TELEDYNE
ANALYTICAL INSTRUMENTS

Sensors for Gas Phase Oxygen Analysis

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Abstract

A discussion of gas phase oxygen analysis is presented. Particular emphasis is given to the construction, principle of operation, and performance characteristics of the various types of Micro-fuel Cells manufactured by Teledyne Analytical instruments (TAI). Micro-fuel Cell is the trade name for TAI's disposable electrochemical oxygen transducer.

A second, non-disposable trace level oxygen sensor is discussed. The additional requirements and special calibration techniques related to analyzers utilizing this type of oxygen sensor are described. Finally, other analysis techniques are summarized and comparisons drawn.

Introduction

Of all gases, oxygen plays a unique part in human existence. Without it, life as we know it could not exist. The nature and measurement of oxygen has, therefore, always been an important challenge to scientists.

Modern technological advances both in industry and medicine have resulted in an increased demand for accuracy in oxygen measurements. The application of oxygen analyzers ranges from the measurement of the atmosphere inside an incubator containing a premature baby to the monitoring of the oxygen content of process and combustion streams in giant chemical plants and refineries to insure safe and economical operation.

It is the intent here to discuss in detail TAI's Micro-fuel Cell, an electrochemical oxygen transducer around which an entire line of analyzers has been developed and successfully marketed. At the end of this discussion, the principle of operation of other oxygen analyzers will be reviewed and comparisons of each analysis technique, relative to that of the Micro-fuel Cell, will be made.

The Micro-fuel Cell

TAI's Micro-fuel Cell is an electrochemical transducer. A transducer is a device that converts one form of energy to another. For example, a loudspeaker is a transducer that converts electrical energy into mechanical energy (sound). A microphone is a transducer that is the reciprocal of this; mechanical energy is converted to electrical energy.

The most common electrochemical transducer is a battery which transforms chemical energy into electrical energy. Although less well known, a fuel cell performs the same transformation. The primary difference between a battery and a fuel cell is the place where the chemical energy is stored. In the instance of batteries, the chemical energy is stored inside the device itself. With fuel cells the chemical energy is stored externally; the rate at which the chemicals are fed into the fuel cell determines the amount of energy or power that is obtained.

Principle of Operation

The Micro-fuel Cell then is a fuel cell (strictly speaking, a hybrid fuel cell) where part of the chemical energy is stored within and the other chemical reactant (oxygen) comes from outside the device. Most fuel cells are power devices, i.e. the hydrogen-oxygen fuel cells that are used to power the manned space vehicles used by NASA in the space program. The oxygen sensing cell under discussion here provides power normally in the 1 to 200 microwatt range, hence the name Micro-fuel Cell.

All types of electrochemical transducers have three major component parts; an anode, a cathode, and an electrolyte. In the Micro-fuel Cell, the cathode is the sensing electrode or the site where oxygen is reduced.

$$4e^- + O_2 + 2H_2O \longrightarrow 4OH^- \quad (1)$$

In the above reaction, four electrons combine with one oxygen molecule (in the presence of water from the electrolyte) to produce four hydroxyl ions. This cathodic half-reaction occurs simultaneously with the following anodic half reaction:

$$\mathrm{Pb} + 2\mathrm{OH}^- \longrightarrow \mathrm{PbO} + \mathrm{H_2O} + 2e^- \quad (2)$$

The anode (lead) is oxidized (in a basic media) to lead oxide and in the process two electrons are transferred for each atom of lead that is oxidized.

The sum of half-reactions (1) and (2),

$$\mathrm{O_2} + 2\mathrm{Pb} \longrightarrow 2\mathrm{PbO} \quad (3)$$

results in the overall reaction (3). From this reaction it can be seen that the Micro-fuel Cell should be very specific for oxygen providing there are no gaseous components in the sample stream capable of oxidizing lead. The only likely compounds that meet this requirement are the halogens (iodine, bromine, chlorine, and fluorine.)

Physical Construction

The Micro-fuel Cell ***(Figure 1)*** is designed as a disposable unit and when the lead anode is consumed due to the sensing of oxygen, the cell is simply discarded. The cell is, therefore, maintenance free requiring no replacement of membranes or electrolyte and no cleaning of electrodes. It is about 1.25" in diameter and .75" thick. The rear of the cell is fitted with a contact plate composed of two concentric metal foils which are electrically common to the anode and cathode and mate to spring loaded contacts in the various cell holding devices used throughout the product line.

The anode is composed of lead and is configured in such a manner (proprietary) so as to maximize the amount of metal available for reaction. The cathode is a convex metal disc approximately .75" in diameter with numerous perforations to facilitate continued wetting of the upper surface with electrolyte and assure minimum internal resistance during the oxygen sensing reaction. The external surfaces of the cathode are plated with an inert or noble metal, normally gold. Silver, rhodium, and platinum are also used in special cases.

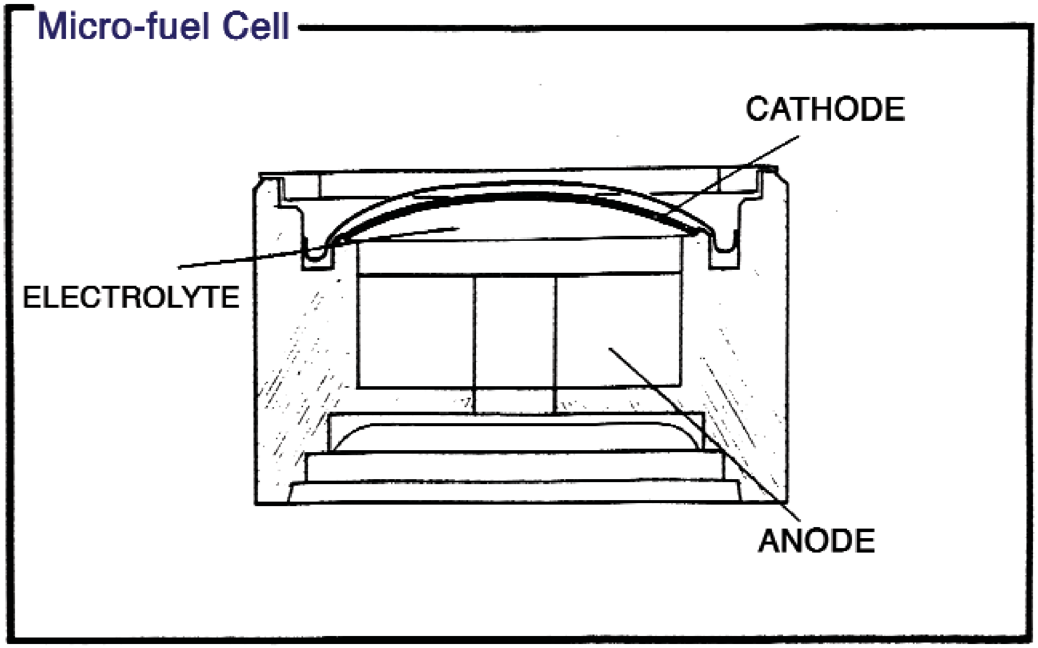


Figure 1

The rear of the cell (inside the contact plate) is fitted with a flexible membrane that is designed to accommodate internal volume changes that occur throughout the life of the cell. If it were not for this volume compensating membrane, the membrane covering the cathode would move to accommodate the internal volume changes resulting in changes in output not related to oxygen concentration.

The sensing membrane (covering the cathode) is made of Teflon whose thickness is very accurately controlled. The entire space between these two membranes is filled with electrolyte (an aqueous solution typically of potassium hydroxide). This results in all surfaces of the anode and cathode being "bathed" in a common pool of electrolyte.

The main body of the cell is fabricated from high density polyethylene. This results in an oxygen sensor that can be placed in virtually any atmosphere or sample stream without any concern that the components of the sampled media will react with the cell assembly.

