

# Oxygen Measurement in Natural Gas

## Application Background

Natural Gas Fuel is primarily methane. If it were pure methane, it would be very simple to transport and use. But it comes out of the well as a mixture of many different chemicals, many of which are considered contaminants in this fuel. After 'sweetening' (removing the acidic components, CO<sub>2</sub> and H<sub>2</sub>S), processing and transporting the gas, Oxygen (O<sub>2</sub>) is usually listed as one of these contaminant gases.

Oxygen in the pipeline is a contaminant for any customer in this supply chain because oxygen reacts with the other constituents of the gas. This document will address measuring oxygen in the natural gas fuel. At the end of the pipe the fuel is burned. This is also where oxygen plays a major role in this industry. Ensuring there is sufficient O<sub>2</sub> for complete combustion, while limiting the parasitic heat loss of heating the combustion air, can help to maximize the efficiency of the burner.

## Where Does The Oxygen Come From?

In the natural gas well, oxygen is a rare occurrence and then only in extremely small concentrations. There are significant sources for the O<sub>2</sub> content in the pipeline. Leakage, maintenance activities, and vacuum extraction processes are the main methods that introduce O<sub>2</sub> into the gas pipeline stream.

The problem with the presence of oxygen in this fuel has increased because producers use vacuum to extract as much natural gas as possible from plays that are nearly depleted. Vacuum pumps exacerbate the issue of leakage and have the potential to pull air into the inlet of the compressor as well as into the fuel. Keep in mind the scope of the volume of gas involved in this industry as many pipelines can carry enormous quantities of gas daily at very high pressures. If the gas contains 0.2% oxygen, it can be a very large volume of this contaminant and still be within specification.

Oxygen also comes from leaks in the pipeline or in processing equipment. Leakage of O<sub>2</sub> into the pressurized gas is not as intuitive, since the escaping gas won't totally prevent the outside environment from ingressing against it. The issue is one of relative vapor pressure. The problem happens when the vapor pressure of oxygen in air, which is roughly 157 mmHg, and the oxygen vapor pressure inside the pipe at 1000 psig with 200 ppm<sub>v</sub> oxygen is just 10.5 mmHg. This represents a pressure ratio of nearly 15:1 pushing the oxygen into a leak in the pipe even at 1000 psig.

**Oh, The Damage A Little Leak Can Do!**



A Natural Gas stream at 1000 psig with <200 ppm<sub>v</sub> O<sub>2</sub> has a leak.

Outside the pipe is 20.7% O<sub>2</sub>.

The Natural Gas will be pushed out of the leak by a pressure ratio of ~69:1.

Oxygen will 'leak' into the pipe pushed by a pressure ratio of **15:1!**



Maintenance activities can be sources of additional leakage and contamination. Pipelines and processing equipment should be isolated if possible to reduce this contamination and ingress of air into the process/pipeline. Once the maintenance activity has been completed, the equipment should be purged with an inert gas, e.g. argon, which is not reactive, or natural gas.

At the point of use the mixture of fuel to air is critical. The O<sub>2</sub> comes from the ambient air to support the combustion process. Large natural gas customers' concern in burning is efficiency so monitoring the O<sub>2</sub> content in the exhaust of the burner is a measure of the efficiency. This measurement also provides a safety alert should the O<sub>2</sub> level fall below a lower limit.

## Why Is O<sub>2</sub> Measurement Important?

There are several reasons why O<sub>2</sub> is undesirable in natural gas. These reasons drive the need to monitor this contaminant.

- O<sub>2</sub> does not add to the heating value of the gas and is not of benefit.
- O<sub>2</sub> combines with other chemical gases, especially H<sub>2</sub>S, to form acids.
- O<sub>2</sub> degrades amine, which inhibits the process of removing CO<sub>2</sub> and H<sub>2</sub>S from the gas chemically.
- O<sub>2</sub> can degrade some mercaptans reducing the effectiveness of these odorants in the gas.
- O<sub>2</sub> accelerates corrosion in the mechanical components that come in contact with the gas.

