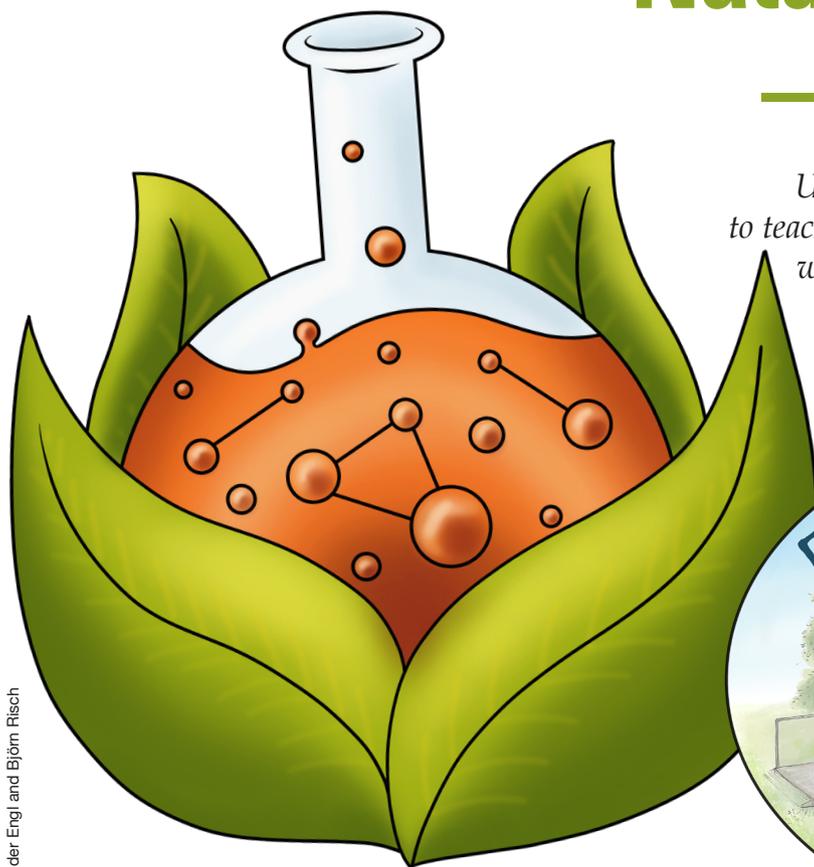


Natural Chemistry – Outdoors!

Use fluorescence and sunscreen to teach chemistry to high school students while immersed in the outdoors



Alexander Engl and Björn Risch

By **Alexander Engl** and **Björn Risch**

THERE IS A BROAD CONSENSUS that experiences in nature positively affect physical and mental health and social development. Children who play outside several times a week are generally happier than those who don't, especially if those outdoor settings are stimulating ones. Since youth now spend an increasing amount of time in a virtual world, too often they become alienated from nature. And they experience fewer sensory opportunities than those who have regular contact with the natural world.

Richard Louv identified this problem as nature-deficit disorder: "the human costs of alienation from nature: among them diminished use of the senses, attention difficulties, and higher rates of physical and emotional illnesses."¹ In spite of this however, "nature" as a place of learning is not sufficiently integrated into science classes.

The concept for teaching chemistry outdoors is intended to make youth more aware of nature and the processes occurring there. The central idea is to shift parts of chemistry lessons outdoors, ideally into natural settings. Such outdoor lessons help students to better connect with the natural world and hopefully enjoy much more their time spent outside.

In order to better understand environmental processes, we encourage students to work in small groups and conduct

outdoor experiments using natural items that they have collected. There is another less obvious benefit of conducting experiments outdoors. The impacts of environmental stressors, such as UV radiation, are not immediately visible to most people. When outdoor experiments are set up to investigate those impacts, it helps the participants to better appreciate those impacts.

In contrast to traditional chemistry lessons which many students find abstract and complex, the objective of our *Natural Chemistry* approach is to build a bridge between chemistry instruction and every-day, natural phenomena. The starting point of our program is the "Outdoor Mobile", a former circus caravan that has been converted into an environmental outdoor student laboratory. This caravan is primarily used to store the materials and act as a meeting place for debriefing what has been learned. While it is very helpful for us, you will not need a mobile caravan in order to implement the concepts outlined in this article.

