Saving Your Students' Skin. Undergraduate Experiments That Probe UV Protection by Sunscreens and Sunglasses

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In recent years, exposure to ultraviolet (UV) radiation has been linked to a number of human health problems, including sunburn, skin cancer, premature aging of the skin, cataracts, and immune suppression (*1–3*). At the same time, evidence of aerosol-induced damage to the earth's primary UV filter, the ozone layer, has increased (*4*), and skin cancer rates have risen to more than 900,000 cases per year (*5*), further intensifying concern over exposure to UV radiation.

UV radiation penetrates the ozone layer over two wavelength regimes, UVB (290–320 nm) and UVA (320–400 nm). UVB acts directly on biological molecules, causing skin cancer, skin aging, and the familiar delayed sunburn that arises 12–24 hours after exposure (*1*, *6*, *7*). In contrast, UVA acts indirectly through reactive oxygen species, causing an "immediate" sunburn that diminishes within 2 hours after exposure, and potentially plays a role in skin cancer and delayed sunburn (*6*, *7*).

Concern over such adverse health effects has led to the development of sunscreens and sunglasses, which provide the skin and eyes with UV protection. Sunscreens and sunglasses protect primarily by absorbing UV radiation, dissipating the absorbed energy as heat before it can damage photosensitive biological molecules (*8*, *9*). In addition, sunscreens and sunglasses may provide extra protection by reflecting or scattering UV radiation (*8*, *9*).

A sun protection factor (SPF) for rating the UVB (i.e., delayed sunburn) protection provided by sunscreens was developed in the 1970s by Plough (*10*) and was recently codified by the Food and Drug Administration (*11*). The SPF is defined by the ratio (*9*, *11*)

$$\mathrm{SPF} = \frac{\mathrm{MED(protected\,skin)}}{\mathrm{MED(uprotected\,skin)}} \tag{1}$$

An MED is the smallest dose (in $\mathrm{J/m^2}$) of UV radiation that produces a delayed sunburn on skin. In eq 1, "protected skin" means skin covered with 2 $\mathrm{mg/cm^2}$ of sunscreen, and "unprotected skin" means uncovered skin. The SPF also can be estimated from absorption measurements as the reciprocal of the effective transmission of UV radiation through the sunscreen (*11*, *12*).

Because UVA is not a primary cause of delayed sunburn, UVA protection is not well represented by the SPF. Industry attempts to develop simple, absorption-based methods to quantify UVA protection, such as directly measuring the fraction of blocked UVA rays, have met with resistance, provoking scolding from the FDA and litigation between rival sunscreen manufacturers (*10*). The FDA currently is attempting to identify a physiological analog of delayed sunburn to use in determining UVA protection (*13*).

The UV protection provided by the best sunglasses is much better than that provided by the best sunscreens. Many sunglasses now block close to 100% of both UVA and UVB, and the Skin Cancer Foundation's Seal of Recommendation for sunglasses soon will be bestowed only on those sunglasses that block at least 90% of both UVA and UVB rays (*14*). Ironically, while the FDA ponders what physiological response to use to quantify UVA protection by sunscreens, UVA protection by sunglasses is quantified simply in terms of the fraction of radiation blocked, using standards established by the American National Standards Institute (ANSI).

The purpose of this article is to describe absorption spectroscopy experiments that allow undergraduate science students to explore the mechanisms by which sunscreens and sunglasses provide UV protection. The experiments expose students to absorption phenomena in a familiar and engaging context with significant medical and environmental relevance.

Theory

The absorption of radiation can be described by the Beer–Lambert law (*15*, *16*),

$$-\log\left(\frac{I(\lambda)}{I_0(\lambda)}\right) = \varepsilon(\lambda)c\,l \tag{2}$$

which states that when radiation of wavelength λ passes through an absorbing sample, its intensity, I, decreases exponentially. Here $I_0(\lambda)$ is the intensity of the incident radiation at wavelength λ, $I(\lambda)$ is the intensity of the transmitted radiation, and $\varepsilon(\lambda)$ is the decadic molar extinction coefficient. The quantity $-\log(I/I_0)$ is termed the absorbance; it is simply the logarithm of the reciprocal of the fraction of transmitted radiation.

