A Practical Science Investigation for Middle School Students: Designing a Simple Cost Effective Chemical Solar Radiation Dosimeter

Downs, N.\(^1\), Larsen, K.\(^1\), Parisi, A.\(^1\), Schouten, P.\(^2\),\(^1\), Brennan, C.\(^4\)

\(^1\) Faculty of Sciences, University of Southern Queensland, Toowoomba, Australia.  
\(^2\) School of Engineering, Griffith University, Gold Coast, Australia.  
\(^3\) Toowoomba State High School, Education Queensland, Australia.  
\(^4\) Hervey Bay State High School, Education Queensland, Australia.

Abstract

A practical exercise for developing a simple cost-effective solar ultraviolet radiation dosimeter is presented for use by middle school science students. Specifically, this exercise investigates a series of experiments utilising the historical blue print reaction, combining ammonium iron citrate and potassium hexacyanoferrate to develop an ultraviolet sensitive solution. The activity is intended for implementation into courses of study based on the new Australian science curriculum, and the strand Chemical reactions matter. The activity investigates rates of reaction and examines the influence of an invisible physical catalyst, solar radiation. The developed photochemical dye was tested for use as a solar dosimeter by painting or soaking various common materials with the solution. A soaked cloth dosimeter was determined to be the most practically appropriate. Its use as a ‘magic cloth’ or polyethylene filtered ultraviolet radiation dosimeter, capable of being calibrated to incoming solar radiation is discussed. The exercise is presented as a practical guide that can be followed by middle school aged science students beginning studies in physics, chemistry or the environment. The experiment may also be extended and applied to senior chemistry investigations.

Authors’ Accepted Version of
(Deposited with blanket permission of the publisher.)
**Introduction**

A common photochemical reaction involves mixing an iron citrate solution with hexacyanoferrate. This reaction is a chemical reaction involving light as a catalyst and has been repeated historically for early solar photocopying before the advent of laser copiers. The process is known as blueprinting. Early copies or blueprints were made by placing transparencies of an original document or image over a material, commonly paper, soaked or painted with the blueprint reactants. Upon exposure to sunlight darker regions of the document or image were prevented from developing upon the underlying paper by not being exposed to sunlight, while transparent regions of an original document or image turned the blueprint reactants from yellow to blue. The original non-developed blueprint dye could be washed from the exposed or developed blueprint leaving a copy in blue and white.

The blueprint reaction is a cyanotype reaction that is performed using an iron (III) salt and an iron (II) salt. These include, ammonium iron (III) citrate (also known as ammonium ferric citrate, generally of the molecular formula FeC₆H₅O₇NH₄OH) and potassium hexacyanoferrate (II) (also known as potassium ferrocyanide, generally of the molecular formula K₄Fe(CN)₆). These common blue print compounds mixed as aqueous solutions are utilised here to prepare a cyanotype ultraviolet (UV) sensitive dye usually known as Prussian blue or Turnbull’s blue (Housecroft & Constable 2006). Specifically the cyanotype solution is developed to produce a compound that absorbs light at a peak wavelength of approximately 700 nm and is therefore deep blue in colour (Rodgers 2002).

The general formula for the reaction of these two Fe²⁺ and Fe³⁺ components is as follows (Cotton et al. 1999):

\[
\text{Fe}^{\text{III}}\text{(aq)} + \text{K}_4\text{[Fe}^{\text{II}}\text{(CN)}_6\text{]}\text{(aq)} \rightarrow \text{Fe}^{\text{III}}\text{[Fe}^{\text{II}}\text{(CN)}_6\text{]}\text{3.4H}_2\text{O} \quad (1)
\]

The above equation is the general reaction equation for the solutions used. The reaction to produce the Prussian blue or blueprint dye can also be carried out using other combinations of Fe II and Fe III salts, such as ferrous ammonium sulfate and potassium hexacyanoferrate (III) (Rodgers 2002). This reaction can be used to develop copies of transparencies as a practical classroom activity but it can also be used to develop a simple cost effective ultraviolet dosimeter.

A chemical dosimeter is a material which undergoes a measureable chemical change that can be calibrated to a known radiation source. Dosimeters are often produced in a badge form so that they can be worn by individuals that need to monitor the radiation which they are exposed to. A common use for a chemical dosimeter might be to monitor the level of ionising radiation for example in a nuclear facility. Non-ionising radiation such as UV radiation which causes sunburn can also be monitored in this way.