The Natural Chemistry units are designed for senior high school students with the following criteria in mind:²

1. Experiments take place outside of the classroom ("nature is my lab")
2. Minimal laboratory equipment and chemicals are used and reactions occur from naturally occurring substances
3. Environmental processes are demonstrated on real objects
4. The focus is on basic chemical concepts

5. Digital media, such as GPS devices or tablet computers, are used

Our program's philosophy is best seen in the following, multi-part activity. The first part of the activity uses model experiments to understand the curse and blessing of UV radiation.³ It will enable students to answer questions related to the effectiveness of sunscreen, clothing material, and skin types. In the second part, we look at natural sunscreens derived from plants such as horse chestnuts. With an extract of the bark, we take a closer look at the phenomenon of fluorescence and we show the dependency on the pH value of the fluorescence dye.

Decades of research have shown that an increase in knowledge does not necessarily lead to a change in behavior.⁴ For this reason, environmental education programs should focus on active and experiential engagement in real-world environmental problems, rather than the transfer of knowledge.⁵ Issue-based, project-based, and investigation-focused programs in real-world (place-based) nature settings will commonly achieve the desired outcomes. Natural Chemistry responds to these findings by actively involving students in the learning process – outdoors!

Alexander Engl has studied chemistry and biology and is currently a Ph. D. student in the Department of Chemistry Education at the University of Koblenz-Landau in Landau, Germany. **Björn Risch** is a Professor of Chemistry Education at the University of Koblenz-Landau (Campus Landau). They would like to thank the *Fonds der Chemischen Industrie* (FCI) for funding the project.

Notes

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Activities

Activities 2 and 3 can be found at <http://greenteacher.com/natural-chemistry-outdoors/>

1. Sunscreen in a Model Experiment

Part A: Production of photo-sensitive cyanotype filter paper

The photo-sensitive cyanotype filter paper displays UV radiation by changing color. This demonstrates the powerful effect of UV radiation. Follow these instructions to create some for the experiment.

Materials: Beaker (50 mL), graduated cylinder (50 mL), glass rod, petri dish (≥ 7 cm), tweezers, 5 regular filter papers (≥ 7 cm), shoe box, paper towels, safety gloves, waste container

Chemicals: 2.5 g green ammonium ferric (III) citrate, 1 g potassium ferricyanide (III), distilled water

Time: 10 minutes

Safety instructions: Wear latex safety gloves to prevent your skin from being stained blue.

Procedure

- Put on latex safety gloves.
- Using the graduated cylinder, measure 25 mL of distilled water.
- Place the 50 mL beaker in the shoe box to avoid as much UV radiation as possible.
- In this beaker, prepare 1 g potassium ferricyanide (III) and 2.5 g green ammonium ferric (III) citrate in 25 mL of distilled water.
- Mix beaker chemicals with a glass rod.
- For best results, place the petri dish inside the shoe box beside the beaker for the next steps to keep it shaded or place it on the counter beside the box.
- Pour part of the solution from the beaker into a petri dish and put all five filter papers in the dish to soak up the poured solution.
- Using the tweezers, lift the filter papers from the petri dish and pat the filter papers dry using paper towels.
- Remove the beaker from the shoe box and store the filter

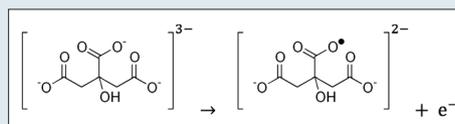
papers in the shoe box until required.

- Expose one of the five filter papers to UV radiation from the sun. You can also cut a small paper template to put over the exposed filter paper to show the difference between the fully exposed and covered portions.
- Leave the remaining papers in the shoe box.

Disposal: Collect the remaining solution in the beaker and petri dish and the one UV exposed filter paper to place in a waste container. (Hold onto the other four filter papers, for later use, as mentioned below.)

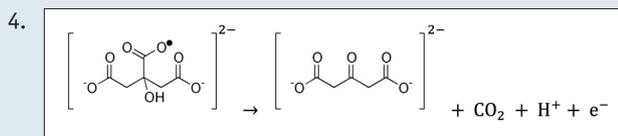
Explanation: The basis for these sunscreen experiments is the cyanotype process, which involves a photochemical-induced reaction between ammonium ferric (III) citrate and potassium ferricyanide (III) (red prussiate). If a watery solution of the two chemicals is exposed to sunlight (or an alternative source of UV radiation such as an ultraviolet lamp, overhead projector etc.), a distinctive blue color forms within a minute. Exposure to high-energy UV radiation causes an electron of the citrate ligand (from the ammonium ferric (III) citrate) to be transferred to the ferric (III) ion of the ammonium ferric (III) citrate, which is in turn reduced to a ferric (II) ion:

