

Trace H_2S , H_2O , CO_2 and O_2 measurements for natural gas, biogas and fuel gas in refining and petrochemical application

Los Gatos Research (LGR)



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

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Introduction

This new analyzer performs with unsurpassed reliability, minimal maintenance and no consumables, measuring multiple target gases in complex matrices with a single instrument.

Key benefits

- Higher sensitivity and accuracy than any other H_2S process analyzer
- Superior precision than any traditional TDLAS analyzer
- Faster than traditional TDLAS analyzers
- Simultaneously measures H_2S , H_2O , CO_2 and O_2
- Zero consumable costs
- Zero field calibration required
- Tolerant to wide variations in background composition
- No scrubbing or drying of sample stream required
- Widest linear dynamic ranges offering broad applicability
- 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

Background – H₂S corrosive, toxic and regulated

Hydrogen Sulfide (H₂S) is a common trace gas encountered throughout refining and petrochemical processes and product streams. It is a problem here – as well as in related industries because H₂S is both corrosive and toxic. Corrosion occurs primarily in the presence of moisture when H₂S forms hydrosulfuric acid, which readily reacts with ferrous and other metals. Incidentally, conventional grade concrete is also susceptible to attack by this acid, presenting detection/mitigation problems in subterranean construction (e.g., subways, roadways) above shallow oil/gas deposits. And because H₂S is produced by decay, it is always present in untreated biogas. H₂S is also incredibly toxic to humans – it is a fast-acting poison at a fundamental cellular level. H₂S and organic sulfides (mercaptans) also have a noxious smell – a characteristic ‘bad eggs’ odor – even in trace amounts, which is generally undesirable but useful for positive safety reasons. As a result, there are many applications to measure trace H₂S. Moreover, the majority of these applications are regulated by government and industry bodies in addition to contractual requirements. The LGR-ICOS from ABB is a next-generation H₂S analyzer that can provide superior performance, higher user confidence and better value in all these applications compared to any legacy technique.

Controlling H₂S in fuel gas – eliminating SO₂ emissions

There are a number of separate H₂S analysis applications in the oil/gas industry for products and process streams. Most of these have a pass/fail ‘not to exceed’ specification for the H₂S content, typically in the 4 – 50 ppm range. Some simply impact product value, others are more highly regulated. For instance, removing H₂S from refinery fuel gas and flare gas is a standout application as determined by many government regulatory agencies. H₂S content is often regulated because when combusted, the sulfur is converted into sulfur dioxide (SO₂) an often-regulated acidic atmospheric pollutant and irritant. As a result, for example, in the USA, EPA regulation 40 CFR Part 60, Subpart J, paragraph 60.105 (a) (4) specifies that, “Instead of the SO₂ monitor in paragraph (a)(3) of this section for fuel gas combustion devices subject to §60.104(a)(1), an instrument for continuously monitoring and recording the concentration (dry basis) of H₂S in fuel gases before being burned in any fuel gas combustion device.” The span range for the H₂S analyzer is effectively 0 – 300 ppm.

Avoiding corrosion problems in natural gas pipelines

The presence or elimination of H₂S (and other sulfides) in natural gas is so important it has its own descriptor: sour versus sweet. Sour gas is any gas with a H₂S content exceeding a given value, usually a few tens of ppm. Removal of the H₂S by scrubbing or other means creates ‘sweet’ gas, which has a higher sale value. One of the main end user benefits to removing H₂S is the issue of pipeline corrosion by hydrosulfuric acid; pipes constructed of steel and metallic weld seams can be even more susceptible to acid attack when higher concentrations of H₂S are present in the gas. Consequently, H₂S content is often specified / measured in conjunction with moisture content. There are numerous methods for sweetening natural gas but the predominant one used in large-scale operations is the amine process. H₂S must be measured immediately before and after this process reactor.

Detecting H₂S in biogas

Biogas is an increasingly popular sustainable energy product both politically and economically. Today, it is often introduced as an alternative fuel source to natural gas. Biogas is produced by natural, usually anaerobic decay of organic materials, such as in landfills. The broad spectrum of organics that can give rise to biogas and the wide range of decay conditions mean that biogas has a correspondingly wide variation in composition. The main value component, methane (CH₄) alone can vary from 50 % to >80 %. H₂S (and moisture) is a ubiquitous by-product from the decay process. For biogas used as an energy source in stationary or mobile internal combustion engines, it is important to lower the H₂S content below 10 ppm to reduce engine maintenance requirements and overly frequent oil changing. Both wet and dry scrubbing methods are used for this purpose, depending on the volume involved. For example sodium hydroxide can be the basis of a scrubbing liquid. On the other hand, when biogas is used as an alternative to natural gas, pure H₂S is sometimes added at the producer stage to reach a 6 ppm target as a human safety odor indicator. So in this end user application, it's important to know exactly how much H₂S is already present in order to correctly hit this target.

