Measuring Dissolved Oxygen

Many applications of perfluorocarbons (PFCs) use their high gas solubility, and so naturally the question arises, how can this solubility be measured. There is not a simple answer! The standard method for measuring oxygen dissolved in water is with a dissolved oxygen meter; for PFCs this has a number of problems that are discussed below. Alternative methods are briefly reviewed as well.

Dissolved Oxygen Meter

The usual technique is with a dissolved oxygen meter. This typically incorporates an electrolysis cell containing KCl solution and an ion selective electrode, and can be galvanic or polarographic. There are pros and cons between the two types, but we believe they will both have the same problem with PFCs.

The electrolysis cell is in contact with the sample via a membrane that allows oxygen through. Thus the oxygen is partitioned between the cell solution and the sample; the more oxygen in the sample, the more there will be in the cell solution. This is calibrated at air and zero, so the real concentration in the cell is irrelevant. The unit expresses the results as a percentage against the calibration, or will convert this to a ml/g figure based on the known solubility figure for water. Salinity affects gas dissolving ability, which in turn will affect how the oxygen partitions between the sample and the cell. For this reason the unit must be given the salinity of the sample for readings in ml/g. What these meters do is tell you how close to being fully saturated with oxygen the sample is.

This whole technique therefore falls down for determining the oxygen dissolving ability of a liquid. If the sample is a PFC, the sample may have twenty times as much oxygen dissolved in it compared to a water sample. But because the solubility is so much higher, the amount of oxygen that passes through the membrane is correspondingly lower. Far less oxygen partitions into the cell, about a twentieth as much. So the concentration of oxygen in the cell is actually the same. If the sample is a liquid that is saturated with air, then it will always give a result that the sample is fully saturated with air, and no more than that.

What this means is that a dissolved oxygen meter is great at measuring relative solubility (i.e., the percentage of fully saturated that the sample is), but no use for measuring the absolute solubility (how much oxygen will dissolve).

There are two further possible problems. Some units have a limited scale, and cannot cope with solutions with more than about 25% oxygen in them. It may also be the case that the membrane is damaged by PFCs. Although membranes can be polyethylene, a quicker response is obtained with PTFE or silicone membranes, both of which are liable to swell with

PFCs, which might block the oxygen transfer. Both these problems are readily surmountable, but must be considered.

Chromatography

Using gas-liquid chromatography with a thermal conductivity detector might be a possibility; we have thought about trying this but are unsure how we would calibrate and how we could ensure no changes while the sample was introduced to the column. For an absolute value, the sample would have to be introduced without changing the temperature or pressure of the sample, perhaps into a sample loop type arrangement.

Measuring the Volume

It is our belief that measures for the FLUTEC liquids were performed using this technique (by ISC/RTZ who originally developed and marketed these liquids). One method is in this paper (top of the third page):

http://symp15.nist.gov/pdf/p193.pdf

The basic principle is straightforward. The liquid is degassed by boiling (perhaps under vacuum). A known volume of oxygen is added to the system. The volume of the system is adjusted to achieve the pressure at which measure is desired, and the volume of oxygen dissolved can be determined from the gas volume in the system.

Winkler Titration

This was the standard method many years ago, before dissolved oxygen meters were available. See procedure here:

http://www.epa.gov/glnpo/monitoring/sop/chapter_5/LG501.pdf

I am doubtful this would work for a perfluorocarbon.

Glucose Assay

This has been used for measuring the oxygen in an emulsion, using a "Glucose (GO) Assay Kit" from Sigma. The kits are designed for measuring something else, but this paper seems to outline how it can be done.

"Enzymatic method for determining oxygen solubility in perfluorocarbon emulsions", MG Freire et al, Fluid Phase Equilibria, 231 (2005) 109-113

AKJ

Aug/2011 (update Jan/2012)