MAGNETO-PNEUMATIC OXYGEN ANALYZER - THE “FORGOTTEN” OXYGEN MEASUREMENT SOLUTION

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ABSTRACT
In the process analysis portfolio for the measurement of oxygen, there are a range of analysis technology approaches available. The most common include zirconia oxide probes, electrochemical sensors, paramagnetic dumbbell analyzers and most recently, tunable diode lasers. The use of TDL analyzers for oxygen measurement has been growing due to its ability to perform the analysis without the need for the sense elements to directly contact the sample. This makes it ideal for harsh applications where dirty and corrosive process streams would damage or interfere with the sense elements that are used in the other oxygen measurement solutions.

However, there is an often forgotten, alternative approach for the measurement of oxygen that also avoids the sense element touching the sample — magneto-pneumatic oxygen analyzers. This class of oxygen analyzer works on the paramagnetic principle popularized in the classical dumbbell or magnetic wind analyzers, but does so by using an alternating pressure principle for the actual measurement.

This paper will discuss the magneto-pneumatic oxygen measurement principle, especially in comparison to the classical paramagnetic as well as the TDL approaches. Examples of applications will also be given to illustrate where the unique properties of this measurement approach were successfully implemented in harsh process measurement applications.
INTRODUCTION

Oxygen plays an important role in a number of chemical processes in the hydrocarbon processing industry, both as a key component in combustion processes as well as chemical processes. It is therefore understandable that the measurement of oxygen is second only to the measurement of moisture throughout the process industry. It is also only natural that a number of measurement techniques have been developed and refined over the years for on-line oxygen analysis.

The classical approaches for oxygen measurements are as varied as the applications they are used in and will be briefly reviewed below. There is also a “new” laser-based approach that is rapidly growing in popularity. However, there is one oxygen measurement technique that is available that has many of the favorable properties of the laser-based analyzer while retaining the straightforward nature of the classical measurement solutions — magneto-pneumatic oxygen analyzers. The magneto-pneumatic approach offers some unique features that make it ideal for a range of applications but it is often “forgotten” due to the overwhelming usage of the classical measurement techniques.

CLASSICAL PROCESS OXYGEN MEASUREMENT TECHNIQUES

As mentioned above, the range of classical process oxygen analyzer techniques are as varied as the applications they are used in. Each of the approaches, as any analyzer, has both advantages and disadvantages that dictate where they can best be used. To better understand where the magneto-pneumatic approach is best suited, it is worth spending a moment to review the most popular process oxygen techniques.

ZIRCONIA OXIDE OXYGEN PROBES

A very popular method of measuring oxygen, particularly in combustion monitoring applications, is with zirconia oxide (ZrO$_2$) ceramic probes. When ZrO$_2$ is heated above 350°C, it becomes a conductor of oxygen ions. By putting a suitable metallic layer on the surface of the ZrO$_2$ (typically platinum), oxygen ions will be formed. If a probe is configured similar to Figure 1, the difference in the partial pressure of the oxygen in the reference gas (often atmospheric oxygen at 20.64%) and the oxygen present in the process gas results in a potential voltage difference between the two metallic layers that can then be measured.

This approach provides a simple and affordable means to measure oxygen. And since the ZrO$_2$ needs to be kept at an elevated temperature, it is very popular for hot, combustion control applications. Furthermore, being able to reference the analyzer with the atmosphere simplifies calibration and operation of the analyzer.
FIGURE 1: KEY ELEMENTS OF A ZIRCONIA OXIDE OXYGEN ANALYZER

But there are some issues with this technique. If there are significant amounts of hydrocarbons, carbon monoxide or hydrogen present, they will react with the oxygen on the probe’s surface to give an artificially low reading. There is also the safety concern that the hot probe could act as an ignition source if the hydrocarbon levels in the process stream are significantly high. But this safety issue is avoided in extractive versions of this measurement technique. Finally, since the probe must be in contact with the process sample, the life of the probe can be reduced due to coating by particulates as well damage from any corrosive compounds present.

