Experiment 8

Sunscreens

or

How I learnt to stop worrying and love UV radiation
The Task
In this experiment you will examine the ability of various commercial sunscreens to absorb UV radiation.

Skills
At the end of the laboratory session you should be able to:
• prepare a sample and run a UV spectrum,
• prepare solutions of various relative concentrations.

Other Outcomes
• You will gain an understanding of how sunscreens protect us from the sun.
• You will gain an understanding of the various wavelengths of UVA, UVB and UVC radiation and the different abilities of sunscreens to absorb them.
• You will verify the Beer-Lambert law.

The Assessment
You will be assessed on your ability to perform a baseline correction when running a UV spectrum.
Introduction

The sun is a yellow dwarf star approximately $1.5 \times 10^8$ km distant from Earth. The light emitted by the sun can be approximated as that of a black body with a surface temperature of $\sim 5250 \, ^\circ C$, the temperature of its photosphere.

While this spectrum peaks in the visible, a significant proportion of the sun’s radiation is emitted at ultraviolet (UV) wavelengths. This ionising radiation has been known to cause skin cancers in humans, including the lethal malignant melanoma. In 2005 there were 10,684 new cases of melanoma diagnosed. In that same year, melanoma was responsible for 1272 deaths.

Scientists can be exposed to additional sources of UV radiation, including ultraviolet lamps and UV lasers (such as Excimer lasers or frequency doubled lasers). Several such lamps and UV lasers are used in the School of Chemistry.

**Types of UV radiation:**

Ultraviolet radiation is often broken up into 3 subtypes, based on its wavelength and the risk that is posed.

**UVA: 400 nm - 315 nm:** The least harmful subtype of UV. UVA reportedly causes such adverse effects as loss of collagen, a decrease in the quantity of blood vessels and an alteration of connective tissue of the dermis. While protection from UVA is desirable, it is not included in SPF ratings for sunscreens.
**UVB: 315 nm - 280 nm:** This radiation is responsible for tanning and sunburn and is the class of radiation most responsible for skin cancers.

**UVC: 280 nm - 100 nm:** While this form of radiation is highly dangerous, it is absorbed by the atmosphere and therefore poses a limited threat. Most UVC is absorbed in the ozone layer, due to the photodissociation of ozone.

\[
\text{O}_3(g) \xrightarrow{\text{UVC}} \text{O}_2(g) + \text{O}(g)
\]

Therefore, in areas where the ozone layer has been depleted (such as at the Earth’s poles) UVC can represent a serious hazard. In the late 20th Century, as a direct result of the danger posed by UVC radiation, international legislation was introduced controlling the use of ozone depleting chemicals.

**Sunscreens**

The body’s natural defence against UV radiation is melanin, a complex aromatic polymer synthesised in cells called melanocytes in response to UVB radiation. It is a brown-black pigment that absorbs harmful UV radiation and converts its energy into heat. To reduce the risk of skin cancer and sunburn, many humans use protective clothing, glasses and chemical sunscreens whilst in the sun. Sunscreens work in a similar fashion to melanin - they form a layer above the skin which absorbs dangerous UV radiation. They are rated by a sun protection factor, SPF.

\[
\text{SPF} = \frac{\text{MED for skin with sunscreen (2 mg cm}^2\text{)})}{\text{MED for skin without sunscreen}}
\]

where “minimal erythemal dose” (MED) is the length of time that one can stay in the sun before getting sunburnt.

Figure 2: Molecular structures of some compounds allowed in Australian sunscreens

See Skill 13 if you need help interpreting the above structures.
Safety

Chemical Hazard Identification

2-propanol - flammable, avoid contact with your skin.
commercial sunscreens - non-hazardous

Risk Assessment and Control

Low risk.

The UV spectrophotometer (obviously) emits dangerous UV radiation. Follow the operating instructions carefully.

When using the UV lamps (Part E), do not look directly at the UV light nor place your hands under the light.

Waste Disposal

All solutions are to be placed in the residues container provided.

Experimental

This experiment is to be carried out in groups of 4.

Part A  UV Spectra of Sunscreens

Measurements will be made with a UV spectrophotometer which is located in the Instrument Room at the back of the laboratory. Full operating instructions for these instruments can be found in the Appendix 18.1 of this experiment (page E18-8). Other important considerations are:

•  The special cuvettes are made of silica and are transparent to UV radiation. They are fragile and expensive so handle them with care. Handle them by the opaque sides only - do not touch the transparent windows of the cuvettes

•  Make up all solutions in the main laboratory - fill and empty the cuvettes before entering the instrument room. Do not make a mess in the Instrument Room.

A1)  Turn on the spectrophotometer - it takes about 10 minutes to warm up.

A2)  Perform a baseline correction as follows. Insert a cuvette containing 2-propanol. Set the wavelength range to 500 - 190 nm. Push F1. (It takes several minutes to run a spectrum, so move onto (A3) whilst you’re waiting.

