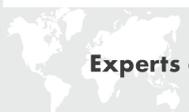


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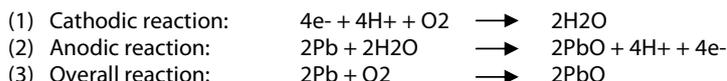
Trace Oxygen Sensors

The trace oxygen sensor can be considered as a lead-oxygen battery which incorporates a lead anode, an oxygen cathode made of gold, and an alkaline electrolyte. Oxygen molecules enter the electrochemical cell through a non-porous fluorine resin membrane and are reduced at the gold electrode. The current that flows between the electrodes is directly proportional to the oxygen concentration in the gas mixture being measured.

All models are a sealed, disposable, aqueous based galvanic cell designed to generate a linear electrical current output directly proportional to the partial pressure of oxygen in a gaseous sample stream. The sensors are maintenance free requiring no replacement of membranes or electrolyte and no cleaning of electrodes. For convenience, when expired, the cells are simply discarded.



In order to explain the chemical reaction the trace sensors filled with potassium hydroxide is a good example. In the chemical reaction (1) four electrons are transferred for each oxygen molecule undergoing reaction. All sensors are using a lead anode and an oxygen cathode with an aqueous potassium hydroxide electro-lyte. Oxygen in the sampled gas diffuses through the membrane and is reduced on the surface of the cathode. A corresponding oxidation reaction (2) occurs at the anode and an electrical current is produced that is directly proportional to the partial pressure of oxygen.



If the sample gas pressure is known, the signal may be interpreted as a volumetric concentration of oxygen. It is designed for measurement of oxygen in inert gas background gases.

The sensing membrane (covering the cathode) is made of PTFE and is mounted over a metal perforated electrode. The space between the membrane and the electrode is filled either with an aqueous alkaline or an acid electrolyte. In normal operation, all portions of the anode and cathode are immersed in the electrolyte. The main body of the cell

is fabricated from high density PVDF. The supporting ring at the face of the sensor is constructed of stainless steel. This results in an oxygen sensor that is chemically resistant to most sampling atmospheres.

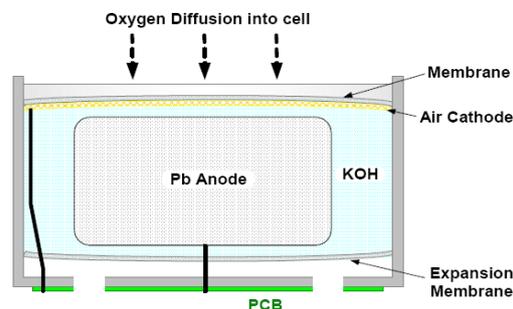


Figure 1: schematic cross-section of a KOH sensor, 2 electrode leads (black) soldered at the PCB

The signal output of the sensor is obtained at two concentric metal foils located at the back end of the cell. Whereas the inner concentric foil is connected to the anode and thus represents the negative polarity and the outer foil is connected to the cathode as positive signal output terminal.

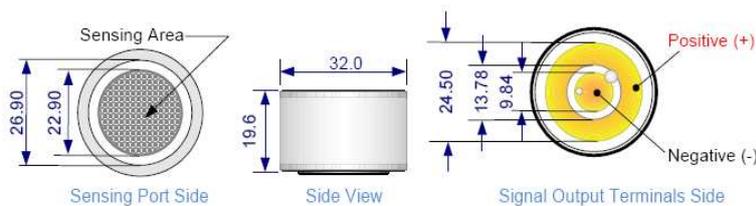


Figure 2: Three side view of trace gas sensor. Do not block the venting holes to be seen on the Signal Output Terminals Side. Through this holes between the concentric metal foils the expansion membrane “breathes” when sudden pressure transients on the sensing area occur.

