ABB MEASUREMENT & ANALYTICS | APPLICATION NOTE

A better method for real-time measurement of trace acetylene, ammonia and other impurities in ethylene

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The LGR-ICOS™ Series 950 is a next-generation, laser-based, industrial process analyzer that provides better sensitivity, accuracy, precision and speed than other laser methods

Measurement made easy

A better method for real-time measurement of trace acetylene, ammonia and other impurities in ethylene

Introduction

Reliable measurements of trace impurities during ethylene production allows improved process control and ultimately greater product yield and quality. This new analyzer performs with unsurpassed reliability, minimal maintenance and no consumables, measuring multiple target gases with a single instrument.

Key benefits

- Higher performance (sensitivity, precision, accuracy and speed) compared with all other process analyzers
- Fast (seconds) response allows rapid process control
- Multi-gas capabilities available (including acetylene, methyl acetylene, ammonia, methane, CO, CO_2 and H_2O)
- Zero consumable costs
- Zero field calibration required
- Tolerant to wide variations in background composition
- No chemical scrubbing or drying of sample stream required
- Widest linear dynamic ranges available
- No out-of-range shock, fastest recovery times to process upsets
- Developed for applications that require hazardous area certifications, including CSA/UL, Class 1 Division 1 and 2, ATEX Zone 1 and 2, and IECEx

The importance of ethylene

Ethylene (C_2H_4) is one of the most important chemical commodities, with total worldwide production already past 150 million tons. As the simplest alpha olefin, ethylene has pre-eminence as a feedstock for the plastics industry, for producing key polymers such as polyethylene, polystyrene and polyvinyl chloride (PVC). It is also used in other important industrial-scale reactions, such as oxidation and hydration, to generate end products like ethylene oxide and ethylene glycol, as well as important intermediates like ethyl acetate.

A large fraction (> 90 %) of the world's ethylene is generated from petrochemical sources, principally from endothermic cracking of hydrocarbon streams (e.g., naphtha) in the presence of steam. Even with an optimized olefin cracker, the C_2 fraction then includes varying amounts of both acetylene (C_2H_2) and ethane (C_2H_6). The amounts vary with source hydrocarbon and other process specific parameters; acetylene can be as high as 0.95 % by weight. High purity ethylene is generated by converting the acetylene into ethylene using a multi-stage hydrogenation reactor followed by a C_2 separator to separate the ethane.

Like all refinery processes, purity is a statistical concept; the ethylene product stream always includes a residual small amount of acetylene and possibly other undesirable impurities, such as ammonia (NH_3), carbon monoxide (CO), carbon dioxide (CO_2), or methane (CH_4). The tolerable level, and hence specifications, for these gases depend on the intended end use of the ethylene product.

In particular, polymerization is extremely sensitive to certain impurities, and hence polymer-grade ethylene has some of the highest purity specifications. The problem is that the polymerization catalysts are very sensitive to any impurity that has a stronger ligand binding affinity than ethylene. Standout examples are acetylene, ammonia and carbon monoxide (CO). Even parts-per-million concentrations of these chemicals can disrupt the polymerization process, causing unwanted branching and premature chain terminations. And ultimately, their presence leads to poisoning of the (costly) catalyst, which must then be replaced.

Targeting acetylene at the refinery

Optimization of the hydrogenation reactor is key to maximizing ethylene stream purity and minimizing costs. This reactor consists of one or more beds with a catalyst – usually precious metal based supported on an inert matrix. Hydrogen is added to the process stream just prior to this reactor. The entire process is a trade-off between competitive reactions. Too little hydrogenation and acetylene may not be eliminated to the polymer grade target level (typically <5 ppm). Conversely, overdriving the process hydrogenates too much of the ethylene to produce ethane. This just adds to the ethane which is adequately removed in the C2 separator. But, ethane has lower value, and this stream is often reprocessed to make ethylene, so this unwanted ethylene hydrogenation should be minimized. Optimization of reactor parameters such as temperature, pressure, flow rate, hydrogen feed, etc., thus requires real-time monitoring of the acetylene content at two critical process locations – immediately before and after the hydrogenator.

