

TECHNICAL NOTES

Issue 8-1

ppm Dissolved Oxygen Measurement

INTRODUCTION

Dissolved oxygen (D.O.) levels are used as a general indicator of water quality. Oxygen is essential to life and vital for countless aquatic forms. D.O. level control is critical in numerous applications ranging from the monitoring of industrial waste water to environmental surveillance.

WHAT IS DISSOLVED OXYGEN?

Dissolved oxygen (D.O.) is the amount of oxygen gas dissolved in a given quantity of solvent (usually water) at a given temperature and atmospheric pressure. As such, it should not be confused with combined oxygen as found in the water molecule, H₂O. It is usually expressed as a concentration in parts per million or mg/l. It can also be expressed as percent saturation, where saturation is the maximum amount of oxygen that can theoretically be dissolved in water at a given altitude and temperature.

Aerobic bacteria plays a key role in the measurement of dissolved oxygen levels both from an environmental and industrial perspective. Microorganisms such as bacteria are responsible for the decomposition of organic waste. When organic matter such as dead plants, manure, sewage and food waste

are present in a water supply, the bacteria will begin to break down this waste. Much of the available dissolved oxygen is consumed by aerobic bacteria, robbing other aquatic organisms of the oxygen they require to live. Biological Oxygen Demand (BOD) is a measure of the oxygen used by microorganisms to decompose this waste. Water supplies containing organic waste will also contain bacteria to break down this waste. When BOD levels are high, dissolved oxygen levels decrease because the available oxygen in the water is being consumed by the bacteria. Since less dissolved oxygen is available in the water, fish and other aquatic organisms may not survive. Hence, measurement of D.O. and BOD levels are vital in order to maintain sufficient oxygen levels to sustain the natural ecosystem. The use of aerobic bacteria for the decomposition of organic waste has become a fundamental aspect of wastewater treatment. Bacterial attack in the presence of oxygen results in the biochemical breakdown of sewage into inorganic byproducts, specifically, carbon dioxide, water and sludge. This oxidation process, known as the activated sludge process, is the most widely used method of secondary waste treatment today. The process typically occurs in an aeration basin and is achieved by aerating or bubbling pure oxygen through the wastewater. The oxygen, which is depleted by the bacteria, is replenished to allow the process to continue. When the measured D.O. falls below a specified concentration, air is added to the basin which provides oxygen to sustain the microorganisms and mixes the waste. Without enough dissolved oxygen, beneficial bacteria

will die; conversely, too much oxygen is wasteful and inefficient resulting in unnecessary energy expenses. To maintain optimal dissolved oxygen levels, on-line analytical instruments are employed to measure and control the concentration of D.O.

DISSOLVED OXYGEN SENSOR DESIGN

For the continuous monitoring of dissolved oxygen, the sensor style most commonly encountered utilizes a membrane-type design with the following characteristics:

- **ELECTRODES** – provide the reaction site needed for the reduction of oxygen molecules and generation of electrons
- **MEMBRANE** – a gas permeable membrane separates the measurement cell from the sample and allows only dissolved oxygen to diffuse into the cell
- **ELECTROLYTE** – facilitates the transfer of dissolved oxygen and provides an electrical path to complete the current loop and removes metal oxide by-products from the electrodes in order to keep their surfaces clean to react

The operation of a membrane sensor begins with the diffusion of oxygen through the membrane into the electrolyte. Since oxygen pressure within the measuring cell is essentially zero (oxygen gas is reduced at the cathode), the oxygen pressure in the sample causes it to diffuse through the membrane to the cathode. The amount of oxygen reduced on the cathode depends upon the amount of pressure exerted on the membrane by the oxygen in the sample referred to as the partial pressure of oxygen. Oxygen is only one of a number of gases present whose individual partial pressures make the total gas pressure in the water. Dissolved oxygen must diffuse freely through the membrane in order for the sensor to function properly. Other factors affecting the rate of oxygen diffusion include membrane thickness and temperature. A thinner membrane offers faster diffusion and

temperature affects the permeability of the membrane and the solubility of oxygen which in turn affects the rate of diffusion. Most D.O. sensors contain a temperature sensor that accounts for these variables in calibration.