Limitations of traditional methods

There are a number of established methods for detecting trace H₂S, each with its advantages and limitations.

Lead acetate colorimetry (paper tape)

In this method, the trace gas is passed through a humidifier chamber to ensure a high water content and is then flowed over an exposed section of a lead acetate impregnated paper tape strip. The moist H₂S reacts with the white lead acetate to form a brown stain due to lead sulfide. The stained tape is quantitatively read by an integrated light source and photometer. In spite of its relatively crude concept, the paper tape method is still widely used, which is arguably a testament to the limitations of alternative technologies. Its main limitations are the cost and disposal requirements of the consumable tape and crosstalk issues with other organosulfides, which can also cause tape darkening. It is thus more quantitative when used to measure total sulfur, where the sample gas is pre-treated to reduce all these sulfides to H₂S.

Gas chromatography

Gas chromatography has excellent specificity for H₂S – much better than the paper tape method. Its two main limitations are slow speed and the cost of consumables – the replaceable columns have a finite lifetime. The speed is instrument specific, but it typically takes about 5 minutes from injection to analyzed data. The column then needs to be completely purged before the next injection. Some instrument manufacturers mitigate this somewhat by using two columns, alternating between sampling and purging of the two columns.

Tunable Diode Laser Absorption (TDLAS)

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 such as natural gas or biogas are low signal and spectral interferences, i.e., cross sensitivity. The 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, for example, H₂S and moisture (H₂O). Plus certain first generation TDLAS instruments perform differential spectroscopy for their H₂S measurements that require dual-channel operation with a consumable scrubber used to continually generate a reference gas.

Other methods

In addition to these leading methods, a host of other minor technologies have been used in attempts to get better data, faster data or lower cost data – with varying degrees of success. These include electrochemical sensors, UV absorption, and flame photometry detection (FPD). Their niche uptake confirms that none of these has been demonstrated to have broad applicability.

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, Off-Axis Integrated Cavity Output Spectroscopy (OA-ICOS), deliver a unique and comprehensive set of benefits to trace H₂S applications.

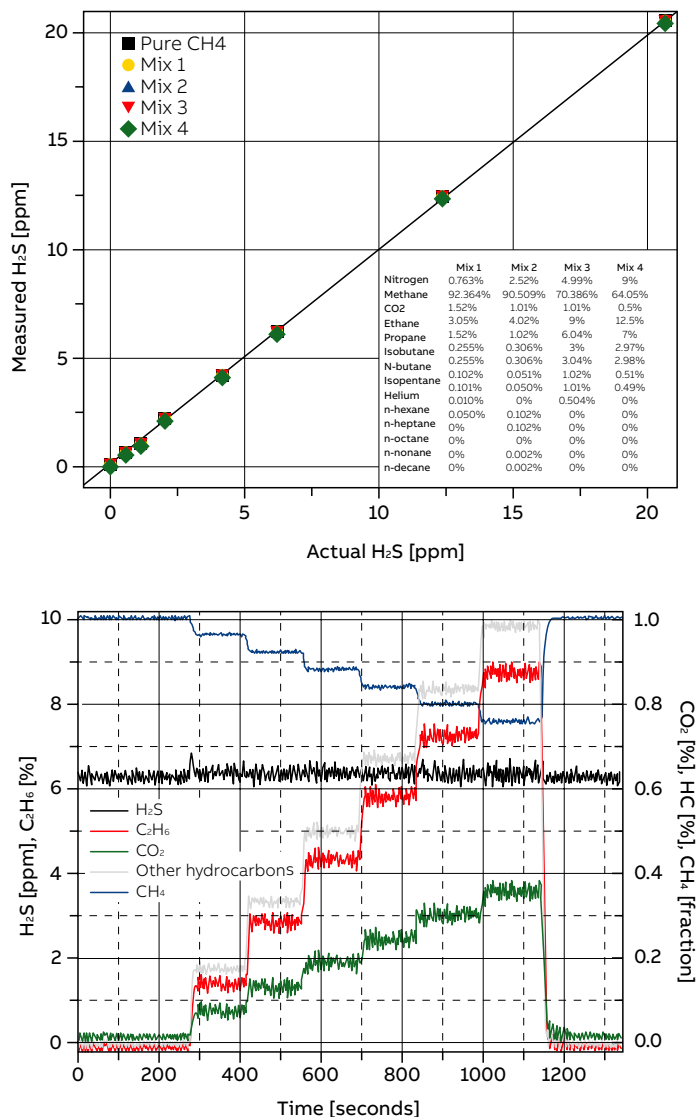


Figure 1 The inherently high sensitivity and selectivity of the patented technology allows the LGR-ICOS analyzer to detect and accurately quantify H₂S in complex flows containing (top) different and (bottom) varying matrices

