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Green Chemistry

A Project
Submitted
To
Governors State University

By
Mary Lynn Koster

In Partial Fulfillment of the
Requirements for the Degree
Of
Masters in Science

January, 2015

Governors State University

University Park, Illinois

Dedicated to my husband, Timothy Lee Koster, my parents (Norman and Marilyn Weaver), my children and their spouses (Michael and Ursula Koster, Thomas Koster, Marie and Evan Gress, Karissa Koster), and my extended Family, Friends, Professors, and all others who have encouraged my academic pursuits. Above all my Heavenly Father, who gave me life and breath and put chemistry as a passion in my heart.

Jeremiah 29:11-13 New International Version (NIV)

For I know the plans I have for you," declares the LORD, "plans to prosper you and not to harm you, plans to give you hope and a future. Then you will call on me and come and pray to me, and I will listen to you. You will seek me and find me when you seek me with all your heart.

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Abstract

In the academic year of 2014-2015, Governors State University will be accepting and enrolling freshman into the university. Therefore, the chemistry department will be offering general chemistry for the first time in its history. Now is the time to introduce the concept of Green Chemistry. Green Chemistry is not a new class but a philosophy that the department or at least the individual experiments within a lab course needs to look at. There are 12 Principles of Green Chemistry:

1. Prevention
2. Atom Economy
3. Less Hazardous Chemical Syntheses
4. Designing Safer Chemicals
5. Safer Solvents and Auxiliaries
6. Design for Energy Efficiency
7. Use of Renewable Feedstocks
8. Reduce Derivatives
9. Catalysis
10. Design for Degradation
11. Real-time Analysis for Pollution Prevention
12. Inherently Safer Chemistry for Accident Prevention ¹

Experiments from a laboratory class will be selected to apply the Principles of Green Chemistry, the experiments will be selected, and modifications to the experiments will be made.

Introduction

Before Green Chemistry, there came a pioneer woman by the name of Rachel Carson in 1962 who would start the environmental push. In her book, Silent Spring, she writes; “The history of life on earth has been a history of interaction between living things and their surroundings. To a large extent, the physical form and the habits of the earth’s vegetation and its animal life have been molded by the environment. Considering the whole span of earthly time, the opposite effect, in which life actually modifies its surroundings, has been relatively slight. Only within the moment of time represented by the present century has one species – man – acquired significant power to alter the nature of his world.”²

American Experience, a DVD aired on Public Television, stated, “[the] essence of Rachel Caron’s Book is that we [the public] have to come to terms with nature. We have to work with nature and not against it.”³ The publishing of Silent Spring in 1962 was the start of caring for the environment and the world in which we live. The Environmental Protection Agency (EPA) was created in 1970⁴, inspired by the outcry of the public and the result of the articles published about Silent Spring and from the government realizing that something had to be done, to protect the environment and human health.⁵ The EPA started to established rules and regulations on what chemicals and by products, which could possibly be expelled into the air, soil, and water. In 1997, The Green Chemistry Institute (GCI) was launched. The EPA defined Green Chemistry as “the design of chemical products and processes that reduce or eliminate the use or generation of hazardous substances. Green chemistry applies across the life cycle of a chemical product, including its design, manufacture, use, and ultimate disposal. Green chemistry is also known as

sustainable chemistry.”⁶ and then in 1998 “Paul Anastas and John C. Warner co-authored the groundbreaking book, *Green Chemistry: Theory and Practice*”.⁷ Within the book, they came up with benchmarks to help define what Green Chemistry is. (See Figure 1 for the complete list of The 12 Principles of Green Chemistry with definitions. See Figure 2 for the short version put out by the American Chemical Association.)

The 12 Principles of Green Chemistry

1. **Prevention**

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

2. **Atom Economy**

Synthetic methods should be designed to maximize the incorporation of all materials used in the process into the final product.

