

**DELTA F CORPORATION**  
**APPLICATION NOTE NO.**  
**107**



## **Risks in Using Zirconium Oxide Analyzers for Trace Oxygen Measurements**

Zirconium oxide oxygen analyzers are used in many applications, including stack gas emissions and boiler trim control. However, the use of these analyzers in trace O<sub>2</sub> applications is not without risk from both measurement dependability and safety perspectives. Significant errors can be introduced by using zirconium oxide oxygen analyzers in trace oxygen measurements. Nearly all gas monitoring applications contain residual amounts of reducing gases (such as H<sub>2</sub>, CO, NH<sub>3</sub>, and all hydrocarbons), even in applications thought to be "clean" (without reducing gases). The oxygen reading errors introduced by a ZrO<sub>2</sub> analyzer, due to the effects of one or more reducing gases that may be present as contaminants, place many oxygen-sensitive production processes at risk.

### ZrO<sub>2</sub> Sensor - Principal of Operation

Zirconium oxide (ZrO<sub>2</sub>) sensors, otherwise known as high temperature electrochemical sensors (or hot probes), consist of a cell made of yttria stabilized zirconia ceramic forming a crystal lattice structure which acts as a solid electrolyte. Typically, the cell is shaped like a test tube where the inner and outer surfaces are each coated with an ultra-thin layer of porous platinum which act as the cathode and anode electrodes. At high temperatures (above 1200°F or 650°C), openings in the crystal lattice permit the movement of oxygen ions. As long as the oxygen partial pressures are equal on both sides, the movement of ions within the lattice is random, and there is no net flow within the lattice. When a sample gas is introduced on one side, oxygen ions migrate within the crystal lattice to form a concentration gradient from the higher O<sub>2</sub> partial pressure side to the lower pressure side. The gradient is determined by the ratio of the O<sub>2</sub> partial pressures between a sample gas on one side of the lattice and a reference gas, (typically ambient air) on the other side of the lattice. This concentration gradient of oxygen ions within the ZrO<sub>2</sub> lattice produces a voltage potential between the two platinum electrodes (E, E<sup>0</sup>) according to the Nernst Equation:



where R is the Universal Gas Constant, T is absolute temperature, n is the number of molecules, F is the Faraday Constant, and Q is the concentration ratio of products to reactants. The voltage can be related to an oxygen concentration in the sample gas relative to the reference gas, but the voltage is also highly temperature dependent. As is apparent, the relationship between the voltage and the O<sub>2</sub> partial pressure change in the gas sample is logarithmic. Equal partial pressures will produce a zero voltage condition. The voltage increases as sample O<sub>2</sub> concentration decreases.

Theoretically, the logarithmic relationship should permit signal resolution at extremes of partial pressure differential. In reality, interference from reducing gases that are present even in high purity inert gases, will cause false low readings. Reducing gases are any gases that can be oxidized (combusted) by reaction with oxygen, such as CO, H<sub>2</sub>, NH<sub>3</sub> and all hydrocarbons.

Because platinum is an excellent catalyst material, the platinum electrodes of the zirconium oxide sensor act in the high normal operating temperature to catalyze reactions between oxygen and other gas constituents in the gas sample, such as ppm or ppb levels of residual hydrocarbon vapors. The oxygen which is being reacted with the residual reducing gas is consumed in the proximity of the platinum cathode electrode. The resulting lower concentration of oxygen at the surface of the cathode electrode is what causes the false low reading because the O<sub>2</sub> no longer exists at the measurement site. There is no way to tell that the zirconium oxide oxygen analyzer is giving false low readings unless the sample is checked by a different type analyzer.

Reactions between the reducing gas and oxygen molecules will take place in near perfect stoichiometric balance because of the superb catalytic properties of the platinum measuring electrodes. For example, two molecules of H<sub>2</sub> present will react one O<sub>2</sub> molecule forming H<sub>2</sub>O in the process. Therefore, if the background gas contains 10 ppm of H<sub>2</sub>, a 5 ppm drop in indicated O<sub>2</sub> readings by a ZrO<sub>2</sub> analyzer can be expected. However, if even minuscule amounts of residual oil vapors are present, such as the vapors emitted from a human finger print, a more dramatic error will result from the stoichiometric proportioning. Two C<sub>12</sub>H<sub>26</sub> heavy hydrocarbon molecules will consume 37 oxygen molecules. Therefore, if the background gas contains 10 ppm of the hydrocarbon, ***a nearly 200 ppm measurement error by the ZrO<sub>2</sub> analyzer will result.***

## Advantages and Disadvantages

Zirconium oxide oxygen analyzers have fast speed of response. Also, due to the high operating temperature requirement, they make an ideal choice for oxygen measurements in combustion applications because the sensor can be inserted into the stack or exhaust directly for in-situ measurements. Because combustion applications measure percent O<sub>2</sub> levels, the error caused by catalytic reaction of the residual hydrocarbons in the post-combustion gas is not significant.

