Green Chemistry in the General Chemistry Laboratory

A case study prepared by Beyond Benign as part of the Green Chemistry in Higher Education program: A workshop for EPA Region 2 Colleges and Universities

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Table of Contents

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Introduction:
A university laboratory manual is used for examples of traditional laboratory experiments performed in introductory chemistry courses. This case study will highlight alternative green chemistry experiments that can be used in the general chemistry laboratory, providing options for faculty.

Background:
This case study is a result of an EPA Region 2 Source Reduction grant[1] titled *Green Chemistry in Higher Education: A Workshop for Region 2 Colleges and Universities*. The Green Chemistry in Higher Education workshop was carried out at Siena College on July 18-21, 2013. 29 faculty members participated from 20 different institutions in New York and New Jersey. The workshop consisted of three main focus areas: green chemistry case studies for lecture and course work, green chemistry laboratory exercises, and toxicology and environmental impact.

Two faculty members from Monmouth University participated in the EPA Region 2 Green Chemistry in Higher Education workshop: Dr. Jia Luo, and Dr. Ellen Rubinstein. Both faculty members are lecturers and teach general chemistry lecture and laboratory courses. Dr. Rubinstein shared their General Chemistry I and II Laboratory Manuals for use as a model general chemistry laboratory course. Suggestions for alternative laboratories are outlined in this case study, with an estimate of the benefits of implementing green chemistry laboratory experiments.

[1] **Disclaimer: Although the information in this document has been funded wholly or in part by the United States Environmental Protection Agency under assistance agreement X9-96296312 to Beyond Benign, it has not gone through the Agency's publications review process and, therefore, may not necessarily reflect the views of the Agency and no official endorsement should be inferred.**

Above Photo: Dr. Mike Cann speaking with the participants of the Green Chemistry in Higher Education workshop at Siena College on July 19, 2013.

Overview: Six of the most commonly used general chemistry laboratory experiments are summarized below, along with the typical chemicals used and hazards associated with them. Suggested greener alternatives are provided for each of the general chemistry experiments. A longer description of each of the labs and replacements, along with literature references, is provided in this case study.

Colorimetry: Beer's Law

Chemicals and Hazards: Crystal violet is a *suspected carcinogen with high acute human toxicity, high aquatic toxicity and is very persistent*.

Greener Alternatives: Food Dyes: i.e., Allura Red (FD&C Red #40). Food dyes generally have low toxicity and can be disposed of down the drain.

Hess's Law

Chemicals and Hazards: Magnesium and hydrochloric acid: *magnesium is a pyrophoric and water-reactive solid and hydrochloric acid is corrosive and causes severe burns*.

Greener Alternatives: Measuring the enthalpy change for vinegar (acetic acid) and baking soda (sodium biarbonate) (endothermic reaction), or hydrogen peroxide (3-6%) and beef liver for an exothermic reaction.

The Chemistry and Qualitative Analysis of Anions

Chemicals and Hazards: Barium chloride: *high human and aquatic toxicity*; Silver nitrate: *moderate human toxicity, high aquatic toxicity*; Nickel (II) chloride: *high human and aquatic toxicity*; Cadmium chloride: *high human and aquatic toxicity*; Lead (II) nitrate: *high human and aquatic toxicity*

Greener Alternatives: Barium, nickel, cadmium and lead should be substituted. Calcium chloride can be used as a substitute for barium chloride.

Identification of an Unknown Organic Compound

Chemicals and Hazards: Hexane has *high human chronic toxicity and high aquatic toxicity*; other organic solvents are also used, including: benzene, carbon tetrachloride, chloroform, methanol, nitrobenzene all of which have high human toxicities with most having high chronic toxicity and high aquatic toxicity

Greener Alternatives: Heptane can be substituted for hexane for solubility testing. It has lower human health toxicity, but similar solvent properties. Less hazardous solvents should be chosen as unknowns for analysis by students.

Molar Mass Determination by Freezing Point Depression

Chemicals and Hazards: 2-methyl-2-propanol is a *flammable liquid*; the unknown organic compounds can be: naphthalene, p-nitrotoluene, or similar halogenated aromatic compounds, all have *high human and aquatic toxicity, and chronic human toxicity*

Greener Alternatives: Freezing point depression can be measured using unknown fatty acids (lauric, palmitic, and myristic acids) instead of organic solvents and aromatic hydrocarbons.

Determining the Rate Law for a Chemical Reaction

Chemicals and Hazards: Crystal violet is a *suspected carcinogen with high acute human toxicity, high aquatic toxicity and is very persistent*.

Greener Alternatives: Vitamin C clock reaction

Traditional Experiment:

Students are introduced to colorimetry techniques and use them to determine the unknown concentration of a sample of a dye solution using Beer's Law.

Crystal violet is typically used in this experiment. It is used in rate law experiments to measure the fading of the purple dye as the crystal violet reacts with sodium hydroxide.

Crystal violet has both chronic and acute human health concerns. It is a suspected carcinogen and has high acute toxicity. Crystal violet is also highly toxic to aquatic organisms, with long-lasting effects. Crystal violet is highly persistent.

Colorimetry: Beer's Law
Traditional Experiment

Chemicals avoided per 100 students: 2.25 L crystal violet, 0.6 gallons of hazardous waste

Table 1. Environmental, health and safety hazards for crystal violet:

Human health toxicity:†	Aquatic toxicity:†	H-statements:†, ‡
Suspected carcinogen, High acute toxicity LD50, oral, mouse - 96 mg/kg; LD50, oral, rabbit - 150 mg/kg	*High toxicity* EC50 (daphnia, 48 hr) - 0.24-5mg/l; EC50 (algae, 72 hr) - 0.025 - 0.8 mg/l	H302, H315, H318, H351, H400, H410

Table 2. Chemicals, cost and waste disposal for traditional Beer's Law experiment (per 100 students):

Chemical	Total per student group (2 students):	Total per 100 students:	Waste disposal cost:*	Waste disposal cost savings:
Crystal violet (10 μM aq. solution)	45 mL	2.25 L (0.59 gal)	$11.79/gallon	$6.96
Water	45 mL	2.25 L (0.59 gal)	$11.79/gallon	$6.96
TOTAL		**4.5 L (1.2 gal)**		**$13.92**

† Human health, aquatic toxicity data and H-statements were gathered from Globally Harmonized Safety Data Sheets, which can be obtained from Sigma-Aldrich [http://www.sigmaaldrich.com/united-states.html].

‡ H-statements (Hazard statements) are part of the European Union's Globally Harmonized System of Classification and Labeling of Chemicals. It is a set of standardized phrases about the hazards of chemical substances. A full list of H-statements can be found here: http://en.wikipedia.org/wiki/GHS_hazard_statement

***** Waste disposal cost are based on EPA's P2 Cost Calculator [http://www.epa.gov/p2/pubs/resources/measurement.html#calc, Accessed July 1, 2014]

Colorimetry: Beer's Law
Greener Alternatives

Chemicals avoided per 100 students: 2.25 L crystal violet, 0.6 gallons of hazardous waste

Greener alternatives:

Food dyes have been found to be suitable alternatives to crystal violet for the typical experiments. The use of food dyes also provides a context for students to understand more about dyes and how to determine the concentration of dyes in beverages. The use of food dyes allow for the solutions to be disposed of down the drain and therefore eliminates the cost of hazardous waste disposal associated with this experiment.

Several model laboratory experiments can be found on-line, including the following:

1) Spectrophotometric Determination of a Food Dye, Exton, D.B. General Chemistry in the Laboratory, 2nd Edition, McGraw-Hill Learning Solutions, ISBN 0-07-804433-5.
    a. Description: Students determine the concentration of Allura Red (FD&C Red #40) in Kool-Aid by creating a Beer-Lambert plot of the dye. Students perform a calculation to determine how much waste they would create if they did the experiment with copper (II) sulfate, a chemical commonly used in this type of experiment.
2) Visible Spectrophotometry, Analysis of a Food Dye in a Commercial Beverage: Skill Building Lab, 2011, Sharmaine S. Cady, East Stroudsburg University [http://www.esu.edu/~scady/Experiments/FoodDyes.pdf, accessed July 1, 2014].
    a. Description: Students determine the concentration of two food dyes in a sports beverage by creating a Beer-Lambert plot created by a calibration curve of known concentrations of food dye.
3) Stevens, Karen E., Using Visible Absorption to Analyze Solutions of Kool-Aid and Candy, J.Chem.Ed., 83 (10), **2006**, 1544-1545.
    a. Description: Students analyze the absorption spectra of Kool-Aid and different candies and determine the exact concentration of dye in a sample by preparing a Beer's law plot.

Above picture from Dye Diet: Eat Food, Not Food Additives! [Accessed February 2, 2015, http://www.dyediet.com/2011/04/28/soft-drinks/how-much-dyes-do-we-drink/]

Traditional Experiment:

Hess's Law

Traditional Experiment

Chemicals avoided per 100 students: 12.5 g magnesium, 10L 1.0 M hydrochloric acid

This experiment involves the use of calorimetry to measure the enthalpy of a reaction for the combustion of magnesium by applying Hess's Law. The experiment is measured using Vernier probes to measure the temperature as a function of time.

Magnesium is combined with hydrochloric acid and magnesium oxide in this reaction.

Magnesium is a pyrophoric solid and can catch fire spontaneously if exposed to air or in contact with water. Magnesium oxide has low to moderate toxicity and is not of high concern for substitution, however there is a lack of data for some toxicity endpoints. Hydrochloric acid is corrosive and can cause severe burns at high concentrations.

