SUNSCREEN EFFECTS IN SKIN ANALYZED BY PHOTOACOUSTIC SPECTROSCOPY

Fernanda Henrique dos Anjos[a], Paula Cristina Bueno Rompe[a], Roberta R. Batista[a], Airton Martin[b], Antônio M. Mansanares[c], Edson C. da Silva[c], Daniel Acosta-Avalos[a], Paulo Roxo Barja[*a]

[a] Universidade do Vale do Paraíba (UNIVAP), Research and Development Institute (IP&D II), Laboratory of Photoacoustics Applied to Biological Systems (FASBio), Av. Shishima Hifumi 2911, São José dos Campos, SP Brazil 12244-000;

[b] Universidade do Vale do Paraíba (UNIVAP), Research and Development Institute (IP&D II), Laboratory of Raman Spectroscopy, Av. Shishima Hifumi 2911, São José dos Campos, SP, Brazil 12244-000;

[c] Universidade Estadual de Campinas (UNICAMP), Instituto de Física Gleb Wataghin (IFGW), Cidade Universitária Zeferino Vaz, Campinas, SP, Brasil 13083-970

ABSTRACT

In the photoacoustic technique, the signal is proportional to the heat produced in a sample as a consequence of modulated light absorption. This technique allows the spectroscopic characterization of multilayer systems: as the thermal diffusion length varies with the light modulation frequency, one can obtain the depth profile of the sample by analyzing the frequency-dependence of the signal. As the photoacoustic signal depends on thermal and optical properties of the sample, structural changes in the system under analysis account for signal variations in time. In this work, photoacoustic spectroscopy was used to characterize samples of sunscreen and the system formed by sunscreen plus skin. Measurements used a 1000W Xe arc lamp as light source, for wavelengths between 240nm and 400nm. This range corresponds to most of the UV radiation that reaches Earth. Skin samples were disks of about 0,5cm diameter. The absorption spectrum of sunscreen was obtained. Finally, photoacoustics was employed to monitor the absorption kinetics of the sunscreen applied to skin samples. This was done by applying sunscreen in a skin sample and recording the photoacoustic spectra in regular time intervals, up to 90 minutes after application. According to measurements, light absorption by the sunscreen plus skin system stabilizes between 25 and 45 minutes after sunscreen application. Results show that this technique can be utilized to monitor drug delivery and farmacokinetics in skin samples.

Keywords: Photoacoustic spectroscopy, skin, sunscreen

1. INTRODUCTION

The photoacoustic effect was discovered by Alexander Graham Bell in 1880, when he noticed that the incidence of modulated sunlight in a solid diaphragm surface produced sound as a result. Observing this effect, Bell showed that the acoustic signal intensity was influenced by the light absorption coefficient of the sample [1].

The photoacoustic technique constitutes an experimental option with many applications in the study of optical properties as absorption and transmission of electromagnetic radiation. Many biological materials subjected to studies, as biological membranes, bone samples or tissue structures are hardly soluble and, biologically, they present the function of a solid

[*] barja@univap.br

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matrix. Such materials are difficult to study by conventional techniques, because they are significantly changed when solubilized. Photoacoustic spectroscopy allows the analysis of the correspondent intact biological tissues, becoming an important research and diagnosis tool in (bio)medicine and biology [2].

Photoacoustic methods find good perspectives of utilization in the study of biological systems, because this technique can be used to analyze optical properties of samples that are not amenable because of the excessive light scattering, or in completely opaque samples [2]. One of the most important possibilities of the photoacoustic technique is to perform a bulk analysis of opaque samples. Photoacoustics is a non-destructive method which gives qualitative and quantitative information on the material under analysis. The molecular absorption properties of a material are normally studied through the transmission and/or reflection coefficients of this material to a determined radiation, while photoacoustics is based upon direct absorption of the incident light. As a conclusion, the photoacoustic technique can be employed in the characterization of opaque materials and complex biological systems [3].

Photothermal techniques have been frequently utilized in the analysis of biological systems as plant leaves and animal tissues. The photoacoustic technique can be employed in the characterization of human skin and in pharmacokinetics studies of topically applied drugs as well [4].