3.1 Signal Output

The output of all sensors is limited by the partial pressure of the oxygen entering the cell. Oxygen is consumed in the cathodic reaction and likewise, Lead is also consumed proportional to the anodic reaction given above. In air (20.9% or 209,000 ppm) and at standard temperature and pressure, the cell for example generates $460\mu\text{A} + 120\mu\text{A}$ or roughly 2 nano amps for each 1 ppm. Since this particular cell generates an extremely low output at low ppm concentrations, the amplification circuit Interface should be designed to have maximum resolution without adding error due to the sum of electronic component inaccuracies. The circuit should be designed to have minimal electronic noise. It is recommended to keep the amplification circuit physically close to the sensor in order to minimize contact with external electromagnetic "noise" from the ambient environment.

3.2 Temperature

In order to obtain accurate readouts that vary only with changes in oxygen concentration, temperature must be taken into account. The rate at which oxygen molecules interact with the cathode is governed by diffusion through the sensing membrane and a thin film of electrolyte between the membrane and cathode. Since all diffusion processes are temperature sensitive, a varying output current can be expected with changes of temperature (at a constant level of oxygen).

None of the trace gas sensors have a temperature compensating network incorporated.

Each of the cell itself has a positive temperature coefficient of 2.44% per °C at 25°C, thus a negative temperature coefficient as external arrangement is mandatory to obtain accurate readings.

Figure 4 shows a typical plot of the cell's temperature dependence along with minimum and maximum deviations.

As to further temperature compensation coefficients/polynoms, please refer to the according specifications of each species.

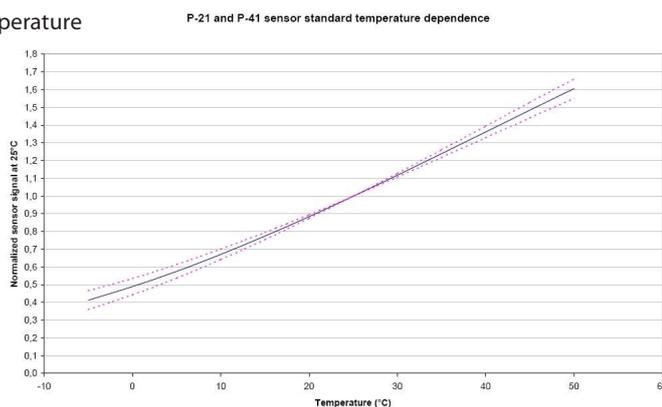


Figure 3: Standard temperature characteristic of trace oxygen cells

Each trace gas sensor must be thermally stable when calibrated and allowed to thermally stabilize after temperature transients.

For best performance, we recommend:

- Allow adequate time for the sensor to equilibrate to a new ambient temperature.
- For best results, perform the calibration procedure at a temperature close to the temperature where analysis will occur.

3.3 Pressure Effects

All trace gas sensors sense the partial pressure of oxygen in the sample gas mixture and hence its output is affected by changes in the overall sample pressure and variations in atmospheric pressure. The flux of oxygen to the working electrode is dependent upon the partial pressure gradient of oxygen across the diffusion barrier (cell membrane). This means that the cell's output signal is directly proportional to the partial pressure of oxygen in the gas mixture. Any changes in atmospheric pressure will therefore result in an equivalent change in output current of the cell. It is important that this characteristic is considered when designing instruments to ensure that back pressure is not applied to the cell when using pumped gas feeds.

So, instrument readouts in volume-ppm's are only correct when the total pressure of the gas being analysed does not change or is compensated for through correlation to a separate pressure signal. In the first case, if the sample pressure is controlled to be constant, then the instrument should be calibrated at a similar pressure and flow rate to the measured sample gas. In the second case, if measuring pressure using a separate sensor, then the oxygen concentration can be calculated based on the absolute pressure of the sampled gas.

3.4 Humidity Effects

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. Humidity, or in other words gaseous water vapor, is just another constituent and its amount of volume (partial pressure of H₂O) contributes to the total pressure. Non-condensing humidity has no effect on the performance of sensors other than diluting the gas. All trace gas sensors can be used in applications where the relative humidity of the sample gas ranges from 0 to 99%, non-condensing. However, it should be noted that water vapor exerts its own pressure in the same manner as oxygen does in a sample gas stream.