A3)  You have a series of commercially available sunscreens. In small labelled 25 mL conical flasks dissolve the amount of sunscreen that covers the end of a toothpick in ~15 mL of 2-propanol. Do this for each sunscreen. Note: The zinc cream doesn’t dissolve properly, but enough enters solution to take a spectrum.
(A4) Record the UV - spectrum of each sunscreen. If the absorbance overflows (is “maxed out”), no reading is possible and you need to dilute the sample and try again. **Record your observations in your logbook.** Pay particular attention to any areas where the sunscreen does and does not absorb.

**For your logbook**

*Rate all the sunscreens on their ability to provide protection against UVA and UVB?*

*Does the tanning oil provide any protection from the sun?*

*Which sunscreen(s) would offer the best protection in Antarctica? Why?*

*The laser spectroscopy lab in the Madsen Building has lasers with the following wavelengths: 355 nm, 308 nm, 266 nm, 248 nm and 193 nm. Would any of the sunscreens provide protection for all these wavelengths from diffuse reflected light from these lasers?*

**Part B  Concentration dependence**

The absorption of radiation can be described by the Beer-Lambert law,

\[ A = \varepsilon cl \]

where \( A \) is the absorbance, \( c \) is concentration, \( l \) is the path length and \( \varepsilon \) is a constant called the molar extinction coefficient.

(B1) Take one of the samples and make a series of dilutions (Skill 4.5) to give 4 new concentrations - the most dilute should be about 5 - 10 % of the concentration of the initial sample. **Record the various relative concentrations in a table in your logbook.**

(B2) Record the UV spectrum of each of these samples.

(B3) Select a particular wavelength and graph the absorbance versus concentration for all five spectra.

**For you logbook**

*How does your graph agree with the Beer-Lambert law?*

*How does this relate to the practicalities of use of commercial sunscreens?*
Part C  The case of the serial killer

You are now part of the forensic team on the trail of a notorious serial killer. He must clearly be stopped. The investigation has narrowed the suspects down to Billy and Bob.

A white singlet top, believed to belong to the killer, was found at the last murder site. A quick examination revealed that the singlet is covered in coconut oil. A search showed that Billy had Reef dark sun tan oil in his sports bag and Bob had LeTan coconut sunscreen oil (SPF4) in his kitchen. A fabric sample from the top is provided.

(C1) Using your forensic kit of 2-propanol, a test tube, a pair of scissors, a stirring rod, a dropper, a paper clip, a rubber band and a UV-Vis spectrophotometer, identify the murderer and make the world a safer place.

Part D  Eye protection

The eyes of humans are also susceptible to ultraviolet radiation. To determine what protection is provided record the absorption spectra of safety glasses, sunglasses and regular glass and silica.

(D1) Run a new baseline correction with nothing in the beam path (i.e. no cuvette).

(D2) Place the material in the beam path and record the spectrum. To run the silica spectrum, use an empty cuvette. To run the glass, use a conical flask with the neck in the beam path.

(D3) Pay attention to the wavelengths at which the material is opaque.

For you logbook

What glasses provide protection for UVA, UVB and UVC?

Which glasses provide protection against diffuse reflections from the lasers mentioned in Part A? (This is important as even diffuse reflections from class IV lasers can cause eye damage.)

Part E  The science of practical jokes

You and a friend are to attend a party that will take place under black lights. Your friend is planning to wear his finest white shirt which he has asked you to collect from the dry cleaners. You, however, have a reputation as a practical joker to uphold and plan to write an embarrassing message on his shirt in sunscreen. Will the trick work or will you merely have wasted perfectly good sunscreen? Test your theory using the UV lamps provided.

References:
Appendix 8.1

Operating Instructions for the SHIMADZU UVmini-1240 (Room 218)

THE CUVETTES
1. Two special cuvettes will be issued to you by your demonstrator.
2. They are made of silica and are transparent to UV radiation. They are fragile and expensive so handle them with care. Handle them by the opaque sides only - do not touch the transparent windows of the cuvettes.

START UP
1. Switch on via the power switch located on the back of the instrument.
2. Allow the spectrophotometer to warm up (up to 10 minutes).
3. When the instrument is ready, a list of the instrument’s functions, titled “Mode Menu” is displayed on the screen.
4. Press 2 on the keypad to select spectrum measurement mode. The following reminder appears:
   Caution!
   Please correct baseline data before measurement.
5. Press Enter to proceed.

CHANGING PARAMETERS
1. To change between absorbance (ABS), % transmittance (T%) or energy (E) measurement modes, press 1 to display the menu containing the options: ABS, T% and E. Use the ↑ and ↓ arrow keys to select the desired mode, then press Enter.
2. To select the wavelength range of 500 nm - 190 nm, press 2 and then key in 500 enter followed by 190 enter.

BASELINE CORRECTION
1. For baseline correction, place the blank sample into the instrument and press F1 to measure the baseline.

SAMPLE MEASUREMENT
1. After the instrument indicates that baseline measurement is complete, replace the blank with the sample to be measured and press [Start/Stop] once.
2. The printer automatically prints the spectrum after each measurement.
3. To re-print the spectrum, press Print while the spectrum is still displayed on the screen.

INSTRUMENT SHUTDOWN
1. If you are the last person to use the instrument for the session, make sure it is switched off, firstly at the back and then at the mains.
2. Make sure both cuvettes have been rinsed clean and returned to your demonstrator.