Table 3. Environmental, health and safety hazards of chemicals in Hess's Law experiment:

Chemical:	**Human health toxicity:**†	**Aquatic toxicity:**†	**H-statements:**†, ‡
Magnesium	*Pyrophoric and water-reactive solid*		H250, H260
Magnesium oxide	*Low toxicity*	*Low toxicity*	
Hydrochloric acid	*Causes severe burns and eye damage*		H290, H314, H335

Table 4. Chemicals used, cost and waste disposal for traditional Hess's Law experiment (per 100 students):

Chemical	**Total per student group (2 students):**	**Amount:**	**Waste disposal cost:***	**Waste disposal cost savings:**
Magnesium	0.25 g	12.5 g	$1.35/lb	$0.04
Hydrochloric acid (1.0 M)	200 mL	10 L	$11.79/gal	$31.13
Magnesium oxide	1.3 g	65 g	$1.35/lb	$0.19
TOTAL		**10 L and 77.5 g**		**$31.36**

† Human health, aquatic toxicity data and H-statements were gathered from Globally Harmonized Safety Data Sheets, which can be obtained from Sigma-Aldrich [http://www.sigmaaldrich.com/united-states.html].

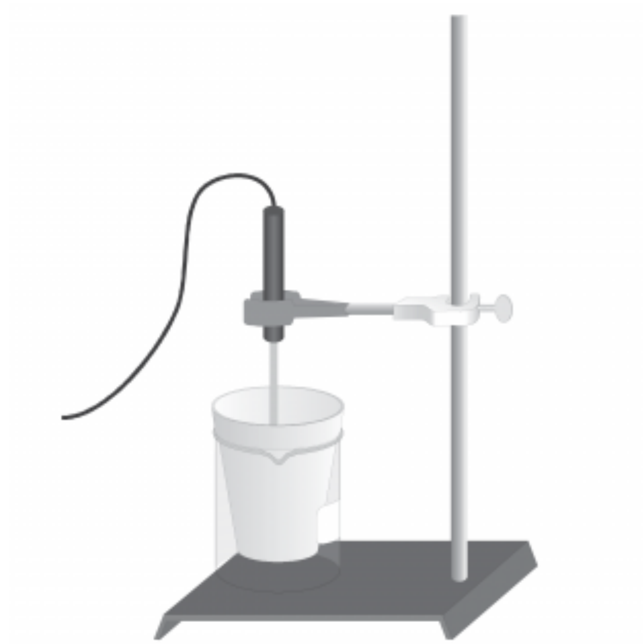
‡ H-statements (Hazard statements) are part of the European Union's Globally Harmonized System of Classification and Labeling of Chemicals. It is a set of standardized phrases about the hazards of chemical substances. A full list of H-statements can be found here: http://en.wikipedia.org/wiki/GHS_hazard_statement

* Waste disposal cost are based on EPA's P2 Cost Calculator [http://www.epa.gov/p2/pubs/resources/measurement.html#calc, Accessed July 1, 2014]

Hess's Law

Greener Alternatives

Chemicals avoided per 100 students: 12.5 g magnesium, 10L 1.0 M hydrochloric acid



Greener alternatives:

Magnesium poses a safety hazard for students and instructors as a pyrophoric and water-reactive solid. There are many alternatives to using magnesium, including the following:

1. Sodium hydroxide is a viable alternative that poses some health risks due to the potential to cause burns, but it is not a pyrophoric solid: Chemistry with Vernier, Experiment #18, Additivity of Heats of Reaction: Hess's Law, http://www.vernier.com/experiments/cwv/18/additivity_of_heats_of_reaction_hesss_law/ [Accessed February 2015].
2. Calcium carbonate or sodium bicarbonate can be used in place of magnesium with hydrochloric acid in this reaction.
3. A simple substitute to demonstrate an endothermic reaction is the use of vinegar (acetic acid) and baking soda (sodium bicarbonate). Or, citric acid and sodium bicarbonate. In this reaction, the students should be able to see the temperature drop by about 5°C.[2]
4. To demonstrate an exothermic reaction, hydrogen peroxide (3 - 6%) can be used with beef liver as a catalyst. The temperature for this reaction should increase by about 5°C.[2]

Above photo from Vernier
http://www.vernier.com/experiments/cwv/18/additivity_of_heats_of_reaction_hesss_law/

2. Green Chemistry in the High School: Lessons from Beyond Benign, "Exothermic and Endothermic" lesson [http://www.beyondbenign.org/K12education/highschool.html Accessed February 2015]

Traditional Experiment:

This experiment involves observing reactions to learn the chemistry of select anions and to understand solubility rules. The experiment includes the determination of the anion in three unknown salts through experimenting with precipitation reactions.

The table below outlines the typical chemicals used, along with amounts and waste disposal costs.

A table of the chemicals used and a summary of the health and aquatic toxicity is provided on the following page.

The Chemistry and Qualitative Analysis of Anions

Traditional Experiment

Hazardous chemicals avoided: barium chloride, nickel (II) chloride, cadmium chloride, silver nitrate, sodium sulfide

Table 5. Chemicals in traditional experiment:

Chemical:	Total per student group (2 students):	Total per 100 students:	Waste disposal cost:†	Waste disposal cost savings:
Sodium sulfate	0.2 g	10 g	\$1.35/lb	\$0.03
Barium chloride, 0.1 M solution	1 mL (est.)	50 mL	\$11.79/gal	\$0.15
Sodium carbonate	0.2 g	10 g	\$1.35/lb	\$0.03
Sodium phosphate	0.2 g	10 g	\$1.35/lb	\$0.03
Sodium sulfite	0.2 g	10 g	\$1.35/lb	\$0.03
Nitric acid, 3M	1 mL (est.)	50 mL	\$11.79/gal	\$0.15
Sulfuric acid, 3M	1 mL (est.)	50 mL	\$11.79/gal	\$0.15
Sodium chloride	0.1 g	5 g	\$1.35/lb	\$0.02
Silver nitrate, 0.1M	1 mL (est.)	50 mL	\$11.79/gal	\$0.15
Sodium bromide	0.1 g	5 g	\$1.35/lb	\$0.02
Potassium iodide	0.1 g	5 g	\$1.35/lb	\$0.02
Sodium nitrate	0.1 g	5 g	\$1.35/lb	\$0.02
Iron (II) sulfate (1M in 1M H_2SO_4)	0.5 mL (est.)	25 mL	\$11.79/gal	\$0.78
Sulfuric acid, concentrated	0.5 mL (est.)	25 mL	\$11.79/gal	\$0.78
Ammonium molybdate	0.1 g	5 g	\$1.35/lb	\$0.02
Dichloromethane	0.5 mL (est.)	25 mL	\$11.79/gal	\$0.78
Chlorine solution (bleach) (sodium hypochlorite)	0.5 mL (est.)	25 mL	\$11.79/gal	\$0.78
Hydrochloric acid	0.2 mL (est.)	10 mL	\$11.79/gal	\$0.03
9 anions used for identification of unknown samples‡	1 drop			
TOTAL		**310 mL and 65 g**		**\$4.15**

† Waste disposal cost are based on EPA's P2 Cost Calculator [http://www.epa.gov/p2/pubs/resources/measurement.html#calc, Accessed July 1, 2014]

‡ A list of typical unknowns is provided in the Appendix A.

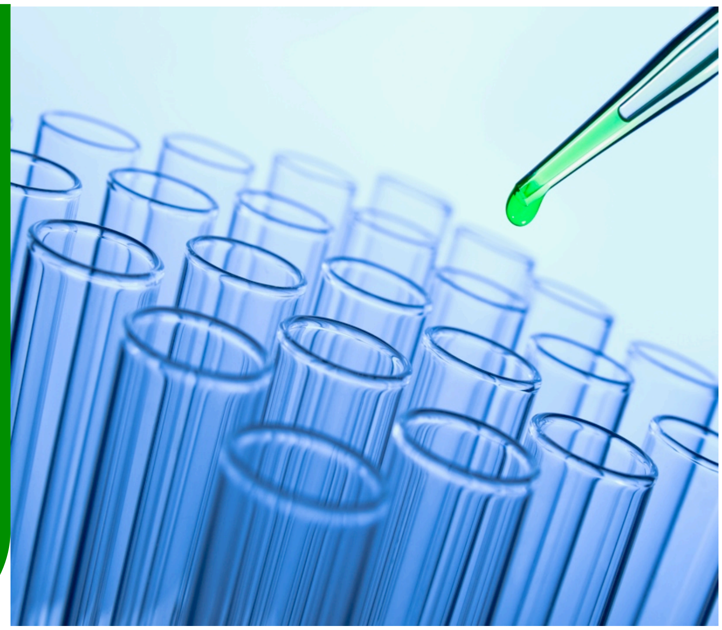
Table 6. *Health and aquatic toxicity data for chemicals in traditional experiment.*

