ABB MEASUREMENT & ANALYTICS | APPLICATION NOTE

Measuring trace O_2 at ppm levels

Los Gatos Research (LGR)

The LGR-ICOS™ Process Analyzer from ABB is a new, smart, industrial analyzer that provides a simple, robust and sensitive method of directly measuring trace O_2 for purity verification and combustion efficiency in 'zero' gases, combustion effluents, HyCO, and other hydrocarbon gases and mixtures.

Measurement made easy

Introduction

ABB's new LGR-ICOS Process Analyzer measures trace oxygen with unprecedented accuracy and precision.

Every so often, a new analytical technology is developed that provides a powerful new solution with important improvements in the form of superior results, greater speed, lower costs, and/or simplicity of use. This Application note shows that the new LGR-ICOS Process Analyzer represents such a breakthrough for measuring trace oxygen in a range of industrial gases, because it offers clear advances in not just one or two, but all **four** of these areas: superior precision, lower investment and maintenance costs, faster speed and simplicity of use.

Key benefits

- Higher sensitivity (< 0.5 ppm) and higher accuracy (0.3 %) than any other O_2 analyzer
- Ideal for a wide range of background gases, including natural gas, inert gases, pure hydrocarbons, and HyCO
- Measures O_2 content directly, with no chemistry or electrochemistry
- No consumable costs
- No need for frequent, expensive calibration
- No crosstalk with hydrocarbons or strong oxidizers
- No drying or other pretreatment of samples required
- Wide linear dynamic range that can be adjusted from 0 to 1 % O_2 to 0 to 100 % O_2
- No oxygen shock, no recovery time needed
- Developed for General Purpose and Hazardous Area installations (various certifications available including CSA/UL; Class 1, Division 1 or 2; ATEX Zone 1 or 2; IECEx)

Background

Molecular oxygen (O_2) is a ubiquitous atmospheric gas associated with myriad natural and industrial processes. Moreover, oxygen is reactive and corrosive and tends to 'stick' to surfaces. Consequently, trace oxygen is often important to minimize yet difficult to remove, which is a challenge in numerous applications. This challenge is compounded by the practical difficulties of making **quantitative** measurements with the requisite sensitivity, accuracy and confidence.

In the important part-per-million (ppm) measurement range, legacy technology typically utilizes fuel-cell-based electrochemistry. More recently, some analyzers have been developed based on chemistry and optical (laser) absorption or even direct absorption. These all have limitations such as low sensitivity, consumables, cross-talk, out-of-range 'shock', etc., all contributing a negative cost impact.

In this Application note, we describe how a new type of robust and simple-to-use optical analyzer -ABB's LGR-ICOS™ trace oxygen analyzer-meets the challenges noted below:

- addressing natural gas handling/transport corrosion issues in natural gas
- verifying ultra-pure and zero gases in the 5.0 to 7.0 range, including alkanes, alkenes, inert gases, and bath (e.g., nitrogen) gases
- achieving ultra-high Btu combustion efficiency

The new analyzer is based on proven fourth-generation technology, described later in this application note. Thousands of similar units are already installed in demanding industrial, scientific, and government installations. The unique combination of advantages of this oxygen analyzer make it an ideal solution for a range of trace oxygen measurement applications.

Avoiding corrosion problems in natural gas

Oxygen is corrosive to both metals and non-metal surfaces because it is such a reactive gas. This is a particular problem in handling natural gas which is anoxic in its raw extracted form. The extensive use of pumps and long mileages of pipeline inevitably lead to small air leaks with resultant O2 levels in the 1-100 ppm range. This can cause progressive oxidation, and when present together with any moisture contamination, trace oxygen can also cause ferrous corrosion damage through electrolytic reactions:

- $O_2 + 4H_2O + 4e^- \rightarrow 4OH^-$ cathodic reactions
- $2H_2 + 2e^- \rightarrow H_2 + 2OH^-$
- $Fe \rightarrow Fe^{++} + 2e^-$ anodic reaction

And, of course, pipes inevitably include welded seams and joints, most notably the long seam created by arc welding or butt welding. These seams contain filler metals which may be even more susceptible to oxygen related corrosion.

These types of corrosion can occur in both transmission and distribution pipelines. And the direct and indirect costs of this corrosion damage, particularly in remote locations, have led to extensive implementation of methods to successfully scrub and clean the gas streams. The cost impact of any corrosion and industry/government regulations associated with leaks also means that the effectiveness of trace oxygen elimination must be routinely verified.

The challenge of measuring O_2 is three-fold in these applications. First, there is the general problem of measuring O_2 at the ppm level. Second, natural gas is a complex and varying matrix, so species crosstalk can be a challenge. Third, several other trace components of natural gas can actually degrade some oxygen analyzers. Until now, addressing these three challenges with legacy electrochemical analyzers has involved work-arounds such as frequent calibration and replacement of consumable parts. Unfortunately, methods based on direct laser absorption have not previously offered the requisite sensitivity and accuracy.