The use of the photoacoustic technique in dermatology actually began in 1977 with Rosencwaig. Research involving the application of cosmetics started in 1978, one topic being the investigation of the ultra-violet (UV) protection factor of commercially available sunscreens [5].

The UV radiation is divided in three wavelength regions: UVA (320-400nm), UVB (280-320nm) and UVC (190-280nm). The UVA radiation comes primarily from the sun (but can be artificially emitted) and reaches deep layers of dermis and epidermis. The UVB radiation is responsible for the tanning and is biologically relevant. The UVC radiation is mostly blocked by the atmosphere before reaching Earth, playing a minor role in photochemical reactions [6].

In the last decades, it has been reported a significant increase in the human exposure to UV radiation. This is due to the diminution of the stratospheric ozone, noticed not only in the south hemisphere but also in some regions of the North hemisphere (intermediate latitudes, for instance). This augments the hazard potential of the UV radiation. Particular problem is the increase in ambient UVB level, considered an induction factor to human skin cancer [7].

The ultra-violet radiation presents benefic effects as the stimulation of the vitamin D synthesis. On the other hand, UV radiation is also responsible for adverse effects to human health as the diminution of the immune system activity and the increase of skin cancer incidence, with consequent augmentation of the mortality levels. Recently, it has been shown that, among other effects, UV radiation induces DNA damages that may be responsible to the lessening of the immune response [8].

With the progressive diffusion of the information on the effects of the UV radiation, people have been alert to the necessity of adopting photoprotective measures. As a consequence, industry research in this field are uninterrupted, with periodic reformulation of sunscreens in order to assure improvements in quality and efficacy. The development of many new formulations utilizes associations of different agents to guarantee absorption of the radiation between 290nm and 400nm [9].

2. MATERIALS AND METHODS

The photoacoustic setup employed in this study was composed by the following equipments: 1) Xenon arc lamp (Oriel, mod. 6128, 1000 W); 2) Chopper (PAR, mod. 192); 3) Monochromator (Oriel, mod. 77250); 4) Lock-in amplifier (PAR-EG&G, mod. 5210); 5) Photoacoustic cell (homemade). The chopper and the photoacoustic cell microphone are connected to the lock-in amplifier, and the lock-in is connected through a general purpose interface bus to a microcomputer for data acquisition. The typical time constant used is 1s, which gives the time response of the setup. Photoacoustic measurements were carried out at 70 Hz.

The xenon arc lamp was used to provide radiation with wavelengths between 240nm and 400nm, which corresponds to the most of ultraviolet radiation from the sun that passes through the atmospheric ozone layer reaching Earth.

The first photoacoustic spectroscopy measurement was performed with black carbon powder. This material can be considered a perfect absorber, and its absorption spectrum serves to characterize the emission spectrum of the arc lamp. All the remaining measurements were normalized to the lamp spectrum.

Afterwards, the absorption spectrum of the sunscreen was obtained. Measurements were done with a commercially available sunscreen with Sun Protection Factor 15.

After these procedures, a new sample of the product was applied in an human abdomen skin sample with diameter 0,5cm. Skin samples were supplied by the Skin Cells and Epidermis Laboratory of the Hospital of the Campinas State University (UNICAMP), obtained from aesthetic surgeries and conserved in physiological serum 0,9%. The sunscreen was applied following the instructions of the producer.

The product was applied over all the surface of the sample, uniformly. Then photoacoustic spectroscopy measurements were performed on the bilayer system “skin + sunscreen”, for different time intervals after applications: 0 minutes (immediately after application of the sunscreen), 25 minutes, 45 minutes, 70 minutes and 90 minutes.

3. RESULTS AND DISCUSSION

The obtained results are represented in the following figures. Photoacoustic spectroscopic measurements of the isolated sunscreen show a relative absorption level superior to 80% in the wavelength region between 245nm and 350nm. Data are shown in Fig. 1.