- Oxidation:

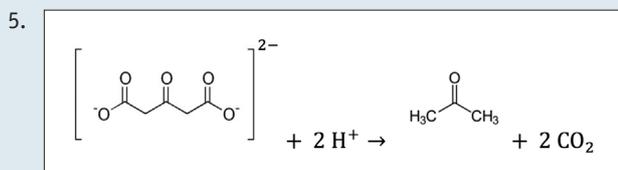


- Reduction: $\text{Fe}^{3+} + e^- \rightarrow \text{Fe}^{2+}$

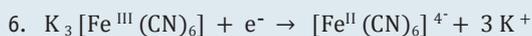
The resulting ferric (II) ions in chemical equation (2) react with the potassium ferricyanide (III) to form Prussian blue. The simply oxidized citrate radical releases a second electron and forms acetonedicarboxylic acid due to decarboxylation.



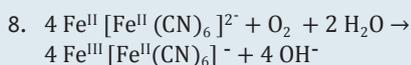
The acetonedicarboxylic acid can undergo decarboxylation two more times, with the Fe³⁺ ions being reduced. The final products are acetone and carbon dioxide:



If the UV radiation is very strong, white color can form on the filter paper. There is a transfer of electrons from the ferric (II) citrate to the ferric (III) ion of the potassium ferricyanide (III). This forms a ferric (II) ferricyanide complex, which reacts with the unbound ferric (II) ions to form so-called Prussian white. This process is called the solarization effect.



The Prussian white reacts with atmospheric oxygen to form Prussian blue. Contrary to the insoluble Prussian blue in chemical equation (3), the complex contains a ferric (II) ion.



Part B: Sunscreen by Reflection

These three model experiments compare different options for skin protection from UV exposure such as cream, clothing and skin types.

Materials: 3 cyanotype filter papers from Part A, 3 glass sheets, a paintbrush, template of different skin types (see figure 4), a piece of silk fabric, a piece of cotton fabric, 2 clothes pegs, waste container

Chemicals: Sun cream, hand cream

Time: 15 minutes

Procedure

- Put a cyanotype filter paper between two sheets of glass. Using the paintbrush, apply thin layers of hand cream and sun cream side by side to the top glass sheet. The same quantities should be used of each and the thickness of the layers applied should be identical.
- The pieces of silk and cotton fabric should be placed side by side over a second piece of cyanotype filter paper and fixed with clothes pegs, if necessary.
- Place the template of different skin types on a third cyanotype filter paper and weigh it down with a glass sheet.



Alexander Engl and Björn Ritsch

Students prepare photo-sensitive cyanotype filter paper for sunscreen in a model experiment.

- Expose these three prepared cyanotype filter papers to UV radiation from the sun.

Disposal: Collect the exposed filter papers in a waste container.

Explanation: A comparison between the hand cream and the sun cream reveals different colors on the cyanotype filter paper. The hand cream provides no protection from UV radiation so a photochemically induced reaction occurs, resulting in a blue color. The sun cream, on the other hand, prevents this process and the filter paper remains virtually yellow-green. Mineral sun creams contain the primary light-screening substance titanium dioxide, in the form of nanoparticles that reflects or absorbs the UV radiation.

Silk and cotton also leave different shades of color on the cyanotype filter paper. Thin fabrics that are not densely interwoven, such as silk, provide very little protection against UV radiation, although people often like to wear these lightweight fabrics in the summer.

The third model experiment demonstrates the protective effect of different skin types. A color template consisting of four brown tones with varying degrees of transparency provides a basis for this experiment. After the experiment, the different shades of the color scale are reflected by different degrees of blue color on the filter paper. The color scale is intended to represent the different concentrations of melanin in skin. Melanin is the color pigment that is produced when skin is sun-tanned. The results illustrate the differences between the skin types with regard to their ability to resist UV radiation. The varying formation of Prussian blue symbolizes the exposure of the deeper skin layers to UV radiation.



Invisible UV radiation forms a distinctive blue color due to the cyanotype process. Sun cream, cotton, or sun-tanned skin prevents this process and the filter paper remains virtually yellow-green.

Part C: Sunscreen Through Absorption

This experiment is concerned with the protection mechanisms of plants in strong sunlight.