Targeting ammonia at the refinery

Traces of nitrogen and sulfur compounds are virtually inevitable in any process stream derived from fossil hydrocarbon sources. Ammonia is a common problem in ethylene cracking streams, where it can originate from refinery gasses, fuel gas feeds, or from hydrogen cracking of nitrogen compounds in the source hydrocarbons. Moreover, ammonia is a notoriously 'sticky' chemical that can persist on surfaces and react with many chemicals; most important for ethylene customers, it binds to polymerization catalysts, disrupting chain lengths and branching ratios and ultimately poisoning the catalyst. For this reason, polymer-grade ethylene is specified as <100 ppb NH_3.

Until recently, the most common method of monitoring for trace ammonia was as part of a GCMS panel online monitoring after the C_2 splitter. In an interesting case study presented at an AIChE conference (EPC Conference, Houston, TX) in 2006, engineers from the BASF FINA steam cracking plant (Port Arthur, TX) described how several customers began to report detecting ammonia in their ethylene. Moreover, this ammonia had not been detected in the GC/MS data. Subsequent analytical testing using a variety of laboratory methods confirmed the presence of ammonia, and engineers were eventually able to trace the main cause as a saturated upstream drier. This is just one example of the vigilance and detection sensitivity required for measuring ammonia.

Screening incoming ethylene purity

Polymerization to produce polyethylene and other products is an increasingly competitive business, with profit margins that reflect this competition and the industry's maturity. At the same time, subtle variations and innovations in catalysts are a means of minimizing the cost of polymerization and squeezing higher margins, by maximizing yields and throughput. As a result, the cost impact of catalyst poisoning cannot be overstated. This cost impact includes both the cost of the expensive catalyst itself and the down time for the reactor. Thus, there is little tolerance for impurity issues with ethylene suppliers. These issues can and results in financial claims and perhaps even litigation. Some impurities also can occasionally arise after production and acetylene removal, namely during storage and transport.

The potential financial damages from feeding a reactor with polymer grade ethylene that is actually out of specification mean that it is usually screened before use. The polymerization industry uses a variety of methods for this, including GC/MS. In the case of ammonia, methods also include paper tape colorimetry, filled tube colorimetry, and old fashioned (slow) analytical chemistry. This analytical chemistry might involve scrubbing the ethylene with water, followed by standard testing for solvated ammonia.

Limitations of existing analyzer technologies

The ideal analyzer for quantifying impurities in ethylene should have several characteristics. First, it needs high specificity with little cross interference. This is because ethylene may contain numerous unwanted impurities like acetylene and ammonia, and depending on the sampling point, varying amounts of other hydrocarbons such as ethane and propylene. Second, it must have high sensitivity, precision and accuracy; end uses like polymerization have a critical demand for certain impurities at <100 ppb. Third, it must be fast; flares often spike with a steep onset curve, and need to be detected immediately. Fourth, it should be robust and easy to use, with low or zero maintenance requirements, and no need for a highly skilled operator. And, finally, it should have low cost of ownership; in the current economic climate, ethylene producers and users are working on smaller than ever margins.

Unfortunately, none of the older established methods meet all of these criteria

Gas Chromatography (GC), Gas Chromatography/Mass Spectrometry

The legacy technology for on-line monitoring of acetylene and ammonia in ethylene is gas chromatography, sometimes in the form of GC/MS. Gas chromatography and gas chromatography/mass spectrometry have excellent specificity, although as the BASF FINA study showed, they do not always have the requisite sensitivity. The three drawbacks of GC are its slow speed and cost of consumables. The speed can range from 5 to 20 minutes depending on the target gas. Moreover, ethylene plant protocols typically require 2 or 3 data points indicating a process excursion before any mitigation action is considered. Using several columns/instruments in tandem can reduce the measurement interval but increase costs. However, this work-around has no effect on response time. The main consumables costs are the replaceable columns and various calibration and carrier gases.

