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Catalog No. AP8367

Publication No. 8367

Ash Water Titration

Student Laboratory Kit

Introduction

The 12 Principles of Green Chemistry guide us to use catalysts to improve the energy and atom efficiency of reactions. The principles also guide us to use renewable feedstocks. In this experiment, we can see how waste from one process can be used productively in another. Specifically, biodiesel can be made from waste vegetable oil, a renewable feedstock that was traditionally discarded by the food preparation industry. To prepare biodiesel from the vegetable oil, base is needed as a catalyst. In this lab we will focus on the catalyst and its source from another "waste material"—wood ash, the material left following the combustion (burning) of wood.

Concepts

- Acid-Base Titrations
- Catalysis
- Renewable Feedstocks
- Extractions
- Green Chemistry

Background

Much of what makes this world modern is the result of the application of chemistry and chemical reactions. Oil and gasoline, prescription drugs, plastics, solvents, and fertilizers, to name a few, are all products of chemistry. Over time, many of the processes used to create these products were found to have unintended consequences and be quite harmful, whether to workers, the consumers or to the environment. In response to these pressing issues, green chemistry was developed as an approach to creating safer chemical products and processes from the initial design stage. The principles of green chemistry provide a framework for scientists to use when designing new materials, products, processes and systems. The principles focus on sustainable design criteria and provide tools for innovative solutions to environmental challenges. These principles are listed below.

Prevention

It is better to prevent waste than to treat or clean up waste after it has been created.

Atom Economy

Synthetic methods should be designed to maximize the incorporation of all materials used in the process into the final product, leaving few or no atoms behind.

Less Hazardous Chemical Syntheses

Synthetic methods should be designed to use and generate substances that possess little or no toxicity to human health and the environment.

Designing Safer Chemicals

Chemical products should be designed to be fully effective while minimizing or eliminating their toxicity.

Safer Solvents and Auxiliaries

Minimize the use of auxiliary substances (e.g., solvents, separation agents, etc.) wherever possible and make them innocuous when used.

Design for Energy Efficiency

Energy requirements of chemical processes should be recognized for their environmental and economic impacts and should be minimized. If possible, synthetic methods should be conducted at ambient temperature and pressure.

Use of Renewable Feedstocks

Renewable raw material or feedstock should be used whenever technically and economically possible.

Reduce Derivatives

Unnecessary derivatization (use of blocking groups, protection/deprotection, temporary modification of physical/chemical processes) should be minimized or avoided if possible, because such steps require additional reagents and can generate additional waste.

Catalysis

Catalytic reagents are superior to stoichiometric reagents.

Design for Degradation

Chemical products should be designed so that at the end of their function they break down into innocuous products that do not persist in the environment.

Real-time Analysis for Pollution Prevention

Analytical methodologies need to be further developed to allow for real-time, in-process monitoring and control prior to the formation of hazardous substances.

Inherently Safer Chemistry for Accident Prevention

Substances and the form of a substance used in a chemical process should be chosen to minimize the potential for chemical accidents, including releases, explosions and fires.

Experiment Overview

Wood ash has been used as a valuable source of base throughout history. In this experiment we will extract the basic substances from a sample of wood ash and then determine their base potential compared to sodium hydroxide, the base often used in the production of biodiesel.

Materials

Wood ash, 30–50 g	300 mL Erlenmeyer flask
Potassium hydrogen phthalate (KHP)	50 mL Erlenmeyer flask, 2
Deionized water	Coffee filter, or Fluted filter paper (15cm diameter), 2
Phenolphthalein indicator	Burette, 50 mL
400 mL beaker	Balance
250 mL volumetric flask	Funnel

Safety Precautions

Phenolphthalein indicator solution contains alcohol and is a flammable liquid; it is toxic by ingestion. Do not use near flames or other sources of ignition. The base extracted from wood ash is slightly toxic by ingestion and skin absorption and is irritating to skin and eyes. Wear chemical splash goggles, chemical-resistant gloves, and a chemical-resistant apron. Wash hands thoroughly with soap and water before leaving the lab.

Procedure

Part A. Preparation of ash water (base):

1. Put a small beaker on the balance, then place an opened fluted filter paper into the empty beaker, and zero the balance.
2. Scoop about 30–50 g of wood ash into the filter. Accurately record the mass of the wood ash.
3. Transfer the wood ash from the filter paper to a 400-mL beaker. Do this gently to avoid making a lot of dust. Don’t worry if a little of the ash sticks to the filter paper.

4. Add 150-mL deionized water to the ashes in the beaker. Do this slowly to avoid making a lot of dust. Stir the resulting slurry with a glass stirring rod for about 1 minute.
5. Suspend a funnel over a 300-mL Erlenmeyer flask, placing the filter paper used in the earlier step inside the funnel.
6. Stir the ash water beaker well and pour as much as possible into the funnel without overflowing the filter paper. Don't worry if a little bit of ash gets into the filtered water. Wait until some of the liquid drains through the funnel then stir the slurry again and pour more into the funnel. Repeat until all of the slurry has been poured into the filter.
7. At this point it is likely that some of the ash is still in the beaker. If so, scrape as much as possible into the filter.
8. Obtain an additional 100-mL deionized water and use it in several small portions to rinse the residue from the beaker into the filter.
9. After the dripping stops and no liquid is visible in the ashes in the filter, remove the filter paper and discard the used ashes as directed by your instructor.
10. Obtain a new fluted filter paper and filter the ash water from the Erlenmeyer flask into a 250-mL volumetric flask. Add deionized water as needed to bring the 250-mL volumetric flask to the mark. (Remember to measure the volume by looking at the bottom of the meniscus.) The ash water is now ready for titration.

Part B. Titration of ash water

1. Label two 50-mL Erlenmeyer flasks A and B.
2. Zero a piece of weighing paper and obtain approximately 70 to 80-mg (0.070 to 0.080 g) of potassium hydrogen phthalate (KHP) acid.
3. Record the exact mass of the KHP.
4. Transfer the KHP to Erlenmeyer A.
5. Repeat steps 2 and 3 and transfer the KHP to Erlenmeyer B.
6. Add about 10-mL deionized water to the KHP in each flask and swirl to dissolve the solid.
7. Add 2 drops of phenolphthalein indicator to the acid solution in each flask and set aside.
8. Fill a 50-mL buret with filtered ash water, taking care to remove the air bubble from the tip.
9. Place a white sheet of paper under the 50-mL flask containing the acid so you can clearly see the color change.
10. Titrate the KHP solution with filtered ash water quickly with flask A to estimate the endpoint of the reaction.
11. Repeat the titration slowly with flask B to get an exact reading, to a light pink end point.
12. Calculate the molarity of the ash water base, using the fact that at the titration endpoint the moles of acid equals moles of base.

Data

	Trial 1	**Trial 2**
Mass, Empty Filters		
Mass, Ash and Filter		
Mass, Ash		
Mass, KHP		
Initial Buret Volume		
Final Buret Volume		
Volume Base		

Name: ______________________________

Post-Lab Questions

1. Determine the NaOH base equivalence by multiplying the moles of wood ash titrated by the molar mass of NaOH.

2. Determine the wood ash to base equivalence by dividing the answer to question 1 by the mass of wood ash used.

3. To make 1L of biodiesel from fresh vegetable oil, about 4g of NaOH is needed. What mass of ash would be needed to obtain sufficient base to make 100 gallons of biodiesel?

4. Wood ash found at an old campsite would not work well for this method. Why not?

5. Discuss how the use of wood ash as catalyst in the production of biodiesel aligns with the principles of green chemistry. Use the descriptions of the 12 principles of green chemistry found in the introduction section as a reference.

Teacher's Notes

Ash Water Titration—Renewable Resources for the Preparation of Biodiesel

Materials Included in Kit

Wood ash, 500 g

Phenolphthalein indicator solution, 100 mL

Potassium hydrogen phthalate (KHP), 25 g

Additional Materials Required *(for each lab group)*

400 mL beaker

250 mL volumetric flask

50 mL Erlenmeyer flask, 2

300 mL Erlenmeyer flask, 1

Coffee filter, or fluted filter paper (15cm diameter), 2

50 mL burette

Balance

Funnel

Safety Precautions

Phenolphthalein indicator solution contains alcohol and is a flammable liquid; it is toxic by ingestion. Do not use near flames or other sources of ignition. The base extracted from wood ash is slightly toxic by ingestion and skin absorption and is irritating to skin and eyes. Wear chemical splash goggles, chemical-resistant gloves, and a chemical-resistant apron. Wash hands thoroughly with soap and water before leaving the lab.

