

Meeting H₂S and Total Reduced Sulfur Measurements in Refineries with a TCD-based GC

In late 2010, the United States Environmental Protection Agency (EPA) published new standards of performance in 40CFR60 subpart Ja that impact refinery emissions monitoring.

Changes to existing monitoring regulations

Historically, refineries were required to measure the hydrogen sulfide (H₂S) concentration in refinery fuel and flare gases. The new requirements mandate the measurement of H₂S & total reduced sulfur (TRS) – defined as H₂S, carbonyl sulfide (COS) and carbon disulfide (CS₂) – in flare gas streams and sulfur recovery unit (SRU) emissions.

	Typical concentration	Typical Measuring range
Hydrogen (H ₂)	20-30%	
Oxygen/Nitrogen (O ₂ /N ₂)	2-10%	
Carbon Monoxide (CO)	1-5%	
Carbon Dioxide	1-5%	
Methane (C ₁)	20-35%	
Ethane (C ₂)	5-15%	
Ethylene (C ₂ ⁻)	5%	
C3+	5-30%	
H ₂ S	<100 ppm	0-320 ppm
TRS	<200 ppm	0-320 ppm
BTU	900 BTU	300-3000 BTU

Figure 1 - shows a typical composition of the refinery flare gas. The actual chemical composition can vary dramatically due to several processing units that contribute light gases into the flare gas. Due to this fluctuation, it is common for refineries to put online analyzers on the flare gas lines to also track the changes in BTU value for improved flare combustion.

Challenges associated with existing monitoring equipment

Over the years, many refineries have found that their choice of H₂S analyzer involved high levels of maintenance. Lead acetate analyzers were maintenance-intensive due to their very mechanical design. Lead acetate analyzers also required

special disposal procedures for the spent lead tape. Refineries using online gas chromatographs with flame photometric detectors (FPD) were also seeing high levels of maintenance required to keep the FPDs flame lit and operating properly. Tunable diode lasers (TDL) struggled with performance issues, as the varying hydrocarbon content in the sample streams often interfered with the targeted wavelength.

Refinery engineering and operation teams also discovered the high installation and operational costs associated with lead acetate analyzers and gas chromatographs with FPDs. In addition to on-going utility requirements, such as disposal charges for the tape cartridges and the flame fuel and flame air gas cylinder costs, FPD-based gas chromatographs also required tight environmental temperature control to ensure reliable performance.

Emerson's thermal conductivity detector solution

The online gas chromatograph from Emerson is a solid alternative for making the traditional H₂S measurement, as well as the recently introduced TRS measurement. Rather than using a complicated, difficult-to-maintain FPD detector, Rosemount Analytical gas chromatographs use a much simpler and rugged thermal conductivity detector (TCD) – even for measurements in the low parts-per-million range.

Thermal conductivity detectors work on the principal that all compounds have unique thermal conductivity properties. By comparing the thermal conductivity of the component to be measured against the properties of a reference gas (usually the chromatograph carrier gas), very precise measurements can be made. The Rosemount Analytical TCD detector can measure compounds such as H₂S, COS and CS₂ down to the 3 ppm detection levels – perfect for H₂S & TRS monitoring applications where the typical measuring range is 0-320 ppm.

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The Rosemount Analytical gas chromatograph can also perform the daily high and low validation checks that are mandated by the regulations. Introduction of validation gases can be set up on an automated basis. The software of the analyzer can also automatically check the results for alarm conditions and log the data automatically.

Using a second TCD enables other measurements to be made in the flare gas such as the BTU content. Many refineries prefer to keep the BTU value of the flare gas above a certain level – typically 300 BTU – to optimize their flare operations. Knowing the BTU content of the feed gas optimizes the amount of pipeline quality natural gas that is required to maintain the energy content above the 300 BTU minimum.

In addition to exceptional analytical capability, Rosemount Analytical gas chromatographs offer the lowest cost of ownership in the industry. Most process measurements can be made at or near the sample point greatly reducing the overall lifetime cost of the measurement. Expenses such as shelters, air conditioning, heating, and long/heated sample lines can

be minimized or completely eliminated in most applications. Furthermore, Rosemount Analytical gas chromatographs are designed to operate unattended for long periods of time without adjustment. When adjustments are required, all components are easily accessible and can be performed in the field in minutes with standard tools.

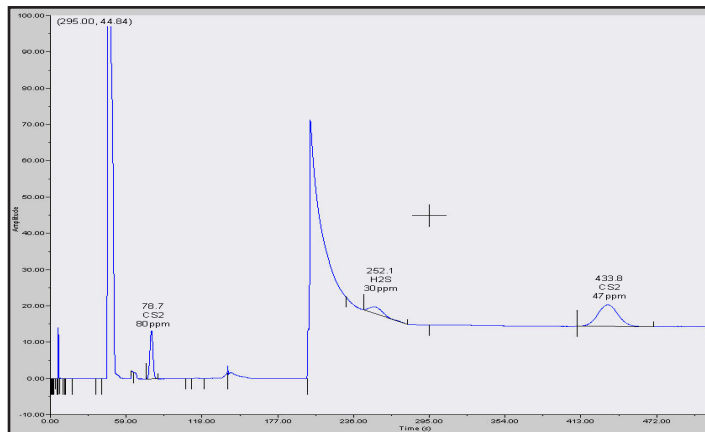


Figure 2 - Typical chromatogram of ppm level H₂S, CS₂ and COS using a thermal conductivity detector on the Rosemount Analytical gas chromatograph

Analyzer #	Stream	Components Measured	Measurement Objective
1	Refinery Fuel Gas	H ₂ S & Total BTU	Used to determine H ₂ S emissions and optimize energy content of fuel gas
2	Flare Gas	H ₂ S, TRS & Total BTU	Used to determine sulfur emissions and optimize flare combustion
3	SRU Recycle	TRS & H ₂ S	Verify SRU performance and monitor emissions

Figure 3 - Sample gas chromatograph applications related to emissions monitoring in a refinery

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