3. **Less Hazardous Chemical Syntheses**

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

4. **Designing Safer Chemicals**

Chemical products should be designed to effect their desired function while minimizing their toxicity.

5. **Safer Solvents and Auxiliaries**

The use of auxiliary substances (e.g., solvents, separation agents, etc.) should be made unnecessary wherever possible and innocuous when used.

6. **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.

7. **Use of Renewable Feedstocks**

A raw material or feedstock should be renewable rather than depleting whenever technically and economically practicable.

8. **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 waste.

9. **Catalysis**

Catalytic reagents (as selective as possible) are superior to stoichiometric reagents.

10. **Design for Degradation**

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

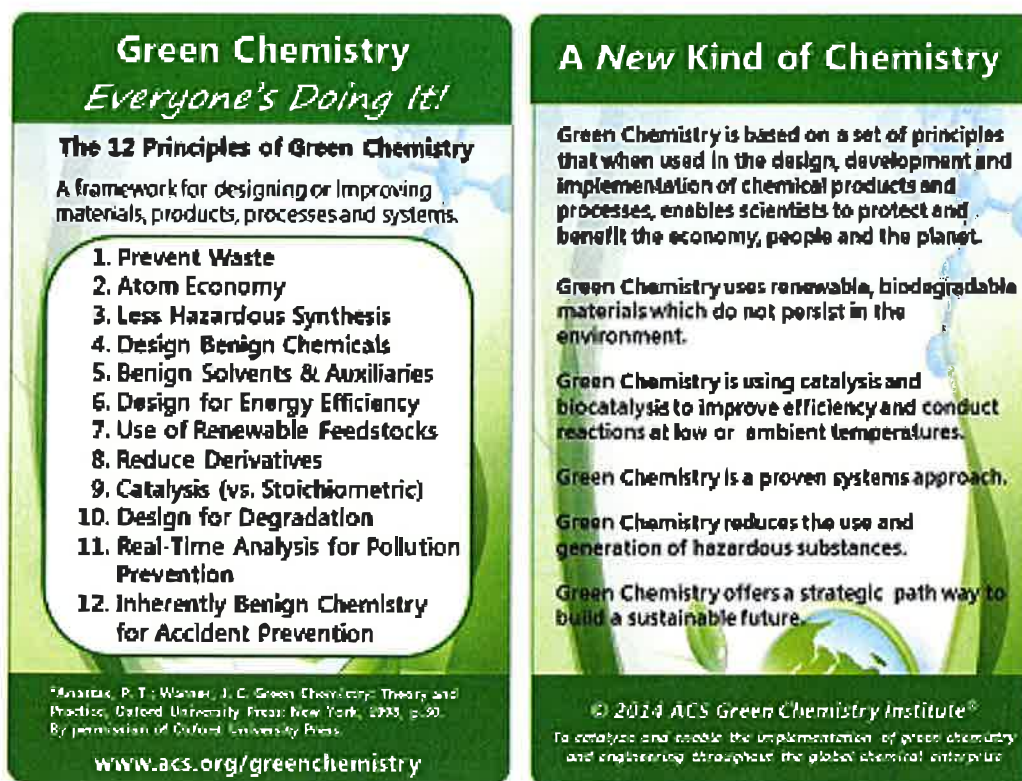
11. Real-time analysis for Pollution Prevention

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

12. 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.⁸

Figure 1: American Chemical Society (ACS) pocket guide



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The Chemistry Department at Governors State University (GSU) is at a prime time to approach and embrace the concept of Green Chemistry using The 12 Principles of Green Chemistry listed in Figure 1 and 2. The academic year, 2014/2015, brought freshman to the GSU campus for the first time. GSU has created General Education Themes in January of 2013 to guide the lower division curriculum. One of the themes that match up with the Green Chemistry is sustainability, which concentrates on stewardship involving long-term maintenance

and responsibility for the resources we are given, be it the environment, society, or ourselves.¹⁰ Also in GSU's mission statement, the University would like the graduates of GSU to be stewards of their future and to be a steward of the environment.¹¹ When the students learn more about Green Chemistry and realize that what they do individually can have an impact on the space around them.