Disposal

Please consult your current *Flinn Scientific Catalog/Reference Manual* for general guidelines and specific procedures governing the disposal of laboratory waste.

Tips

- In addition to demonstrating the application of several of the principles of green chemistry, this experiment can serve as a substitute for the traditional acid-base titration lab, which typically reacts HCl with NaOH to a pink endpoint.
- As an extension, use wood ash from different sources and compare how the different samples equate to each other and NaOH. Also, run a titration in parallel using NaOH to observe directly the amount of NaOH needed to titrate an equivalent amount of KHP.
- As an extension, vary the temperature of the water used to extract base from the wood ash to determine effects on the endpoint of the titration. Also, compare the end point achieved from base obtained from the first extraction to a second or third extraction. Do these two things together to maximize the extraction, that is, to derive as much base from the wood ash as possible.
- As an extension, evaporate the base down to use as a catalyst in the preparation of biodiesel.
- You can get additional wood ash from your fireplace, a pizza parlor that uses a wood oven, a fireplace store or a store that sells wood stoves. It is necessary to strain the wood ash with a colander to remove bits of charcoal, foreign matter, etc. It is recommended that the ash be strained twice. It is advisable to do this outdoors since a great deal of dust is usually produced. Use protective equipment such as a mask to avoid exposure to dust. The grey/white ash is what is needed – black charred wood should be kept to a minimum. If you choose to use wood ash from a fire pit make sure that it is dry and has never been rained on.

Sample Data

	Trial 1	**Trial 2**
Mass, Empty Filters (g)	3.15	3.17
Mass, Ash and Filter (g)	53.52	53.25
Mass, Ash (g)	50.37	50.08
Mass, KHP (g)	0.070	0.068
Initial Buret Volume (mL)	0.00	20.20
Final Buret Volume (mL)	20.20	40.05
Volume Base (mL)	20.20	19.85

Calculations

Molarity of wood ash (base):

Moles base = Moles Acid = 0.070 g × 1 mole KHP/204.22 g = 3.43×10^{-4} moles KHP

Volume base needed to reach endpoint (L) × Molarity base = moles KHP

Molarity base = moles KHP/Volume base needed to reach endpoint (L);

= 3.43×10^{-4} moles/0.0202 L = 0.0170 M

Answers to Post-Lab Questions

1. Determine the NaOH base equivalence by multiplying the moles of wood ash by the molar mass of NaOH.

   moles wood ash = molarity wood ash x volume of ash water

   moles wood ash = 0.0170 M × 0.250 L = 0.00425 moles wood ash

   NaOH base equivalence: 0.00425 moles wood ash × 40.0 g/1 mole = 0.170 g

2. Determine the wood ash to base equivalence by dividing the answer to question 1 by the mass of wood ash used. This represents how much wood ash is needed to extract a given amount of base.

   0.170 g/50.37 g = 0.00338

3. To make 1L of biodiesel from fresh vegetable oil, about 4g of NaOH is needed. What mass of ash would be needed to obtain sufficient base to make 100 gallons of biodiesel?

   100 gallons biodiesel × (1 L/0.264 gallons) × (4 g NaOH/1 L biodiesel) × (50.37 g wood ash/0.170 g NaOH)

   = 448,930.48 g wood ash = 448.93 kg wood ash

4. Wood ash found at an old campsite would not work well for this method. Why not?

   Wood ash found at an old campsite will likely have spent significant time exposed to the elements, in particular rain and moisture. As a result some of the base will be extracted from it naturally over time and the wood ash will be less and less equivalent to NaOH. That is, less base will be extracted from wood ash found at an old campsite than from fresh wood ash.

5. Discuss how the use of wood ash as catalyst in the production of biodiesel aligns with the principles of green chemistry. Use the descriptions of the 12 principles of green chemistry found in the introduction section as a reference.

   To prepare biodiesel from vegetable oil base is needed as a catalyst. This experiment examines the extent to which wood ash can be used as a substitute for NaOH and aligns with several of the principles of green chemistry, as detailed below.

   Prevention: *waste wood ash is still useful for the extraction of base; left over wood ash can be recycled/composted, and base isolated can be used in further preparation of biodiesel.*

   Use of Renewable Feedstocks: *used wood ash as a base that can be used with another renewable feedstock (vegetable oil) to produce biodiesel.*

   Safer Solvents and Auxiliaries: *no organic solvents were used.*

   Design for Energy Efficiency: *experiment was run at ambient temperature and pressure.*

References

Credit: Irv Levy, Department of Chemistry, Gordon College

Anastas, P.T.; Warner, J.C. *Green Chemistry: Theory and Practice,* Oxford University Press: New York, **1998.**

Materials for *Ash Water Titration—Student Laboratory Kit* are available from Flinn Scientific, Inc.

Catalog No.	Description
AP8367	Ash Water Titration—Student Laboratory Kit

Consult your *Flinn Scientific Catalog/Reference Manual* for current prices.

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Catalog No. AP8366

Publication No. 8366

Design and Function: Blackberry Solar Cell

Introduction

Solar energy, the conversion of sunlight to electricity, has enormous potential as a clean source of renewable energy that demonstrates several of the principles of green chemistry. The field of Green Chemistry was founded in the 1990s with the goal of applying chemical principles to prevent pollution. The approach calls for the design of chemical products and processes that will reduce the use and generation of hazardous substances. Although solar energy has powered satellites and spacecraft for almost 50 years, it accounts for less than 1% of electricity generated in the United States today. An important factor limiting the use of solar energy is the trade-off between cost and efficiency. High- performance solar cells require large, high-purity silicon crystals, which are very expensive to produce. Less expensive forms of silicon are not as efficient. Photovoltaic cells that do not depend on silicon may offer a better balance between cost and efficiency. Dye-sensitized solar cells mimic the process that occurs in photosynthesis to harvest sunlight and convert it to electricity. Build a dye-sensitized solar cell and learn about the principles behind its operation.

Concepts

- Green Chemistry
- Solar Energy
- Photoelectric Effect
- Photovoltaic Cell
- Nanotechnology
- Semiconductors
- Electrochemistry
- Materials Chemistry

Background

Green Chemistry

Much of what makes this world modern is the result of the application of chemistry and chemical reactions. Oil and gasoline, prescription drugs, plastics, solvents, and fertilizers, to name a few, are all products of chemistry. Over time, many of the processes used to create these products were found to have unintended consequences and be quite harmful, whether to workers, the consumers or to the environment. In response to these pressing issues, green chemistry was developed as an approach to creating safer chemical products and processes from the initial design stage. The principles of green chemistry provide a framework for scientists to use when designing new materials, products, processes and systems. The principles focus on sustainable design criteria and provide tools for innovative solutions to environmental challenges. These principles are listed below.

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Renewable raw material or feedstock should be used whenever technically and economically possible.

Reduce Derivatives

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Catalysis

Catalytic reagents are superior to stoichiometric reagents.

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Chemical products should be designed so that at the end of their function they break down into innocuous products that do not persist in the environment.

Real-time Analysis for Pollution Prevention

Analytical methodologies need to be further developed to allow for real-time, in-process monitoring and control prior to the formation of hazardous substances.

Inherently Safer Chemistry for Accident Prevention

Substances and the form of a substance used in a chemical process should be chosen to minimize the potential for chemical accidents, including releases, explosions and fires.

Solar Cells

A solar cell, also called a photovoltaic cell, is a light-sensitive semiconductor device that uses the *photoelectric effect* to convert sunlight into electricity. A semiconductor is a material whose electrical conductivity increases with temperature or when irradiated with light. The increase in conductivity is due to electrons being promoted from the valence band to the conduction band. The energy difference is called the band gap energy and determines how much energy must be supplied for the material to conduct electricity.

Conventional solar cells contain a silicon diode as the semiconductor. The diode is created by joining n-type silicon (silicon doped with an impurity that has one more valence electron than silicon) to p-type silicon (silicon doped with an impurity that has one fewer valence electron than silicon). The different properties of the materials at the p–n junction give rise to a potential difference at the interface. Light striking the silicon surface excites electrons from the valence band to the conduction band and creates "electron-hole pairs." Electrons move toward the positive side of the junction, "electron holes" toward the negative side, and the resulting flow of electrons generates an electric current. The main factor limiting the use of solid-state solar cells is cost. In order to obtain maximum efficiency in the conversion of sunlight into electricity, large, high-purity silicon crystals are required.

In 1991, Michael Grätzel of the Swiss Federal Institute of Technology in Lausanne, Switzerland, reported a new type of solar cell called a dye-sensitized solar cell (DSC). Since the first DSC prototype was demonstrated more than 20 years ago, the technology has been commercialized to build solar panels for roofs and buildings.