Oxygen Measurements

In reaction (1) four electrons are transferred for each oxygen molecule undergoing reaction. In order to be reacted, an oxygen molecule must diffuse through both the sensing membrane and the thin film of electrolyte maintained between the sensing membrane and the upper surface of the cathode. The rate at which oxygen molecules reach the surface of the cathode determines the electrical outlet. This rate is directly proportional to the concentration of oxygen in the gaseous mixture surrounding the cell.

As in ***Figure 2***, this proportionality is linear with the sensor exhibiting an absolute zero, i.e. in the absence of oxygen the cell produces no output.

Calibration: Given these two conditions (linearity and absolute zero), single point calibration is possible. The oxygen concentration in air (20.945%) is a very convenient reference gas to use, and it is accurate to three or four significant figures throughout the entire earth's surface.

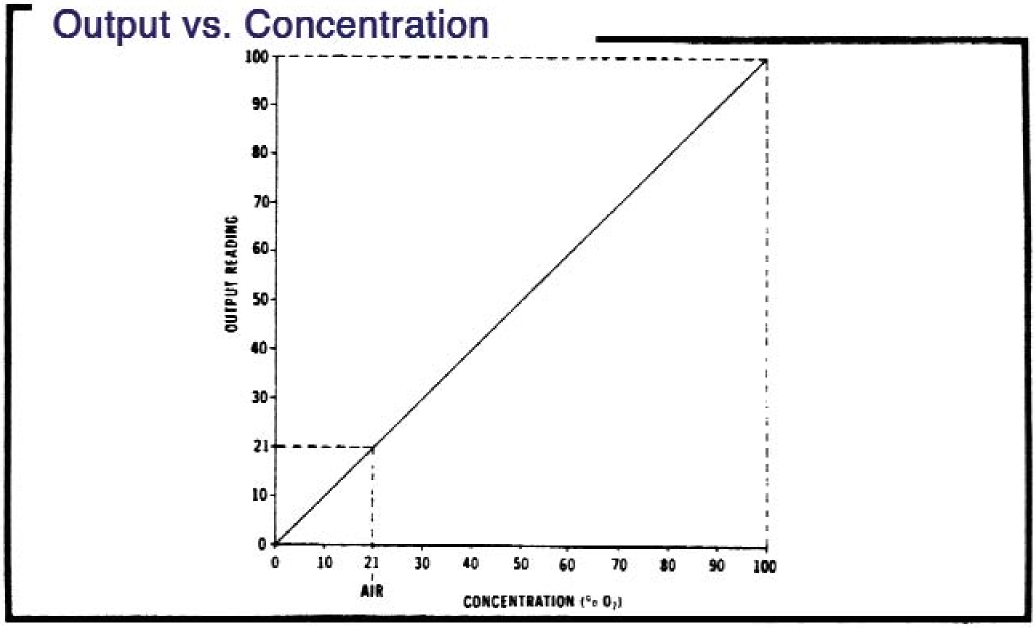


Figure 2

In calibrating a given oxygen analyzer, it is best to use a calibration or reference gas whose oxygen content is near or equal to the full scale reading. In Figure 2, both air and 100% oxygen are shown as potential calibration gases. In theory, any known concentration of oxygen could be used. Air and 100% oxygen were chosen because they are the easiest and most economical to obtain. In this case, however, air is not the better of the two gases to use for calibration. Any error in reading the readout meter or an error in the meter reading during the setting of the span control would be multiplied by a factor of 5 for subsequent readings at or near full scale. This results from attempting calibration at a point only 1/5 of full scale. In this case, 100% oxygen would be the calibration gas of choice.

Since air is such a convenient reference and the Micro-fuel Cell's readings are independent of the sample gas' flow rate (they can give accurate reading in static gas samples such as ambient air), multiple ranges are generally provided in the more sophisticated instruments, one of which is always 0 – 25%. 20.94% is about 84% of full scale which will provide good calibration accuracy which is degraded only slightly when switching to the other ranges included.

Concentration Units: Although most of the oxygen analyzers manufactured by TAI are set up to readout the concentration of oxygen in percentage units, the Micro-fuel Cell (and all other analysis techniques) are actually sensitive to the partial pressure of oxygen in the sample gas mixture. Readouts in percent are permissible only when the total pressure of the gas being analyzed does not change.

To illustrate, assume that an analyzer with a percent readout was calibrated in air at sea level. The span control would be adjusted until the analyzer reading was 20.94% (assuming that degree of readability was available). If the analyzer were then elevated to higher and higher altitudes, the reading would begin to drop and continue to do so as long as the analyzer is raised. The percent of oxygen in the atmosphere is the same regardless of the altitude, i.e. the ratio of oxygen molecules does not change; the molecules merely get farther and farther apart. The Micro-fuel Cell's output is a function of the number of molecules of oxygen per unit volume which is decreasing as the analyzer is raised in altitude.

Figure 3 illustrates how the output of the cell increases when the total pressure is increased (the opposite of the previous illustration). In this case as with the previous one, the percent oxygen does not change.

Dalton's Law of Partial Pressures states that the total pressure exerted by a mixture of gases is the same as the sum of the individual pressures exerted by the constituent gases. Or, stated another way, in a mixture of gases, every gas exerts the same pressure that it would if it alone were confined in the same volume.

$$P(\text{total}) = P(1) + P(2) + P(3) + \ldots$$

For air this becomes:

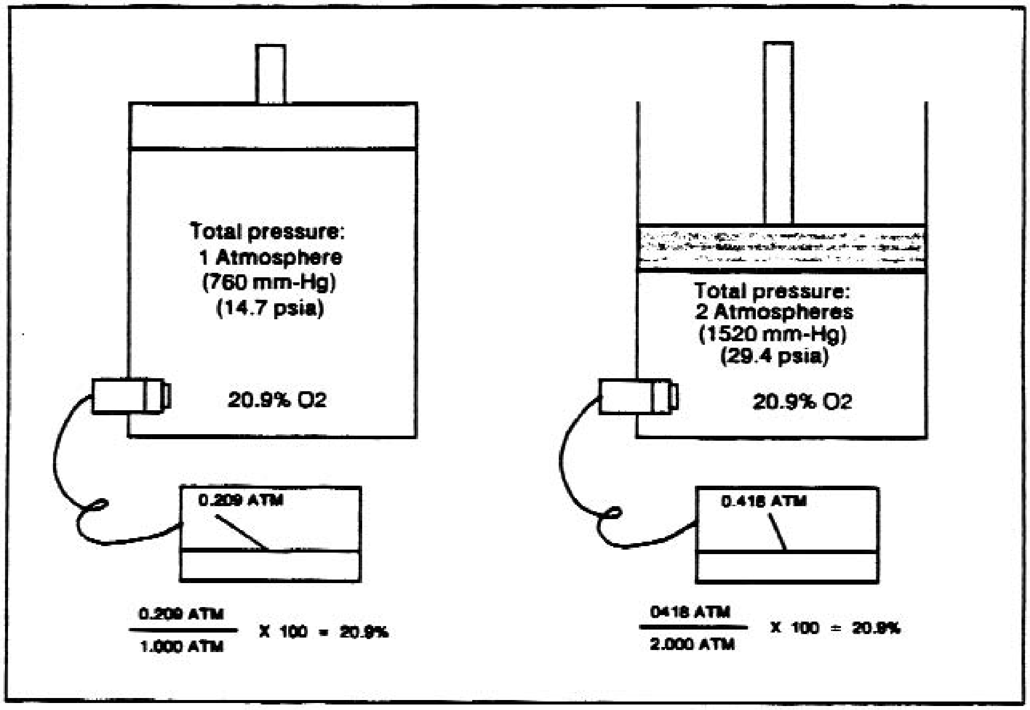

Concentration Units

Figure 3

P(total) = P(O2) + P(N2) + P(Ar) + P(Ne) + …

The amount of argon, neon, and other trace gases present in air is less than 1%. Ignoring their contribution and assuming a dry gas mixture (no water), the expression becomes:

P(total) = P(O2) + P(N2)

At sea level, P(total) would be 1.00 atmospheres, 760 millimeters of mercury, or 14.7 pounds per square inch (absolute). Other partial pressure units could be used. In each of the three units above, the concentration of oxygen and nitrogen would be: 0.209 atm, 159 mm-Hg, and 3.07 psia for oxygen; and 0.791 atm, 601 mm-Hg, and 11.6 psia for nitrogen.