Chemical:	Human health toxicity:†	Aquatic toxicity:†	H-statements:†, ‡
Sodium sulfate	*Low toxicity*; LD50 (oral, mouse) - 5,989 mg/kg	*Moderate aquatic toxicity;* LC50 (fish, 96 hr) - 120 mg/l; LC50 (fish, 96 hr) - 4,380 mg/l	H402, H412
Barium chloride	*High human health toxicity via ingestion and inhalation;* Oral LD50's: 90 mg/kg (dog); 76 mg/kg (guinea pig); 70 mg/kg (mouse); 170 mg/kg (rabbit)	*Moderate acute aquatic toxicity* and *high chronic aquatic toxicity* LC50 (fish, 96 hrs) - 46 mg/l EC50 (daphnia, 48 hr) - 14.5 mg/l;	H301, H332, H412
Sodium carbonate	*Low toxicity;* LD50 (oral, rat) - 4,090 mg/kg; LC50 (inh, rat, 2 hr) - 5,750 mg/l	*Low toxicity;* LC50 (fish, 96 hr) - 300 mg/l; EC50 (daphnia, 48 hr) - 265 mg/l	H319
Sodium phosphate	*Low toxicity*, can cause skin and eye irritation	*Moderate aquatic toxicity;* LC50 (fish, 96 hr) - 28.5 mg/l	H315, H318, H335, H412
Sodium sulfite	*Low toxicity*; LD50 (oral, rat) - 3,560 mg/kg; LC50 (inh, rat, 4 hr) >5,500 mg/m3	*Low toxicity;* LC50 (fish, 96 hr) - 660 mg/l	None
Nitric acid	*Causes severe burns*		H272, H314
Sulfuric acid	*Causes severe burns and eye damage*		H314, H318
Sodium chloride	*Low toxicity*;LD50 (oral, rat) - 3,550 mg/kg; LC50 (inh, rat) > 42,000 mg/m3; LD50 (dermal, rabbit) > 10,000 mg/kg	*Low toxicity*; LC50 (fish, 96 hr) 5,840 mg/l; LC50 (daphnia, 48 hr) 1,661 mg/l	None
Silver nitrate	*Moderate toxicity;* LD50 (oral, rat) - 1,173 mg/kg	*Very high acute and chronic aquatic toxicity;* LC50 (fish, 96 hr) - 0.029 mg/l; LC50 (fish, 96 hr) - 0.006 mg/l; EC50 (daphnia, 48 hr) - 0.0006 mg/l	H272, H302, H314, H410
Sodium bromide	*Low toxicity*;LD50 (oral, rat) 3,500 mg/kg; LD50 (dermal, rabbit) > 2,000 mg/kg	*Low toxicity*; LC50 (fish, 96 hr) 160,000 mg/l; EC50 (daphnia, 48 hr) 5,800 mg/l	None
Potassium iodide	*Moderate toxicity;* LD50 (oral, mouse) 1,000 mg/kg	*Moderate toxicity;* LC50 (fish, 96 hr) 2,190 mg/l; EC50 (daphnia, 24 hr) 2.7 mg/l	H302, H315, H319
Sodium nitrate	*Moderate toxicity;* LD50 (oral, rat) 1,267 mg/kg; LD50 (oral, rabbit) 2,680 mg/kg; LD50 (intra, mouse) 175 mg/kg	*Low toxicity*; LC50 (dish, 96 hr) 6,650 mg/l; EC50 (daphnia, 24 hr) 6,000 mg/l	H272, H302, H315, H319
Iron (II) sulfate	*Moderate toxicity;* LD50 (oral, mouse) 1,520 mg/kg	*Low toxicity*	H302, H315, H319
Ammonium molybdate	*Low toxicity*	*Moderate toxicity;* LC50 (fish, 96 hr) 320 mg/l; LC50 (fish, 96 hr) 420 mg/l; EC50 (daphnia, 48 hr) 140 mg/l	H402, H412
Dichloro-methane	*Moderate toxicity, suspected carcinogen;* IARC Group 2B Possibly carcinogenic to humans; LD50 (oral, rat) 2,000 mg/kg; LC50 (inh, rat) 52,000 mg/m3; LD50 (dermal, rat) 2,000 mg/kg	*Low toxicity*; LC50 (fish, 96 hr) 193 mg/l; EC50 (daphnia, 48 hr) 1,628 mg/l	H315, H319, H351, H335, H336, H373
Sodium hypochlorite solution	*Causes severe burns and eye damage*	*Very high acute and chronic aquatic toxicity*	H314, H410
Hydrochloric acid	*Causes severe burns and eye damage*		H290, H314, H335
9 anions used for unknown samples*			

† Human health, aquatic toxicity data and H-statements were gathered from Globally Harmonized Safety Data Sheets, which can be obtained from Sigma-Aldrich [http://www.sigmaaldrich.com/united-states.html].
‡ H-statements (Hazard statements) are part of the European Union's Globally Harmonized System of Classification and Labeling of Chemicals. It is a set of standardized phrases about the hazards of chemical substances. A full list of H-statements can be found here: http://en.wikipedia.org/wiki/GHS_hazard_statement
* A list of typical unknowns is provided in the Appendix A, along with toxicological information.

The Chemistry and Qualitative Analysis of Anions
Greener Alternatives

Hazardous chemicals avoided: barium chloride, nickel (II) chloride, cadmium chloride, silver nitrate, sodium sulfide



Greener alternatives:

The laboratory exercise teaches students to use the following solubility rules to predict reactions and precipitates:

- All sodium, potassium and ammonium salts are soluble.
- All nitrates are soluble.
- All chlorides are soluble except silver chloride; lead chloride is slightly soluble.
- All sulfates are soluble except for lead sulfate and barium sulfate: calcium sulfate and silver sulfate are slightly soluble.
- All carbonates and hydroxides are insoluble except those of sodium, potassium and ammonium: calcium hydroxide is slightly soluble.

Barium chloride is used to demonstrate the precipitation of sulfite and sulfate and is of the highest concern from the listed chemicals in this experiment. Barium chloride is used to demonstrate the precipitation of barium sulfite. A suggested alternative to barium chloride for this experiment is calcium chloride. Calcium chloride has high solubility in water (74.5 g/100 mL, 20C). If reacted with aqueous sodium sulfate or sodium sulfite, the calcium will precipitate out due to the low solubility in water (calcium sulfite 0.0043 g/100 mL, calcium sulfate 0.21 g/100 mL). This simple substitution should be suitable for the purposes of this experiment and calcium chloride is significantly less toxic than barium chloride (Table 7).

Table 7. Toxicity data for barium chloride versus calcium chloride:

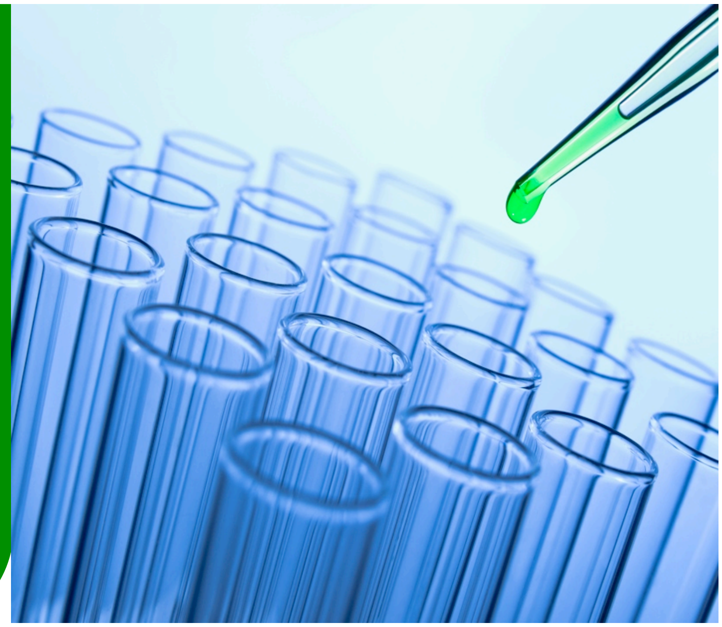
Chemical:	**Human health toxicity:**†	**Aquatic toxicity:**†	**H-statements:**†,‡
Barium chloride	*High human health toxicity via ingestion and inhalation;* Oral LD50's: 90 mg/kg (dog); 76 mg/kg (guinea pig); 70 mg/kg (mouse); 170 mg/kg (rabbit)	*Moderate acute aquatic toxicity* and *high chronic aquatic toxicity;* LC50 (fish, 96 hrs) - 46 mg/l; EC50 (daphnia, 48 hr) - 14.5 mg/l;	H301, H332, H412
Calcium chloride	*Low human health toxicity* LD50 (oral, rat) – 2,301 mg/kg	*Low aquatic toxicity* LC50 (fish, 96 hr) – 10,650 mg/l; EC50 (daphnia, 48 hr) – 2,400 mg/l	H319

† Human health, aquatic toxicity data and H-statements were gathered from Globally Harmonized Safety Data Sheets, which can be obtained from Sigma-Aldrich [http://www.sigmaaldrich.com/united-states.html].

‡ H-statements (Hazard statements) are part of the European Union's Globally Harmonized System of Classification and Labeling of Chemicals. It is a set of standardized phrases about the hazards of chemical substances. A full list of H-statements can be found here: http://en.wikipedia.org/wiki/GHS_hazard_statement

The Chemistry and Qualitative Analysis of Anions *Greener Alternatives*

Hazardous chemicals avoided: barium chloride, nickel (II) chloride, cadmium chloride, silver nitrate, sodium sulfide



Greener alternatives, continued:

Silver nitrate is also of higher concern for the chemicals used in this experiment. Silver nitrate and lead nitrate are typically used to demonstrate the precipitation of halides, such as chloride. Silver nitrate is the better choice of the two options due to the high health hazards associated with lead nitrate. Silver nitrate has moderate human health toxicity and high aquatic toxicity. To date, there are no suitable alternatives for demonstrating the solubility rule: all chlorides are soluble except for silver chloride; lead chloride is slightly soluble.

