Improved solutions for natural gas quality analysis

Asad Tahir, Emerson, USA, offers an analysis of the advances in analyser technology which have improved natural gas composition and sulfur content evaluation.

Natural gas suppliers and pipeline companies have many choices when looking for sources of supply. Gas can come from a variety of domestic fields (Figure 1), from other countries via pipeline or LNG tanker, and from alternative sources such as biomethane. The common element is compositional variability, often reaching the limits of what is considered commercial natural gas.

Regulatory agencies and pipeline companies around the world define natural gas quality by limits on components other than methane (CH_4). While there is some variation, most include specification ranges for:

- Wobbe index.
- Calorific value.
- Relative density.
- Total sulfur content.
- Hydrogen sulfide content.
- Water content.
- Hydrogen content.
- Carbon dioxide content.
- Oxygen content.

Variability can create a variety of problems for large-scale users, particularly for use as a fuel for gas turbines or sophisticated fired heaters, where the Btu rating (calorific value) is critical. For gas turbines, the Wobbe index indicates additional characteristics affecting its suitability as a fuel. For some users, contaminants can be just as important. For most, the least desirable contaminants relate to sulfur, which influences the price and quality of gas being transferred.

All fossil hydrocarbon fuels carry sulfur and its various compounds over a wide range of concentrations, from traces (ppb) to percentages. In addition to elemental sulfur, forms found in natural gas include, but are not limited to:

- Hydrogen sulfide.
- Carbonyl sulfide.
- Dimethyl sulfide.
- Tetrahydrothiophene.

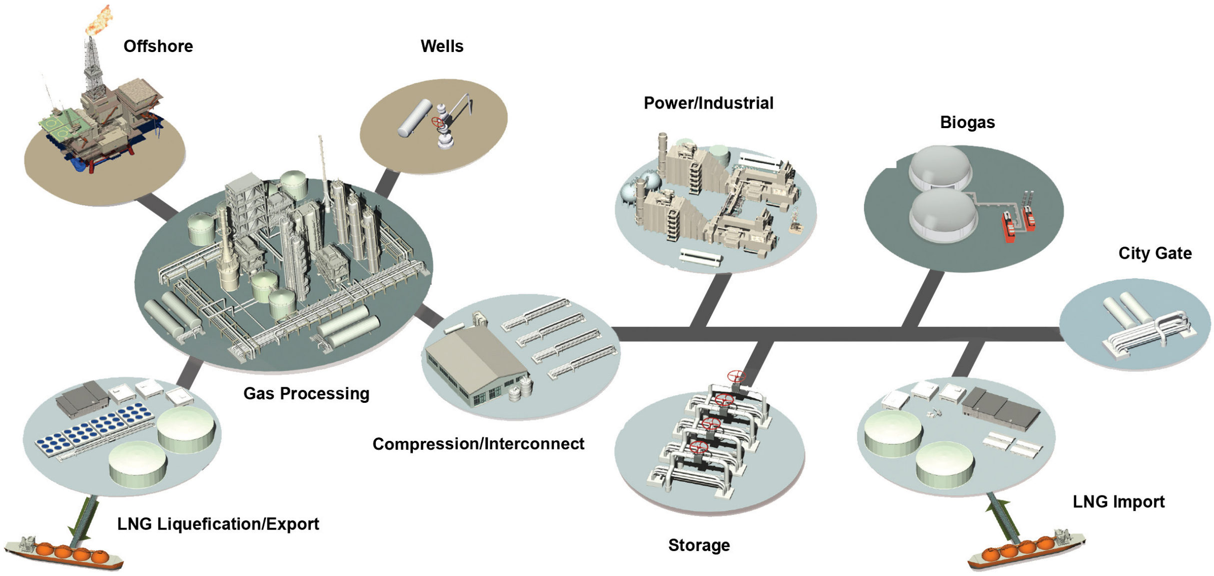

Figure 1. The complexity of the entire natural gas distribution chain calls for quality evaluations at many points.

