Cyanotypes and sunscreens

Several years ago, we published a Bulletin article about the cyanotype process [1], an obsolete photographic process that is ideal for the classroom. As it used inexpensive iron salts and can be handled and developed in a laboratory without the need for a darkroom.

Here we share a variation of this process, developed in association with St Andrew's University [2], that can be used in place of UV beads for teaching about ultraviolet light and sunscreens.

Background

Sun cream protects our skin from harmful damage caused by ultraviolet radiation (UV). Exposure to UV light can result in molecules gaining sufficient energy for bonds to be broken. When UV light breaks bonds, free radicals are formed. Free radicals have unpaired electrons and, as a result, are highly reactive.

Sun cream contains compounds that absorb the UV light so that free radicals are not formed, therefore reducing/preventing damage to the skin. This experiment demonstrates the absorption of UV light using different strengths of sun cream against a control.

It uses a light sensitive solution (based on that used in the cyanotype photographic process) which changes colour from green to dark blue on exposure to UV light.

You will need

- Ethanedioic acid solution (8 g per litre)
- Potassium hexacyanoferrate III solution (30 g per litre)
- Iron III nitrate solution (12 g per litre)
- Petri dishes (or beakers)
- Source of UV light
- Sun cream
- Bottle wrapped in aluminium foil for the combined reagent
- Colorimeter

Health & safety

Iron III nitrate and potassium hexacyanoferrate III are irritant to skin, eye and respiratory system while ethanedioic acid is harmful if swallowed or in contact with skin. Avoid raising dust when making up solutions and wear eye protection and possibly gloves. The solutions are of low hazard.

Preparation

1) Make up the three solutions to the concentrations given above. For each test, you need about 20 cm^3 to cover the bottom of the Petri dish, so for 3 samples and a control you will need:
   - 40 cm^3 of ethanedioic acid solution
   - 1 cm^3 of potassium hexacyanoferrate III
   - 40 cm^3 of Iron III nitrate solution
2) Put 40 cm^3 of the ethanedioic acid solution in the light-proof bottle.
3) Add 1 cm^3 of the potassium hexacyanoferrate III to the oxalic acid solution.
4) Add 40 cm^3 of iron III nitrate solution to the reagent bottle and swirl to mix.
5) If using Petri dishes, wrap the bottom half of each in aluminium foil to prevent light coming in through the side. (Or use any other method to light-proof it).
6) Leave one of the lids untouched and apply sunscreen to the other three. Try to ensure you add the same amount of sunscreen in each case.

The experiment

1) Pour about 20 cm^3 of the combined reagent into each Petri dish, replace the lids and then expose to the light source.

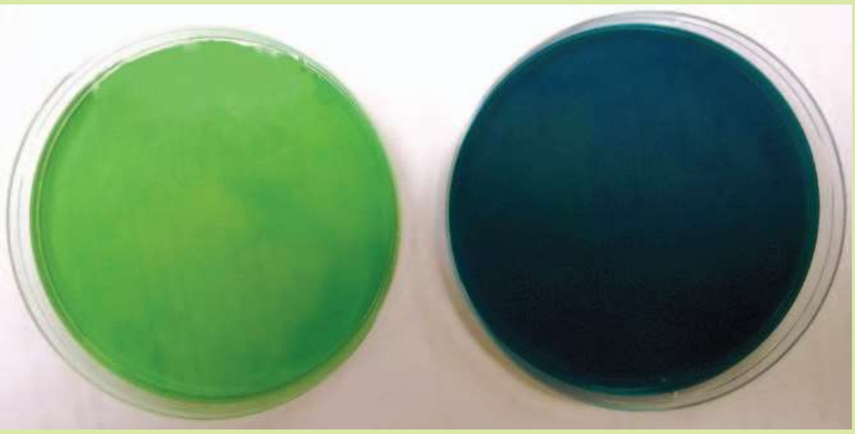


Figure 1 *- The colour changes.*

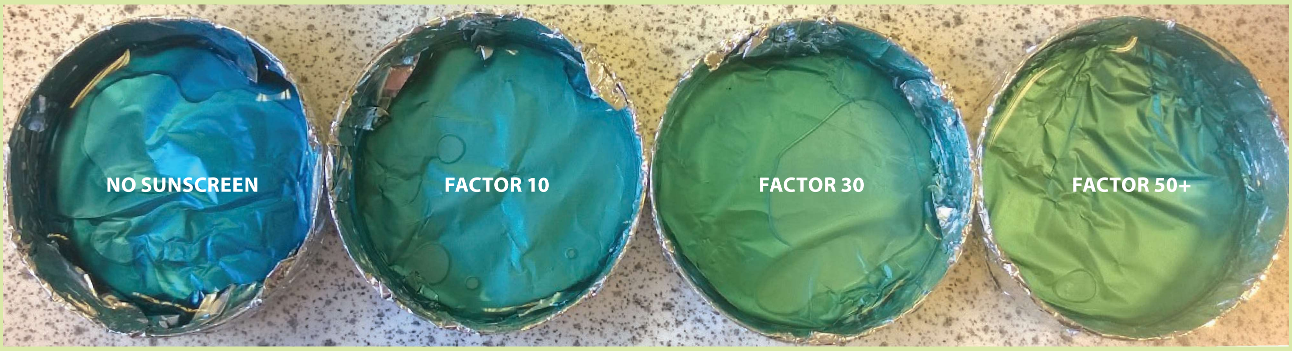


Figure 2.