Potassium iodide could potentially be substituted with sodium iodide. The human health toxicity associated with sodium iodide is lower, however the aquatic toxicity is higher:

Table 8. Toxicity information for potassium iodide versus sodium iodide:

Chemical:	**Human health toxicity:**†	**Aquatic toxicity:**†	**H-statements:**†, ‡
Potassium iodide	*Moderate toxicity* LD50 (oral, mouse) 1,000 mg/kg	*Moderate toxicity* LC50 (fish, 96 hr) 2,190 mg/l; EC50 (daphnia, 24 hr) 2.7 mg/l	H302, H315, H319
Sodium iodide	*Low human health toxicity* LD50 (oral, rat) – 4,340 mg/kg	*High toxicity* LC50 (fish, 96 hr) – 860 mg/l; EC50 (daphnia, 48 hr) 0.17 mg/l	H315, H319, H400, H410

† Human health, aquatic toxicity data and H-statements were gathered from Globally Harmonized Safety Data Sheets, which can be obtained from Sigma-Aldrich [http://www.sigmaaldrich.com/united-states.html].

‡ H-statements (Hazard statements) are part of the European Union's Globally Harmonized System of Classification and Labeling of Chemicals. It is a set of standardized phrases about the hazards of chemical substances. A full list of H-statements can be found here: http://en.wikipedia.org/wiki/GHS_hazard_statement

Traditional Experiment:

In this experiment, students measure the density, freezing point, boiling point, and solubility in two solvents for an unknown organic liquid.

The unknown can be a number of different organic solvents. A comparison table of the possible unknowns are listed on the following page, along with human health and aquatic toxicity data.

Identification of an Unknown Organic Compound

Traditional Experiment

Hazardous chemicals avoided: Hexane, chloroform, benzene, nitrobenzene

Water and hexane are typically used as solvents for the solubility experiments and the experiment is typically performed at the small scale. The chemicals used and estimated amounts are listed below:

Table 9. Chemicals used, amounts and waste disposal costs for traditional identification of an unknown organic compound experiment:

Chemical:	**Total per student group (2 students):**	**Total per 100 students:**	**Waste disposal cost:**†	**Waste disposal cost savings:**
Water	5 drops (est. 0.32 mL)	est. 16 mL	$11.79/gal	$0.05
Hexane	5 drops (est. 0.32 mL)	est. 16 mL	$11.79/gal	$0.05
Unknown*	5 drops (est. 0.32 mL)	est. 16 mL	$11.79/gal	$0.05
TOTAL		**48 mL**		**$0.15**

*Typical unknowns include benzene, chloroform, nitrobenzene, or other halogenated solvents. The list of typical unknowns is in Table 10 on the following page.

Key to the table on the following page:

- NFPA (National Fire Protection Association) codes can be found here: http://en.wikipedia.org/wiki/NFPA_704#Red
- Human health, aquatic toxicity data and H-statements were gathered from Globally Harmonized Safety Data Sheets, which can be obtained from Sigma-Aldrich [http://www.sigmaaldrich.com/united-states.html].
- H-statements (Hazard statements) are part of the European Union's Globally Harmonized System of Classification and Labeling of Chemicals. It is a set of standardized phrases about the hazards of chemical substances. A full list of H-statements can be found here: http://en.wikipedia.org/wiki/GHS_hazard_statement

Table 10. Health and safety information for typical unknowns.

Chemical:	Flammability:	Human health toxicity:	Aquatic toxicity:	H-statements:
Acetic Acid	*NFPA Code: 2* Flash Point: 40°C	*Causes severe burns and eye damage; Moderate acute toxicity;* LD50 (oral, rat) 3,310 mg/kg, LC50 (inh, rat, 4 hr) 11.4 mg/l, LD50 (dermal, rabbit) 1,112 mg/kg	*Low toxicity;* LC50 (fish, 96 hr) >1,000 mg/l; EC50 (daphnia, 48 hr) >300.82 mg/l	H226, H314, H318
Acetone	*Flammable NFPA Code: 3* Flash Point: -20°C	*Low toxicity;* D50 (oral, rat) 5,800 mg/kg; LC50 (inh, rat, 8 hr) 50,100 mg/m3; LD50 (dermal, guinea pig) 7,426 mg/kg	*Low toxicity;* LC50 (fish, 96 hr) 5,540 mg/l; LC50 (daphnia, 48 hr) 8,800 mg/l	H225, H319, H336
Acetonitrile	*Flammable NFPA Code: 3* Flash Point: 2.0°C	*Moderate toxicity;* LD50 (oral, rat) - 1,320 - 6,690 mg/kg; LC50 (inh, mouse, 4 hr) - 3587 ppm; LC50 (inh, rat, 4 hr) - 26.8 mg/l	*Low toxicity;* LC50 (fish, 96 hr) - 1,640 mg/l; EC50 (daphnia, 48 hr) - 3,600 mg/l	H225, H302, H332, H312, H319
Benzene	*Flammable NFPA Code: 3* Flash Point: -11.63°C	*High toxicity; IARC Group 1: Carcinogenic to Humans;* LD50 (oral, rat) - 2,990 mg/kg; LC50 (inh, rat) - 44,700 mg/m3; LD50 (dermal, rabbit) - 8,263 mg/kg	*High toxicity;* LC50 (fish, 96 hr) - 5.9 mg/l; LC50 (fish, 96 hr) - 15-32 mg/l; EC50 (daphnia, 48 hr) - 22 mg/l; EC50 (daphnia, 48 hr) - 9.2 mg/l; EC50 (algae, 72 hr) - 29 mg/l	H225, H315, H319, H340, H350, H304, H401
Carbon tetrachloride	Non-flammable	*High toxicity;* IARC Group 2B: Possibly carcinogenic to humans; LD50 (oral, rat) - 2,350 mg/kg; LC50 (inh, rat) 8000 ppm; LD50 (dermal, rabbit) 20,000 mg/kg	*Moderate toxicity;* LC50 (fish, 96 hr) - 24.3 mg/l	H301, H331, H311, H317, H351, H372, H402, H412
Chloroform	Non-flammable	*High toxicity;* IARC Group 2B: Possibly carcinogenic to humans; LD50 (oral rat) 908 mg/kg; LD50 (dermal, rabbit) 20,000 mg/kg	*Moderate toxicity;* LC50 (fish, 48 hr) - 162 mg/l; LC50 (fish, 96 hr) 97 mg/l; LC50 (fish, 96 hr) 121 mg/l; EC50 (daphnia, 24 hr) 79 mg/l	H302, H332, H315, H319, H351, H361, H336, H373, H402
Cyclohexane	*Flammable NFPA Code: 3* Flash Point: -20°C	*Low toxicity;* LC50 (oral, rat) 12, 705 mg/kg; LC50 (inh, rat, 4 hr) 34,000 mg/l	*High toxicity;* LC50 (fish, 96 hr) 34.7 mg/l; LC50 (fish, 96 hr) 4.53 mg/l; EC50 (daphnia, 48 hr) 3.78 mg/l; EC50 (algae, 72 hr) 3.4 mg/l	H225, H315, H336, H304, H401, H411
Diethyl ether	*Highly Flammable; NFPA Code: 4; Flash Point: -45°C*	*Low toxicity;* LD50 (oral, rat) 1,215 mg/kg; LD50 (dermal, rabbit) 14.2 g/kg	*Low toxicity;* LC50 (fish, 96 hr) 2,560 mg/l; EC50 (daphnia, 24 hr) 165 mg/l	H224, H302, H319, H336
Ethyl acetate	*Flammable NFPA Code: 3* Flash Point: -4°C	*Low toxicity;* LD50 (oral, rat) 5, 620 mg/kg; LC50 (inh, mouse) 45,000 mg/m3; LD50 (dermal) 18,000 mg/kg	*Low toxicity;* LC50 (fish, 96 hr) 350 - 600 mg/l; LC50 (fish, 96 hr) 220 - 250 mg/l; EC50 (daphnia, 24 hr) 2,300 - 3,090; LC50 (daphnia, 48 hr) 560 mg/l; EC50 (algae, 24 hr) 4,300 mg/l	H225, H319, H336
Glucose (20% in water)	Non-flammable	*Low toxicity*	*Low toxicity*	None
Hexane	*NFPA Code: 3* Flash Point: -26°C	*High chronic toxicity, Reproductive and Developmental hazard*	*High aquatic toxicity;* LC50 (fish, 96 hr) 2.5 mg/l; EC50 (daphnia, 48 hr) 3,878 mg/l	H225, H304, H315, H336, H361, H373, H401, H411
2-Propanol	*Flammable NFPA Code: 3* Flash Point: 13°C	*Low toxicity;* LD50 (oral, rat) 5,045 mg/kg; LC50 (inh, rat) 1600 ppm; LD50 (dermal, rabbit) 12,800 mg/kg	*Low toxicity;* LC50 (fish, 96 hr) 9,640 mg/l; EC50 (daphnia, 24 hr) 5,102 mg/l;	H225, H319, H336
Methanol	*Flammable NFPA Code: 3* Flash Point: 11-12°C	*High toxicity;* Ingestion causes blindness; LD50 (oral, rat) 1,187 - 2,769 mg/kg; LC50 (inh, rat) 128.2 mg/l; LC50 (inh, rat) 87.6 mg/l	*Low toxicity;* LC50 (fish, 96 hr) - 15,400 mg/l; EC50 (daphnia) 10,000 mg/l;	H225, H301, H311, H331
Nitrobenzene	*NFPA Code: 2* Flash Point: 88°C	*High toxicity;* IARC Group 2B: Possibly carcinogenic to humans; LD50 (oral, rat) 349 mg/kg; LC50 (inh, rat) 556 ppm; LD50 (dermal, rat) 2,100 mg/kg	*Moderate toxicity;* LC50 (fish, 96 hr) 92 mg/l; LC50 (fish, 96 hr) 44 mg/l; EC50 (daphnia, 24 hr) 50 mg/l; EC50 (algae,72 hr) 51.6 mg/l	H227, H302, H331, H351, H361, H372, H401, H411
1-Propanol	*NFPA Code: 3* Flash Point: 22°C	*Low toxicity;* LD50 (oral, rat) - 8,038 mg/kg; LC50 (inh, rat) - 20000ppm; LC50 (dermal, rabbit) 4,000 mg/kg	*Low toxicity;* LC50 (fish, 96 hr) - 1,000 mg/l; EC50 (daphnia, 48 hr) 3,642 mg/l	H225, H318, H336
2-Methyl-2-Propanol	*NFPA Code: 3* Flash Point: 11°C	*Low toxicity* LD50 (oral, rat) 2,743 mg/kg; LD50 (dermal, rabbit) 2,000 mg/kg	*Low toxicity* LC50 (fish, 96 hr) 6,140 mg/l; EC50 (daphnia, 48 hr) 933 mg/l	H225, H319, H335