In a given sample of gas with a constant absolute pressure, the more humidity that is present, the less the partial pressure of the oxygen constituent will be. In measuring oxygen in a gas sample with the trace gas sensor, if you calculate in terms of volume or ppm, then you must also consider the contribution of the relative humidity (RH). If the RH remains generally constant from the time that a calibration was made in comparison to when a gas sample is measured, then the offset due to RH will be minimal (it is directly proportional to the amount of humidity that is displacing oxygen).

Concerns on calibrations:

If the sensor is calibrated in dry gas and then the sample gas is humidified, the sensor output will correctly generate a signal that is slightly lower than previously measured. This is due to the dilution of oxygen in the sample gas by water vapor.

This characteristic is important to note in systems where both "wet" and "dry" gas streams exist. Additionally, gas streams of high humidity may tend to condense on the sensor. Condensation on the sensor may eventually affect performance. For this reason, it is recommended that the sensor be mounted in a vertical position, facing downward to prevent condensate from flowing onto the sensing surface.

3.5 Response Time

The trace gas sensors have an extremely fast response time to changes in oxygen concentration once the cell has reached equilibrium in the trace range. Exposure to oxygen in concentrations above 1% by volume may result in temporarily saturating the liquid electrolyte of the sensor and may require additional time to reach equilibrium and a fast response time again.

Exposure to "out-of-range" oxygen concentrations is sometimes referred to as "oxygen shock".

< 180 s from 10,000 down to 1000 ppm

< 10 min from 1000 down to 10 ppm

< 5 h from 10 ppm down to < 1 ppm

3.6 Effect of Changing Altitude

As stated earlier, all trace gas sensors are sensing the partial pressure of oxygen in the sample gas mixture and hence their output is affected by changes in the overall sample pressure and variations in atmospheric pressure. If a sensor is calibrated with regards to volumetric units while at sea level, and then the sensor is raised to a higher altitude, the signal would begin to drop and continue to do so if the sample gas references atmospheric pressure. The volumetric concentration of oxygen in the sample gas is the same regardless of altitude, but the partial pressure of oxygen in the sample may change.

3.7 Influence of Various Gases

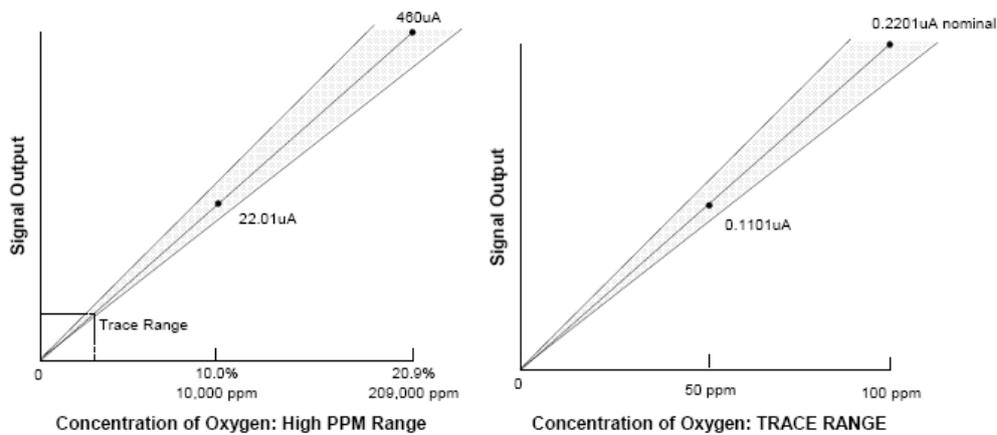
The influence on the sensor from various gases is shown in the Table below. The 'interference level' shown in the table indicates the change ratio between sensor output in oxygen concentrations in gas mixtures containing 0-2000 ppm Oxygen and the contaminant compared to contaminant free gas mixtures. For example, if the interference level of Cl₂ is considered to be 1:2 ratio, then the sensor's output signal in a sample containing Cl₂ plus 100 ppm Oxygen would be equivalent to 300 ppm (100 ppm for the normal oxygen signal and another 200 ppm interference for the chlorine effect).

