

Oxygen Sensors

There are a number of possible methods to measure the concentration of oxygen in a gas sample. By far the most common is the electrochemical sensor to measure the concentration directly. The methods regularly used to measure oxygen are:

Electrochemical sensor
Partial pressure sensor
Zirconia sensor
paramagnetic measurement.

These systems all have advantages and disadvantages for use in a flue gas analyzer, as will be discussed below.

Electrochemical Sensor:

The electrochemical sensor is, as stated above, by far the commonest type used in a flue gas analyzer. The basic functioning of an oxygen sensor is similar to a battery. It functions as a current source. The lifetime depends on the amount of electrolyte and material present for the reaction, as well as the exposure to oxygen, but lies generally in the region of one to two years. The link will lead to a more complete explanation. The major disadvantages of the standard electrochemical oxygen sensor are a cross-sensitivity to carbon dioxide and a tendency to form a carbonate layer on the internal lead electrode when high concentrations of carbon dioxide are encountered regularly. Added to the limited lifetime, this is a serious disadvantage. The great advantage is the simplicity of the sensor and measuring circuit, and a relative lack of sensitivity to pressure changes. This last point is a great advantage for equipment such as flue gas analyzers that is used in all countries and at all levels. The lifetime of the electrochemical sensor can be increased by leaving it open circuit when the instrument is switched off, but this has the disadvantage that the sensor takes about 20 minutes to settle down after reconnection. The commonest solution is to short the terminals of the sensor when not in use. This detracts from the lifetime of the sensor, but means that the sensor can be used immediately after switching on. One possible solution is to disconnect the sensor when the instrument will not be used for a longer period of time, but this is a somewhat unsatisfactory answer, and raises questions about warranty conditions.

Partial pressure sensor:

The partial pressure sensor is very similar in construction to the electrochemical sensor in many ways. This sensor is mainly used for medical or diving purposes, where the effect on the human body is the most important aspect of the measurement. Naturally, this sensor can also be used for other purposes, such as flue gas analyzers. It has the major advantage of not being sensitive to carbon dioxide, which is a major point when biogas measurements are considered. Since this sensor measures the partial pressure of oxygen directly, it is essential to compensate for ambient pressure if a concentration is needed as a result, which is the case with a flue gas analyzer, for instance. With an ambient pressure sensor, the partial pressure sensor can be used outside of the normal pressure range for an electrochemical oxygen sensor (typically atmospheric +/-10 %) and still measure accurately.

Zirconia sensor:

This has always been popular for fixed flue gas analyzers, so-called CEMS. It has advantages, in that it is not sensitive to carbon dioxide, and can also be used inside the stack, not requiring extractive technology. The most common use, however, is for installations where only oxygen is to be measured, for control of a burner system or chemical process, such as heat-treatment. It is also used in the medical sector, and produces very accurate results if used correctly. Below is a short description of the operating theory.

PRINCIPLES OF OPERATION

Pure zirconium oxide is a monoclinic crystalline material that transforms reversibly to a tetragonal form at 1000°C with a large change in volume. If placed in solid solution, however, with 4% to 12% MgO, CaO or Y₂O₃, it is held in the stable isometric (cubic) form which has no transformation in the range of normal flue temperatures. Due to the addition of these stabilizing oxides, oxygen ion vacancies are created in the crystal lattice. The mobility of O²⁻ ions is greatly enhanced, and under specific conditions of temperature and composition, the conductivity is entirely due to oxygen ions. This condition coincides with the existence of the pure cubic crystalline phase, and is responsible for the oxygen sensing capability of stabilized zirconia.

A minimum quantity of the stabilizing oxides will ensure the existence of the pure cubic crystalline phase of zirconia. When this amount is present, the zirconia is said to be fully stabilized. The commercially available zirconia for oxygen sensors will have generally somewhat less than this minimum amount, resulting in a "partially stabilized" electrolyte with a better resistance to thermal fracture. The zirconia in average sensors contains about 6 mole % (10.5 weight %) of Y₂O₃. The cell construction demonstrates a characteristic typical of electrolytes having unity transference numbers for an ionic species; there is an electromotive force displayed at the terminals that can be precisely related to the corresponding molecular concentration at the two surfaces. In the case of cubic zirconia, the cell voltage is given by a form of the Nernst equation,

$$U_C = -0.01528T_K \log_{10}(p_0/p_1) \text{ millivolts}$$

where T_K is the absolute temperature in Kelvin, p₀ and p₁ are the oxygen concentrations at the inner and outer electrodes respectively.

