SYSTECH INSTRUMENTS

Zirconia Oxygen Analysis

The zirconia oxygen analyser is suitable for measurements of ppm to % levels of oxygen in a gas or mixture of gases. The zirconia cell employs a high temperature ceramic sensor containing yttrium stabilised zirconium oxide.

Within an instrument the zirconia cell is mounted in a temperature controlled furnace with the necessary electronics to process the signal from the detection cell. Typically measurements are displayed directly via a digital display as oxygen concentration over the range 0.01ppm to 100%.

Theory

The zirconia cell is a high temperature ceramic sensor. It comprises two electronically conducting, chemically inert, electrodes attached to either side of a solid electrolyte tube. This is shown schematically in Figure 1., overleaf.

The tube is completely gas tight and made of a ceramic (stabilised zirconium oxide) which, at the temperature of operation, conducts electricity by means of oxygen ions. (Note: In sensors of this type, the temperature has to be above 450°C before they become active as an electrolyte conductor). The potential difference across the cell is given by the Nernst equation.

$$E = \frac{RT}{4F} \log_e \frac{P_1}{P_2}$$

where:

E	is the potential difference (volts)
R	is the gas constant (8.314 J mol^{-1} K^{-1})
T	is the absolute temperature (K)
F	is the Faraday constant (96484 coulomb mol^{-1})
P_1 & P_2	are the partial pressures of the oxygen on either side of the zirconia tube

The Nernst equation can therefore be reduced to:

$$E = 0.0496T \log_{10} \frac{P_1}{P_2}$$

Thus, if the oxygen partial pressure at one of the electrodes is known and the temperature of the sensor is controlled, then measurement of the potential difference between the two electrodes enables the unknown partial pressure to be calculated.

Note

The partial pressure of the gas is equal to the molar concentration of the component in a gas mixture times the total pressure of the gas mixture.

$$PO_2 = CO_2\ P_2$$

where:
PO_2 = Oxygen partial pressure
CO_2 = Molar concentration of oxygen
P_2 = Total pressure

e.g. For atmospheric air, CO_2 = 20.9%
P_2 = 1 atmosphere

$$PO_2 = \frac{0.209}{100} \times 1$$

PO_2 = 0.209 atmospheres

Principle of Operation

The zirconia cell used by Systech Instruments, is made of zirconium oxide stabilised with yttrium oxide as the ceramic with porous platinum electrodes.
This cell is shown in Figure 1.

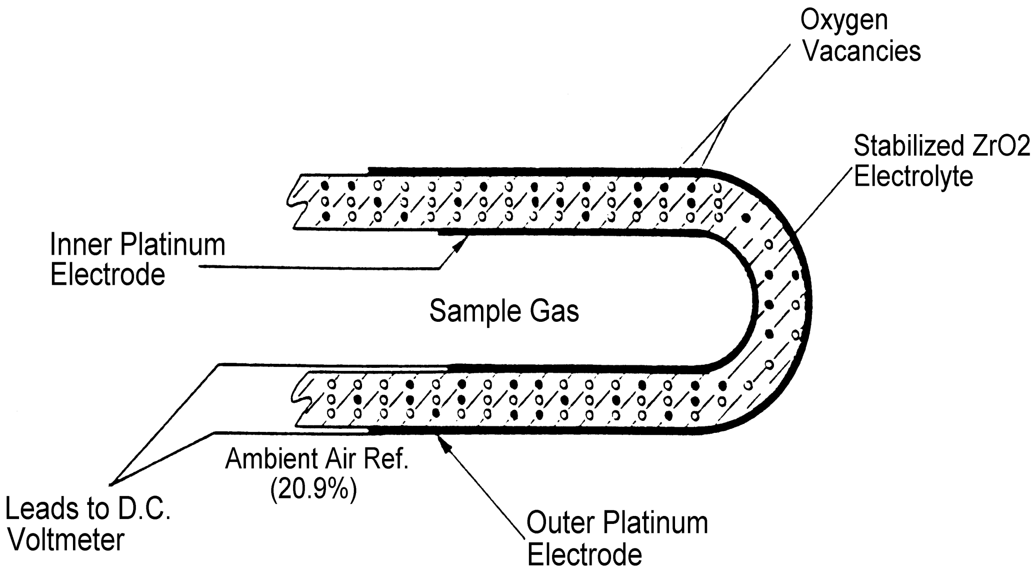

Figure 1

(Enlarged cross sectional representation of the zirconia substrate)

Molecular oxygen is ionised at the porous platinum electrodes.

$$\text{PtO} \rightarrow \text{Pt} + \tfrac{1}{2}\,O_2$$
$$\tfrac{1}{2}\,O_2 + 2e^- \rightarrow O^{2-}$$

The platinum electrodes on each side of the cell provide a catalytic surface for the change in oxygen molecules, O_2, to oxygen ions, and oxygen ions to oxygen molecules. Oxygen molecules on the high concentration reference gas side of the cell gain electrons to become ions which enter the electrolyte. Simultaneously, at the other electrode, oxygen ions lose electrons and are released from the surface of the electrode as oxygen molecules.
The oxygen content of these gases, and therefore the oxygen partial pressures, is different. Therefore, the rate at which oxygen ions are produced and enter the zirconium oxide electrolyte at each electrode differs. As the zirconium oxide permits mobility of oxygen ions, the number of ions moving in each direction across the electrolyte will depend on the rate at which oxygen is ionised and enters the electrolyte at each electrode.