Research task: Not only do people need to be protected from UV radiation, plants also require sunscreen. For example, cacti in the highlands are covered in dense hair which enables them to reflect part of the UV radiation. The horse chestnut, ash, and narra trees or common orange lichen have a different strategy. This experiment shows how UV-active substances absorb sunlight. (Tip: The horse chestnut contains a water-soluble, UV-active substance between its bark and wood.)

Materials: 1 cyanotype filter paper from experiment A, scissors, 2 snap capped vials with a seal, glass rod, tweezers, a horse chestnut twig, waste container

Chemicals: Distilled water

Time: 15 minutes

Procedure (hidden for students)

- Put a small horse chestnut twig into a snap capped vial.
- On one side of the twig, remove up to half of the bark using the scissors.

- With the twig and loose bark in the vial add distilled water and stir several times with the glass rod.
- Use tweezers to extract the bark pieces and twig from the snap capped vial so that it only contains water with the extract of horse chestnut.
- Place the snap capped vial containing the horse chestnut extract and a second snap capped vial containing only distilled water on a cyanotype filter paper and expose it to sunlight.

Disposal: Collect the blue filter paper in a waste container. Keep the horse chestnut extract for subsequent experiments.

Explanation: In addition to sunscreen through reflection, some chemical substances provide light protection by absorbing sunlight and, as a result, reduce the intensity of UV radiation. UV-active substances such as 4-aminobenzoic acid derivatives are used in sun cream for this purpose. Selected substances contained in plants also absorb UV radiation and show the phenomenon of fluorescence. These fluorescent dyes are characterized by an extended conjugated π -electron system, which does not absorb visible light like other dyes, but is stimulated by short-wave UV radiation.



The horse chestnut contains a water-soluble, UV-active substance between its bark and wood. This chemical substance provides light protection by absorbing UV radiation. The left snap-capped vial contains water as a blank; the right snap-capped vial contains horse chestnut extract. The upper shade in the right picture is more yellow-green due to the sunscreen through absorption of the horse chestnut extract.

2. Absorption and Emission: Interplay in the Horse Chestnut

This experiment is about the phenomena of fluorescence using Aesculin as a natural fluorescent dye.

Materials: 7 snap-capped vials with a seal, ultraviolet torch ($\lambda = 366 \text{ nm}$), scissors, beaker (100 mL), glass rod, shoe box (see photo for the location of holes), a horse chestnut twig

Note: the recommended ultraviolet torch is the Pet Urine Detector 365NM Black Light Flash-light: PeeDar-Precision UV LED. It is available on Amazon.

Chemicals: Distilled water

Time: 15 minutes

Procedure

- Using the scissors, cut a hole in the box for the ultraviolet torch and cut another small hole to see into the box.
- Insert an approximately 10-cm-long horse chestnut twig in a beaker (100 mL).
- On one side of the twig, remove up to half of the bark using the scissors.
- Add 50 mL of distilled water to the pieces of bark and the twig and stir several times with the glass rod.
- Place the beaker containing the horse chestnut twig and extract in the shoe box, aligning it with the holes, and put the lid on the box.
- Insert the UV torch into the suitably-sized hole in the box and switch it on. The second hole in the shoe box is used for making observations during the experiment (see figure 6).
- Now turn off the UV torch, remove the beaker, and use the extract to evenly fill six snap-capped vials.
- Fill one snap cap vial with distilled water to serve as the blank.

- Line up the seven snap-capped vials behind one another inside the box in front of the UV lamp hole. The position of the blank can be varied arbitrarily.
- Shine the UV light through the lined up vials, which now block each other, so that the first vial gets full light and the last vial gets the least light (see figure 6).

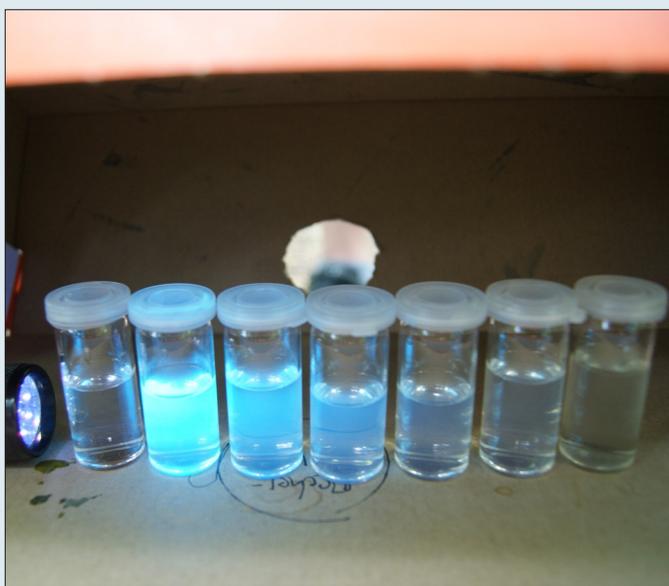
Disposal

All of the solutions can be kept for subsequent experiments.

