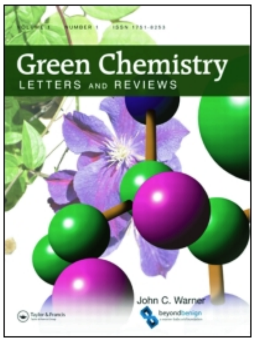

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Extraction of dyes contained in glow sticks using liquid CO_2

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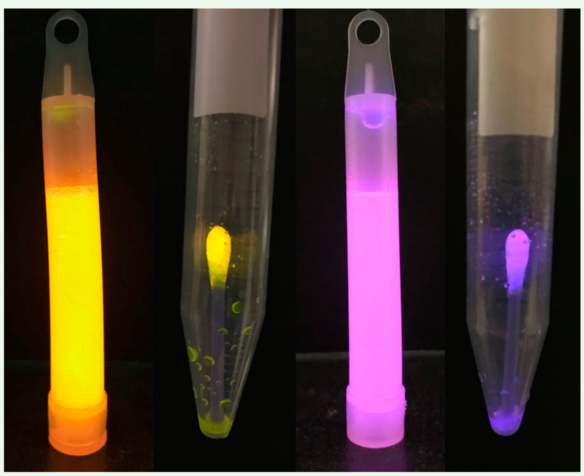
ABSTRACT

Separation of glow stick dyes adhered to a cotton swab using liquid CO_2 provides an engaging demonstration of several chemical concepts including polarity, kinetics, chemiluminescence, and the importance of CO_2 a green solvent. The simple protocol allows access to a broad range of students. Differential polarities of the glow stick dyes allow certain dyes to be preferentially dissolved in liquid CO_2, leaving other dyes adhered onto cotton. Both TCPO (bis(2,4,6-trichlorophenyl)oxalate) and H_2O_2, which together provide the necessary reaction for chemiluminescence, are present in both the extracted liquid and cotton upon dissipation of CO_2. Thus, it is possible to compare the emission spectrum of the extracted fluid to that of the original glow stick and the residue left on the cotton swab. Emission peaks resulting from the presence of polar dyes in the original glow stick and on the cotton are routinely observed to be missing in the extracts.



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Introduction

Both liquid CO_2 and supercritical CO_2 can be used as a substitute for volatile organic solvents in extraction and chromatographic methods (*1–7*). CO_2 can be obtained from and returned to the air in a cyclic fashion, it is neither toxic nor flammable, and its use as a solvent avoids the production of large quantities of waste solvent (*7*). In fact, in a survey of academic researchers, CO_2 was identified as the solvent mostly likely to reduce environmental damage (*8*). Thus, the use of CO_2 as a solvent in separation science can provide avenues to introduce students to the importance of green chemistry and sustainability. Indeed, several experiments that involve the use of liquid CO_2 during extractions and chromatographic separations have appeared in the chemical education literature. For example, the use of liquid CO_2 to extract various organic compounds from orange peels (*1*,*2*), fennel seeds (*3*), cloves (*4*), and essential oils (*5*) has been previously reported.

Chemiluminescence is another topic that has been extensively covered in the chemistry curriculum (*9–14*). In fact, chemiluminescent reactions have even been referred to as the most "exocharmic" reactions known, based on the high interest they generate in students and other observers (*9*). Chemiluminescent reactions have been used to introduce students to topics as varied as fluorescence, kinetics, thermodynamics, chromatography, catalysis, organic synthesis, and principles of

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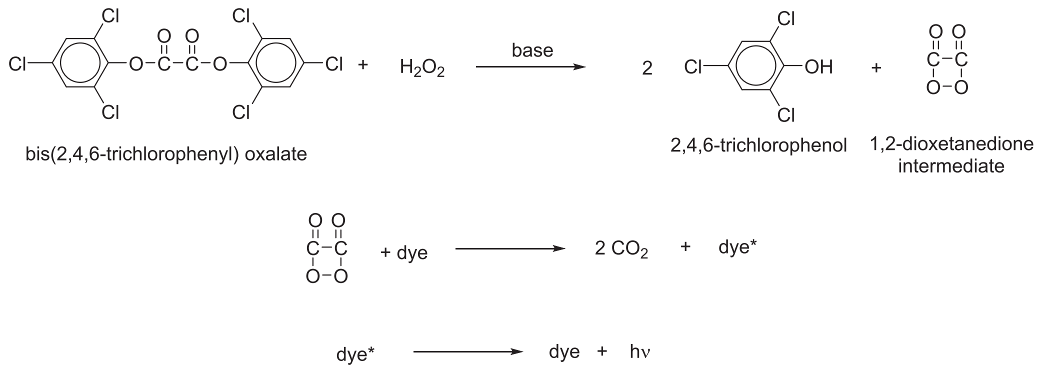