D.O. SENSOR CALIBRATION

At any given temperature and barometric pressure the partial pressure of oxygen in water-saturated air is exactly the same as it is in air-saturated water. Thus a sensor can be calibrated in water-saturated air, using the 20.9% oxygen available in air as the full-scale standard. Both temperature and barometric pressure affect the partial pressure of oxygen in air saturated water vapour. Most D.O. microprocessors are programmed with all the values along with a temperature input. Therefore, correct data is automatically obtained to compute the correct gain, and calibrate the analyzer. This calibration technique will give a 100% saturation reading for the temperature and pressure which the microprocessor displays as ppm dissolved oxygen. To calibrate the D.O. sensor, simply suspend the probe above fresh tap water and auto calibrate.

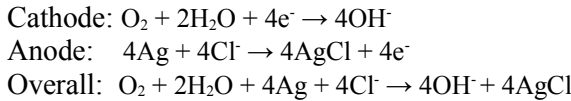
D.O. SENSOR TECHNOLOGY: ELECTROCHEMICAL METHOD

This type of measuring sensor is an electrochemical cell similar to a battery that produces current in the presence of oxygen. The measurement cell consists of a cathode (negative electrode) and an anode (positive electrode) immersed in a filling solution separated from the process by a gas permeable membrane. This separation provides a controlled environment for the electrodes and electrolyte while allowing oxygen to enter from the sample and react.

This article will focus strictly on the electrochemical measurement of membrane-type sensors, specifically, galvanic (spontaneous voltage) and polarographic (applied voltage) measuring cells.

Polarographic Measuring Cell

A polarographic ("Clark" or amperometric) cell consists of a metallic anode (eg. silver) and a metallic cathode (eg. gold or platinum) immersed in an electrolyte, typically an aqueous potassium chloride (KCl) solution. A constant polarizing voltage of -0.7V to -0.8V is applied across the electrodes which causes oxygen to be reduced at the cathode (ie. it is chemically converted to OH⁻). This applied voltage ensures that only oxygen is reduced at the cathode. The resulting current flow is directly proportional to the dissolved oxygen content of the electrolyte. The oxidation-reduction reactions for a typical Clark cell are as follows:



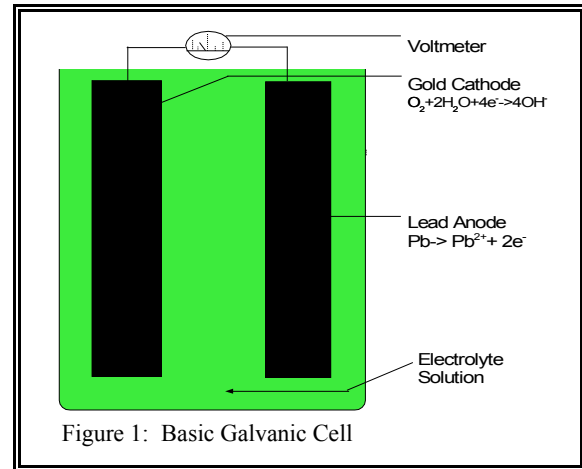
Sensors of this type require a special meter in order to provide the polarizing voltage. Further inherent disadvantages associated with polarographic sensors are as follows:

- ➔ Since the net result of the chemical reaction is AgCl, over time, a build up of AgCl will coat the anode. Once the entire anode is covered, reaction stops and the oxygen probe stops working. However, the probe may be reactivated by cleaning the anode to remove the AgCl deposit.
- ➔ OH⁻ ions result from the overall reaction which alters the pH value of the electrolyte. The electrolyte, which has a near neutral pH, moves into the alkaline range. This causes a zero shift, and over time, the electrolyte will need to be replaced.
- ➔ The net reaction also consumes Cl⁻ ions. Thus the electrolyte will need to be changed as a result of the Cl⁻ ions being consumed over time.
- ➔ The electrode requires an external power source, so as soon as the probe is disconnected, the power supply is cut off. Upon re-connection, the user must wait for the probe to be polarized (ie. for the current loop to be stabilized). This warm-up time can be up to 1 hour and any measurement

taken before this time will typically result in a higher value thus giving a false reading.