Returning to Figure 3, it is evident that when the total pressure of the gas mixture (air) is doubled, the partial pressure of all the constituent gases will double as well. The oxygen reading doubles also since the number of oxygen molecules per unit volume is twice what it was before the total pressure was changed. Therefore, when applying an oxygen analyzer where the total pressure will vary, a readout in partial pressure units should be employed.

Temperature Coefficient: In order to obtain accurate readouts that vary only with changes in oxygen concentration, one final parameter must be taken into account – temperature. The rate at which oxygen molecules hit the cathode is governed by diffusion through the sensing membrane and the film of electrolyte between the membrane and cathode. Since all diffusion processes are temperature sensitive, it is to be expected that the Micro-fuel Cell's electrical output will vary with temperature (at a constant level of oxygen). This variation amounts to about +2.5% per degree Centigrade. This means that for every degree Centigrade of temperature rise, the cell output will increase 2.5%. The cell, therefore, has a positive temperature coefficient of 2.5% per degree Centigrade.

Negative temperature coefficient thermistors are used to compensate for this effect. ***Figure 4*** shows the manner in which this temperature compensation is effected. In most instruments, the compensation curve is matched with an accuracy of ±5% or better. The resultant output function then is independent of temperature (within the above stated accuracy) and varies only with changes in oxygen concentration. Figure 4 also shows two simple circuit diagrams where the Micro-fuel Cell's output is temperature compensated; one involving no amplifier and the other showing a single stage of amplification.

It should be noted that Micro-fuel Cells do have enough output power to drive readout meters directly without amplification or external power supplies. This usually results, however, in single range capability.

Amplification: In most of the oxygen analyzers using Micro-fuel Cells (with the exception of the portable medical and safety instruments), a dual stage amplification circuit is used as shown in Figure 5.

The first stage is an I to E (current to voltage) transducer whose negative feedback loop is used to facilitate range changes. The I to E configuration offers three distinct advantages.

1) The Micro-fuel Cell can be located at a distance (500 feet) from the remainder of the analyzer without preamplification or noise pickup problems.

2) The cell operates into a short (zeroohm load) which

Temperature Compensation

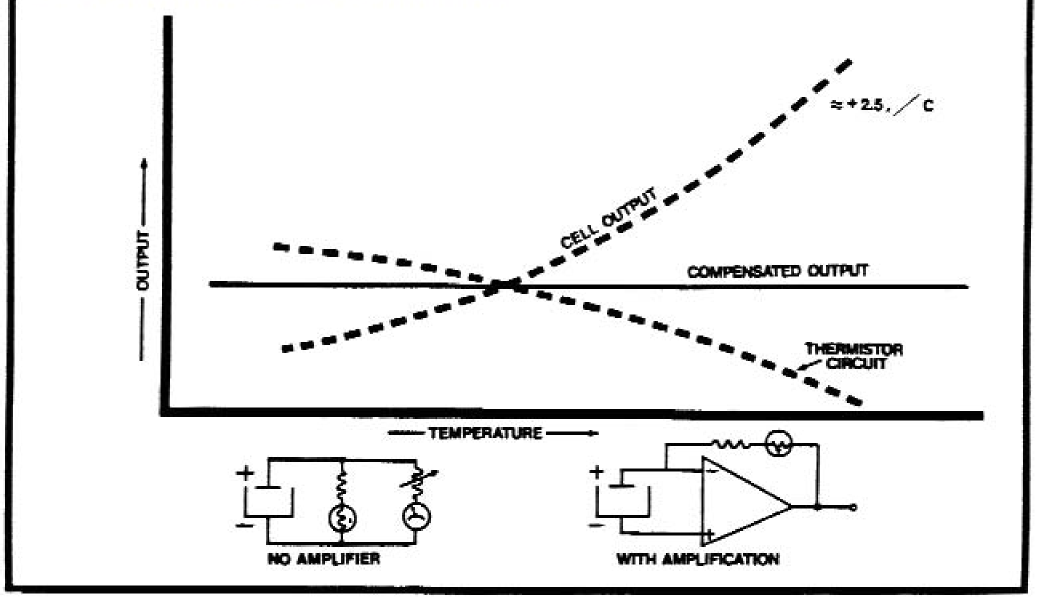


Figure 4

is the ideal for best linearity and rapid response.

3) The effects of amplifier voltage offset are minimized.

An N-channel field effect transistor (FET) is located across the inputs of the I to E transducer to provide a low resistance current path for the cell when the analyzer is turned off (no power). When the gate of the FET is powered, the source to drain resistance is approximately 10 to the 12th power ohms. When negative power is removed, this resistance drops to approximately 30 ohms.

As shown in ***Figure 5***, the output of the first stage of amplification is as follows:

E(out) = -iR(f) (1)

Where E(out) is the output voltage, i is the input current (the current output of the Micro-fuel Cell) and R(f) is the negative feedback resistance. This feedback resistance can be changed (as shown in the diagram) to effect range changes. The cell is connected backwards (+ to – and – to +) because the polarity of transduction is inverted when the amplifier is operated in this configuration. Hence, the minus sign in equation (1).

The second stage of amplification is used to effect temperature compensation. The thermistor must be located remotely or at the same location as the Micro-fuel Cell, and so a total of four conductors (two for the cell signal and two for the thermistor) plus a shield, are required when the sensor assembly is located remotely.

The output of the second stage of amplification is then:

$$E(out) = E(in) \times \frac{(R1 + R2)}{R2} \qquad (2)$$

Where E(out) is the output voltage, E(in) is the input voltage (output of the first stage), R1 is the thermistor resistance, and R2 is the reference resistor. The expression:

$$\frac{(R1 + R2)}{R2}$$

Is the gain of the second stage of amplification.

To complete the amplification circuit of the analyzer, it is only necessary to provide span (calibration) and readout capability. Figure 5 shows these in schematic form.

Amplification

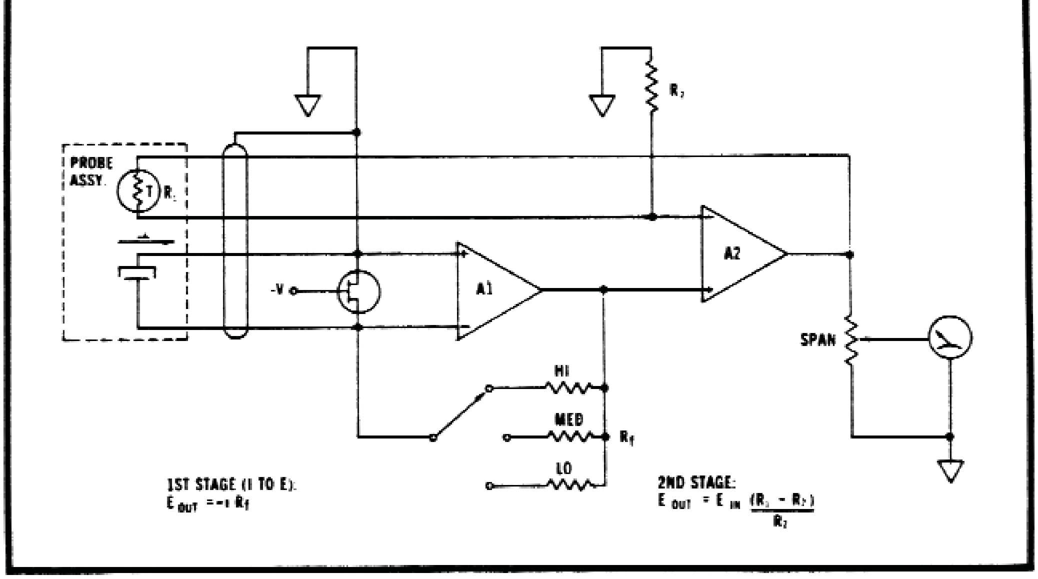


Figure 5

Accuracy: It is now possible to discuss the concept of overall accuracy since the parameters affecting accuracy have been delineated. There are two basic types of errors affecting overall accuracy of a given analyzer:

1) Those that produce a percent of reading contribution, and

2) Those that are a fixed value (usually expressed as a percentage of full scale).

