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Study of Sunscreen Lotions, a Modular Chemistry Project

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Abstract The project described in this paper illustrates the spectrophotometric UV behavior of some representative chemicals used as sun blockers and some over the counter (OTC) sunscreen lotions labeled with different sun protection factor (SPF). The experiments have been carried out in three different solvents, Cyclohexane, Methanol and Dimethyl sulfoxide, which illustrate the solvent effect in the UV spectra. Indices of UV protection have been estimated from the ratios of the areas per unit of wavelength for each UV region (UVA-I, UVA and UVB). Higher indices of UV protection are obtained for higher SPF. The broad spectrum protection (UVA protection) has also been estimated from the critical wavelength value. All OTC sunscreen lotions studied comply with broad spectrum labeling, λ(crit.) ≥370 nm, while the sun blockers studied cannot be classified as such. When comparing the UV spectra for sunscreen lotions that have aged for one year with freshly produced sunscreen, a shift toward the UVB region for aged lotion can be observed. UVA/UVB ratio is the parameter of choice to describe the aging effect, while λ(crit.) is practically insensitive to aging. Sunscreen aging is accompanied by UVA protection failure and therefore renewing sunscreens each season is to be recommended. This project has been carried out for final year students in Chemistry and Pharmacy at different degrees of difficulty.

Keywords Sunscreens, Graduate Lab, UV spectroscopy

1. Introduction

Outdoor activities inevitably result in varying degrees of exposure to sun light. Tanned skin tends to be considered as an outward sign of success and prosperity. Moreover, sun light is well known to have some beneficial effects on health, for example in the bloodstream it increases the number of red blood cells and haemoglobin, as well as facilitates vitamin D3 synthesis through the activation of 7-dehydrocholesterol found in the epidermis [1]. However, excessive exposure is also responsible for skin damage, such as sunburns, aging, skin cancer, adverse effects on the immune system, etc. [2].

Fortunately, the human skin has a natural protection mechanism against solar radiation in the form of skin pigmentation via the formation of melanin. The UV radiation in sun light is mainly responsible for the immediate and persistent skin darkening stimulating the melanocytes, which produce melanin, the dark skin pigmentation. Melanin prevents the mutagenesis of cellular DNA by blocking absorption of UV radiation. Nevertheless, the degree of natural protection against UV damage depends on the skin photo-type and age. Children and young adolescents tend to be more vulnerable to UV radiation.

Solar radiation covers the wavelength range from 150 nm (Ultraviolet) to 4000 nm (Infrared) in the electromagnetic spectrum. The highest intensity falls in the range of visible light. UV radiation can be divided into UVC (200–290 nm), UVB (290–320 nm) and UVA radiation (320–400 nm). Only part of solar UV radiation reaches the Earth's surface, the intensity level is lower for shorter wavelengths and depends on the location, season, clouds and level of air pollution. UVC does not reach the Earth's surface as it is completely absorbed by the atmosphere. UVB radiation also is mainly absorbed by oxygen and ozone, thus the depletion of the ozone layer lowers the degree of absorption. The UVA constitutes 95% of UV radiation that reaches the Earth's surface. Furthermore, the penetration of solar radiation into the skin has an inverse relationship with the energy of the radiation, thus UVA penetrates deeper into the skin [3].

From the earliest times people have been using clothing, umbrellas and hats to avoid the solar radiation's adverse effects. However, the use of chemicals for sun protection was only first documented in the 20th century [4].

Thus, the protective chemicals, sun blockers, are typically applied to the skin as a lotion providing an external armor against the invisible UV radiation [5]. The protection mechanism is similar to that of natural solar protection, i.e. UV light absorption by molecules. The

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influence of substituent, solvent or pH on the wavelength of maximum absorption of chemical absorbers can be analysed based on simple molecular orbital theory. This absorption is linked to the energy gap between the frontier orbitals, occupied and virtual (HOMO and LUMO) [6].

Sun blocking chemicals may be classified according to the kind of protection they offer, either as physical blockers or as chemical absorbers.

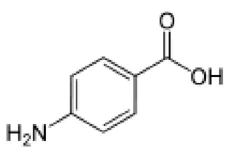
a) Inorganic (physical blockers).

The best-known inorganic UV filters are TiO_2 and ZnO particles. However, TiO_2 is the most commonly used in the UV filters. A maximum concentration of 25% in a UV filter is recommended for each. The known mechanism of physical sun blocking is through light reflection and scattering, but the small (Nano) particles can absorb part of the UV light [7].

b) Organic (chemical absorbers).