The course that showed the most potential for piloting Green Chemistry labs was the Chemistry Science Foundations class. It was chosen because it is a smaller class, about 20 students, it repeats every semester, and this class is usually taken early in the students' college career at GSU.

After Chemistry Science Foundations was identified as the class to do the pilot labs, a search was done on the syllabus to identify the labs that could have potential to either be replaced completely with a Green Chemistry Lab or be modified to incorporate some of The 12 Principles of Green Chemistry. A search was made of the syllabus of what the professor wanted to cover in the labs and the goals that the students would learn from the labs.

A search was done through the lab manuals at GSU and a web search of articles from both the journals and files from other professors or teachers that placed the labs on the web. When the labs were identified, a discussion occurred between the professor and myself to make sure the lab was a good fit for the learning objectives of the particular lab. Then the labs were modified by either replacing a compound within the experiment, reducing the amount of solution used, or the elimination of the compound altogether. The experiment was tested to determine if the results were achieved and to make sure the modification did not affect the results the students should see. A check was also made on the data sheets to make sure there was nothing missing

and the directions were able to be followed as written. Either the modifications were written on the board, told verbally to the students or the complete experiment instructions were rewritten for them. In addition, supplies and chemicals were identified to be ordered.

The labs that were chosen were labs that had been written up in the literature, seen in the textbooks, given in a seminar, given from one chemistry teacher to another, or by examination and trying the experiments with application of The 12 Principles of Green Chemistry.

Materials & Methods

Identification of experiments

The experiments that were identified, after a literature and textbook search, were experiments that GSU has done in the past but needed to be modified to fit into the 12 Principles of Green Chemistry. The labs chosen from Chemistry Science Foundations are (1) conservation of mass, (2) Double Replacement Lab, and (3) Titration – the Percent Acetic Acid in Vinegar. From Analytical Chemistry the lab that has very good potential to be converted to a Green Chemistry Lab is the Iodimetric Titration of Vitamin C.

The professor in charge of the lab approved the experiments to be piloted. The selected lab was tested before the students performed the experiment to make sure the experiment would run smoothly and to make sure the supplies did not need to be ordered. The students then were given the instructions and the data sheet to compete the lab.

The Selection and the Modification

Table 1: Learning Objectives for the experiments that were chosen

Experiment	Objective	Traditional Chemistry	Green Chemistry
Conservation of Mass (See Appendix A)	<ul style="list-style-type: none">• Reinforce the law of Conservation of Mass• Open and Closed systems	-Just told about the Law of Conservation of Mass	*all waste can be disposed of down the drain
Double Replacement (See Appendix B)	<ul style="list-style-type: none">• Writing formulas• Writing equations• Writing balanced equations• Determining if a reaction has occurred	-Used a large quantity of chemicals -Large amount of waste containing heavy metals	*small amount of waste will be collected in the proper waste container
Titration (See Appendix C)	<ul style="list-style-type: none">• Calculate the percent of Acetic Acid in Vinegar C• Compare percentage calculated to the percentage listed on the Vinegar bottle	-Used a large quantity of chemicals	*titration was done in a reaction plate *small amount of chemicals used
Iodimetric Titration (See Appendix D)	<ul style="list-style-type: none">• Calculate the amount of Vitamin C in a tablet and compare to the Vitamin C bottle• Demonstrate the reduction reaction• Improve titration skills	-use of Mercury as an antimicrobial agent in the starch indicator	*removal of Mercury will allow all of the waste to be washed down the drain

