. Although solar radiation is essential for maintenance of life in Earth, excessive exposition to the ultraviolet radiation emitted by the sun may cause sunburns, early aging and even cancer lesions. Sunscreens act absorbing or reflecting ultraviolet radiation; in this way, they protect the skin against the damages caused by excessive absorption of ultraviolet radiation. Sunscreens must present photostability, that is the capacity of a product to be retained in skin without degradation by light incidence. The present study aimed to evaluate, through photoacoustic spectroscopy (PAS) measurements, the photostability of a sunscreen commercially available in Brazil. PAS measurements were performed at 19 Hz, for wavelengths between 270 nm and 400 nm, using a sunscreen with solar protection factor (SPF) 15 applied in skin samples. Photoacoustic spectra of the sunscreen applied to the skin were obtained and analyzed as a function of time after application. Photostability was then evaluated by the comparative study of the integrated areas of the absorption curves for the sunscreen applied to the skin. Results indicate that the sunscreen analyzed was photostable for a large period and was not completely removed by cleaning.

1 Introduction

The ultraviolet (UV) radiation emitted by the sun has positive effects for human skin, as the production of the D vitamin, which prevents rachitism in children and osteoporosis in adults. However, excessive exposition to UV radiation may cause sunburns, skin aging and even cancer lesions in skin [1]. The skin acts as a natural barrier against UV penetration. UV spectra is divided in three regions, according to the wavelength and the biological effects produced: UVC, from 100 nm to 290 nm, is basically absorbed by the ozone layer; UVB (290 nm to 320 nm) reaches epidermis, generating erithema; and UVA (320 nm to 400 nm) reaches deeper skin layers and generates photoaging effects [2].

Sunscreens are products employed to protect skin against the damage caused by UV radiation, being composed by chemical agents that absorb radiation and physical agents that dissipate it by reflection. A sunscreen must present photostability (ability to remain in the epidermal layer without degradation); furthermore, it must be retained in the epidermis, since reaching deeper skin layers could lead to systemic absorption of the product, with deleterious effects [3].

The US Food and Drug Administration (FDA) does not have a standard way of assessing photostability; photostability testing is not required. Also, there is no standard method for

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measuring UVA protection of sunscreen [4]. However, the study of these aspects is required, since they present potentially important consequences to public health. Even in newly developed sunscreens, not all UV filters are sufficiently photostable [5]. The aim of this work was to employ photoacoustic (PA) measurements to evaluate the photostability of a commercially available sunscreen applied to skin.

2 Methodology

The experimental setup utilized in this study is described elsewhere [6,7] and employed a mechanical chopper (EG&G, model 167), a closed PA cell with B&K microphone, a lock-in (PAR-EG&G, model 5210) and a microcomputer for data acquisition. A Xenon lamp (Oriel, model 77250, 1000 W) was employed as light source for spectroscopic measurements; this lamp presents an UV irradiation spectrum very similar to that of the sun, with effective emission in the UVB-UVA region (270–400 nm; actually, shorter wavelengths emitted by the sun are blocked by the ozone layer of the Earth's atmosphere). The experimental system presented a total UV irradiation of about $25\,\mathrm{W/m^2}$; this matches the spectrum of the sun at noon, in a clear summer day and at intermediate latitudes [8,9]. All photoacoustic spectroscopic (PAS) measurements were normalized to the lamp spectrum.

PAS measurements were performed at 19 Hz, for wavelengths between 270 nm and 400 nm, using a sunscreen with solar protection factor (SPF) 15 applied in skin samples ($1\,\mathrm{cm^2}$) obtained from abdominoplasty at the Policlin Hospital from São José dos Campos, Brazil. Skin samples were conserved in physiological serum (0.9%) at low temperature (between 275K and 277 K) for no more than 48 h and, after utilization, they were discarded at the Policlin Hospital. The sunscreen employed was approved by ANVISA, which regulates the commercialization of drugs and cosmetics in Brazil [10]. Sunscreen was homogeneously applied in skin samples following the FDA recommendation ($2\,\mu\mathrm{L/cm^2}$) [11]. After initial PAS measurements of the isolated sunscreen and skin samples, the PA spectra of the system sunscreen+skin were measured and analyzed as a function of time after sunscreen application, with the samples receiving UV irradiation from the light source in the time intervals between successive measurements. The ratio of the irradiation time to the measurement time was 9:1 (27 minutes of irradiation, followed by 3 minutes of measurements, corresponding to intervals of 30 minutes between the beginning of successive measurements).

Four hours after application, the skin sample was cleaned with absorbing paper and the PA spectrum of the cleaned skin was then obtained.