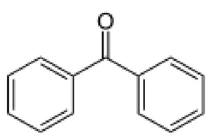
Organic UV filters include different substance classes (functional groups), which can be classified as UVA and/or UVB filters according to their specific absorption characteristics. They are usually aromatic compounds conjugated with double C=C bonds, having the electronic excitation energy in the UV range. The absorption range and their strength are affected by the position and type of substituents [6, 8].

- p-Aminobenzoate derivatives.



This group of derivatives was one of the first marketed as UV filters. Since 2008, most of them have been banned in the EU.

- Benzophenone derivatives.

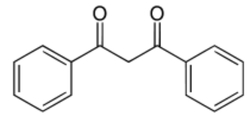


This large family of derivatives shows a very good photo-stability and can be classified as broadband protection over UVB and UVA ranges.

- Camphor derivatives.

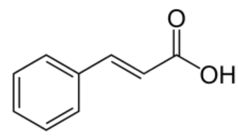
High photostability is a distinguishing feature of this group of derivatives. This property accounts for the fact that they are present in nearly one-third of commercial sunscreens.

- Dibenzoylmethane derivatives.



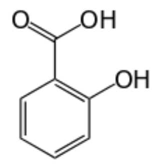
These derivatives are considered as good for UVA protection, but show some degradation in presence of sun light.

- Cinnamate derivatives.



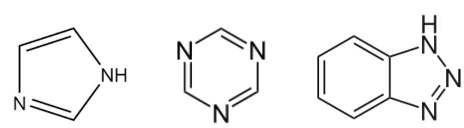
In spite of some photochemical instability, this group of derivatives is one of the most widely used in the manufacture of UV filters. In combination with other UV filters, high SPF values can be achieved.

- Salicylate derivatives.



These derivatives show good water resistance and low skin penetration, there are active in the UVB range.

- N-Heterocyclic derivarives (imidazol, triazin, benzotriazol …).



In order to maximize the effects of topically applied therapeutic drugs, the use of less than 500 Da molecular weight compounds is recommended, known as rule 500 Da [9]. This rule is now no longer strictly applied as new sunscreens are being developed with greater than 500 Da molecular weight. In this way, the absorption through the skin is avoided, minimizing the side effects.

The extension and abundance of the chromophores in these compounds provides protection across the entire UVB and UVA ranges.

These chemicals play an important protective role in skin health, and therefore their degree of effectiveness has to be controlled. The efficacy of sunscreen products for rating UVB (delayed sunburn) is primarily measured by the so-called sun protection factor, SPF, [10-12] which is the ratio between the minimum erythematic dose (MED) with sun block applied and the MED without sun block:

$$\text{SPF}=\frac{\text{MED(protected skin)}}{\text{MED(unprotected skin)}} \tag{1}$$

The SPF value should allow a direct and readily appreciated comparison. However, the “in vivo” SPF determinations depend on many and diverse parameters and criteria for selection of persons for testing, number of subjects, age, skin phototype, how sunscreen is applied and the source of irradiation and/or the time elapsed between exposure and evaluation of the redness of the skin. Furthermore, the "in vivo" method is expensive, time consuming and can raise some ethical issues. Thus, "in vitro" methods have been developed to avoid those difficulties. Nevertheless, there is no widely accepted "in vitro" method, mainly due to the substrate variability [13-16]. In the actual project, a simplified "in vitro" method based on FDA regulations has been used. Thus, different indices of UV protection have been obtained from the UV spectra in solution by computing the area per unit of wavelength:

$$\text{UV area per unit of } \lambda = \frac{\int_{\lambda_1}^{\lambda_2} \varepsilon(\lambda)\, d\lambda}{\lambda_2 - \lambda_1} \qquad (2)$$

where $\varepsilon(\lambda)$ is the extinction coefficient and $d\lambda$ is the wavelength interval between measurements. In fact, the UV area per unit wavelength represents the arithmetic mean of the extinction coefficient in the interval between λ_1 and λ_2.

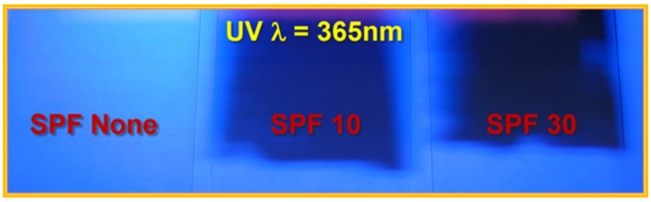


Figure 1. Picture of three glass plates covered with different SPF sunscreens illuminated with a black light from a counterfeit banknotes detector

The UV radiation and the SPF effect can be made visible using a simple UV black light (365nm) counterfeit banknotes detector. Picture in Figure 1 shows three glass plates impregnated with the same amount of sunscreen labeled with different SPF. A darker spot can be noticed when SPF is increased, indicating a higher degree of blocking UV radiation.

