Process Oxygen Monitoring in Vapor Recovery, Flares and Condensing Process Streams

Introduction

There are many organic vapor streams where it is critical to monitor the oxygen concentration to minimize the risk of explosion. For example, the headspace of a refinery wastewater treatment plant oil/water separator can typically contain volatile compound levels exceeding the **Upper Explosive Limits (UEL)** and therefore nitrogen blanketing is carried out to generate a non-combustible atmosphere with acceptably low levels of oxygen. One way to increase safety and minimize the use of nitrogen simultaneously is to control nitrogen blanketing as a function of oxygen concentration in the headspace. The objective is to prevent the oxygen concentration from exceeding the so called **Limiting Oxygen Concentration (LOC)**, which is specific for each product that is blanketed.

The oxygen measurement is typically carried out in the process line where the oil/water headspace is suctioned to one of two thermal oxidizers or flares. When oxygen level exceeds the safe limit of operation, a nitrogen purge of the tank headspace is initiated to keep oxygen at safe levels below upper explosive limits (typically <2% O_2). By measuring the oxygen concentration in the headspace, the nitrogen consumption can be optimized to keep the operating costs low while insuring safe plant operation.

This Application Note will compare the advantages and disadvantages of **Tunable Diode laser Absorption Spectroscopy (TDLAS)** based analyzers versus the more traditional **Paramagnetic Analyzers** as applied to the analysis of oxygen in **Volatile Organic Compounds (VOC)** vapor streams.

A Comparison of Paramagnetic and TDLAS VOC Oxygen Measurements

Magnetic wind and thermo-magnetic type paramagnetic analyzers are suited for many oxygen concentration monitoring applications but this approach has proven to be problematic in many ways for the VOC headspace application.

The following is taken from the literature of a leading paramagnetic analyzer manufacturer.

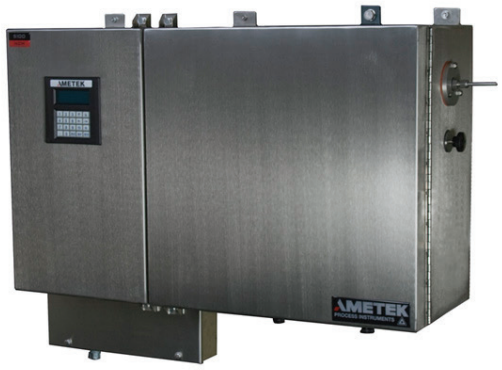
"Paramagnetic analyzers always needs sample conditioning, filtering, pressure / flow control, heating and drying. For example, if streams require heating or contain particulates, high boiling components or inorganic material, sample extraction can result in high maintenance. Sample extraction and conditioning is especially demanding when the measurement involves chemically reactive or unstable or explosive constituents."

High moisture concentrations in the sample streams are a serious problem as moisture significantly decreases the life of the paramagnetic cell. Also, the typical maximum paramagnetic cell operation temperature of <90ºC prevents keeping the sample in vapor phase above the dew point of many gas streams. One method to prevent condensation is to remove water and higher molecular weight hydrocarbons. **Knocking Out (KO)** the moisture using a coalescing filter is an ineffective approach as the filter quickly becomes saturated and moisture carries over to the analyzer. When a thermoelectric sample cooler is used, the sample condensate from the cooler is considered a hazardous pollutant stream and is required, by law, to be pumped back back to the oil/water separator using heat traced transport lines. For this reason, a technology that can measure a hot-wet sample is much preferred over the paramagnetic dry-sample approach.

Several measurement technology options are available for hot/wet sample analysis; however, all have significant drawbacks as compared with **Tunable Diode Laser Absorption Spectroscopy (TDLAS)**. Comparison of these options from the viewpoint of moisture, H_2S, VOC interference, temperature limits, requirement of filter and contact with sample is presented in Table 1 to illustrate why laser spectroscopy is a better option.

TABLE 1: Technologies for Measuring Oxygen in VOC Streams

Technology	Moisture Interference	Temperature Limit	KO Required	VOC Interference	H_2S Interference	Product Contact
Magnetic Wind and Thermomagnetic (Paramagnetic)	Yes	<90ºC	Yes	Yes	No	Yes
Electrochemical Cell	Yes	<40ºC	Yes	Yes	No	Yes
Flourescent Quenching	No	<50ºC	No	Yes	No	Yes
Polarographic	No	<79ºC	No	Yes	Yes	Yes
TDLAS	No	<150ºC	No	No	No	No



Model 5100 HD - The Tunable Diode Laser Absorption Spectroscopy (TDLAS) Solution by AMETEK

It is well known that the results of a paramagnetic measurement are influenced by hydrocarbons present in the sample stream. Table 2 shows the hydrocarbon related errors reported by two paramagnetic analyzer manufacturers. Most paramagnetic oxygen measurements are made on a dry gas sample. Drying the sample stream can result in an error of around +/- 0.6% oxygen at a moisture level of 7%. In contrast the TDLAS measurement is made in a hot/wet manner using a laser wavelength which is totally free from all hydrocarbon and moisture interferences.