UV dosimeters are developed from materials that undergo measureable UV sensitive changes and are typically deployed to measure personal UV exposures (Diffey 1991). They may also be deployed to measure environmental UV exposures in places where electronic
instrumentation may be either too expensive or too difficult to deploy (Parisi et al. 2004). UV sensitive dosimeters are generally available as light sensitive polymer films, which experience a variation in opacity following exposure to UV radiation. They may also take the form of small electronic badges or wrist-bands (Thieden et al. 2004). The objective of this investigation is to complement these previously employed dosimetric devices by developing a new cost effective solar UV radiation dosimeter utilising the blueprint reaction. Such a dosimeter can be cheaply manufactured by school students and calibrated to the incident UV by application of low-cost, readily available electronic UV measurement instrumentation such as the Edison UV checker (Deals Direct 2011).

The cyanotype dosimeter presented in this article can be used to simply indicate the presence of UV radiation or can be further calibrated to measure the radiation received in any particular environment. The design of the dosimeter is left to students depending on what they want to investigate. For example, blueprint solution painted onto paper may be enough to provide an indication of the presence of UV radiation under the shade of a tree or alternatively students may like to attempt the design of a long-term, slow reacting dosimeter. For the investigation presented here, it was found that the UV reaction of a cloth soaked dosimeter filtered by polyethylene film slowed the blueprint reaction sufficiently to enable the production of a calibration continuum and simple environmental UV measurements.

Materials
The materials presented here are divided into three sections for each specific stage of the experiment: developing the UV sensitive solution; investigating the blueprint reaction by painting and soaking with various materials and filters; and making solar radiation dosimeters for calibration to the environmental UV. Students wishing to follow the presented experimental methods below will require all of the materials listed in this section. However, the experimental design can be customised to suit the preferences of individual classrooms and science programmes.

**Essential solution materials:**

- 20 g ammonium iron (III) citrate;
- 8 g potassium hexacyanoferrate (II);
- 200 ml water;
- measuring cylinders;
- beakers;
- glass stirring rod;
- aluminum foil;
- solution bottle or flask with stopper;
- measuring scales;
- spatula;
- personal protective equipment (such as gloves and plastic glasses).

**Additional investigation materials:**

- paint brush;
- tweezers;
- popsicle sticks;
- paper bag;
- cardboard;
- A4 printing paper;
- white cloth;
- filter paper;
- UV light source (sun);
- halogen lamp;
- petri dish (plastic);
- petri dish (glass);
- glass sheet;
- plastic page holder;
- plastic garbage bag (black);
- takeaway box plastic lid;
- section of polycarbonate roof sheeting;
- sunglasses;
- test tubes and tube rack.

**Cloth dosimeter for measuring UV calibration:**
- previously listed essential solution materials;
- white cloth;
- petri dish;
- ceramic tile;
- solar radiation meter.

**Experimental Methods**

1. **Mixing the solution**

The blue print solution is developed and stored in a light-proof container or flask prior to application and eventual exposure to UV radiation. For this experiment, a light-proof container for storing the light sensitive solution was made by wrapping a conical flask in aluminum foil. Two different reactant concentrations were trialed in creating the blue print solution. Best results were achieved by adding 20 g of ammonium iron (III) citrate to the light proof flask and dissolving in 100 ml of tap water. The ammonium iron (III) citrate powder was easily dissolved by gently swirling the mixture for several minutes. Next, 8 g of potassium hexacyanoferrate (II) was dissolved in a beaker with 100 ml of tap water by mixing with a glass stirring rod. This solution was added to the light-proof flask, mixed gently, sealed with a rubber stopper and placed in a cupboard for storage. The combined light sensitive solution was found to be viable, if stored using this method for about a week. After such time the solution began to turn from a yellow-green colour to a darker brown colour.

The two aqueous solutions, before reacting together, are separately stable for several weeks, when stored away from direct sunlight. One may also use smaller quantities of the two components to prepare the cyanotype material, as long as the concentrations and relative volumes of each of the reactants are kept the same.

2. **Solution testing with various media**

The light sensitive blueprint solution can be tested over a period of several days. The solution can be brushed onto various materials; or alternatively, the materials themselves can be soaked in the solution and dried over several minutes by placing on a tile indoors prior to exposure. Care should be taken not to spill the solution as it was found to stain, hence the use of tweezers and personal protective equipment for handling soaked materials is recommended. Also, students should be reminded not to ingest the solution under any circumstances.