A recent review summarizes the regulatory status of different approved UV filters on the market, describing their beneficial and adverse properties and giving an overview of how the efficacy of sunscreens can be evaluated [17]. Studies on sunscreen have been published over time in some chemical education journals. They are pitched at different levels, from high school to graduate, and from different points of view, with varying emphasis on their analysis, synthesis and modelling [18-22]. Most of those papers are based on the analysis of specific absorbance at fixed wavelengths.

In this paper, some representative sun blocker chemicals and some over-the-counter (OTC) sunscreens lotions are analyzed by spectrophotometric UV analysis in three different solvents. Thus, the possible influence of the solvent can also be investigated.

The widespread use of these commercial products makes it worthwhile for students to study them, using simple methodology, from a chemical point of view. The level of complexity of the experimental procedure can be easily adapted to different educational levels, from showing the effect of UV light on sunscreens spread out on a glass plate to more detailed analyses using the spectral area under UV zones. This last analysis permits both the lotion's classification and sun protection capacity, i.e., protection A, B or broad spectrum, to be assessed. A predictable relationship between UV area and the level of SPF can also be obtained. Moreover, a peak shift toward the UVB zone for one year old (aged) sunscreens can be observed, indicating the importance of replacing them each season for better UVA protection.

Additional concerns about the use of sunscreens also come from their absorption into the skin and the free radical formation due to solar radiation (sunscreens radiation stability). Of even greater concern are the effects on the environment. Thus, the extensive usage of these OTC products in public bathing areas, with no restriction on their use and distribution, increases contamination of aquifers. Therefore, a reasonable use of these compounds is recommended to reduce environmental pollution.

2. Objectives

The use and application of UV-Vis spectroscopy is demonstrated by applying it to commonly available products like sunscreens. The importance of the dispersion medium is illustrated by using solvents that differ in polarity, permitivity and H-bond strength [23]. The observed solvatochromic effect forms a starting point for the discussion on how different solvents influence ground and excited states [24]. By using simple spreadsheet calculations, students can estimate and compare the "in vitro" protection efficiency for different chemicals employed. Moreover, the aging effect in the UV protection on the OTC lotions can be studied on the same brand of lotion by using products from previous seasons that have already expired.

3. Experimental

The experimental study has been carried out using chemicals, which are representative of UV blockers with different functional groups and using sunscreens obtained directly OTC with different SPF.

The chemicals investigated have been obtained from Sigma Aldrich [25]:

- 2-Hydroxy-4-methoxybenzophenone, CAS# 131-57-7, Benzophenone-3, Oxybenzone.
- 2-Ethylhexyl 4-methoxycinnamate, CAS# 5466-77-3, Octinoxate.
- 2-Ethylhexyl 2-cyano-3, 3-diphenylacrylate, CAS# 6197-30-4, Octocrylene.
- 2-Ethylhexyl 4-(dimethylamino)benzoate, CAS#

21245-02-3, Padimate O

Commercial sunscreens:

Lancaster Tan Deepener Dry Oil, SPF10 and SPF 15. Active UV components [26]:

- Bis-Ethylhexyloxyphenol Methoxyphenyl Triazine (CAS# 187393-00-6)
- Butyl Methoxydibenzoylmethane (CAS # 70356-09-1)
- Methoxycinnamate (CAS# 5466-77-3)
- Octocrylene (CAS# 6197-30-4)

Eucerin Daily Protection Face Lotion SPF 30. Active UV components [27]:

- Ensulizole (CAS# 27503-81-7)
- Octinoxate (CAS# 5466-77-3)
- Octocrylene (CAS#, 6197-30-4)
- Zinc Oxide (CAS# 1314-13-2)
- Titanium Dioxide (CAS# 13463-67-7)

Avène Stick 50+, one stick from the current season and other from the previous one. Active UV components [28]:

- Butyl Methoxydibenzoylmethane (CAS # 70356-09-1)
- Octocrylene (CAS# 6197-30-4)
- Bis-Ethylhexyloxyphenol Methoxyphenyl Triazine (CAS# 187393-00-6)
- Titanium Dioxide (CAS# 13463-67-7)

Three different solvents, analytical reagent grade, have been selected, one non-polar, Cyclohexane (Cx), and two having a polar character, one protic, Methanol (MetOH) and Dimethyl sulphoxyde (DMSO) as aprotic. The solvents were stored in amber bottles with a 4Å molecular sieve as dessicant.

