High variability of volume and chemical composition of flare gas makes analysis for environmental regulatory compliance a challenge. Different technology combinations offer different capabilities.

Refiners routinely flare gas from the process that is not commercially recoverable. The amount of gas and its chemical composition changes according to operating conditions, but it is primarily methane with a few other products, including sulfur compounds. Steam may be added to reduce visible black smoke from the stack. Operation of a flare stack is typically regulated by local environmental authorities, and refineries may face limits as to the total volume burned along with requirements to monitor the level of sulfur content. If...
unreduced sulfur is included, it may also have to verify that the waste gas has sufficient British thermal units (BTU) content to ensure full combustion of all components and sulfur reduction.

Generally, the two main components that regulators want to monitor are hydrogen sulfide (H₂S) and total reduced sulfur (TRS).

The challenge for refineries is demonstrating compliance with the test methods, procedures and performance specifications cited in relevant regulations. Meeting those can present a variety of technical and economic challenges relating to the variability of flare gas at any given time. For example, measuring the concentration of TRS may span four orders of magnitude. Finding a device that can measure accurately across so wide a range while still meeting requirements of the rule for calibration and validation can be a major technical challenge and may require more than one device. The economic challenge is finding an approach that can do it all reliably, cost effectively, and in conformity with the requirements of relevant specifications.

This article will look at various analyser technologies and consider the approaches that are currently available with a critique of their underlying assumptions and effectiveness. The applicability of any one will have to be evaluated for the specific situation.

Complying with regulations

The US Environmental Protection Agency (EPA) regulates flare gas under Title 40 CFR Part 60 Subpart Ja, which will be mentioned throughout this article, but there are parallel regulations in other jurisdictions to varying degrees. Subpart Ja regulations can be summarised in Table 1. (Strictly speaking, BTU content is not defined in Subpart Ja, but it is included elsewhere in Part 60).

Three main options will be considered available for achieving these measurements, but regardless of the approach, the regulatory environment in which refiners find themselves in any part of the world might leave them with technical solutions that are inadequate to the task at hand. Refiners often find themselves in a gap between compliance requirements and the limitations of available technologies.

One issue already mentioned is that the TRS level can vary enormously leaving the analyser trying to monitor across a concentration range that may far exceed its dynamic range. Some analyser manufacturers compensate by using internal techniques that extend dynamic range by means that change the sample (through dilution), the function of the analyser (electronics, detectors, etc.), or both. Such changes effectively create multiple analysis systems (or analyser regimes), which all have to be validated during routine span checks.

Can gas chromatography do it all?

Gas chromatographs (GCs) are highly configurable, therefore the possibility exists to integrate all three measurements within a single analyser package. This sounds like a useful approach but the reality is more complicated. That single GC has to be configured with three separate channels or analysis trains, each with a dedicated injector, column, detector and oven to perform the measurements defined in Table 1. The result is that it is not a single analyser, but is instead three discrete analysers integrated into a common enclosure and controlled by a common processor.

Achieving a dynamic range that is three to five orders of magnitude, as may be required to measure TRS, could depend on a dilution scheme that roughly requires one dilution regime per 10 fold to 100 fold change in concentration. Consider a GC configured with three different dilution regimes to span TRS concentration in three ranges: low range up to a perhaps 500 ppm; the mid range up to a couple percent; and high range up to perhaps 50%. When combined with analytical trains that also measure H₂S and BTU, the so called single analyser that is really a three in one analyser becomes a five in one proposition.

While a three in one chromatograph is conceptually appealing, the fact that it is three analysers demands the individual calibration and validation of each analysis train, as would be the case for any trio of analysers. Depending on the prevailing regulations, that could mean daily zero/span tests of all three.

To complicate matters further, analysers that depend on dilution schemes rely on hardware that changes the sample by combining it with a diluent. Both the sample gas and diluent have to be metered individually using equipment that typically does not perform consistently across all stream compositions. For example, use of a mass flow controller assumes that the number of grams of gas per litre of sample

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Figure 1. Multiple analysers in a single analyser system with three dilution regimes for TRS.
is constant, which clearly is not the case. An alternative approach that meters a sample for dilution by constant volume volumetric displacement is also problematic, as the dilution ratio varies according to the relationship $P_1 \cdot T_1 = P_2 \cdot T_2$, which demands temperature control to ensure reproducible dilution.

Beyond these problems, using a GC to measure TRS may present other associated issues. Coking may occur in the flame ionisation detector (FID) used to oxidise compounds containing sulfur in reduced oxidation states.

All these factors suggest that working with three diverse applications is beyond the practical capability of one technology. The logical alternative is to consider the next option and assemble a multi analyser system based on technologies that are each optimised for their specific purpose.

**GC with a dedicated TRS analyser**

Following the above logic, the measurement requirements defined in Table 1 are best met by a system that comprises analysers best suited to perform the specific measurements: a gas chromatograph with two separate analysis trains to measure BTU and $H_2S$ combined with a total sulfur analyser to measure TRS as $SO_2$.