The easiest way to make sure they all receive the same level of exposure is just to put all of them on the same window ledge.

2) Within a minute or two, depending on the light, you will see a dark blue colour appearing. The more UV light the dish is exposed to, the darker blue the solution will become (Figure 1).

3) In order to get some quantitative data, after a set time (which will be determined by the particular conditions) remove the dishes from the light source and transfer 3 cm^3 samples of each solution to cuvettes for reading in a colorimeter. Make sure you stir the solutions before taking the sample as the Prussian blue is insoluble and actually forms a suspension of very fine particles. The colorimeter should ideally be using a yellow filter. If using the Mystrica colorimeter, select the red LED.

Results

The bases of small Petri dishes were covered with aluminium foil to prevent light leakage.

The lids were covered as follows with as even a layer of sunscreen as possible with fingers using a 'blob' the size of a small pea. No sunscreen; Sainsbury's Factor 10, Sainsbury's Factor 30, Nivea Factor 50+ (Figure 2).

10 cm^3 of solution was placed into each Petri dish and it was placed in the dark prior to exposure while the other samples were prepared.

Coating	Absorbance
No Sunscreen	2.27
Factor 10	1.665
Factor 30	1.340
Factor 50+	1.137

***Figure 3** - The result table.*

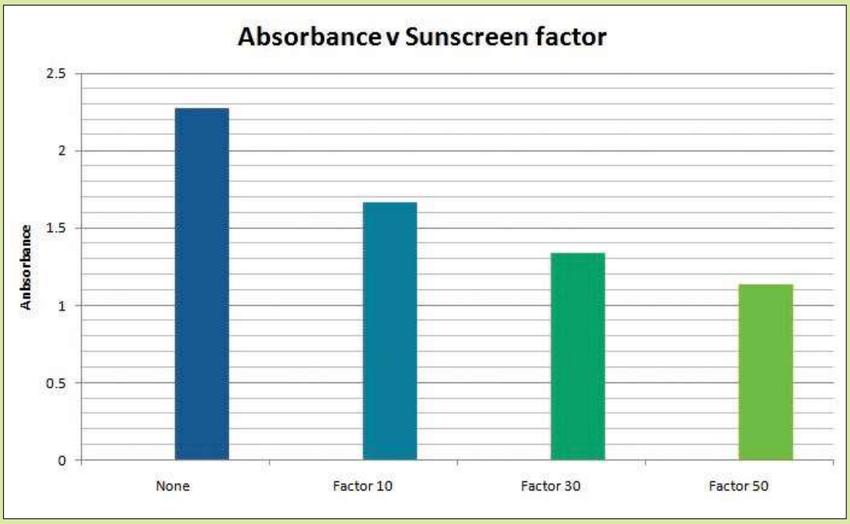


***Figure 4** - The result graph.*

All 4 Petri dishes were placed on the same windowsill for 2 minutes and then removed to more subdued lighting for analysis.

3 cm^3 from each Petri dish was transferred to a cuvette using a Pasteur pipette and the absorbance was taken using a Mystrica colorimeter with the blue LED (465 nm).

The results (Figure 3 and 4) clearly show that increasing the factor of the sunscreen reduced the amount of UV light reaching the solution.

Discussion

In 1842, William Herschel invented a photographic process using iron salts like this. It was called the cyanotype process and was very successful for a short period of time until the more sensitive silver emulsions were invented. The pictures produced are monochrome in shades of blue - from where we get the word blueprint.

The colour is known as Prussian Blue since it was first isolated in Germany. Prussian Blue is essentially iron(III) hexacyanoferrate(II) but there exists a whole range of such iron blues, having compositions which depend on their precise method of preparation. At the molecular level, they all have in common a characteristic cubic structure, but this lattice can accommodate variable amounts of water and metal ions within it, so formulae range from $KFe[Fe(CN)_6].5H_2O$ to $Fe_4[Fe(CN)_6]_3.15H_2O$.