Gas	Concentration	Interference Level
H ₂ S	<5 ppm	no effect
SO ₃	<10 ppm	no effect
SO ₂	<10 ppm	no effect
HCl	<1000 ppm	no effect
HCN	<1000 ppm	no effect
CO ₂	<1000 ppm	no effect
NO ₂	<1000 ppm	1 ppm → 2 ppm O ₂
Cl ₂	<1000 ppm	1 ppm → 2 ppm O ₂

3.8 Linearity

The signal output is determined by the rate at which oxygen molecules reach the surface of the cathode. This rate is directly proportional to the concentration of oxygen in the gaseous mixture surrounding the cell. That is, the output is linear with the sensor exhibiting an absolute zero. In the absence of oxygen the cell produces zero amperage output. There is virtually no baseline output. The signal output is very stable and linear with virtually no significant hysteresis. The output is extremely repeatable but does decay over the life of the sensor.

Linearity Error: $\pm 2\%$ of signal



4.1 Sensor Lifetime, End of Life

As a basic principle the operating life of all trace gas oxygen sensors is inversely proportional to the amount of oxygen the sensor consumes with respect to the amount of lead anode available. This rate is governed by the average or mean concentration of oxygen that the cell is exposed to throughout its life. Most applications for trace oxygen sensors concern the measurement of the oxygen content in dry gas streams. Sensor life will be generally be limited by the loss of water that ultimately results in sluggish response characteristics and failure to give accurate, trace level readings. When measuring dry gas streams the water from the electrolyte tries to reach equilibrium by diffusing slowly back through the sensing membrane. Acceptable performance can be expected until the electrolyte volume is reduced to approximately half of its original volume. Decay of the sensor signal is towards zero output and happens rapidly near the last month of life.

All trace gas oxygen sensors generally provide excellent results over a two year lifespan when exposed to trace levels of oxygen. In extremely dry atmospheres, the life can be shortened to 8-12 months. Periodic exposure to sample gas containing some humidity can help return water concentration within the electrolyte to normal conditions and thus extend the sensor life.

Life is determined by the level of exposure to oxygen, the amount of lead anode remaining, the dryness of the sample gas, and exposure to aggressive sample gases or background gases.

4.2 Shock and Vibrations

Mechanical shock and vibration may affect the inner structure of the sensor and so should be avoided. Temporary fluctuations in the sensor's output signal may result due to shock and vibration. Depending on the severity of vibration or shock imparted on each oxygen sensor, the signal may recover to its original state after the sensor is kept motionless in normal operating temperature. If the mechanical shock or vibration is great, an irreversible change in the output signal may occur due to structural damage within the sensor. Shock absorbing measures should be used to protect the sensor during transportation or when used for applications in where shock or vibration is likely to occur. Although the sensor is a robust package, it should not be exposed to shock greater than 2 G force.

4.3 Position Sensitivity

The sensor should be mounted in a vertical position with the sensing face pointed down. In portable instruments, the sensor may be mounted with the sensing face pointing sideways. The purpose of these orientations is to facilitate keeping the sensing portions of the cell immersed in the electrolyte and to prevent the cathode/ membrane from drying out. If this were to occur, the sensor's output signal would fluctuate.

4.4 Storage

All trace gas oxygen sensors are originally packaged in a hermetically sealed container (aluminium sheath). In addition each of the cells are packed under a Nitrogen atmosphere. The sensors can thus be stored for periods in excess of six months and still provide 90 – 95% of expected life when finally placed in use.

Furthermore, each cell type will give accurate, reliable readings at all times from the very first moment and beyond. It is not suggested, however, that cells be stockpiled or stored any longer than logistics necessitate. IT Gamber and its local distributor maintain a stock of all cells that can be normally shipped within 2 weeks after receipt of order.

A spare cell should be carefully stored in an area that is not subject to large variations in ambient air temperature (between 5 to 25°C), and in such a way as to obviate any possibility of incurring damage. Never disturb the integrity of the cell package until the cell is to be actually used. If the cell package is punctured and air permitted to enter, the cell will immediately start to react to the presence of oxygen.



4.5 Exposure to organic solvents

Prolonged exposure to organic solvents such as Acetaldehyde, Acetamide, Acetone, Ammonia, Benzaldehyde, Dimethyl Formamide, Ethyl Acetate, Methyl Ethyl Ketone, and Tetrahydrofuran may cause the sensor's external housing (PVDF Polyvinylidene Fluoride) to degenerate and degrade over time, resulting in unstable output voltage. Condensation of such solvents on the sensor could cause adverse influence on output signal and response time.