Tunable Diode Laser Absorption Spectroscopy (TDLAS)

More recently, first and second generation optical analyzers based on TDLAS have shown some merit for analyzing trace gases. Optical absorption spectroscopy is used in many applications to quantify a target species. The challenges to detect a trace species in a mixed gas matrix are low signal and spectral interferences, i.e., cross sensitivity. Spectral interferences arise for acetylene in ethylene because all the hydrocarbons absorb near-infrared light in a similar wavelength region. This cross sensitivity problem can be partially addressed by using a tunable diode laser as the light source. The two major limitations in these first-generation laser absorption instruments are low absorption signals requiring long integration times, and the inability to target more than one species with a single instrument. Plus first-generation instruments have to perform differential spectroscopy for some targets, requiring dual-channel operation with a consumable scrubber used to continually generate a reference gas.

Off-Axis Integrated Cavity Output Spectroscopy (OA-ICOS) – proven next-generation analyzers

The typical drawbacks of legacy and optical methods are eliminated with the LGR-ICOS, a fourth-generation, cavity-based absorption spectroscopy analyzer from ABB, already well-proven in laboratory studies, remote field measurements and at-line industrial process monitoring applications. The inherent advantages of its core (patented) technology, OA-ICOS, deliver a unique and comprehensive set of benefits to analyze trace C_2H_2, NH_3, and other ethylene impurities.

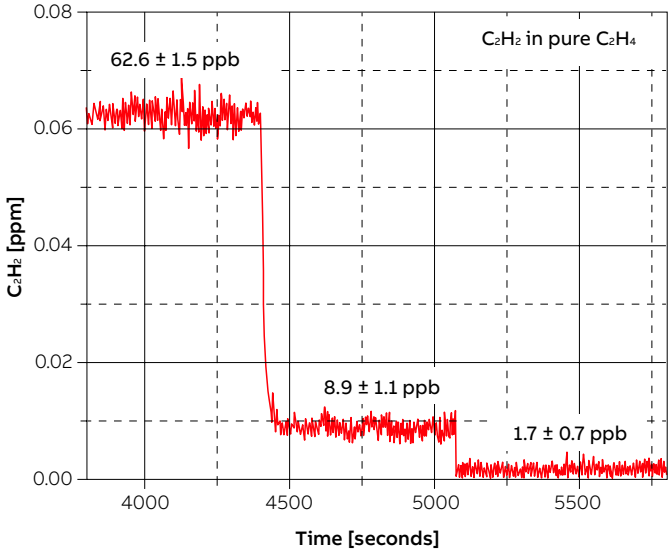

Figure 1 Measured C_2H_2 (1 second data rate) in C_2H_4 illustrates fast response and low ppb-level sensitivity, precision and accuracy

High sensitivity and precision

In simple terms, the OA-ICOS technique addresses the low optical absorption signal by using a tunable laser in conjunction with a high-finesse optical cavity to produce a sampling length of 25 kilometers or more in a compact instrument. This delivers many orders of magnitude better sensitivity than traditional TDLAS. This is an important advantage for detecting a trace hydrocarbon like acetylene in the presence of several other hydrocarbons (ethylene, ethane, methylacetylene, etc.). As a result, trace C_2H_2 and NH_3 can be directly measured with a routine sensitivity (LDL) in the single-digit ppb range (2σ, with 10 seconds of signal averaging). Moreover, low instrument noise enables accuracy of better than 1 % over the entire measuring range of the analyzer.

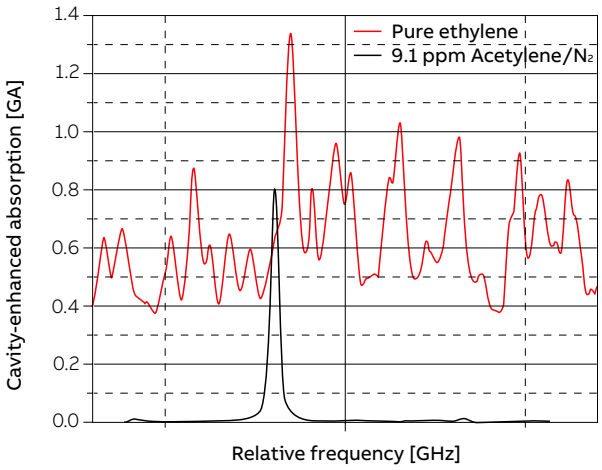

Figure 2 Measured spectroscopic basis sets, used by analysis software, illustrate the unique absorption fingerprints of the target gases

Off-Axis Integrated Cavity Output Spectroscopy (OA-ICOS) – proven next-generation analyzers

Variable background matrix

Limitations of sensitivity and cross-interference mean that earlier optical methods like TDLAS struggle to accommodate changes in the background gas matrix, particularly when measuring acetylene. Because of its use of narrow linewidth lasers (see Figure 2) and a very robust and proprietary multi-variant chemofit (chemometrics) software package, the LGR-ICOS analyzer is the only optical instrument measures C_2H_2 in a highly absorbing and varying background of hydrocarbons with single-digit ppb accuracy and sensitivity (see Figure 1, page 5).