Verifying ultra-pure and zero gases

Many applications need ultra-pure gases in the 5.0 to 7.0 purity range. This includes reactive / process gases, zero and span gases for instrumentation calibration, inert bath gases, pure hydrocarbon gases, and pristine gases for the semiconductor industry. As in the case of natural gas, trace oxygen is a common problem because it is frequently present unless scrubbed. Moreover, its sticky, persistent nature, and its high reactivity make trace oxygen an issue for demanding applications like semiconductor manufacturing, even at the 6.0 level.

Inert gases are expensive because of their limited natural supply; typical air contains only 0.0018 % neon, 0.00011 % krypton and 0.000009 % xenon. Yet there is a growing demand in medicine, electronics and photonics for ultrapure sources of these gases. This includes fluorescent lighting, decorative lighting (especially neon), and plasma displays, and inside the excimer lasers, to name just a few. (These lasers are critical tools in LASIK ophthalmology procedures and in the fabrication of high brightness televisions and smart device displays.) In many of these applications, even trace amounts of a reactive gas like oxygen can have a poisoning or quenching effect disproportionate to the trace amount present.

Automotive is another industry increasingly using ultra-pure gases, most commonly associated with emissions measurement and testing, as well as concomitant use in the R&D of emissions reduction systems. And since (non-electric) automotive engines all involve combustion, i.e., explosive oxidation, trace oxygen is a particularly problematic constituent for any quantitative measurement. For example, one of the gases required under the latest Euro 6 regulations is nitrogen with less than 2 ppm trace oxygen.

Yet another purpose for verifying trace oxygen elimination is for inert packaging gases, usually dry nitrogen, where oxygen would cause product deterioration. Obviously long-life food packaging is a major application here, as well as trans-shipment packaging of exotic chemicals and components that cannot be exposed to oxygen.

Specialty gas suppliers provide solutions to these and many other applications. They thus have a need for a **traceable** quantitative oxygen analyzer suitable for measuring oxygen in diverse gases, all the way through production and purification to cylinder filling stations and the final loading dock. The major drawback of electrochemical instruments here is the cost and time for constant re-calibration. But first-generation laser optical analyzers don't have the requisite sensitivity and overall performance.

Ultra-high BTU combustion efficiency

There is also a growing need to measure trace oxygen in some energy/fuel streams with very high Btu values. Specifically, the downward pressure on natural gas prices and equivalent fuel gas streams in the 1000 Btu/ft³ range makes it ever more attractive for petrochemical refineries to produce gases in the higher thermal range, say 1050-1200 Btu/ft³ – a range often called 'High Heating Value' or HVV in the natural gas market. These fuel gases and synthetic gases are traded with a thermally-based value – rather than the volume-based pricing used in the natural gas industry prior to deregulation. As a result, the higher the Btu, the higher the impact of unwanted trace impurities. So whereas producers, distributors and industrial customers might historically specify trace oxygen in the 1 % range, today there is a demand to measure levels at 0.1 % (100 ppm) and even lower.

The new LGR-ICOS trace oxygen analyzer is ideal for the above applications with none of the frequent calibration, consumables costs and drift of electrochemical sensors. It offers higher sensitivity than first-generation laser optical methods, and is much faster than chromatography, which also suffers from the cost of consumables.

Limitations of traditional methods

The dominant methods of trace oxygen detection rely on the reactivity of oxygen to perform electrochemical or optogalvanic measurements. The most common type is the fuel cell. Here, the gas to be tested enters a small cell at the cathode end. Ultimately trace oxygen causes oxidation of the lead anode and a small electrical current results.

These cells have several limitations. The cell has a finite lifetime and must be replaced often. Other strong oxidizers in the gas stream can cause erroneous signals and also accelerate the aging of the detection cell. In many instances this means testing pre-scrubbed samples only. A common variation on this senses a signal between the electrodes separated by zirconia ceramic. Here the signal is essentially based on concentration (a concentration cell) rather than electrochemical reaction. In others, the detection is based on oxygen diffusion rate to the electrodes – a method that is not quantitatively accurate when used with flammable gases. The other limitations are fairly similar in all cases.

The challenge of measuring trace oxygen is well-illustrated by the applications that resort to measuring the magnetic properties of oxygen! The oxygen molecule has two unpaired electrons making it paramagnetic. The flow rate of a gas containing oxygen through a narrow tube can thus be influenced by a magnetic field. This method requires a sampling unit specifically optimized for the particular sample gas.

Chromatography is even used in some applications, in spite of its known limitations of slow speed, calibration and consumables.