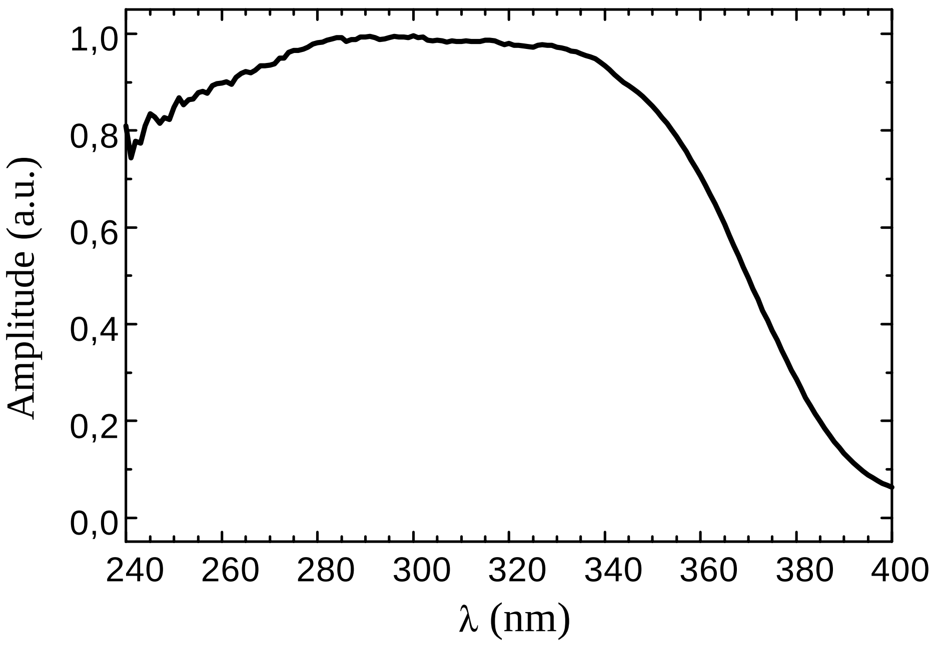

Fig. 1. Absorption spectrum of the sunscreen obtained by photoacoustic spectroscopy. The spectrum was normalized to the amplitude value at 280 nm, that correspond to the maximum observed at the original spectrum. The vertical axis corresponds to the amplitude of the photoacoustic signal in arbitrary units, while the horizontal axis determines the radiation wavelength.

Figure 2 shows the photoacoustic spectroscopy response of the epidermis before sunscreen application. We can observe some absorption peaks. The more evident absorption peaks correspond to: 1) wavelengths between 240nm and 245nm; and 2) wavelengths between 280nm and 285nm.

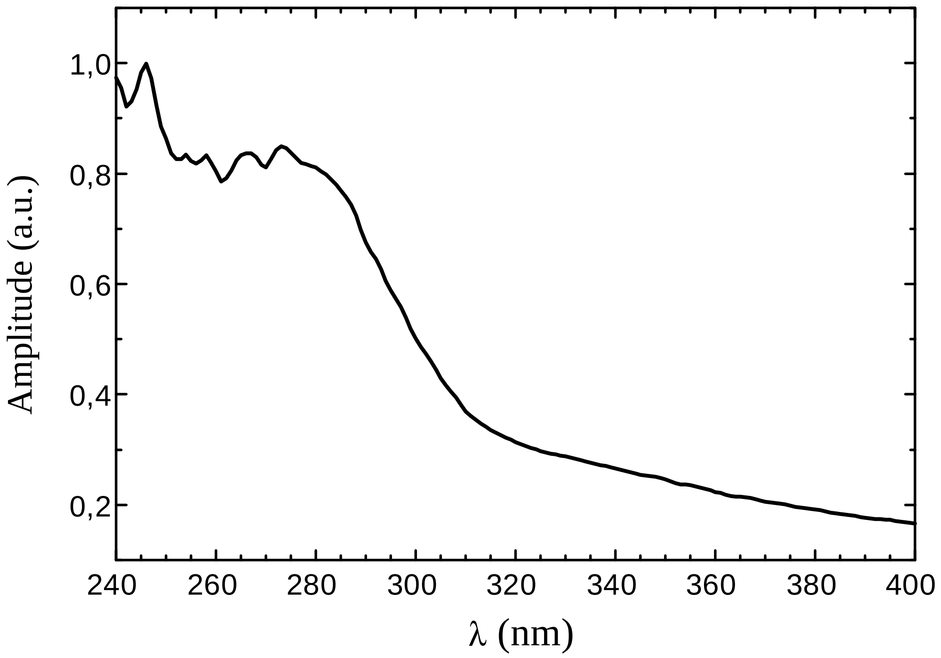

Fig. 2. Absorption spectrum of the epidermis (before sunscreen application) obtained by photoacoustic spectroscopy. The vertical axis corresponds to the amplitude of the photoacoustic signal in arbitrary units, while the horizontal axis determines the radiation wavelength.