Materials and Methods

Sunscreens

The active ingredients in various commercial sunscreens were solubilized for absorption analysis by a simple alcohol extraction. A small amount of each sunscreen was combined with 2-propanol (isopropyl alcohol) in a disposable polypropylene centrifuge tube to yield a desired sunscreen concentration in the range 2.50–20.0 g of sunscreen per liter of 2-propanol. The mixture was shaken to suspend the sunscreen and then heated in a water bath to 45–50 °C for ~1 min,

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accompanied by mild agitation. The mixture was returned to room temperature and either centrifuged or allowed to settle overnight. The supernatant containing the active ingredients was collected for absorption studies. As a practical matter, the supernatant can be prepared in advance and stably stored for at least several months.

Absorbances were measured on a Hewlett Packard 8452A Diode Array Spectrophotometer using a standard quartz cuvette with 1-cm path length. For absorption experiments, the supernatant was diluted with 2-propanol to minimize scattering and to keep the absorbance within measurable limits. Typical dilutions of the supernatant were ~1:100, corresponding to total sunscreen dilutions in the range ~1:5,000 to 1:40,000 (and final sunscreen concentrations in the range ~0.025 to 0.20 g/L). Large sunscreen dilutions are required in our experiments because the thickness of a cuvette is much greater than the thickness of a typical layer of sunscreen applied to the skin. Corrections were made for possible absorption by the cuvette or solvent by subtracting the absorbance of a blank containing 2-propanol.

Sunglasses

The absorption properties of commercially available sunglasses were determined by placing their lenses in the light path of the spectrophotometer. Data were collected without removing the lenses from the frame, using air as a blank. All lenses were positioned normal to the light path to ensure consistent and minimal blockage of radiation by reflection.

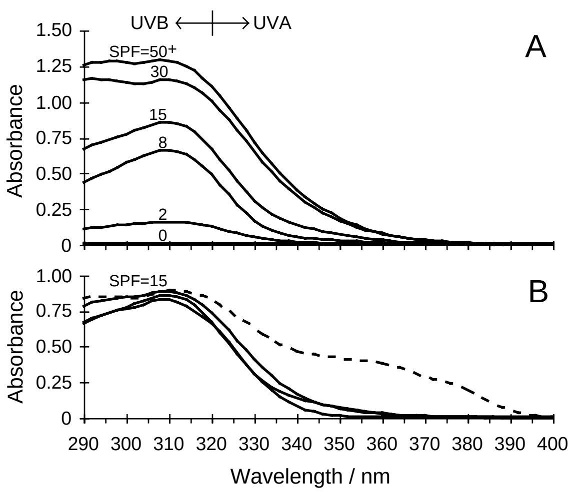

Figure 1. Absorbance vs wavelength for some commercial sunscreens. Sunscreens were extracted at 10.0 g/L and diluted 100-fold for absorption measurements. (A) Effect of SPF on absorbance spectra for various Banana Boat sunscreens. Data are shown for Baby Sunblock Lotion (SPF 50+), Sport Sunblock Lotion (SPF 30+), Sunblock Lotion (SPF 15), Sunscreen Lotion (SPF 8), Dark Tanning Oil with Sunscreen (SPF 2), and Sun Amplifier (SPF 0). The Sun Amplifier has zero absorbance; hence its absorbance curve lies along the horizontal axis. (B) Effect of brand on absorbance spectra. The three solid curves represent (without specific attribution) Oil of Olay Daily UV Protectant (SPF 15), Shade Oil-Free Gel (SPF 15), and Banana Boat Sunblock Lotion (SPF 15). The dashed curve represents Shade UVAguard (SPF 15). Banana Boat sunscreens are marketed by Sun Pharmaceuticals Ltd., Delray Beach, FL; Shade sunscreens are marketed by Schering-Plough HealthCare Products, Inc., Memphis, TN; and Oil of Olay sunscreen is marketed by Olay Company, Inc., Cincinnati, OH.