Why not an optical method? Today, many industrial trace species are measured optically, often by light absorption methods such as FTIR or NIR, because of the high speed, high sensitivity and high specificity potential for some gases. Unfortunately, the oxygen molecule is symmetric with no dipole so it has only a very weak infrared and visible absorption spectra due to electronic transitions. Furthermore, many of these weak lines overlap with strong lines from other gases such as hydrocarbons. In an effort to address the signal overlap (and potential interference) issue, some instrument makers have built absorption spectrometers based on tunable diode lasers or TDLs, with narrow spectra linewidth. However, the very weak absorption of oxygen means that the amount of laser light absorbed is extremely small. As a result, the instrument shot-noise limits these first-generation instruments to a minimum sensitivity of 100 to 200 ppm or worse. They also need frequent calibration.

As an indication of this difficulty, some instrument makers perform an indirect measurement where the oxygen is reacted to create water which is then measured by laser absorption. This complex approach is limited by the requirement of pre-scrubbing of samples to eliminate all water.

The LGR-ICOS trace oxygen analyzer

All these issues are successfully eliminated in the LGR-ICOS Trace Oxygen Analyzer, which now delivers a unique and comprehensive set of benefits to trace oxygen applications.

High sensitivity, precision and accuracy

ABB's patented Off-Axis ICOS technology used in the LGR-ICOS analyzer is a fourth-generation cavity-based absorption spectrometry. In simple terms it addresses the low optical absorption characteristics of oxygen by using a tunable laser in conjunction with an optical cavity to deliver a sampling length of 20 kilometers or more in a compact instrument. This delivers many orders of magnitude boost in sensitivity, which allows it to target carefully choose absorption lines purely on the basis of having no overlap with other common molecules. It no longer matters if these are 'weak' lines because of the extreme sensitivity provided by a 20 km (12.5 mile) pathlength. As a result, trace oxygen can be directly measured with a routine sensitivity (LDL) of better than 0.5 ppm (3σ, with 100 seconds of signal averaging). Guaranteed precision is better than 0.85 ppm (2σ, with just 10 seconds of signal averaging). And absolute accuracy is better than 1 % of full scale deflection (FSD).

This extraordinary sensitivity is shown in Figure 1, where a ≈1 ppm O_2/N_2 sample was measured for over 1 hour. The data shows that the analyzer can measure the 1 ppm sample with a precision of 0.09 ppm (1σ, 100 s) and a corresponding lower detection limit (LDL) of 0.27 ppm.

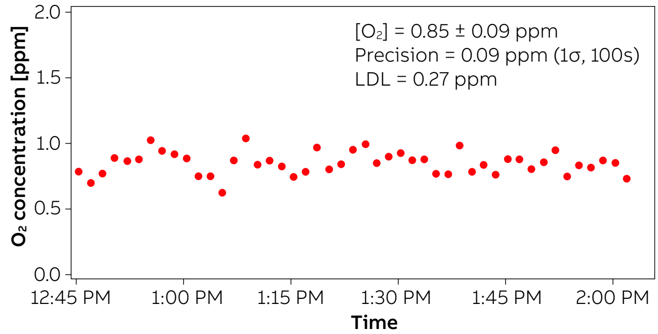

Figure 1 Continuous measurements of an approximately 1 ppm O_2/N_2 gas mixture shows the analyzer's extraordinary precision and LDL

…The LGR-ICOS trace oxygen analyzer

Linear dynamic range

Off-axis integrated cavity output spectroscopy (OA-ICOS) is a direct absorption measurement that avoids problems of detector saturation, delivering a highly linear response over the full dynamic range of the analyzer as shown in Figure 2. Together with the direct measurement with no need for the time, complexity and cost of frequent calibration with zero and/or span gases. In fact, ABB recommends that the analyzer calibration be checked only annually, depending on the application.

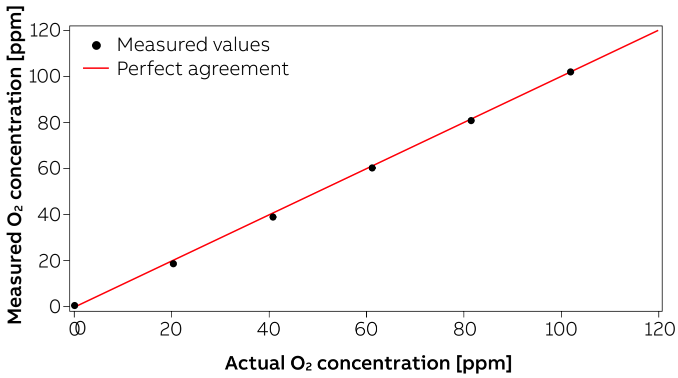

Figure 2 The LGR-ICOS Trace Oxygen Analyzer exhibits excellent measurement linearity. The instrument has a linear response that can be extended up to 1 % or 100 % molecular oxygen.