Identification of an Unknown Organic Compound
Greener Alternatives

Hazardous chemicals avoided:
Hexane, chloroform, benzene, nitrobenzene

Greener alternatives:

A simple alternative for the solubility testing in this experiment is to switch hexane for heptane. Hexane has high human chronic toxicity, including being a reproductive and developmental hazard to humans. It also has high aquatic toxicity. Heptane has lower human toxicity, yet has very similar solvent properties to hexane. Please note that heptane still has high aquatic toxicity and is a flammable solvent. The table below provides a comparison of the flammability, human health toxicity and aquatic toxicity of hexane and heptane.

Table 11. Health and safety information for hexane versus heptane:

Chemical:	**Flammability:***	**Human health toxicity:†**	**Aquatic toxicity:†**	**H-statements:†, ‡**
Hexane	*NFPA Code: 3* Flash Point: -26°C	*High chronic toxicity, Reproductive and Developmental hazard*	*High aquatic toxicity* LC50 (fish, 96 hr) 2.5 mg/l; EC50 (daphnia, 48 hr) 3,878 mg/l	H225, H304, H315, H336, H361, H373, H401, H411
Heptane	*NFPA Code: 3* Flash Point: -4.0°C	*Low toxicity*	*High aquatic toxicity* LC50 (24 hr, fish) 4 mg/l; LC50 (96 hr, fish) 375 mg/l; EC50(daphnia, 48 hr) 1.5 mg/l	H225, H304, H315, H336, H400, H410

The table provided in the previous section should be used to determine which solvents are suitable to provide to students as unknowns. Unknowns should be chosen which have low human health and aquatic toxicity.

* NFPA (National Fire Protection Association) codes can be found here: http://en.wikipedia.org/wiki/NFPA_704#Red

† Human health, aquatic toxicity data and H-statements were gathered from Globally Harmonized Safety Data Sheets, which can be obtained from Sigma-Aldrich [http://www.sigmaaldrich.com/united-states.html].

‡ H-statements (Hazard statements) are part of the European Union's Globally Harmonized System of Classification and Labeling of Chemicals. It is a set of standardized phrases about the hazards of chemical substances. A full list of H-statements can be found here: http://en.wikipedia.org/wiki/GHS_hazard_statement

Traditional Experiment:

Colligative Properties laboratory exercises are commonly performed in general chemistry in order to introduce students to colligative properties and to use the properties to determine the molar mass of a substance. The experiment is typically performed with an organic solvent that has a melting point around room temperature, such as 2-methyl-2-propanol (25°C), or cyclohexane (6.5°C). The warming curve for the pure solvent is typically observed, followed by the introduction of an unknown compound. The freezing point depression is observed and can be measured to determine the molar mass of the unknown

Molar Mass Determination by Freezing Point Depression
Traditional Experiment

Hazardous chemicals avoided: 2-methyl-2-propanol or cyclohexane, naphthalene, p-nitrotoluene, 1,4-dibromobenzene

Chemicals used and hazards:

The chemicals that are typically used in this experiment are listed below, along with a list of the hazards. The amounts are estimated based on a common procedure from one of the most widely used General Chemistry textbooks*, along with a procedure from Monmouth University's General Chemistry II Laboratory Manual.

Table 12. Chemicals used, human health and aquatic toxicity data:

Chemical:	**Amount per student group (2 students):**	**Flammability:**	**Human health toxicity:**†	**Aquatic toxicity:**†
2-methyl-2-propanol	25 mL (0.066 gal)	Flammable; NFPA Code: 3; Flash Point: 11°C	*Low toxicity* LD50 (oral, rat) 2,743 mg/kg; LD50 (dermal, rabbit) 2,000 mg/kg	*Low toxicity* LC50 (fish, 96 hr) 6,140 mg/l; EC50 (daphnia, 48 hr) 933 mg/l
Cyclohexane	10 mL (0.0026 gal)	Flammable; NFPA Code: 3; Flash Point: -20°C	*Causes CNS depression, drowsiness, dizziness,* Low acute toxicity, LD50 (oral, rat) 12,705 mg/kg; LC50 (inh, rat) 34,000 mg/l; LD50 (dermal, rabbit) 2,000 mg/kg	High toxicity: LC50 (fish, 96 hr) 4.53 mg/l; EC50 (daphnia, 48 hr) 0.9 mg/l; EC50 (algae, 72 hr) 3.4 mg/l
Naphthalene	2 g (0.0044 lb)	n/a	*High toxicity* IARC Group 2B: Possibly carcinogenic to humans LD50 (oral, rat) 490 mg/kg; LC50 (inh, rat) 340 mg/m3; LD50 (dermal, rabbit) 20,000 mg/kg	*High toxicity* LC50 (fish, 96 hr) 0.9-9.8 mg/l; LC50 (daphnia, 48 hr) 1-3.4 mg/l
p-nitrotoluene	2 g (0.0044 lb)	n/a	*Moderate toxicity* IARC Group 3: Not classifiable as to its carcinogenicity to humans. LD50 (oral, rat) 2,250 mg/kg; LC50 (inh, rat) 975 mg/m3	*High toxicity* LC50 (fish, 96 hr) 49.7 mg/l; EC50 (algae, 96 hr) 22 mg/l
1,4-dibromo-benzene	0.4 g (0.00088 lb)	n/a	*Moderate toxicity, causes respiratory irritation* LD50 (oral, mouse)3,120 mg/kg	*High toxicity* LC50 (fish, 96 hr) 0.68 mg/l

* "Colligative Properties: Freezing Point Depression and Molar Mass", Experiment 19 in Chemistry The Central Science Laboratory Experiments, 12th Edition, by Nelson, J.H., Kemp, K.C., and Stoltzfus, M., Pearson Education, 2012, p. 237-250.

† Human health and aquatic toxicity data were gathered from Globally Harmonized Safety Data Sheets, which can be obtained from Sigma-Aldrich [http://www.sigmaaldrich.com/united-states.html].

Traditional Experiment, Continued:

The purchasing and waste disposal costs associated with this procedure are estimated in the following table. Purchasing costs were estimated based on prices available from Sigma-Aldrich:[5]

Total amounts of chemicals used and disposed of per class of 100 students:

- ***0.33 gal of 2-methyl-2-propanol or 0.13 gal of cyclohexane***
- ***0.22 lbs. naphthalene, p-nitrotoluene, or 1,4-dibromobenzene***
- ***Estimated 0.5 gallons of liquid waste****

Molar Mass Determination by Freezing Point Depression

Traditional Experiment

Hazardous chemicals avoided: 2-methyl-2-propanol or cyclohexane, naphthalene, p-nitrotoluene, 1,4-dibromobenzene

Table 13. Purchasing and waste disposal costs:

Chemical:	**Amount per 100 students:**	**Waste disposal cost**[6]	**Purchasing cost:**	**Purchasing cost per 100 students:**	**Waste disposal cost per 100 students:**	**Total cost (per 100 students)**
2-methyl-2-propanol	1,250 mL (0.33 gal)	$11.27/gal	$100, 1L	$125.00	$3.72	$128.72
Cyclohexane	500 mL (0.13 gal)	$11.27/gal	$91.40, 1 L	$45.70	$1.47	$47.17
Naphthalene	100 g (0.22 lb)	$1.35/lb	$42.20, 1 kg	$4.20	$0.30	$4.50
p-nitrotoluene	100 g (0.22 lb)	$11.27/gal	$20.10, 100 g	$20.10	$0.30	$20.40
1,4-dibromobenzene	20 g (0.044 lb)	$1.35/lb	$28.80, 100 g	$5.76	$0.06	$5.82
TOTAL (per 100 students):	**0.13 - 0.33 gal and 0.04 - 0.22 lb**			**$49.90 - $145.10**	**$1.53 - $4.02**	**$52.98 - $149.12**

Total purchasing and waste disposal costs per class of 100 students:

- ***$49.90 - $145.10 in purchasing costs***
- ***$1.53 - $4.02 in waste disposal costs***
- ***$52.98 - $149.12 total cost***

* 0.5 gallons of liquid waste is estimated due to the solid waste (naphthalene, p-nitrotoluene, or 1-4-dibromobenzene) being dissolved in the solvent (i.e., cyclohexane) and therefore increasing the volume of the liquid waste.

† Sigma-Aldrich [http://www.sigmaaldrich.com/united-states.html, Accessed July 18, 2014].

‡ Waste disposal costs are based on the EPA Cost Calculator Tool [http://www.epa.gov/p2/pubs/resources/measurement.html#calc, accessed December 2014].

