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In-Vitro Evaluation of Sun Protection Factors of Sunscreens Marketed in Sirte City by Ultraviolet Spectrophotometry

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Abstract The Sunscreen products that contain different active ingredients can affect the sunlight by absorbing, reflect or scatter it depends on the nature of these products. The effectiveness of a sunscreen product can be evaluated by determining the sun protection factor (SPF). This research aimed to determine the sun protection factor (SPF) values of six sunscreens commercial product (creams, lotions and foundations) by UV-Visible Spectroscopy. The Mansur equation was applied to calculate SPF values for each cosmetic product. The sun protections labelled values of these commercially available sunscreens were in the range (10-90%).

Keywords: Sun protection factor, Lotion, Ultraviolet spectrophotometry, Sunscreens, Titanium dioxide, Zinc oxide.

مخبرياً تقدير قيم الـــعامل الوقاية الشمسي (SPF) لبعض الاوقية الشمسية ومنتجات التجميل المتوفرة في اسواق مدينة سرت بواسطة مطيافية الأشعة الفوق بنفسجية والمرئية UV/VIS Spectrophotometer

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ملخص الهدف من هذا البحث هو قياس قيم عامل الحماية من أشعة الشمس (SPF) ومطابقته في المنتج التجاري. في هذه الدراسة، تم قياس قيم الامتصاص لبعض مستحضرات التجميل مثل واقيات الشمس (الكريمات والمستحضرات والأساسات foundations) باستخدام مقياس الطيف الضوئي فوق البنفسجي، ومن ثم تم تطبيق معادلة منصور لحساب قيم الـــ SPF لكل منتج تجميلي ومقارنته بالمنتج التجاري. كانت قيم الحماية من أشعة الشمس (SPF) لهذه الواقيات الشمسية المتوفرة في النطاق (10–90). من مزايا هذه الطريقة التحليلية انها غير مكلفة وسهلة التطبيق بحيث يمكن استخدامها كوسيلة لمراقبة الجودة لتقديم معلومات حول واقيات الشمس ومستحضرات التجميل قبل اختبارها في الجسم الحي. أحد عيوب هذه الطريقة هو أنه لا يمكن استخدامها لحساب قيم الـــ SPF لواقيات الشمس التي تحتوي على مرشحات غير عضوية مثل أكسيد الزنك وأكسيد التيتانيوم وذلك لأنها لا تمتص في مجال الأشعة فوق البنفسجية وانما تقوم بعكس الاشعة. لذ يتم استخدام هذه الطريقة الطيفية كوسيلة تقييم لحساب قيم الـــ SPF في مستحضرات التجميل التي تحتوي على مرشحات عضوية فقط ولا تتضمن مرشحات غير عضوية.

الكلمات المفتاحية: الحماية من أشعة الشمس، اللوشن، مطيافية الأشعة فوق البنفسجية، واقيات الشمس، ثاني أكسيد التيتانيوم، أكسيد الزنك.

Introduction

The short exposure of the human body to ultraviolet rays through sunlight is important in the production of vitamin D, which our body needs to treat many diseases, such as, psoriasis, eczema and jaundice. However, long exposure to these rays has harmful effects on human skin [1-3]. Furthermore, about one million people yearly diagnosed with skin cancer, and about 10.000 die from malignant melanoma [4]. The body areas that frequently exposed to the sun, for instance, head, neck, face, back of the hands, always affected by skin cancer [4].

The ultraviolet rays (UV) are divided into several waves that overlap with each other: [5,6]

i. UVA (320-400 nm): This radiation can be further subdivided into UVAII (320–340 nm) and UVAI (340–400 nm). These rays are directly responsible for pigmentation and tanning due to increased melanin in the skin.
ii. UVB: This radiation is between 290-320 nm, which causes burns to the skin, striking the cells in the skin's layer and destroying the collagen fibres.
iii. UVC: This radiation is between 200-290 nm. This radiation filtered by the atmosphere layer before reaching the earth.

Aromatic molecules conjugated with carbonyl groups consider as the main active ingredients in the composition of sunscreen, which have light-emitting effect from the stable state to the excited state. This general structure allows the molecules to prevent the harmful UV rays from reaching the skin by absorbing the high-energy UV rays and release energy as low-energy rays [7]. Table 1 summarises some of the active ingredients used in sunscreens industry [7-9].

Table (1): Some of the active ingredients allowed by the FDA.