Table 2: The Modifications to the labs

Experiment	The modification
Conservation of Mass (See Appendix A)	<ul style="list-style-type: none">✓ The experiment was conducted in a Ziploc bag with all benign chemicals, which can be disposed down the drain and into the wastebasket.
Double Replacement (See Appendix B)	<ul style="list-style-type: none">✓ The amounts of chemicals were decrease from 3 mL to 2 drops each. The drops were placed on top of each other on a clear plastic overhead projector sheet or a sheet protector over a piece of white paper can be used.✓ The use of a reaction plate (See Figure 3) and disposable pipets (see Figure 4). were used.
Titration (See Appendix C)	<ul style="list-style-type: none">✓ The amounts of chemicals used and needed were decreased from over 100 mL to approximately 10 mL.✓ The use of a reaction plate (See Figure 3) and disposable pipets (see Figure 4). were used.
Iodimetric Titration (See Appendix D)	<ul style="list-style-type: none">✓ After the lab was completed, the instructor and I talked about the removal of the mercury in the starch indicator. The purpose of the mercury in the indicator is to prevent the growth of bacteria.✓ The starch solution would have to be disposed of and made every week, but all of the reactions can be disposed of down the sink instead of the collection of the hazardous waste and a large expense for expensive water.

Tools for Green Chemistry

Figure 2: Reaction Plate ¹²

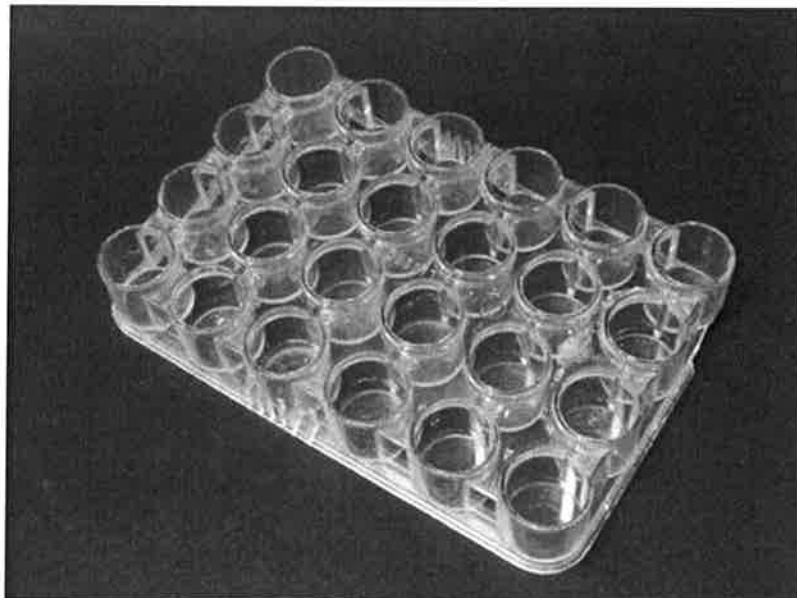


Figure 3: Disposable Pipettes ¹³

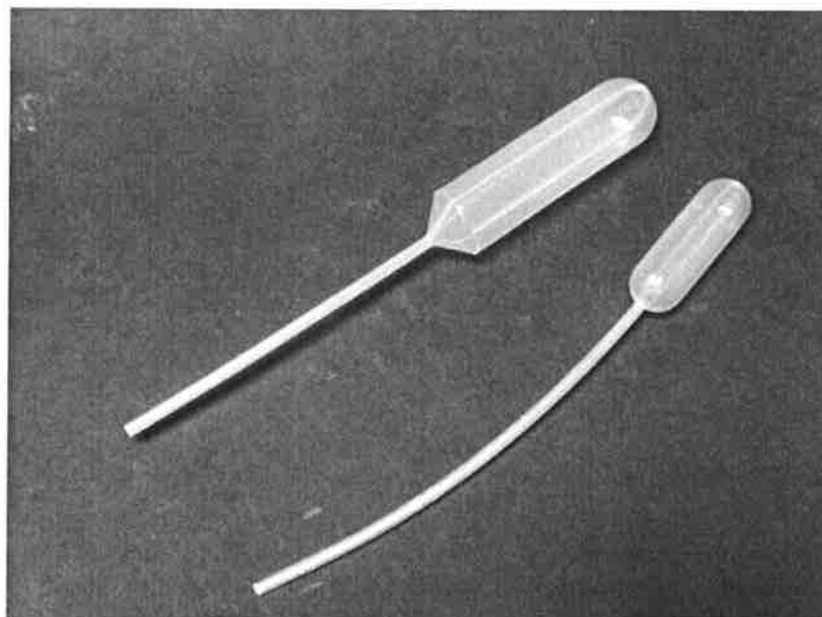


Figure 4: The traditional set up for titrations¹⁴

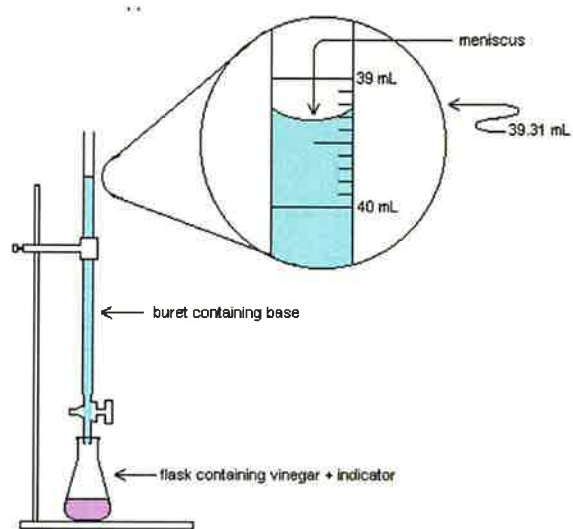


Figure 5: The Green Chemistry set up for titrations¹⁵



Results and Discussion

Conservation of Mass

The experiment was performed and the students were amazed at the temperature changes, color changes (from the acid/base indicator), and the production of gas. The reactants mass of the closed system did not equal the products mass. That was due to the fact that the Ziploc bags were large for the scale and hung off the sides of the scale. Students will need to be informed on how to place the bag in a beaker in order to get the proper weight of the reactants and products.

Double Replaceent Experiment