Figure 1. Reaction mechanism in glow sticks responsible for the emission of light. Note that dye* represents a dye molecule that is in an excited electronic state.

green chemistry (*9–14*). Many of these experiments have focused on the chemistry of glow sticks, which provide very easily obtained sources of chemiluminescent reactions. The use of such simple materials in experiments is attractive for many chemical educators who work at institutions that do not have large budgets or access to expensive equipment. In a previous publication, it was demonstrated how materials contained in an activated glow stick could be separated using column chromatography (*9*). In some cases it was possible for students to observe distinct, actively glowing bands on the column as the separation took place. This experiment was light-heartedly termed "glowmatography" on account of its combination of glow sticks and chromatography.

In this letter, we build upon the body of previously reported work to describe how liquid CO_2 can be used to separate various dyes contained in glow sticks using materials as simple as dry ice, plastic centrifuge tubes (*1*), glow sticks, and cotton swabs. The development of laboratory exercises that use liquid CO_2 rather than supercritical CO_2 is important, because many chemical educators and their students do not have the resources or infrastructure necessary to carry out experiments using supercritical CO_2. However, extractions involving liquid CO_2 are quite easy to perform (*1–5*). Thus, laboratory experiments that incorporate liquid CO_2 as a solvent allow a wider audience of students to learn about the potential benefits of CO_2 as a solvent. Indeed, the experiments reported in this letter introduce students to the same chemical principles taught in the original glowmatography experiment, but without the use of hexane solvent and silica gel stationary phase. In addition, over ten times less glow stick material is required when using this new extraction method. Thus, this new method described represents a substantial move toward a more environmentally friendly study of separation of dyes contained in glow sticks.

Background

The light emitted from a glow stick is powered by the base catalysed reaction between bis(2,4,6-trichlorophenyl) oxalate (TCPO) and hydrogen peroxide (*10*) Figure 1.

In the first step of the reaction mechanism, TCPO (*11*) reacts with hydrogen peroxide to form a reactive dioxetanedione intermediate, C_2O_4. This intermediate collides with a fluorescent dye molecule contained in the glow stick, and upon doing so promotes an electron in the dye to an excited state (dye*). As the electron relaxes back to the ground state, a photon of light is concomitantly emitted. Because the wavelength of the photon emitted depends upon the chemical structure of the dye, various colors of light emission are obtained by placing different dyes or mixtures of dyes within glow sticks (*9*). For example, various rhodamine dyes emit red or orange light, while bis(phenylethynyl)anthracene (BPEA) dyes emit yellow, green, or blue light. In addition to these differences in colors of light emitted, rhodamine dyes tend to be more polar than BPEA dyes (*9*). The experiments reported herein allow students to use liquid CO_2, a non-polar solvent, to extract actively glowing non-polar dyes from an activated glow stick mixture. Direct visualization of the extraction process is possible because it is easy to recognize that the extracted material glows a different color than the original mixture.

Materials and methods

A glow stick (both Supreme Glow and Super Glow brands work, available at https://www.partycity.com/) is activated by breaking the inner glass ampoule. The glow stick is cut open using a PVC pipe cutter. A cotton swab with a plastic handle is cut in half, and the cotton end is dipped into the activated glow stick mixture. Excess liquid is dabbed from the cotton. The swab is placed cotton side up into a Corning 15 mL polypropylene centrifuge tube (Fisher Scientific, manufacturing number 430052). Dry ice is powdered with a hammer, and then added to the centrifuge tube until it is roughly ¾ full. The cap is sealed tight and the assembly is immediately placed into hot water (60–70°C) contained in a 355 mL plastic soda bottle with its top removed. As the dry ice sublimes, pressures sufficient to liquefy CO_2 build inside the centrifuge tube, melting usually occurs within 30 s. Even so, pressure does vent from the tube as evidenced from considerable hissing noise observed as CO_2 gas escapes. On occasion, the dry ice does not liquefy. If not, it is helpful to tighten the seal of the cap on the centrifuge tube. Non-polar dyes contained in the glow stick mixture are preferentially dissolved into the liquid CO_2 that rinses through the cotton, and these dyes collect in the bottom of the centrifuge tube (Figure 2). If available, an emission spectrometer is used to collect the emission spectra of the glowing extract and the glowing residue remaining on the cotton. In addition, the emission spectrum of a second cotton swab that has been dipped into the activated glow stick mixture – but that has not gone through the CO_2 extraction process – is also recorded. All processes are carried out by students except the collection of emission spectra. Emission spectra were carried out in the dark using an Ocean Optics USB4000 spectrometer with an optical resolution of 1.0 nm FWHM; integration time was set at 5 s. Light emitted from extracts and material adhered to cotton swabs were collected via a fiber optic cable attached to the spectrometer. To collect spectra of material on cotton swabs, the end of the fiber optic was held ~3 mm above the surface of the cotton swab. To collect spectra of residues in a centrifuge tube, the fiber optic was inserted into the centrifuge tube and held ~3 mm above the surface of the extract (after removal of the cotton swab).