The blueprint reaction occurs quickly when the dosimeter is placed in sunlight. In order to manufacture a material suitable for use as a dosimeter, students may like to test various materials to see how they influence the photo-reaction rate. Brushing or soaking the material will influence the consistency of the solution when applied to various media. The
The following media were tested and found to be suitable for this investigation: popsicle sticks, paper bags, cardboard, printing paper, filter paper and cloth.

Figure 1: Cyanotype cloth dosimeters placed on a ceramic tile for drying prior to an exposure experiment. A large Petri dish was used for soaking the dosimeters and can be seen in the left of the image.

Once a selected material is painted or soaked it can be placed in sunlight and the blueprint reaction observed. Upon exposure in sunlight, the solution turns from yellow to dark blue in a matter of minutes depending upon the available UV and the medium used. The blueprint solution left in liquid form inside open test tubes or measuring cylinders can also display a photo-reaction.

Figure 2: The cyanotype aqueous solution exposed to sunlight in a large measuring cylinder shows the beginnings of the blueprint reaction near the top of the cylinder. Mixing processes caused by variations in compound densities take place during an exposure event, eventually influencing the colour of the entire tube.

3. Slowing the reaction by using filters
The photo-reaction occurs in the presence of UV. On Earth, the solar UV spectrum occurs immediately below the visible spectrum in the range 290 to 400 nm and consists of the UVA (320 to 400 nm) and UVB (290-320 nm) wavebands. It is the higher energy (short wavelength) UVB radiation that is primarily responsible for sunburn in human skin (CIE 1987). This radiation can however be blocked by non-quartz glass. Placing glass sheets over blueprint dosimeters should therefore slow the photo-reaction provided the reaction is most sensitive to radiation of the shorter UV wavelengths. A cost effective UV meter like the UV Checker (Deals Direct 2011) will confirm that no UVB radiation penetrates the glass sheet. It was found for this investigation, that glass sheets do not significantly slow the blue print photo-reaction, suggesting that lower energy UVA radiation can initiate a response. This may be due to there being a significantly higher proportion of UVA available in terrestrial sunlight.

The following filters were investigated to determine if reaction time could be reduced: projection transparencies (acetate), glass and plastic petri dishes, sunglasses, polycarbonate roof sheeting and black garbage bags (polyethylene). Out of these items the sunglasses were found to be the most effective UV filter. The black garbage bag film was also found to be an effective UV filter, supporting the findings obtained previously by Schouten et al. (2010). Students may wish to experiment with the influence of filter thickness or use various filter combinations to determine which may be used as the most appropriate UV filters for their dosimeters.

4. Physical factors that influence reaction time

After selecting a suitable media and filter the rate of the photo-reaction can be tested under different conditions. A simple experiment to determine the influence of cloud cover, time of day (solar elevation) or season can be performed by timing how long it takes for the blueprint solution to turn from yellow to green to blue. Similarly, blueprint dosimeters placed under indoors ambient lighting or a UV fluorescent tube (such as those available for use in aquariums) will indicate the presence of UV radiation.

5. Calibration of Cloth dosimeters

A total of seven cloth dosimeters were manufactured and calibrated to the incident UV using the UV checker pocket meter. Alternatively other low cost UV meters could be used for the calibration process. The meter used for this investigation lists the erythemally effective or human sunburning effective UV radiation. As a guide, perceptible sunburn begins to appear in fair skinned individuals after receiving approximately 200 Jm⁻² of erythemally effective UV radiation.

Figure 1 shows the cloth soaked dosimeters prior to exposure. The dosimeters were each covered by black polyethylene garbage bag film and exposed over a period of 90 minutes. During the exposure period as the dosimeters were removed, the incident UV irradiance was recorded in mWm⁻² (Table 1) and each dosimeter was photographed to present a reaction continuum upon which later cloth dosimeters can be calibrated. This reaction continuum is presented in Figure 3.
Results

The UV irradiance was measured using the Edison UV checker. This is a simple point and click instrument which requires students to hold the instrument so that the receiver is orientated vertically (Downs et al. 2008). In this position, the total or global erythemal UV irradiance received by the cloth soaked dosimeter is measured by reading the value in mWm\(^{-2}\) several times over a 90 minute exposure interval. Here, the irradiance in mW is a measure of the radiant solar energy being received per second. The total sunburning energy received is calculated over the exposure interval by multiplying by the interval time in seconds. Sunburning or erythemal energy is expressed in Joules per square meter (Jm\(^{-2}\)). The cumulative exposure is the total energy received after successive measurements of the UV irradiance (Table 1).