Explanation

Aesculin is a substance occurring in the leaves, seeds and bark of the horse chestnut (*Asculus hippocastanum*). This substance is soluble in polar solvents such as water and it fluoresces blue. Fluorescence occurs when UV absorption and visible light emission interact. High-energy, short-wave, and invisible UV radiation excites electrons of the aesculin molecule. As a result of this absorption, the aesculin molecule temporarily transforms into an unstable state. However, the excited electrons immediately return to the energetically more favorable ground state. The energy resulting from this process is released in the form of visible light (emission).

The blue light of the extract in the lined-up tubes diminishes from one snap-capped vial to the next. The first aesculin solution absorbs the majority of the UV radiation, producing the most intensive fluorescence in this tube. Only a small proportion of the UV radiation passes through all of the snap-capped vials, which is why the last tube with aesculin solution hardly emits light at all. Regardless of the sequence of the tubes and the position of the blank, the weakening of fluorescence is identical because water does not absorb UV radiation.



Fluorescence occurs when UV absorption and visible light emission interact. The picture on the left shows the blue fluorescence of horse chestnut extract on the left side and ash extract on the right side. The blue fluorescence in the second picture diminishes from one snap capped vial to the next. The first snap-capped vial serves as a blank containing water.

3. Acid-base reaction with horse chestnut extract

This research task is about the pH dependency of the fluorescent dye. Acid-base reactions illustrate reversible fluorescence changes.

Research task: Verify the extent to which the fluorescence of the horse chestnut extract depends on the pH value of the solution. Also show how possible changes can be reversed. To enable comparison, use water as a blank and unchanged horse chestnut extract as a control sample.

Materials: 7 snap-capped vials from experiment 2, ultraviolet torch ($\lambda = 366 \text{ nm}$), felt-tip pen, small spoon, glass rod, shoe box, pH indicator paper, pipette, waste container

Chemicals: Lemon juice, baking soda, 5% hydrochloric acid and 5% lye in eyedroppers

Time: 15 minutes

Safety instructions: Safety goggles should be worn when handling acidic and alkaline solutions.

Procedure

Unless students are unable to work out a solution by themselves, please keep the following hidden from them. If they cannot, the following steps will help guide them. Note too that in Germany, students over 10 are allowed to work with hydrochloric acid and lye. Please check local regulations.

Part 1

- Drip lemon juice or hydrochloric acid into three snap-capped vials containing horse chestnut extract.
- Use a snap-capped vial with distilled water as the control sample.
- Use one snap-capped vial with horse chestnut extract as a blank.
- Put these five vials into the shoe box and expose them to ultraviolet radiation using the UV torch. Observe how the pH levels affect the fluorescence.

Part 2

- Add baking soda to a sixth snap-capped vial with horse chestnut extract.
- Add lye to a seventh snap-capped vial with horse chestnut extract.
- Place these two vials also into the box.
- Shine the UV lamp into the box to observe how the pH levels affect the fluorescence.

Part 3

- Use one of the three vials with acid from part 1 that contains extract and either lemon juice or hydrochloric acid.
- Either baking soda is spooned into it or lye is dripped into it to change the pH level.
- Place all seven vials (horse chestnut extract with lemon juice; horse chestnut extract with hydrochloric acid; horse chestnut extract with baking soda; horse chestnut extract with lye; horse chestnut extract with lemon juice and baking soda or with hydrochloric acid and lye; horse chestnut extract as a blank; distilled water) into the box and shine the UV light to compare the fluorescence and see how the change in pH has affected the solution.

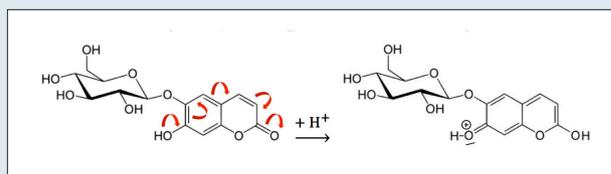
Disposal

Collect all remaining solutions in a waste container.