Molar Mass Determination by Freezing Point Depression *Greener Alternatives*

Hazardous chemicals avoided: 2-methyl-2-propanol or cyclohexane, naphthalene, p-nitrotoluene, 1,4-dibromobenzene

Greener Alternatives:

"A Greener Approach for Measuring Colligative Properties", by McCarthy, S.M. and Gordon-Wylie, S.W., J. Chem. Ed., 2005, 82(1), 116-119:

This experiment involves the melting point depression of an unknown fatty acid rather than an unknown aromatic hydrocarbon or organic solvent. Students can use the waste from this lab to make soap or biodiesel. Materials used include stearic acid and an unknown fatty acid (lauric, palmitic, or myristic), along with a small amount of 2-propanol to wash the unknown solid out of the test tube. A comparison table is provided for the fatty acids below:

Table 14. Chemicals used, human health and aquatic toxicity data:

Chemical:	**Amount per student group (2 students):**	**Human health toxicity:**†	**Aquatic toxicity:**†
stearic acid	9 g (0.02 lb)	*Low toxicity* LD50 (oral, rat) > 2,000 mg/kg; LD50 (dermal, rabbit) > 5,000 mg/kg	*Low toxicity*
lauric acid	2 g (0.0044 lb)	*Moderate toxicity* LD50 (oral, rat) > 5,000 mg/kg; Can cause eye damage	*High toxicity* LC50 (fish, 96 hr) 5 mg/l; LC50 (daphnia, 48 hr) 3.6 mg/l
palmitic acid	2 g (0.0044 lb)	*Low toxicity* LD50 (oral, rat) > 5,000 mg/kg	*High toxicity*, LC50 (fish, 96 hr) > 1,000 mg/l; EC50 (daphnia, 48 hr) > 4.8 mg/l
myristic acid	2 g (0.0044 lb)	*Low toxicity* LD50 (oral, rat) > 10,000 mg/kg; Can cause skin irritation	*Low toxicity*

† Human health and aquatic toxicity data was gathered from Globally Harmonized Safety Data Sheets, which can be obtained from Sigma-Aldrich [http://www.sigmaaldrich.com/united-states.html].

Molar Mass Determination by Freezing Point Depression
Greener Alternatives

Hazardous chemicals avoided: 2-methyl-2-propanol or cyclohexane, naphthalene, p-nitrotoluene, 1,4-dibromobenzene

***Greener Alternatives, Continued*:**

The purchasing and waste disposal costs associated with this procedure are estimated in the following table. Purchasing costs were estimated based on prices available from Sigma-Aldrich:†

Total amounts of chemicals used and disposed of per class of 100 students:

- ***1 lb of stearic acid***
- ***0.22 lbs of lauric acid, palmitic acid or myristic acid***
- ***1.22 lbs of fatty acids total***
- ***0-1.22 lbs of waste generated***

Table 15. *Purchasing and waste disposal costs:*

Chemical:	**Amount per 100 students:**	**Waste disposal cost‡**	**Purchasing cost:**	**Purchasing cost per 100 students:**	**Waste disposal cost per 100 students:**	**Total cost (per 100 students)**
stearic acid	450 g (0.99 lb)	$1.35/lb	$66.00, 1 kg	$29.70	$1.34	$31.04
lauric acid	100 g (0.22 lb)	$1.35/lb	$68.00, 1 kg	$6.80	$0.30	$7.10
palmitic acid	100 g (0.22 lb)	$1.35/lb	$241.00, 100 g	$241.00	$0.30	$241.30
myristic acid	100 g (0.22 lb)	$1.35/lb	$64.60, 100 g	$64.60	$0.30	$64.90
TOTALS:*	**1.2 lbs.**			**$36.50 - $270.70**	**$1.64**	**$38.14 - $272.34**

Total purchasing and waste disposal costs per class of 100 students:

- ***$36.50-$270.70 in purchasing costs***
- ***$1.64 in waste disposal costs***
- ***$38.14 - $272.34 total cost***

† Sigma-Aldrich [http://www.sigmaaldrich.com/united-states.html, Accessed July 18, 2014].
‡ Waste disposal costs are based on the EPA Cost Calculator Tool [http://www.epa.gov/p2/pubs/resources/measurement.html#calc, accessed December 2014].

Traditional Experiment:

Determining the Rate Law for a Chemical Reaction
Traditional Experiment

Hazardous chemicals avoided: crystal violet, potassium nitrate, ammonium persulfate, potassium iodide

This experiment is typically performed one of two ways. The first is a reaction between crystal violet and sodium hydroxide.

In the first procedure students determine the order of the reaction between crystal violet and sodium hydroxide with respect to reactant and calculate the rate constant for the reaction at room temperature. A colorimeter can be used to determine how the concentration of crystal violet changes over time.

Chemicals used and hazards:
The chemicals that are typically used in this experiment are listed below, along with a list of the hazards.

The amounts are estimated based on a procedure from Monmouth University's General Chemistry lab manual.

Table 16. Chemicals, amounts and toxicity data for tradition experiment:

Chemical:	**Amount per student group (2 students):**	**Human health toxicity:†**	**Aquatic toxicity:†**	**H-statements:†,‡**
Crystal violet (10 μM aqueous solution)	18 mL	*Suspected carcinogen, High acute toxicity;* LD50, oral, mouse - 96 mg/kg; LD50, oral, rabbit - 150 mg/kg	*High toxicity;* EC50 (daphnia, 48 hr) - 0.24-5mg/l; EC50 (algae, 72 hr) - 0.025 - 0.8 mg/l	H302, H315, H318, H351, H400, H410
Sodium hydroxide, 0.05 - 0.1M	2 mL	*Corrosive, causes severe burns to skin and eyes*	*Moderate toxicity;* LC50 (fish, 96 hr) 125 mg/l; LC50 (fish, 96 hr) 45.4 mg/l; EC50 (daphnia, 48 hr) 40.38 mg/l	H290, H314, H318, H402

Table 17. Chemicals used the traditional reaction:

Chemical:	**Total per 100 students:**	**Waste disposal cost:***	**Purchasing cost:**	**Purchasing cost per 100 students:**	**Waste disposal cost per 100 students:**	**Total cost (per 100 students):**
Crystal violet (10 μM aqueous solution)	900 mL (0.24 gal)	$11.79/gal	$49.70, 50 g	$0.01	$2.83	$2.84
Sodium hydroxide, 0.05 - 0.1M	100 mL (0.026 gal)	$11.79/gal	$55.90, 500 g	$0.05	$0.31	$0.36
TOTAL	**1 L (0.26 gal)**			**$0.06**	**$3.14**	**$3.20**

† Human health, aquatic toxicity data and H-statements were gathered from Globally Harmonized Safety Data Sheets, which can be obtained from Sigma-Aldrich [http://www.sigmaaldrich.com/united-states.html].
‡ H-statements (Hazard statements) are part of the European Union's Globally Harmonized System of Classification and Labeling of Chemicals. It is a set of standardized phrases about the hazards of chemical substances. A full list of H-statements can be found here: http://en.wikipedia.org/wiki/GHS_hazard_statement
* Waste disposal cost are based on EPA's P2 Cost Calculator [http://www.epa.gov/p2/pubs/resources/measurement.html#calc, Accessed July 1, 2014]

Traditional Experiment, continued:

The second type of experiment for determining the rate law for a chemical reaction is a clock reaction, which typically involves measuring the effect of concentration upon the rate of the reaction of peroxydisulfate ion with iodide ion.

In this experiment, students will measure the rate of a reaction and determine the rate law by measuring the amount of peroxydisulfate that reacts as a function of time.

Determining the Rate Law for a Chemical Reaction

Traditional Experiment

Hazardous chemicals avoided: crystal violet, potassium nitrate, ammonium persulfate, potassium iodide

Chemicals used and hazards:
The chemicals that are typically used in this experiment are listed below, along with a list of the hazards. The amounts are estimated based on a common procedure from one of the most widely used General Chemistry textbooks.†

Table 18. Chemicals used, human health and aquatic toxicity data:

Chemical:	**Amount per student group (2 students):**	**Human health toxicity:‡**	**Aquatic toxicity:‡**
potassium iodide, 0.2 M (MW = 166 g/mol)	122.5 mL (4.07 g/122.5 mL) (0.032 gal)	*Moderate toxicity,* LD50 (oral, mouse) 1,000 mg/kg	*Moderate toxicity,* LC50 (fish, 96 hr) 2,190 mg/l; EC50 (daphnia, 24 hr) 2.7 mg/l
starch solution, 1%	4.1 mL	*Low toxicity*	*Low toxicity*
sodium thiosulfate, 0.4 M (MW = 158.11)	32 mL (2.02 g/32 mL) (0.008 gal)	*Low toxicity,* Lethal dose (humans) 0.5-5 g/kg	*Low toxicity,* LC50 (fish, 96 hr) 24,000 mg/l
disodium Ethylenediaminetetraacetic acid, 0.1 M (MW = 372.24g (dihydrate))	0.5 mL (0.019g/0.5 mL)	*Low toxicity,* LD50 (oral, rat > 2,000 mg/kg)	*Low toxicity,* LC50 (fish, 96 hr) > 500 mg/l; EC50 (daphnia, 24 hr) > 100 mg/l
potassium nitrate, 0.2 M (MW = 101.1 g/mol)	129.5 mL (2.62 g/129.5 mL) (0.034 gal)	*High toxicity IARC Group 2A: Probably carcinogenic to humans,* Reproductive & developmental hazards LD50 (oral, rat) 3,750 mg/kg	*Moderate toxicity,* LC50 (fish, 96 hr) 22.5 mg/l; EC50 (daphnia, 72 hr) 226 mg/l

† "Rates of Chemical Reactions I: A Clock Reaction", in Chemistry The Central Science Laboratory Experiments, 12th Edition, by Nelson, J.H., Kemp, K.C., and Stoltzfus, M., Pearson Education, 2012.