The procedure for the solubilization of some samples was improved by using an ultrasound bath, product of Selecta [29]. The sunscreens with high degree of solar protection can include in their formulation TiO_2 and ZnO solid particles as inorganic sun blockers. Solutions having particles in suspension were filtered through a 0.45 µm Nylon filter to obtain clear working solutions.

In order to get absorbance values in the optimal range (0.5–1.5), a 100mL of stock solution approx. 10^{-3} mol/L for each compound and solvent were prepared and stored in amber bottles. From them, working diluted solutions (approx. 10^{-5} mol/L) were prepared to fulfill the optimal absorbance range in the corresponding solvent. In the case of sunscreens, the same absorbance criterion was observed, but the solution concentrations were expressed in g/L.

Spectrophotometric measurements were performed with a Shimadzu UV Spectrophotometer Mini-1240 controlled by UVProbe version 2.31 software. A digital UV spectrum can be easily stored on any common spreadsheet saved from a text file. If the spectrophotometer only generates the spectrum as a hard copy graphical output, it is possible to obtain the spectrum in digital format by scanning the spectrum image by using freely available digitization software like WinDig [30].

Hellma UV range Quartz Suprasil [31] precision spectrophotometric cells, with 10mm path length, were employed.

4. Results and Discussion

Experimental UV spectra were recorded from 250 nm to 400 nm every 0.5 nm for each compound in the three solvents. These spectra in digital format were stored on a spreadsheet, one for each compound. Using a spreadsheet template, included in the supplemental material, the spectra are transformed to allow a better comparison with the plot of molar extinction coefficient, ε, vs. wavelength, λ.

In this way, a direct comparison of the absorption capacity can be done independent of the actual sun blocker or sunscreen compound concentration. Figure 2 shows the spectra as ε vs. λ plots, for the Padimate O, CAS# 21245-02-3. The UVB (290–320nm) and UVA (290–400nm) regions are shaded in the plot.

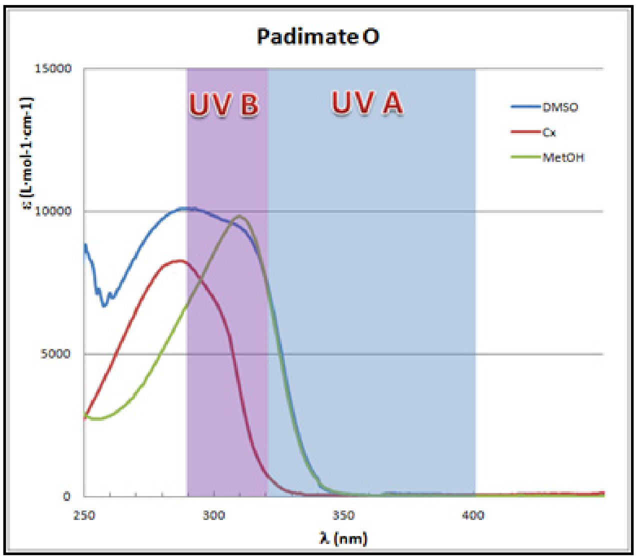


Figure 2. Padimate O UV-Vis spectra in different solvents

The extinction coefficient represents a measure of how strongly a chemical species attenuates light at a given wavelength. The area under the plot ε vs. λ in a UV wavelength range (per unit wavelength), provides a quantitative protection index against the UV radiation in the spectral zone, eqn. (2).

It is important to note that a constant amount of 2 mg per square centimeter of substrate [10] is applied, in agreement with FDA recommendations for in vitro testing of externally applied drugs. Thus, the area under the plot, ε vs. λ should be correlated with the UV protection in vitro. In fact, this protection index is close to that reported for in vitro testing in accordance with the FDA recommended procedure, since in both cases the estimated area is proportional to the mass or molar extinction coefficient.

