

Application Note D-2



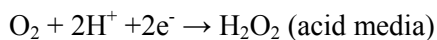
Subject: Deaeration...How and Why?

WHY?

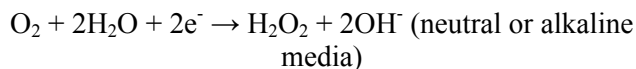
Polarography is a highly sensitive technique for detecting and determining electroactive substances. Oxygen is capable of dissolving in aqueous solutions to the extent of forming a one millimolar solution at room temperature and pressure and the polarographic reduction of oxygen complicates the polarographic determination of other electroactive materials. The electrochemical reactivity of oxygen is a boon for those involved in determining dissolved oxygen in a variety of media (natural waters, physiological fluids, sewage, etc.) but not for the analyst concerned with the electroanalysis of substances other than oxygen. Since it can be present in solutions in high concentrations and since it is electroactive, oxygen must be removed from the analyte prior to polarographic analysis.

Problems arise both from the voltammetric behavior of oxygen itself and from the associated chemical reactions that take place.

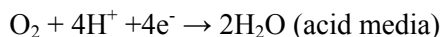
Oxygen is reduced at the dropping mercury electrode in two stages. The first stage involves the reduction of oxygen to hydrogen peroxide and/or hydroxide ion.



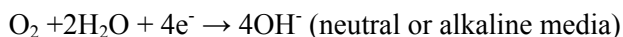
$$E_{1/2} = -0.05 \text{ V vs. SCE}$$



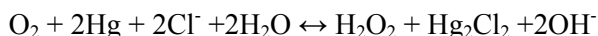
The second stage involves the reduction of oxygen to hydroxide ion or water.



$$E_{1/2} = -0.5 \text{ to } -1.3 \text{ V vs. SCE}$$



It is thus evident that two types of complications can arise if oxygen is not removed. The hydrogen peroxide produced from the first reaction can produce invidious effects on other electroactive species present in solution since it can function as both an oxidizing agent and a reducing agent. More significantly, however, pH changes can occur in the vicinity of the dropping mercury electrode due to the reduction of oxygen. The resultant increase in pH in the vicinity of the dropping mercury electrode can precipitate heavy metal ions and thus diminish their diffusion currents. Also, those species (i.e., organics) whose reduction involves hydrogen ions will be adversely affected due to the localized increase in pH at the dropping mercury electrode. Deaeration prior to polarographic analysis is also necessary to prevent the following reaction:



The above non-electrochemical process, which can occur in neutral, unbuffered metal salt solutions containing metallic mercury and dissolved oxygen, require that the latter be removed by rigorous deaeration procedures.

Polarograms of 10^{-4} M Pb^{2+} in 0.02M KCl before and after deaeration (Figure 1) illustrate in dramatic fashion the necessity of removing dissolved oxygen prior to polarographic analysis.

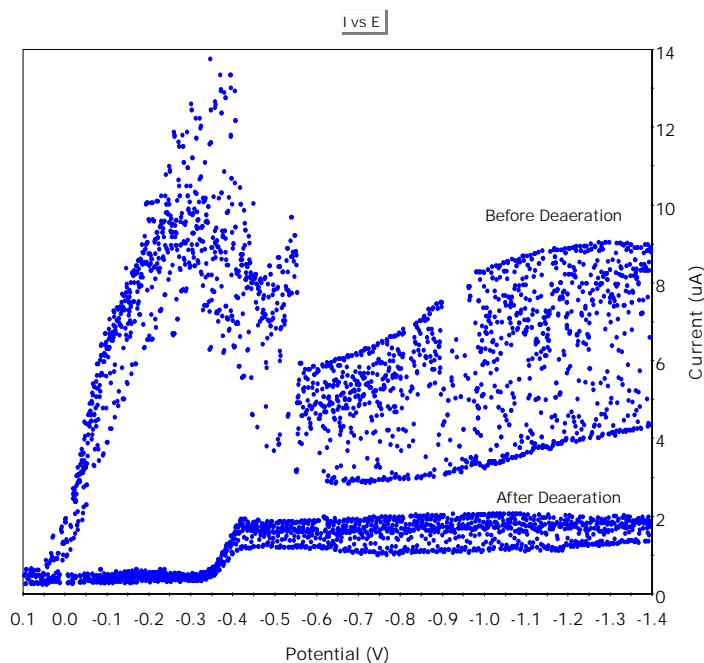


FIGURE 1: 10-4 M Pb²⁺ in 0.02M KCl. Electrodes: DME. Scan Rate: 2 mV/sec.

HOW

Although dissolved oxygen can be removed chemically from alkaline solutions by addition of sodium sulfite, by far the most convenient method of removing oxygen is to deaerate the analyte solution with pre-purified nitrogen gas. For high concentrations of analytes, ordinary pre-purified nitrogen direct from the tank (containing a few parts per million oxygen) can be used. At trace levels, however, direct tank nitrogen is unsuitable for deaeration purposes and an oxygen scrubbing system is required to remove the last traces of oxygen.

Several methods, of varying degrees of convenience, are available for this final purification process. The first method involves passage of the nitrogen stream through a heated quartz tube containing copper turnings heated to 450° - 500° C. While the ability of this system to remove traces of oxygen is extremely good, it lacks convenience since the time required to reach operating temperature can be lengthy. Furthermore, the copper turnings must be rendered grease free prior to packing and periodic renewal of the turnings is necessary for efficient operation.

Vanadous chloride solutions can be used for oxygen scrubbing (Figure 2). These solutions are prepared most

readily by boiling two grams of ammonium metavanadate with 25 mL of concentrated hydrochloric acid, diluting to 250 mL and reducing with a few grams of heavily amalgamated zinc.* The blue or green vanadium solution which results is reduced to the vanadium (II) stage by passing nitrogen gas through it until a clear violet color is obtained. When exhausted (as evidenced by loss of violet color), the vanadous chloride solutions can be regenerated by addition of a few mL of concentrated hydrochloric acid and/or more amalgamated zinc.

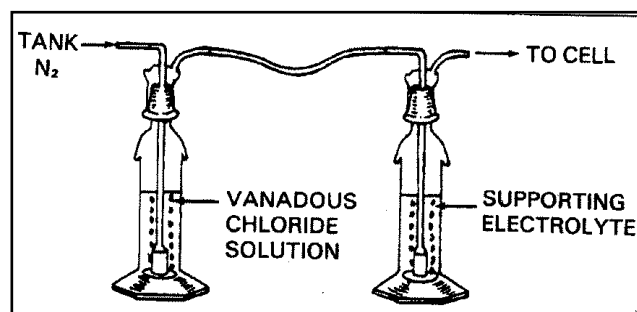


FIGURE 2

Another system offered by Supelco, Inc.** uses a rechargeable catalytic column which is housed in a split-sided furnace. The catalyst will last up to one year between recharges in typical installations. This system provides the most convenient arrangement at a reasonable cost.

COMMENTS

1. For longest service and most efficient operation, any oxygen scrubbing system must be kept out of contact with air while not in use.
2. The oxygen-free nitrogen stream should be pre-saturated by passing through a gas washing bottle filled with a quantity of supporting electrolyte. This prevents evaporation of any volatile constituents from the analyte and insures that the nitrogen stream is in equilibrium with the analyte/
3. One further point worth mentioning is that anodic voltammetry with graphite or platinum electrodes, and the like, does not normally require deaeration, since oxygen is not anodically active.

* Zinc is amalgamated easily in the presence of mercury in a dilute solution of hydrochloric acid.

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