Dye-sensitized solar cells are *photoelectrochemical cells*. The anode is nanocrystalline titanium oxide, a wide band-gap semiconductor, and the cathode is carbon or platinum. An iodine/iodide electrolyte solution serves as a redox catalyst in the solar cell. Nanocrystalline titanium oxide (particle size 10–50 nm) is deposited as a thin film onto the surface of a conductive glass or polymer sheet. The coating is heated to anneal the titanium oxide particles and improve their electronic conduction and then stained with a dye to make it sensitive to visible light. [The band gap energy of titanium oxide is about 3 eV, corresponding to ultraviolet light energy (about 400 nm). Thus, in the absence of a dye, titanium oxide requires ultraviolet light to initiate the photoelectric effect.] Using a nanocrystalline form of titanium oxide increases the effective surface area of the dye and improves the efficiency of light and energy absorption. The maximum possible voltage for a titanium oxide–based solar cell using iodine as the redox catalyst is about 0.9 V—this is the difference between the Fermi level (conduction band) of TiO_2 and the standard reduction potential of iodine.

The function of the dye in a dye-sensitized solar cell is similar to the light-harvesting reaction of chlorophyll during photosynthesis. Chlorophyll and other accessory pigments absorb visible light and the resulting excited state (high-energy) electrons travel down a series of intermediate electron acceptors with progressively lower reduction potentials. In a DSC, the dye absorbs visible light, which promotes an electron from the ground state to an excited state. The excited state electrons are transferred to the conduction band of titanium oxide, leaving oxidized dye molecules on the surface. The electrons migrate through the titanium oxide film and travel through the external circuit to the cathode. The dye is regenerated by accepting an electron from an iodide ion in the electrolyte solution. Iodide ions, acting as a redox catalyst, are regenerated by reduction of iodine at the cathode.

The components of a dye-sensitized solar cell are illustrated in the following schematic diagram (Figure 1), and the working principles are summarized in steps 1–6:

1. Dye molecule absorbs visible light.
2. An electron in the dye (S) is promoted to a "photo-excited state" (S*).
3. S* transfers an electron into the conduction band (E_f) of TiO_2.
4. The oxidized dye accepts an electron from the redox catalyst (I^-).
5. Electrons migrate through the external circuit to the cathode.
6. Iodine is reduced to iodide at the cathode, thus regenerating the redox catalyst.

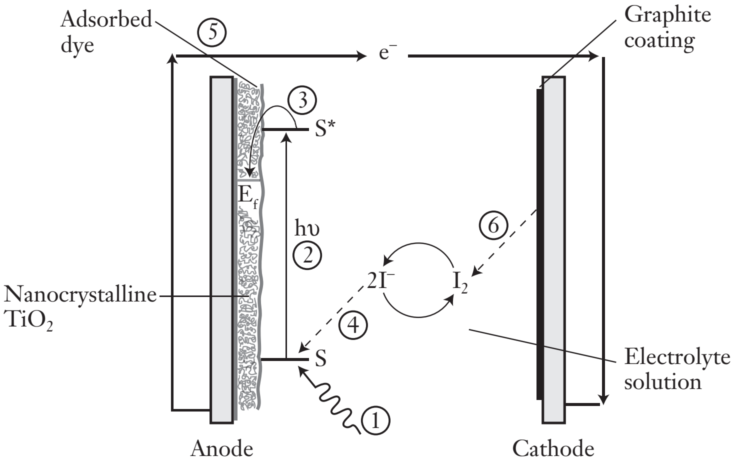


Figure 1.

Experiment Overview

The purpose of this activity is to build a dye-sensitized solar cell (DSC) and measure its electrical characteristics. The DSC is built using conductive glass plates as supports for the anode and the cathode. The anode is nanocrystalline titanium oxide that is stained with a dye to absorb visible light, and the cathode is graphite. The cell is filled with an iodine/iodide electrolyte solution that acts as a redox catalyst.

Materials

Transparent indium tin oxide (ITO) coated glass slide, 2
Iodine/Potassium iodide electrolyte solution, 2–3 drops
TiO_2 nanocrystalline paste
Pencil
Beral pipet, thin stem
Culture (petri) dish, 1
Binder clips, 2
Microscope slide, plastic
Blackberry
Spatula
Paper towel
Mortar and Pestle
Multimeter
Blackberry

Safety Precautions

The solvent for the iodine/potassium iodide electrolyte solution is propylene glycol, a combustible organic liquid. Polyethylene glycol is toxic by ingestion. Iodine in this solution is irritating to skin, eyes and the respiratory tract. Nanocrystalline titanium oxide is a fine dust and may be harmful if inhaled. Avoid breathing the fine particle dust and avoid contact of all chemicals with eyes and skin. Wear chemical splash goggles, chemical-resistant gloves, and a lab coat or chemical-resistant apron.

Name: ______________________________

Pre-Lab Questions

1. What is the function of each of the following components in a dye-sensitized solar cell?
   a. Titanium oxide

   b. Conductive glass

   c. Natural dye

   d. Iodine/iodide electrolyte solution

2. What are the advantages of dye-sensitized solar cells compared to conventional solar cells? What are the possible disadvantages?

3. Describe how a dye-sensitized solar cell mimics the process that occurs in photosynthesis.

Procedure

Part A. Titanium Oxide Anode

1. Obtain an ITO-coated glass slide and determine which side the ITO coating is on by using a multimeter set to ohms. Place the mutlimeter probes on the surface of the glass. The conductive side will register a reading of 10-30 ohms.
2. Tape the glass slide, conductive side up, to a clean surface with two layers of tape, as shown in Figure 2. The tape should mask about 5 mm of glass on each short side of the slide. (The tape will control the thickness of the titanium oxide coating).
3. Using a Beral-type pipet, add a thin line of TiO_2 suspension all the way across both the top and bottom of the glass slide (Figure 3a).

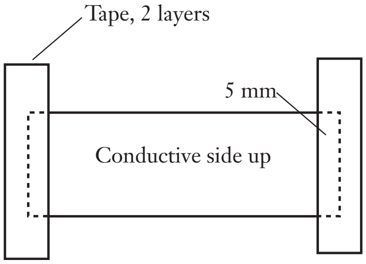
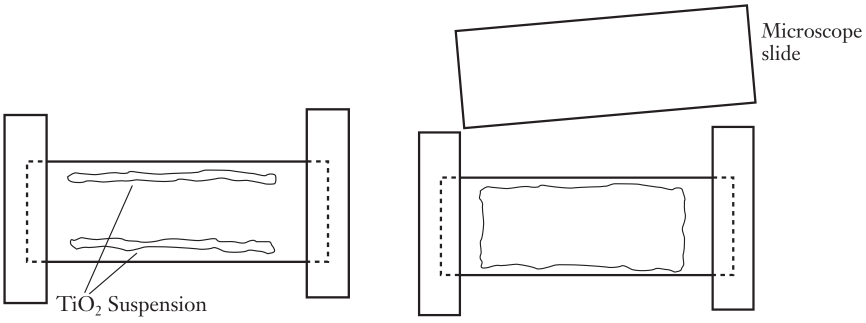


Figure 2.



3a.

3b.

