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A Comparison between Polargraphic and Galvanic Dissolved Oxygen Sensor Technologies

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- ***Galvanic Sensors Reduce Maintenance and Startup time.***
- ***Polargraphic and galvanic sensors are used to measure dissolved oxygen electrochemically. The amount of maintenance each type requires differs.***

Abstract

Engineers and chemists working in plants, in the field, and in laboratory environments use electrochemical techniques to measure dissolved oxygen—the volume of oxygen contained in water. Knowing dissolved oxygen values is important, because they affect the health of aquatic ecosystems. Dissolved oxygen measurements are also important for waste-water treatment and aquaculture, such as fish farming.

The two sensing technologies used to measure dissolved oxygen—polargraphic and galvanic sensing systems—are both based on electrochemical cells.

An electrochemical cell converts chemical energy to electrical energy or applies electrical energy to force a chemical reaction to occur. It has three important components—a cathode, anode, and electrolyte. The cathode, usually Ag, Zn, or another metal, is oxidized during the electrochemical reaction used to measure the dissolved oxygen. Electrons pass from the cathode to the anode, where oxygen is reduced. Ions diffuse through the electrolyte, providing charge movement that closes the circuit.

If engineers choose electrode materials so that no external potential is required, the system is galvanic. In a polargraphic system, an external voltage is applied to the cell. Galvanic sensors offer some advantages over polargraphic ones—stability, the ability to operate for months without replacing the electrolyte.

Polargraphic cells, which were developed in 1956, are based on an ampreometric cell polarized at about 800 mV. An external power source, usually the oxygen meter's battery, supplies the polarization voltage. In addition to the anode, cathode, an electrolyte, a polargraphic cell has a semi-permeable membrane. Oxygen passes through this membrane, which is impermeable to ionic salts, and reacts with a gold cathode, producing hydroxide ions. At the anode, which is made of silver, oxidation occurs, giving electrons and silver chloride.

To avoid errors caused by inappropriate polarization values, which can be as high as 20%, most meters provide power to the probe even when it is turned off. This drains the battery, and users must ensure that each meter has an adequate supply of power. If they disconnect the probe, cutting off the power supply, the must wait 10-50 minutes for polarization values to climb back up to 800 mV.

After an extended time, silver chloride produced at the anode builds up on this electrode. When the anode is completely covered, it can’t be used until analysts remove the silver chloride deposits with an abrasive material or acid.

Another limitation is that gaseous sulfur dioxide is converted to hydrogen sulfide, a toxic gas, at high pH. The sulfide ions attack the silver, forming a silver-sulfide coating. Analysts also may need to remove this coating from the polargraphic-cell anode.

The hydroxide ions produced at the cathode make the electrolyte—a neutral potassium chloride solution—more basic. Increasing the pH makes the electrolyte potential more negative and causes a zero shift. Silver chloride precipitation also changes the potassium chloride electrolyte solution, because it consumes chloride ions. These two reactions make it necessary for analysts to change the probe electrolyte solution as often as every two weeks.

Galvanic cells, which were developed in 1964, are similar to polargraphic cells but use different electrode materials. The anode is made of lead or zinc, and the cathode is made of gold or silver. Using these dissimilar metals generates an 800 mV electromotive potential in the presence of an electrolyte. The zinc or lead is oxidized, giving electrons. These electrons reduce oxygen at the cathode surface to produce hydroxide. With a zinc electrode, the hydroxide ions are precipitated by zinc ions as zinc hydroxide, which is converted to zinc oxide.

Galvanic cell benefits include reduce anode maintenance; constant electrolyte solution pH, volume, and concentration; elimination of sulfide poisoning; and no warm-up time.

Even though zinc is consumed, probes can last up to five years. When the electrochemical reaction produces zinc oxide, it doesn’t coat the anode surface. An anode made of zinc alloy materials has a non-uniform and porous electrode surface. The oxide falls off this surface, exposing new zinc metal. This eliminates the need to periodically clean and polish the electrode.

Another benefit of electrochemical zinc oxide production is that excess hydroxide ion doesn’t build up in the electrolyte solution. This lengthens the usable life of the galvanic-sensor electrolyte solution and eliminates interference problems caused by other species present in alkaline solution, such as ammonia. Metal-oxide precipitation has the additional effect of not removing chloride ion from the electrolyte solution, which further lengthens its useful life.

Because the sliver cathode has electrons flowing toward it, it has a net negative charge. This repels the sulfide-poisoning problems.

With two dissimilar metals providing the electric potential, users don’t need to wait for polarization to occur when the sensor is turned on. There is, therefore, no waiting for the sensor to warm up, as is the case for polargraphic systems. An additional benefit is that current is not drawn from the battery supply to keep the probe polarized while the meter is not in use.

Abstract

Electrochemical measurement of dissolved oxygen is widely accepted as a technique suitable for most field, plant and laboratory applications. Within this technique there are two major categories of sensing technologies. These are polargraphic sensing systems and galvanic sensing systems. This article will describe the significant advantages of galvanic sensing systems over polargraphic sensing systems. We will discuss the details of polargraphic sensing systems and isolate the specific deficiencies that create difficulties for the user. We will then describe the advantages of galvanic sensing systems that overcome the deficiencies of polargraphic sensing systems.

Summary Table 1: Polargraphic vs. Galvanic Sensor Systems for Dissolved Oxygen

Characteristic	Polargraphic	Galvanic
Anode Chemistry	AgCl based, coats and isolates anode thus requiring frequent anode polishing.	ZnO based, freely flakes off the anode leaving exposed Zn for reaction. Does not require anode polishing.
Cathode Chemistry	OH- based. OH- must be absorbed by the electrolyte. Electrolyte becomes unstable and alkaline creating a zero shift. Eventually probe cannot be calibrated without electrolyte change.	OH- based but leads to $Zn(OH)_2$ then ZO and H_2O. No zero shift. ZO does not affect electrolyte chemistry. H_2O is added back as it is used. Electrolyte is highly stable.
Electrolyte Chemistry	KCl based to provide Cl ions that are used in anode chemistry. This depletes the electrolyte in a short time (as little as two weeks).	H_2O based (selected salts added to carry charge). H_2O is consumed and replaced so the electrolyte is very stable.
Sulfide Resistance (high pH only)	None, Ag2S coats and isolates anode thus requiring frequent anode polishing.	Excellent b/c ZnS at anode will flake off b/c anode is a zinc alloy.
Maintenance	Frequent electrolyte changes and anode polishing.	Very little except occasional membrane and electrolyte changes
Polarization	Requires probe to be polarized for 10 min to 1 hour and remain polarized before use. Shut off meter or unplug probe and re-polarization is required. Drains batteries, holds up measurement cycle.	Not required. Ready to read. Probe is ‘Self Polarized’ as long as electrolyte is present. Less battery drain. More dependable for field use.

We have shown there are compelling reasons to select galvanic sensor systems over polargraphic sensor systems whenever possible. Galvanic sensors have no significant technical drawbacks, while polargraphic sensor systems have many. Fortunately, galvanic sensor systems are available from better quality instrument suppliers and are already becoming more affordable. In addition, manufacturers of galvanic sensor systems are offering replacement components and designs that make every aspect of using their sensors easier for users, regardless of experience. Anyone who uses polargraphic dissolved oxygen sensor systems should look into switching to galvanic sensor systems at the soonest opportunity.