Figure 2. (Left) Liquid CO_2 extraction of dyes contained in orange glow stick fluid. Note the slight yellow tint of the liquid CO_2 that surrounds the cotton swab. (Right) Cotton swab and extract after extraction procedure and warmed to room temperature.

Results

Fluid from an activated, orange light stick is applied to a cotton swab and placed in a centrifuge tube as described in the Materials and Methods. This is an elegant manner of providing polar material that remains suspended above the bottom of the centrifuge tube. The stalk of the cotton swab is made of polypropylene, analysed by FTIR, and therefore neither of the dyes absorb onto the stalk, making analysis of both extract at the bottom of the centrifuge tube and the residue remaining on the cotton tip quite easy and convenient. The centrifuge tube is filled with powdered dry ice and sealed. When the liquid CO_2 forms, it drips through the cotton swab. The glowing stops due to the decrease in temperature, and the liquid CO_2 takes on a faint orange-yellow color from dyes that dissolve in the liquid CO_2 (Figure 2, left). Dyes extracted from the cotton collect on the bottom of the centrifuge tube as the CO_2 escapes. After all the CO_2 escapes, the cap is removed and the contents of the centrifuge tube are allowed to warm up. Upon reaching about room temperature, both the residue on the cotton and the extract begin to glow again (Figure 2, right). The light emitted from the cotton swab is a noticeably different color than the light emitted from the extract (Figure 2, right), due to differential solubility of dyes in the liquid CO_2. While the emission spectrum of the glowing residue adhered to the cotton (Figure 3, thin line) is somewhat dimmer than fresh glowing glow stick mixture adsorbed onto a cotton swab (Figure 3, bold line), the spectra are otherwise quite similar. Both spectra show peaks at about 550, 620, and 675 nm. On the other hand, the peaks at 620 and 675 nm are clearly diminished in the emission spectrum of the extracted material on the bottom of the centrifuge tube (Figure 3, dotted line). These results indicate that liquid CO_2 tends to extract yellow-green emitting dye (s), but not red emitting dye(s) from the cotton. Given the non-polar nature of liquid CO_2 and the polar nature of the cellulose in the cotton, it is likely that the red-orange emitting dye(s) are more polar than the yellow-green emitting dye(s). When the experiment is repeated using a pink light stick, the emission spectra of fresh glow stick mixture (Figure 4, bold line) and residue adhered to

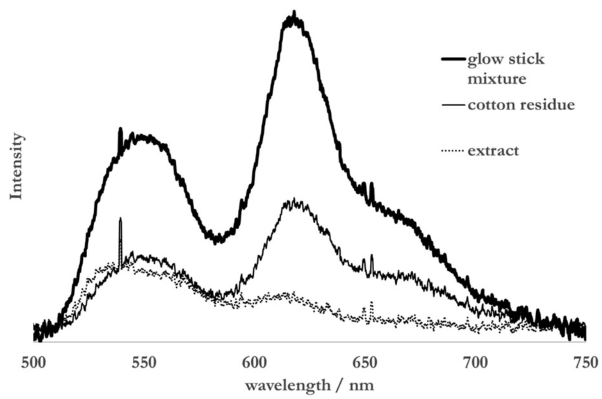

Figure 3. Emission spectra of orange glow stick material prior to and following extraction procedure as described in the text. Fresh glow stick mixture (bold line), residue on cotton swab (thin line), extract (dotted line).