Concentration		Weight/g	x ml to 10ml	
C (DMSO)(mol/L)=	2,54502E-05	0,0368	0,25	
C (Cx)(mol/L)=	2,90464E-05	0,0420	0,25	
C (MetOH)(mol/L):	2,69025E-05	0,0389	0,25	
			Mol. Weight	
			361,49	
Area	L/(mol·cm)	L/(g·cm)		
UV A (400-320)			Mean Area	
DMSO	1283,2649	3,55	1084,757	3,001
Cx	773,9759	2,14		
MetOH	1197,0291	3,31		
UV B (320-290)			Mean Area	
DMSO	10058,1973	27,82	7750,990	21,442
Cx	7044,1778	19,49		
MetOH	6150,5959	17,01		
UVA I (340-400)		L/(mol·cm)	Mean Area	
DMSO	543,7085	1,50	409,237	1,132
Cx	238,4113	0,66		
MetOH	445,5899	1,23		

Figure 3. Part of the Octocrylene spreadsheet snapshot displaying the calculated area under UV zones

Figure 3 shows a sample spreadsheet which reports the Octocrylene areas obtained for the three solvents in L/(mol·cm) and L/(g·cm). Those areas have been easily estimated on the spreadsheet using the trapezoidal rule. The trapezoid bases are the $\varepsilon(i)$ values, and the heights are $\lambda(i+1)$-$\lambda(i)$ = 0.5 nm, so each trapezoid area is:

$$\text{Trapezoid area} = \left[\varepsilon(i)+\varepsilon(i+1)\right]*\left[\lambda(i+1)-\lambda(i)\right]/2$$
$$\int_{\lambda_1}^{\lambda_2}\varepsilon(\lambda)\,d\lambda \cong \sum_{\lambda_1}^{\lambda_2}\text{Trapezoid area} \qquad (3)$$

Figure 2 shows the influence of solvent on the Padimate O UV ε vs. λ plots. Padimate O spectra for both polar solvents are shifted to longer wavelengths, i.e. a bathochromic shift.

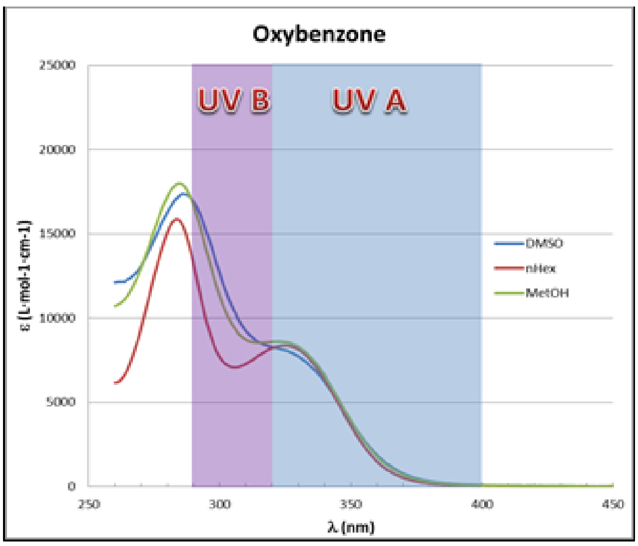


Figure 4. Oxybenzone UV-Vis spectra in different solvents

This is an indication of the different interaction with the solvent in the UV absorption process, that is, the solvatochromic effect. Thus, the energy in the electronic transition from ground state to the excited state is lower for polar solvents. In this case, the bathochromic shift implies that the excited state has a stronger polar character compared with the ground state, causing it to be stabilized in a polar environment [24]. Nevertheless, for other compounds the effect is absent as illustrated by the Oxybenzone spectra of Figure 4.

The UVA area in the case of Padimate O is more than 10 times larger in the presence of polar solvents. The solvatochromic effect should be taken into account in the design of a sunscreen were the media used in its formulation can have different degrees of polarity [23].

Thus, in this study, for each sample the mean value of three solvents spectral areas has been used as a measure of the degree of UV protection.

As can be noticed in Figures 2 and 4, the area under the part of the corresponding UVB zone is larger than that for the UVA zone for each solvent. This is a common feature of all the compounds and solvents studied.

Table 1. Mean Spectral Area of UVA and UVB for the Sun Blockers Studied

Blocker /Area	UVA-I	UVA	UVB
	L/(mol·cm)		
Octinoxate	328	3280	37500
Oxybenzone	1360	2980	10300
Octocrylene	409	1080	7750
Padimate O	71.4	643	7830

Table 1 summarizes the sun blocker's mean (three solvents) spectral areas per unit of wavelength for UVA-I (340–400 nm), UVA (320–400 nm) and UVB (290–320 nm) regions. Actually, these values are the arithmetic mean of the extinction coefficient in the specified UV range, see eqn. (2).