The precipitation and gas production reactions produced excellent results. The students did have issues with the reactions that produced heat. The heat production could not be felt, but if the student looked closely at the overhead projection sheet, they could see a small amount of condensation.

Titration

The titration went fast and the students could get at least 5-8 titrations completed in less than an hour. The issue that occurred was that students did not know what a drop was and they would lose count of the drops. If the students need to be extremely accurate and precise, the traditional method should be used. Most of the students calculated out the percent of acetic acid in vinegar close to what the bottle stated as the percentage.

Iodimetric Titration

The experiment without the mercury in the starch indicator was not performed during the Analytical Chemistry Fall 2014 semester.

Conclusion

Conservation of Mass

The experiment is effective just the way it is written in Appendix A. As an instructor there will be a need to teach about the use of the scale and how properly to place bulky items on a scale

Double Replacement Experiment

The experiment as it is written in Appendix B, needs to have a verbal or written on the board of how to drop drops of chemicals on top of each other. In addition, the disposal of the chemicals needs to be placed in hazardous disposal and the overhead sheets need to be washed with soap and water and rinsed very well. The other reactions that need to be looked at closely would be the ones that only produce a temperature change. Those reactions would either be have to be completed in a test tube or as a demo and then allow the students to feel the test tube.

Titration

The experiment is effective just the way it is written in Appendix C. The only drawback to this experiment is lack of the use of science measuring tools such as the buret or the volumetric pipet. If the student was to be going onto analytical chemistry, then this way of doing a titration would not be appropriate. Using the reaction plate does not teach a skill but the concept of titration.

Iodimetric Titration

The experiment in Appendix D needs to be rewritten to remove the mercury from the written experiment or it can be stated verbally or written on the board for the students to follow.

