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## DETERMINATION OF TRACE OXYGEN IN NATURAL GAS

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### Introduction

The necessity for trace oxygen measurements is increasing with requirements below 100 or 10ppmv. An understanding of the considerations when choosing technology for measuring Oxygen is useful especially for remote locations or locations with high levels of corrosive contaminants such as CO<sub>2</sub> and H<sub>2</sub>S. This paper discusses a variety of measurement methods used in natural gas such as Galvanic Cell method, the Quench Florescence method and the Gas Chromatograph method.

Oxygen can be found in various types of natural gas streams. These streams include vacuum systems and traditional pipeline systems. Vacuum systems include landfills, vacuum oil recovery systems, and coal mine methane, all of which can contain percent-level oxygen whereas traditional pipelines typically contain only 100 ppm of oxygen.

When oxygen is found in a natural gas stream, it can cause various problems including degradation of process chemicals (for example, amine) and increased corrosion in pipelines. Pipeline specifications are normally set at 10 ppmv to 2000 ppmv (depending on the region or the system). At percentage levels, oxygen is dangerous in the presence of natural gas and hydrocarbon gases due to the flammability of the mixture.



Figure 1: Diatomic oxygen molecule with double bond

### Physical

Molecular	32 g/mole
Boiling Point	-182.95°C, -297.31°F
Gas density (STP)	1.354 kg/m <sup>3</sup>
Compressibility Factor (STP)	0.9994
Specific gravity (STP)	1.105
Limiting O <sub>2</sub> Concentration in CH <sub>4</sub>	12%
STP	“Standard Temperature and Pressure” = ~20°C and ~1 Bar

### Measurement Concentration Units

PPM/V = Parts Per Million by Volume

PPM/W = Parts Per Million by Weight

Percent = % of total gas (10,000 PPM/V = 1% molar ratio by volume)

## Why Measure?

- Personal Safety – O<sub>2</sub> mixed with natural gas can be explosive
- Corrosion Protection – O<sub>2</sub> when combined with CO<sub>2</sub> and H<sub>2</sub>S can cause corrosion and pitting in steel
- Contractual Agreements – Many custody transfer contracts have oxygen limits from 10 to 2000 ppmv
- Gas Processing – Protection of scavengers in natural gas processing plants is important economically and important for process control

## Where does oxygen come from?

Typically oxygen does not come from underground or from the well where natural gas is produced. Oxygen is typically introduced into natural gas through unintended leaks and generally occurs in natural gas gathering, vapor recovery systems, and compression systems. For example, boosters and VRU's may take gas from an overhead space and cycle on and off. A fast responding oxygen measurement system will enable the operators to correlate oxygen spikes with certain operational activities.

Additionally, oxygen may be introduced by maintenance activities or construction. For example, it is common to purge a compressor with natural gas after it has been rebuilt before bringing it back into service. An oxygen measurement is a convenient method to determine that the purging is complete.

## Sampling for On-line Measurement

Gas sampling for on-line O<sub>2</sub> analysis is fairly straightforward. Refer to ASTM D5503 "Standard Practice for Natural Gas Sample-Handling and Conditioning Systems for Pipeline Instrumentation". For accurate measurement it is critical that the gas sample containing a representative concentration of O<sub>2</sub> reach the analyzer in the shortest period of time possible. The response time of most analyzers can be many times faster than the delivery time of the gas sample from the sample tap to the analyzer unless the velocity of the sample is considered in the design.

The sample extraction system will typically consist of a sample probe (to obtain a sample from the center of the flowing gas), a regulator to reduce pressure as close as possible to the sample tap, and a sample transport line made of stainless steel tubing. The probe and tubing should be heated to avoid condensation if the dew point of the gas is near the lowest ambient temperatures known for the region in which it is installed. A heated regulator should be used if the pressure drop is significant enough to cause a drop in temperature (i.e. the Joule-Thomson effect) enough to create condensation in the regulator.

If the analyzer is sensitive to corrosive compounds in the stream, such as H<sub>2</sub>S or CO<sub>2</sub>, then the sample system may require a scrubber system immediately upstream of the analyzer to eliminate the offending compounds. The scrubber systems (one or more ~1-liter containers with solid material used to scrub the gas) must be maintained to avoid breakthrough of the offending gases. The spent materials from the scrubber(s) must be disposed of in accordance with the appropriate regulations. The material must be handled in accordance to the MSDS and DOT rules.