These two error types are expressed graphically in ***Figure 6***.

The most significant percent of reading error is that contributed by the matching of the thermistor curve to the output versus temperature curve of the Micro-fuel Cell. As mentioned earlier, this is normally accomplished with an accuracy of better than ±5%. A second percent of reading error, although much less significant, is that imposed during range changing. Typically resistors having a tolerance of ±1% are used. However, in the more sophisticated multi-ranged analyzers, resistors of closer tolerances or selected resistors are used to decrease this error contribution.

The major percent of scale type error is that contributed by the readout device. Meters can be counted on for linearity errors from ±0.5% to ±2% depending on the quality of the meter. In the case of taut band meters, linearity errors are the only significant error involved. (The others are either insignificant or are "spanned out" during calibration.) Pivot and jewel type meter movements can add repeatability errors due to the increased friction of the movement bearings. This can add another ±1% or so. If recorders or digital meters are used to readout the analog signals, then errors of ±0.25% and ±0.1% respectively can be achieved.

A typical overall accuracy statement for analyzers incorporating a meter readout would be ±2% of full scale at constant temperature or ±5% of reading throughout the operating temperature range, whichever is greater. Figure 6 shows this specification graphically.

It is important to keep in mind that these accuracy specifications are worst case and, for example, if measurements are made at the same temperature at which calibration was accomplished, there will be no temperature compensation error. In this case, only readout errors would be operative. Small temperature variations (i.e. 10 - 20°F) will produce a maximum of ±1% of reading error.

Cell Warranty and Classification

TAI manufactures a number of different types of Micro-fuel Cells. The differences are due to differing application requirements. Varying the thickness of the sensing membrane, for example, offers a trade off in speed of response and long life. Thinner membranes produce relatively rapid response and shorter life whereas thicker membranes produce slower response characteristics and longer life.

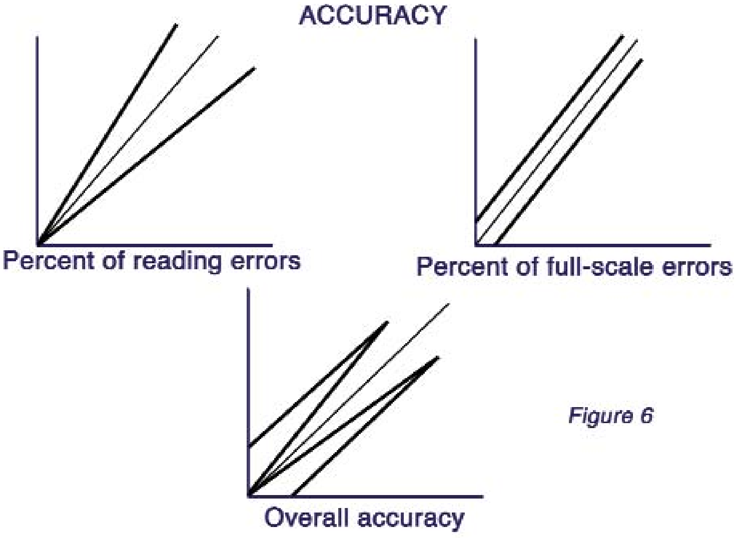


Figure 6

Cell Life: The life of a cell is generally limited by the amount of lead anode material available inside the cell and the rate at which it is consumed. This rate is governed by the average or mean concentration of oxygen that the cell is exposed to throughout its life. If a given cell would last for 12 months in air, it would be expected to last only 21/100 or approximately 1/5 as long as in 100% oxygen.

If cells are used to monitor the oxygen content of dry gas streams, their life will be limited generally by the loss of water which ultimately results in sluggish response characteristics and failure to give accurate, low level readings. The water from the electrolyte, in these cases, diffuses slowly through the sensing membrane and life limitation is primarily a function of membrane thickness.

Good performance can be expected until the electrolyte volume is reduced to approximately half its original volume (2 – 3 millimeters). With the thicker sensing membranes, the time required to accomplish this reduction in electrolyte volume is about 12 months. In the case of thinner membranes, this time is reduced to about 6 months.

Warranty: The various cell classes are warranted usually for a 6 or 12 month period based upon the above considerations, and in the event of failure due to manufacturing or material defects, the cell will be replaced. All warranty replacements are on a prorated basis.

For information on the complete line of Teledyne's Micro-fuel Cells, please visit our website at:

www.teledyne-ai.com

Packaging and Handling

All Micro-fuel Cells are packaged in special gas barrier bags. Most cells are originally packaged in air, but after the bag is sealed the cell reacts with the oxygen inside the bag. Eventually oxygen in the bag is consumed and the cell is in a relatively inert environment inside the bag. The barrier bag transmits negligible amounts of oxygen and almost no moisture. The cell can thus be stored for periods in excess of one year and still provide 90 – 95% of expected life when finally placed in use. It is not suggested, however, that cells be stock piled nor stored any longer than logistics necessitate. TAI maintains a stock of all Micro-fuel Cells and normally cells are shipped the same week that orders are received.

After the cell is removed from its barrier bag, it should continue to have a current path at all times. This means the cell should remain installed in the analyzer or, if removed for any reason, the shorting clip should be reinstalled. (Be careful not to puncture the sensing membrane.)

A current path is required so the cell will be ready to give accurate, reliable readings at all times with a minimal waiting period. If the cell is left unshorted for any significant period, oxygen from the air will diffuse into the cell without being reacted. Depending upon the length of time the cell is left unshorted, when the cell is again installed in the analyzer a period of a few minutes to overnight is required for the cell to consume all the oxygen allowed to diffuse inside the cell. The end of this period is recognizable as the point in time when the reading of the analyzer no longer drops but rather stabilizes to some low value (assuming that the oxygen concentration at the cell is not varying.)

In general, it is best not to remove the cell from the analyzer unless there is some indication the cell is not performing properly. The Micro-fuel Cell is rugged and can survive dropping and general rough handling. The only precaution that should be taken is to assure the sensing membrane is not punctured with a sharp object. This is especially critical with cells having thin sensing membranes such as the A-1, B-1, and B-2.

If a cell is contaminated with liquids that are erroneously introduced into the sampling system of the analyzer, the cell can be removed from its holder and cleaned with water or isoprophyl alcohol and dried with a tissue such as Kleenex or Kimwipe. This procedure will in no way impair future performance of the cell. It is important to remove any liquids that condense or otherwise find themselves on the sensing membrane of the cell. Films of liquid impair diffusion through the normal diffusion path and result in erroneously low readings.

Occasionally poor contact between the cell contact plate and the spring loaded contacts inside the cell holder may develop. This is accompanied by erratic and unstable readings. If this occurs, the cell should be removed and the contact plate and holder contacts cleaned with water and / or alcohol. Sometimes it may be necessary to clean the contact plate with cleanser, fine emery cloth, or sand paper.

OPEN TYPE ELECTROCHEMICAL TRACE LEVEL OXYGEN SENSOR

TAI manufactures a series of trace oxygen analyzers which utilize an unsealed (open) configuration electrochemical sensor.

Chemistry

There is no difference in basic chemistry between this cell and the Micro-fuel Cell. The differences are mainly in physical construction. To facilitate the measurement of oxygen in the very low ppm region, a cathode with a large surface area is employed.

The cathode assembly is a radial array of 1/2 inch wide, 2 – 1/2 inch long, 80 mesh silver screen elements ***(see Figure 8)***. This assembly is mounted in an acrylic cell block so that its lower edge (approximately 1/32 inch) is under the surface of the electrolyte. The surfaces of the silver screen wires are treated in such a way so as to hold, by capillary action, a very thin film of electrolyte.

When an external current path is completed between the cathode assembly and the lead anode (mounted concentrically below the cathode), a current is produced proportional to the concentration of oxygen in the gas phase surrounding the cathode of the cell.