Monitoring the oxygen content of this fuel to alert to a potential danger from this contamination is a critical measurement. Limits vary globally and from tariff to tariff ranging widely from a maximum of only 10 ppm to <1% by volume. North American maximum limits are generally found to range from 0.1 to 0.2% by volume. The industry appears to be moving these limits downward across the board due to oxygen's detrimental impact on the gas infrastructure and the economics of processing.

Keep in mind that while using any measurement method, humidity will change the reading. According to Dalton's Law, moisture displaces other molecules and inversely impacts the O<sub>2</sub> concentration.

## Current Measurement Methods:

There are several methods for oxygen measurement in Natural Gas applications. The most common measurement methods are:

- Galvanic (dry electrochemical) Method
- Coulometric (wet electrochemical) Method
- Paramagnetic Method
- Fluorescence Quenching Method (Oxygen Optode)
- Gas Chromatography Method

### Galvanic Method

#### Operation

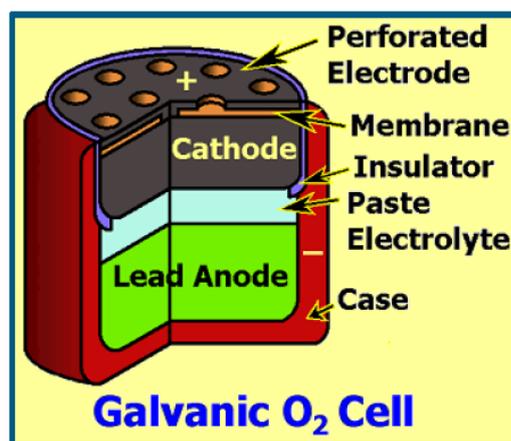
This galvanic sensor (dry electrochemical, coulometric or "echem" method) is analogous to a dry-cell battery that produces a small current in the presence of oxygen. A porous membrane allows the sample to contact the cathode, made of a noble metal, usually gold or silver. The O<sub>2</sub> is reduced by the oxidation of the anode of lead. This cell also contains an electrolyte paste to allow the conduction of the electrons to form the battery. The electrical connections allow the current flow and measuring this current determines the oxygen content at the cell.

#### Sensor Life

This is consumable sensor where the anode is consumed or oxidized during its use at a rate dependent on the quantity of O<sub>2</sub> in the gas. These cells are often sold for the range of oxygen to be measured. To extend cell lifetimes, additional lead is often used for the higher O<sub>2</sub> ranges.

#### Interferences

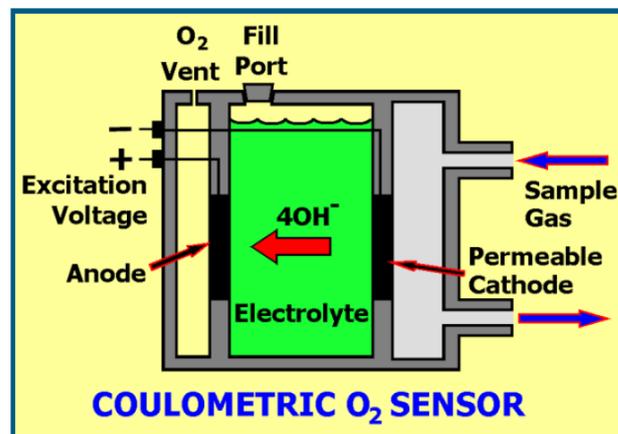
- These cells are immune to interference by most gases.
- CO<sub>2</sub> reacts with the electrolyte in most KOH based sensors and is usually not recommended above a few ppm of CO<sub>2</sub>. Acetic acid based sensors are available for use in backgrounds with more than 0.5% CO<sub>2</sub> present.
- Temperature is compensated using a temperature sensor and algorithm for the final reading.
- Pressure will have little impact if it is equal on both sides of the sensor. Rapid pressure changes are certainly not recommended.



