ABB MEASUREMENT & ANALYTICS | APPLICATION NOTE

Measuring trace impurities in HyCO, regeneration hydrogen and inert gases

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The new LGR-ICOS™ laser process analyzer from ABB provides a simple, robust and sensitive method of simultaneously measuring multiple trace impurities in industrial gases

Measurement made easy

Introduction

From measuring HyCO products to hydrogen recovery, many gas monitoring applications for trace impurities use legacy technologies. These include mass spectrometry, gas chromatography, FTIR and even paper tape-based methods. Each of these has a well-known set of limitations such as costly consumables, limited sensitivity, drift, insensitivity, cross sensitivity between different targets and so on.

A new analyzer from ABB – the LGR-ICOS analyzer – uses fourth-generation cavity enhanced absorption spectroscopy (CEAS), a technology already well-proven for remote atmospheric monitoring, laboratory and medical research, and semiconductor process applications. The LGR-ICOS analyzer is fully optimized for industrial facilities requiring trace gas monitoring in demanding applications.

This publication examines how its high speed, lack of cross sensitivity and high precision make the LGR-ICOS analyzer an ideal analyzer for three important applications:

- monitoring H2S and other impurities in (HyCO) fuel gas
- measuring multiple trace species in recovered hydrogen (for example, for regeneration)
- QC/certification of ultrapure inert gases (for example, from air separation units)

Hydrogen recovery and regeneration

Many refineries are making changes in their processing patterns to adapt to ongoing market changes and thereby re-optimize profitability. For example, some are increasingly processing lower cost heavy and sour crudes while accommodating trends such as the shifting demand from gasoline towards more distillate, and hence a reduction in naphtha reforming. An overall result is increased production of fuel gas and decreased availability of hydrogen. But there is no decline in the demand for hydrogen; in fact, quite the opposite. While a number of refineries are simply re-balancing their hydrogen budget by buying ‘over the fence’ hydrogen, these trends are causing many others to look at increasing the utility and value of their existing hydrogen-rich streams. Specifically, hydrogen purification (recovery and regeneration) is gaining in popularity to improve downstream quality, process efficiency, and/or combustion efficiency, depending on the final destination of the hydrogen. In particular, these applications include hydrogen recovered by pressure swing adsorption (PSA) regeneration catalytic systems and hydrogen from steam methane reformers (SMRs).

The final value and utility of any recovered high-purity hydrogen depends on minimizing trace impurities such as carbon monoxide (CO), carbon dioxide (CO_2) and volatile (saturated and olefin) hydrocarbons such as methane (CH_4). For example, a typical target value for regeneration purposes is <10 ppm CH_4. And, of course, for any excess hydrogen that is exported over the fence for applications such as fuel cells, compositional purity determines value and price. Hence there is a growing need for a robust method of measuring hydrogen purity.

Currently, the most commonly used method for measuring hydrogen purity in refineries is gas chromatography (GC), mainly for want of a superior alternative and in spite of its well-known drawbacks. These include limitations on absolute accuracy resulting in a concomitant need for frequent calibration, slow speed and costly consumables (for example, columns and carrier gases). Slow speed is always a potential issue with GC, particularly in applications that require fast response in process control plant operations. With GC, operator alerts have an inevitable time delay, often meaning the operator has to stop the process before it goes out of specification to avoid contaminating good product or poisoned catalysts. The other major limitation of GC is the cost of routine maintenance. In fact, one of the first things a GC supplier tells a customer is how to open the oven and carefully change the separation column. Also, GC ideally benefits from having a skilled and experienced operator.

In contrast, the LGR-ICOS analyzer requires no consumables and very little maintenance, except for a simple window cleaning procedure included in a recommended annual maintenance check. This cleaning can be accomplished in just a few minutes. The LGR-ICOS analyzer is also very fast; wavelength scanning of the target absorption lines can be completed in only milliseconds.

For recovered hydrogen applications, the other important advantages of the LGR-ICOS analyzer are its ability to simultaneously target multiple specific impurities (for example, CO, CO_2 and CH_4). That’s because the measurement cavity in this analyzer can accommodate multiple tunable lasers. In contrast, earlier cavity-enhanced optical methods, such as cavity ringdown spectroscopy (CRDS), could be configured for multiple targets only by housing several instruments in a single box.

The high spectral resolution of the lasers used in the LGR-ICOS analyzer, and the discrete width of the absorption feature also means that the analyzer is highly selective and exhibits minimal cross-interferences from other background gases.