The four blockers studied present a stronger absorption in the UVB region than in the UVA. Octinoxate has the highest UVB absorption than the rest of the sun blockers studied, being approx. 5 times that obtained for Padimate O. Among them, Octinoxate and Oxybenzone have a distinct UVA; their values are 3 to 5 times higher than those for Octocrylene and Padimate O.

However, it is important to note the difference between the studied behavior of the compounds in the UVA-I and UVA zones. Octinoxate and Oxybenzone have nearly the same value for the UVA range. Nevertheless, in Octinoxate UVA-I the value drops one order of magnitude when compared to the value for the entire UVA range.

As stated earlier, the focus of the development of sunscreen lotions has shifted to broadband protection. This newly recommended criterion can be described quantitatively by using the ratio of the different UV zones and the full UV. In Table 2 are collected different UV area ratios for the sun blockers studied.

Table 2. UV Area Ratio for the Sun Blockers Studied

Blocker/ Ratio	UVA-I/UV	UVA/UV	UVB/UV	UVA/UVB
Oxybenzone	0.28	0.61	2.08	0.29
Octocrylene	0.14	0.38	2.68	0.14
Octinoxate	0.03	0.26	3.01	0.09
Padimate O	0.03	0.21	3.12	0.07

As can be expected the UV ratios obtained are independent of the use of the molar or mass extinction coefficient. So, this parameter can be used for direct comparison of both pure sun blockers and sunscreens, without having to specify a molecular weight. Thus, in the calculation of these parameters for OTC sunscreen products the extinction coefficient by mass has been used.

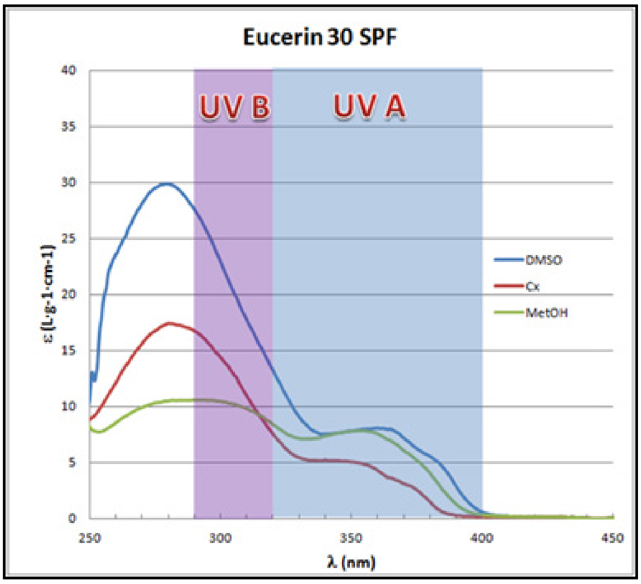


Figure 5. Eucerin SPF 30 UV-Vis spectra in different solvents

Using this parameter, the blockers that have better broad spectrum protection now are Oxybenzone and Octocrylene. Octinoxate and Padimate O have a low UVA-I/UV ratio in part due to their high UVB/UV ratio. In fact, these UV ratio parameters represent the ratio of the extinction coefficient, arithmetic mean, of one UV zone and another.

Figure 5 shows that the ε (in L/(g·cm)) vs. λ (in nm) plots for Eucerin SPF 30 have a marked contribution from the UVA spectral zone as is desirable for a broad spectrum sunscreen. Different values for the extinction coefficient can be observed for the different solvents with some solvatochromic effect.

Table 3 presents the mean spectral area for the sunscreens studied, expressed in L/(g·cm). It is clearly observed in Table 3 that the increase in the SPF for the two Lancaster lotions is correlated with an increase in the mean spectral area.

However, the mean values for the sunscreens having a higher SPF (Eucerin and Avène) are lower than that estimated for those with lower SPF. This can be explained by taking into account the fact that most sunscreens formulations have a combination of organic sun blockers with a concentration below the maximum amount legally allowed. When higher sun protection is necessary, the inclusion of the inorganic sun blockers ZnO and TiO_2 is a good choice because their concentration can reach values of 25% and even in many countries with strict regulations for cosmetics, there is no limit placed on the amount of these inorganic blockers. Their protection mechanism is different from that of the organic sun blockers, based as it is on light reflection and scattering by the solid particles rather than absorption. As was stated in the experimental section, the sunscreen solutions containing solid particles and suspensions were filtered. Therefore, it is not surprising to obtain lower mean values for Eucerin and Avène sunscreens. Nevertheless, after filtration the mean spectral area values for the different UV zones maintain strong UVA characteristics, as can be noted in Table 3.