ELECTROCHEMICAL OXYGEN SENSORS

Electrochemical oxygen sensors tend to operate as galvanic electrodes or fuel cells depending on the design. They are compact devices similar to Figure 2 where oxygen will permeate through a membrane and react with a cathode that is coated with a metal such as gold or platinum. This creates hydroxide ions (OH-) that are then conducted by an electrolyte in the sensor; the ions then react with a metal anode (typically lead) to complete a reaction that liberates electrons. The level of electrons created can be measured and is indicative of the amount of oxygen present in the sample.2

FIGURE 2: KEY ELEMENTS OF AN ELECTROCHEMICAL OXYGEN ANALYZER
Electrochemical oxygen probes have excellent sensitivity, are often used for trace oxygen (ppm levels) and can be used in gas as well as liquid samples. They are also very compact in size. Furthermore, their simple design is very cost effective and generally low in maintenance when used in the proper applications.

But since the electrolyte is consumed in many applications, they have a finite life (typically 1 – 2 years depending on the design and application). But more importantly, electrochemical oxygen sensors are like the ZrO2 probe — the sensor must directly contact the process stream for the measurement to occur. This can lead to plugging of the permeable membranes which leads to measurement error and failure. There is also the damage to the sensor itself that can occur in the presence of corrosive compounds in the stream.

PARAMAGNETIC OXYGEN ANALYZERS

Paramagnetic oxygen analyzers exploit the attraction that oxygen has to magnetic fields. By designing the analyzer to expose the measured sample to a magnetic field, the oxygen molecules are selectively attracted to the magnetic field enabling their measurement. There are three means of measuring the attraction of the oxygen to the magnetic field: 1) a mechanical “dumbbell” sensor, 2) a magnetic “wind” approach, and 3) the magneto-pneumatic approach that is the basis of this paper.

The basic design of the dumbbell-based paramagnetic sensor can be seen in Figure 3a. A small glass dumbbell is suspended on a wire that has a mirror attached to it. One of the glass balls is oriented so that it is in a magnetic field. Any oxygen present in the sample will be attracted to the side of dumbbell where the magnetic field is. This results in a stronger pressure on that side of the glass dumbbell causing the dumbbell to twist. The analyzer measures the amount of the twist with the small mirror mounted on the dumbbell by reflecting a light beam off the mirror to measure the deflection of the mirror caused by the twisting of the dumbbell. This can be measured to give the value of the oxygen in the sample by adjusting a torsion inducing current through the wire to hold the mirror in one location. The level of current is proportional to the amount of oxygen present in the sample.

![FIGURE 3: KEY ELEMENTS OF “DUMBBELL” AND MAGNETIC “WIND” PARAMAGNETIC OXYGEN ANALYZERS](image-url)
The magnetic “wind” approach is a basic thermal conductivity sensor set up in a Wheatstone bridge (see Figure 3b)\(^2\). The oxygen molecules will be attracted to the magnetic field and cool off the measurement filament more than the reference side resulting in a voltage potential that can be measured.

Due to the selectivity of the oxygen to a magnetic field, both of these paramagnetic analyzers offer precise oxygen measurement, and their mechanical simplicity makes them ideal solutions for a wide range of process measurement applications.

However, the “dumbbell” approach is sensitive to vibration and requires careful sample conditioning to prevent damage to the delicate glass dumbbell from particulates or liquids in the stream. While the magnetic wind approach is a much more rugged and robust mechanical design, it is still sensitive to corrosive compounds and is susceptible to errors when background composition changes result in changes to thermal conductivity.

**COMMON ISSUES WITH THE CLASSICAL APPROACHES**

The classical oxygen analyzers discussed above have been used for decades to great success in a wide range of applications. However, they all are limited by the fact that the measurement techniques used requires the sensing elements to directly contact the process sample. While this is not an issue for many applications, for applications with high levels of particulates and/or corrosive compounds present, they often resulted in high levels of maintenance and measurement errors.

The desire for a way to measure oxygen in process samples that did not require the sensing element to directly contact the sample has lead to the growing use of a new measurement technique — tunable diode lasers\(^1\).

**TUNABLE DIODE LASER ANALYZERS**

Tunable Diode Laser (TDL) spectrometers were originally developed by NASA and the Jet Propulsion Laboratory for the measurement of upper atmospheric compounds and were installed on a probe sent to Mars\(^3\). Since then, TDL spectrometers have been developed for a number of process measurements such as moisture analysis\(^1\). One application that is also increasing in popularity for TDL analyzers is the measurement of oxygen.