5.1 Recommended Practises for Sampling System

The trace-gas sensors are versatile devices that can be used to measure gaseous trace oxygen in a variety of applications. It is important to devise the proper sampling system to carry the gas sample to the sensor. Some applications such as monitoring glove boxes can simply monitor the atmosphere by diffusion. No special sampling system may be required. In some cases, you may even be able to install the analyser into the glove box along with the sensor. The remaining types of applications will probably require some form of extraction of sample gas from the process and injecting this sample to the sensor. When devising a system where oxygen to be measured diffuses to the sensor, there are a couple of guidelines to follow:

Diffusion Sampling System

Ensure that the presence of the sensor into the measured process does not admit unwanted contamination. This may be important in high purity applications such as semi-conductor processing or pharmaceutical processing where it is simply forbidden to install a sensor within the process chamber (such as within a glovebox).

- (1) Ensure the glovebox atmosphere is typically in the trace oxygen range. If it regularly goes to atmospheric oxygen levels, then cell life will be shortened and response time to measuring trace oxygen levels will be lengthened.
- (2) Ensure the process environment does not contain contaminants that will damage the sensor. See reliability and characteristics sections of this document for effect of background gases and solvent vapors.
- (3) If the analyser that is connected to the sensor is outside of the glove box or sample environment, then ensure the cabling penetrations into the enclosed area do not allow intrusion of ambient air or moisture.
- (4) Ensure the sampled environment is within normal operating pressures and temperatures.
- (5) Ensure the sensor is protected and the cell membrane cannot be damaged when installed and used within the environment.
- (6) Ensure the sensor is facing downwards so that the internal side of the sensing area remains immersed in electrolyte.
- (7) Ensure that the mounting fixture for the sensor does not impede normal diffusion flow to the sensor face.
- (8) Ensure you have given proper attention to the means to periodically calibrate the sensor. This may require the addition of a flow through head when calibrating. See extractive sampling system below.
- (9) Allow sufficient time to purge the newly installed sensor within the chamber to be measured and ensure exposure to air is minimised (a few minutes is ok).

Extractive Sampling System

- (1) Ensure that all components of the sample delivery system to the sensor are constructed of materials that do not allow oxygen intrusion or permeation into the sampled gas. We suggest using stainless steel tubing and stainless steel flow through head designs to ensure the system is oxygen tight. In some instances, you may be able to combine a high density cell holder (flow through head) that is constructed of high density plastic (such as HDPE or Delrin) along with still using stainless steel tubing.
- (2) Ensure the sampled atmosphere is typically in the trace oxygen range. If it regularly goes to atmospheric oxygen levels, then cell life will be shortened and response time to measuring trace oxygen levels will be lengthened.
- (3) Ensure the sensor is isolated when not in use. This can be accomplished by using stainless steel ball valves on the sample inlet and outlet ports to seal the sensor when not in use. It is usually a good idea to run nitrogen or another inert gas through the cell holder before closing the valves to sweep out any sample at the cell.
- (4) Ensure the sample delivery system does not create pressure above or below the operating parameters given in the specification. As a general rule of thumb, do not go outside of atmospheric pressure + 10%. Remember that the sensor measures the partial pressure of the oxygen in the sampled gas.
- (5) Ensure the sensor is facing downwards in your sampling system so that the internal side of the sensing area remains immersed in electrolyte.
- (6) Allow sufficient time to purge the newly installed sensor within the chamber to be measured and ensure exposure to air is minimised (a few minutes is ok).
- (7) Ensure the gas sampling system is designed to prevent particulates from entering the sensor. Design the system to prevent condensation onto the face of the sensor.
- (8) Ensure the sampling system is designed to reduce any vibration or shock from damaging the sensor.
- (9) Design the sample extraction system to allow a means to admit calibration gas to the sensor.
- (10) Design the sampling system to control the gas delivery to the sensor to a constant pressure (1-3 psig) and constant flow (100 cc/min to 1 litre per minute).
- (11) Design the cell holder so that the sensor can be easily replaced.
- (12) Incorporate temperature compensation or temperature measurement into the cell holder.