Figure 3. Coating the Anode with the Titanium Oxide

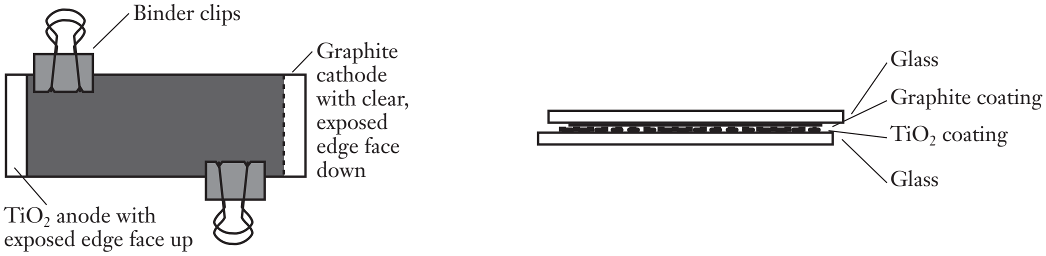
4. Use a clean microscope slide as a “squeegee” by drawing the long, thin edge of the slide to draw the suspension across the glass to coat the entire exposed surface (Figure 3b). Do not lift the slide off the glass. If any uncoated areas remain, push the microscope slide back up to the top of the taped-down slide. (This process must be done quickly to avoid drying out the suspension before the surface is covered.)
5. Allow the TiO_2 to dry for about 2–3 minutes before removing tape slowly as to not damage the conductive glass.
6. Place the glass plate, coated side up, on the surface of a hot plate. Turn the hot plate to a low setting (such as 1 or 2) and heat for about 15 minutes. During this time the titanium oxide coating will turn light brown at the edges and then transition back to its original off-white color of the titanium (Observe the plate during the heating process to avoid overheating and cracking the glass.) Caution: The hot plate is very hot.
7. After about 5 minutes, the titanium oxide coating will turn light brown at the edges. Continue heating the plate until the off-white color of the titanium oxide coating is restored. This will take about 15 minutes. (Observe the plate during the heating process to avoid overheating the plate and cracking the glass.)
8. Turn off the hot plate and allow the glass plate to cool for 5 minutes before attempting to remove it from the surface.
9. Using metal tweezers or forceps, carefully remove the glass plate from the hot plate and place the glass plate on a ceramic pad to cool (about 15 minutes).
10. *Dying the Anode:* Place the blackberry in a petri dish or aluminum pan. Use a spatula to crush the blackberry to extract the juices and remove solid pulp.
11. Place the glass slide with the TiO_2 face down into the aluminum pan. Allow to sit for 3–5 minutes.
12. Remove the TiO_2 slide from the blackberry juice. Use a paper towel to gently blot the excess juice off the slide. Dry the slide as much as possible, but do not remove any of the TiO_2 coating. Do not wipe the slide as this may remove some of the TiO_2 coating.

Part B. Graphite Cathode

13. Obtain another ITO coated glass slide. Determine which side the coating is on by using a multimeter with its setting placed on resistance (Ω). The indium tin oxide coating is on the side of the slide that gives a non-zero reading on the multimeter.
14. Using the tip of a graphite pencil, lay down the carbon catalyst by shading the indium tin oxide coated side of the slide. The graphite may not leave a visible mark.

Part C. Assembly

15. Lay the dyed titanium oxide electrode face up on a clean surface and place the graphite electrode face down on top of the titanium oxide electrode. Stagger the two plates so that part of the anode and part of the cathode will be exposed. Each plate extends out about 5 mm on either side of the glass “sandwich” and there is a clean, exposed surface on each plate. (The exposed surfaces serve as contact points for alligator clip leads to a multimeter.) See Figure 4.



4a. Top view 4b. Side view

Figure 4. Assembling the Solar Cell “Sandwich”

16. Use the 2 small binder clips to hold the slides together.
17. Carefully add 2–3 drops of iodine/potassium iodide electrolyte solution to one side of the solar cell “sandwich” in the area where the exposed glass meets the opposite electrode. The liquid will seep between the layers by capillary action.
18. Tilt the cell slightly and gently unclip and clip the binder clips to draw liquid throughout the cell. It may help to place a paper towel along the bottom edge of the cell.
19. Set the multimeter to measure the cell potential in volts (1–10 V). Connect the titanium oxide electrode to the negative lead and the graphite electrode to the positive lead. (The titanium oxide is the anode and the graphite is the cathode. Do not reverse the leads because a reverse bias may damage the cell.)
20. Measure and record the voltage of the solar cell under normal light illumination in the classroom.
21. Place the solar cell, photoanode side down, on an overhead projector stage or in front of a 100-W light source. Measure and record the solar cell voltage when illuminated.
22. Place the solar cell in the dark (for example, under a cardboard box “canopy”) and measure and record the dark solar cell voltage.
23. Set the multimeter to measure current in milliamps (1–20 mA). Connect the titanium oxide electrode to the negative lead and the graphite electrode to the positive lead.
24. Replace the solar cell on the overhead projector stage or in front of a bright lamp and measure and record the current.

Data

	Dyed Solar Cell (Prepared fresh)			**Dyed Solar Cell (After 1 week)**
Light Source	None	Classroom Light	Overhead Projector	Overhead Projector
Voltage				
Current				

Name: ______________________________

Post-lab Questions

1. Titanium oxide is the most common pigment in white paints. Using the normal, inexpensive source of this pigment in a DSC does not work however. What is the function of nanocrystalline TiO_2 in a solar cell?

2. Predict how you would expect the voltage and the current produced by a DSC to change of the size of the solar cell were increased from 1″ × 3″ to 3″ × 3″.

3. What are the advantages and disadvantages of placing solar panels on the southern versus the western side, respectively, of a home?

4. Discuss how the design of solar panels, or small cells, from the components used in this experiment align with some the principles of green chemistry. Use the descriptions of the 12 principles of green chemistry found in the introduction section as a reference.

Teacher's Notes

Blackberry Solar Cell

Materials Included in Kit

- Transparent indium tin oxide (ITO) coated glass slide, 14
- Iodine/Potassium iodide electrolyte solution, 25 mL
- Nitric acid, 0.1 M, 50 mL
- Titanium oxide, pre-measured, 4 g
- Beral pipet, thin stem, 30
- Binder clips, 14
- Culture (petri) dish, 7
- Lens paper, 4″ × 6″, 3
- Microscope slides, plastic, 7

Additional Materials Required *(for each lab group)*

- Blackberry
- Spatula
- Pencil
- Paper towel
- Mortar and Pestle
- Multimeter

Safety Precautions

The solvent for the iodine/potassium iodide electrolyte solution is propylene glycol, a combustible organic liquid. Polyethylene glycol is toxic by ingestion. Iodine in this solution is irritating to skin, eyes and the respiratory tract. Nanocrystalline titanium oxide is a fine dust and may be harmful if inhaled. Avoid breathing the fine particle dust and avoid contact of all chemicals with eyes and skin. Wear chemical splash goggles, chemical-resistant gloves, and a lab coat or chemical-resistant apron.

Disposal

Please consult your current *Flinn Scientific Catalog/Reference Manual* for general guidelines and specific procedures governing the disposal of laboratory waste. Excess titanium oxide suspension may be placed in the trash according to Flinn Suggested Disposal Method #26a. Excess iodine/potassium iodide solution may be reduced with excess sodium thiosulfate solution according to Flinn Suggested Disposal Method #12a. After disassembly, the solar cell components may be rinsed with water and then placed in the trash according to Flinn Suggested Disposal Method #26a.

Tips

- The nanocrystalline titanium oxide suspension is pre-measured. Each brown bottle contains 2 g of solid. You do not need to mass the solid. Instead add approximately 5 mL of 0.001 M HNO_3 directly to the bottle, then tightly cap and shake vigorously. Next, pour the contents into a mortar and grind into a paste. This paste can be applied to the slides.
- To prepare 100 mL of ≈ 0.001 M HNO_3 from 0.1 M HNO_3; add ≈ 1 mL of 0.1 m HNO_3 to 99–100 mL water and mix.
- Solar cells may be prepared in assembly line fashion—plan on about two hours for Parts A–C. There are two good stopping points if the complete set-up and demonstration cannot be completed at one time. The undyed, titanium oxide– coated anode may be stored completely submerged in a dilute nitric acid solution in the dark. (Do not store the dyed electrode—some of the dye will rinse off in the solvent.) The graphite-coated plates should be stored in any safe location where they will not be accidentally disturbed. Alternatively, the anode and cathode may be clamped together and stored in the dark before the electrolyte solution is added.
- The solar cells are reusable and may be stored for several weeks in the dark. The cell voltage will decrease during storage, but the cell current is fairly stable. The electrolyte layer may be replenished by adding a few more drops of electrolyte solution as needed to ensure complete coverage.
- Conductive glass is produced by depositing a thin, transparent coating of fluorine-doped tin oxide (SnO_2 : F) on the glass by pyrolysis. Tin oxide is a wide-band-gap semiconductor.
- In a voltaic cell, the anode is considered the negative electrode, the cathode the positive electrode.
- Experiment with different dyes to see how they affect the solar cell. Extract other fruits and flowers with water or ethyl alcohol and use the resulting dye solutions to stain the titanium oxide film. Nearly all fruits and flowers that are bright red, blue or purple contain a class of pigments or natural indicators called anthocyanins. Anthocyanins are derivatives of

cyanidin with a varying number of hydroxyl (OH) and glucoside (OGl) groups attached to the aromatic rings in the structure (Figure 6).