TABLE 2: Paramagnetic Matrix Gas Interferences

Gas	Volume %	Interference % Oxygen Vendor A	Interference % Oxygen Vendor B
Propane	10	-0.10	-0.09
Methane	40	-0.08	-0.07
Ethane	10	-0.06	-0.05
Butane	10	-0.15	-0.13
Ethylene	10	-0.03	-0.02
Carbon Dioxide	10	-0.03	-0.03
Total Interference		-0.44	-0.39

TDLAS is a non-contact analysis technique with long-term stability, high specificity and excellent accuracy/precision selectivity. A laser based oxygen sensor offers the advantage of fast response time, non-intrusive and path averaged measurements in comparison with conventional techniques such as paramagnetic and zirconium sensors. In an application such as monitoring the headspace of a tank that can become explosive, the above mentioned attributes help assure the safe operation of the vapor processing unit.

The AMETEK model 5100 HD is an extractive type analyzer designed for hot/wet sample analysis. The 5100 HD can be configured to analyze not only oxygen but also H_2S, H_2O, CO_2, CO, CH_4, C_2H_2 and many other small gas molecules. There is no sample conditioning required for the analyzer system other than particulate filtering and assuring the sample does condense at the maximum integrated oven temperature of 150ºC. The model 5100 HD uses a sealed reference cell containing the analyte gas for continuous on-line analyzer verification and offers high specificity, and sensitivity. The analyzer uses a completely digital implementation of the **Wavelength Modulation Spectroscopy (WMS)** approach so changing the experimental protocol is simply a matter of uploading a file.

The model 5100 HD has been the choice of many customers as an alternative to paramagnetic based oxygen analyzers in process tank headspace applications. Analytical performance of the analyzer was evaluated at number of customer sites with varying process pressures and temperatures. An accuracy of ~0.1% and a repeatability of ~0.03% oxygen was demonstrated for a variety of experimental conditions. Data from a side-by-side long term comparison of the AMETEK 5100 HD with a paramagnetic analyzer is shown in Table 3. During the twelve month evaluation the TDLAS analyzer showed 100% up time versus 94% for the paramagnetic analyzer.

TABLE 3: Reliability Results from Paramagnetic/TDLAS Comparison

	Paramagnetic Analyzer	AMETEK TDLAS
Time Interval in Months	12	12
Number of Failures	11	0
MTBF (Years)	9.1×10^{-2}	$\rightarrow \infty$
Availability	94%	100%

Cost of Installation and Maintenance

The monitoring of oxygen in a nitrogen sparged process vessel headspace is a critical application that demands an analyzer with a near 100% availability. The AMETEK 5100 HD provides a integrated heated sample compartment **(up to150ºC)** containing the stainless steel gas cell and the sample conditioning system. All that is required for installation is mounting the analyzer back pan and attaching a heated transfer line (depending on the dew point of the gas stream). Paramagnetic analyzers require complicated external sample conditioning systems to prevent cell degradation from moisture H_2S, and volatile organic compounds.

The semiconductor diode laser source used in the 5100 HD TDLAS has a MTBF of more than eight years. As noted earlier, degradation of paramagnetic cells in these applications is unavoidable and replacements are often required every two months.

The 5100 HD real-time verification algorithms combined with the internal reference cell provide a continuous indication that the analyzer is operating properly. The Wavelength Modulation Spectroscopy (WMS) data collection eliminates any concentration effects resulting from moderate cell contamination and any major fouling of the analysis cell results in an alarm output. The gas cell can be cleaned by plant technicians in less than an hour minimizing down time in case of a cell contamination due to liquid condensation.

TABLE 4: Costs Associated with TDLAS versus Paramagnetic for Oxygen in Organic Volatiles

	TDLAS	Paramagnetic	Savings
Base Analyzer Price	$28K[2]	$15K	-$7K
Sample Conditioning	$3K	$20K	+$17K
Installation	$8K	$12K	+$4K
Yearly Maintenance (5-yr total)[1]	$5K	$25K	+$20K
Total	$44K	$72K	(TDLAS SAVINGS) +$34K

[1] Includes Sample Conditioning Maintenance and Replacement Parts

[2] Typical analyzer pricing. The actual base analyzer price is dependent on the specific configuration.

Conclusion

Monitoring oxygen in nitrogen sparged process vessel headspace is a critical application that demands an analyzer with a near 100% availability because of the plant safety considerations. The built-in verification feature of the AMETEK TDLAS minimizes the frequency of zero and span gas validations. The AMETEK 5100 HD TDLAS Analyzer provides best of class connectivity with current loop, Modbus and Ethernet communications. The fast response, elimination of sample conditioning, immunity to interference from moisture, H2S, and VOC's make the laser based AMETEK model 5100 HD TDLAS a superior and dependable choice.

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