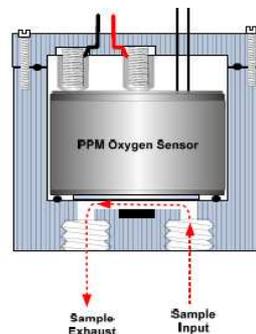


5.2 Installation

A variety of methods may be used to effectively install the sensor into a newly designed analysing system. For ambient measurements such as those in which oxygen is measured within a sealed glovebox, the sensor does not require a complicated sample delivery system. However, in this instance some method should be provided to be able to expose the sensor to calibration gases to compensate for drift.

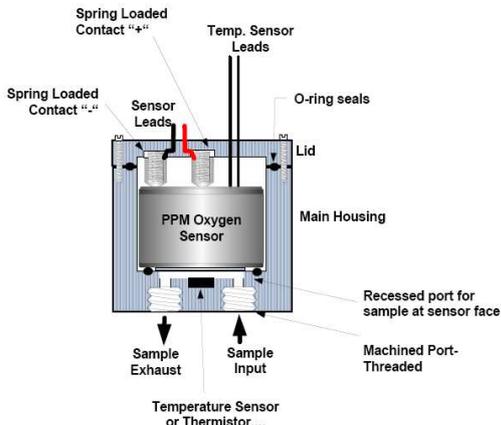
To maintain a liquid electrolyte interface between the anode and cathode, it is recommended that the sensor be mounted in a vertical, upright position so that the sensor face is pointing downwards.

For applications where the sample gas must be extracted from the measured point and injected to any of the oxygen sensors, we recommend that you use a sealed sampling head. The sensor should be mounted within a sealed cavity that has sample gas input and exhaust ports. The sample gas pressure and flow should be controlled to be steady and not to exceed the range listed in the specifications sheet.

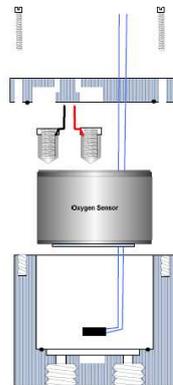


The wetted materials of construction for the sensor gas delivery system should be of a material that does not permit oxygen diffusion nor allow oxygen to stick to its surface. Generally, stainless steel is preferred although some plastics and aluminums may be usable. In general, oxygen sticks to plastic surfaces and diffuses through plastic tubing. Some surfaces of metal tubing and housings such as those made from copper or brass can get oxidized and dramatically slow down oxygen purging. Best to use stainless steel.

The following sketches depicting a suggestion for a sensor sampling system:



Sketch 1 Assembled view



Sketch 2 Exploded View

5.3 Procedure of Unpacking Cells, Sensor Replacement

All trace oxygen cells are designed to operate for extended lifetime before replacement becomes necessary. Reasons for end of life were already pointed out above in this application note. A good sign of this is when drop of output signal leads to an increased calibration frequency. At this time it is advisable to keep a spare cell ready for replacement.

In order to keep the maintenance time short we recommend to remove the old cell from the analyser's receptacle before you start unpack the new cell for immediate installation. As each sensor is packed under nitrogen atmosphere this way of handling shortens the time where the cell gets oxygen saturated by ambient air pressure and thus guaranties a quick run-in ready for low ppm-O₂ measurements in your application.

Never leave sensors unpacked at ambient air pressure for longer than 30 minutes!

Doing so will have significant impact on lifetime. When a new sensor is installed it may take one to two hours or longer to reach equilibrium to calibration gas. The amount it take to come to that level is a function of how long the sensor was exposed to air during replacement. Therefore, it is important that when a new sensor is installed, the time between when it was unpacked and first exposed to calibration gas should be kept to an absolute minimum.



Figure 4:

- Left packaging style a hermitically sealed aluminium sheath
- Top right, top view on the sensor w/ lid + conducting fleece
- Bottom right depicts sensor, lid with venting hole and a conducting black fleece to short-cut terminal when not in use.