the cotton (Figure 4, thin line) both show peaks at 445, 475, 620, and 675 nm. On the other hand, while the peaks at 445 and 475 nm appear in the emission spectrum of the extract, the peaks at 620 and 675 nm are almost absent (Figure 4, dotted line). These results suggest that liquid CO_2 extracts a substantial amount of non-polar, blue emitting dye(s) from the pink glow stick fluid, leaving red emitting dye(s) adsorbed on the cotton. The spectra are consistent with the more pronounced blue color observed in the extract than on the residue adhered to the cotton (Figure 5). This extraction method can be successfully applied using glow sticks of other colors, but orange and pink glow sticks tend to provide the greatest contrast in color between the extract and residue adhered to the cotton. Results from experiments using glow sticks of other colors, as well as a student laboratory sheet, can be found in the supporting information.

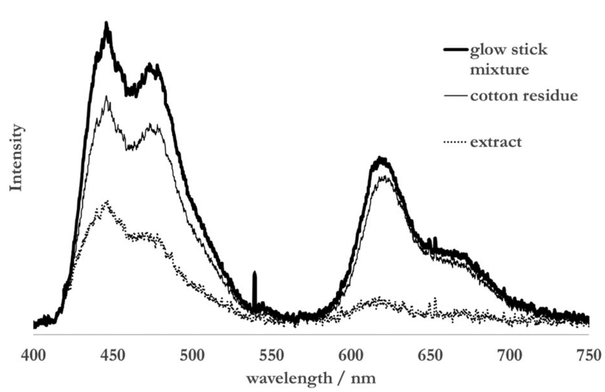

Figure 4. Emission spectra of pink glow stick material prior to and following extraction procedure as described in the text. Fresh glow stick mixture (bold line), residue on cotton swab (thin line), extract (dotted line).

Figure 5. Cotton swab and extract after extraction procedure performed on pink glow stick material. Both the cotton swab and extract have been warmed to room temperature.

Discussion

Using liquid CO_2 to extract dyes from activated glow stick mixtures provides a simple, colorful, and motivating way to introduce students to the importance of sustainable solvents. The process is easy to carry out, allowing students at a wide variety of institutions to participate in these experiments. Nevertheless, the process allows for the discussion of several chemical topics including chemiluminescence, molecular polarity, solubility, kinetic mechanisms, emission spectroscopy, and intermolecular forces.

During the extraction process, it is interesting to note that the glow stick material adsorbed on the cotton loses its glow. This is not surprising, given that it is well known that the kinetics of the chemical reaction in glow sticks substantially decreases with temperature (*14*,*15*). However, it is unexpected that both the residue on the cotton swab and the extract begin glowing again after being warmed back to room temperature following the extraction process (Figure 2, right and Figure 5). In order for chemiluminescence to occur, TCPO, H_2O_2, and dye(s) must be present (Figure 1). Therefore, both the cotton residue and extract contain TCPO and H_2O_2. The presence of TCPO in the extract is likely due to the fact that both TCPO and liquid CO_2 are non-polar. The presence of H_2O_2 on the cotton is probably due to hydrogen bonding and other dipole–dipole interactions between the peroxide and cotton cellulose. That some H_2O_2 ends up in the extract implies that H_2O_2 dissolves in liquid CO_2. This may occur to some extent if O-H groups on the peroxide act as hydrogen bond donors, while the oxygen atoms on CO_2 act as hydrogen bond acceptors. Similarly, TCPO adhered to the residue could occur by O-H groups on cellulose and oxygen atoms on TCPO acting as hydrogen bond donors and acceptors, respectively. In any event, it is fortuitous that these compounds are present in both the cotton residue and extract, allowing both to recover easily visible chemiluminescence upon warming.

In conclusion, the experiments reported here provide an enlightening and colorful way for students to gain experience using CO_2 as an environmentally friendly solvent. Dyes in glow stick mixtures can be extracted somewhat selectively using simple and inexpensive materials. The protocol is straightforward enough that it can be carried out by non-science majors. On the other hand, interpreting the results of these experiments requires a knowledge of a rich assortment of physicochemical topics. As such, we have used this experiment in settings that range from outreach events to undergraduate research projects.

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Disclosure statement

No potential conflict of interest was reported by the authors.

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Thomas S. Kuntzleman is professor of chemistry at Spring Arbor University and an associate editor of the Chemical Education Xchange. He earned an MS from the University of North Carolina at Greensboro and a PhD from the University of Michigan. He is interested in the chemistry of everyday phenomena as well as the design of chemical-educational experiments that use inexpensive and easily obtained materials.