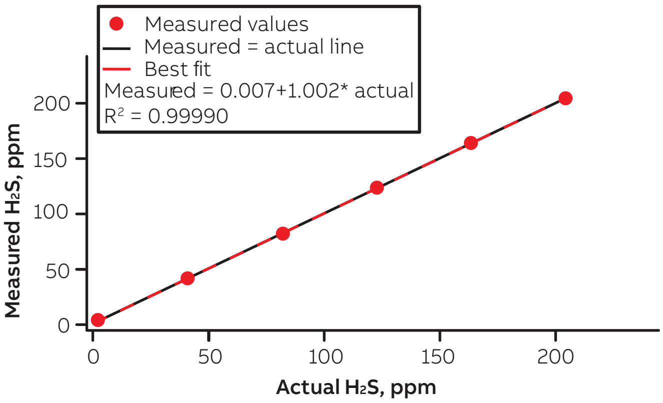

Figure 1 Measurements of H2S recorded by the analyzer show excellent linearity and accuracy over a dynamic range exceeding 3 orders of magnitude

Unlike other optical methods, the laser-based LGR-ICOS analyzer reports data over an extremely wide dynamic range – often up to 6 decades. Thus, the analyzer is well suited for reporting, for example, methane in complex process streams containing hundreds of ppm or in high purity gases at single-digit ppb levels. As an example of excellent linearity and dynamic range, Figure 1 shows measurements of H_2S recorded from 0 to 200 ppm, with a LDL of 5 ppb.

An additional advantage for the LGR-ICOS analyzer is the ability to combine the monitoring of multiple streams of widely varying concentrations with a single analyzer rather than multiple analyzers covering shorter ranges of measurement. Table 1 shows selected examples of LGR-ICOS analyzer performance in inert gas matrices. Trace measurements with unmatched sensitivity, precision and accuracy show superior performance for both quality assurance and process efficiency applications.

Analyzer configuration	Gas analyte	Measurement range		Precision (2σ, 10 sec)	LDL (3σ, 10 sec)	Accuracy (% of reading)	Response time T 90/10
		Low	High				
$CH_4 + CO + CO_2 + H_2O$	CH_4	0 – 50 ppb	0 – 100 %	0.5 ppb	0.75 ppb	< 1 %	< 15 sec
	CO	0 – 5 ppm	0 – 5000 ppm	50 ppb	75 ppb	< 1 %	< 15 sec
	CO_2	0 – 10 ppm	0 – 1 %	100 ppb	150 ppb	< 1 %	< 15 sec
	H_2O	0 – 10000 ppm	0 – 70000 ppm	10 ppm	15 ppm	< 1 %	< 15 sec
$H_2S + CO_2$	H_2S	0 – 1 ppm	0 – 5000 ppm	10 ppb	15 ppb	< 1 %	< 15 sec
	CO_2	0 – 25 ppm	0 – 20 %	250 ppb	375 ppb	< 1 %	< 15 sec
Trace O_2	O_2	0 – 50 ppm	0 – 20 %	500 ppb	750 ppb	< 1 %	< 15 sec
% V/V O_2	O_2	0 – 1 %	0 – 100 %	85 ppm	130 ppm	< 1 %	< 15 sec

Table 1 Performance of LGR-ICOS analyzer for trace impurities in inert gases, HyCO, and hydrogen. Measurement accuracy is better than 1 % of reading until precision limited. Measurement range is continuous between low and high ranges (please inquire for details).

HyCO (SynGas) applications

HyCO, often called SynGas and historically sometimes called Power Gas, is a mixture of CO, H_2 and usually CO_2, together with various impurities, that are dependent on the specific origin of the particular HyCO stream. There are numerous sources of HyCO, including steam reforming of natural gas, coal gasification and recycling (for example, from waste to energy conversion plants). It is no longer commonly used for domestic delivery and consumption but its high calorific value and plentiful supply at the typical refinery make HyCO and separated HyCO products (CO and H_2) desirable combustion fuels in an overall scheme of maximizing refinery profit. In addition, HyCO and its separated products have significant value as a crucial intermediate resource or feedstock for the production of hydrogen, ammonia, methanol and synthetic hydrocarbon fuels.

Raw HyCO is often contaminated with light sulfides (H_2S, OCS and small mercaptans). The value of the HyCO product and its utility for both combustion and as a chemical feedstock is greatly enhanced by removing these sulfides from the HyCO mixture and/or from the separated CO and H_2 constituents. This is typically accomplished by the use of mixed (iron and other) metal oxides. CO_2 and trace moisture (H_2O) are the other common and potentially problematic impurities that are usually removed in 'HyCO driers'.

As a result, there is a need to monitor trace levels of H_2S, H_2O and CO_2 in pure hydrogen and purified CO. There is also a need to monitor derived mixtures of CO and H_2 in dry HyCO. This is currently accomplished by gas chromatography (GC), non-dispersive infrared (NDIR) or ultraviolet (UV) absorption. The advantages and disadvantages of using GC with HyCO are very similar to those discussed previously in the context of hydrogen for regeneration.

