

Determination of the Formula of a Hydrate: A Greener Alternative

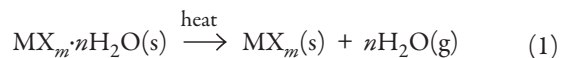
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Green chemistry is defined as “the utilization of a set of principles that reduces or eliminates the use or generation of hazardous substances in the design, manufacture, and application of chemical products” (1). While efforts to incorporate the principles of green chemistry into parts of the undergraduate curriculum (especially organic chemistry) are gaining momentum, the infusion of green chemistry across the entire chemistry curriculum has not been widely seen. With these efforts in mind, we are striving to introduce first-year students to the principles of green chemistry with the emphasis on how they can be applied in the laboratory setting. Specifically, the first and third of the Twelve Principles of Green Chemistry (1) apply to this lab.

- Principle 1: It is better to prevent waste than to treat or clean up waste after it is formed.
- Principle 3: Wherever practicable, (synthetic) methodologies should be designed to use and generate substances that possess little or no toxicity to human health and the environment.

Stoichiometry is one of many fundamental concepts that first-year undergraduate students learn (2–4). In the case of hydrated salts, we generally discuss the stoichiometry (or molar ratio) of water molecules to cations within the crystal lattice. This application of stoichiometry can be explored in the laboratory by dehydrating a known mass of hydrated salt over a flame, followed by determination of the mass of the dehydrated salt (5).¹



The mass difference can then be used to calculate the ratio of

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formula units of salt to water molecules, provided the molar mass of the dehydrated salt is given.

The laboratory experiment we desired to make “greener” used both barium and calcium hydrate salts. While the calcium salt does not pose any major health issues (6), barium, in comparison, possesses a National Fire Protection Association (NFPA) health rating of 3 (poison) and has been investigated as a tumorigen. In addition, barium has been shown to bioaccumulate in the environment (7). From a green chemistry standpoint, this conflicts with Principle 3, which stresses the use of safer solvents and reagents and reaction conditions. In addition, both the calcium and barium salts were discarded after the lab, which conflicts with Principle 1 that advocates prevention of waste. Our alternative discussed below and compared to the original reagents in Table 1, shows lower health risks, lower reactivity, higher permissible exposure limits (PEL), and the added benefit of lower cost (9).

To improve the “shade of green”, we looked for a more environmentally friendly alternative to barium in addition to negating the issue of waste. The number of hydrated metal salts that can be considered “green” initially limited us. We also sought to find a metal salt that displayed a distinct color change upon dehydration to give an added visual aspect to the lab. After attempts with metal hydrates such as magnesium sulfate heptahydrate, copper sulfate pentahydrate, and zinc sulfate heptahydrate, we chose copper(II) chloride dihydrate ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$). The hydrated form is bright blue, but upon dehydration the color dramatically changes to chocolate brown. In comparison, the barium and calcium salts used in the original protocol were white in color and remained so upon dehydration.

The original experimental protocol called for heating with a Bunsen burner to carry out the dehydration process. To overcome this safety hazard and the original need for natural gas, we used a 110 °C oven to carry out the dehydration, which is an intrinsically safer method of heating.

Table 1. Purity, NFPA Ratings, Permissible Exposure Limits (PEL), and Costs of Salts Used

Salt	Purity	Health ^a	Flammability ^a	Reactivity ^a	PEL ^a / (mg m ⁻³)	Cost ^b (per 100 g)
$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	ACS	2	0	0	15	\$20.20
$\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$	ACS	3	0	0	0.5	\$14.60
$\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$	Reagent	2	0	0	1	\$6.20 ^c

^aData taken from refs 5–7. ^bData from 2005–2006 Sigma-Aldrich. ^cDetermined from price of a 500 g bottle.

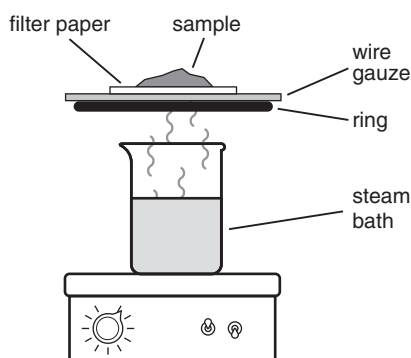


Figure 1. Apparatus used for sample rehydration.

Procedure

In a typical procedure, the dihydrate salt (typically 0.5–0.8 g) was placed into a crucible. The crucible was then placed in a numbered muffin tin with the lid positioned so that water vapor could escape. To identify the sample, the number corresponding to the position in the tin was recorded. The tins were then placed in the oven by the instructor or laboratory assistant for a 30-minute period. Afterwards, the closed crucible was allowed to fully cool for 15 minutes. An initial dehydrated mass was determined after cooling and the crucible returned to the muffin tin for an additional 10-minute heating period. Following the second heating, the samples were again allowed to cool, and finally the mass of the crucible and sample were determined. If a sample showed a mass discrepancy greater than 0.003 g compared to the first heating, it was returned to the oven for an additional 10-minute period. A third heating was not needed in any of the lab sections. This batch heating simplifies the procedure and keeps all students on the same time schedule.