## Coulometric Method

### Operation

This coulometric sensor (Clark Cell, amperometric, wet electrochemical or polarographic method) is analogous to a wet-cell battery that produces a small current in the presence of oxygen. In other words, there is a chemical ion exchange where the current flowing under an applied excitation between two electrodes in a solution is enabled by oxygen. Like the galvanic cell above, a porous membrane allows the oxygen to diffuse into the wet cell. The cell is filled with a KOH solution where the anode, made of a noble metal, usually silver, and the gold cathode are mounted. The oxygen in the sample is electrolyzed and moved from the cathode to the anode driven by an applied voltage. The current is directly related to the concentration of oxygen in the sample. The electronics scale and translate this current into a useable value.



The cell reacts quickly to changes in oxygen in the sample and is not consumed in the process. The analogy of the dry-cell vs. wet cell batteries is similar where the wet-cell is rechargeable and the old style dry-cell is not.

### Sensor Life

Because the electrodes are not consumed during the measurement or exposure to oxygen, this cell has a long life reaching 5 years of service in many applications. To prevent cell damage, the level of the KOH solution must be maintained by adding distilled water.

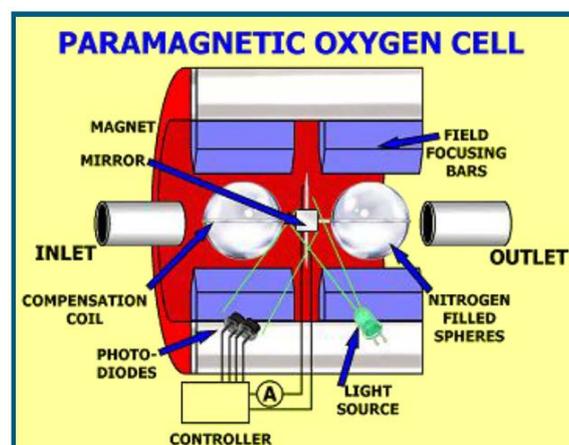
### Interferences

Although even moderate concentrations of acid gases can damage the cell, additional protective electrodes can be installed to minimize these acidic chemical effects.

## Paramagnetic Method

### Operation

The Paramagnetic Method uses an unusual property of oxygen molecules - they can be attracted by a strong magnetic field. The sensor is essentially measuring the displacement of other gases by the concentration of the O<sub>2</sub> molecules. Magneto-dynamic sensors have glass spheres filled with nitrogen that would be displaced by the concentration of O<sub>2</sub> in the strong field. Current through a coil to counteract this force is proportional to the O<sub>2</sub> content.



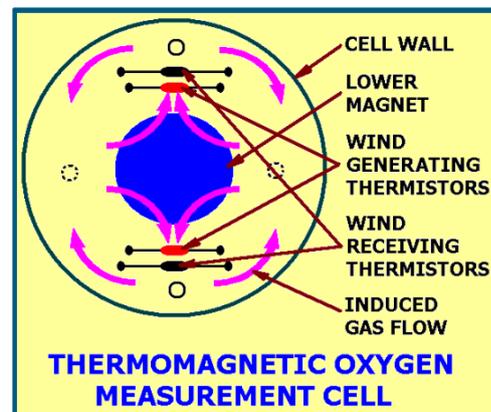
Thermo-paramagnetic cells have no moving parts and are able to detect the flow of a "molecular wind" using a "hot wire" detection technique. The "wind" is created as the oxygen molecules attracted to the strong magnetic field inside the cell find a heated escape route of heated thermistors. This heated gas transfers some of that heat to a sensing thermistor and this transfer is proportional to the flow of gas, i.e. oxygen concentration. For use in hazardous/classified locations the cell is mounted in a suitable enclosure.

### Sensor Life

There are no consumables in this sensor and the drift rate is very low. Sensor lifetimes are limited only by the presence of any corrosive components in the gas and by accumulations of particulates.

### Interferences

Any background gas that is present in the sample that differs from the calibration will have an effect on the measurement. This can be remedied by an offset in the field adjustment or calibrated out in the factory.

