

Determinations of Sun Protection Factor (SPF) of some sunscreens marketed in Kurdistan Region by UV-Visible spectrometry and study their Rheological properties

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Abstract

The sunscreen products contain active ingredients able to absorb, reflect and scatter the UV rays. The *in vitro* sun production factor (SPF) of some sunscreen emulsions marketed in Kurdistan Region can be estimated by ultraviolet-visible spectrophotometer. Fifteen different commercially available samples of sunscreen emulsions of various manufacturers were selected and assessed *in vitro* SPF values, pH values and rheological profile analysis. The SPF labeled values was in the range of 15 to 100. The values of the 33% of the analyzed samples are in close agreement with labeled SPF, 13% of SPF values above the labeled amount and 54% SPF values under the labeled amount. All samples of sunscreen emulsions exhibited pH values 6.2 to 7.9 and rheological profiles indicated that the all sunscreens have pseudoplastic properties.

Keywords: Sunscreens, *In vitro* Sun Protection Factor, Rheology and pH

1. Introduction

The short period exposure human body to UV radiation from the sunlight is required by our bodies to produce vitamin D, treat several diseases, including rickets, psoriasis, eczema and jaundice. Also, it is useful for disinfection and sterilization. But the long period exposure of ultraviolet radiation has the harmful effect on human skin. The UV radiation is classified into three regions UVA (320- 400 nm), UVB (280-320) and UVC (200-280 nm). The UVA radiation damages skin cells and DNA, being responsible for aging of skin and skin cancer [1], the UVB radiation is not completely filtrated out by the ozone layer, it causes skin burns and UVC radiation is filtrated by atmosphere [2]. For these reasons, several types of sunscreens such as moisturizers, creams, lotions, shampoos, mousses and other skin care protections have been used as most important substance to protect human skin from UV radiation. All sun protection products are designed to absorb or reflect the sun's UV radiation in order to prevent the skin cells from photodamage [3].

The efficacy of sunscreens can be expressed by the sun protection factor (SPF). The determination of SPF has been performed for a long time *in vivo* on human volunteers according to the COLIPA method. However the *in vivo* testing on volunteers is time-consuming, complex and expensive, particularly when information concerning to the protection against long wavelength (UVA) is required [4]. It is based on the minimal erythema dose (MED) on protecting skin, divided by the UV energy required to produce a MED on unprotected skin

$$\text{SPF} = \frac{\text{Minimal erythemal dose in sunscreen protected skin (MED}_p\text{)}}{\text{Minimal erythemal dose in unprotected skin (MED}_u\text{)}} \quad (1)$$

The minimal erythemal dose (MED) is defined as the lowest time interval or dosage of UV light irradiation sufficient to produce a minimal, perceptible erythema on unprotected skin. Therefore, much effort has been used to develop technique to determine SPF of *in vitro* for assessing the photoprotection of sunscreen compounds.

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The assessment of SPF *in vitro* can be done by two methods. The first method is measuring of absorption or the transmission of UV radiation through sunscreens product films in quartz plates or biomembranes, and the second method is determining absorption characteristics of sunscreen agent based on spectrophotometric analysis of dilute solutions [5, 6]. By UV spectrophotometric technique and employing a simple formula developed by Mansur equation. The *in vitro* SPF can be calculated by following equation:

$$SPF = CF \times \sum_{290}^{320} EE(\lambda) \times I(\lambda) \times Abs(\lambda) \quad (2)$$

Where EE (I) - erythemal effect spectrum; I(I)-solar intensity spectrum,; Abs-Absorbance of sunscreen product; CF-correction factor(=10). The value of EE x I are constant and predetermined [7] as shown in Table 1.

Table 1: Normalized product function used in the calculation of SPF

Wavelength (λ nm)	EE x I (normalized)
290	0.051
295	0.0817
300	0.2874
305	0.3278
310	0.1864
315	0.0839
320	0.018

The aim of this research was to determine the *in vitro* SPF values of several foreigner sunscreens Marketed in Kurdistan region claimed good protection against both UVA and UVB radiation based on their labeled SPF. Moreover, the physical properties of sunscreens are important to show the stability, storage, end-using of the sunscreens. The formulations that are commercially available include a combination of these agents to cover a wide spectrum of UV radiation. This sunscreen agent's action may vary from blocking, reflecting and scattering sunlight. Chemical sunscreens absorb UV rays, whereas physical sunscreens reflect or scatter light [8].