The experiments from Science Chemistry Foundations were a not a complex change. Some were just dropping the amounts used or finding a new way to look at the lab. The Analytical experiment is where a large savings in the lab occurred. But just removing mercury there would be no expense involved in the disposal of 8 liters of water with a minute amount of mercury.

Green Chemistry already exists in the GSU chemistry department. Organic chemistry has micro-scaled the labs which has cut cost and hazardous waste production. Biochemistry and Analytical biochemistry uses small amounts of chemicals to run the experiments in the lab and the products can be disposed of down the drain or into the wastebasket without hazardous waste collection. Analytical chemistry with one chemical dropped (mercury in the starch solutions) from the experiment (Iodimetric Titration) brought the experiment high hazardous waste producing lab to a lab with a very small amount of waste.

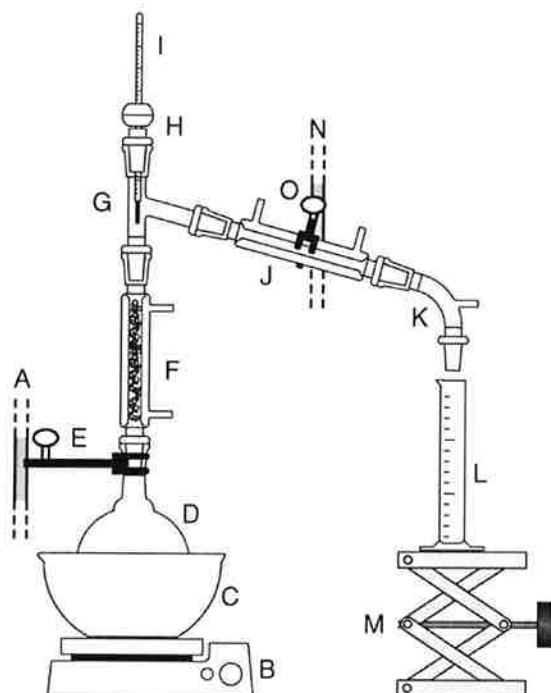
Future Studies

GSU and the Chemistry department can utilize green chemistry concepts by

1. Do a cost analysis is for hazardous waste disposal

2. Being aware of the 12 principles of Green Chemistry that have been laid out by numerous articles and web site.
3. Being conscious of what chemicals are being used in the experiment
4. Being conscious on how to dispose of the hazardous waste and the chemicals within the reaction
5. How much is product or was is going to be produced
6. Running the experiment beforehand to see if the amounts of chemicals used could be scaled back
7. Teach the students about the impact of their actions have on the environment
8. Integrate green chemistry concepts into all chemistry experiments taught for majors and non-majors. Be very deliberate about pointing out where the Green Chemistry is happening or what has been replaced to make this experiment a Green Chemistry experiment.
9. Recycle the acetone waste in the organic lab. Figure 7 is an example of a simple solvent recovery system. The Journal of Education article explains how the students would pour the acetone waste in the vessel after the organic experiments. The following week the students would test the acetone for the purity and use the recovered acetone for their experiment. ¹⁶

Figure 6: Recovery Apparatus¹⁷



Acetone Recovery Apparatus. Macroscale fractional distillation apparatus: (A) ring stand, (B) stirrer-hot plate, (C) hot water bath, (D) still pot (100 mL roundbottom flask), (E) buret clamp, (F) fractionating column (a condenser lightly packed with steel sponge), (G) distillation head, (I) thermometer, (H) thermometer adapter, (J) condenser attached to (N) a second ring stand via (O) a second clamp, (K) vacuum adapter, (L) 50 mL graduated cylinder (acetone receiving vessel), and (M) a lab jack to hold the receiving vessels in place.

Acetone Recovery Apparatus

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J. Chem. Educ. **2011** 88 , 1724-1726

Appendices A

Appendices B

Appendices C

Appendices D