Results

Sunscreens

The absorption properties of various commercial sunscreens, each diluted to the same extent, are analyzed in Figure 1. Figure 1A shows absorbance spectra for a series of Banana Boat sunscreens with different SPFs. Data were highly reproducible, yielding errors of ≤ 2%. An increase in SPF is accompanied by two primary changes in the absorbance spectrum. First, the overall absorbance increases, reflecting either an increase in the concentration of active ingredients (*8*, *11*) or the substitution of ingredients that absorb a higher percentage of the incident radiation (i.e., that have a higher extinction coefficient) (*8*). Second, the shape of the absorbance spectrum changes, reflecting the addition of new ingredients with different absorption properties (*11*, *17*). The addition of new ingredients is necessary because federal regulations restrict the total concentration of specific compounds that can be found in a sunscreen; however, even if the limit on one ingredient is reached, another legally can be added (*11*, *17*).

Figure 1A also shows that the absorbance increases at an ever-diminishing rate as SPF is increased. This saturation effect is to be expected. The SPF can be estimated as the reciprocal of the effective fraction of UV radiation transmitted (*11*, *12*). This implies that absorbance should vary approximately logarithmically with SPF and that SPF 2, SPF 30, and SPF 50 sunscreens should absorb ~50%, ~96.7%, and ~98% of the incident burning UV, respectively. This relatively slow increase in absorbance at high SPF has caused high-SPF sunscreens to be labeled a consumer scam (*18*) and has led the FDA to propose that SPFs be capped at 30 (*11*). However, high-SPF sunscreens do attenuate the transmitted radiation as is required to justify their higher protection claims.

Different sunscreens typically contain different active ingredients, as shown in Table 1; this is true even if their SPFs are the same. Figure 1B shows absorbance spectra for four sunscreens from three manufacturers, each of which has SPF 15. Three of the sunscreens have nearly identical absorbance spectra despite having different compositions, and all four are similar in the UVB regime used in determining SPF. However, the Shade UVAguard has a much greater absorbance in the UVA, which reflects the presence of the UVA absorber Parsol 1789 (avobenzone). The reproducibility of the absorbance spectrum in the UVB shows that sunscreens with the same SPF provide the same level of protection, independent of composition. The reproducibility also indicates that the propanol is extracting essentially all of the UV-absorbing materials from the sunscreens.

Sunscreen data also can be used to introduce students to the Beer–Lambert law. Figure 2 shows the absorbance maximum plotted against sunscreen concentration for three different sunscreens. The data were fitted well by straight lines, confirming aspects of the Beer–Lambert law. The best-fit slopes decrease with decreasing SPF, reflecting the lower absorbance of lower SPF sunscreens. The absence of a plateau in the absorbance as sunscreen concentration is increased demonstrates that the extraction procedure is not saturating the alcohol over an eightfold range in extraction concentrations. This is particularly important to demonstrate for the high-SPF sunscreens.

In these experiments, the path length was fixed at 1 cm. However, students also could design experiments to measure absorbance as a function of path length.

Table 1. Active Ingredients of Sunscreens, by SPF Rating and Brand

Ingredient	Banana Boat, SPF Rating						Sunscreen, SPF 15			
	0	2	8	15	30+	50+	Oil of Olay	Shade Gel	Banana Boat	Shade UVAguard
Avobenzone (Parsol 1789)[a]										●
Ethylhexyl *p*-methoxycinnamate		●		●	●	●	●	●	●	
2-Ethylhexyl-2-cyano-3,3-diphenylacrylate						●				
2-Ethylhexyl salicylate					●	●				
Octyl methoxycinnamate										●
Octyl salicylate								●		
Oxybenzone[b]			●	●	●	●		●	●	●
Padimate O		●	●	●					●	
2-Phenylbenzimidazole-5-sulfonic acid							●			
Titanium dioxide						●				

NOTE: The first 9 ingredients are chemical sunscreens, which *absorb* UV radiation and dissipate the energy as heat. This is the primary process underlying UV protection by sunscreens. The 10th ingredient, titanium dioxide, is a physical sunscreen, which *scatters* UV radiation. Note that as the SPF increases the number (as well as the concentration) of active ingredients increases; and for a fixed SPF, the composition of commercial sunscreens can differ significantly, sometimes with little change in overall absorption characteristics (see Fig. 1B).