Figure 2. Basic natural gas analysis can be covered by a C6+ analyser, such as Emerson's Rosemount™ 370XA Gas Chromatograph. Its enclosure permits field mounting in most areas classified as hazardous.

- Tertiary butyl mercaptan.
- Methyl mercaptan.
- Ethyl mercaptan.
- Isopropyl mercaptan.
- Normal propyl mercaptan.

Gas is usually considered sour if hydrogen sulfide (H_2S) content is above 5.7 mg/m^3. Sulfur is a problem because it is corrosive, shortening the life of processing equipment, and burning it creates sulfur dioxide (SO_2), a heavily-regulated pollutant. Many sulfur compounds are also toxic.

Naturally, sulfur content affects the value of natural gas since it must be removed, treated, or its effects mitigated – each of which adds cost for a user or pipeline company. The most common amine process for sulfur removal can recover it in a form suitable for sale. The yellow sulfur piles outside gas processing facilities account for about 15% of total sulfur production, which mitigates removal costs. Nonetheless, these cleaning methods are not totally effective and can leave 2 – 5% of the original content in the gas.

Consequently, it remains critical for those in the delivery chain to monitor overall gas composition and sulfur content in its entirety continuously, since it can vary greatly with changes in gas sources. If the pipeline switches from a conventional gas field supply to a mix from various shale sites, or from gas processed by a less effective removal

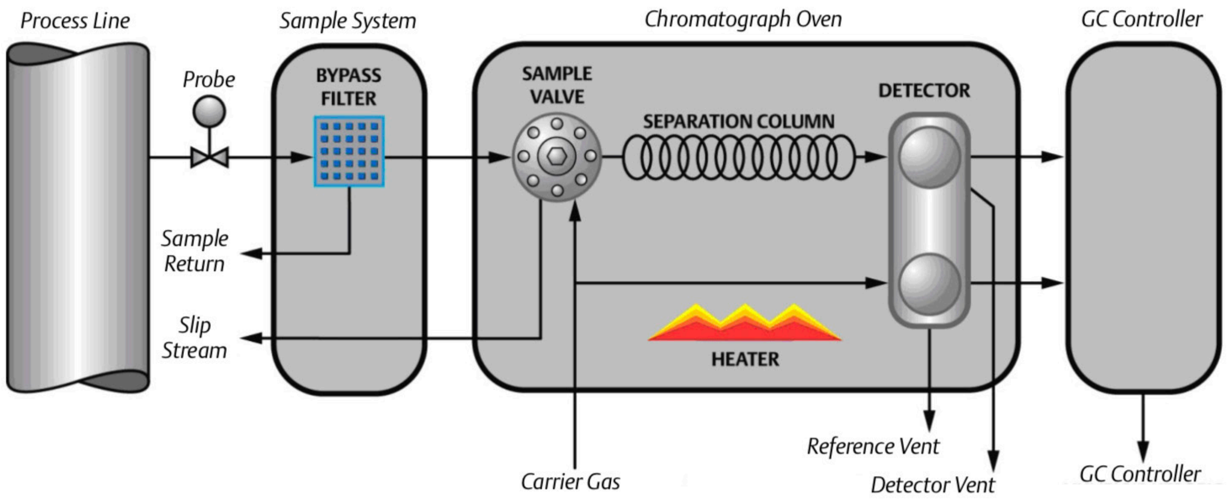

Figure 3. The main components of a basic GC include a sample valve which mixes the sample with carrier gas, the actual separation column, and the thermal conductivity detector.