Galvanic Measuring Cell

By using electrodes in contact with an electrolyte, a spontaneous chemical reaction occurs in the presence of oxygen. In this reaction, the cathode reduces the oxygen into



hydroxide, releasing four electrons for each oxygen molecule. These electrons flow through the electrolyte, proportional to the oxygen concentration in the electrolyte. Common electrode materials include gold, silver, copper, and lead, with potassium hydroxide (KOH) as the most frequently used electrolyte. The cathode must be a noble metal (such as silver or gold) for the cathode potential to reduce molecular oxygen when the cell circuit is closed. The anode should be a base metal (iron, lead, cadmium, copper, zinc, or silver) with good stability and without the tendency for passivation. Galvanic technology overcomes many of the disadvantages affiliated with polarographic sensors, for example:

- ➔ No warm-up (polarization) time required. The probe is ready to measure since it is 'self polarized' as long as electrolyte is present. Less battery drain on meter.
- ➔ Provides an absolute zero measurement as galvanic current is zero when zero oxygen is present.
- ➔ Non-depleting electrolyte. The fill solution

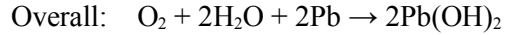
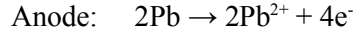
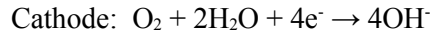
is water-based with selected salts added to carry the charge. H₂O is consumed and replaced rendering the electrolyte stable and thus reducing frequency of replacement.

- ➔ Overall reaction produces water and a metallic oxide. The metallic oxide flakes off the anode leaving an exposed anode for continuous reaction. Therefore, anode polishing is not required.
- ➔ No zero shift. Metallic oxide does not affect electrolyte chemistry. Water is added back as it is used. Electrolyte highly stable.

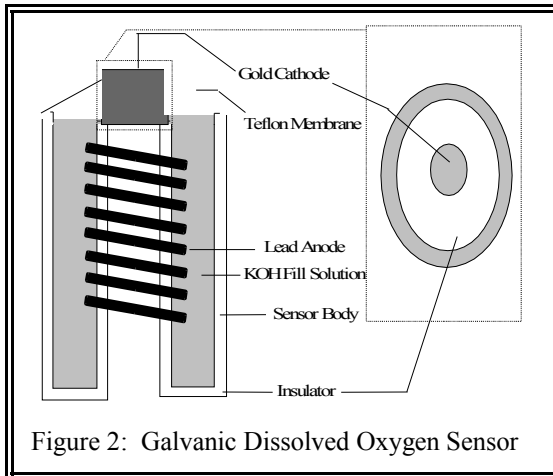
IC CONTROLS PPM D.O. SENSORS

Due to the advantages of galvanic cells and limitations of polarographic cells, IC Controls

hydroxide (KOH) as the electrolyte. The chemical reactions within the cell are as follows:



IC Controls currently offers three D.O. sensor designs; Models 802, 814, and 825. All three sensors share the same cell chemistry and offer three membrane options; standard response, fast response, and a ruggedized membrane. The fast response membrane is thinner but less durable whereas the ruggedized membrane is thicker but with slower response. Each sensor employs the same method of calibration which is simply achieved using air over potable water as the standard.



dissolved oxygen sensors utilize galvanic technology. The measuring cell has a gold cathode, a lead anode and uses potassium

SUMMARY

There are a variety of waste-water dissolved oxygen sensor technologies, each with its own advantages and disadvantages. One sensor technology will not be suitable in all applications. However, in comparing polarographic and galvanic technologies, compelling evidence was presented to substantiate the superiority of a galvanic sensor. Galvanic sensors have no significant technical drawbacks whereas polarographic sensors have many. Galvanic systems are virtually maintenance free with the exception of occasional membrane changes and regular calibration. For these reasons, IC Controls has opted to utilize only galvanic technology for its ppm line of dissolved oxygen measurement.