Humidification

In a functioning analyzer, the sample gas is made to flow over the cathode and, unless the sample gas is saturated with water vapor (100% relative humidity), the water-based electrolyte would eventually dry out. It is therefore necessary to humidify the sample gas prior to its entering the cell.

Figure 9 shows the flow schematic for the Series 306 of trace oxygen analyzers. Humidification water is stored in the reservoir. In the absence of sample gas flow, the level of water will be the same in the reservoir and the humidifier column. With the sample bubbling through the humidifier, the level drops in the humidifier column to a level equal to the point in the reservoir tank where the sample bubbles through the tank just prior to venting. The sample is allowed to "blanket" the tank prior to exhausting to the atmosphere so all oxygen dissolved in the humidification water will be expelled rather than added to the sample stream.

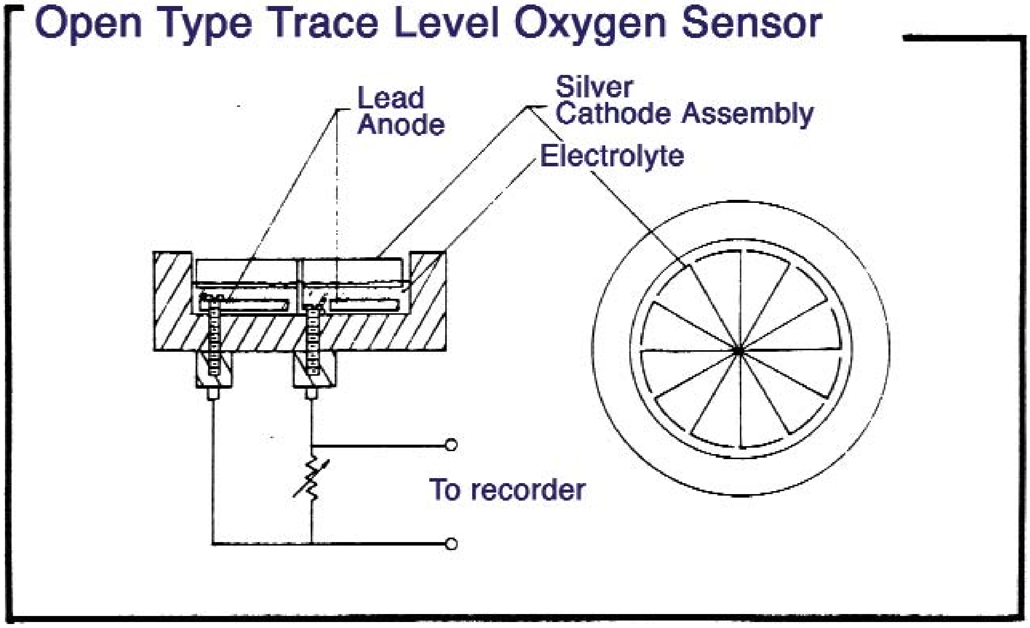


Figure 8

Calibration

The Series 306 is not referenced to air as is their Micro-fuel Cell counterpart. A Faraday type calibration is utilized which relies upon the electrolysis of water at a known current rate into a known flow rate of sample gas. Faraday's Law states (in this case) that 96,500 coulombs of electricity will electrolize 8 grams (one gram equivalent weight) of oxygen from water. By measuring the current flowing through the calibrator (coulombs / second), a direct measure of the concentration of oxygen added to a sample stream is made possible. Figure 10 summarizes this process.

Without going into details of the mathematical conversions, the following relationship holds:

$$C(O_2) = 25i \text{ ppm } O_2 \text{ added}$$

Where $C(O_2)$ is the concentration of oxygen added to the sample stream; 25 is the constant of proportionality; and i is the current in milliamperes that flows through the calibrator electrodes. In Figure 10, f(i) refers to the voltage that is capable of being read out on the recorder, which is required for readout with the oxygen analyzer.

Other Oxygen Analysis Techniques

The following section summarizes other oxygen analysis techniques. Comparisons to the Micro-fuel Cell method of analysis will be made at the end of each summary. At the conclusion of this section, a tabular comparison of the basic electrochemical techniques will be made.

Paramagnetic Analyzers

In an oxygen molecule, two of the electrons in the outer shell are unpaired. Because of this, the magnetic movement of the molecule is not neutralized, thus making the oxygen molecule strongly paramagnetic (attached by a magnetic field). This property of the oxygen molecule allows an analysis cell to be constructed wherein two diamagnetic spheres filled with nitrogen are mounted at the ends of a connecting bar to form a dumbbell shaped assembly. This assembly is mounted horizontally on a vertical torsion suspension. A quartz fiber or platinum ribbon is normally use for this purpose. Electromagnetic or electrostatic feedback is used to maintain the dumbbell at a reference or zero position. The spheres of the dumbbell assembly are coated with a thin metallic coating when electrostatic feedback is employed.

Figure 11 shows the basic configuration of an electromagnetic feedback paramagnetic oxygen analyzer. The dumbbell is mounted inside a stainless steel housing having a glass window. At the center of the dumbbell assembly is a small mirror upon which is focused a light beam. The differential output from the

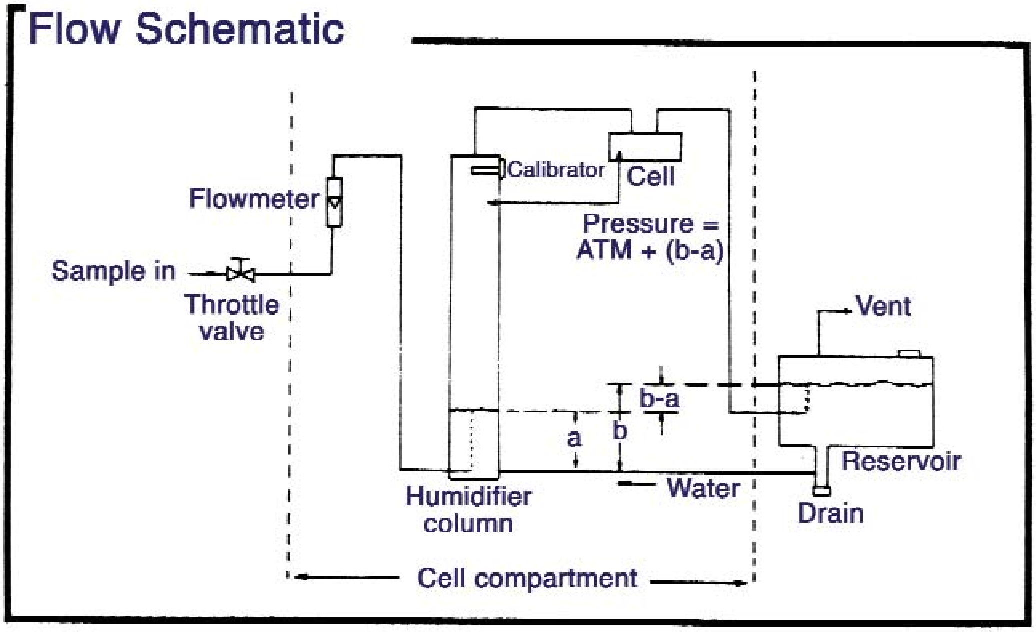


Figure 9

twin photocell is amplified and fed back to a coil around the dumbbell. With an oxygen free gas in the cell, the torsion suspension is rotated (mechanical zeroing) until there is a zero signal output from the photocells. With a calibration gas in the cell, the gain of the amplifier is adjusted so the feedback current reading corresponds to the concentration of oxygen in the calibration gas. The current required to keep the dumbbell at the zero position is a measure of the magnetic susceptibility of the sample gas.