2. Material and methods

2.1 Reagents and samples

Ethanol (Merck®) analytical grade. Commercially available sunscreen emulsions of various manufactures were purchased from local pharmacies. The samples are shown in Table 2.

2.2 Apparatus

UV-visible spectroscopy measurement was carried out using a double-beam spectrophotometer Cary 100 scan, equipped with 1 cm quartz cell, computer and printer Epson FX-850, pH meter and Brookfield LV viscometer.

2.3 Methods

The fifteen commercially available sunscreens were selected for the assessment of *in vitro* SPF, pH and rheological profile. 1.0 g of marketed sunscreen formulations was weighed individually, transferred to 100mL volumetric flask and finally diluted to volume with ethanol. Further, it was kept for the ultrasonication for 15 min and filtered through cotton filter, discarded the initially ten mL. Afterwards 5.0 ml aliquot was transferred to a 25mL volumetric flask and the volume was adjusted with ethanol [8]. The absorbance of samples in solution form was measured in the wavelength range of 290 to 320nm, every 5nm wavelength interval, and the same was performed in triplicate for each sample and finally the Mansur equation was applied to calculate the SPF. The pH was measured with a Quimis® pHmeter. The electrode was introduced into each sample and the reading performed after stabilization. The rheological profile was assessed with a Brookfield L-V viscometer by taking a 150 ml of each sunscreen at 25°C.

3. Results and Discussion

The effectiveness of a sunscreen formulation to protect skin from sunburn, aging, cancer and other skin damage can be evaluated by the SPF number. The estimated SPF values provide awareness to users for how long they can stay in the sun before burning. To prevent any damage may cause to skin by UV rays, the sunscreen

products should have sufficient SPF values and wide range of absorbance between 290 to 400 nm, to absorb and reflect enough amount of UV ray photons.

The SPF values of fifteen commercially available products found in the Kurdistan Region’s market were evaluated by UV-Visible spectrophotometer by applying Mansur mathematical equation. The Calculated SPF values are shown in Fig. 1 and the SPF values found in samples E, I, K, L and M are in close agreement with labeled SPF, whereas, the SPF values for sample J and O are above labeled SPF and the rest of the samples are under labeled SPF as shown in Fig. 2.

Fig. 1: Labeled and calculated SPF against samples

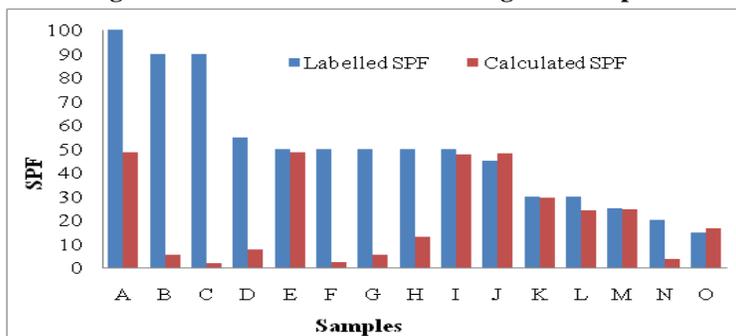


Fig. 2: Percentage of calculated sunscreen formulation.

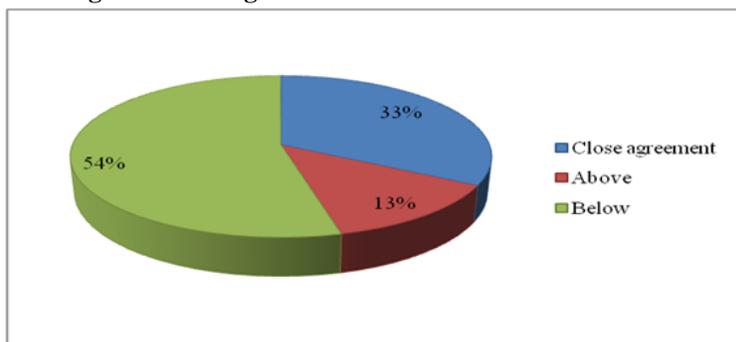


Table 2: Active Ingredient and labelled SPF values of commercially available formulation found at Kurdistan’s market.