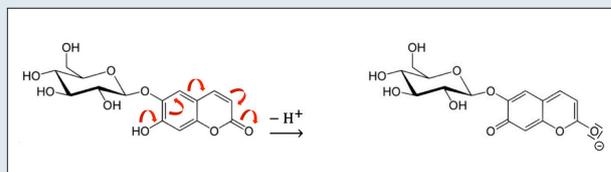
Explanation

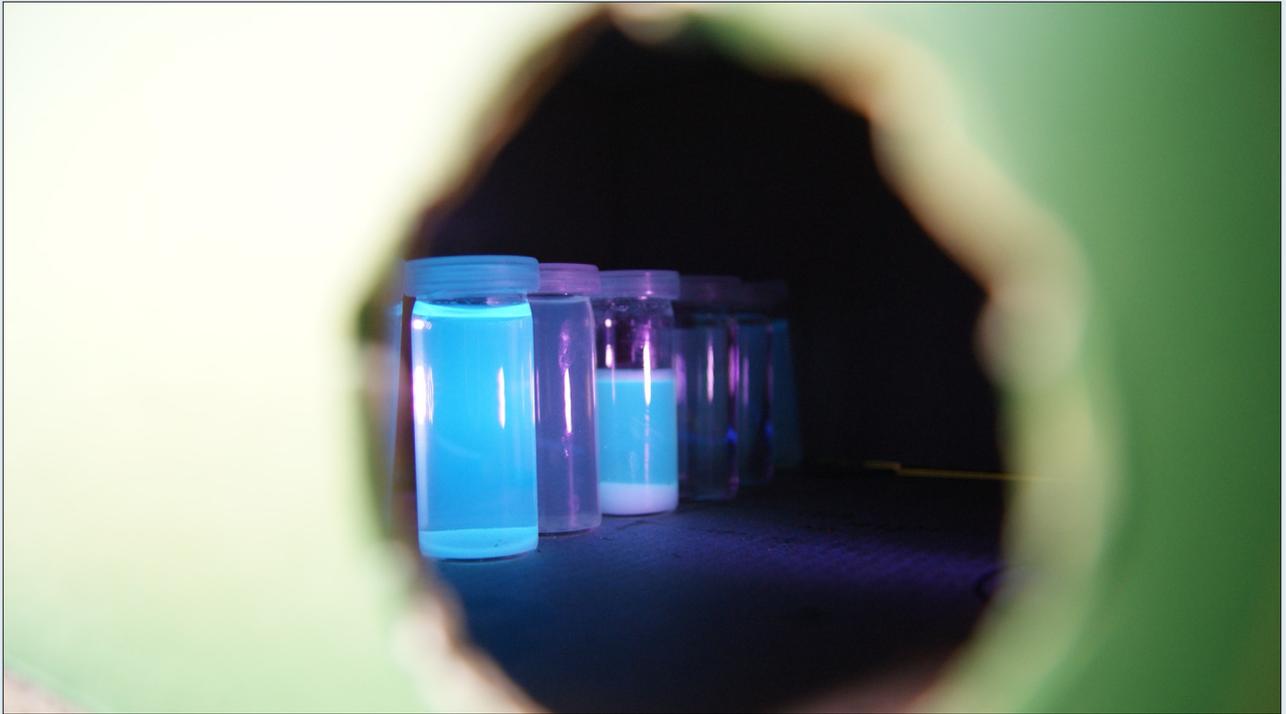
The aesculin molecule is prevented from fluorescing by adding acid. Bases, on the other hand, intensify fluorescence of the aesculin molecule. A neutralization reaction causes the base in part three of the experiment to move the acidic pH value of the horse chestnut extract into a neutral area, making the solution fluoresce blue again. The fact that the fluorescence of aesculin is dependent on the pH value can be explained by the structure of the molecule. In an acidic environment, the molecule is protonated, destroying the conjugated π -electron system and resulting in no more UV radiation being absorbed. In a basic milieu, the deprotonated molecule is stabilized by resonance structures and the free electron pairs of the oxygen atoms extend the conjugated π -electron system, causing fluorescence to acquire more intensity.

9. protonated



10. deprotonated





The fluorescence of the horse chestnut extract depends on the pH value of the solution. Acids like lemon juice or hydrochloric acid prevent it from fluorescing and bases like baking soda or lye intensify fluorescence. In the picture above, the first snap-capped vial serves as a blank containing horse chestnut extract, the second snap-capped vial contains horse chestnut extract and lemon juice, and the third snap-capped vial contains horse chestnut extract and baking soda.