Paramagnetic analyzers are, in general, best suited for laboratory applications and in instances where suppressed ranges (90 – 100%, 95 – 100%, etc.) are required. The major disadvantage in industrial applications are:

1. Sample gases must be scrupulously cleaned and rendered free of all particulate matter and condensibles.

2. The dumbbell assembly is fragile and expensive to replace. Also, this maintenance must be performed at the factory.

3. The analyzer cannot read accurately under conditions of shock and vibration and is position and tilt sensitive.

4. The analyzer cannot tolerate wide variations is sample flow rates due to movements of the dumbbell assembly caused by turbulences resulting from too high a flow rate.

The Micro-fuel Cell requires less stringent sample conditioning and can tolerate some particulate and condensible vapors in the sample stream. In the event that the cell is contaminated to the point where accurate readings are no longer possible, the cell can be removed, cleaned, and reinstalled in a matter of minutes. This is not the case with the paramagnetic analyzer.

Magnetic Wind Analyzers

This type of analyzer (also called thermal magnetic) uses a combination of techniques – thermal conductivity and paramagnetic. The analysis cell consists of two side tubes with an interconnecting tube passing through a strong magnetic field ***(Figure 12)***. Inside the tube there is a heated filament which forms one arm of a Wheatstone bridge. Sample gas passes up the two side tubes and into the cross tube. Oxygen

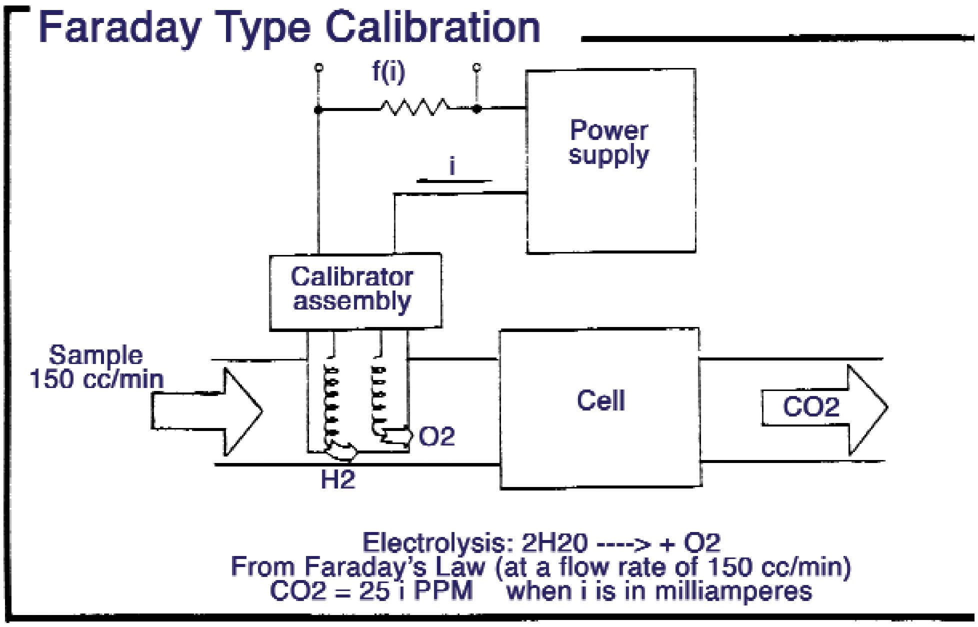


Figure 10

present in the left hand tube is attracted into the magnetic field. Upon entering the field, the oxygen is heated by the filament and its magnetic susceptibility is reduced. The heated gas is pushed across the cross tube by other cold gases entering at the left. The effect is as though there were a continuous flow of gas through the tube. This gas flow cools the filament, thus changing its resistance. This change in resistance unbalances the bridge and produces a signal proportional to the oxygen content of the sample gas.

Thermal magnetic analyzers suffer from the same basic problems as the paramagnetic analyzer without being as fragile or shock sensitive. However, these analyzers are plagued with several inherent sources of error that are unique:

1) The filament temperature is affected by changes in the thermal conductivity of the carrier gas, causing the calibration to be correct for only one gas mixture. If that mixture is changed, a new calibration mixture must be used. When the sample mixture varies during the required sampling interval, the resultant errors can be substantial.

2) Hydrocarbon vapors in the sample stream react on the hot filament causing changes in temperature and significantly large errors. These hydrocarbons must be removed if their concentration level is high enough. In those instances, oxygen reading errors will result due to the reduction in sample volume.

3) The cross tube must be perfectly horizontal to avoid errors due to gravitational flow effects.

Paramagnetic Analyzer

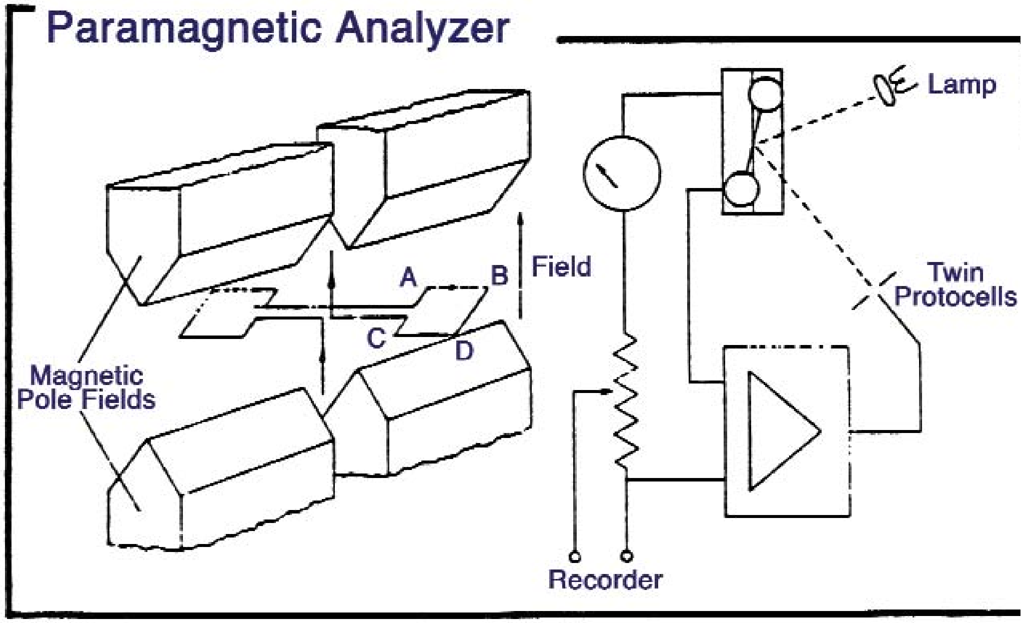


Figure 11

Other Electrochemical Techniques

In addition to the Micro-fuel Cell type of electrochemical sensor, there are two other similar devices often encountered. These are the polarographic sensor and the high temperature ceramic sensor (zirconium oxide).