- Commercial dye–sensitized solar cells utilize organometallic complexes as the dye. The ligands in the coordination compound have been specially designed to coordinate with the titanium oxide coating and also to undergo efficient charge transfer to the titanium oxide conduction band.
- Construct an undyed solar cell and compare its electrical properties versus a dye-sensitized solar cell. The band gap energy for titanium oxide is 3–3.2 eV, corresponding to long-wavelength ultraviolet light (400 nm). An undyed titanium oxide solar cell will therefore require ultraviolet light for photoinitiation. In our experience, the maximum cell voltage for an undyed solar cell was 0.25 V in sunlight, as opposed to 0.45 V for a dye-sensitized solar cell on an overhead projector. Theoretically, the maximum cell voltage is equal to the voltage difference between the Fermi level of the semiconductor and the standard reduction potential of the redox catalyst. For titanium oxide and iodine, the theoretical cell voltage is 0.9–1.0 V. An undyed solar cell may be converted to a DSC by disassembling the cell, rinsing the photoanode with ethyl alcohol, and then dyeing the titanium oxide.

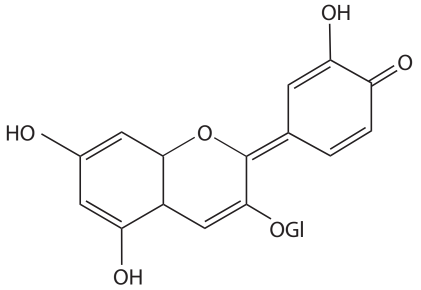


Figure 6. General Structure of Anthocyanin Dyes

- Connect two cells in series and measure the combined voltage and current. The voltage is additive when cells are connected in series. The current, however, does not change when cells are connected in series—the same current flows through each cell. Connect two cells in parallel and measure the combined voltage and current. The current is additive when cells are connected in parallel. The voltage should be the average of the individual voltages of each cell in the parallel circuit. Optimum performance is usually obtained with a parallel–series circuit (Figure 7).
- For best results have your students go outside to test the solar cells. One of the advantages of the dye-sensitized solar cell is the ability to conduct electricity even on a cloudy day.

Sample Data

	Dyed Solar Cell (Prepared fresh)			**Dyed Solar Cell (After 1 week)**
Light Source	None	Classroom Light	Overhead Projector	Overhead Projector
Voltage	0.01 V	0.23 V	0.42 V	0.35 V
Current	N/A	0.23 mA	0.73 mA	0.71 mA

Answers to Pre-Lab Questions

1. What is the function of each of the following components in a dye-sensitized solar cell?

   a. Titanium oxide

   Titanium oxide is a semiconductor. Electrons that are transferred from excited dye molecules enter the conduction band of titanium oxide. Electrons migrate from the anode to the cathode via an external circuit.

   b. Conductive glass

   A conductive surface is needed for both electrodes to complete the external circuit for migration of electrons from the anode to the cathode through the solar cell.

   c. Natural dye

   The dye absorbs visible light and acts as a "sensitizer" for the titanium oxide. Titanium oxide by itself does not absorb visible light.

   d. Iodine/iodide electrolyte solution

   The iodine/iodide electrolyte solution acts as a redox catalyst to regenerate the reduced form of the dye at the anode.

2. What are the advantages of dye-sensitized solar cells compared to conventional solar cells? What are the possible disadvantages?

   Dye-sensitized solar cells do not require expensive, high-purity silicon for their manufacture. However, DSC are not as efficient as conventional solar cells.

3. Describe how a dye-sensitized solar cell mimics the process that occurs in photosynthesis.

   Photosynthesis involves energy transfer from the sun to chemical potential energy in cells and living organisms. Special pigments in a cell absorb light energy, resulting in promotion of an electron to a higher energy level. Excited-state electrons are then transferred to other pigment and enzyme molecules, resulting in the reduction of H_2O *to* O_2 *(and* $NADP^+$ *to NADPH for synthesis of glucose).*

Answers to Post-Lab Questions

1. Titanium oxide is the most common pigment in white paints. Using the normal, inexpensive source of this pigment in a DSC does not work however. What is the function of nanocrystalline TiO_2 in a solar cell?

   The nanocrystalline form of TiO_2 *has a very large surface area. The large surface area is necessary to increase the capture or transfer of electrons to the conduction band.*

2. Predict how you would expect the voltage and the current produced by a DSC to change if the size of the solar cell were increased from 1″ × 3″ to 3″ × 5″.

   The voltage of a DSC is an intrinsic property of the materials used in the solar cell and thus should not depend on the size of the cell. The current of a DSC should increase as the size of the solar cell increases, because there is a greater flow of electrons. ***Instructor's note:*** *The current of a DSC is usually expressed in milliamps per square centimeter* (mA/cm^2)*.*

3. What are the advantages and disadvantages of placing solar panels on the southern versus the western side, respectively, of a home?

   The general consensus is to array solar panels facing south (in the Northern hemisphere) so that they get the most exposure to sun- light. This results in maximum sunlight/electricity during the day. Peak electricity usage in most homes occurs in the late afternoon, however, so a west-facing panel will also work.

4. Discuss how the design of solar panels, or small cells, from the components used in this experiment align with some the principles of green chemistry. Use the descriptions of the 12 principles of green chemistry found in the introduction section as a reference.

   Solar energy does not rely primarily on combustion produces and therefore is not a significant contributor of CO_2 *into the atmosphere. In this respect, the solar cells discussed herein are green alternatives to petrochemical based energy sources. Some of the raw materials used in the construction of this solar cell are biodegradable and renewable, e.g. the blackberry. Moreover, the fabrication procedure is quite safe with nitric acid, a corrosive hazard, used only sparingly. With respect to prevention, the synthesis described herein does indeed prevent production of significant waste and also prevents production of harmful pollutants during application of the solar cell itself.*

References

Bohrmann-Linde, C.; Tausch, M., "Photogalvanic Cells for Classroom Investigations: A Contribution for Ongoing Curriculum Modernization," *J. Chem. Educ*. **2003**, 80, 1471–1473.

Grätzel, Michael, "Molecular Voltaics that Mimic Photosynthesis," *Pure Appl.* Chem. **2001**, 73, 459–467.

Warner, John. "Construction of Solar Energy Devices with Natural Dyes". *Greener Approaches to Undergraduate Chemistry Experiments*. American Chemical Society, Washington D.C. 2002.

Anastas, P.T.; Warner, J.C. *Green Chemistry: Theory and Practice,* Oxford University Press: New York, **1998.**

Materials for *Design and Function: Blackberry Solar Cell* are available from Flinn Scientific Inc.

Catalog No.	Description
AP8366	Design and Function: Blackberry Solar Cell

Consult your *Flinn Scientific Catalog/Reference Manual* for current prices.

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Catalog No. AP8368

Publication No. 8368

Investigating the Toxicity of Road Deicers

Student Laboratory Kit

Introduction

Road deicers are effective at preventing ice from forming and reducing accidents during winter months. Certain road deicers have unintended environmental impacts. Green chemistry promotes the design of chemical products and processes that reduce or eliminate the use and generation of hazardous substances. This experiment introduces the idea that certain chemicals can be hazardous if allowed to leach into the environment. You will compare the ecotoxicity of three common ionic salts used as road deicers—sodium chloride, magnesium chloride and calcium chloride—by measuring germination rates and lengths of lettuce seeds in aqueous solutions of each alcohol.

Concepts

- Green Chemistry
- Serial dilutions
- Ecotoxicity
- Aqueous Solution Chemistry

Background

Much of what makes this world modern is the result of the application of chemistry and chemical reactions. Oil and gasoline, prescription drugs, plastics, solvents, and fertilizers, to name a few, are all products of chemistry. Over time, many of the processes used to create these products were found to have unintended consequences and be quite harmful, whether to workers, the consumers or to the environment. In response to these pressing issues, green chemistry was developed as an approach to creating safer chemical products and processes from the initial design stage. The principles of green chemistry provide a framework for scientists to use when designing new materials, products, processes and systems. The principles focus on sustainable design criteria and provide tools for innovative solutions to environmental challenges. These principles are listed below.

Prevention

It is better to prevent waste than to treat or clean up waste after it has been created.

Atom Economy

Synthetic methods should be designed to maximize the incorporation of all materials used in the process into the final product, leaving few or no atoms behind.

Less Hazardous Chemical Syntheses

Synthetic methods should be designed to use and generate substances that possess little or no toxicity to human health and the environment.

Designing Safer Chemicals

Chemical products should be designed to be fully effective while minimizing or eliminating their toxicity.

Safer Solvents and Auxiliaries

Minimize the use of auxiliary substances (e.g., solvents, separation agents, etc.) wherever possible and make them innocuous when used.

Design for Energy Efficiency

Energy requirements of chemical processes should be recognized for their environmental and economic impacts and should be minimized. If possible, synthetic methods should be conducted at ambient temperature and pressure.