Fast response

The LGR-ICOS is also very fast because of digital scanning of the embedded solid-state lasers; wavelength scanning of the target absorption lines can be completed in just milliseconds. Speed of response to changes in target gas concentrations is primarily limited by the flow time through the instrument (less than 15 seconds).

Multiple target gases

Many ethylene testing/screening applications require simultaneous monitoring of C_2H_2, NH_3 and possibly also CO or CO_2. The LGR-ICOS analyzer is the only optical instrument that can deliver high precision and accurate measurements of all of these, enabling very cost-effective and robust stream analysis with a single instrument. In contrast, legacy TDLAS systems require bundling multiple instruments – one per target gas – in a single enclosure, or by installing several individual analyzers side-by-side in a single shelter or analyzer house.

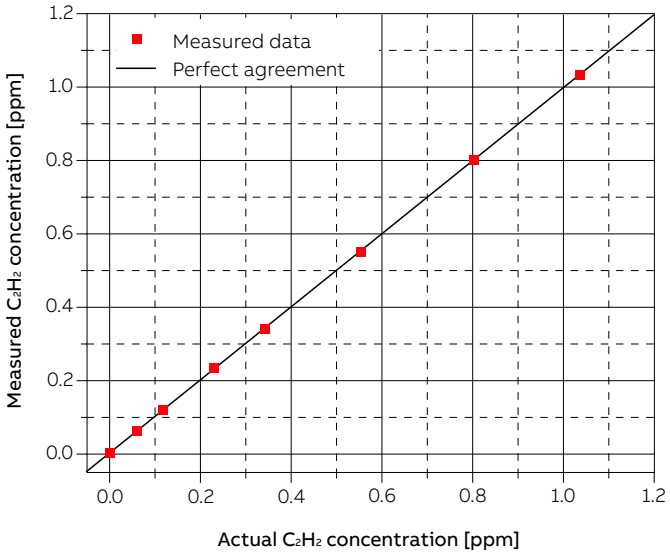

Figure 3 Measurements of acetylene in high purity ethylene illustrate the inherent measurement linearity. The analyzer can measure acetylene concentrations exceeding 100 ppm.

Linear dynamic range – superior accuracy

LGR-ABB's OA-ICOS delivers a highly linear response over the large dynamic range of the analyzer, see figure above. Together with the robust chemofit software and the absence of cross sensitivity, this results in accuracy better than 1 % of full scale deflection (FSD), across the instrument's entire measurement range, for C_2H_2 and/or NH_3, or any other target gas.

Immune to process upsets – zero recovery time

Unfortunately, during at-stream ethylene measurements, various types of process anomalies can occur. The high specificity and fast response of the LGR-ICOS analyzer means its superior performance (sensitivity, precision and accuracy) is not impaired even by out-of-range process upsets.

Automated ease-of-use

Although the LGR-ICOS analyzer is based on high resolution spectroscopy measurements, all this is completely transparent to the operator. Automated operation can be easily software configured to report the target gas concentration at set intervals, and/or to signal an alarm when a customer-set threshold value is exceeded.

No chemical scrubbing required

Unlike other, less-sensitive, analyzers, LGR-ICOS analyzers report gas concentrations quickly, directly and continuously without the need for chemical scrubbing. As a result, LGR-ICOS analyzers do not have consumables and cannot suffer from inaccuracies caused by scrubber aging or breakthrough.

