TECHNICAL NOTES

Issue 8-3

ppb Dissolved Oxygen Measurement

INTRODUCTION

Dissolved oxygen (D.O.) measurement is one indicator of water quality because oxygen is a common element contributing to corrosion reactions. This corrosion reaction provides the need for low level D.O. control since dissolved oxygen is responsible for costly replacement of piping and equipment by corrosive attack on metals.

> ***WHAT IS DISSOLVED OXYGEN?***
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> *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. It is usually expressed as a concentration in parts per million or mg/l. For trace levels of dissolved oxygen, parts per billion is the unit typically used. D.O. 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 pressure and temperature.*

Corrosion is a state of deterioration in metals caused by oxidation or chemical action starting at its surface. Hard and porous metal oxide corrosion deposits have little strength and form rapidly in the presence of water and oxygen. The most serious aspect of oxygen corrosion is that it results in pitting. Pitting is a localized form of corrosion by which metal oxide filled cavities or holes are produced in the material. Pitting is considered to be more dangerous than uniform corrosion because it is more difficult to detect and predict. Pits can produce system failures even though only a relatively small amount of metal has been lost. Rapid corrosion will progress inside a boiler water and steam system, for example, unless dissolved oxygen can be virtually eliminated. Unchecked corrosion eventually results in expensive repairs or equipment failures and subsequent replacement. For this reason, water with the least possible amount of dissolved oxygen is used. Therefore, in order to control trace levels of D.O. in Boiler feedwater supplies, on-line analytical instruments are employed to monitor and maintain the desired D.O. levels.

DISSOLVED OXYGEN SENSOR DESIGN

For the continuous monitoring of dissolved oxygen concentrations, the most common sensor design utilizes a membrane. Membrane sensors typically share 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 – provides an electrical path to complete the current loop between

the cathode and anode.

A membrane sensor operates by diffusing oxygen through the membrane into the electrolyte. Since oxygen pressure within the measuring cell is essentially zero, 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. Dissolved oxygen must be allowed to 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 whereas a thicker membrane a slower diffusion rate. Temperature affects the permeability characteristic of the membrane and the solubility of oxygen which affects the rate of diffusion. D.O. sensors contain a temperature sensor so that these variables can be accounted for 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. For accurate calibration, temperature and pressure values must be input into the analyzer. This calibration technique will give a 100% saturation reading for the temperature and pressure and provide the best calibration accuracy. To calibrate the D.O. sensor, simply suspend the probe above fresh tap water and let the analyzer 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. Although other D.O. measurement techniques exist, 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. The applied voltage is carefully selected to ensure 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:

Cathode: $O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$
Anode: $4Ag + 4Cl^- \rightarrow 4AgCl + 4e^-$
Overall: $O_2 + 2H_2O + 4Ag + 4Cl^- \rightarrow 4OH^- + 4AgCl$

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

- ➔ Since the net result of the chemical reaction is AgCl, 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 are produced and Cl^- are consumed in the overall reaction which alters the chemistry of the electrolyte. This causes a zero shift, and over time, the

electrolyte will need to be replaced.

- ➔ The need for an external power source to be applied to the electrode means that 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. Polarization can take up to 1 hour and any measurement taken before this time will typically result in a false high reading.

Galvanic Measuring Cell

By using carefully selected electrodes in contact with an appropriate 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. Electrons flow through the

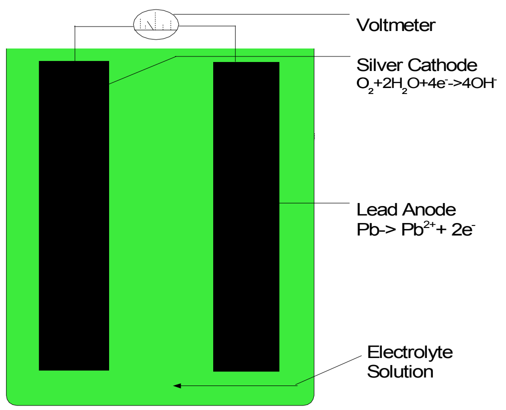

Figure 1: Basic Galvanic Cell

electrolyte, the magnitude of which is 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 in order 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 polarization time required. The probe is ready to measure since it is 'self polarized' as long as electrolyte is present.
- ➔ Provides an absolute zero measurement as galvanic current is zero when zero oxygen is present.
- ➔ Non-depleting electrolyte. The reaction consumer and produces OH^- at the same rate which as means no drift or zero shift.
- ➔ Overall reaction produces metallic hydroxide which flakes off the anode leaving exposed anode for continuous reaction. Therefore, requires reduced anode polishing.