Table 3. Mean Spectral Area of UVA and UVB for the Sunscreens Studied

Sunscreen/Area	UVA-I	UVA	UVB
	L/(g·cm)		
Lancaster 10 SPF	2.73	3.23	10.9
Lancaster 15 SPF	10.6	12.5	26.0
Eucerin 30 SPF	4.64	4.63	14.5
Avène 50 SPF (fresh)	5.46	6.30	11.8
Avène 50 SPF (aged)	3.66	3.53	11.6

In addition, it can be observed from Table 3 that for all sunscreens the mean spectral area for UVA-I and UVA have comparable values. As stated previously, this fact is in contrast with the values for the sun blockers studied. This is a consequence of the sunscreen's design being based on the recommendation of broadband protection.

Table 4. UV Area Ratios for the Sun Sunscreen Lotions Studied

Sunscreen/Ratio	UVA-I/UV	UVA/UV	UVB/UV	UVA/UVB
Lancaster 10 SPF	0.55	0.63	2.01	0.31
Lancaster 15 SPF	0.63	0.74	1.71	0.44
Eucerin 30 SPF	0.59	0.69	1.85	0.39
Avène 50 SPF (fresh)	0.72	0.83	1.48	0.58
Avène 50 SPF (aged)	0.60	0.67	1.89	0.35

Table 4 collects the UV area ratios for the sunscreen lotions studied. Looking at these values it is noted that the index of UVA-I protection falls within the range 0.55 to 0.72 which corresponds to a FDA classification of "Medium" to "High" protection [10].

As was stated before, another parameter that can be used as an indicator for the degree of UV protection is the critical wavelength, λ(crit.), up to which 90% of the cumulative area under the full UV spectrum (290–400 nm) is covered. A large critical wavelength is indicative of better UV protection. A product with a λ(crit.) $\geq$ 370 nm is considered to have broad spectrum protection. This parameter can be easily estimated from ε vs. λ plots stored as spreadsheets. Table 5 shows that λ(crit.) values for the sun blockers studied are between 315 nm and 345 nm. These low UV protection λ(crit.) values are in agreement with low UVA-I mean areas and UVA-I/UV ratios for these compounds. However, λ(crit.) values for all sunscreen lotions are consistent with their classification as providing broad spectrum protection. Moreover, their high values seem to be independent of the fact that inorganic sun blocker for sunscreen solutions with high SPF have been removed.

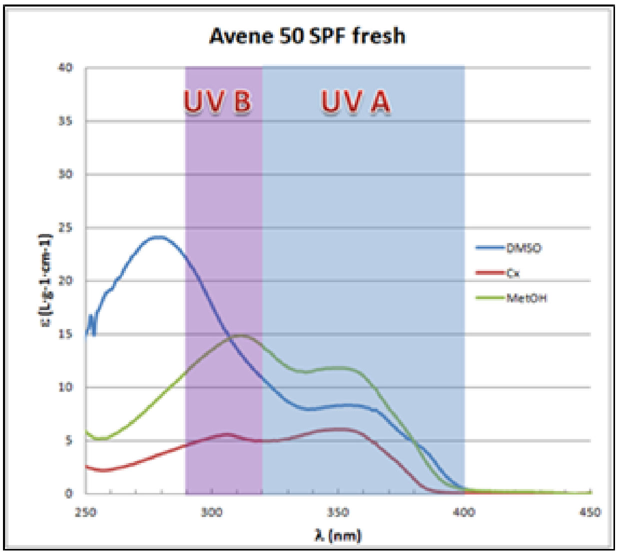


Figure 6. Avène SPF 50 fresh UV-Vis spectra in different solvents

Another interesting comparative analysis can be performed on the data collected corresponding to the Avène sunscreen lotion under aging conditions, one product freshly purchased and another from the previous year.