Magnetic Wind Analyzer

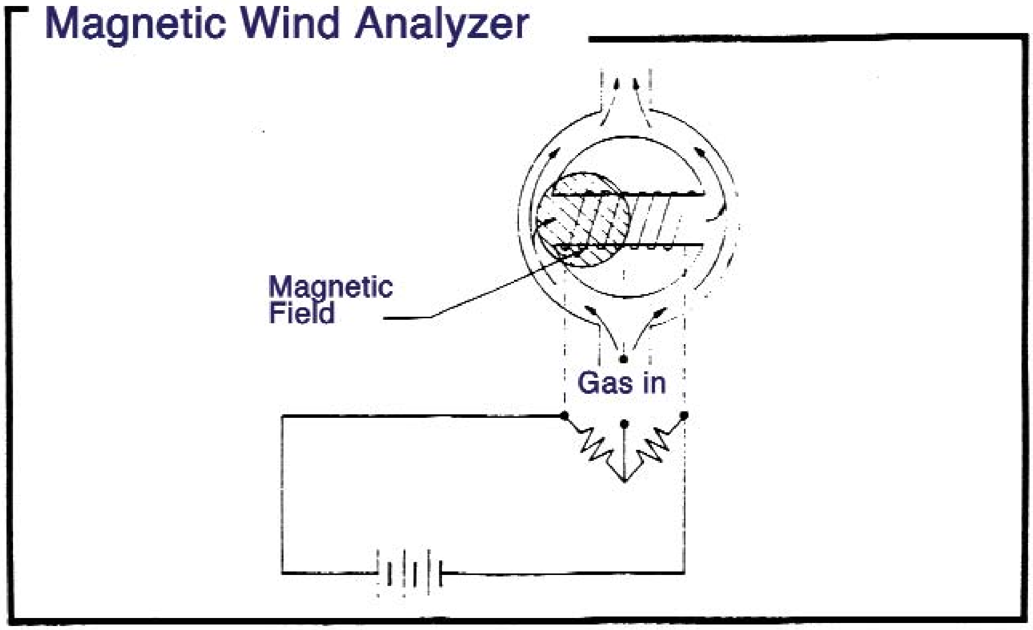


Figure 12

The Polarographic Sensor: The main difference between this type sensor and the Micro-fuel Cell is the source of the driving potential. In the Micro-fuel Cell, the driving potential is obtained through the proper choice of anode material, copper, cadmium, lead, tin, zinc, etc. Any of these anode metals would exhibit a driving potential sufficient to cause a current to flow in the presence of oxygen. In the polarographic cell, the anode is usually silver and the cathode is gold. It is necessary that an external potential of about 0.7 volts be applied between the electrodes (minus the cathode) before the following half-reaction can occur:

Cathodic reaction:

$$4e^- + O_2 + 2H_2O \longrightarrow 4OH^- \quad (1)$$

Anodic reaction:

$$Ag^+ + Cl^- \longrightarrow AgCl + e^- \quad (2)$$

Overall reaction:

$$4Ag^+ + O_2 + 2H_2O + 4Cl^- \longrightarrow 4AgCl + 4OH^- \quad (3)$$

It should be noted that the cathodic reaction (1) is identical to the cathodic reaction in the Micro-fuel Cell. The reaction at the silver anode occurs in a neutral potassium chloride electrolyte. This is the source of chloride ions (Cl-) in reaction (2).

Unlike the Micro-fuel Cell where the composition of the electrolyte does NOT change as the oxygen sensing reaction proceeds, the polarographic cell electrolyte is constantly changing. Hydroxyl ions (OH-) are being substituted for chloride ions (Cl-). When the electrolyte becomes depleted of Cl-, it must be replenished. This involves taking the cell apart and consequently the membrane must be replaced as well ***(Figure 13)***. Alternatively, the entire sensor may be replaced.

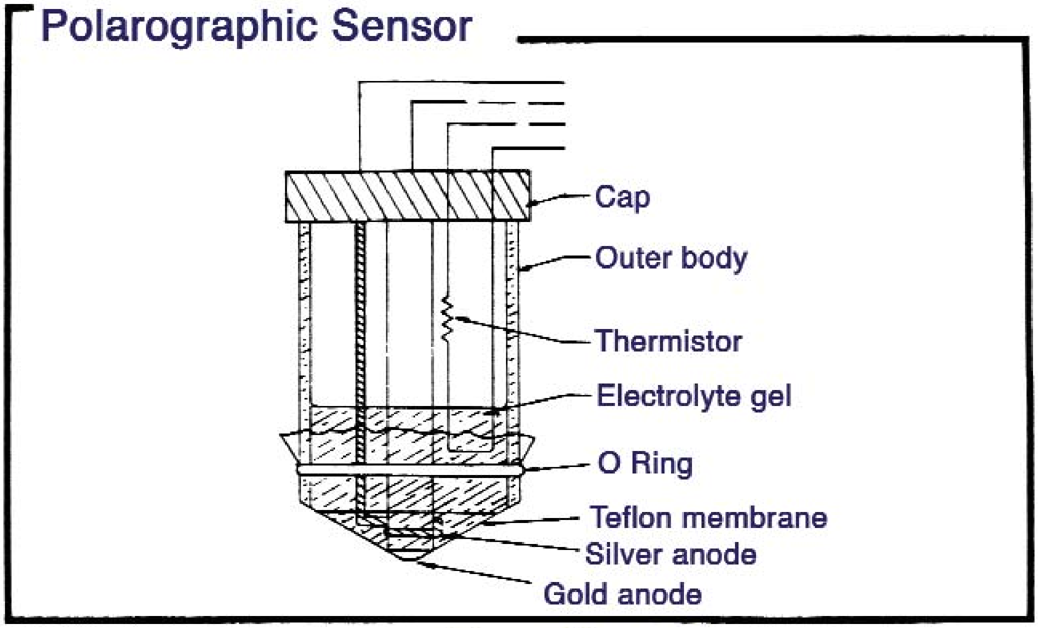


Figure 13

Depending upon the design of the sensing assembly, the maintenance cycle can vary from a few hours to several months. If the sample gas is dry, this will tend to shorten the cycle since polarographic sensors generally utilize small electrolyte volumes and the water in the electrolyte evaporates relatively quickly.

Unlike the Micro-fuel Cell, polarographic sensors are unable to measure at the trace oxygen level. This is because of the residual of background current that is produced due to the externally applied potential which results in the electrolysis of water. This residual current is normally insignificant if the range of measurement is, for example, 0-25%. However, a range of 0-1% (0 – 10,000 ppm) will have an offset of from 0.01 to 0.05% oxygen equivalent. Often this becomes greater in cells that are used and have undergone several maintenance cycles.

And finally, polarographic cells always require amplification because of their relatively low output and their need for an external polarizing voltage.

High Temperature Ceramic Sensor. ***Figure 14*** shows the arrangement of the major components of the high temperature ceramic sensor. The sensing cell consists of a calcium stabilized zirconium oxide solid electrolyte with porous platinum electrodes on its inner and outer surfaces. A temperature controlled furnace maintains the sensing cell at approximately 800 degrees C (1472 F). At this temperature the ceramic electrolyte will conduct oxygen ions (O=) and the half-reaction at each electrode is:

$$\text{Reference: } O_2 + 4e^- \longrightarrow 2O^{=}$$

$$\text{Sample: } 2O^{=} \longrightarrow O_2 + 4e^-$$

The above equations hold as long as the reference gas is higher in concentration than the sample gas. If the sample oxygen level exceeds the reference, than the O= and electron flow reverse and the output will be of opposite polarity. The open circuit voltage for the two half reactions is:

$$E = \frac{RT}{nF} \text{ in } \frac{P(O_2)\ \text{reference}}{P(O_2)\ \text{sample}}$$