No consumable costs and simple maintenance

The LGR-ICOS Process Analyzer also requires no consumables and very little maintenance, except for the simple window cleaning procedure included in a recommended annual maintenance check. And because this fourth- generation analyzer does not require the ultra-precise alignment of older optical methods like first-generation CRDS, this cleaning can be accomplished in just a few minutes.

Fast response

The LGR-ICOS instrument is also very fast because of the digital scanning of the embedded solid-state diode lasers; wavelength scanning of the target absorption lines can be completed in only milliseconds. The analyzer provides a data rate of faster than 1 Hz with a gas flow through T90-10 time of less than 15 seconds.

No crosstalk with multiple gases – no pre-scrubbing required

Another important advantage is immunity from crosstalk with other species. Specifically, the high spectral resolution of the lasers used in the LGR-ICOS Process Analyzer, and the narrow width of the absorption feature means that the analyzer is highly selective and exhibits minimal cross-interferences due to other background gases. The reason for this inherent advantage can be see clearly in Figure 3, which shows the raw spectral datadata that is rarely seen or used by an operator. This figure clearly shows how the analyzer can measure trace oxygen in an inert background of nitrogen, as well as a 1,3-butadiene matrix. Similar data has been measured for natural gas, hydrogen chloride, and ethylene backgrounds.

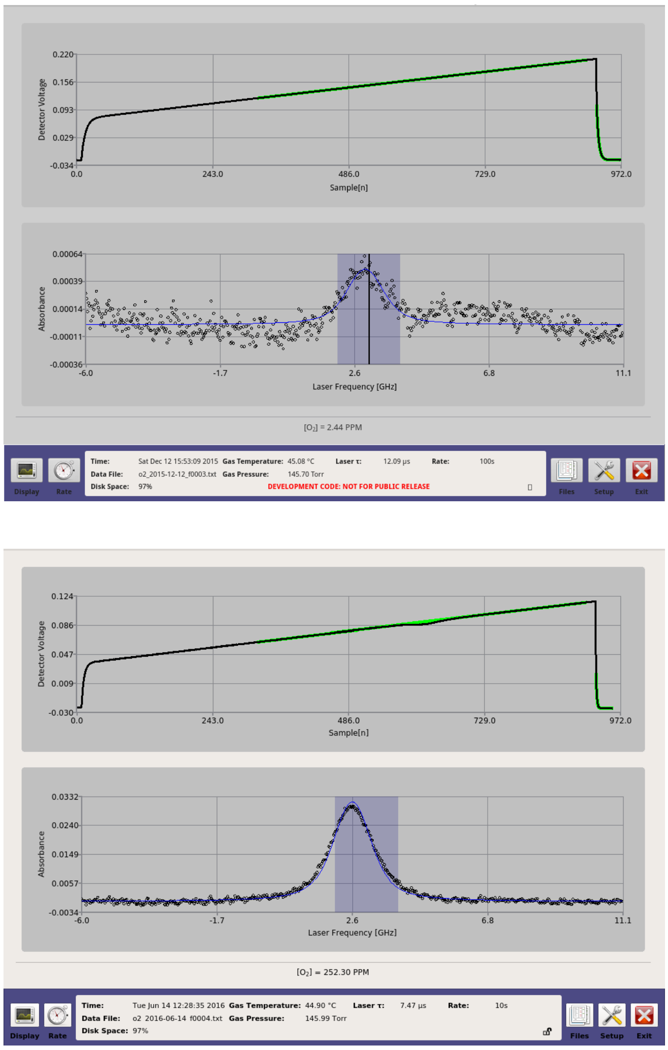

Figure 3 Raw, measured spectra of 2 ppm oxygen in nitrogen (top) and 250 ppm oxygen in 1,3-butadiene (bottom). The analyzer can readily measure low-levels of oxygen in both inert/pure backgrounds, as well as complex hydrocarbons.

No oxygen shock, zero recovery time

The LGR-ICOS Process Analyzer has a very fast response to changing oxygen concentration; it is able to accommodate swings as high as 80 % of FSD with full accuracy and precision after just 15 seconds. And unlike legacy instruments based on electro-chemistry which go into overload with out of range high oxygen concentrations, there is no such risk of oxygen shock with this new analyzer, and no corresponding dead time, or recovery time.

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ABB Inc.
Measurement & Analytics
3400 Rue Pierre-Ardouin
Quebec (Quebec)
G1P 0B2
Canada
Tel: +1 418 877 2944
Fax: +1 418 877 2834
Email: icos@ca.abb.com

abb.com/measurement

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