While the design of TDL analyzers vary between manufacturers, they all exhibit features similar to Figure 4. A tunable diode laser of the appropriate wavelength (typically around 760 nanometers for oxygen) is beamed through the sample to be measured. A detector then measures the loss of signal due to the absorption by oxygen with the concentration calculated by Beer-Lambert law.
FIGURE 4: KEY ELEMENTS OF A TUNABLE DIODE LASER OXYGEN ANALYZER

One nice feature of a TDL-based analyzer is that the laser diode and detector are isolated from contact with the process sample by isolation windows. This characteristic makes the TDL-based oxygen analyzer ideal for applications that are high in particulates and/or where there may be corrosive compounds present. However, there is another option for these types of applications that many users may not realize is available — magneto-pneumatic oxygen analyzers.

A challenge for TDL-based analyzers is there is no way to calibrate the analyzer in the field like a traditional analyzer would be calibrated. For most applications, this is not an issue as the laser used in TDL-based analyzers has little to no drift over time. This means the calibration done at the factory is adequate for a length of time that is often measured in years depending on the manufacturer. It is then a simple matter of “challenging” the analyzer with a validation sample to confirm the analyzer is still operating at factory-level performance. When calibration of the TDL analyzer is needed, the instrument would be sent back to the factory for a ‘tune-up’. But for applications where routine calibration is mandated, such as EPA applications, work-around solutions must be used that may or may not be accepted by the government agency.

MAGNETO-PNEUMATIC OXYGEN MEASUREMENT TECHNIQUE

PRINCIPLES OF OPERATION

As previously described, oxygen is attracted to magnetic fields and there are two popular paramagnetic analyzer designs used in the process industry to monitor oxygen. However, a third measurement technique based on the paramagnetic properties of oxygen exists called the magneto-pneumatic technique. It offers some unique benefits that are important when there is a need for non-contacting measurements.

The magneto-pneumatic technique uses an asymmetrical magnetic field similar to the dumbbell and the magnetic wind methods but looks for changes in pressure rather than mechanical or thermal conductivity changes. The basis of the magneto-pneumatic oxygen measurement approach is the increase in the oxygen partial pressure at the higher magnetic field strength. This increase in oxygen pressure can be determined from Curie’s Law of magnetism. By using a
flowing reference technique (see Figure 5), the temperature effects cancel out, resulting in the following equation:

$$\Delta p = \frac{1}{2} \times H_{\text{max}}^2 \times (k_{O_2} - k_{\text{ref}}) \times \mu_0$$  \hspace{1cm} (1)

Where:
\(\Delta p\) = pressure difference between a reference gas and the oxygen partial pressure
\(H_{\text{max}}\) = maximum magnetic field strength
\(k_{O_2}\) = paramagnetic constant of oxygen
\(k_{\text{ref}}\) = paramagnetic constant of the reference gas
\(\mu_0\) = magnetic field constant

**FIGURE 5: PRESSURE IMBALANCE CAUSED BY OXYGEN’S ATTRACTION TO A MAGNETIC FIELD**

Figure 6a shows how this increase in pressure caused by the oxygen migrating to the magnetic field can be used to determine its concentration. In this configuration, the sample to be analyzed enters the measurement chamber and then exits. At the same time, a flowing reference gas (typically pure nitrogen) is split into two paths and enters the measurement chamber. One of the two reference paths is exposed to a magnetic field as it enters the chamber. Any oxygen present in the sample will be attracted to the magnetic field and will cause a back pressure on the flowing reference path of the magnetic side (see Figure 6b). This will result in a back flow of the flowing reference across the bridge connecting the two paths that can be measured with a flow sensor. The level of flow is proportional to the amount of oxygen in the process sample. By then turning the magnetic field on and off, a continuing measurement of the pressure contribution of the oxygen as compared to the reference gas can be made. This is why this technique is also referred to as the “pulsing pressure” measurement technique.

