

Dramatic Demonstration of Oxygen Sensing by Luminescence Quenching

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As shown throughout this symposium, luminescence of metal complexes is a powerful mechanistic tool and forms the basis for a variety of practical devices. In particular, oxygen quenching of Ru(II)- α -diimine complexes forms the basis of a class of oxygen sensors utilizing oxygen deactivation (quenching) of the emission. These systems are suitable for remote fiber optic analysis in numerous biomedical applications, including *in vivo* measurements and biological oxygen demand (BOD) in natural waters, and in a variety of industrial applications such as wind tunnel monitoring of pressure on aircraft. We present here a dramatic demonstration of oxygen quenching of the oxygen sensors [Ru(bpy)₃]Cl₂, (bpy = 2,2'-bipyridine) and [Ru(Ph₂phen)₃]Cl₂, (Ph₂phen = 4,7-diphenyl-1,10-phenanthroline). The demonstration is suitable for large rooms and clearly demonstrates the principles of quenchometric oxygen analysis. The theory and the quantitative equation are given in the companion article (1).

Demonstration

[Ru(bpy)₃]Cl₂ and [Ru(Ph₂phen)₃]Cl₂ were obtained from G. Frederick Smith Chemical Co. [Ru(bpy)₃]Cl₂ is also available from other sources, including Alpha and Aldrich Chemical Companies. Three 100-mL glass bottles are filled with equal-concentration methanol solutions of either complex. [WARNING: methanol liquid and vapor are toxic and exposure should be minimized.] The experiment will also work with the less toxic 95% ethanol. A concentration of 10 μ M [Ru(bpy)₃]Cl₂ works well, but optimum results in different-sized bottles or test tubes will be obtained with somewhat different concentrations. The solution can be made up by simply dissolving enough complex to give a light yellow solution. Very little complex is required: a few crystals on the tip of a spatula is generally adequate. The solutions are stable indefinitely; we are using ones prepared several years ago. Oxygen gas is bubbled through two of the solutions and the bottles are tightly capped, while the third is left open to the air.

The bottles are arranged as shown in Figure 1 (step 1), with the oxygenated solutions in jars A and C and the air-saturated solution in bottle B. Excitation is provided by a disco-style fluorescent black light. Because the bulb emits some visible light, it is best to arrange the lamp so that it is shielded from the audience, which can only see the front faces of the bottles. Additionally, yellow cellophane can be used to block the lamp's blue emission and improve contrast. The yellow-orange glow of the air-saturated solution is clearly much brighter than the barely visible luminescence of the heavily quenched oxygen saturated solutions.

To create an oxygen-free, unquenched solution, a small piece of dry ice is added to bottle A (step 2). The vigorous bubbling purges the solution of all oxygen gas in a few sec-

onds, and a spectacular increase in the solution luminescence results. The purged sample emission is now far more intense than the emission of the air-saturated solution. Visually, the relative intensities of the three jars are monotonically and highly dependent on the solution's oxygen concentration, which clearly demonstrates the analytical utility.

For a traveling demonstration, we have found that portable oxygen cylinders supplied by medical houses for patients work very well. The smallest home-care cylinder lasts for at least 10 or 20 experiments. We did this demonstration repeatedly at a poster session at the Memphis ACS meeting in 1995, using a black cardboard box to eliminate interference from the room lights. For only a single demonstration, tightly capping the bottle will hold the oxygen for several days.

Of course, practical quenchometric oxygen sensors are more complex. These systems use solid-state supports rather than fluid media. To date the most widely used molecule is [Ru(Ph₂phen)₃]²⁺ (Ph₂phen = 4,7-diphenyl-1,10-phenanthroline), which is much more luminescent than [Ru(bpy)₃]Cl₂ and more efficiently quenched. See the companion article for details (1). For purposes of the demonstration, then, [Ru(Ph₂phen)₃]²⁺ provides a more intense color change on going from an oxygen-saturated solution to an oxygen-free solution. However, the degree of quenching is so great for [Ru(Ph₂phen)₃]²⁺ in the air-saturated solution that its luminescence is barely discernible compared to the intensely luminescent deoxygenated solution. For this reason, the demonstrator may wish to show both complexes.

In summary, we present a simple, inexpensive, easily and safely set up demonstration of a qualitative oxygen analyzer based on luminescence quenching. The demonstration is dramatic enough to impress even nonscientists and may be useful in inspiring college, high school, and even elementary students to consider a science career. In spite of its simplicity, the demonstration involves a great deal of chemistry and photophysics and, thus, provides an excellent introduction to such topics as sensor preparation, luminescence quenching, and other excited-state processes.

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Literature Cited

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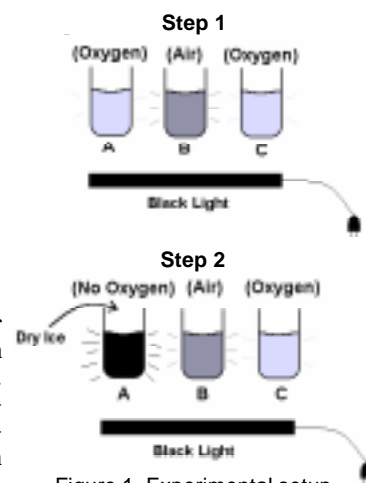


Figure 1. Experimental setup.

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