AMETEK®

PROCESS INSTRUMENTS

APPLICATION NOTE

PROCESS OXYGEN MONITORING IN VAPOR RECOVERY, FLARES AND CONDENSING PROCESS STREAMS

This application note compares the advantages and disadvantages of tunable diode laser absorption spectroscopy (TDLAS) based analyzers with the more traditional paramagnetic analyzers, as applied to the analysis of oxygen (O_2) in volatile organic compound (VOC) vapor streams.

There are many organic vapor streams where it is critical to monitor O_2 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 lower explosive limits (LEL) and, therefore, nitrogen (N_2) blanketing is carried out to generate a non-combustible atmosphere with acceptably low levels of O_2. One way to simultaneously increase safety and minimize the use of N_2 is to control N_2 blanketing as a function of O_2 concentration in the headspace. The objective is to prevent the O_2 concentration from exceeding the limiting oxygen concentration (LOC), which is specific for each product that is blanketed.

The O_2 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 the O_2 level exceeds the safe limit of operation, a N_2 purge of the tank headspace is initiated to keep O_2 at safe levels, below upper explosive limits (typically <2% O_2). By measuring the O_2 concentration in the headspace, the N_2 consumption can be optimized to keep operating costs low while ensuring safe plant operation.

ADVANTAGES OF A TDLAS ANALYZER

TDLAS is a non-contact analysis technique with long-term stability, high specificity and excellent accuracy/precision selectivity. A laser-based O_2 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 5100HD is an extractive-type analyzer designed for hot/wet sample analysis. The 5100HD can be configured to analyze not only O_2 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 maintaining the sample in a gas phase and removing any particulates. The 5100HD uses a sealed reference cell containing the analyte gas for continuous optical system 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 5100HD has been the choice of many customers as an alternative to paramagnetic-based O_2 analyzers in process tank headspace applications. Analytical performance of the analyzer was evaluated at a number of customer sites with varying process pressures and temperatures. Data from a side-by-side long-term comparison of the 5100HD with a paramagnetic analyzer is shown in Table 1. During the 12-month evaluation the TDLAS analyzer showed 100% uptime, versus 94% for the paramagnetic analyzer.

	Paramagnetic Analyzer	AMETEK TDLAS
Time interval in months	12	12
Number of failures	11	$\overset{\infty}{\rightarrow}$
MTBF (years)	9.1×10^{-2}	0.60
Availability	94%	100%

Table 1. Reliability results from paramagnetic vs. TDLAS comparison

COST OF INSTALLATION AND MAINTENANCE

The monitoring of O_2 in a N_2-sparged process vessel headspace is a critical application that demands an analyzer with a near-100% availability. The 5100HD provides an integrated heated sample compartment (up to 150°C (302°F)) containing the stainless steel gas cell and the sample conditioning system. All that is required for installation is mounting the analyzer back panel, making electrical and communication connections, and attaching a transfer line. Paramagnetic analyzers require complicated external sample conditioning systems to prevent cell degradation from moisture, H_2S, and volatile organic compounds.

The laser diode used in the 5100HD has a mean time between failures (MTBF) of more than eight years.

As noted earlier, degradation of paramagnetic cells in these applications is unavoidable and replacements can be required every two months.

The 5100HD real-time verification algorithms combined with the internal reference cell provide a continuous indication that the analyzer is operating properly. 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 a technician in less than an hour, minimizing downtime in case of a cell contamination due to liquid condensation.

PARAMAGNETIC VS. TDLAS VOC MEASUREMENT

Magnetic wind and thermomagnetic-type paramagnetic analyzers are suited for many O_2 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 need 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. One method to prevent condensation is to remove water and higher molecular weight hydrocarbons. Knocking out 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 to the oil/water separator using heat-traced transport lines. For this reason, a technology that can measure a hot-wet sample is preferred over the paramagnetic dry sample approach.

Several measurement technology options are available for hot-wet sample analysis; however, all have significant drawbacks when compared with 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 2 to illustrate why laser spectroscopy is a better option.

Technology	Moisture interference	Temperature	KO required	VOC interference	H_2S interference	Product contact
Magnetic wind and thermomagnetic (Paramagnetic)	Yes	<110°C (230°F)	Yes	Yes	No	Yes
Electrochemical cell	Yes	<40°C (104°F)	Yes	Yes	No	Yes
Fluorescent quenching	No	<50°C (122°F)	No	Yes	No	Yes
Polargraphic	No	<79°C (174.2°F)	No	Yes	Yes	Yes
TDLAS	No	<150°C (302°F)	No	No	No	No

Table 2. Technologies for measuring O_2 in VOC streams

It is well known that the results of a paramagnetic measurement are influenced by hydrocarbons present in the sample stream. Table 3 shows the hydrocarbon-related errors reported by two paramagnetic analyzer manufacturers. Most paramagnetic O_2 measurements are made on a dry gas sample. Drying the sample stream can result in an error of around ±0.6% O_2 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.

Gas	Volume %	Interference % oxygen Vendor A	Interference % oxygen Vendor B
Propane	10	-0.10	-0.09
Methane	40	-0.08	-0.07
Ethane	10	-0.08	-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

Table 3. Paramagnetic matrix gas interferences

CONCLUSION

Monitoring O_2 in a N_2-sparged process vessel headspace is a critical application that demands an analyzer with near-100% availability because of plant safety considerations. The built-in verification feature of the AMETEK 5100HD TDLAS analyzer minimizes the frequency of zero and span gas validations. Lower total cost of ownership, fast response time, elimination of sample conditioning, immunity to interference from moisture, H_2S, and VOCs all make the laser-based 5100HD a superior and dependable choice.

5100HD TUNABLE DIODE LASER ANALYZER

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