Cumulative exposure is calculated by summing the erythemally effective UV received in each exposure interval where the exposure in each interval in Jm\(^{-2}\) is calculated by multiplying the average irradiance of the interval by the number of seconds in that interval. For example, in the first 5 minute exposure, the average irradiance received was 7 mWm\(^{-2}\) or 7 mJs\(^{-1}\)m\(^{-2}\). Multiplying by 300 seconds in the 5 minute interval gives an exposure of 2.1 Jm\(^{-2}\). Exposures in each interval listed in Table 1 are added to the previous exposure to determine the cumulative exposure received by each dosimeter. The cumulative exposure sums to a total of 105.6 Jm\(^{-2}\) meaning a fair skinned person exposed to this level of solar UV radiation would be unlikely to experience a perceptible sunburn. Cloth dosimeters manufactured by students can be exposed to sunlight and compared to Figure 3 to determine the approximate exposure received. Alternatively, using the techniques presented, students may like to develop their own calibration charts.

Table 1: A calibration table for cloth soaked cyanotype dosimeters.

<table>
<thead>
<tr>
<th>Exposure duration (minutes)</th>
<th>Erythemally effective UV Irradiance (mWm(^{-2}))</th>
<th>Cumulative erythemally effective UV exposure (Jm(^{-2}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>7</td>
<td>0</td>
</tr>
<tr>
<td>5</td>
<td>7</td>
<td>2.1</td>
</tr>
<tr>
<td>10</td>
<td>7</td>
<td>4.2</td>
</tr>
<tr>
<td>20</td>
<td>19</td>
<td>12.0</td>
</tr>
<tr>
<td>30</td>
<td>22</td>
<td>24.3</td>
</tr>
<tr>
<td>40</td>
<td>19</td>
<td>36.6</td>
</tr>
<tr>
<td>60</td>
<td>21</td>
<td>60.6</td>
</tr>
<tr>
<td>90</td>
<td>29</td>
<td>105.6</td>
</tr>
</tbody>
</table>
Figure 3: A continuum of the blue print photo-reaction shown for 6 polyethylene filtered exposure levels, from left: 2.1 Jm$^{-2}$, 4.2 Jm$^{-2}$, 12.0 Jm$^{-2}$, 24.3 Jm$^{-2}$, 36.6 Jm$^{-2}$, 60.6 Jm$^{-2}$ and one unfiltered cloth dosimeter (far right) receiving a total erythemally effective exposure of 105.6 Jm$^{-2}$.

Conclusions

The presented investigation provides students with the opportunity to study the environmental influence of physical UV radiation on the rate of a chemical reaction. This investigation may be applied as part of a relevant study or written assessment item within second term year 10 studies of Chemical reactions matter outlined in the Australian Science curriculum (ACARA 2011). The investigation can be applied to develop student understanding of a physical property that is otherwise non-detectable by manufacturing inexpensive chemical UV dosimeters. The task can be related to other scientific fields such as radiation and protection dosimetry and atmospheric science. Students may like to perform a literature review to investigate how different types of radiation are detected using different types of chemical and solid-state dosimeters. It may be appropriate for students to question why dosimeters are important for human health monitoring for both long and short-term applications.

The cyanotype dosimeter can be utilised as an environmental monitor of solar UV. Students involved with the design and construction of such dosimeters have the opportunity to think about the environment they live in and how local factors such as tree shade, or reflections from nearby buildings can influence the rate at which an observable reaction takes place, and in turn how these factors influence the amount of UV present. They may consider such questions as:

- How much UV radiation is available on any given day?
- When is there most likely to be the most radiation available?
- What does this have to do with the position of the sun in the sky?
- How might this radiation affect me personally?
- How much radiation is needed to maintain a healthy lifestyle?

Considering these factors is essential for the health and long-term wellbeing of all Australians. It is important to maintain a balance between sufficient sunlight exposure to maintain adequate vitamin D levels while preventing overexposure to sunlight which can lead to skin cancer and various other eye disorders. For students, beginning to develop these ideas during their middle school years will help them to develop lifelong habits that promote better future health outcomes while improving their own understanding of science as a human endeavour.

Acknowledgements
The authors would like to thank Year 10 Science Student, Jason Longshaw from Darling Downs Christian School for assisting with testing the experiments presented in this investigation.

References