The GC for BTU content and $H_2S$ is effectively the only technology available today that is suitable for the ranges seen in flare gas. Some have attempted to measure $H_2S$ spectrometrically, in particular by tunable diode laser (TDL) spectrometry, but background interference and dramatic variations in $H_2S$ line shapes may severely limit the accuracy of TDL for this application. If that were not the case, TDL certainly could be used to measure $H_2S$; however, in the case where both BTU and $H_2S$ must be measured, the argument for introducing yet another technology simply to measure $H_2S$ is difficult to make on practical and financial grounds.

Similarly, although the spectrometric analysis of BTU content is possible in streams such as natural gas, this approach generally has difficulty in accurately differentiating between compounds heavier than butane, which in turn encumber the accurate determination of fuel value.

Though gas chromatography is the default technology for analysing BTU content and $H_2S$ in flare gas, one analyser cannot do both. There are actually two analysers, each configured for a specific task. This suggests using the three in two analyser option, pairing the two GCs with a total sulfur analyser shown in Figure 2. A large number of refiners have adopted this approach after taking into account all technical, economic and regulatory considerations.

**Wide range TRS measurement**

Refiners are familiar with analysers that verify sulfur levels in gasoline and diesel to meet regulatory specifications. Typically, these analysers rely on ultraviolet fluorescence (UVF), which selectively quantifies sulfur on the basis of electrons excited by UV radiation. Though suitable for single range measurement of sulfur in motor fuels at levels below 50 ppm, application of these technologies to measure TRS up to percent levels in flare gas suffers the same limitation as GCs discussed earlier. Dilution schemes must be implemented because the core sensor technology lacks the dynamic range necessary to measure TRS across the nearly three orders of magnitude required for the

**Figure 2.** Multiple analysers in a single analyser system.

**Figure 3.** Three analyser trains for three analyses. Patent pending.

0 – 5000 ppmv minimum range, much less that required to make measurements at percentage levels. The implications of dilution for TRS analysis are as much of a problem for conventional sulfur analysers as they are for TRS analysis by gas chromatography.

There is a new excimer ultraviolet fluorescence (EUVF) technology for TRS measurement that does not require dilution schemes and associated questions. The solution still uses a process GC to measure BTU content and $H_2S$, but it is paired with new EUVF analyser technology, designated as the EF.60107, for measuring TRS. This type of analyser is now installed and operating at a major US refinery. It can measure TRS across four orders of magnitude, from 100 ppmv to 1 million ppmv (100%), without the need to dilute the sample. Therefore, the solution incorporates three analytical trains, not four or five, because it requires no dilution to span the full range of possible TRS concentrations.

Figure 4 presents results for analysis of $H_2S$ for TRS using this new approach. With a measurement interval of only 100 s, the results (blue) appear to be nearly continuous, whereas the
conventional GC results (maroon) exhibit stair step characteristics due to its 10 min analysis cycle time, characteristic of most GCs. Note that essentially all of the sulfur in the flare gas stream was in the form of H$_2$S, necessitating for purposes of clarity the offset of the results from the new approach relative to those from the conventional GC.

Even before making a rigorous statistical comparison between the two sets of results, Figure 4 permits important qualitative assessments. First, the new device’s response to actual changes in stream composition appears to be nearly instantaneous, when compared with the GC results.

Second, the higher amplitudes of the periodic oscillations and the sharpness of the associated peaks gives further evidence that the EUVF based technology does not suffer from dilution or sample carryover effects between measurements. Instead, each 100 s interval measurement represents the result for a discrete sample. Equally important, Figure 4 shows that it tracks the GC in revealing the broad contours of process variation.

Third, due to the limited variation of total sulfur in the process stream, the data set does not reveal the full dynamic range and linear response of the new approach. Using a factory calibration based on 100% H$_2$S, the agreement of the new EUVF analyser with a certified standard containing 5882 ppm H$_2$S was within a difference less than ±0.1%, relative. Results shown in Figures 4 and 5 were obtained after a zero/span calibration with that gas to obtain the following calibration equation:

$$\text{ppm H}_2\text{S} = 0.999185 \times R_{\text{EUVF}} + 30.89$$

Where $R_{\text{EUVF}}$ (the reading from the EUVF analyser) = reading of the EUVF analyser based on the original factory calibration.

This approach produces results at a rate that is six times higher than the conventional GC (one result every 100 s versus one result every 10 mins or 600 s). Figure 4 shows almost 1000 results from the EF.60107 compared with only 164 from the GC over a defined time period.

To reveal the relationship between results from the two analysers in greater detail, Figure 5 shows only those results for the analyser that corresponds in time to the GC results. The data reduction in Figure 5, compared with Figure 4, suggests that the responsiveness of the new analyser technology provides a more accurate accounting of total sulfur, evidenced by the fact that high values are higher and low values are lower, compared with results from the GC.

**Conclusion**

Many conventional analyser technologies must overcome limits to their measuring range through dilution and other engineered adjustments that effectively create analyser regimes that regulators may not find acceptable. Compared with conventional approaches available until now, the dilution free, three for three approach offers refiners distinctive benefits including improved performance, unambiguous fulfilment of regulatory requirements, and lower lifecycle costs.