Typically, the analyzer will also have a sample conditioning system (SCS) immediately upstream of the analyzer to further reduce pressure to atmospheric levels, to control the flow rate to the analyzer, and to filter solids and liquids that may have been caught in the stream. Additionally, the SCS will have a bypass loop which splits the gas flow into two parallel paths; one that flows through the analyzer (the filtered gas) and one that bypasses the analyzer (the bypass can carry "dirty" gas that was removed by the filtration). The bypass also allows the user to demand a higher flow rate of gas from the sample tap thus increasing the velocity of the stream to the analyzer. For this reason it is sometimes referred to as a speed loop. ASTM D5503 has detailed descriptions and diagrams explaining this.

## Measurement Technologies

There are several technologies for measuring concentrations of O<sub>2</sub>. This section briefly describes the more popular methods used:

**Gas Chromatography (GC)** – A standard natural gas GC with thermal-conductivity detector (TCD) will report a concentration that has nitrogen (N<sub>2</sub>) and oxygen (O<sub>2</sub>) as a combined value. Optionally, the GC can be configured by the factory to measure oxygen separately too. However this is not the most common way to do the measurement because of the added complexity. An additional switching valve and columns are required which increases the complexity of the analyzer especially during maintenance and troubleshooting and increases the time required for the measurement. The minimum detection level of the GC will typically be 100 ppmv.

The advantage is that the measurement will not be compromised by high levels of H<sub>2</sub>S or other corrosives because the GC separates all of the compounds. Additionally, if the end user is very familiar and comfortable with GC's and must have a GC on site for other measurements, then adding the option for oxygen may be advantageous.

**Electrochemical** – The most common method of measuring oxygen at this time is the electrochemical or "galvanic" method. It is a chemical sensor that quantitatively measures oxygen by electrical output produced by the sensor that utilizes an electrolytic solution, and a cathode and anode. A gaseous sample at a constant flow rate is passed over the electrochemical cell. Oxygen diffuses into the sensor through a membrane and reacts chemically at the sensing electrode to produce an electrical current proportional to the oxygen concentration present in the gas. The sensor cell is a consumable and replaceable component with an expected life measured in weeks or months depending on the application factors. After the cell is replaced, the instrument is recalibrated.

Interferences such as H<sub>2</sub>S, oxides of sulfur or oxides of nitrogen can produce false readings and reduce the expected life of the cell. Scrubbers are used to remove these compounds. For gas streams with these compounds, or with high concentrations of CO<sub>2</sub>, the analyzer manufacturer must be consulted to determine if the instrument will perform and to make recommendations for successful implementation.

The advantage of this type of analyzer is the relatively low upfront cost. However, it will require a high level of attention to be sure the analyzer is working properly over time. The cell may fail unsafe (failure with a permanent low reading) so regular validation is important. Care must be put into the disposal of the spent electrochemical cells because they can be messy and may be considered hazardous waste in some areas. If scrubbers are used, maintenance and disposal of spent material must be considered.

**Quench Fluorescence** – Quench Fluorescence (QF) is a technique that has been used for several decades in the pharmaceutical and other industries for measuring dissolved oxygen in liquid streams. Recent developments have made the technology available for trace measurements (detection limit of 0.5ppmv) in vapor phase. QF sensing is an optical technique that uses a substance that when excited by light, will "fluoresce" with a very predictable emission of return light. When oxygen is present, the emission will be quenched (or dampened) in proportion to the concentration of the oxygen in the stream. The sensor is immune to high levels of H<sub>2</sub>S or other corrosives in natural gas and requires very little maintenance. The advantage is that the overall cost to operate the analyzer is very low. However the upfront cost is higher compared to electrochemical cells.

## Calibration/Validation

Regardless of the technology employed, it is imperative that calibration or validation be performed periodically to insure accuracy. Some analyzers are susceptible to calibration drift, zero drift, desensitizing or interferences. Periodic validation & calibration assures the user that the calibration of the analyzer stays accurate. Depending on the analyzer make and model, and the criticality of the measurement, calibration or validation once a month, once a quarter or semiannually is sufficient. In the case of the electrochemical sensor, a calibration is required each time the cell is replaced.

## Conclusion

Measurement of O<sub>2</sub> is becoming more critical as gas quality requirements become more stringent. Whether the purpose is to control below the explosive limits of oxygen and fuel or for corrosion control, it is critical for personal safety and pipeline quality. Several technologies exist to perform this function and care should be taken to select the technology and brand of instrument that best suits the application requirements. Upfront costs as well as the cost of operation over time should be considered in the decision.