

Considerations of the Effect of Atmospheric Pressure Changes on Potentiometric Zirconia Oxygen Sensor Measurements

Introduction

The potentiometric zirconia oxygen sensor is an electrochemical device employing a high temperature stabilized zirconium oxide ceramic electrolyte. The sensor is in the form of a tube closed at one end, with electrodes, usually platinum, deposited onto the inner and outer surfaces.

Theory

The tube is completely gas tight at the temperature of operation, which is commonly in the range 500 to 750°C. It conducts electricity by means of oxygen ions. The potential difference across the cell is given by the Nernst equation:

$$E = 2.303 \frac{RT}{4F} \log_{10} \frac{p_1}{p_2}$$

where:

E is the potential difference / volts

R is the gas constant / $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$

F is the Faraday constant / $96484 \text{ coulomb mol}^{-1}$

p_1 and p_2 are the partial pressures of oxygen outside and inside the zirconia tube, respectively.

Note

The partial pressure of a gas in a mixture is equal to the volume fraction of the gas times the total pressure of the gas mixture. So for oxygen in air at standard atmospheric pressure of 1013 mbars, the mole fraction = $\frac{20.9}{100} = 0.209$

Therefore $p_1 = 0.209 \times 1013 = 211.7 \text{ mbars}$

Calculation

If the gas sample is vented to the atmosphere, there will be a pressure drop (Δp) between the sensor inlet and the exit of the outlet tube. The pressure of the gas sample inside the zirconia tube = $\Delta p +$ total external pressure. At the recommended flow rate of 150 ml/min the back pressure due to, for example, 5m of 1/8" tubing is about 20 mbars. If longer runs of tubing are required, 3/4" tubing is recommended to minimise backpressure.

We consider the case of the sensor being zeroed and calibrated at low atmospheric pressure (e.g. 980 mbars), and then being used at a higher atmospheric pressure (e.g. 1040 mbars). We will calculate the sensor output and the instrument readings for samples of 1 ppm and 1% oxygen.

The Nernst equation can be reduced to:

$$E = 0.0496T \log_{10} \frac{p_1}{p_2}$$

Note that E is now in mV. We take the operating temperature as 650°C.

Case 1 – with an external total pressure of 980 mbars

For 1ppm oxygen $p_1 = 0.209 \times 980 = 204.8$ mbars
 $p_2 = 1 \times 10^{-6} \times (980 + 20) = 1 \times 10^{-3}$ mbars

The sensor potential will be $E = 0.0496 \times (273.3 + 650) \times \log_{10} \frac{204.8}{1 \times 10^{-3}} = 243.24$ mV

For 1% vol oxygen $p_1 = 0.209 \times 980 = 204.8$ mbars
 $p_2 = \frac{1}{100} \times (980 + 20) = 10.0$ mbars

The sensor potential will be $E = 0.0496 \times (273.3 + 650) \times \log_{10} \frac{204.8}{10.0} = 60.05$ mV

Case 2 – with an external total pressure of 1040 mbars

For 1ppm oxygen $p_1 = 0.209 \times 1040 = 217.4$ mbars
 $p_2 = 1 \times 10^{-6} \times (1040 + 20) = 1.06 \times 10^{-3}$ mbars

The sensor potential will be $E = 0.0496 \times (273.3 + 650) \times \log_{10} \frac{217.4}{1.06 \times 10^{-3}} = 243.26$ mV

For 1% vol oxygen $p_1 = 0.209 \times 1040 = 217.4$ mbars
 $p_2 = \frac{1}{100} \times (1040 + 20) = 10.6$ mbars

The sensor potential will be $E = 0.0496 \times (273.3 + 650) \times \log_{10} \frac{217.4}{10.6} = 60.07$ mV

Comparison of the Sensor Potential for Case 1 and 2

For 1ppm oxygen

The percent change in $E = [(243.26/243.24) \times 100] - 100 = 0.008\%$
i.e. the sensor potential E is 0.008% greater at 1040 mbars.

For 1% vol oxygen

The percent change in $E = [(60.07/60.05) \times 100 - 100] = 0.033\%$
i.e. the sensor potential E is 0.033% greater at 1040 mbars.

Comparison of the Sensor Potential for Case 1 and 2

We said that the instrument was calibrated at 980 mbars. Therefore the theoretical readings are normalised to 1.00 ppm and 1.00% vol oxygen for the two gas concentrations at that pressure.

By substituting the sensor potentials from case 2 into the equations for case 1 we can solve for p_2 and determine the theoretical readings.

For 1 ppm oxygen the equation for the sensor potential is:

$$243.26 = 0.0496 \times (273.3 + 650) \times \log_{10} \frac{204.8}{p_2}$$

By solving the equation for p_2 we find that the oxygen partial pressure would be 9.999E-04 mbars and the instrument reading would be 0.999 ppm.

For 1% vol oxygen the equation for the sensor potential is:

$$60.07 = 0.0496 \times (273.3 + 650) \times \log_{10} \frac{204.8}{P_2}$$

By solving the equation for p_2 we find that the oxygen partial pressure would be 9.999 mbars and the instrument reading would be 0.999% vol.

Conclusion

Under normal operating conditions the effect of changes in atmospheric pressure on the measurement of oxygen concentrations using the zirconia oxygen sensor is negligible. Barometric pressure correction is not required.

August 2012

By Dr Malcolm Taylor PhD, GRSC