Spectrophotometric determination of UV protection provided by cosmetic products with sunscreen properties

Agata WAWRZYŃCZAK, Izabela NOWAK – Faculty of Chemistry, Adam Mickiewicz University, Poznań

Please cite as: CHEMIK 2011, **65,** 7, 655-660

Introduction

It is well known that overexposure to the sunlight, particularly to UV rays, may cause many skin defects, like sunburns (erythema), premature skin aging (wrinkles), photosensitivity, suppression of the immune system or even skin cancers. For many years, sunscreens have been recommended by dermatologists, not only as a protective measure against excessive amounts of sunlight, but also because of their contribution to the prevention of skin photodamage [1]. All of cosmetic products with sunscreen properties are designed to absorb or reflect the sun's UV radiation in order to protect the skin cells from damage.

UV radiation is a part of the electromagnetic spectrum that lies in the range of 200 and 400 nm (Fig. 1) and it is usually divided into three regions:

- UVA: 320÷400 nm
- UVB: 280÷320 nm
- UVC: 200÷280 nm

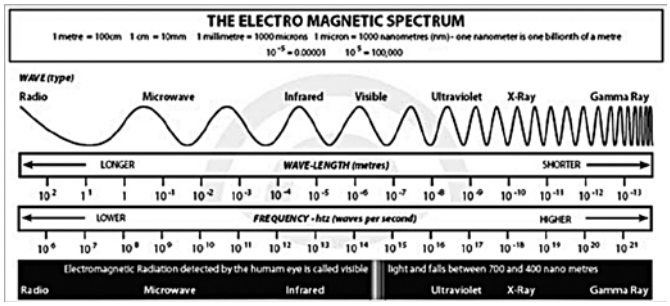

Fig. 1. The electromagnetic spectrum

Of the total solar UV radiation that reaches the Earth's surface, only 6% is in the UVB region and 94% in the UVA. UVC, the highest energy region, is completely absorbed by the ozone layer in the stratosphere, because these waves possess a relatively short range, according to the equation1, which proves that the higher energy, the shorter wavelength.

$$E = h \cdot \nu = h \cdot \frac{1}{\lambda}$$

Eq. 1. The correlation between the quantum energy and the wavelength

(E – energy, h – Planck constant, ν – frequency, λ. – wavelength).

The potential of UV radiation to cause skin damage rises exponentially with decreasing wavelength. UV light at 280 nm is 1000 times more damaging than the light at 340 nm, therefore, a sunscreen's ability to block UVB radiation seems to be the most important to prevent the negative effects of sun exposure [2]. However, a number of studies have shown that not only UVB irradiation is strongly damaging, but also UVA irradiation causes severe negative effects in the human skin [3÷5]. Therefore, a common test method for measuring UVA protection levels have become at least as important as UVB influence examination.

The article covers different methods for measuring UVA protection, with a strong emphasis on spectrophotometric techniques.

Measurement of the UV protection factor of sunscreens

Destructive influence of UV radiation, particularly from the UVA range, occurs on the biochemical, the cellular and on the functional level of the human skin. These effects are mostly mediated by free radicals, e.g. reactive oxygen species, and the visible signs of their activity are often a result of long-term, accumulative reactions. Hence, it is critical for sunscreens formulations to protect the skin against the effects of both: short-wavelength UVB and long-wavelength UVA.

UVB protection

The level of sun protection performance of the sunscreen products is indicated by the Sun Protection Factor (SPF), which can be defined as a time factor for the protection of the skin compared to exposure without any protection (eq. 2).

$$SPF = \frac{time\ or\ dose\ to\ minimal\ erythema\ on\ protected\ skin}{time\ or\ dose\ to\ minimal\ erythema\ on\ unprotected\ skin}$$

Eq. 2. Calculation of the SPF number

Most often SPF parameter is measured according to the so-called *in vivo* procedure, in which tests on volunteers are conducted. 2 mg of the product are applied on the 1 cm^2 of the volunteer's skin, followed by the UV radiation exposure. Irradiation is continued until the first skin reddening occurs. Afterwards the procedure is repeated, but without using any sunscreen products. These experiments allow measurements of time periods that can be directly used to calculate the value of SPF (according to the eq.2).

