Laboratory Evaluation for
Liquid CO₂ Extraction of D-limonene from Orange Peel


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Submitted by Doug Raynie at South Dakota State University based on evaluations completed by participants of the Green Chemistry in Education Workshop in Eugene, Oregon, July 15-20, 2006.

Evaluation

Liquid CO₂ Extraction of D-Limonene from Orange Rind

This experiment is a good, highly visible demonstration of the use of alternative solvents for chemical processes. Liquid carbon dioxide is nontoxic, nonflammable, inexpensive solvent. The experiment is high on the "wow" factor for students. The experiment works well if all guidelines in the experimental description are followed. (Note: there may be difficulties performing this experiment at high altitude.) This is a relatively fast experiment (less than 1 hour + characterization time), so it can easily be combined with other extraction or natural products experiments (such as steam distillation). In fact, if the experiment is not worked into the laboratory curriculum, it may also be an effective classroom demonstration.

This experiment may work for other samples, in addition to orange rind. While carbon dioxide is used for coffee decaffeination, dry cleaning, and other processes, these techniques require approaches beyond the limits of this experiment, so the focus should remain on natural products. Lemon zest provides a mixture that is easily characterized by GC-MS. For powdery samples, like ground spices, the sample may be dispersed with sand to allow better permeation by the carbon dioxide. For wet sample, like tomato, the sample should be mixed with a drying agent (diatomaceous earth (Celite)) is preferred; sodium sulfate is acceptable) until a free-flowing powder is obtained. Alternatively, the sample may be freeze-dried prior to extraction. With wet samples, the moisture will freeze, preventing effective extraction.

During the experimental procedure, the copper wire loop is sufficient to hold orange rind. Some students may need to attempt the extraction two or three times to achieve an effective sealing of the cap and tube. For granular products, filter paper or wire mesh is needed to hold samples away from the bottom of the tube. Using a pencil or laboratory spatula to occasionally submerge the tube in the water results in better CO₂ liquefaction. The more finely ground the dry ice, the better the CO₂ will liquefy. Due to the small mass of material extracted and the lack of ability to assess extraction completeness, determination of extraction yield may be omitted. Sufficient sample is obtained for characterization by NMR, IR, and GC-MS.

In the organic laboratory, the experiment demonstrates the isolation of natural products. However, the experiment may be used elsewhere in the curriculum. For example, in physical chemistry, a discussion of phase equilibria and partitioning can be discussed (and perhaps coupled to the Shoemaker and Garland experiment on phase equilibria of binary mixtures). In the analytical laboratory, extraction selectivity and characterization aspects can be emphasized. As a middle school demonstration, organic-soluble inks can be extracted from paper with the added demonstration that the paper comes out dry after the extraction. In any of these cases,
students can comment on the other processes where CO₂ replaces organic solvents (e.g., coffee decaffeination, dry cleaning, chromatography mobile phases, etc.). Non-science majors and the general public can be engaged in conversations on the role of GRAS ("generally regarded as safe") solvents and food processing safety.

In actuality, the safety concerns are minimal, if the procedure is followed exactly as written. While an occasional cap may eject from the centrifuge tube, safety concerns are not significant. Safety glasses must be worn at all times. There is some safety concern due to the pressure build-up during the CO₂ liquefaction. The stated polypropylene tubes must be used (do not substitute). Glass cylinders should not be used. Gloves should be available for handling dry ice.