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# Spectroscopic scale protection factor (SSPF) of solar ultraviolet radiation molecular screens. I. Salicylidene compounds

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**Abstract**

We have found a new absolute scale of solar ultraviolet radiation protection factor for molecular screens, called spectroscopic scale protection factor (SSPF). This scale, based on the solar-action spectra of these molecular screens, is obtained under a 20° zenith angle of the sun actinic flux spectra at the earth's surface.

In order to compare this scale versus the usual sun protection factor (SPF) scale which uses homosalate (SPF = 4.2) as a standard compound, we have determined the electronic absorption spectral properties of a salicylidene compound series. Since these aromatic compounds present a good photostability behavior, a broad absorption band and a high molar absorption coefficient in the UV-A and UV-B regions, we have established their potential use as a solar ultraviolet radiation molecular screen according to the SSPF data. 

*Keywords:* Molecular screens; Sun protection factor (SPF); Salicylidenes; Spectral bands; Solar actinic flux

## 1. Introduction

It is a well known fact that a global depletion of the stratospheric ozone levels is occurring and will continue into the next century ([1–3]). Several world wide international organizations of meteorology, as well as universities and other centers for atmospheric research, have putforth significant efforts to organize monitoring network of solar ultraviolet radiation (SUR) at the earth's surface, and these SUR networks are mainly constituted by band spectroradiometers involving sensors of UV (total), UV-A (320 to 400 nm) and UV-B (290 to 320 nm). Therefore, a public awareness of the damaging effects of overexposure to the sun, as well as, the photochemical damage of different organic materials at industrial scale, are being considered as sources of new research in the interest to reduce these new solar problems at the earth's surface.

The solar photochemical damage on the organic material are caused predominantly by the ultraviolet region of the electromagnetic spectrum, particularly by the UV-B region, due to the absorption bands of a broad class of polymer compounds.

On the other hand, overexposure to UV-B causes skin cancer and has also been linked to a suppression of the human immune system, although recent research has shown that UV-A generate risk of skin cancer too ([4,5]). Therefore, protection against UV light can also be accomplished through the use of molecular screens in polymers when these materials are used directly as transparent polymer-glass to the UV-A solar radiation.

There is not a simple quantitative method for determining a photochemical protection factor between different molecular screens. At sunscreen level, there is a sun protection factor (SPF) concept, which is defined as the UV energy required to produce a minimal erythemal (sunburn) dose (MED) on protected skin divided by the UV energy required to produce a MED on unprotected skin ([6])

$$\mathrm{SPF} = \mathrm{MED}_{\mathrm{protected}}/\mathrm{MED}_{\mathrm{unprotected}}$$

The dose can be measured in intensity of light or in length of exposure, the latter being the more common method of SPF determination. The Food and Drug Administration in the USA has defined homomenthyl salicylate (homosalate) as a

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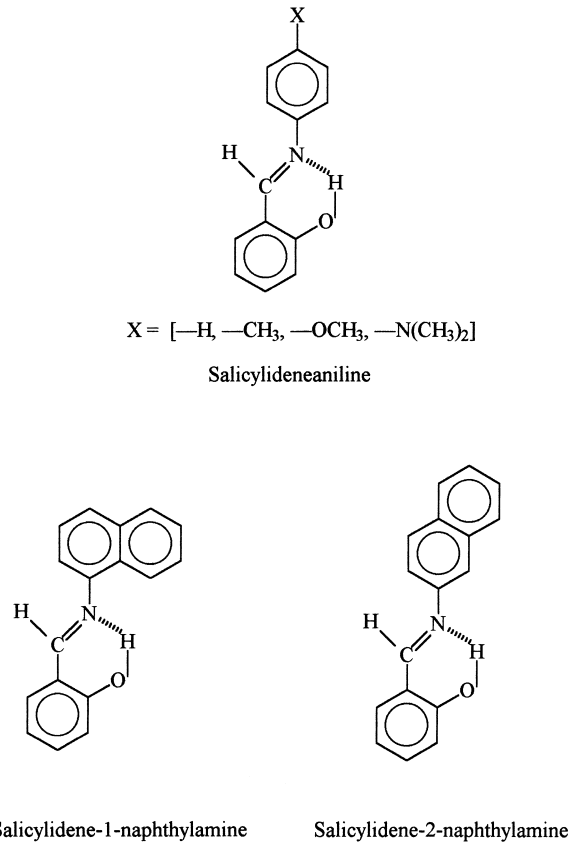


Fig. 1. Salicylidene compounds.

standard compound, where an emulsion with a given formula containing 8% of this compound has an SPF value of 4.24 ([7]).