Figure 3 shows the photoacoustic spectra of the bilayer system composed by the sunscreen applied in the skin, for different times after application. The initial curve (0 minutes, continuous line) corresponds to the measurement performed immediately after sunscreen application and reproduces essentially the photoacoustic spectrum of the applied sunscreen.

The next curve (25 minutes, dashed line) shows a general decrease in the absorption level, indicating sunscreen penetration. The last three curves (45, 70 and 90 minutes) are similar among themselves, showing the stabilization of the system "skin + sunscreen".

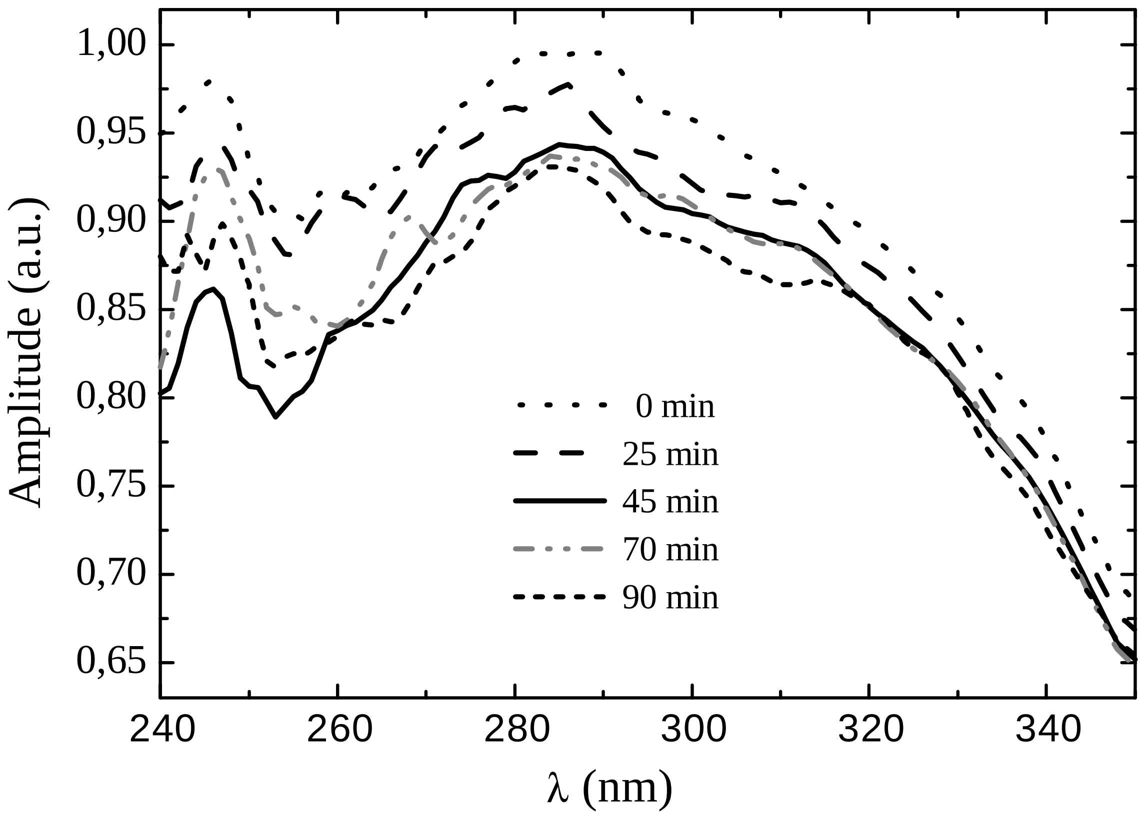

Fig. 3. Absorption curves of the system "skin (epidermis) + sunscreen" obtained by photoacoustic spectroscopy for different times after sunscreen application on the skin sample. The vertical axis corresponds to the amplitude of the photoacoustic signal in arbitrary units, while the horizontal axis determines the radiation wavelength.