Sample	Active Ingredient	Labeled SPF
A	Benzophenone-3, Octocrylene, Titanium Dioxide, Octyl Methoxy Cinnamate	100
B	Alkyl benzoate, Octocrylene, Titanium Dioxide, Butyl methoxy dibenzoil methane	90
C	Alkyl benzoate, zinc dioxide, Ethyl Hexyl Methoxy Cinnamate	90
D	Benzophenone, Titanium Dioxide, Ethyl Hexyl Methoxy Cinnamate	55
E	Phenethyl benzoate, Benzophenone-3, Octocrylene, Titanium Dioxide, Butyl methoxy dibenzoil methane	50
F	Alkyl benzoate, Octocrylene, Titanium Dioxide, Butyl methoxy dibenzoil methane	50
G	Alkyl benzoate, Octocrylene, Titanium Dioxide, Butyl methoxy dibenzoil methane	50
H	Benzyl Benzoate, Octocrylene, Butyl methoxy dibenzoil methane	50
I	Alkyl benzoate, Octocrylene, Titanium Dioxide, Ethyl Hexyl Methoxy Cinnamate	50
J	Phenethyl benzoate, Benzophenone-3, Octocrylene, Titanium Dioxide, Ethyl Hexyl Methoxy Cinnamate, Butyl methoxy dibenzoil methane	45
K	Alkyl benzoate, Tocopheryl Acetate, Titanium Dioxide, Ethyl Hexyl Methoxy Cinnamate, Butyl methoxy dibenzoil methane	30
L	Alkyl benzoate, Tocopheryl Acetate, Titanium Dioxide, Ethyl Hexyl Methoxy Cinnamate, Butyl methoxy dibenzoil methane	30
M	Alkyl benzoate, Zinc dioxide, Titanium Dioxide, Ethyl Hexyl Methoxy Cinnamate	25
N	Alkyl benzoate, Titanium Dioxide, Zinc oxide	20
O	Titanium Dioxide, Ethyl Hexyl Methoxy Cinnamate, Cetyl Ethyl Hexanoate	15

Fig. 3 shows higher differences between labeled and calculated values for sunscreens with labeled SPF 90, 100, 55 and 50 except for sample E and J. But lower differences observed for sunscreens labeled SPF 45, 30, 25, 20 and 15 compare to calculate SPF.

The high SPF values are more difficult to calculate *in vivo* due to the high SPF leads to great uncertainty and biological variation of the volunteers [6] or contain insufficient amount of active agents to absorb or reflect UV rays.

Fig. 3: Differences between labeled and calculated SPF values against samples

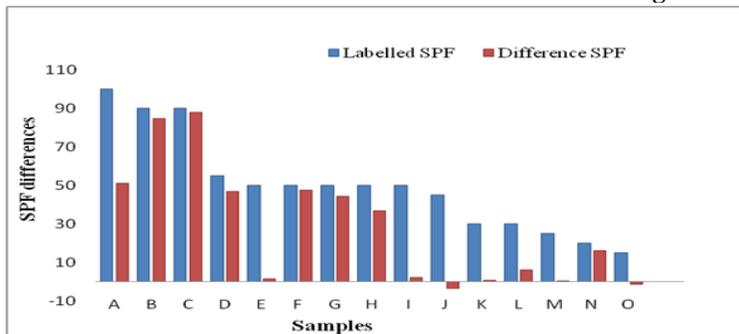
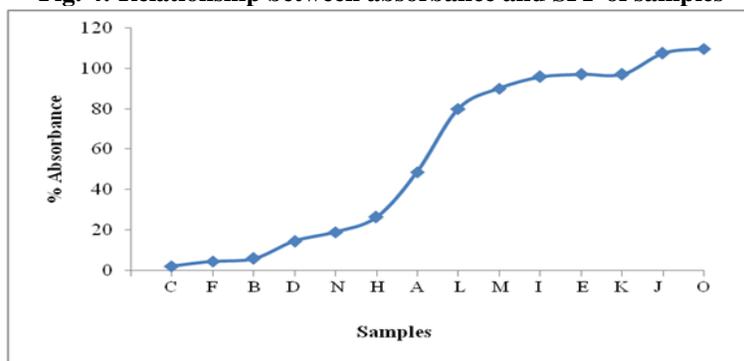


Fig. 4 shows maximal absorbance of samples was analyzed by UV-Visible spectrophotometer. The sample O shows higher absorbance than all samples. This is may be due to sample O has sufficient active agent to absorb UV rays compare to other samples or it has more sunscreens substance amount than other samples.