Since this biological method, based on the skin exposure to the UV radiation, depends on several factors such as the skin type, the solar intensity variations skin response, the air and humidity conditions, etc., their usefulness is limited and only can be considered as a complex method for qualitative analysis.

During the last years, we have initiated a program of research about the photochemical stability of a series of organic aromatic compounds ([8,9]), and based on this systematic study, we have found good photostable systems such as the salicylidene compound series (Fig. 1) ([10]). Therefore, we have been interested to develop a physical method for classifying these compounds according to the UV-solar protection factor. Since the SPF biological method needs a referencial organic compound (homosalate), in the present work we have introduced a new concept denominated spectroscopic scale protection factor (SSPF), based on the integrated area of the action spectra (IAS) which is originated by the UV-solar spectrum and the absorption spectra of the compound under study.

In spite of the salicylidene compounds being irritants, and they cannot be used as topical compounds, their use is attractive in polymeric films or UV-transparent solid polymeric matrix. Therefore, we have applied this method to several molecular screen compounds derived of salicylidene, and from the SPF and the SSPF values we have determined the best photoprotector compounds.

## 2. Materials and methods

The salicylidenic Schiff's bases (Fig. 1) were synthesized by a condensation procedure stirring equimolar quantities of salicylaldehyde and the aniline in methanol solution ([11]). The synthesized compounds are: salicylidene (Anil-H), salicylidene-*p*-methylaniline (Anil-Me), salicylidene-*p*-methoxyaniline (Anil-OMe), salicylidene-*p*-dimethylamineaniline (Anil-$NMe_2$), salicylidene-1-naphthylamine (Anil-1-Napht) and salicylidene-2-naphthylamine (Anil-2-Napht).

Twice recrystallizations were done in methanol at low temperature. Each compound under study were structurally determined by infrared and $^1$H-NMR spectroscopy and physical properties were previously confirmed.

Reactives and solvents were purchased from Aldrich. The compounds were purified by sublimation before use and fresh solutions in ethanol were prepared for spectral registration. The absorption spectra were registered in a Perkin Elmer Lambda 11 UV/Vis at 20°C in quartz cells.

## 3. Results and discussion

In Table 1 we present the spectral absorption band maxima and the molar absorption coefficients of the salicylidene compounds.

In order to calculate the SSPF values for the salicylidenes, we have determined the action spectra of every compound under study. In this case, it is necessary to know the actinic UV-solar flux at the earth's surface (Io). In Fig. 2 we show the actinic flux at the earth's surface as a function of wavelength calculated by Demerjian et al. ([12]) at 20° zenith angle. This UV-solar spectral function has been simulated by means of a polynomial function ([13]) defined by $f_0(\lambda)$, where

$$f_0(\lambda) = a_4\lambda^4 + a_3\lambda^3 + a_2\lambda^2 + a_1\lambda + a_0$$

and the $a_i$ parameters are presented in Table 2. This polynomial function has been incorporated in every absorption spectrum $A(\lambda)$, as can be seen in Figs. 3 and 4 and the

Table 1
Spectral absorption band maxima and molar absorption coefficient of the salicylidene series

| Compounds | $\lambda_{max}$ (nm) | $\varepsilon$ (l/mol cm)$\times 10^4$ |
|---|---|---|
| Anil-H | 338 | 1.32 |
| Anil-Me | 341 | 1.50 |
| Anil-OMe | 349 | 1.99 |
| Anil-$NMe_2$ | 384 | 2.72 |
| Anil-1-Napht | 351 | 1.57 |
| Anil-2-Napht | 344 | 1.82 |

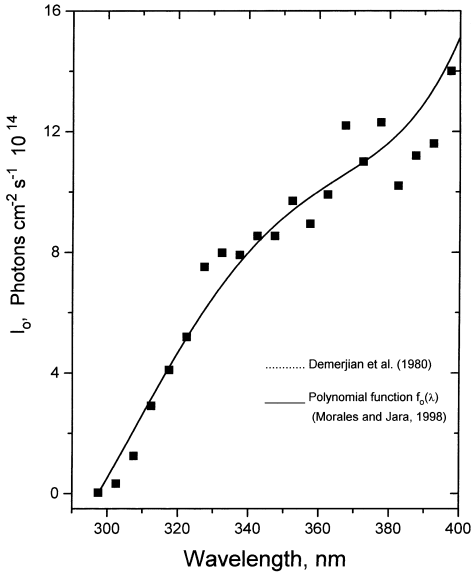


Fig. 2. Actinic flux at the earth's surface at 20° zenith angle $f_0(\lambda)$.