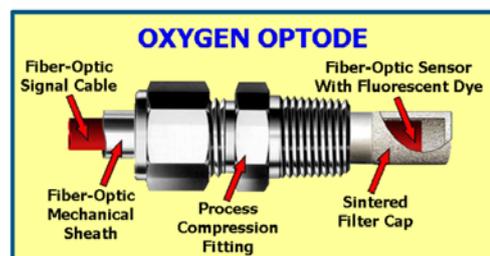
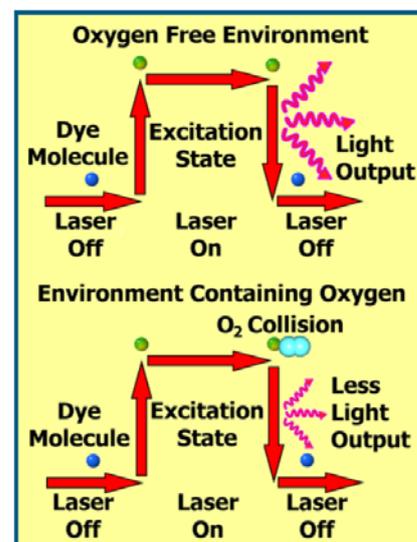


## Oxygen Optode or Fluorescence Quenching Method

### Operation

Many chemicals have the property of fluorescence, i.e. they can be excited by an external source to produce this luminescence. Some of these same materials lose this property in the presence of other non-associated chemicals. Specific to the measurement of oxygen, a specific chemical deposit/dye of an optical fiber gives an opportunity to measure the O<sub>2</sub> content in a sample.

The sensitive chemistry is either coated onto an optical fiber, or the tip of the fiber is dyed with the chemical. As all fluorescent materials require excitation, the optical fiber is excited by pulsing it with a laser light of the required wavelength. Between the pulses of light, the light generated by the chemical fluorescence is measured by a spectrometer. Oxygen content of the sample counteracts the fluorescence in a proportional way. The more O<sub>2</sub>, the less light is generated from exciting the chemical to fluoresce. This light is more sensitive at low levels of oxygen in the sample.



### Sensor Life

Sensor lifetime is good, but it is often recommended that it be reconditioned annually for best performance. Any chemical interaction that might impact the chemical dye will cause the sensor to lose its ability to measure accurately.

## Interferences

Since this sensor depends on the density of the O<sub>2</sub> molecules it is pressure and temperature sensitive and these effects must be compensated. Samples that contain particulates can cause backscatter and interfere with the accuracy. Proper sample handling is essential because any sensor contamination that slows equilibration will slow response speed and may cause significant errors.

## Gas Chromatography Method

### Operation

GCs can provide the oxygen content in natural gas but require an additional “molecular sieve” column to discriminate O<sub>2</sub> from any nitrogen in the gas. This measurement method does not provide this data point in the standard GC configuration for BTU analysis, but requires that accessory column along with its supporting valve system. Cycle times for the GC are extended to provide the time for the O<sub>2</sub> analysis. The installed base of field GCs is very large because they are used to determine the heating value of the gas. Very few of these have the required column installed and most cannot be retrofitted for this feature.

In addition to the special column and valving, the calibration gas mixture is also required to contain a representative concentration of oxygen in the mixture. Calibration gas must be used in order to ensure that the GC remains accurate. Field GCs can detect down 0.01% O<sub>2</sub> LDL so they would detect the minimum concentration needed to meet most tariff quality specifications with the smallest range of 0-1% O<sub>2</sub>.



### Sensor Life

Sensor lifetime is governed by the sample quality provided to the chromatograph. If even a slightly contaminated sample is supplied to the columns, they will eventually plug and lose their ability to provide accurate sample analysis.

## Interferences

Without the correct column and proper sample conditioning system, nitrogen can strongly influence the data peak where oxygen is found. This is due to their proximity and drives the need for a special column to separate these two gases ahead of the detector.