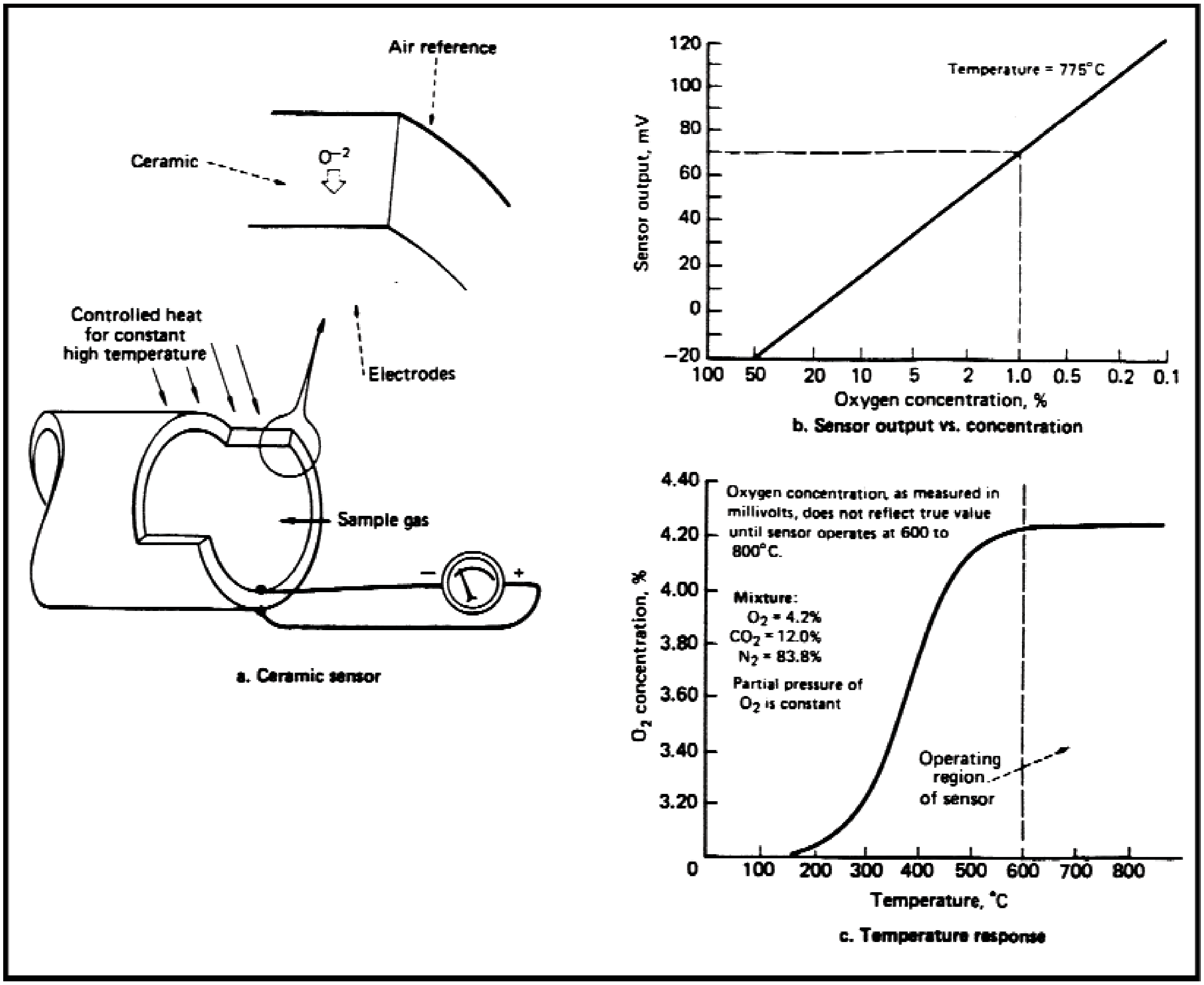


Figure 14

Converting from natural log to log (10) this becomes:

$$E = 0.050 \log \frac{P(O2)\ \text{reference}}{P(O2)\ \text{sample}}$$

As can be seen from these equations, the relationship between the output voltage and the sample oxygen level is logarithmic. For every decade drop in sample oxygen concentration, the output voltage increases 50 millivolts.

The manufacturers of the high temperature ceramic sensor analyzers state their instruments can handle hot, wet, even dirty and corrosive sample gases without a sample conditioning system. They also claim ability to sense ppm quantities of oxygen under the same conditions.

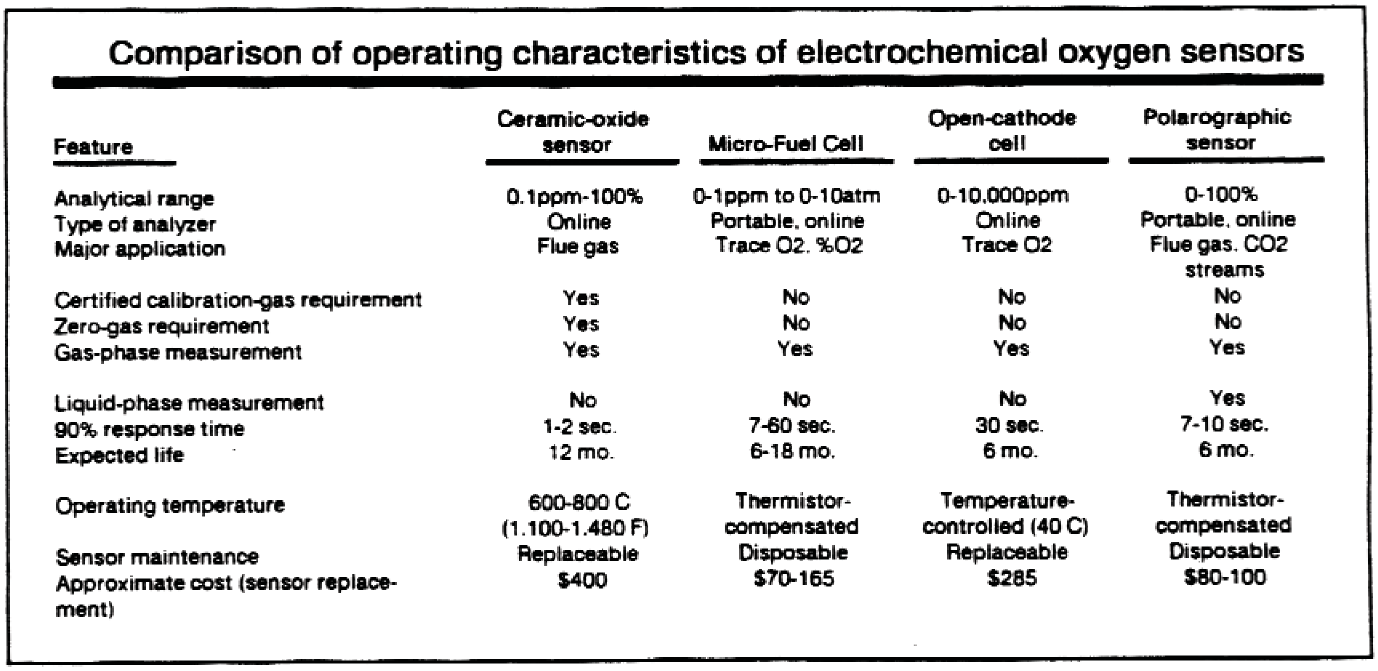
There is no question they can operate at high temperatures and handle samples with high water content since their sensor is operating at almost 1500° F. However, this by itself is no real advantage if the oxygen content of sample gases cannot be measured reliably or accurately.

The main objection to this type of analysis technique is that at this elevated temperature, any and all oxidizable materials in the sample will combine with oxygen stoichemetrically and consequently will subtract from the oxygen available. The reading is, in effect, the net oxygen content of the monitored sample. This phenomenon almost completely eliminates the possibility of using the high tempeature ceramic analyzer for trace oxygen analysis since there is always some hydrocarbons and/or oxidizable inorganic gases that contaminate almost any sample stream.

Also the output of this analyzer is logarithmic and reversed from normal readouts (i.e., the high concentration is at the low end of the scale). Moreover, there is not true zero level. As a result, these output signals do not lend themselves to directly driving conventional recorders or data acquisition systems.

Comparison of Electrochemical Techniques

Figure 15 is a comparison of the four basic types of electrochemical sensors, the Micro-fuel Cell, the polarographic sensor, the open cathode sensor, and the high temperature, ceramic sensor. This comparison is made on the basis of versatility, cost, and maintenance. **§**



Comparison of operating characteristics of electrochemical oxygen sensors

Feature	Ceramic-oxide sensor	Micro-Fuel Cell	Open-cathode cell	Polarographic sensor
Analytical range	0.1ppm-100%	0-1ppm to 0-10atm	0-10,000ppm	0-100%
Type of analyzer	Online	Portable, online	Online	Portable, online
Major application	Flue gas	Trace O_2, %O_2	Trace O_2	Flue gas, CO_2 streams
Certified calibration-gas requirement	Yes	No	No	No
Zero-gas requirement	Yes	No	No	No
Gas-phase measurement	Yes	Yes	Yes	Yes
Liquid-phase measurement	No	No	No	Yes
90% response time	1-2 sec.	7-60 sec.	30 sec.	7-10 sec.
Expected life	12 mo.	6-18 mo.	6 mo.	6 mo.
Operating temperature	600-800 C (1,100-1,480 F)	Thermistor-compensated	Temperature-controlled (40 C)	Thermistor-compensated
Sensor maintenance	Replaceable	Disposable	Replaceable	Disposable
Approximate cost (sensor replacement)	$400	$70-165	$285	$80-100

Figure 15