Table 2
$f_0(\lambda)$ Polynomial function of the actinic flux at the earth's surface at 20° zenith angle, where $\lambda$ is the UV-wavelength and $f_0(\lambda)$ is given by

$$f_0(\lambda) = a_4\lambda^4 + a_3\lambda^3 + a_2\lambda^2 + a_1\lambda + a_0$$

| Parameters | Value | sd |
|---|---|---|
| $a_0$ | 4234.0923 | 501.39877 |
| $a_1$ | −51.846146 | 5.78352 |
| $a_2$ | 0.23520611 | 0.02494 |
| $a_3$ | −4.693092E-4 | 0.00005 |
| $a_4$ | 3.4852772E-4 | 3.4022E-8 |

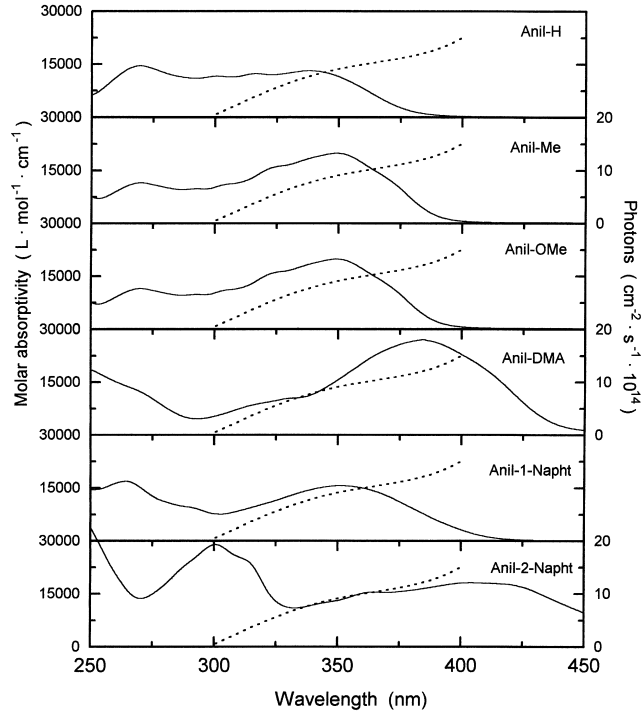


Fig. 4. Spectral absorption bands of salicylidene compounds (———) and the actinic flux at the earth's surface at 20° zenith angle (. . .).

integrated areas of the action spectra (IAS) for every compound under study have been calculated according to

$$\mathrm{IAS}_{\mathrm{compound}} = \int_{\lambda} A(\lambda) f_0(\lambda)\mathrm{d}\lambda$$

Obviously, we can generate a SSPF scale for different zenith angle polynomial functions of the actinic UV-solar flux at the earth's surface (Io), however we have chosen 20° zenith angle as the typical angle for the highest solar intensity at medium latitude. Anyway, since we are defining

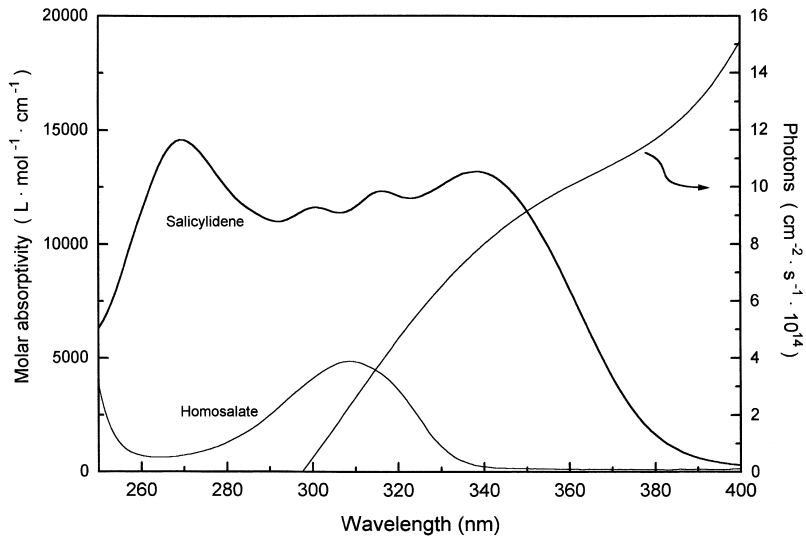


Fig. 3. Spectral absorption bands of salicylidene, homosalate and the actinic flux at the earth's surface at 20° zenith angle.