Fig. 4: Relationship between absorbance and SPF of samples



The rheological study of different sunscreen samples was tested in different shear rate and 25°C. All marketed sunscreens were showed pseudoplastic or shear thinning behavior because of decreasing viscosity with an increasing shear rate as shown in Fig. 5. The sunscreen formulations with a pseudoplastic flow produce a coherent protective film covering the skin surface and this activity is important for adherence to skin. The pH of commercial sunscreen samples was found almost a neutral around pH 7 and compatible with human’s skin[9] as shown in Fig. 6.

The variation of emulsion used in the formulations by interaction of vehicle components such as esters, emollients and emulsifiers used in the formulation, the pH system and viscosity and emulsion rheological properties, which can be increased and decrease UV absorption of each sunscreen [2].

Fig. 5: Rheograms of commercial marketed samples

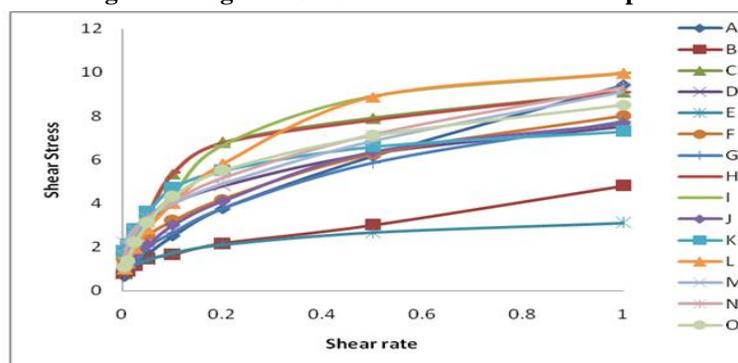
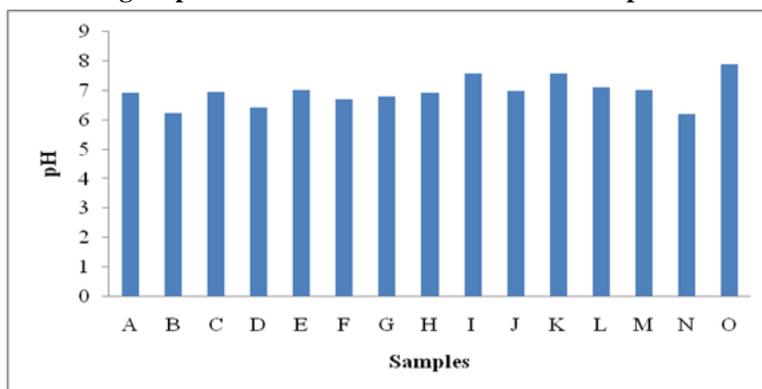


Fig. 6: pH values of commercial sunscreen samples.

4. Conclusions

The calculated SPF values of some sunscreen formulations marketed in Kurdistan Region show 33% of the analyzed samples are in close agreement with labeled SPF, 13% of SPF values above the labeled amount and 54% SPF values under the labeled amount. According to our results, the significant difference observed between real and labeled SPF, the sample A, B, C and D have a difference of 51.3, 84.5, 88.1 and 47.1 respectively, when compared to SPF 100, 90, and 55. The samples of E, F, G, H and I have a difference of 1.5, 47.7, 44.8, 36.8 and 2.1 respectively, when compared to SPF 50. The samples of J, K, L, M, N and O have difference of -3.4, 0.6, 6, 0.2, 16.1 and -1.5 respectively, when compared to SPF 45, 30, 25, 20 and 15. The rheological profiles indicated that the all formulations are pseudoplastic as the shear rate increases the viscosity decrease. The pseudoplastic is desirable property needed by all types of sunscreens to produce a coherent protective film covering the skin surface and distributed active ingredients. The analyzed pH indicated, all samples have almost neutral pH, which is compatible with human's skin.

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