Use of Renewable Feedstocks

Renewable raw material or feedstock should be used whenever technically and economically possible.

Reduce Derivatives

Unnecessary derivatization (use of blocking groups, protection/deprotection, temporary modification of physical/chemical processes) should be minimized or avoided if possible, because such steps require additional reagents and can generate additional waste.

Catalysis

Catalytic reagents are superior to stoichiometric reagents.

Design for Degradation

Chemical products should be designed so that at the end of their function they break down into innocuous products that do not persist in the environment.

Real-time Analysis for Pollution Prevention

Analytical methodologies need to be further developed to allow for real-time, in-process monitoring and control prior to the formation of hazardous substances.

Inherently Safer Chemistry for Accident Prevention

Substances and the form of a substance used in a chemical process should be chosen to minimize the potential for chemical accidents, including releases, explosions and fires.

Experiment Overview

In this lab you will assess the toxicities of aqueous solutions of three potential road deicers—sodium chloride, calcium chloride and magnesium chloride—by examining the effect these substances have on germination of lettuce seeds. The procedure introduces toxicity measurements, while using standard equipment and common techniques such as serial dilution and volumetric measurement. The experiment involves setting up Petri dishes with wetted filter paper on which the seeds are placed. Data including germination percentage and average root length are collected and correlated to salt identity and concentration.

Materials

- Petri dishes, 7
- Filter paper, 7
- Lettuce seeds, 30–50
- Aqueous solutions:
  - 10% NaCl, 10 mL
  - 10% $CaCl_2$, 10 mL
  - 10% $MgCl_2$, 10 mL
- Graduated cylinder, 10 mL
- Deionized water, 50 mL
- Test tubes, 6
- Test tube rack
- Graduated plastic pipet or micropipettor, 1
- Sharpie marker, 1
- Kimwipes

Safety Precautions

The chemical used in this lab are considered nonhazardous. Still, all standard laboratory safety procedures should be followed. Wear chemical splash goggles and chemical resistant gloves.

Procedure

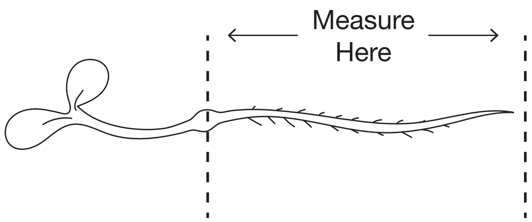
Preparing Lettuce Seeds for Germination:

1. Using a permanent marker, label a test tube with the deicer assigned by your teacher (e.g. 10% $CaCl_2$).
2. Fill the test tube with 10 ml of the stock (10%) solution.

3. Use the permanent marker to label 5 additional test tubes:
    - 1%
    - 0.1%
    - 0.01%
    - 0.001%
    - 0.0001%
4. Using a pipette, add 9ml of distilled water to test tubes 2 to 6.
5. Remove 1ml of your stock solution from test tube 1.
6. Using serial dilution, complete 1/10 dilutions from tubes 2 to 6. In other words, to make the 1% solution mix 1 mL of 10% solution with 9 mL of water. To make the 0.1% solution mix 1 mL of 1% solution with 9 mL of water, and so on.
7. Label 7 Petri dishes as follows: 10%, 1%, 0.1%, 0.01 %, 0.001%, 0.0001% and "control."
8. Place a filter paper into the bottom of each Petri dish.
9. Put 5 ml of each test tube solution into its associated (labelled) Petri dish.
10. Add approximately 40 lettuce seeds to each of the Petri dishes.
11. Stack and place Petri dishes into a single zip lock bag and seal to retain moisture.
12. Place in a well-lit location, but out of direct sunlight.
13. Allow seeds to germinate over 5 to 7 days. Be sure to check on the germinating seeds daily if possible.
14. Construct a data table to record your observations.
15. Record your observations daily in the data table.
16. After germination is complete, use the figure below as a model to measure growth of the seed (length indicated in figure).
17. Record results in a data table.

Obtaining data after one week:

1. Count the number of seeds germinated in each Petri dish and record in the table as shown on the next page. (*Use forceps; be careful not to break roots! If part of a root breaks, ignore that root in the following step.)
2. Measure the length of root of all germinated seeds with unbroken roots. Record the data. ***Measuring protocol:*** Before measuring, dry all the seeds by patting them with a Kimwipe to remove as much moisture as possible. For each sprout, measure the root length (not the shoot or seed itself) to the nearest mm. Measure when the root is straight. (If the root is curved, try to measure it as you roll it along a ruler.) Calculate the average length (mean) for each plate of seeds. Do not include seeds that did not germinate or seeds with broken roots when calculating average.



http://ei.cornell.edu/toxicology/bioassays/lettuce/data.asp

3. Dispose filter papers and seedlings in the waste container provided by your instructor.

Name: ______________________________

Data

	Petri dish 1 (10%)	Petri dish 2 (1.0%)	Petri dish 3 (0.1%)	Petri dish 4 (0.01%)	Petri dish 5 (0.001%)	Petri dish 6 (0.0001%)	Control
# of seeds germinated (count)							
as a percentage							

	Petri dish 1 (10%)	Petri dish 2 (1.0%)	Petri dish 3 (0.1%)	Petri dish 4 (0.01%)	Petri dish 5 (0.001%)	Petri dish 6 (0.0001%)	Control
Mean root length							

Post-Lab Questions

1. Based on your data do ionic compounds appear to be a green option for use as road deicers? Explain.

2. Based on the results of this experiment would you feel comfortable using ecotoxicity data to estimate human toxicology data? That is, would you feel comfortable ingesting a chemical that did not prevent germination and growth in a vast majority of lettuce seeds? Explain.

Teacher's Notes

Investigating the Toxicity of Road Deicers

Materials Included in Kit *(For 14 groups of students working in pairs)*

Petri dishes, 100

Filter paper, 9 cm, 100

Lettuce seeds, 20,000 (1 oz)

Sodium chloride, 10% solution, 500 mL

Calcium chloride, 120 g

Magnesium chloride, 300 g

Additional Materials Needed *(for each lab group)*

Graduate cylinder, 10 mL

Deionized water

Plastic pipet or micropipettor, 1

Sharpie marker, 1

Kimwipes

Preparation of 10% Aqueous Solutions

10% $CaCl_2$: Dissolve 10 g of $CaCl_2$ in 90 mL of distilled or deionized water. Clearly label the solution.

10% $MgCl_2$: Dissolve 10 g of $MgCl_2$ in 90 mL of distilled or deionized water. Clearly label the solution.

Safety Precautions

The chemicals used in this lab are considered nonhazardous. Still, all standard laboratory safety procedures should be followed. Wear chemical splash goggles and chemical resistant gloves.

Disposal

Please consult your current *Flinn Scientific Catalog/Reference Manual* for general guidelines and specific procedures, and review all federal, state and local regulations that may apply, before proceeding. Leftover solids may be disposed of according to Flinn Safety Disposal Method #26a. Solutions may be disposed of accroding to Flinn Safety Disposal Method #26b.

Tips

- Point out to students that many of the products we purchase for personal use contain chemicals and those chemicals generally find their way into the environment very easily. For example, the chemicals used in road deicers leach into the ground and may affect plant growth such as observed in this lab experiment. Therefore, if greener chemicals can be used to accomplish an objective, in this case melting road/sidewalk ice, in a cost effective way, they should be used.
- This is a nice demonstration of a straightforward way of measuring ecotoxicity (and its relationship to toxicology) that need not be limited to ionic compounds. For example, the effects of other compounds such as alcohols on lettuce seed growth could be measured using the same protocol.
- Serial dilutions are commonly performed in analytical laboratories and hospital labs. This is a valuable technique to introduce students to, and one that is not often taught in introductory courses. This particular experiment is a nice way to introduce green chemistry, ecotoxicity, and introductory analytical chemistry in a single stroke.
- If time permits each lab group may set up trials for each compound. Or, each lab group can be assigned a single compound for investigation and the lab groups can share data at the end of the data collection period.
- Set up another, subsequent experiment to run as a challenge in which students must determine the cut-off concentration at which the aqueous solutions deter germination and growth. Students can be left to determine how many new solutions must be prepared to make such as determination. For example, they may see that seeds grow in 3% solutions but not in 4% solutions and iteratively test until they settle on 3.5% as the cut-off. Also, they may find that the cut-off differs between the three compounds. This is a nice approach that challenges students' experimental design skills and their ability to function in a guided-inquiry lab environment.
- Radish seeds can also be used for this experiment. You may want to have some students use radish seeds and others use lettuce seeds to see how that influences the results.