UV filter (Molecular Formula)	Up to % conc.	Absorbance
p-Aminobenzoic acid ($C_7H_7NO_2$)	15%	UVB
Padimate O ($C_{17}H_{27}NO_2$)	8%	UVB
Phenylbenzimidazole sulfonic acid ($C_{13}H_{10}N_2O_3S$)	8%	UVB
Cinoxate ($C_{14}H_{18}O_4$)	6%	UVB
Dioxybenzone ($C_{14}H_{12}O_4$)	3%	UVB, UVAII
Oxybenzone ($C_{14}H_{12}O_3$)	10%	UVB, UVAII
Homosalate ($C_{16}H_{22}O_3$)	15%	UVB
Menthyl anthranilate $C_{17}H_{25}NO_2$)	5%	UVB
Octocrylene $C_{24}H_{27}NO_2$)	10%	UVB
Titanium dioxide(TiO_2)	25%	Physical
Zinc oxide (ZnO)	25%	Physical
Sulisobenzone ($C_{14}H_{12}O_6S$)	10%	UVB, UVAII

Photosensitivity can be defined as significant burning or irritation after sun exposure to the sun and other sources of UV rays [3]. Photosensitivity depends on the skin type and in the following Table 2 shows the response of various skin types of ultraviolet rays [10].

Table (2): The response of various skin types to ultraviolet rays.

Skin type and its Response to UV rays	Genotype
Type I is infected with sunburn and it has pigmentation easily.	Red or blond hair Blue or brown eyes
Type II often occurs in burns andpigmentation.	Hair is red or blond or brown Blue eyes or hazelnuts or brown eyes.
Type III has moderate burns which are gradually stained.	Caucasian skin
Type IV suffers minor burns and it has easily pigmented.	Dark brown hair White or light brown skin
Type V rarely gets burned and it has easily pigmented.	Structure Complexion (Middle East & Spain)
Type VI does not get burned and it has easily pigmented.	Black skin

The efficacy of a sunscreen is usually expressed by sun protection factor (SPF) which is the dose of UV rays required to produce minimal erythema dose (MED) on protected skin after application of 2 mg/cm^2 of product divided by the UV rays to produce MED on unprotected skin. High SPF numbers give the false impression they can provide enhanced protection when that is not the case. A well-formulated sunscreen with an SPF 30 still only protects the skin from about 97% to 98% of the sun's rays [2].

Reliable, fast, and simple *in vitro* method of measuring the SPF is to screen the absorbance of the product between the wavelength range 290-320 nm at every 5 nm periods. Mansur equation is applying to calculate SPF [4,11-12]. This study was carried out in the spring of June 2018 and ended in November of 2018 on six sunscreens (creams, moisturisers and Foundations) from different brands. This study aims to calculate the absorption (ABS) of active substances in local available commercial sunscreens by using ultraviolet spectrophotometer in ultraviolet light UVB range of 290-320 nm and then calculate the value of solar protection factor (SPF) according to Mansur's method.

Materials and methods

Chemicals and equipment

Sunscreens were purchased from some pharmacies and shops in the local market in Sirte city. Absolute ethanol (95%) was purchased from Merk. Spectrophotometric determination of UV absorbance was carried out in 1 cm path length cuvette (quartz), using JENWAY6305 UV/Visible spectrophotometer (single beam). Samples mixing were carried out using Vortex mixer (Bio Cote).

Sample preparation for spectrophotometric SPF measurement

One gram of the sample was weighed and dissolved by ethanol in 100 mL volumetric flask, followed by vigorous mixing with a vortex mixer for 5 min and then filtered, the first 10 mL was discarded. Then, 5 mL aliquot was diluted with ethanol in 50 mL volumetric flask. Finally, a 5.0 mL was transferred to a 25 mL volumetric flask and the volume completed to the mark with ethanol.

Absorption measurement

The absorbance of prepared solutions was measured in the range of 290-320 nm, each time the wavelength range is changed by 5 nm in each measurement.

Calculation of solar protection factor (SPF)

The Mansur mathematical equation (1) was used to calculate the SPF values of the samples (A- F).

$$SPF = CF \times \sum_{290\,nm}^{320\,nm} EE(\lambda) \times I(\lambda) \times ABS(\lambda) \quad (1)$$

Where: CF is the correction factor (=10); "EE", the erythemal effect of radiation at wavelength λ; "I", the intensity of the solar spectrum; and "ABS", the absorbance at wavelengths 290-320 nm. "EE", "I", and "ABS" are values obtained or applied for every wavelength (λ). The values for each of the [EE(λ) x I(λ)] are constants have been reported by the authors as normalized based on the work by Sayre et. al., and were shown in Table 3 [4,11,12].