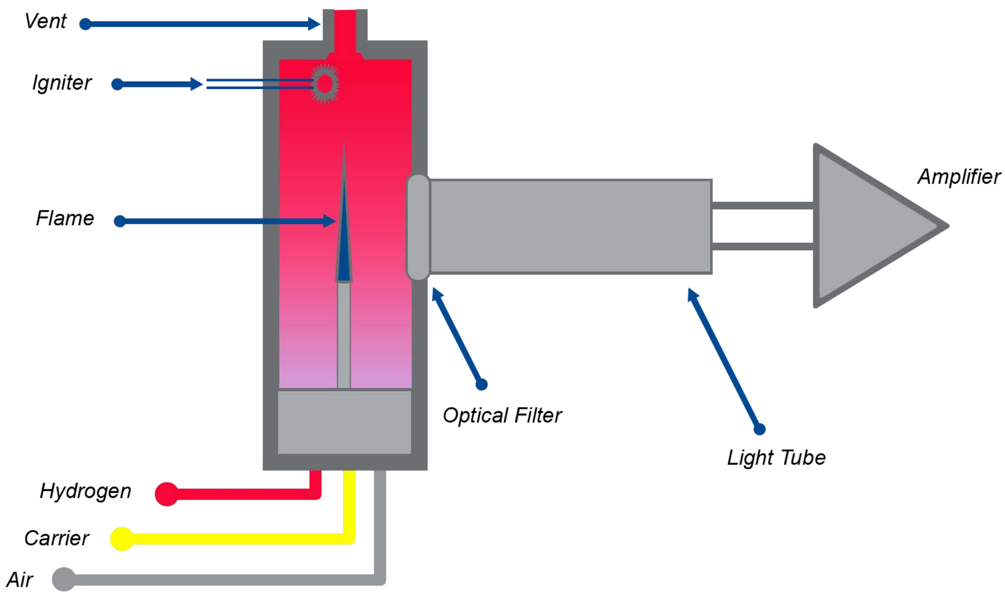

Figure 4. A flame photometric detector injects the sample gas into a stream of hydrogen mixed with air. As the gas burns, the light tube collects photons which are converted into an electrical signal. This method is able to detect and quantify trace amounts of sulfur and sulfur compounds.

facility, there can be significant fluctuations, while still remaining within the bounds of what is considered to be commercial natural gas.

Pipeline operators must pay particular attention to composition due to operational and equipment durability concerns. The corrosiveness of sulfur affects pipeline integrity, as well as valves and compressors. If heavy hydrocarbons condense into liquids, these require more energy to push through the pipe and increase the frequency of pipe cleaning. Heavy components can also form hydrates able to damage equipment and clog pipes.

Non-fossil sources

The natural gas supply picture is changing as many countries move to a low-carbon energy sector built on various types of renewables. One of the fastest growing renewable sources is biogas (sometimes called biomethane), a purified form of digester gas generated by the decomposition of organic waste in a sealed digester. This type of gas can be collected from many possible sources, including vegetation and animal waste.

Purification is necessary because the gas from these processes contains a mix of products, including carbon dioxide (CO_2), ammonia (NH_3), and hydrogen sulfide. Some locations burn minimally processed digester gas on-site, while others upgrade it into higher-value biogas for sale via the pipeline grid.

The chemical composition of digester gas varies according to the process and feedstock, so the distribution of other components also varies. If the producer wants to deliver processed biogas to a pipeline operator, it must ensure the composition meets minimum requirements. For example, in its 'Biogas Interconnect Facility Requirements' document, TransCanada Corp. tells producers:

"The Biogas delivered into TransCanada pipelines must meet the gas quality standards specified in the Tariff for each TransCanada pipeline. At a minimum, the following equipment (more specifically defined in the TransCanada specifications and standards) is required at all interconnections with biogas facilities:

- Gas chromatograph.
- Oxygen analyser.
- Hydrogen sulfide/total sulfur analyser.
- Moisture analyser.
- Filter separator.
- Quality assurance valve.
- Corrosion coupon holder.

Additional equipment may be required as necessary to ensure that the biogas delivered meets the gas quality standards of the TransCanada pipeline. Remote operated shutdown valves will be required and activated when gas quality is out of spec."[1]

This equipment must be available at any point where gas could be added to the pipeline system. Note particularly that it requires hydrogen sulfide and total sulfur measurements among the specifications. Should anything drift out of range, the pipeline can shut off the supply from the offending source.