Once a final constant mass is achieved, the amount of water driven off can be found by subtracting the final mass after heating from the initial mass of salt used and dividing the difference by the formula mass of water. To find the ratio of formula units of salt to water, the final mass of dehydrated salt and formula mass of the dehydrated salt are used to determine the number of moles of dehydrated salt. The moles of dehydrated salt are then divided by the moles of water driven off to determine their ratio.

Finally, each sample was rehydrated, allowing it to be recycled (Principle 1). Figure 1 shows a typical rehydration setup where the dehydrated sample was placed on a large piece of filter paper that is supported by a wire gauze, ring, and ring stand. A boiling water bath was then positioned under the sample. Simple movement of the salt within the steam with the aid of a rubber policeman effectively rehydrated the sample. In general the rehydration could be completed in about a 15–20 minute period. We also found that if rehydration by a steam bath was not carried out, the salt could also be left out overnight on the counter-top and would absorb enough water from the atmosphere to return to its original hydrated form. We recommend steam rehydration since it adds a valuable lesson and since the students enjoy watching the rehydration process.

With proper care and technique, the recovered hydrate can be dehydrated and rehydrated at least seven times with consistent, reproducible results. The possibility of further cycling may be possible, but was not pursued. It must be noted that while the rehydration process is quite efficient, there is always some sample that becomes absorbed in the filter paper. On one occasion, a student group managed to dissolve nearly their entire sample into the filter paper. This was due to the lack of sample movement when exposed to the steam and a “puddling” effect of the hydrated crystals.

While not required of our students, an approximate recycling efficiency of about 95% was also determined by mass determination following rehydration. By comparison of the final mass with the initial mass, an approximate quantity of salt retained within the filter paper can be determined. Proper disposal should be followed depending on the quantity of copper salt entrained within the paper.

Hazards

Copper(II) chloride dihydrate is harmful by inhalation and ingestion; is a skin, eye, and respiratory irritant; and repeated exposure can lead to copper poisoning.

Summary

This experiment offers many opportunities for students to apply concepts that may have already been covered in the course, including the mole concept, writing chemical formulas from names, naming compounds based on formulas, along with slightly more advanced topics such as unit cells and crystal lattice structures. In addition, with the emergence of green chemistry within the undergraduate curriculum, the laboratory provides a greener approach and encourages students to consider the toxicity and exposure risks of the reagents in use and environmental and disposal issues of the generated waste in the original procedure. Toxicity differences are emphasized by asking students to consult the MSDS for the appropriate chemicals. They are then asked to make their own judgment on the green aspects of the lab.

We believe this laboratory redesign offers clear advantages over the original protocol. By implementing the principles of green chemistry, we reduced the overall risk of the laboratory but have not altered the fundamental learning objectives. The dramatic color change observed upon dehydration and subsequent rehydration not only adds to the educational aspects of this experiment (by allowing the opportunity to discuss why the color changes), but is also appealing to the students. In addition, the use of the oven for dehydration rather than a Bunsen burner removes the issues of open flames and the concern of open gas ports upon lab completion. Finally, by having students rehydrate the copper salt, the experiment demonstrates an important aspect of green chemistry: sustainability.

Acknowledgments

This work was made possible by the generous financial support of the W. M. Keck Foundation and the Howard Hughes Medical Institute.

Note

1. An Internet search using keywords “formula of a hydrate” will generate many laboratory procedures demonstrating the original dehydration procedure.

Literature Cited

1. Anastas, P. T.; Warner, J. C. *Green Chemistry: Theory and Practice*; Oxford University Press: Oxford, 1998.
2. Chebolu, V.; Storandt, B. C. *J. Chem. Educ.* **2003**, *80*, 305.
3. Song, Y.; Wang, Y.; Geng, Z. *J. Chem. Educ.* **2004**, *81*, 691.
4. Pinto, G. *J. Chem. Educ.* **2005**, *82*, 1509.
5. Schaeffer, R. W.; Chan, B. C.; Marshall, S. R.; Blasiolo, B.; Khan, N.; Yoder, K. L.; Trainer, M. E.; Yoder, C. H. *J. Chem. Educ.* **2000**, *77*, 509.
6. Calcium Sulfate Dihydrate, MSDS. <http://www.jtbaker.com/msds/englishhtml/c0495.htm> (accessed Feb 2008).
7. Barium Chloride Dihydrate, MSDS. <http://www.jtbaker.com/msds/englishhtml/b0372.htm> (accessed Feb 2008).
8. Cupric Chloride Dihydrate, MSDS. <http://www.jtbaker.com/msds/englishhtml/c5863.htm> (accessed Feb 2008).

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