Table (3): Normalized product function used in the calculation of SPF.

Wavelength (nm)	EE x I (normalized)
290	0.0150
295	0.0812
300	0.2874
305	0.3278
310	0.1864
315	0.0837
320	0.0180

Appling absorbance values in Mansur equation (1) to calculate the SPF values for these analysed samples (A-F) as shown in Table 4.

Table (4): The SPF values for the analysed samples.

Sample (Type)	Brand	Actives Ingredients	SPF	Calc. SPF
A (Foundation)	Max Factor	non specified, AntiUV SPF10	10	9.3
B (cream)	Garnier	non specified, AntiUV SPF30	30	18.63
C (Foundation)	Final Touch	TiO_2	40	1.3
D (Foundation)	Final Touch	TiO_2	45	0.14
E (lotion)	Dulgon	non specified, AntiUV SPF50	50	10.12
F (cream)	Uriage	Ethylhexyl methoxycinnamate, ZnO, TiO_2, alkyl benzoate	90	17.16

Results and discussion

The measurement of SPF considers as the ultimate method to determine the efficiency of sunscreen formulation. Whenever the SPF is high, the sunscreen offers more protection against UV-light. The natural defence mechanisms of the human body assistance by the sunscreen that helps in protecting against the harmful UV rays from the sun. Its function depends on sunscreen ability to absorb, reflect or scatter the sun's rays [16,17]. The labelled SPF values were in the range of 10 to 90. The samples (A, B and E) with SPF values are 10, 30, and 50. The active ingredients for these sunscreens are not labelled. The samples C and D with SPF values 40 and 45 are classified as physical sunscreens so their calculated SPF did not match the product. The sample F with SPF 90 containing organic and inorganic filters as active ingredients afford only SPF value 17.16, which give an indication that the UV absorbency by both used organic and inorganic filters (Ethylhexyl methoxycinnamate, alkyl benzoate, ZnO and TiO_2) will affect the SPF of this kind of products. Furthermore, the protection value of sample A is very close to the value of the product, while the rest of the samples B, C, D, E, F fell much less. Likewise, several reported methods obtained similar results using the same spectrophotometric method for evaluation of SPF in the cosmetic product[4-5, 13-15]. The following Figure 1 shows the results of the SPF protection values of the analysed samples and compared them with the values on commercial product [4.5]

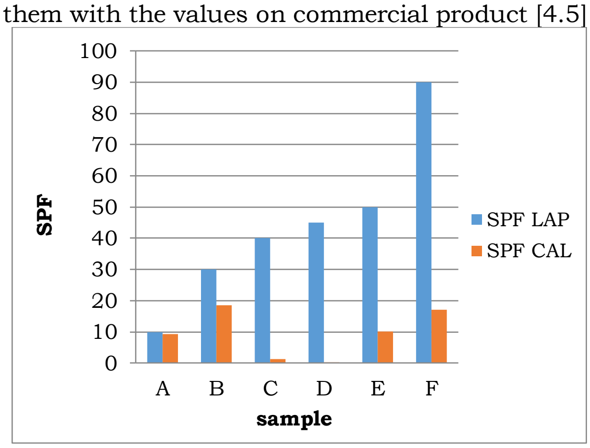

Figure (1) Comparison of labelled SPF values on the product and the calculated.

on the other hand, there are many other factors that can affect protection values, these factors may include: the value of pH, the degree of viscosity, the interaction of active substances with some other components of the sunscreen, the temperature, and the exposure of product to the sun which can increase or decrease the absorption of ultraviolet rays of the sunscreen.

Conclusions

In conclusion, measuring the SPF value of the sunscreen is the best way to determine its effectiveness so that the higher the SPF value provides the more excellent protection against ultraviolet radiation. The UV spectrophotometric method is used for the *in vitro* determination of SPF values in many cosmetic formulations. The obtained results of all the tested sunscreen product showed lower calculated SPF when compare with the labelled SPF values. The current method could be useful in the quality control process, during the production until the final product. This method showed good results with the sunscreen that contain organic filters as active ingredients compared to that contain inorganic filters, such as zinc oxide and titanium oxide, as an active ingredient due to this, inorganic filters cannot absorb in the area of ultraviolet radiation, which causes dispersion and light reflex of UV rays and does not fit with the calculation by Mansur equation.

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