As already mentioned, the photoprotection of the topical sunscreens against the exposure for solar UV radiation is mostly determined by the phototesting of human volunteers. However, this *in vivo* testing is a time-consuming process. As a consequence, scientific methods for evaluating the SPF values of sunscreens have been developed. Early *in vitro* studies relied on either spectrophotometric assay of dilute solutions of sunscreening agents or the determination of the transmission spectrum of thin films of products. Nowadays, they are based mostly on diffuse transmittance measurements, obtained using a UV-Visible spectrophotometer equipped with a diffuse reflectance accessory.

The international standard for quantifying the damaging effects of UV radiation on the human skin is CIE Erythemal Action Spectrum [6]. In order to calculate UV protection factors according to the CIE directions, the percent transmission of a sunscreen lotion sample across the whole UV spectrum has to be measured. In the next step these values should be weighted by the so-called erythemal weighting factors at different wavelengths [6].

The greatest benefit of this particular method is that the lotion can be tested directly in a measuring cell, without any dilution or previous sample preparation. Nevertheless, it is worth mentioning that *in vitro*

methods of SPF analysis may quite often produce very high SPF values on chemical sunscreens compared to *in vivo* measurements. However, physical sunscreens have *in vitro* SPF measurements closer to their advertised values [2].

All methods for SPF value evaluation are specified according to some standards, for example COLIPA International Sun Protection Factor Test [7], and are regularly updated.

UVA protection

The sun protection factor (SPF), which is measured according to the COLIPA protocol [7], indicates only the efficacy of UVB protection but does not adequately cover the UVA part of the sunlight. Since the harmful effects of the UVA radiation have been established, the need for a common test method for UVA protection measurements became even more urgent.

Up to now several *in vivo* methods for evaluation of the UVA protection have been described, like PPF (Phototoxic Protection Factor), PFA (Protection Factor UVA), IPD (Immediate Pigment Darkening) and PPD (Persistent Pigment Darkening), among which the last two are the most prominent ones [8, 9]. Similarly to the SPF evaluation, also these tests should be conducted according to some specified standards, for example COLIPA guidelines [10]. *In vivo* tests for UVA protection factors are the most common. They are performed with volunteers and usually are based on measurements of the skin pigmentation caused by UVA radiation.

Immediate Pigment Darkening (IPD) method involves the evaluation of an immediate darkening of the skin pigment and the appearance of a low intensity erythema hidden by the pigment. However, there are some limitations in this test. The pigment reaction, induced by UVA radiation on the skin surface, is relatively easy to detect only on subjects with a type III or IV phototype. When it comes to a I or II type phototype subjects, this phenomenon does not apply. Moreover, the appearance of an immediate pigment darkening is quite difficult to be seen on volunteers with a dark phototype skin. Thus, the IPD method does not always give a precise reading.

The Persistent Pigment Darkening (PPD) is a method of measuring UVA protection, similar to the SPF method of measuring UVB light protection. It means that, theoretically, a sunscreen with a PPD value rating of 5 should permit tolerance of 5 times as much UVA as without protection. During this test, volunteers are irradiated with a UVA light source (320÷400 nm) and skin changes, yielding in a persistent pigment darkening, are observed after 2÷24 hours after the irradiation has been stopped. To determine the final value of UVA-PF, the response of the sunscreen protected and unprotected skin is compared [9]. The advantage of the PPD method, when comparing with IPD, is that the residual colour that has developed after exposure to the radiation is stabilized and allows more precise readings. Even though, the PPD response is stable and reproducible, its clinical significance may be questionable, because the PPD action spectrum for wavelengths shorter than 320 nm is not defined, and the response can be covered by other UV skin responses during outdoor sun exposure [9].

In vivo testing for sunscreen protection values is a time-consuming process, particularly when information concerning the protection against long wavelength of UV spectra (UVA) is required. Because of this, some attempts to establish effective and undemanding *in vitro* methods for UVA protection factors have been made.