Analysing natural gas

Natural gas analysis typically requires the detection of specific components or groups:

Table 1. Analytical detection techniques for hydrogen sulfide and total sulfur in flue gas, fuel gas, and natural gas

Application vs detection technique	Lead acetate paper	Tunable diode laser	Gas chromatographic FPD	Gas chromatographic TCD
H_2S in flue gas	X	X	X	X
H_2S in fuel gas	X	X	X	X
H_2S in natural gas	X	X	X	X
Total sulfur	X		X	

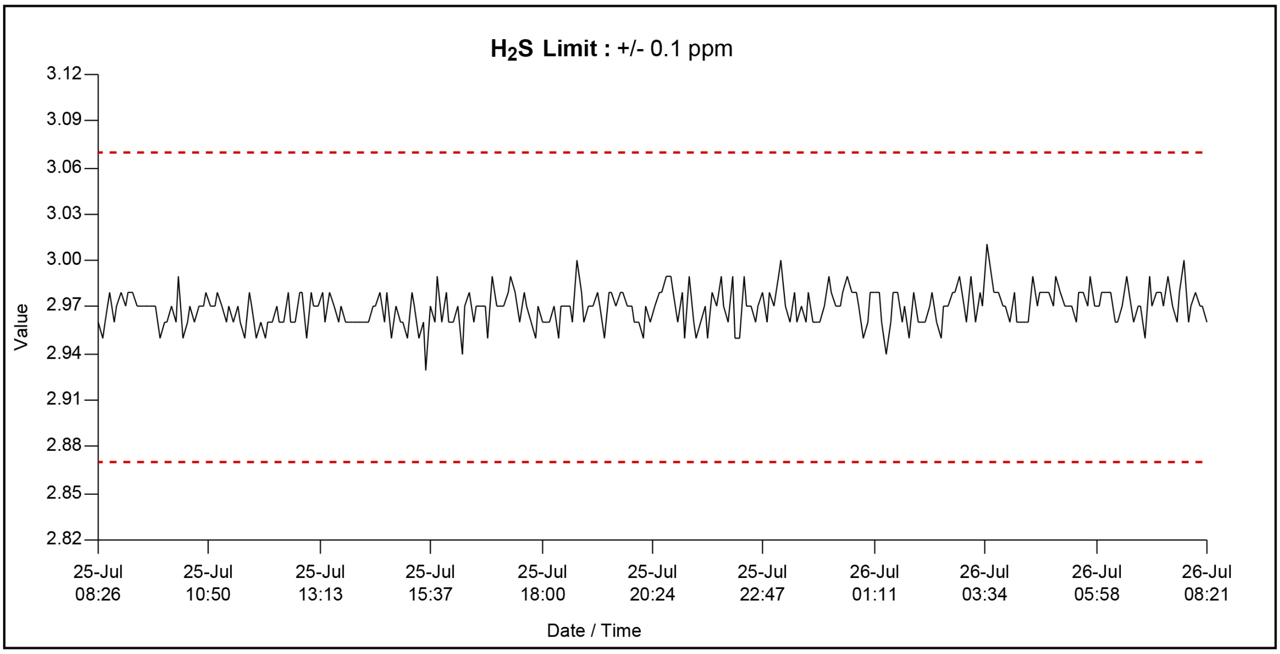

Figure 5. μFPDs provide a linear response over typical ranges of 0.2 to 10 ppm.

- Combustible gases – methane, hydrogen, plus heavier hydrocarbons up to C9+.
- Ballast gases – nitrogen, carbon dioxide, water vapour.
- Contaminants – sulfur, hydrogen sulfide, mercaptans.

The first two groups determine Btu content, plus factors such as dew points for heavier hydrocarbons. This type of analysis is usually performed with gas chromatographs (GCs). A relatively simple GC can handle most common components, including hydrocarbons through C6 (Figure 2).