## Current Measurement Methods Summary:

Method	Positive Points	Negative Points
Coulometric	<ul style="list-style-type: none"> <li>High accuracy and stability</li> <li>Long sensor life</li> <li>Acid gas resistance with optional additional electrodes</li> <li>Can handle oxygen shock</li> <li>Fast response</li> <li>No false low readings</li> <li>Mid-range pricing</li> </ul>	<ul style="list-style-type: none"> <li>Requires rebuilding to clean the anode every 5-6 years</li> <li>Electrolyte needs to be replenished regularly with distilled water</li> <li>Longer warm up time</li> <li>Low pressure only, some to 100 psig max.</li> </ul>
Fluorescence Quenching	<ul style="list-style-type: none"> <li>Fast response</li> <li>Immune to H<sub>2</sub>S</li> <li>No interferences in natural gas</li> <li>Reliable</li> <li>Minimal Maintenance</li> <li>Long sensor Life</li> <li>Easy to calibrate</li> </ul>	<ul style="list-style-type: none"> <li>Higher initial cost</li> <li>Requires temperature and pressure correction</li> <li>Sensor will not tolerate chemicals that attack the fluorescent coating/dye</li> <li>Sample pressures to 200 psig</li> </ul>
Galvanic	<ul style="list-style-type: none"> <li>Fairly easy to use</li> <li>Portable, light and easy to power from batteries</li> <li>This technology is competitive so cells are plentiful</li> <li>Low initial cost relative to other technologies</li> <li>Robust sensor</li> <li>Sensing is independent of an external power source</li> <li>Short warm-up time</li> <li>Pressure to 30 atm if both inlet and outlet are at equal pressure</li> </ul>	<ul style="list-style-type: none"> <li>Being a consumable transducer, the instrument needs monthly, or even more frequent, calibration.</li> <li>Can become slower to respond as the cell ages.</li> <li>Cells exposed to high oxygen levels including exposing the cells to the atmosphere fail prematurely.</li> <li>Cells fail low or "Unsafe" giving a false sense of security.</li> <li>High oxygen exposure translates into longer recovery time to return to a "normal" low reading</li> <li>Cells cannot tolerate overpressure or vacuum when there is a significant pressure differential between the inlet and exhaust.</li> <li>H<sub>2</sub>S degrades the sensor components – a scrubber needs to be fitted.</li> <li>Sensors/cells have a limited shelf life.</li> <li>Atmospheric pressure operation is recommended.</li> </ul>
Gas Chromatography	<ul style="list-style-type: none"> <li>Familiar instrument to Instrument Technicians</li> <li>Consolidates measurements into one instrument</li> </ul>	<ul style="list-style-type: none"> <li>Higher instrument cost and complexity</li> <li>Calibration gases are more expensive</li> <li>Lower detectible limit is ~100 ppm<sub>v</sub></li> <li>Low pressure only</li> </ul>
Paramagnetic	<ul style="list-style-type: none"> <li>Medium priced instrument</li> <li>Sensors can be calibrated on-site using a calibration gas source plumbed to the sensor or air.</li> </ul>	<ul style="list-style-type: none"> <li>Can be sensitive to changes in the flow rate of the sample gas</li> <li>The presence of minute particulates and moisture can interfere with the accuracy in some designs</li> </ul>



## Sampling for Oxygen Measurement in Natural Gas

In natural gas, sampling is required with all oxygen measurements due to the lack of pressure capability of all these sensing technologies. Optimal performance of all the technologies above can be achieved by controlling pressure, flow and temperature, as well as having a clean sample free from liquids. Sample systems should include the following basic characteristics:

- Sample probe per API 14.1 with optional pressure reduction and filtration/liquid rejection
- Short Sample lines
- High bypass or fast loop design to maximize speed of response
- Liquid removal with membrane bypass filters
- Particulate filtration
- Pressure regulation using a heated regulator to manufacturers' specification
- Flow control to manufacturers' specification
- Temperature control within the sample system enclosure for minimum drift
- Minimum components to reduce incidence of leakage
- Ability to easily valve in a calibration gas to the sensing element
- Block and bleed valving for safe servicing

All of these issues should be addressed in the design of the sample system for oxygen measurement in natural gas. Stabilizing all possible variables will aid in the accuracy and stability of all sensing elements.