Interaction of light with the ethanedioate ions leads to their oxidation and releases carbon dioxide and an electron (equation a) which then reduces Fe(III) to Fe (II):

a) $C_4H_4O_6^{2-} + hv = 2CO_2 + 2C(OH_2) + 2e^-$
b) $Fe^{3+} + e^- = Fe^{2+}$

The Fe(II) formed combines with CN^- present in the solution to form the complex $[Fe(CN)_6]^{4-}$ which, in turn, gives the insoluble blue Prussian blue, $Fe(III)_4[Fe(CN)_6]_3$:

c) $Fe^{2+} + 6\,CN^- = [Fe(CN_6)]^{4-}$
d) $[Fe(CN_6)]^{4-} + 4\,Fe^{3+} = Fe(III)_4[Fe(CN_6)]_3$

Turner *et al* [3] have determined that the cyanotype reagent responds to all three sections of the UV spectrum, A, B and C as well as to violet light to some degree.

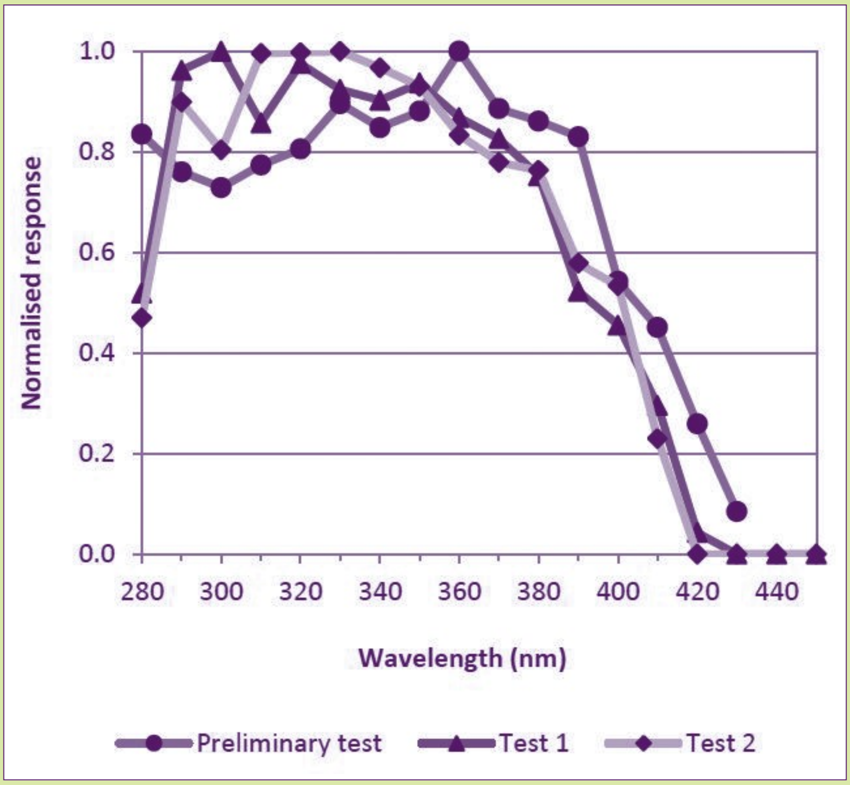


***Figure 4** - Sensitivity of cyanotype paper: Turner et al [3].*

References

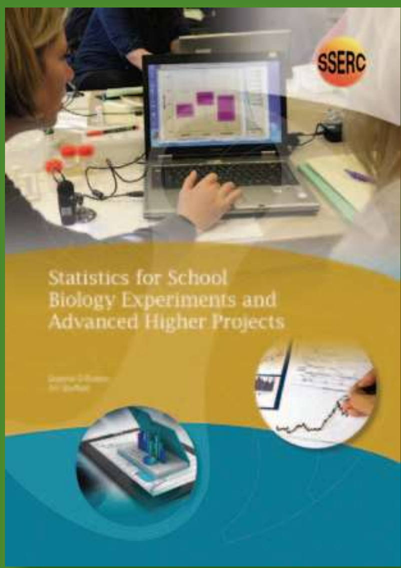
[1] SSERC Bulletin, **234**, http://www.sserc.org.uk/index.php/bulletins226/2010/234.

[2] Thanks to Iain Smellie and Megan Russell at St Andrews University for developing this particular recipe for the solution.

[3] From Ultraviolet to Prussian blue: A spectral response for the cyanotype process and a safe educational activity to explain UV exposure for all ages. Turner, J, Parisi, AV, Downs, N and Lynch, M. University of Southern Queensland, Toowoomba, Australia. https://www.academia.edu/8928524/From_Ultraviolet_to_Prussian_blue_A_spectral_response_for_the_cyanotype_process_and_a_safe_educational_activity_to_explain_UV_exposure_for_all_ages.

Coming soon....

In a recent issue of the Bulletin (Issue 250, Spring 2015) we announced the publication of a new guide entitled 'Advanced Higher Biology Project investigations' written by Jim Stafford.



We are delighted to say that Jim has recently teamed up with Professor Graeme Ruxton from St Andrew's University to produce a new guide entitled 'Statistics for School Biology Experiments and Advanced Higher Projects'.

As was the case for Advanced Higher Biology Project investigations, a copy of this new, exciting resource will be sent to all schools and colleges in the near future. Further copies of the guide will be available through the SSERC website.