These types of GCs use a packed column (Figure 3), combined with a thermal conductivity detector (TCD) for the actual quantification.

For users needing to quantify additional components, including heavier hydrocarbons for critical dew points, a C9+ GC uses a double column/detector set in a two-stage configuration.

Quantifying sulfur in its various forms is a different matter. A basic GC using only a TCD can detect sulfur, but only where there are relatively high levels, and it cannot differentiate specific compounds. Depending on the application, this may be sufficient.

However, in most situations where sulfur is a concern, the measurement will likely call for higher resolution than can be provided by a TCD-based GC. Many regulatory bodies call for measurements below 3 ppm, which is outside the practical range of a GC that is equipped with only a TCD.

Do multiple components require multiple analysers?

Table 2. Analytical detection techniques and their dynamic measurement ranges and limit of detection (LOD) for hydrogen sulfide and total sulfur in gases. LOD values for TCD are very conservative

Application vs range/detection limit of analytical detection	Lead acetate paper	Tunable diode laser	Gas chromatographic FPD	Gas chromatographic TCD
H_2S in flue gas	0.010 ppm – % level 10 ppb LOD	0 – 20 ppm 5 ppm LOD	50 ppb – 100 ppm 10 ppb LOD	0.5 ppm – % level 0.5 ppm LOD
H_2S in fuel gas	0.010 ppm – % level 10 ppb LOD	0 – 20 ppm 5 ppm LOD	50 ppb – 100 ppm 10 ppb LOD	0.5 ppm – % level 0.5 ppm LOD
H_2S in natural gas	0.010 ppm – % level 10 ppb LOD	0 – 20 ppm 5 ppm LOD	50 ppb – 100 ppm 10 ppb LOD	0.5 ppm – % level 3 ppm LOD*
Total sulfur	0.010 ppm – % level 10 ppb LOD		200 ppb – 500 ppm 40 ppb LOD	

*TCD's detection of H_2S at >3 ppm is dependable and steady. Detection at levels <3 ppm can be less accurate

Figure 6. Detailed natural gas analysis calls for a C9+ analyser, such as Emerson's Rosemount 700XA Process Gas Chromatograph.

Table 3. C9+ analysis with total sulfur

Methane	65 to 100 mole %
Ethane	0 to 20 mole %
Propane	0 to 10 mole %
n-Butane	0 to 5 mole %
Iso-Butane	0 to 5 mole %
n-Pentane	0 to 1 mole %
Iso-Pentane	0 to 1 mole %
Hexane	0 to 0.7 mole %
Nitrogen	0 to 20 mole %
Carbon dioxide	0 to 20 mole %
Heptane	0 to 1 mole %
Octane	0 to 0.5 mole %
Nonane	0 to 0.5 mole %
Sulfur measurement analysis	
H_2S	0.2 to 10 ppm
COS	0.2 to 10 ppm
RSH+	0.3 to 30 ppm
Total sulfur (calculated)	0.2 to 50 ppm

Depending on the extent of the analysis required, facilities using traditional methods often end up using multiple analysers. If total sulfur, hydrogen sulfide, and multiple additional compounds must be quantified, the solution normally involves specialised analysers because conventional wisdom says that no single technology can perform everything.

Lead acetate tape analysers

If hydrogen sulfide is the greatest concern, the old approach calls for lead acetate tape machines. This is a long-standing technology and can be accurate with high sensitivity, but most only measure hydrogen sulfide, although some also measure carbon dioxide. While they require little calibration, they are maintenance-intensive due to their mechanical design. They also rely on consumables that add maintenance and operating cost and reduce the availability of the analyser. Lead acetate paper tape (CAS 6080-56-4)[2] is classified as a hazardous waste according to US and EU regulations (RCRA Code D002/D003, EU 16 05 06)[3], requiring hazardous waste disposal. Proper disposal of used tape incurs additional operating costs, and failure to do so can lead to a violation and a fine.