‡ Human health and aquatic toxicity data was gathered from Globally Harmonized Safety Data Sheets, which can be obtained from Sigma-Aldrich [http://www.sigmaaldrich.com/united-states.html].

Traditional Experiment, continued:

The purchasing and waste disposal costs associated with this procedure are estimated in the following table. Purchasing costs were estimated based on prices available from Sigma-Aldrich:[5]

Total amounts of chemicals used and disposed of per class of 100 students:

- ***204 g potassium iodide (1.6 gal 0.2M solution)***
- ***367 g ammonium persulfate (2.2 gal 0.2M solution)***
- ***130.9 g potassium nitrate (1.7 gal 0.2M solution)***
- ***5.9 gallons liquid waste***

Determining the Rate Law for a Chemical Reaction

Traditional Experiment

Hazardous chemicals avoided: crystal violet, potassium nitrate, ammonium persulfate, potassium iodide

Table 19. Purchasing and waste disposal costs:

Chemical:	**Amount per 100 students:**	**Waste disposal cost[6]**	**Purchasing cost:**	**Purchasing cost per 100 students:**	**Waste disposal cost per 100 students:**	**Total cost (per 100 students)**
potassium iodide, 0.2 M (MW = 166 g/mol)	1.6 gal (203.5 g/1.6 gal)	$11.27/gal	$200.50, 500 g	$81.60	$18.03	$99.63
starch solution, 1%	0.054 gal	$11.27/gal	$63.60, 500 mL	$26.08	$0.61	$26.68
ammonium persulfate, 0.2M (MW = 228.2 g/mol)	2.15 gal (367.4 g/2.15 gal)	$11.27/gal	$69.30, 500 g	$50.92	$24.23	$75.15
sodium thiosulfate, 0.4 M (MW = 158.11)	0.4 gal (101 g/0.4 gal)	$11.27/gal	$45.50, 250 g	$18.38	$4.51	$22.89
disodium Ethylenediaminetetraacetic acid, 0.1 M (MW = 372.24g (dihydrate))	0.0065 gal (0.95 g/0.0065 gal)	$11.27/gal	$34.30, 100g	$0.33	$0.07	$0.40
potassium nitrate, 0.2 M (MW = 101.1 g/mol)	1.7 gal (130.9 g/1.7 gal)	$11.27/gal	$69.30, 500g	$18.15	$19.16	$37.30
TOTAL (per 100 students):	**5.9 gal**			**$195.46**	**$66.61**	**$262.07**

Total purchasing and waste disposal costs per class of 500 students:

- ***$195.46 in purchasing costs***
- ***$66.61 in waste disposal costs***
- ***$262.07 total cost***

[5] Sigma-Aldrich [http://www.sigmaaldrich.com/united-states.html, Accessed July 18, 2014].

[6] Waste disposal costs are based on the EPA Cost Calculator Tool [http://www.epa.gov/p2/pubs/resources/measurement.html#calc, accessed December 2014].

Determining the Rate Law for a Chemical Reaction
Greener Alternative

Hazardous chemicals avoided: crystal violet, potassium nitrate, ammonium persulfate, potassium iodide

***Greener Alternative*:**

The Vitamin C Clock Reaction is an ACS safer laboratory experiment ("Getting Off to a Safe Start: Using safer starting materials for chemical reactions" in Introduction to Green Chemistry, American Chemical Society, 2002, p. 5-11.) that replaces traditionally used chemicals described previously.

In the greener approach to the Clock Reaction, iodine solution is reacted with hydrogen peroxide in order to measure the rate law for the reaction. Liquid starch is used as the indicator for the I_3^- product and vitamin C (ascorbic acid) is used in the reaction in order to consume the I_3^- product in this reaction.

Table 20. The human health and aquatic toxicity data for the chemicals in the vitamin C clock reaction:

Chemical:	**Amount per student group (2 students):**	**Human health toxicity:‡**	**Aquatic toxicity:‡**
2% Lugol solution (2 g iodine, 2.1 g NaI, in 100 mL water)	7.5 mL	*Low toxicity, Iodine: (LD50 oral, rat) 14000 mg/kg; (LD50 oral, mouse) 22000 mg/kg; Sodium iodide: (LD50 oral, rat) 4340 mg/kg; (LD50 oral, mouse) 1000 mg/kg; Ethyl alcohol 200 Proof: (LD50 oral, rat): 7060 mg/kg; (LD50 oral, mouse) 3450 mg/kg; (LC50 inh, rat, 8 hr): 20000 ppm 8 hours; (LC50 inh, mouse, 4 hr): 39000 mg/m 4 hours*	*High toxicity Iodine: (LC50 fish) 1.7 mg/l, 96 hr; EC50 fish 0.2 mg/l, 48 hr; Sodium iodide: LC50 (fish, 96 hr) 860 mg/l; EC50 (daphnia, 48 hr) 0.17 mg/l*
Starch solution (liquid laundry starch)	3 mL	*Low toxicity*	*Low toxicity*
Vitamin C tablets (500mg vitamin C/250 mL)	75 mL	*Low toxicity*	*Low toxicity*
Hydrogen peroxide (3%)	25 mL	*Low toxicity, LD50 (oral, mouse) 2000 mg/kg; LD50 (dermal, rat) 4060 mg/kg; LC50 (inh, rat) 2000 mg/m*	*Low toxicity*

‡ Human health and aquatic toxicity data was gathered from Globally Harmonized Safety Data Sheets, which can be obtained from Sigma-Aldrich [http://www.sigmaaldrich.com/united-states.html].

Determining the Rate Law for a Chemical Reaction
Greener Alternative

Hazardous chemicals avoided: crystal violet, potassium nitrate, ammonium persulfate, potassium iodide

***Greener Alternative, Continued*:**

The purchasing and waste disposal costs associated with this procedure are estimated in the following table. Purchasing costs were estimated based on prices available from Sigma-Aldrich:[†]

Total amounts of chemicals used and disposed of per class of 500 students:

- ***0.5 gal Lugol solution (2g iodine, 2.1g NaI, 50mL ethanol, 50mL water)***
- ***5.2 gal aqueous solutions (starch solution and vitamin C table solution)***
- ***1.7 gal 3% hydrogen peroxide***
- ***7.5 gallons liquid waste***

Table 21. Purchasing and waste disposal costs:

Chemical:	**Amount per 100 students:**	**Waste disposal cost[6]**	**Purchasing cost:**	**Purchasing cost per 100 students:**	**Waste disposal cost per 100 students:**	**Total cost (per 100 students)**
2% Lugol solution[7] (2 g iodine, 2.1 g NaI in 100 mL water)	375 mL (0.099 gal)	$11.27/gal	$54.10, 1L	$20.29	$1.12	$1.12
Starch solution (liquid laundry starch)	150 mL (0.04 gal)	$11.27/gal	$2.97, 64 fl oz (0.5 gal)	$0.24	$0.45	$0.69
Vitamin C tablets (500 mg tablets) (solution is 500mg vitamin C/250 mL)	3.750 mL (0.99 gal)	$11.27/gal	$4.37, 120 tablet bottle	$2.00	$11.16	$13.16
Hydrogen peroxide (3%)	1,250 mL (0.33 gal)	$11.27/gal	$1.77, 16 oz bottle (0.125 gal)	$4.67	$3.72	$8.39
TOTAL (per 100 students):	**1.5 gal**			**$27.20**	**$16.45**	**$43.65**

[†] Sigma-Aldrich [http://www.sigmaaldrich.com/united-states.html, Accessed July 18, 2014].

[‡] Waste disposal costs are based on the EPA Cost Calculator Tool [http://www.epa.gov/p2/pubs/resources/measurement.html#calc, accessed December 2014].

Additional Resources for Green Chemistry in General Chemistry and beyond:

Greener Educational Materials (GEMs) Database (University of Oregon)

- Website: http://greenchem.uoregon.edu/gems.html
- Description: Searchable database with Green Chemistry educational materials uploaded by faculty members and educators world-wide
- Most curriculum is available for download (free-of-charge) or with primary literature information
- Google map of Green Chemistry educators

American Chemical Society's Green Chemistry Institute

- Website: www.acs.org/greenchemistry
- Description: Green Chemistry Resources for educators and students
- Experiments and Curriculum available for download
- List of ACS books on Green Chemistry

Green Chemistry Commitment

- Website: www.greenchemistrycommitment.org
- Description: A program of Beyond Benign to adopt Green Chemistry Learning Objectives in higher education.
- Case studies are available, university highlights, and curriculum resources

Beyond Benign

- Website: www.beyondbenign.org
- Description: Green Chemistry Curriculum available on-line (free-of-charge)
- Regional Outreach and Community Educational Events

GCEdNet – Green Chemistry Education Network

- Website: http://cmetim.ning.com/
- Description: A place where Green Chemistry educators share resources
- Blogs, discussions and chat rooms

University of Scranton Greening Across The Chemistry Curriculum

- Website: http://www.scranton.edu/faculty/cannm/green-chemistry/english/drefusmodules.shtml
- Description: Green Chemistry modules available for download
- Power point presentations, hand-outs available

Carnegie Mellon University Institute for Green Science

- Website: http://igs.chem.cmu.edu/
- Description: Green Chemistry modules available for download
- Power point presentations, hand-outs available

Appendix A
Comparison Table of Chemicals used in a Typical Qualitative Analysis Experiment