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References

[1] McKenzie, L.C.; Thompson, J.E.; Sullivan, R.; Hutchison, J.E. Green Chemical Processing in the Teaching Laboratory: A Convenient Liquid CO_2 Extraction of Natural Products. *Green Chem.* **2004,** *6*, 355–358. doi:10.1039/B405810K.

[2] Buckley, H.L.; Beck, A.R.; Mulvihill, M.J.; Douskey, M.C. Fitting It All In: Adapting a Green Chemistry Extraction Experiment for Inclusion in an Undergraduate Analytical Laboratory. *J. Chem. Educ.* **2013**, *90* (6), 771–774. doi:10.1021/ed300510s.

[3] Bodsgard, B.R.; Lien, N.R.; Waulters, Q.T. Liquid CO_2 Extraction and NMR Characterization of Anethole From Fennel Seed: A General Chemistry Laboratory. *J. Chem. Educ.* **2016**, *93* (2), 397–400. doi:10.1021/acs.jchemed.5b00689.

[4] Barcena, H.; Chen, P. An Anesthetic Drug Demonstration and an Introductory Antioxidant Activity Experiment with "Eugene, the Sleepy Fish". *J. Chem. Educ.* **2016**, *93* (1), 202–205. doi:10.1021/ed5008469.

[5] Baldwin, B.W.; Kuntzleman, T.S. Liquid CO_2 in Centrifuge Tubes: Separation of Chamazulene From Blue Tansy (Tanacetum Annum) Oil via Extraction and Thin- Layer Chromatography. *J. Chem. Educ.* **2018**, *95* (4), 620–624. doi:10.1021/acs.jchemed.7b00610.

[6] Schaber, P.M.; Larkin, J.E.; Pines, H.A.; Berchou, K.; Wierchowski, E.; Marconi, A.; Suriani, A. Supercritical Fluid Extraction Versus Traditional Solvent Extraction of Caffeine From Tea Leaves: A Laboratory-Based Case Study for an Organic Chemistry Course. *J. Chem. Educ.* **2012**, *89* (10), 1327–1330. doi:10.1021/ed200536e.

[7] Clarke, C.J.; Tu, W.-C.; Levers, O.; Brohl, A.; Hallet, J.P. Green and Sustainable Solvents in Chemical Processes. *Chem. Rev* **2018,** *118*, 747–800. doi:10.1021/acs.chemrev.7b00571.

[8] Jessop, P.G. Searching for Green Solvents. *Green Chem.* **2011,** *13*, 1391–1398. doi:10.1039/C0GC00797H.

[9] Kuntzleman, T.S.; Comfort, A.E.; Baldwin, B.W. Glowmatography. *J. Chem. Educ.* **2009,** *86* (1), 64–67. doi:10.1021/ed086p64.

[10] Kuntzleman, T.S.; Rohrer, K.; Schultz, E. The Chemistry of Lightsticks: Demonstrations To Illustrate Chemical Processes. *J. Chem. Educ.* **2012**, *89* (7), 910–916. doi:10.1021/ed200328d.

[11] Pay, A.L.; Kovash, C.; Logue, B.A. General Chemistry Laboratory Experiment to Demonstrate Organic Synthesis, Fluorescence, and Chemiluminescence Through Production of a Biphasic Glow Stick. *J. Chem. Educ.* **2017,** *94* (10), 1580–1583. doi:10.1021/acs.jchemed.7b00194.

[12] Jilani, O.; Donahue, T.M.; Mitchell, M.O. A Greener Chemiluminescence Demonstration. *J. Chem. Educ.* **2011,** *88* (6), 786–787. doi:10.1021/ed100597n.

[13] Wieczorek, R.R.; Sommer, K.S. Demonstrating the Antioxidative Capacity of Substances with Lightsticks. *J. Chem. Educ.* **2011**, *88* (4), 468–469. doi:10.1021/ed900043a.

[14] McCluskey, C.L.; Roser, C.E. Lightstick Kinetics. *J. Chem. Educ.* **1999,** *76* (11), 1514–1515. doi:10.1021/ed076p1514.

[15] JCE Editorial Staff. The Effects of Temperature on Lightsticks. *J. Chem. Educ.* **1999,** *76* (1), 40A–40B. doi:10.1021/ed076p40.