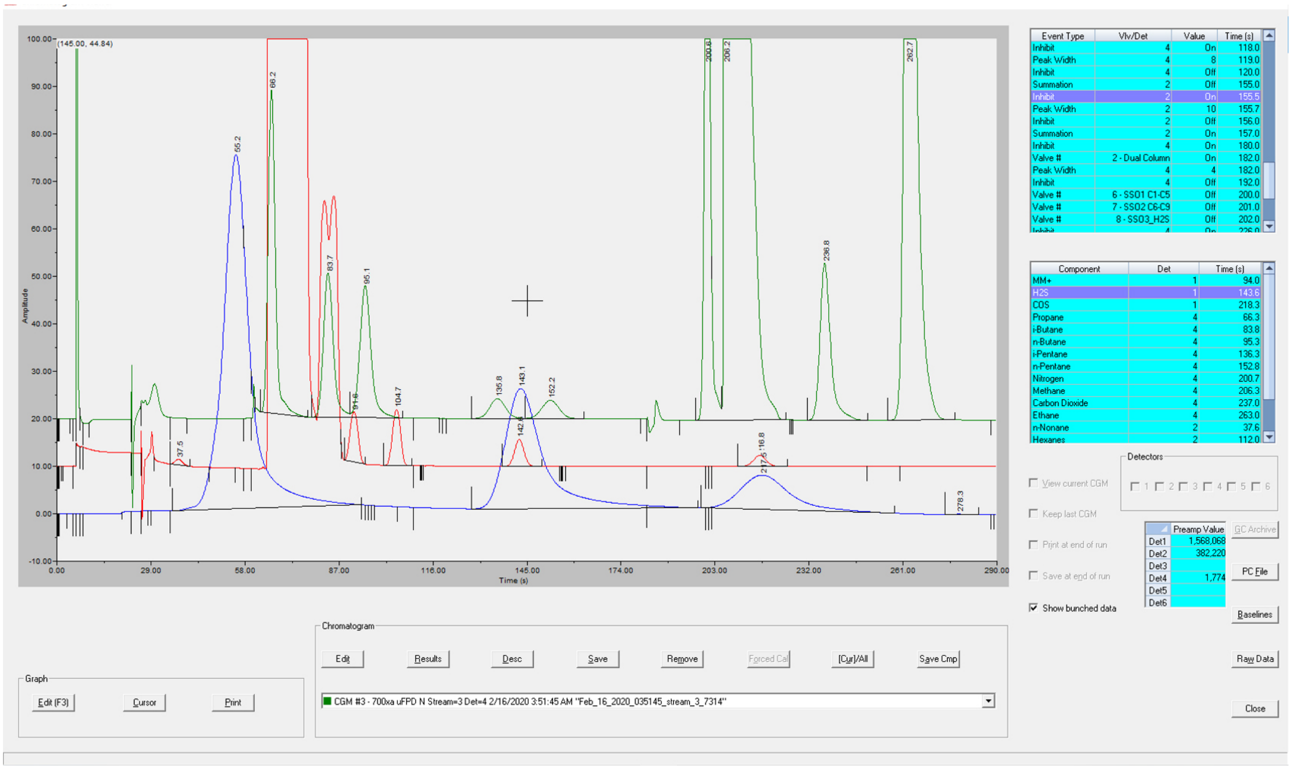

Figure 7. A GC's chromatogram provides a visual indication of the various components measured by a detector as a series of peaks.

Tunable diode laser analysers

Many tape machines are being supplanted by tunable diode laser spectroscopy analysers, which are capable of measuring hydrogen sulfide with low limits well below 1 ppm. These are relatively inexpensive but have few other capabilities in this context. They can also quantify carbon dioxide and water vapour in the gas stream, but that is all. Their measurement performance is also susceptible to cross-interference from hydrocarbons which can lead to misreading. In addition, they cannot speciate and quantify all mercaptans and sulfur compounds.