Sample Data (These data represent values measured after one week of growth)

Data for NaCl, $MgCl_2$ and $CaCl_2$ appear in the top, middle, and bottom rows, respectively.

	Petri dish 1 (10%)	**Petri dish 2 (1.0%)**	**Petri dish 3 (0.1%)**	**Petri dish 4 (0.01%)**	**Petri dish 5 (0.001%)**	**Petri dish 6 (0.0001%)**	**Control**
# of seeds germinated (count)	0 0 0	40/40 40/40 40/40	40/40 40/40 40/40	40/40 40/40 40/40	40/40 40/40 40/40	40/40 40/40 40/40	40/40 40/40 40/40
as a percentage	0%	100%	100%	100%	100%	100%	100%

	Petri dish 1 (10%)	**Petri dish 2 (1.0%)**	**Petri dish 3 (0.1%)**	**Petri dish 4 (0.01%)**	**Petri dish 5 (0.001%)**	**Petri dish 6 (0.0001%)**	**Control**
Mean root length	0.0 cm 0.0 cm 0.0 cm	0.5 cm 0.5 cm 0.5 cm	3.5 cm 3.7 cm 3.5 cm	3.5 cm 3.0 cm 5.0 cm	4.0 cm 3.0 cm 3.5 cm	3.7 cm 4.5 cm 6.0 cm	3.5 cm 3.3 cm 3.0 cm

Answers to Post-Lab Questions

1. Based on your data do ionic compounds appear to be a green option for use as road deicers? Explain.

   Yes, ionic compounds appear to be a greener option for use as road deicers, at least when used in concentrations less than or equal to 1%. In these solutions, germination and significant growth occurred (against controls) in nearly all seeds, in all three compounds' aqueous solutions with concentrations 1% or lower.

   However, no data was collected for solution concentrations in excess of 1%. Therefore it cannot be stated that road deicers, when used at such concentrations, are green or not green.

2. Based on the results of this experiment would you feel comfortable using ecotoxicity data to estimate human toxicology data? That is, would you feel comfortable ingesting a chemical that did not prevent germination and growth in a vast majority of lettuce seeds? Explain.

   No. The data obtained in this experiment are not sufficient to draw conclusions about toxicity with respect to humans. We do not know whether these compounds will not harm humans, only that they do not prevent germination and growth of lettuce seeds when used in concentrations less than or equal to 1%.

References

Green Chemistry Laboratory Activities: Comparative Terrestrial Ecotoxicity of Road Salts and Common Alcohols. Travise A. Crocker, Irvin J. Levy and Timothy J. Swierzewski, Abstracts of the 240th ACS National Meeting, CHED 209 Boston, MA, August 2016.

Anastas, P.T.; Warner, J.C. *Green Chemistry: Theory and Practice,* Oxford university PRess: New York, **1998.**

Green Chemistry: *Investigating the Toxicity of Road Deicers—Student Laboratory Kit* and supporting supplies are available from Flinn Scientific, Inc.

Catalog No.	**Description**
AP8368	Investigating the Toxicity of Road Deicers—Student Laboratory Kit

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Catalog No. AP8365

Publication No. 8365

Recycling Polylactic Acid to Make a Household Surface Cleaner

Introduction

Biobased polymers are plastics derived from renewable biomass sources. This lab features polyactic acid, a polymer derived from corn. Several of the 12 principles of green chemistry are featured in this lab: the use of renewable feedstocks as starting material and pollution prevention by converting a waste cup into a usable cleaner. This lab demonstrates how to chemically convert plastic cups made from polylactic acid into household cleaning agents, and is an example of how green chemistry applies to consumer products.

Chemical Concepts

- Green Chemistry
- Acid-Base Chemistry
- Hydrolysis Reactions
- Aqueous Solution Chemistry
- Titrations
- Polymers

Background

Much of what makes this world modern is the result of the application of chemistry and chemical reactions. Oil and gasoline, prescription drugs, plastics, solvents, and fertilizers, to name a few, are all products of chemistry. Over time, many of the processes used to create these products were found to have unintended consequences and be quite harmful, whether to workers, the consumers or to the environment. In response to these pressing issues, green chemistry was developed as an approach to creating safer chemical products and processes from the initial design stage. The principles of green chemistry provide a framework for scientists to use when designing new materials, products, processes, and systems. The principles focus on sustainable design criteria and provide tools for innovative solutions to environmental challenges.

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Design for Degradation

Chemical products should be designed so that at the end of their function they break down into innocuous products that do not persist in the environment.

Real-time Analysis for Pollution Prevention

Analytical methodologies need to be further developed to allow for real-time, in-process monitoring and control prior to the formation of hazardous substances.

Inherently Safer Chemistry for Accident Prevention

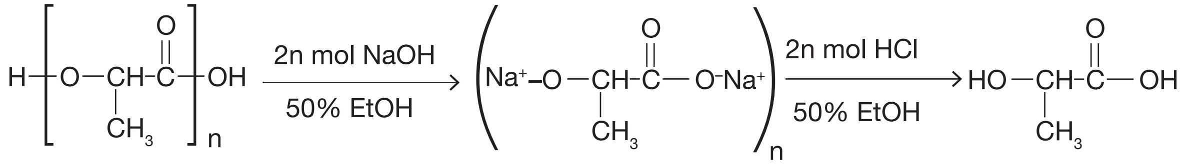
Substances and the form of a substance used in a chemical process should be chosen to minimize the potential for chemical accidents, including releases, explosions and fires.

Experiment Overview

In this lab you will convert a polylactic acid cup into a household surface cleaner. Polylactic acid is a polymer derived from corn, a renewable resource, in contrast to the majority of commercial plastics which are derived from petroleum, a non-renewable resource. In addition, polylactic acid biodegrades on a reasonable time scale (~180 days) relative to other plastic polymers such as polyethylene (HDPE/LDPE), polyethylene terephthalate (PET) and polystyrene (PS) which can persist in the environment for 500 to 1000 years without biodegrading. This is environmentally problematic because the world produces approximately 200 billion pounds of plastics and nearly half of this plastic winds up in landfills each year.

Polylactic acid (PLA) is derived from natural resources. Lactic acid, which is derived from corn, is the monomer used to create this polymer. PLA degrades under compost conditions into CO_2, H_2O, and humus, all benign components. Also, the CO_2 released during degradation returns the carbon to the atmosphere with no overall net gain. Since the polymer is made from a corn feedstock, the process uses significantly less petroleum than traditional polymers. It is categorized under plastic resin code #7 or #0 ("other plastics"). While it is recyclable, currently there are no municipal recycling facilities that accept PLA.

Instead of disposing PLA products into landfills or compost facilities, another option of handling them at the end of the products' useful life is to reuse them as other products. One thing to do with PLA materials is to convert them into an antimicrobial cleaning solution. In order to do so the PLA polymer must be depolymerized via hydrolysis in basic solution, a reaction that results in the deprotonation of lactic acid monomers and formation of sodium lactate. Subsequently, sodium lactate monomers are protonated using hydrochloric acid to form lactic acid. See Figure 1 below.



$$\mathrm{H{-}\left[O{-}\underset{CH_3}{CH}{-}\overset{O}{\overset{\|}{C}}\right]_n{-}OH \xrightarrow[\text{50\% EtOH}]{\text{2n mol NaOH}} \left(Na^+{}^-O{-}\underset{CH_3}{CH}{-}\overset{O}{\overset{\|}{C}}{-}O^-Na^+\right)_n \xrightarrow[\text{50\% EtOH}]{\text{2n mol HCl}} HO{-}\underset{CH_3}{CH}{-}\overset{O}{\overset{\|}{C}}{-}OH}$$

Figure 1. The reaction scheme describing the depolymerization of polylactic acid into sodium lactate, and subsequent protonation of sodium lactate to form lactic acid.

Materials

- Hydrochloric acid solutions, HCl, 6 M
- Balance, 0.01-g precision
- 1.4 M NaOH in 1:1 ethanol/water, 100 mL
- 100-mL graduated cylinder
- 250-mL Erlenmeyer flask
- Heat resistant gloves
- Ice water bath
- Magnetic stir bars, 1
- Permanent marker
- Pipet
- Polylactic acid cup
- Stirring hot plate
- Stirring rod
- Thermometer
- Watch glass
- Weigh boat

Safety Precautions

Concentrated hydrochloric acid and aqueous sodium hydroxide are highly toxic by ingestion or inhalation and is severely corrosive to skin and eyes; can cause severe body tissue burns. Wear chemical splash goggles and chemical resistant gloves.