Simple maintenance

This new ABB process analyzer also requires very little maintenance. Estimated preventive maintenance is approximately four hours annually, which includes a simple mirror and/or sample cell cleaning procedure, if indicated by the analyzer's diagnostic software. And, because this fourth-generation method does not require the ultra-precise alignment of older optical methods, like CRDS or TDLAS Herriot cell instruments, this cleaning can be accomplished in just a few minutes. ABB recommends a single span gas verification per target during the annual maintenance routine check. This verification can be performed manually with a single span gas, at a concentration within the analyzer's linear measuring range.

Successful field trial data – first generation

An earlier form of the technology, configured for acetylene and methylacetylene, and using an earlier version of the analysis software, was evaluated in a proof-of-concept study. This was conducted jointly with the Dow Chemical Company, initially in the laboratory, and then for an extended period online at the company's Freeport, TX olefin cracker, just downstream of the C_2 hydrogenators(s).

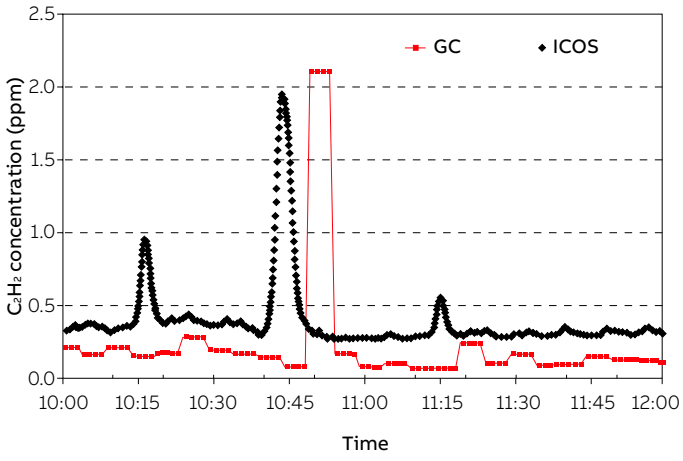

Figure 4 Fast response of the OA-ICOS analyzer allows quantification of time-dependent processes that conventional GC technology can miss

Initial tests verified that the instrument is capable of measuring 0.050 ppm of acetylene, has a precision of ±0.025 ppm, and can accurately determine acetylene concentrations with comparable accuracy to a gas chromatograph (±0.1 ppm) in an actual process stream composition matrix under plant operating conditions. Even with earlier, less sophisticated chemometric software, the acetylene measurement was robust and unaffected by significant matrix variations. Subsequently, the prototype analyzer was installed in a hydrocarbon facility for field-trials in parallel with existing gas chromatographs, where its rapid response (less than 30 seconds) allowed it to measure transient acetylene and methyl acetylene fluctuations that were too fast for the conventional (GC) methodologies. And, unlike those methodologies which require consumables, the laser-based analyzer demonstrated an extended dynamic range that enabled measurement of very high acetylene levels (0 to 1000 ppm) during abnormal plant operations.

Finally, two OA-ICOS laser analyzer systems with stream-switching capabilities were implemented in the Dow Freeport facility with automated stream handling/switching enabling monitoring of more than one reactor. As in the laboratory, analyzer again out-performed the optimized GC, as shown in Figure 4, and more correctly reflected actual process conditions. Following this controlled study, data from the analyzer were then used to optimize the Freeport facility's startup operation and to minimize recovery time during plant excursions, resulting in lower environmental impact and increased product quality.

Summary

Occasionally, a new analytical technology is developed that provides a powerful solution, with important improvements in the form of superior results, greater speed, higher functionality/value, and/or improved simplicity of use. This Application note shows that the new LGR-ICOS Series 950 process analyzers represent such a breakthrough for measuring trace acetylene and/or ammonia in ethylene applications because they offer clear advances in not just one or two, but all **five** of these areas.

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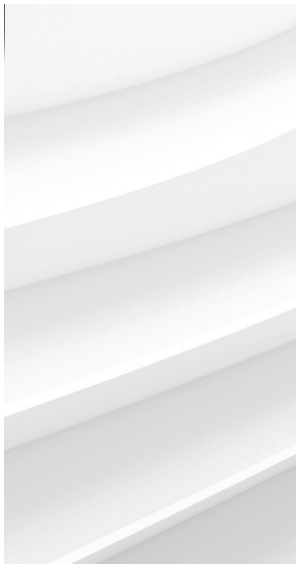

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