This approach for the measurement of oxygen offers a couple of important features. Since the measurement element (the flow sensor) never directly contacts the sample (only the reference gas), samples with minor amounts of particulates or samples that are corrosive can be analyzed without damaging the instrument. Also, if there are other paramagnetic compounds present in the sample (such as the oxides of nitrogen), they can be added to the reference gas to cancel out the interference.
Since both the TDL analyzer and Magneto-Pneumatic analyzer share a number of important characteristics, it is useful to compare the two to better identify the best way to apply each of them.

**COMPARISON OF MAGNETO-PNEUMATIC ANALYSIS TO THE TDL TECHNIQUE**

For many oxygen measurement applications, all of the measurement techniques discussed in this paper have a role to play. But the classical oxygen techniques all exhibit a common limitation in that the measuring element directly contacts the sample. So for an application where the sample is high in particulates or corrosive compounds, the options were limited. However, both the magneto-pneumatic and TDL techniques offer the ability to perform the measurement while avoiding damage to the measurement elements.

Table I provides a summary of some of the features between the magneto-pneumatic and TDL analyzer methods. Bear in mind that there are many still technical, product solution and operational sample stream details and objectives to consider when deciding which technology should be applied.

While magneto-pneumatic analyzers tend to be lower cost than TDL-based analyzers for oxygen measurement, cost is not the only criteria for solution selection. At the risk of oversimplifying the decision of which analyzer should be used in a specific application for oxygen measurement, in general, the magneto-pneumatic design is very well suited for extractive designs, especially when the sample is already being extracted for other measurements.
TABLE I. FEATURE COMPARISON BETWEEN MAGNETO-PNEUMATIC ANALYZER AND TDL ANALYZER

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<thead>
<tr>
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<th>Magneto-Pneumatic Analyzer</th>
<th>Tunable Diode Laser Analyzer</th>
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<tbody>
<tr>
<td>System Configuration</td>
<td>Extractive Analyzer</td>
<td>In-situ or Extractive Analyzer</td>
</tr>
<tr>
<td>Sample Conditioning</td>
<td>Always needs sample conditioning but non-contacting nature of the measurement principle makes it compatible with many dirty and corrosive samples.</td>
<td>If in-situ design is possible, TDL eliminates the maintenance associated with extractive designs. However, in-situ designs can complicate calibration/validation requirements as well as complicate analyzer access for maintenance.</td>
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<tr>
<td>Response Time</td>
<td>Measurement response time depends mainly on the sample transport lag, which can range from seconds to over a minute.</td>
<td>Extractive TDLs have the similar sample transport lag issues. But TDL analyzers are often dependent on measurement averaging which can range from a few seconds to nearly a minute.</td>
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<tr>
<td>Cross Interference</td>
<td>Although oxygen has very high paramagnetic properties, other compounds can exhibit a paramagnetic response. In those cases, the flowing reference needs to be tailored to compensate for this.</td>
<td>The wavelength that oxygen uses to measure by TDLs is selected with typical cross interferences below minimum detectability.</td>
</tr>
<tr>
<td>Pressure Sensitivity</td>
<td>Minimal when sample conditioning techniques are used.</td>
<td>For in-situ TDL analyzers, changes in process pressure (and temperature) can have an impact on the measurement reading and should be compensated for if the process pressure can change significantly (typically more than 1 atmosphere).</td>
</tr>
<tr>
<td>Background Composition</td>
<td>Other than the unlikely presence of other paramagnetic compounds that can be compensated for, little effect is seen in the measurement due to changes in sample composition.</td>
<td>Both in-situ and extractive TDL analyzers are sensitive to measurement errors when the background composition changes significantly (referred to as collisional broadening). The amount of change tolerated depends on the design and application but can be impacted with changes as low as 10% of the normal amount.</td>
</tr>
<tr>
<td>Calibration / Validation</td>
<td>Traditional external reference standards can be introduced to calibrate or validate the analyzer or the entire analytical system. For some environmental monitoring applications, this may be a requirement.</td>
<td>In-situ calibration / validation is possible in many designs by insertion of a known sample into the optical flow path. The known sample is often either a filled gas cell or a fixed volume filled with a known gas. These techniques are becoming more accepted by many environmental regulatory agencies, but not all.</td>
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Magneto-pneumatic is also well equipped to handle applications where the process sample can change dramatically both in composition and pressure. In-situ TDL analyzers, on the other hand, are ideal for applications where the samples contain a high amount of particulates or where the need is to measure across a wide distance, such as a combustion zone of a process heater.
EXAMPLES OF APPLICATION SOLUTIONS

To better illustrate where the use of magneto-pneumatic analyzers are best used, is a collection of success applications for magneto-pneumatic analyzers.