The major disadvantage is the relatively short life span and high replacement cost of the zirconium oxide sensor. Sensors typically require replacement every 12-24 months of continuous use due to the gradual diffusion of the platinum of the electrodes into the ZrO<sub>2</sub> crystal lattice, eventually shorting the two electrodes together. Further, as the sensor ages, it becomes more unstable and, therefore, more difficult to keep in calibration.

Because of their sensitivity to reducing gas, zirconium oxide analyzers are not well suited to trace O<sub>2</sub> analysis. Even high purity inert gases contain some levels of H<sub>2</sub> or hydrocarbons that are residual from gas production and transport, or tube manufacturing processes. Moreover, applications where accidental mixing of higher concentrations of reducing gas and oxygen (air) is possible should be avoided due to the safety risk of combustion. The highly catalytic platinum sensing electrodes operating at high temperatures can induce runaway reactions, and, therefore, can act as a potential ignition source.

## Interference from Reducing Gases

Interference from reducing gases can take place in applications where it is least expected. Most high purity bulk gas distribution piping is constructed of stainless steel tubing. Large amounts of H<sub>2</sub> and hydrocarbons are absorbed into the walls of the tubing during various heat treating steps during its production. Very low residual trace levels will outgas for weeks or months into the high purity inert gas once the piping system has been placed into service. This reducing gas component of high purity gas is typically not anticipated, but it can cause serious errors if a zirconium oxide analyzer is used during commissioning to certify that O<sub>2</sub> levels are within specifications.

Other than by cross-checking with another type of O<sub>2</sub> analyzer, there is no way to distinguish between accurate readings within spec., and false low readings which are masking an out-of-spec oxygen condition. Even if checked against a bottled O<sub>2</sub> standard, the errors may not be noticeable because the background gas has changed, thereby removing the potential source of reducing gas. Also, O<sub>2</sub> levels are typically much higher than in process conditions so the relative error from the calibration gas should be much less.

In other process applications, gaseous byproducts of the process can be a source of reducing gas constituents which will cause a zirconium oxide analyzer to give false low readings. In *Solder Reflow* applications, circuit boards are assembled with surface mount components and are sent on a conveyer through a furnace, usually blanketed with nitrogen. In the process, the boards are gradually heated as they progress through the furnace to a point where the solder in the solder paste on the individual components begins to flow. An oxygen-free condition is critical to the solder joint quality on small lead geometries.

The volatile organic content of the solder paste is vaporized during the process. Assuming an oven volume of 8 ft<sup>3</sup> at 250°C and atmospheric pressure, a forced convection flow of 160 cubic feet per minute, 10 grams of solder paste on the boards, an average molecular weight of 150 grams/mole using a C<sub>10</sub> hydrocarbon as typical, and a "Volatile Content" of 10% by weight, a concentration of 63 ppm of volatiles can be calculated using the Ideal Gas Law,  $PV = nRT$ .

***The resulting oxygen reading error reported by a zirconium oxide analyzer will be 960 ppm !*** Because of this zirconium oxide analyzer manufacturers recommend or supply activated carbon filters to remove the hydrocarbons so the analyzer output will not continuously read zero oxygen. Unfortunately, these filters are not reliable and there is no convenient way to identify when the filter is full. Why take the risk in false low readings?

## Delta F Difference

The Delta F Non-Depleting Electrode Coulometric sensor is an ambient temperature electrochemical device, so it inherently poses no risk upon exposure to reducing gases. Unlike other ambient temperature electrochemical sensors which all operate on a galvanic principal (depleting anode electrode), the Delta F sensor's life span is indefinite. It uses carbon-based electrodes which are not consumed in the oxygen measuring process. Oxygen in the sample gas is reduced at the cathode electrode. At the anode electrode, it is oxidized back into molecular O<sub>2</sub>, which vents out of the sensor. Whereas galvanic sensors use a consumable lead (or cadmium) anode as the driving force for the electrochemical reaction, Delta F uses an

externally applied 1.3 VDC potential, and the electrodes undergo no chemical change. As a result, much better measurement stability is achieved, less calibration is required, and periodic sensor replacement (or rebuilding) is eliminated.

Delta F analyzers perform flawlessly in applications ranging from inert to pure reducing gases, such as H<sub>2</sub>, CO, natural gas, ethylene, propylene, butadiene, and others. Performance features unmatched in the industry, include:

- Extremely Stable, Long-Term, Drift-Free Operation
- Five Year Sensor Warranty (conditional)
- Factory Calibration to NIST Traceable Standards
- Acid Gas Operation (with STAB-EL™ option)
- Quick Start-up

## Recognized for Quality

Delta F's Quality Management System has been certified to ISO-9001 by Lloyd's Register Quality Assurance Ltd. This assures you of the highest quality product design, manufacturing, and service.

Delta F Oxygen Analyzers can be ordered with a full scale range of 0-2 parts per billion (ppb) to as high as 0-25 percent. For specific product recommendations, contact Delta F Corporation, 4 Constitution Way, Woburn, MA 01801-1087, Tel. (781)935-4600, FAX (781)938-0531, e-mail [marketing@delta-f.com](mailto:marketing@delta-f.com).