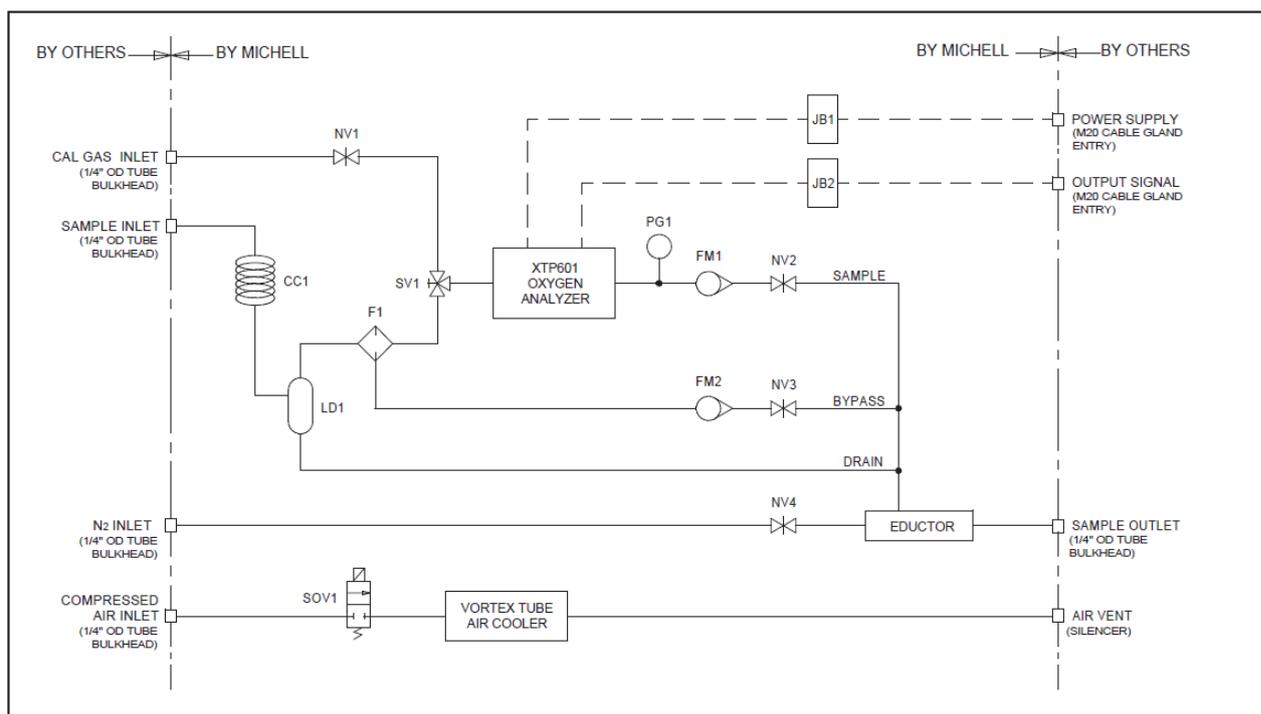
## Michell's Solution: Measuring Correctly

### Thermo paramagnetic analyzer

Use a thermal paramagnetic transmitter connected to the natural gas sample from the pipeline. The sample system must include pressure reduction and membrane filtration to ensure a clean gaseous sample to the sensor.

### How should the instrument be connected?

The connections for the analyzer should be simple - from a pressure reducing sample probe in the pipeline to the sample system as described below. This system includes the membrane filter ahead of the XTP601 then the sample is exhausted to a vent or flare. For added convenience a calibration gas can be connected but should have no path for the calibration gas to return to the pipeline (see flow diagram on the next page.)





## Cost justification: What can happen if the O<sub>2</sub> is not monitored correctly?

If oxygen level is too high in the gas:

- Corrosion can substantially decrease the life of the pipeline and/or gas processing components.
- O<sub>2</sub> degrades amine which inhibits the process of chemically removing CO<sub>2</sub> and H<sub>2</sub>S from the gas
- It can degrade some mercaptans reducing the effectiveness of these odorants in the gas.

All of these important issues can become very expensive if O<sub>2</sub> is not monitored and much more costly than installing an oxygen measuring system so that proper operation is maintained.

## What should be used for this application

Use an XTP601 with a sample system and choose any additional options or accessories that may be needed. Consult with your Michell Representative for sample system recommendations.