Chemical:	Human health toxicity:	Aquatic toxicity:	H-statements:
Barium chloride	*High human health toxicity via ingestion and inhalation;* Oral LD50's: 90 mg/kg (dog); 76 mg/kg (guinea pig); 70 mg/kg (mouse); 170 mg/kg (rabbit)	*Moderate acute aquatic toxicity* and *high chronic aquatic toxicity*; LC50 (fish, 96 hrs) - 46 mg/l; EC50 (daphnia, 48 hr) - 14.5 mg/l;	H301, H332, H412
Potassium chloride	*Low human health toxicity;* Oral LD50 - 2.6 g/kg (rat), 0.142 g/kg (intravenous, rat)	*Moderate acute and chronic aquatic toxicity;* LC50 (fish, 96 hr) – 880 mg/l; EC50 (daphnia) – 83 mg/l	H402, H412
Sodium phosphate	*Low human health toxicity*, can cause skin and eye irritation	*Moderate acute and chronic aquatic toxicity;* LC50 (fish, 96 hr) – 28.5 mg/l	H315, H318, H335, H412
Silver nitrate	*Moderate human health toxicity;* LD50 (oral, rat) – 1,173 mg/kg	*Very high acute and chronic aquatic toxicity;* LC50 (fish, 96 hr) - 0.029 mg/l; LC50 (fish, 96 hr) – 0.006 mg/l; EC50 (daphnia, 48 hr) – 0.0006 mg/l	H272, H302, H314, H410
Nickel (II) chloride	*High acute and chronic human health toxicity, including carcinogenicity, reproductive and developmental hazards;* LD50 (oral, rat) - 186 mg/kg; on CA Prop 65 list as known carcinogen	*Very high acute and chronic aquatic toxicity;* EC50 (daphnia, 48 hr) – 6-9.3 mg/l; EC50 (algae, 96 hr) – 0.006-0.012 mg/l	H301 + H331, H315, H317, H334, H341, H350, H360, H372, H410
Sodium sulfide	*High acute toxicity;* LD50 (oral, rat) - 246 mg/kg	*Very high acute and chronic aquatic toxicity;* LC50 (fish, 96 hr) - 0.032 mg/l; LC50 (daphnia, 48 hr) – 75 mg/l	H251, H290, H301, H314, H410
Cadmium chloride	*High acute and chronic human health toxicity, including carcinogenicity, reproductive and developmental hazards;* LD50 (oral, rat) - 107 mg/kg; LC50 (inh, rat) > 4.5 mg/m3; IARC Group 1 Carcinogen; on CA Prop 65 List as known carcinogen	*Very high acute and chronic aquatic toxicity;* LC50 (fish,96 hr) – 1,500 μg/l; EC50 (daphnia, 48 hr) – 0.036 mg/l; EC50 (algae, 72 hr) – 0.070 mg/l	H301, H330, H340, H350, H360, H372, H410
Sodium acetate	*Low toxicity;* LD50 (oral, rat) - 3,530 mg/kg; LC50 (inh, rat) > 30,000 mg/m3; LD50 (dermal, rabbit) > 10,000 mg/kg	*Low toxicity;* LC50 (fish, 120 hr) - 13,330 mg/l; LC50 (fish, 24 hr) – 5,000 mg/l; EC50 (daphnia, 48 hr) > 1,000 mg/l	None
Lead (II) nitrate	*High acute and chronic human health toxicity, including carcinogenicity, reproductive and developmental hazards;* LD50 (intravenous, rat) – 93 mg/kg; LD50 (intraperitoneal, mouse) - 74 mg/kg; IARC Group 2A: Probably carcinogenic to humans	*Very high acute and chronic aquatic toxicity;* LC50 (fish, 96 hr) - 1.5 mg/l; LC50 (fish, 96 hr) – 0.4-1.3 mg/l; EC50(daphnia, 48 hr) - 0.5-2.0 mg/l	H272, H302 + H332, H318, H360, H373, H410
Copper (II) sulfate	*Moderate human health toxicity;* LD50(oral, rat) – 482 mg/kg; LD50 (intraperitoneal, rat) – 20 mg/kg; LD50 (subc, rat) – 43 mg/kg; LD50 (intravenous, rat) – 48.9 mg/kg	*Very high acute and chronic aquatic toxicity;* LC50 (fish, 96 hr) - 1-2.5 mg/l; EC50 (daphnia, 48 hr) - 0.024 mg/l	H302, H315, H319, H410
Sodium nitrate	*Moderate human health toxicity;* LD50 (oral, rat) 1,267 mg/kg; LD50 (oral, rabbit) – 2,680 mg/kg; LD50 (intravenous, mouse) – 175 mg/kg	*Low aquatic toxicity;* LC50 (fish, 96 hr) – 6,650 mg/l; EC50 (daphnia, 24 hr) - 6,000 mg/l	H272, H302, H315, H319, H335
Ammonium chloride	*Moderate human health toxicity;* LD50 (oral, rat) - 1,650 mg/kg	*High acute and chronic aquatic toxicity*; LC50 (fish, 96 hr) - 209 mg/l; LC50 (fish, 96 hr) – 3.98 mg/l; LC50 (daphnia, 48 hr) – 161 mg/l	H302, H319, H411
Sodium carbonate	*Low toxicity;* LD50 (oral, rat) - 4,090 mg/kg; LC50 (inh, rat, 2 hr) – 5,750 mg/l	*Low toxicity;* LC50 (fish, 96 hr) - 300 mg/l; EC50 (daphnia, 48 hr) - 265 mg/l	H319

Appendix B
Guidelines for human and aquatic toxicity values

The following guidelines are used to determine human toxicity values (low, moderate, high and very high). They are derived from Clean Production Action's Green Screen®[†] and adapted for Washington State Department of Ecology's Quick Chemical Assessment Tool (QCAT):[‡]

Acute Mammalian Toxicity LD50 (Oral, Dermal), LC50 (Inhalation):

Very High (v)	***High (H)***	***Moderate (M)***	***Low (L)***
GHS Category 1 or 2; Risk Phrases R26, R27, R28; Hazard Phrases H300, H310, H330; Technical Criteria: Oral LD50 ≤ 50 mg/kg; Dermal LD50 ≤ 200 mg/kg; Inhalation (g) LC50 ≤ 500 ppm; Inhalation (v) LC50 ≤ 2 mg/l; Inhalation (dust, mist) LC50 ≤ 0.5 mg/l	GHS Category 3; Risk Phrases R23, R24, R25; Hazard Phrases H301, H311, H331; Technical Criteria: Oral LD50 > 50 but ≤ 300 mg/kg; Dermal LD50 > 200 but ≤ 1,000 mg/kg; Inhalation (g) LC50 > 500 but ≤ 2,500 ppm; Inhalation (v) LC50 > 2.0 but ≤ 10.0 mg/l; Inhalation (dust, mist) LC50 > 0.5 but ≤ 1.0 mg/l	GHS Category 4; Risk Phrases R20, R21, R22; Hazard Phrases H302, H312, H332; Tech. Criteria: Oral LD50 > 300 but ≤ 2,000 mg/kg; Dermal LD50 > 1,000 but ≤ 2,000 mg/kg; Inh. (g) LC50 > 2,500 but ≤ 20,000 ppm; Inh. (v) LC50 > 10.0 but ≤ 20.0 mg/l; Inh. (dust, mist) LC50 > 1.0 but ≤ 5.0 mg/l	GHS Category 5; Hazard Phrases H303, H313, H333; Tech.l Criteria: Oral LD50 > 2,000 mg/kg; Dermal LD50 > 2,000 mg/kg; Inh. (g) LC50 > 20,000 ppm; Inh. (v) LC50 > 20.0 mg/l; Inh. (dust, mist) LC50 > 5.0 mg/l

The following guidelines are used to determine aquatic toxicity values (low, moderate, high and very high). They are derived from Clean Production Action's Green Screen and adapted for Washington State Department of Ecology's Quick Chemical Assessment Tool (QCAT):

Acute Aquatic Toxicity LC50 or EC50:

Very High (v)	***High (H)***	***Moderate (M)***	***Low (L)***
on Canadian DSL list as Inherently Toxic to Aquatic Organisms; GHS Category 1; Risk Phrases R50, Hazard Phrases H400; Technical Criteria: 96 hr LC50 (fish) ≤ 1 mg/l, 48 hr EC50 (crustacea) ≤ 1 mg/l, 72 or 96 ErC50 (algae) ≤ 1 mg/l	GHS Category 2; Risk Phrases R51, Hazard Phrases H401; Technical Criteria: 96 hr LC50 (fish) > 1 but ≤ 10 mg/l, 48 hr EC50 (crustacea) > 1 but ≤ 10 mg/l, 72 or 96 ErC50 (algae)> 1 but ≤ 10 mg/l	GHS Category 3; Risk Phrases R52, Hazard Phrases H402; Technical Criteria: 96 hr LC50 (fish) > 10 but ≤ 100 mg/l, 48 hr EC50 (crustacea) > 10 but ≤ 100 mg/l, 72 or 96 ErC50 (algae) > 1 but ≤ 100 mg/l	Technical Criteria: 96 hr LC50 (fish) > 100 mg/l, 48 hr EC50 (crustacea) > 100 mg/l, 72 or 96 ErC50 (algae)> 100 mg/l

[†] Washington State Department of Ecology Quick Chemical Assessment Tool [http://www.ecy.wa.gov/programs/hwtr/ChemAlternatives/QCAT.html, Accessed February 2015].

[‡] Clean Production Action Green Screen® for Safer Chemicals [http://www.greenscreenchemicals.org/method/?/Greenscreen.php, Accessed February 2015].

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