IC CONTROLS PPB D.O. SYSTEMS

Due to the advantages of galvanic cells and limitations of polarographic cells, IC Controls dissolved oxygen sensors utilize galvanic technology. The ppb measuring cell has a silver cathode, a lead anode and uses

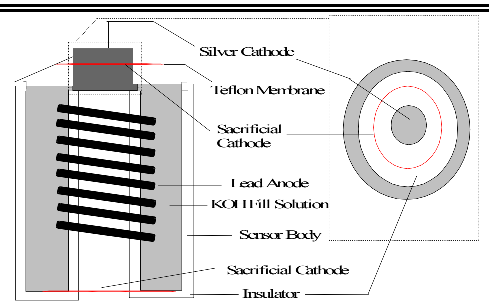

Figure 2: Galvanic ppb Dissolved Oxygen Sensor

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

Cathode: $O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$
Anode: $2Pb \rightarrow 2Pb^{2+} + 4e^-$
Overall: $O_2 + 2H_2O + 2Pb \rightarrow 2Pb(OH)_2$

Dissolved Oxygen sensors that measure in the ppb range require an additional component within the measuring cell. Residual dissolved oxygen in the electrolyte can migrate to the cathode, add to the overall reaction and result in false high readings. Therefore, a "sacrificial" cathode is used to capture D.O. before reaching the sensing element. This is not an issue with ppm sensors since the residual level is low enough to have no effect on the sample reading. IC Controls uses two sacrificial cathodes in its ppb sensors; one silver ring is placed around the sensing tip and another silver ring is situated at the base of the sensor body. These silver rings consume any dissolved oxygen that has diffused into the fill solution thereby avoiding detection by the sensing electrode. As a result, false high readings from oxygen are prevented and a more accurate reading is obtained. IC Controls currently offers two ppb systems; a portable D.O. unit, model 869, and the model 865-25.

MODEL 869: Portable DO Analyzer

The model 869 offers ppb D.O. measurement for portable use mounted on a stainless steel stand. The 869 offers two sensor and flow cell configurations; a CPVC option and a stainless steel option for ultra low level accuracy. .

MODEL 865-25: Trace-Level ppb DO Analyzer

The model 865-25 is designed to monitor the oxygen continuously in steam and water circuits. The 865-25 is a complete package with the analyzer, sensor, flow cell, and sampling system all conveniently mounted on a stainless steel backplate. The sample panel includes on-line calibration, magnetite grit bypass and a siphon-drain system. The bypass helps protect the electrode membrane, extending its life, by diverting magnetite grains and other solids to drain. This bypass also provides a convenient point to obtain grab samples and maintains a constant pressure at the sensor.

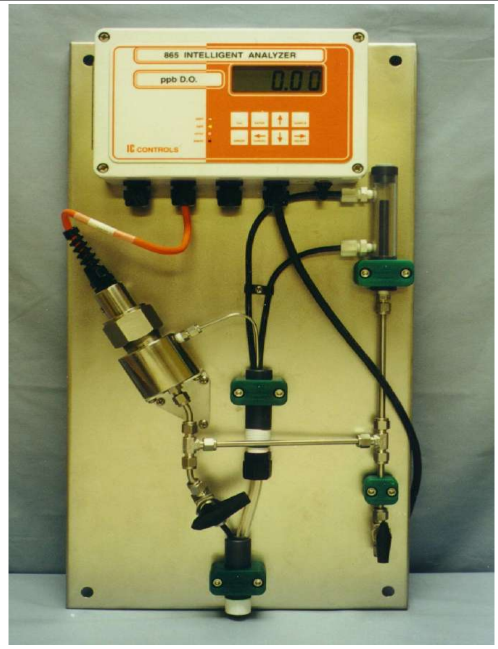

Figure 3: Model 865-25

SUMMMARY

There are a variety of 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, IC Controls saw compelling evidence to substantiate the superiority of a galvanic sensor and has opted to utilize only galvanic technology for its ppb line of dissolved oxygen measurement.

Common applications :

- ➔ boiler feedwater monitoring
- ➔ high purity cooling water
- ➔ deaerator evaluation
- ➔ food and beverage
- ➔ breweries
- ➔ semiconductor manufacturing
- ➔ off shore oil drilling

For further product information, please refer to our website at www.iccontrols.com or direct inquiries to *sales@iccontrols.com*.