3 Results and discussion

Absorption curves were initially obtained for the isolated skin samples (with an absorption band in the 280 nm region) and also for the isolated sunscreen, that presented high absorption in the UVB region and a decreasing level of absorption for wavelengths above 360 nm (Figure 1), showing a more effective protection against UVB radiation, responsible for the occurrence of erithema. Figure 1 also presents the absorption curve of the system sunscreen+skin. Analysis of the results obtained must consider that UVB radiation is highly absorbed by epidermal constituents (mainly melanin), which avoids its penetration in the dermal layer; on the other side, UVA radiation is most likely to reach the dermal layer, being absorbed by melanocytes and possibly generating melanoma precursors [2]. This is why most modern sunscreens include UVA absorbers, even if such substances are not required for SPF determination tests. For the sunscreen under study, the critical wavelength (defined as the wavelength at which the absorption level falls to 50% of the maximum value) is of about 380nm for the isolated sunscreen and about 360 nm for the sunscreen *in situ*. The American Academy of Dermatology recommends that sunscreens with broad-spectrum label should have a critical wavelength of more than 370 nm [5]. The absorption curves (N = 3) of the system sunscreen+skin were then obtained

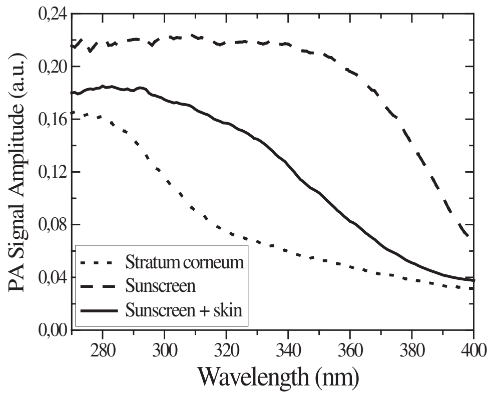

Fig. 1. Absorption spectra of skin (stratum corneum) and sunscreen.

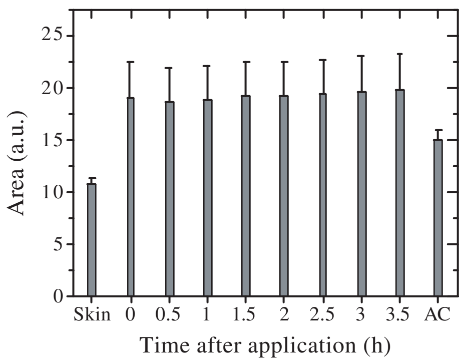

Fig. 2. Area under the absorption curves as a function of time after sunscreen application (average for N = 3; error bars indicate standard error; AC: skin after cleaning).

for different times after sunscreen application (in 30 min intervals), and photostability was evaluated through the area below the absorption curve, which remained essentially constant up to 3.5 h after application, showing good photostability for the product under analysis (Figure 2).

After cleaning the skin samples with absorbing paper, the area below the absorption curve falls significantly, and the new absorption curve obtained (Figure 3) resembles that of the skin alone, but the higher amplitude indicates that sunscreen removal was not complete.

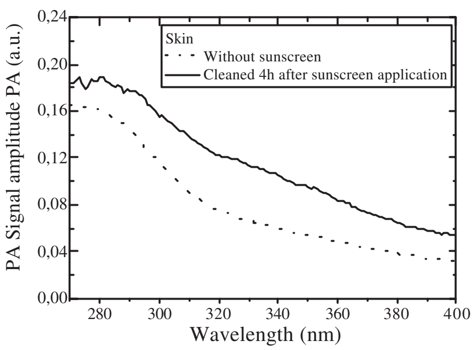

Fig. 3. Absorption spectra for the skin before sunscreen application and for the sunscreen+skin system after cleaning.

Many factors affect the performance of a sunscreen; the amount of sunscreen is the most important factor, since people generally apply a lower quantity than that employed in standard tests [12]. Other factors that affect photostability include: water immersion; sunscreen vehicle, skin oil content and environmental factors (wind, humidity etc). Our results showed photostability in the sunscreen+skin system, but samples were kept in a closed PA cell, thus being isolated from environmental factors. This was confirmed by additional measurements (data not shown) using another experimental setup, with a tungsten lamp as light source (irradiation of about 100 W/m^2, with effective emission in the UVA/visible region). The fact that the sunscreen was only partially removed by cleaning suggests that there may have been penetration/incorporation of the product into the corneum layer, as reported by another recent study [13].

4 Conclusion

The results obtained indicate that the sunscreen evaluated presents good photostability, when applied in the concentration recommended by the FDA. However, the influence of environmental factors in photostability remains to be investigated in the future, preferentially through *in vivo* measurements.

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