NDIR instruments provide the benefit of rugged simplicity and low cost. The well-known limitation of NDIR is a lack of specificity. The instrument compares broadband infrared absorption characteristics in several pre-set bands of the infrared spectrum. Where two or more trace impurities absorb in the same spectral region, the onboard computer can sometimes estimate relative composition based on absorption values in one of the other spectral windows. One of the worst culprits for cross sensitivity is H_2O, which is present in nearly every source of unpurified HyCO. UV absorption is used for some HyCO applications because sulfides produce a strong and distinctive

UV absorption signal compared to H_2O and CO_2. The problem is that so do other compounds that are sometimes found in HyCO. So again, the issue is cross sensitivity. Both methods typically need frequent calibration. UV absorption methods are typically limited to low ppm concentrations. As a result, UV absorption and NDIR are best suited to monitoring the processing of streams of well-characterized composition where uncertainties are few. They are also suitable for looking for significant process changes. They are a poor match where absolute precision is required, or where HyCO composition is complex and/or subject to variation.

In contrast to these broadband, low-resolution methods, the LGR-ICOS analyzer is a precision analytical tool based on quantitative absorption measurements using narrow line tunable lasers. The laser bandwidth is typically less than 3 MHz, which is many orders of magnitude narrower than UV absorption or NDIR measurements and much narrower than the typical interval between absorption lines from different species – see Figure 2, page 5. As a result, the LGR-ICOS analyzer is often immune to interference between multiple species, even in complex mixtures like HyCO.

Many HyCO monitoring applications need to measure or certify more than one trace impurity. The high spectral resolution of the LGR-ICOS analyzer means that it is ideal for these uses. Also, unlike earlier cavity-based optical analyzers like CRDS, multiple lasers can be incorporated in a single instrument where necessary, enabling simultaneous measurement of a large number of factory-specified targets. No other optical method offers this multi-species analysis capability in a high precision format.

Ultrapure industrial gases

The customizable flexibility of the LGR-ICOS analyzer makes it ideal for suppliers and consumers of a range of ultrapure gases. For example, it is particularly useful for QC and certification of inert gases such as nitrogen and argon, produced from high volume, high purity (for example, cryogenic) air separation units from key on-line sampling through to final loading station testing. Cryogenic air separation has been commercialized for a century now, and process refinements have evolved in parallel with ongoing advances in compression machinery, heat exchangers, distillation technology and gas expander technology. Yet, until the LGR-ICOS analyzer, the state of stream and product analysis methodology has been fairly stagnant. The high sensitivity and absolute accuracy mean that this new analyzer is also an excellent match for suppliers and users of reagent grade calibration gases, such as hydrogen, argon, nitrogen and neon. And the same advantages make the LGR-ICOS analyzer a superior instrument for QC/QA of gases used as inert pressurization blankets in industrial catalyst beds and chemical storage tanks (for example, nitrogen).

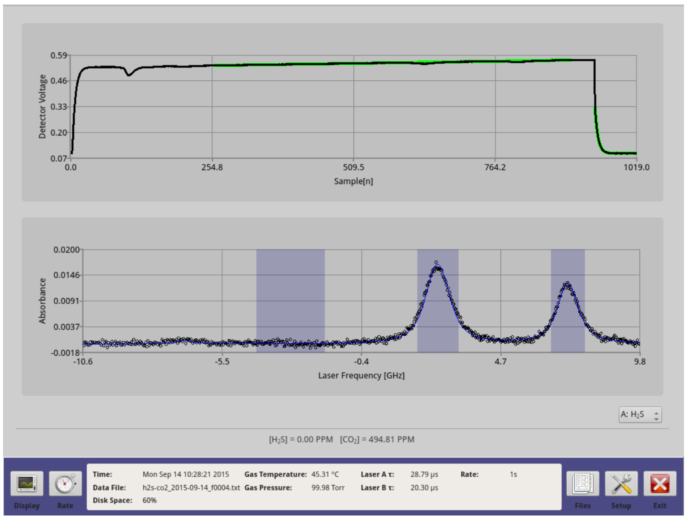

Figure 2 LGR-ICOS analyzer produces and locally stores highly resolved absorption spectra of multiple gases in a single scan

The high spectral resolution of the laser resolves individual absorption features with no cross interference. The broad utility and flexibility of OA-ICOS technology, compared to older spectroscopic methods such as FTIR, UV fluorescence and NIR, offers clear superiority in the key areas of accuracy and sensitivity. OA-ICOS technology is well-established and routinely used for parts per billion data precision in many of the gases monitored for purity in these industrial gas applications.

Summary

Every so often, a new analytical technology is developed that provides a powerful new method of performing existing product analysis with important improvements over conventional methods in the form of superior results, greater speed, lower costs and/or simplicity of use.

The new LGR-ICOS analyzer represents such a breakthrough for measuring trace gas impurities in 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
- simplicity of use

Please contact your local ABB Sales office to discuss your application detail and obtain a quotation according to your specific sample stream composition.

Notes

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