[a] UVA absorber, not included in the FDA's tentative final monograph on sunscreens (*11*).

[b] UVA absorber, included in the FDA's tentative final monograph on sunscreens (*11*).

Sunglasses

The absorption properties of various sunglasses are analyzed in Figure 3. Results are shown for four different glasses, including traditional glass sunglasses, plastic prescription sunglasses, and yellow-lensed "blue-blockers". All the glasses provide excellent protection in the UVB, absorbing more than 99.9% of the radiation in this wavelength regime. All also provide excellent UVA protection, significantly exceeding that available with the best sunscreens. UVA protection is especially good at shorter UVA wavelengths.

At longer UVA wavelengths, differences in the protection provided by the different sunglasses become apparent. If the glasses are not designed to block visible light, or if they are designed for good color rendition, their absorbance must be constant beyond ~400 nm. For this reason, absorption by the eyeglasses and conventional sunglasses falls off above ~350 nm. In contrast, absorption by the two yellow-lensed glasses is nearly constant through 400 nm.

Differences in absorption also are manifest for visible light. A flat absorbance profile in the visible indicates perfect color rendition, whereas a curved absorbance profile indicates color distortion. Good color rendition is provided by both the Ray Ban and plastic sunglasses, the former reducing the light intensity by about 90% over the entire visible spectrum.

Perhaps the most interesting difference in absorbance spectra is found between the Ambervision sunglasses and the Ray Ban Shooting Glasses, both of which have lenses that

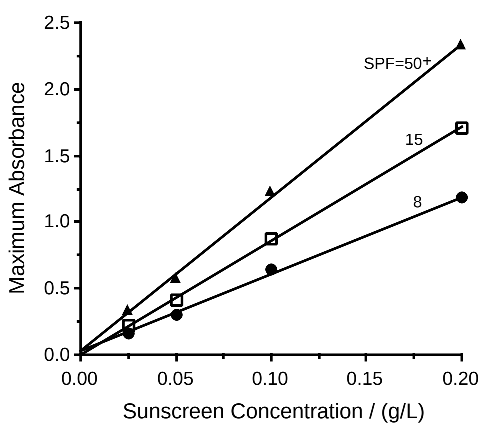

Figure 2. Maximum absorbance vs relative sunscreen concentration for various sunscreens. Sunscreens were extracted at 2.50–20.0 g/L and diluted 100-fold for absorption measurements. Data are shown for Banana Boat Baby Sunblock Lotion (SPF 50+), Shade UVAguard (SPF 15), and Banana Boat Sunscreen Lotion (SPF 8). Maximum absorbances were at 308, 312, and 310 nm, respectively. Data were fitted to straight lines. Fitting coefficients were ≥ .998; the best-fit slopes are 11.6, 8.5, and 5.8, respectively, in units of L/g.

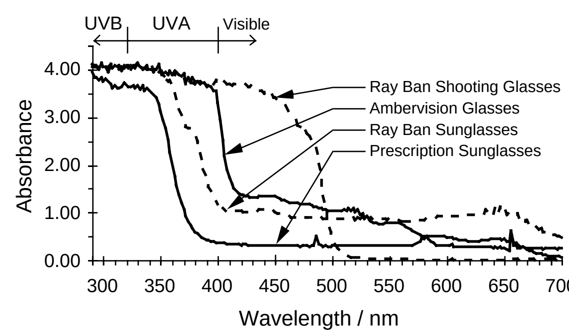

Figure 3. Absorbance vs wavelength for various sunglasses. Data are shown for Ray Ban Shooting Glasses, Ambervision sunglasses, Ray Ban sunglasses, and a pair of prescription sunglasses, as indicated. Lens thicknesses fell in the range 2.0–2.5 mm. Ray Ban glasses are marketed by Bausch and Lomb, Rochester, NY; Ambervision glasses are marketed by TeleBrands, Roanoke, VA. The prescription glasses were obtained at Four Eyes, Berkeley, CA.