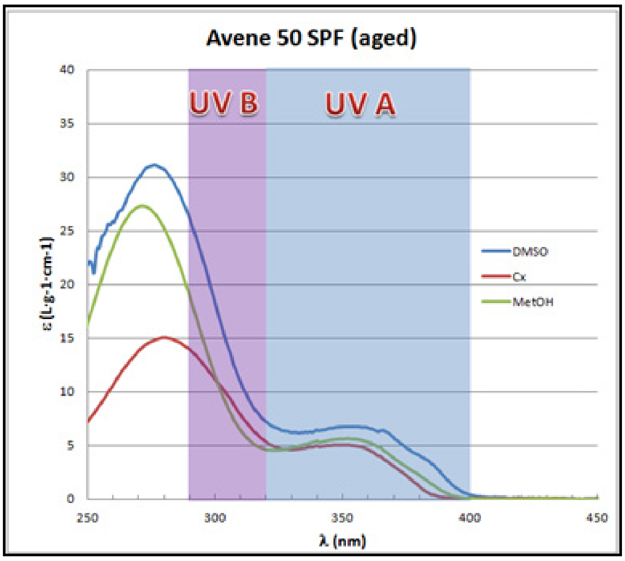


Figure 7. Avène SPF 50 aged UV-Vis spectra in different solvents

Figures 6 and 7, displays the ε vs. λ plots in different solvents for the fresh and aged product, respectively. These plots show that the ε in the UVA zone is lower for the aged product. The opposite occurs in the UVB zone, where the ε values are larger for the aged product. The data for Avène lotion collected in Tables 3 and 4 quantify these observations.

Table 3 shows the UVA-I and UVA mean spectral areas for fresh Avène are 5.46 L/(g·cm) and 6.30 L/(g·cm) respectively. Those values are significantly higher than those for the aged sunscreen, 3.66 L/(g·cm) and 3.53 L/(g·cm). Additionally, in Table 4, the UVA-I/UV, UVA/UV and UVA/UVB ratios are larger for the fresh product, indicating a better UVA protection for the recently prepared product. At the same time, the UVB/UV ratio is larger for the aged product.

A reasonable hypothesis that may explain the spectral variation over time is based on the gradual degradation of the sunscreen's active ingredients. The aging processes are usually related to chemical oxidation by atmospheric oxygen. The aging can occur by an oxidative cleavage of the double bonds in the sun blocker molecules, leading to a loss of double bond conjugation. The resulting products will have a lower contribution in the UVA region and an increasing one in the UVB region [6, 8].

Table 5. Critical Wavelength Ranges for the Sun Blockers and Sunscreen Lotions Studied

Sun blocker	λ(crit.)/nm	Sunscreen Lotion	λ(crit.)/nm
Oxybenzone	344–345	Lancaster 10 SPF	363–371
Octocrylene	332–340	Lancaster 15 SPF	364–373
Octinoxate	324–329	Eucerin 30 SPF	363–72
Padimate O	313–326	Avène fresh 50 SPF	367–371
		Avène aged 50 SPF	363–370

Also interesting to note is the low sensitivity of λ(crit.) values to aging, see Table 5. Figures 6 and 7 show that the greater increase in absorptive strength for the aged product takes place at wavelengths less than 290 nm, which are not taken into account in the λ(crit.) estimation of UV protection. Taking into account that UV ratios are calculated as ratios of arithmetic means, and that the UVB contribution is always greater than that of UVA, the UVA/UVB ratio will be more sensitive to aging than the UVA/UV ratio, see eqns. (4).

$$\frac{(\mathrm{UVA}/\mathrm{UV})_{\mathrm{Fresh}}}{(\mathrm{UVA}/\mathrm{UV})_{\mathrm{Aged}}} \approx 1.2; \quad \frac{(\mathrm{UVA}/\mathrm{UVB})_{\mathrm{Fresh}}}{(\mathrm{UVA}/\mathrm{UVB})_{\mathrm{Aged}}} \approx 1.7 \quad (4)$$

Thus, the aging effect displayed in Table 5 is better expressed by comparing UVA/UVB ratios. Therefore, in light of the fact of the sunscreen's aging significantly affecting the broad spectrum protection it should be strongly recommended to renew the OTC products every season.

5. Conclusions

This experimental study is proposed as a final year project for students of Chemistry and/or Pharmacy. Readily available lab equipment that is commonly employed, the relative ease with which these experiments can be carried out, together with the use of OTC products for everyday use, would make it a very attractive project for students.

The mean UV area by wavelength and the UV ratios are suitable parameters, which qualitatively and semi-quantitatively describe the UV blocking effect for both sun blockers' active components as well as OTC sunscreen products. It is worthwhile to take into account the influence of the solvent and/or excipients on the UV-Vis shift, as some products lose some of their UVA protection capacity in polar solvents. The procedure can be employed to compare fresh and aged OTC products, being the UVA/UVB mean area ratio the parameter of choice to characterize protection levels. The aging effect is more important in the UVA region. Thus, the use of freshly prepared sunscreens rather than reuse of aged stock from the previous season is recommended.

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