COLIPA guidelines are dedicated mainly to liquid and emulsion-type sun protection products [10]. The test for UVA protection factors (UVAPF) evaluation should be based on the assessment of UV transmittance through a thin film (0.75 mg/cm^2) of the sunscreen sample spread on a roughened substrate, before and after exposure to a controlled dose of UV radiation from a strictly defined UV source. This method allows *in vitro* measurements of UVAPF values, which are shown to correlate quite well with *in vivo* results, determined with PPD method, the latter being considered as a reference. COLIPA guidelines also give detailed specifications of the DR UV-vis spectrophotometer that can be used in UVAPF measurements [10]. The most important one is that spectrophotometer input optics should be designed for diffuse illumination and/or diffuse collection of the transmitted irradiance through the roughened PMMA (polymethylmethacrylate) plate, both with or without the sunscreen layer spread on its surface. The lamp used to measure the transmittance has to emit a continuous spectrum of radiation within the range of 290÷400 nm. The level of irradiance should be sufficiently low, so that the photostability of the product is not disproportionately impaired. For example, a xenon flash lamp may be a convenient solution. It is worth noticing that the UV-dose during one measurement cycle should not exceed 0.2 J/cm^2. More detailed equipment specifications, as well as the measurement and calculation method can be found in the COLIPA guideline publication [10].

Australian standard (AS) method uses spectrophotometer for measurements of the solar radiation transmitted by a sunscreen product to yield a percentage of UVA radiation absorbed by the product. According to this test, a product is designated as a long wave protector only if it transmits less than 10% of the incoming UV radiation between 320 and 360 nm. Though, this method assures that the product may provide a broad spectrum of the protection, nevertheless, it cannot guarantee the appropriate level of UVA protection for people with extreme photosensivity. Furthermore it doesn't take the photounstability into account.

Boots Star Rating System is based on a ratio of UVA/UVB transmitted radiation. Areas under the curve in the UVA and UVB region are calculated for each sunscreen product, leading to a coefficient between 0 and 1, which can be also assigned as a star value (Tab. 1).

Table 1

Corresponding coefficient values and Boots Stars assignments

UVA/UVB	0 - 0.2	0.21 - 0.4	0.41 - 0.6	0.61 - 0.8	0.81 - 0.9	> 0.91
Boots Stars	none	*	**	***	****	*****
Protection category	none	minimum	moderate	good	superior	ultra

Broad Spectrum Rating (Critical Wavelength) method is based exclusively on the spectrophotometric analysis of products applied to a suitable substrate and allows elimination of the studies on human or animal objects. The absorbance spectrum obtained by spectrophotometric assay is reduced to a single index by determining so-called critical wavelength value (λ_c), at which the spectral absorbance of the product reaches 90% of the area under the curve from 290 to 400nm. Broad Spectrum Rating method relies only on the shape of the UV absorption spectrum and not on its amplitude. The problem of this test is quite small correlation with *in vivo* results. [11].

APP method (UVA Protection Percentage) was proposed by Sayre and Agin to determine the percentage of UVA radiation blocked by a given sunscreen. This technique provided an efficient measure, but did not reach widespread use due to potential operator influence, difficulty in obtaining the substrate, and lack of recognition by the FDA. [12].

Conclusion

In recent years the harmful effects of the UVA radiation have been more comprehensively established. Since the commonly used SPF value covers only the UVB range protection, quick and simple tests for UVA blocking properties should be invented.

In vitro test methods to determine the UVA protection of sunscreen products have been already developed and they can give meaningful information about UVA protection. However, no complete procedure has been yet correlated with *in vivo* test results, giving reliable and reproducible results The main problem of all these *in vitro* methods is that they do not quantitatively measure the magnitude of protection, but only the relative broadness of the UVA absorbance.