The major disadvantages of the zirconia sensor are a strong cross-sensitivity to any combustible gases and a sensitivity to dirt in the gas. Whilst this is not a problem in medical applications, a flue gas analyzer is often required to measure dirty gases where combustibles may be found.

Paramagnetic sensor:

The paramagnetic oxygen sensor is a highly accurate measurement technique for oxygen concentration. The major disadvantage to this method is the price. Below is the theory of this type of measurement:

Magnetic properties of gases

All paramagnetic measuring instruments available on the market today utilize the paramagnetic properties of oxygen. Oxygen is one of very few gases with a strong magnetic susceptibility. The movement of the electrons within a molecule generates magnetic moments. A distinction must be made in this context between:

- orbital magnetic moment: movement of electrons around the nucleus, within the orbitals
- spin magnetic moment: the electron's own rotation

External magnetic fields influence these magnetic moments, causing them to align. The orbital magnetic moment responds diamagnetically, in other words aligns in the opposite direction to the external field, thereby weakening it. In contrast, the spin magnetic moment responds paramagnetically, i.e. aligns parallel to the external field and hence strengthens it. Depending on the structure of a molecule, the orbital and spin magnetic moments will be more or less strongly marked, which in turn results in the different magnetic properties of gases. Oxygen has strong paramagnetic properties, while nitrogen responds diamagnetically.

Principle of measurement

There are various different principles of paramagnetic measurement, though in recent years the magnetomechanical or "dumb-bell" principle has come to be used in most measuring instruments. The principle of measurement is based on a sensor in which a dumb-bell comprising two nitrogen-filled spheres is arranged in rotational symmetry within a magnetic field. The gas to be measured passes through the sensor. If the sample gas contains oxygen, the oxygen is drawn into the magnetic field on account of its paramagnetic properties as described above, thereby strengthening the field. The nitrogen inside the glass spheres has the opposite magnetic polarization and is forced out of the field, causing the dumb-bell to rotate. The degree of rotation is directly proportional to the oxygen concentration. To reduce sensitivity to vibration, the dumb-bell's rotation is no longer measured directly in modern sensors. Instead, a mirror is attached at the dumb-bell's rotational axis and symmetrically reflects a beam of light onto a pair of photocells. When the dumb-bell starts to rotate, a potential difference is generated at the photocells. The resulting current is amplified and conducted around the dumb-bell through windings. The current flow generates an electromagnetic countermoment which causes the dumb-bell to return to its original position. The current needed to maintain the dumb-bell in its null position is directly proportional to the oxygen concentration.

Despite years of using the standard electrochemical sensor, the partial pressure sensor is now becoming very attractive due to its lack of reaction to CO₂. This is a cumulative action, where the lead electrode slowly reacts with carbon dioxide to form lead carbonate, and effectively shield the electrode from further reaction. There are appropriate ambient pressure sensors on the market at a reasonable price, which makes it quite possible to change the type without great difficulty. The Photon will be fitted with the partial pressure sensor as standard, as will any flue gas analyzer intended for use with biogas or fitted with a CO₂ sensor in excess of 25 % carbon dioxide. There will in future be a conversion kit, allowing standard electrochemical oxygen sensors to be converted to the partial pressure sensor in most flue gas analyzers.

The zirconia sensor is well-known in most countries and is required in some countries. Despite its disadvantages and higher cost, it will remain popular for its simplicity of use. It will in future at some point be possible to connect a zirconia sensor to the stationary analyzers, to cover this need. Nevertheless, it will never be the mainstay of oxygen measuring technology for portable flue gas analyzers.

The paramagnetic sensor is a wonderfully accurate piece of technology, but both too expensive and too fragile for use in portable equipment. The paramagnetic sensor is used in many CEMS constructions, often as a standard requirement.

For portable use, the partial pressure sensor will possibly become the sensor of choice for many flue gas analyzer applications in the future, not least for its increased lifetime of about five years.