The mechanism of this ion transfer is complex, but it is known to involve vacancies in the zirconia oxide lattice by doping with yttrium oxide.

The result of migration of oxygen ions across the electrolyte is a net flow of ions in one direction depending upon the partial pressures of oxygen at the two electrodes. For example in the Nernst equation:

$$E = 0.0496T \log_{10} \frac{P_1}{P_2}$$

If P1>P2, ion flow will be from P1 to P2, i.e. a positive E.M.F.
If P1<P2, ion flow will be from P2 to P1, i.e. a negative E.M.F.
If P1=P2, there will be no net ion flow, i.e. a zero E.M.F.

Principle of Operation (cont)

In the zirconia analyser, the Nernst equation is written

$$E = 0.0496T\log_{10}\frac{PO_2 sample}{PO_2 reference}$$

The analyser uses air as a reference, a constant oxygen concentration of 20.9%, and the zirconia cell is mounted inside a furnace whose temperature is controlled to 650°C (923 K).

Thus, our Nernst equation further reduces to:

$$E = 45.78\log_{10}\frac{PO_2 sample}{0.209}$$

The analyser electronically calculates the oxygen partial pressure, and therefore oxygen concentration, of a sample gas with unknown oxygen concentration. This is accomplished by measuring the potential, E, produced across the zirconium cell electrodes, substituting for E in the Nernst equation and anti-logging to obtain PO_2. The cell potential output is shown in Figure 2.

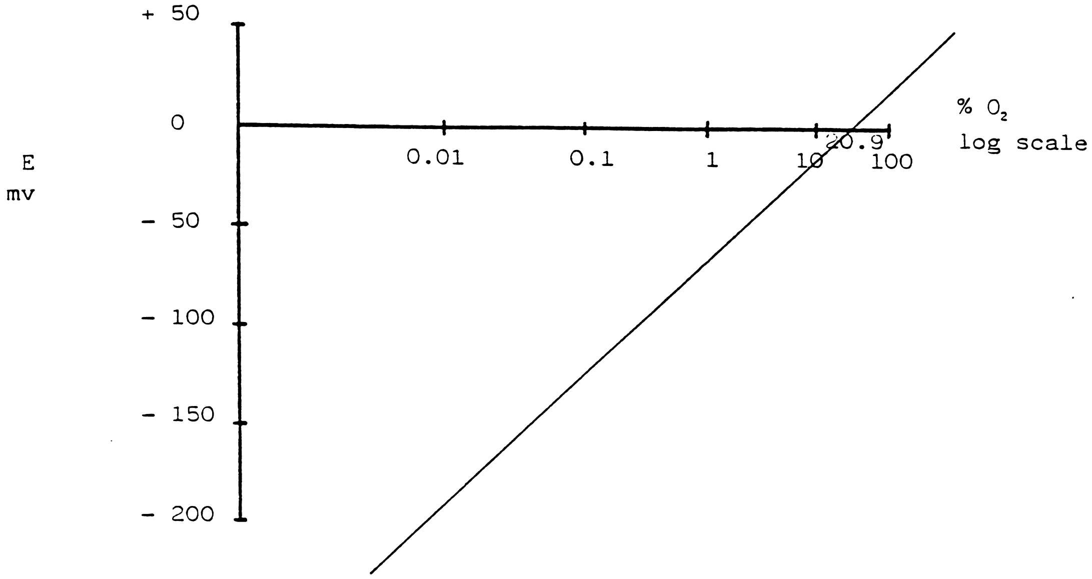

Figure 2 Graph of cell potential vs. oxygen concentration of zirconia cell.

By anti-logging the equation, the output signal can be displayed directly on a digital readout meter as oxygen concentration in ppm or %.

Calibration

As the zirconia instrument uses a measurement principle which conforms to the Nernst equation. Therefore it only requires a single calibration point. With ambient air the output from the zirconia sensor will be zero. Routine calibration of the instruments should be performed using ambient air.

Factory calibration consists of calibration of the electronics to accept the millivolt input signal from the detection cell and checking that the instrument then reads correctly on air, 20.9%. The instrument is then further checked for correct reading on ppm oxygen content in nitrogen.

Applications

The zirconia analysers may be used for measurement of oxygen at any level between 0-100% in gases or gas mixtures.

The only restriction on the instrument’s usage is that the gas to be measured must not contain combustible gases or any material that will poison the zirconium oxide detection cell.

Any combustible gas, e.g. CO, H_2, hydrocarbons such as methane, in the sample gas entering the instrument will combine with any oxygen in the sample gas in the furnace due to the high temperature at which the furnace is kept. This will actually reduce the amount of oxygen in the sample gas and cause the instrument to give an incorrect low reading.

Materials that will poison the detection cell are:

Halogens	e.g. Chlorine
Halogenated Hydrocarbons	e.g. Methylchloride
Sulphur containing compounds	e.g. Hydrogen Sulphide
Lead containing compounds	e.g. Lead Sulphide

Gases or gas mixtures containing any of the above are not suitable for oxygen determination with a zirconia type oxygen analyser.

Typical applications for the Model 800, ZR893, Gaspace and Mapcheck, are with industrial gas producers, industrial gas users and food packaging companies:

Gas Producers		for ensuring product quality by measuring for an oxygen impurity or for monitoring for oxygen purity.
Gas Users	-	to ensure reliability of inert gas blankets
	-	to ensure quality of gases used as production materials in the chemical industry.
Food packaging		to ensure the correct oxygen levels are present in packages containing modified or controlled atmospheres.

The applications are discussed in greater detail in the applications guide.

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