are predominantly yellow. Both glasses are designed to improve clarity by blocking scattered light. Because atmospheric scattering is proportional to $1/\lambda^4$ (*16*), this means blocking blue light. The Ray Ban glasses block everything in the blue, out to ~500 nm; beyond this their absorbance is zero and nothing is blocked. In contrast, the Ambervision glasses block everything out to ~425 nm; beyond this their absorbance falls gradually to zero.

Discussion

Concern over UV-induced damage to the skin and eyes has led to a burgeoning market for sunscreens and sunglasses. Sunscreen sales alone now exceed $500 million per year (*18*). Along with these growing sales has come an interest in better quantifying and characterizing the UV protection provided by sunscreens and sunglasses and in developing improved products.

In many countries, and in this article, absorption spectroscopy is the method used to characterize UV protection. The appeal of this method is its relative simplicity and its clear relationship to mechanisms of action. Moreover, absorption spectroscopy measurements can yield results for sunscreen protection that are essentially equivalent to those obtained using the more complicated SPF methods mandated in the United States (*9*, *11*).

Potential Variations

The experiments described here provide a starting point for a variety of other experiments. First, the same methodology can be used to characterize the absorption properties of other materials, including car windows and special window coatings. Second, experiments analogous to those described can be performed on the individual active ingredients in sunscreens. For example, some sunscreen ingredients, such as oxybenzone, are available commercially, and their individual absorbance spectra thus can be obtained (*12*). Third, as noted under Results, a pseudo-Beer's law analysis of commercial sunscreens can be used to correlate absorbance at one wavelength with sunscreen SPF (*12*). Finally, the composition of sunscreens can be determined by standard analytical techniques, such as chromatography (*19*).

Absorption by sunscreens can also be measured without using a cuvette. A small amount of sunscreen can be spread onto transparent packing tape at the 2 mg/cm^2 dose used in SPF determinations and the sunscreen absorbance measured through the tape (*11*, *20*). The relatively low UV absorbance of the tape can be eliminated by using the tape as a blank. The disadvantages of this method are that it is difficult to apply films of sunscreen that are even and reproducible, and that the nonactive lotion ingredients of the sunscreen can cause scattering that complicates the signal.

Potential Pitfalls

Several criteria must be satisfied for the sunscreen studies to yield accurate results. First, the cuvette employed for the sunscreen studies must not absorb significantly in the UV. A variety of commercially available quartz cuvettes satisfy this criterion. Second, the concentration of photoabsorbant (active) material must be high enough that a measurable amount of the incident radiation is absorbed, yet low enough that a measurable amount of radiation reaches the detector. Ideal absorbances lie in the range of 0.1 to 2.0 (*15*). Outside this range, the differences between different sunscreens will be more difficult to discern. With typical sunscreens, good signals can be obtained with sunscreen-to-solvent dilutions of ~1:10,000.

In addition, if the sunscreen concentration is too high, or if the photoabsorbant materials are not extracted and analyzed separately, insoluble materials can cause scattering that contaminates the absorption signal. A scattering signal is readily identified by its persistence into the visible, where the active ingredients in the sunscreens do not absorb. Scattering can be minimized by reducing the concentration of scatterers. Some sunscreens (such as the Banana Boat 50+ analyzed here) contain compounds, typically inorganics such as zinc oxide and titanium dioxide, that function by scattering or reflecting incident sunlight rather than absorbing it (*8*, *9*, *11*).

Absorbance by sunglasses cannot be optimized by dilution. Thus, for wavelengths where the absorbances of all sunglasses exceed the maximum measurable on the spectrophotometer ($A_{max} \approx 4$ for the Hewlett Packard 8452A), performance cannot be distinguished. However, since an absorbance of 4 corresponds to 99.99% absorption, this is not a significant limitation.

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