Following this thinking, if the application calls for the measurement of a long list of variables – including total sulfur, hydrogen sulfide, Btu content, carbonyl sulfide, mercaptans, and others – it may be necessary to have several analysers, each using different technologies.

This is a solution, but it is very costly, and it requires many consumables and excessive maintenance, along with extensive personnel training to create internal experts. Moreover, it has not yet been discussed how any of these technologies can differentiate various sulfur compounds. Fortunately, there is one analyser technology that delivers exactly the capabilities needed.

Gas chromatographic flame photometric detector

Arguably, the most complete analysis of sulfur and its compounds, outside of a laboratory environment, is available with a gas chromatographic flame photometric detector (FPD). The working principle employed is that sulfur produces a unique blue flame in the presence of burning hydrogen and air (Figure 4). Photons from the blue emission are then filtered and passed through a photomultiplier tube. These signals are amplified and processed in the electronic compartment or controller.

Usually a FPD stage is used in combination with a GC – where the column separates the individual sulfur compound species – which are then detected, identified, and measured using the FPD.

Given this capability, why are these not more common? Traditional gas chromatographic FPD analysers are equipped with large air-bath ovens and are typically too expensive, bulky, and finicky for field use. They require elaborate, air-purged enclosures that add significant capital and operating costs tied to installation, utilities, heat tracing, long sample lines, climate control, and HVAC, especially in hot climates since air-bath ovens generate a lot of latent heat, driving up total cost of ownership. Fortunately, as FPD technology has evolved, it has become far more practical and economical. New miniaturised micro-FPD (μFPD) versions are suitable for integration into a field-mountable and explosion-proof transmitter-style analyser, where the μFPD performs as one more stage added to a multi-purpose GC, significantly reducing cost and footprint, plus eliminating the need for running purge lines.

Tables 1 and 2 provide a comparison of the technologies discussed, their applications and measuring ranges.

Recent analysers using this μFPD technology are highly sensitive to compositional changes and can typically measure hydrogen sulfide with repeatability less than 0.1 ppm (Figure 5) at limit alarm points. This kind of accuracy is critical as the maximum hydrogen sulfide plus carbonyl sulfide level for European gas transmission pipeline networks is 3.3 ppm.

While such comprehensive measurements would have called for multiple analysers a few years ago, these variables are now on the list of the values measured by Emerson's Rosemount 700XA GC, an explosion-proof analyser equipped with a μFPD (Figure 6) and designed for in-situ or close-to-tap field mounting. Mercaptans, carbon dioxide, and carbon monoxide can also be measured and reported.

With everything included, a C9+ GC with a μFPD can measure a comprehensive list of components (Table 3 and Figure 7).

All this can be achieved from a single standalone, field-mountable analyser, reducing operator training and simplifying installation because of lower requirements for power and environmental controls. This results in reduced capital and operating costs by as much as 50%, and footprint by as much as 40%. Purge air and shelters are no longer necessary, even in the outdoor plant environments where these analysers are typically deployed.

Durability and easy operation

Today's analysers are not the complex, fragile, bulky, and expensive devices of yesteryear. The need for consumables is much lower, and improved operator interfaces allow automated processing, remote connectivity, and audit checks while reducing the need for specialised training. The reduced size and fragility of internal valves and sensors makes it possible to reduce the footprint of a GC and eliminate the need for specialised enclosures. Some designs available today are explosion-proof and ATEX/IECEX safety rated – meaning that they are field installable without an enclosure – even in Class 1, Division 1 areas, eliminating the need for costly air-purged enclosures in any environment.

The ability to capture the data necessary to build a complete picture of natural gas characteristics is far easier than ever before. The need for multiple dedicated single analysers has been supplanted by GCs with μFPD technology, resulting in today's simpler, smaller, less expensive, and more versatile offerings. Gas producers, pipeline companies, and end users are taking advantage by getting the measurements they need without the complications, expense, and maintenance requirements of older technologies and solutions.

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