Translation into English by the Author

Literature

1. Tarras-Wahlberg N., Stenhagen G., Larko O., Rosen A., Wennberg A.M., Wennerstrom O.: J. Invet. Dermatol. 1999, **113,** 547.
2. Allen M.W., Bain G., Thermo Fisher Scientific, Appl. Note nr 51463, www.thermo.com.
3. Kligman L.H., Akin F.J., Kligman A.A.: J. Invest. Dermatol. 1985, **84**, 272.
4. Kligman L.H.: J. Soc. Cosmet. Chem. 1994, **45,** 21.
5. Diffey B.L.: Phys. Med. Biol. 1980, **25,** 405.
6. CIE (International Commission on Illumination) Research Note, A reference action spectrum for ultraviolet induced erythema in human skin, CIE J. 1987, 6, 1722.
7. COLIPA, European Cosmetic, Toiletry and Perfumery Association, Colipa SPF Test Method, 94/289, 1994.
8. Cole C., VanFossen R., Skillman: J. Acad. Dermatol. 1992, 26,178.
9. Chardon A., Moyal D., Hourseau C., Sunscreens , Marcel Dekker Inc.: 1997, 559.
10. COLIPA, European Cosmetic, Toiletry and Perfumery Association, Colipa Method for the in vitro determination of UVA protection provided by sunscreen products, Guideline 2007.
11. Diffey B.L.: Int. J. Cosmet. Sci. 1994, **16,** 47.
12. Sayre R.M., Agin P.P.: J. Am. Academy. Dermatol. 1990, 23, 429.

Agata WAWRZYŃCZAK - Ph.D., is an adjunct at the Applied Chemistry Group, Faculty of Chemistry, the Adam Mickiewicz University (AMU). She obtained the Master's degree in 2003 and doctoral degree in 2007 in chemistry at AMU. Her scientific interest is focused on synthesis, modification and characterisation of heterogeneous catalysts and cosmetic chemistry. She is a co-author of 20 scientific papers, 1 patent and 38 presentations at national and international conferences.

Izabela NOWAK - D.Sc., is an Associate Professor and Head of the Applied Chemistry Group. She was granted from TEMPUS a scientific fellowship at the University of Reading, U.K., in 1992÷1993, where she wrote her M.Sc. thesis. She received her M.Sc. in chemistry in 1993 from the Adam Mickiewicz University (AMU) in Poznan, Poland, where she also obtained a Ph.D. in chemistry in 1996. She received a postdoctoral training at the Leverhulme Centre for Catalysis in Liverpool. In 2006, she was awarded the degree of D.Sc. (habilitation) for the research on synthesis, characterization and catalytic properties of nanoporous materials for the liquid-phase oxidation processes. Her current scientific interests are focused on synthesis and modification of novel ordered materials, textural/structural/surface/acid-base/redox properties of thereafter, heterogeneously catalyzed synthesis of fine and intermediate chemicals and modern synthesis strategies for cosmetics and cosmeceuticals. She has published more than 80 papers, 3 patents, and made more than 140 presentations at symposiums and conferences.

Future materials for Grand Challenges of our time FUMAT 2011

Poland, Warszawa, 22-23 September 2011

European Industrial Technologies Conference on Materials will be a major event concerning materials. It will be organized during the Polish Presidency of the Council of the EU in cooperation with the European Commission. FUMAT 2011 will be an opportunity to gather together the actors from the scientific community, the industry and the policy makers from across Europe, and discuss the open question: How materials of the future can contribute to the strategies and solutions for the grand societal challenges? The Conference will involve thematic sessions related to areas where materials can play a key role in our quest to answer that question.

The Conference will focus on:

- The application of Future Materials in different sectors (energy, ICT, transport, safety and security).
- Human aspects of materials development (quality of life, health, job creation, etc)
- R&D in materials bridging research and application
- International partnership with focus on East European countries (Eastern partnership)
- dissemination of knowledge and societal acceptance.

The objectives of the conference are:

- To support the EU policies in view of Grand Challenges and EU2020 strategy in fields relevant to materials
- To discuss the directions of material development, which aregoverned by factors such as the technological progress, by the societal and political needs, but also financial capabilities.
- To increase the society's awareness about the importance of R&D in materials, as well as to discuss the ways to widen the societal acceptancefor the newly developed technologies.

more: http://www.fumat2011.eu