The spectrum shown in Fig.4 corresponds to the difference between the photoacoustic spectrum of the bilayer system "skin + sunscreen" (figure 3, instant 0) and the photoacoustic spectrum of the untreated skin (Fig. 2). In this way, it is possible to notice the effect of the sunscreen applied to the skin. It can be observed in Fig. 4 that sunscreen increases UV protection from about 310 nm to 340 nm, that correspond with a spectral region where normal skin is not protected (Fig. 2).

From these results, we can observe that this specific sunscreen is particularly effective for ultraviolet radiation at UV range from 280nm to 340nm. This attests that the sunscreen utilized in this work can offer a good protection against UVA and UVB radiation.

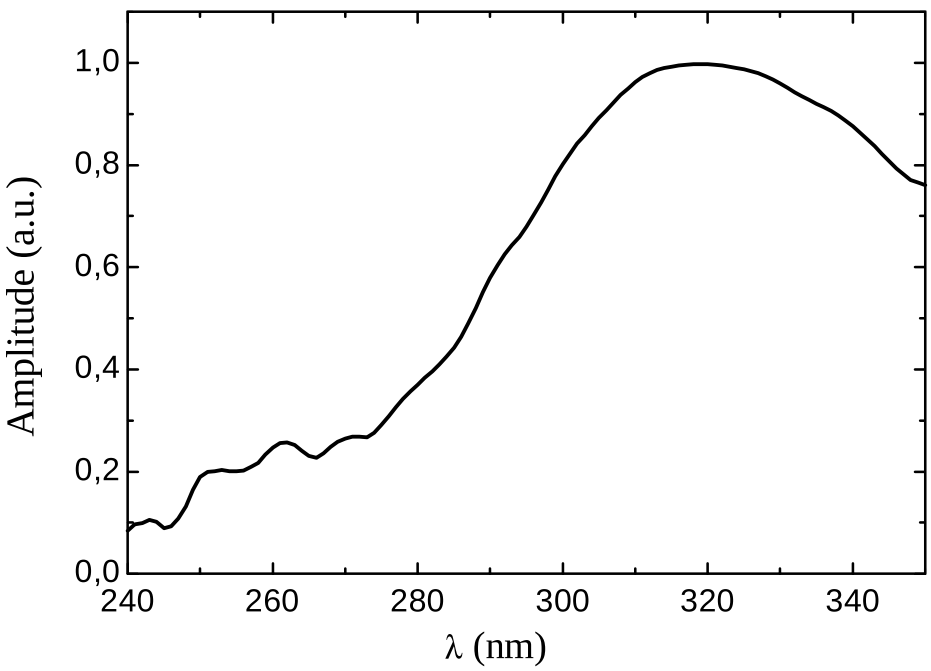

Fig. 4. Photoacoustic spectrum of the sunscreen *in situ* (applied to the skin). This "difference spectrum" was obtained from the data in fig. 2 and (the first curve of) fig. 3.

4. CONCLUSIONS

This work attests that photoacoustics can be a valuable technique in the analysis of the protection offered by commercially available sunscreens. Time evolution of the absorption spectra agrees with the instructions given by the producers about the need of applying the sunscreen at least 30 minutes before exposition to sun rays, in order to allow stabilization of the system. Also, as emphasized in the instructions for use (presented in the label of the sunscreen), it is important to periodically reapply the sunscreen. This is confirmed by the progressive decrease in the level of ultraviolet absorption as a function of the time. The decrease observed in the photoacoustic signal amplitude as a function of time is associated to the kinetics of sunscreen absorption.

According to the results obtained, we conclude that the product analyzed presents an effective absorption of the ultraviolet rays that are dangerous to the human body. However, we must emphasize that the amount of the product actually applied to the skin can affect the level of photoprotection acquired by the user [9]. A more detailed analysis of the protector effect as a function of the amount of substance applied is a perspective for future work in this field using the photoacoustic technique. Besides that, as a low-cost diagnosis technique, photoacoustics can become a useful tool in the characterization of sunscreens from different producers and with different sun protection factors.

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