5.4 How to Dispose Cells

At the end of each of the oxygen sensors lifetime cells should not be disposed off in normal public waste as they contain some lead and acid/ electrolyte. Care should be given not to puncture the sensor or take it apart. Please, contact your local authorities for environmental legislation to relevant local waste disposal.

6.1 Linearity over Range

The oxygen sensors are extremely sensitive over its operating range. It is a current limiting cell and the output curve will start to flatten out as you approach oxygen concentrations in excess of 25% by volume when new. It is recommended to design your system to operate primarily in the 0 to 10,000 ppm range of oxygen to maintain good response times. As the sensor ages, the curve to flat line shifts towards zero concentration of O₂.

6.2 Electronic Layout

In principle all trace gas sensors do have enough output power to drive readout meters directly without amplification or external power supplies. This usually results, however, in single range capability. However, in most of the oxygen analysers using trace gas sensors a single stage amplification circuit is used as shown in Figure 5.

Since all cells deliver an output current that is strongly proportional to the partial pressure of oxygen at the sensing area the first stage (OP1) amplification should be linear and designed to be an I to E (current to voltage) converter. The current output from the sensor is then applied to the input of a buffer amplifier that converts the current to a voltage and produces a low impedance signal (U_{out}) proportional to the sensor output.

This I to E configuration offers three distinct advantages.

- 1) The cell operates into a short (zero-ohm load) which is the ideal for best linearity and rapid response.
- 2) The effects of amplifier voltage offset are minimised.
- 3) sensors can be located at a distance (up to 1 meter, 3 feet) from the remainder of the analyser without pre-amplification or noise pickup problems.

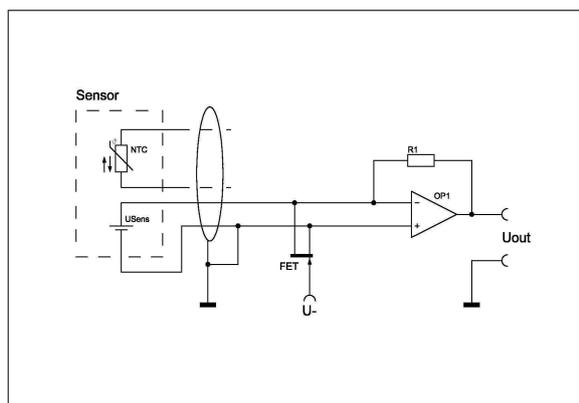


Figure 5: A typical electronic configuration of a first stage amplifier OP1.

An N-channel field effect transistor (FET) is located across the inputs of the I to E converter to provide a low resistance current path for the cell when the analyser is switched off (not in operation). When the gate of the FET is powered, the source to drain resistance can be considered as "open circuit" (approx. 10 to the 12th power ohms). When negative power is removed, this resistance drops to almost "closed circuit" (approx. 30 ohms).

With reference to Figure 5, the output of the first stage of amplification is as follows:

$$U_{out} = -I \times R1$$

Where U(out) is the output voltage, I is the input current (the current output of the according sensor) and R1 is the negative feedback resistance. This feedback resistance can be changed in order to match the amplification span to the adjacent electronic, an A/D converter for instance. 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 the above equation.

A possible second stage of amplification can be used to effect temperature compensation. It is strongly recommended to place the thermistor remotely or at the same location as the cell.

6.3 Intrinsic Safety Considerations

As per the general requirement of EN 50014 in section 1 clause 1.3 a device as defined may not exceed at any time one of the physical values 1.2 V; 0.1 A; 20 μ J or 25 mW.

There are 2 cases to consider:

Case 1: "Open circuit"

A batch of cells were tested to work on a load of 1×10^9 Ohm at 20.9 Vol% O₂; 1013mBar, 50°C.

The max. output voltage did not exceed 820 mV.

Case 2: "Short circuit" and "Operating condition"

A batch of fresh cells were tested to work on a load of 10 Ohm at 20.9 Vol% O₂; 1013mBar, 50°C. The short circuit has been performed and the transient function recorded.

At no time the peak current of the core cells exceeded values of: 899 μ A.

As a result the maximum output power generated was not more than: 740 μ W.

Hence, according to the above each sensor of trace gas family for itself is an intrinsically safe device.

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