CHLOR-ALKALI PLANT

The production of chlorine is important in the pulp and paper industry as a bleaching agent as well as for the manufacture of a number of compounds such as vinyl chloride monomer (VCM). Chlorine and caustic are manufactured by the electrolysis of sodium chloride brine (salt water). The measurement of oxygen in the chlorine product stream is needed since oxygen is a by-product of the chlorine production. The typical measuring range is 0 – 5% for oxygen with a balance of chlorine (and low levels of moisture).

This has been a difficult application for traditional oxygen analyzers since the chlorine and moisture are extremely damaging to the sense elements of those designs, so this is an ideal example of where the non-contacting nature of the magneto-pneumatic design can address a difficult application.

ETHYLENE OXIDE PLANT

Ethylene oxide is an important feedstock for the manufacture of glycols, detergents, etc., and is manufactured by reacting ethylene with oxygen in the presence of a catalyst (typically silver-based). The levels of oxygen are controlled in the feed to the reactor to avoid runaway reactions that can occur if the oxygen levels exceed 20%. A typical measuring range of the oxygen would be 0 – 10% with the goal to stay as close to the upper range as possible for maximizing plant production while operating in a safe manner.

Magneto-pneumatic oxygen analyzers are ideal for this application due to their extremely fast response time (typically less 2 seconds). And with the ability to avoid any measurement errors caused by corrosion, contamination or compositional changes, confidence in the measurement is dramatically improved for this critical plant safety application.

MARINE DOCK VAPOR RECOVERY

During the loading and unloading of barges and ships at dockside storage facilities, it is important to do it in a safe manner. One critical factor is maintaining a safe inert gas blanket to keep inert conditions within the storage holds of the ships. This blanketing gas is typically nitrogen where the oxygen level is kept below the flammable limit, typically a 0 – 10% range for the oxygen. The measurement can be a challenge due to the frequent presence of entrained hydrocarbon liquids that can be present in the sample and can damage other oxygen sensor and probe designs.

Once again, the non-contacting nature of the magneto-pneumatic design reduces the risks associated with permanent damage of the sensor in the case of liquid hydrocarbon breakthrough.
AIR SEPARATION PLANT

Air separation plants are a good example of how the use of the flowing reference can be used to perform a critical measurement. To verify the purity of the oxygen product manufactured, it is important that the process oxygen analyzer has a very tight measuring range for the tightest precision. It is not unusual to see requests for a 98 – 100% measuring range with ±0.5% of span precision. This had been a challenge for traditional oxygen analyzers as well as TDLs since their ranges are based off of zero; so the error of measurement makes such a range impractical.

For this application, the magneto-pneumatic oxygen analyzer would use a flowing reference that would contain 98% oxygen. This would give a true elevated zero measurement. The precision would be based on a 2% span and not the 100% span seen with other designs.

CEMENT PLANT

As a final example of where the magneto-pneumatic oxygen analyzer has been used successfully is within cement plants. For example, oxygen is typically measured with a range of 0 – 5% at the kiln inlet, calciner and cyclone pre-heater. But the corrosive nature of the stream compositions has challenged traditional designs for reliability.

CONCLUSION

Reliable oxygen measurement is critical to a wide range of applications in the process industry and the analytical field has responded by developing a number of measurement approaches to address these needs. However, as is often the case, not all analytical techniques are well suited for all applications. For applications that are corrosive, high in particulates or entrained liquids or for applications that need an elevated measuring range, the magneto-pneumatic oxygen analyzer is a possible solution that is often overlooked.

It is also important to recognize that as technology progresses, emerging measurement solutions will continue to add to the choices of measurement solutions. A prime example of this is the increasing use of tunable diode laser analyzers for oxygen analysis.
REFERENCES