Procedure

1. Put on safety glasses, gloves and apron/lab coat.
2. Cut PLA cup into small pieces using scissors. The smaller the pieces, the faster the reaction. Do not use any green parts. (If there is ink writing on the cup do not use those pieces).
3. Place PLA pieces into a weigh boat.
4. Measure 5 g of PLA pieces on a balance.
5. Add 5 g of PLA pieces into the 250 mL Erlenmeyer flask using a funnel.
6. Using the graduated cylinder, measure 100 mL of the pre-made solution (1.4 M NaOH in 1:1 ethanol/water).
7. Add the solution and magnetic stir bar into the flask.
8. Place the flask onto the hot plate.
9. Turn on the heating function of the hot plate and heat the solution to 90°C (reduce the heat if the flask begins to vigorously boil).
10. Heat and stir the solution until the PLA pieces have completely dissolved. Use a stirring rod to stir the solution. Alternatively, the stir function on a stir-plate will safely stir the solution. Record observations as reaction proceeds in the data table provided.
11. After the PLA pieces have completely dissolved and the solution is pale yellow, turn off the hot plate. Temperature should be 80°C–90°C.
12. Use heat resistant gloves to remove flask from hot plate. Place the flask in an ice water bath and allow the solution to cool until it is below 60°C. This mixture is now called "hydrolyzed PLA".
13. Using the plastic pipette, transfer 1–2 drops of the solution to the watch glass.
14. Test the pH of the hydrolyzed PLA by wetting a pH strip in the watch glass. Record the pH.
15. Slowly add 50 drops of 6 M HCl into the flask. **Mix well.**
16. Dip the glass stirring rod into the solution then touch it to the mouth of the flask to remove big drops of liquid. The wetted tip can then be touched to a strip of blue litmus paper to test its pH. Note whether the solution is acidic or basic.
17. Record whether the solution is acidic or basic after each test (thoroughly mix the solution after adding 6 M HCl before testing it).
18. Repeat steps 15–17 until an acidic pH is obtained. Each strip of litmus paper can be used several times.
19. Measure the final pH of the solution using a pH strip. Aim for a pH range of 4–5. The solution now contains lactic acid and sodium chloride (NaCl).

20. Using a funnel, transfer the lactic acid solution into the squirt bottle.
21. Spray the solution onto a dirty surface and wipe clean with a paper towel.

Post-Lab Questions

1. How much NaOH is required to completely react with the PLA.
2. Why is the Acidification step required?
3. Describe the appearance of the plastic before it is placed in solution and after it is placed in the solution.
4. Describe the appearance of the solution before the reaction starts and after the reaction is complete.
5. What is the pH of the solution after the reaction stops and before any HCl is added?
6. Does the plastic degrade under base hydrolysis conditions?
7. Explain how the conversion of polylactic acid cups into a cleaning agent is an example of green chemistry in action.

Data

Time	# Minutes	Temperature (°C)	Observation
	0		
	2		
	4		
	6		
	8		
	10		

# Drops 6M HCl	Color of Litmus Paper After Addition	pH	Acid or Base?
50			
100			
150			
200			
250			
300			
350			

Teacher's Notes

Recycling Polylactic Acid to Make a Household Surface Cleaner

Materials Included in Kit

- Polylactic acid cup, 15
- Ethyl alcohol, anhydrous, 1000 mL
- Hydrochloric acid solution, 6M, 500 mL
- Sodium hydroxide solution, 6M, 400 mL
- Litmus Paper, Blue, Vial

Additional Materials Needed (for each lab group)

- 100-mL graduated cylinder
- 250-mL Erlenmeyer flask
- Balance, 0.01-g, precision
- Heat resistant gloves
- Ice water bath
- Label tape
- Magnetic stir bars
- Permanent marker
- Pipets, disposable
- Stirring hot plate
- Weigh boat

Safety Precautions

Concentrated hydrochloric acid, and solid and aqueous sodium hydroxide are highly toxic by ingestion or inhalation and is severely corrosive to skin and eyes; can cause severe body tissue burns. Wear chemical splash goggles and chemical resistant gloves. Please consult the appropriate Safety Data Sheets for further safety, handling and disposal information.

Disposal

Please consult your current *Flinn Scientific Catalog/Reference Manual* for general guidelines and specific procedures governing the disposal of laboratory waste.

Tips

- This experiment can be done in a more quantitative way by titrating the basic solution, as opposed to adding drops qualitatively. This experiment can therefore serve as a substitute to traditional acid-base titration labs. In addition, the use of a pH meter or probe can be substituted for pH paper.
- Green chemistry will likely be a new topic for students. Given that it is not a regular part of high school curricula nor most undergraduate curricula it may help to spend a bit of time on the 12 principles as part of your pre-lab lecture. The Beyond Benign website (www.beyondbenign.org) includes information on how green chemistry can be further integrated throughout a chemistry curriculum.
- The 1.4 M NaOH solution in 1:1 ethyl alcohol:water can be prepared ahead of the lab or prepared by students as part of the experiment. To prepare 100 mL of the solution, the following procedure should be followed: dispense 23.33 mL of 6M NaOH into a small beaker and add approximately 40 mL each of ethyl alcohol and distilled deionized water. It is not necessary to perform more quantitative measurements because the exact stoichiometry of the reaction is not a concern. That is, this preparation should give enough NaOH to promote base hydrolysis of the PLA cup.
- Have the students handle and cut up the PLA pieces before putting on their gloves. The pieces should be about the size of an adult thumbnail. Wait to hand out the NaOH until they have added the PLA pieces to the flask.

Sample Data

Time	# Minutes	Temperature (°C)	Observation
	0	24.0	Clear, colorless
	2	65.0	Off yellow, cloudy
	4	74.1	Off yellow, cloudy
	6	81.2	Boiling, off yellow, clear, dissolution of plastic complete
	8		
	10		

# Drops 6M HCl	Color of Litmus Paper After Addition	pH	Acid or Base?
50	Lavender	11	Base
100	Lavender	11	Base
150	Lavender	11	Base
200	Lavender	10	Base
250	Lavender	10	Base
300	Lavender	8	Base
350	Pink	4.5	Acid

Answers to Post-Lab Questions

1. How much NaOH is required to completely react with the PLA.

   5 g PLA cup × (1 mole PLA monomer/72 g) × (2 mole NaOH/1 mole PLA monomer) = 0.1388 moles NaOH

2. Why is the Acidification step required?

   The acidification step converts sodium lactate to polylactic acid. In other words, the acidification step is taken to protonate the monomers following the depolymerization step.

3. Describe the appearance of the plastic before it is placed in solution and after it is placed in the solution.

   Prior to being placed in solution the plastic is clear and colorless. Once placed in solution the plastic retains its color but begins to dissolve.

4. Describe the appearance of the solution before the reaction starts and after the reaction is complete.

   Prior to the reaction beginning the solution is clear and colorless. Once the reaction is complete the solution is a pale yellow color.

5. What is the pH of the solution after the reaction stops and before any HCl is added?

   After the reaction stops and before the any HCl is added the solution is very basic. That is, the approximate pH is greater than 12. We know the pH is high prior to adding acid because even after the addition of 50 drops of 6 M HCl the pH is still in the basic regime, at around 11.

6. Does the plastic degrade under base hydrolysis conditions?

   The plastic doesn't degrade (or decompose) under base hydrolysis conditions. Rather, the plastic depolymerizes. On a macroscopic scale, you will observe that the plastic dissolves in basic solution. Upon dissolution, the plastic, or polylactic acid polymer, breaks down into monomers of sodium lactate. Subsequently these sodium lactate monomers are protonated in an acidification step.

7. Explain how the conversion of polylactic acid cups into a cleaning agent is an example of green chemistry in action.

   Polylactic acid (PLA) is derived from a renewable feedstock (corn). Furthermore, it biodegrades to environmentally benign decomposition products on a short time scale. Its use in consumer products is therefore preferable to the use of petroleum-based plastics such as HDPE and LDPE. Moreover, the conversion of PLA cups that would otherwise be discarded to a landfill reduces environmental impact to an even greater degree.

References

Gurney, Rich. *Hydrolysis of Post-Consumer Polylactic Acid Waste*, Chmistry, Simmons College, **2008.**

Anastas, P.T.; Warner, J.C. *Green Chemistry: Theory and Practice,* Oxford University Press: New York, **1998.**

Recycling Polylactic Acid to Make a Household Surface Cleaner is available from Flinn Scientific, Inc.

Catalog No.	Description
AP8365	Recycling Polylactic Acid to Make a Household Surface Cleaner

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