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 deliver a sampling length of 25 kilometers or more in a compact instrument. This delivers many orders of magnitude better sensitivity than traditional TDLAS, which allows OA-ICOS to target carefully chosen absorption lines purely on the basis of having no overlap with other common molecules. As a result, trace H₂S can be directly measured with a routine sensitivity (LDL) in the single-digit ppb range (2 σ , with 10 seconds of signal averaging). And low instrument noise enables guaranteed accuracy of better than 1 % over the measuring range for the lifetime of the analyzer.

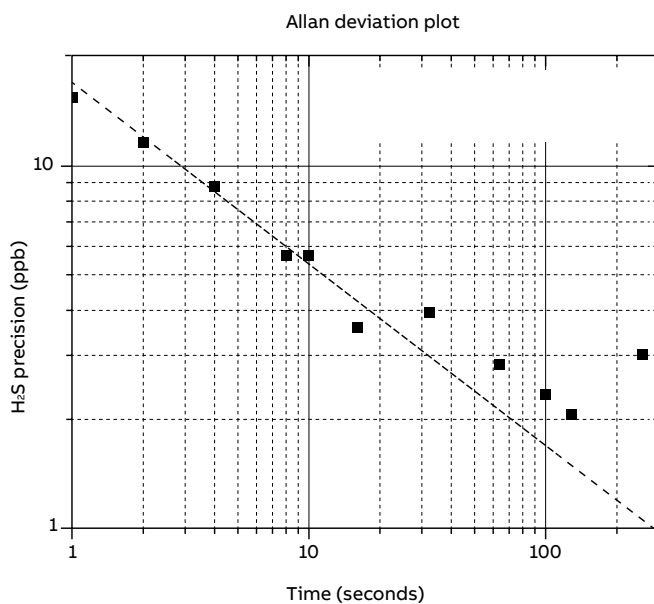


Figure 2 Precision versus averaging time – this Allan plot for the LGR-ICOS Trace H₂S Analyzer shows that with just 10 seconds of averaging, the precision in >92 % CH₄ is better than 10 ppb

Fast response

The LGR-ICOS analyzer is also very fast because of the digital scanning of the embedded solid-state lasers; wavelength scanning of the target absorption lines can be completed in only milliseconds. Speed of response in T90/10 to H₂S gas concentrations within the measuring range is less than 15 seconds.

Multiple target gases

Many H₂S applications require simultaneous monitoring of moisture (H₂O), CO₂ and O₂. 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 from different manufacturers side-by-side in a single shelter or analyzer house.

Linear dynamic range – superior accuracy

LGR-ABB's OA-ICOS delivers a highly linear response over the full dynamic range of the analyzer, see Figure 1, page 4. 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.

...OA-ICOS – proven next generation analyzers

Variable background matrix

Trace H₂S is not the only component that varies in natural gas and biogas. For example, the methane/ethane/propane varies significantly depending on the source of the gas. Because of its use of narrow linewidth lasers and a very robust and proprietary multi-variant chemofit (chemometrics) software package, the LGR-ICOS analyzer is the only optical instrument that can measure H₂S in a highly absorbing background of hydrocarbons with accuracy and sensitivity (Figure 1, page 4).

Immune to process upsets – zero recovery time

Unfortunately during at-stream H₂S measurements, various types of process anomalies can occur. For example, the CO₂ level might spike from say 100 ppm to 2 % or higher. The high specificity and fast response of the LGR-ICOS analyzer means its superior performance (sensitivity, precision and accuracy) is not impaired by process upsets.

Single channel instrument – no scrubbing required

The linear response from ppb to high ppm concentrations and robust calibration of the LGR-ICOS analyzer enables direct single channel measurement, without need for continuous differential calculations using a scrubbed sample (as in earlier traditional TDLAS instruments), and with no need for frequent calibration or any calibration at all in the field. No scrubbing means no consumables or 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 during the annual maintenance routine check. This verification can be performed manually with a single span gas of a concentration anywhere within the analyzer's linear measuring range.

Summary

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, 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 H₂S, H₂O, CO₂ and O₂ in a range of natural gas, fuel gas and biogas applications because they offer clear advances in not just one or two, but all **four** of these areas.

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