Table 3
Spectroscopic scale protection factor (SSPF) of salicylidene compounds

| Compounds | IAS $10^5$ | SSPF | SS(UV-A) | SSPF(UV-B) |
|---|---|---|---|---|
| Anil-H | 54.1 | 54.1 | 47.7 | 6.3 |
| Anil-Me | 64.9 | 64.9 | 58.2 | 6.7 |
| Anil-OMe | 96.5 | 96.5 | 89.8 | 6.7 |
| Anil-$NMe_2$ | 167.7 | 167.7 | 163.4 | 4.3 |
| Anil-1-Napht | 92.2 | 92.2 | 87.4 | 4.9 |
| Anil-2-Napht | 131.6 | 131.6 | 119.0 | 12.6 |
| Homosalate | 4.02 | 4.02 | 1.67 | 2.35 |

Table 4
Sun protection factor (SPF) relative to homosalate

| Compounds | SPF |
|---|---|
| Anil-H | 57.0 |
| Anil-Me | 68.4 |
| Anil-OMe | 101.7 |
| Anil-$OMe_2$ | 176.8 |
| Anil-1-Napht | 97.3 |
| Anil-2-Napht | 138.8 |
| Homosalate | 4.24 |

a spectroscopic scale protection factor, this zenith angle must be considered as a referencial data for the defined scale.

Thus, the integrated area of the action spectra permits us to generate a new scale of sun protection for molecular screens. If we consider the $IAS_{compound}$ divided by $10^5$, the magnitude order of the integrated area, we have a simple number (SSPF) that permits an easy comparison between different molecular screen compounds. Furthermore, we can define this protection factor on all the UV-spectral ranges, or in every UV-A and UV-B segments, i.e., we can determine an UV-A spectroscopic scale protection factor (UV-A SSPF) and an UV-B SSPF, in absolute units, without introducing a standard compound.

Contrarily to the SPF method, where it is necessary to consider a particular standard compound, homosalate, which has different optical behavior in both UV-A and UV-B regions, our SSPF scale permit us to compare molecular screens in terms of their absolute optical properties in both spectral ranges. By following our method can be used in order to establish a partial spectral range scale such as SSPF(UV-A) and SSPF(UV-B), according to

$$\mathrm{SSPF(UV\text{-}A)} = 10^{-5} \int_{\mathrm{UV\text{-}A}} A(\lambda) f_0(\lambda) \mathrm{d}\lambda$$

and

$$\mathrm{SSPF(UV\text{-}B)} = 10^{-5} \int_{\mathrm{UV\text{-}B}} A(\lambda) f_0(\lambda) \mathrm{d}\lambda$$

or determine the total solar ultraviolet spectral range (SSPF) as

$$\mathrm{SSPF} = \mathrm{SSPF(UV\text{-}A)} + \mathrm{SSPF(UV\text{-}B)}$$

In Table 3 we have calculated the corresponding SSPF, SSPF(UV-A) and SSPF(UV-B) for every compound under study, including the homosalate compound.

The sun protection factor (SPF) of the salicylidene compounds have been determined relative to homosalate (SPF = 4.2) in order to establish a standard comparison. Thus, these SPF were determined according to the following equation:

$$\mathrm{SPF_{compound}} = 4.2(\mathrm{IAS_{compound}})/\mathrm{IAS_{homosalate}}$$

where $IAS_{compound}$ and $IAS_{homosalate}$ are the integrated area of the action absorption spectra in ethanol of the (UV-A + UV-B) region. The SPF calculations relative to homosalate (SPF = 4.24) are shown in Table 4

From Table 4 it is interesting to observe that salicylidene *p*-dimethylamineaniline (Anil-$NMe_2$) and salicylidene 2-napthylamine (Anil-2-Naft) are the best protector molecular screens, being over 30 times bigger than homosalate.

Finally, we can establish that our SSPF data agrees to those of the classical SPF method, but, at the same time, our scale emerges as a more versatile and easier method than the older. Mainly, the versatility of our SSPF scale permits to determine the protection factor of the total and the both partial the UV-solar spectral ranges, without changing the magnitude order of the old scale.

New photostable compounds are being studied in order to determine these new spectroscopic scale protection factors.

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