Flare Emissions Monitoring

APPLICATION NOTE

EPA Refinery Sector Rule (RSR) 40 CFR 63

Flare Gas Compliance with Total Composition Monitoring

January 30, 2019 is the compliance deadline for the latest update to the US EPA Refinery Sector Rule (RSR). This will require additional monitoring and gas analysis when regulated material is sent to the flare. The MAX300-RTG, environmental gas analyzer, provides a rapid, speciated analysis of vent gas composition that many refineries are currently using for EPA compliance.

According to new requirements in the General Provisions, flares used as Air Pollution Control Devices (APCD) are expected to achieve 98% Hazardous Air Pollutant (HAP) destruction efficiencies. These updated requirements include monitoring of the pilot flame, visible emissions, flare tip velocity, net heating values, and dilution parameters, as well as maintaining a Flare Management Plan and a Continuous Parameter Monitoring System Plan. The Net Heating Value of the gas in the Combustion Zone (NHV_{CZ}) is of particular importance as it has a direct impact on combustion efficiency. As a result, the RSR update mandates a $NHV_{CZ} \geq 270$ Btu/scf, based on a 15 minute block average, when regulated material is sent to the flare for at least 15 minutes. For flares actively receiving perimeter assist air, NHV_{dil} must be greater than or equal to 22 Btu/ft^2, when regulated material is sent to the flare. To meet this requirement, continuous direct measurements of refinery vent gas must be made. High variability, sulfur content, and corrosivity can make these samples difficult for many analytical techniques.

The MAX300-RTG, real-time gas analyzer, is currently used at many US refineries for NSPS Subpart Ja sulfur monitoring. The analyzer measures the full, speciated composition of the flare gas and delivers continuous updates of NHV, H_2S, and Total Sulfur several times per minute (Fig. 1). Rapid updates of NHV are critical for compliance because the refinery must be able to both monitor and control the gases at the flare tip within the regulated 15 minute block. The additional information provided by full speciation can be used at RSR sites for Ja sulfur compliance, validating or replacing existing sulfur analyzers, as well as for operational control and accurate root cause analysis.

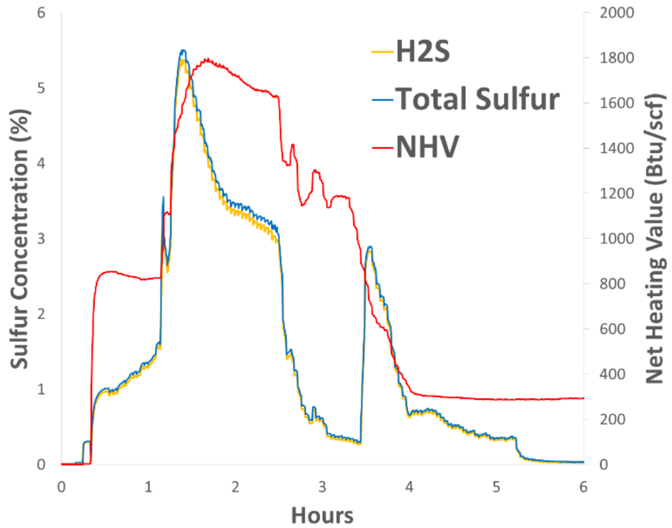


Figure 1. Net Heating Value and Sulfur in refinery flare gas reported by the MAX300-RTG. These data were recorded during a high-sulfur event and calculated from a fully speciated analysis consisting of 31 individual components. Total composition analysis time is <20 seconds.

Net Heating Value Monitoring for RSR Compliance

The regulation provides multiple ways to calculate the Net Heating Value of the gas in the Combustions Zone (NHV_{CZ}) for RSR reporting, but all methods use the Net Heating Value of the Vent Gas (NHV_{VG}) as an input. In fact, several parameters, including NHV_{CZ}, NHV_{dil}, and each flare's specific maximum tip velocity (V_{max}), are determined based on NHV_{VG}, making this value one of the key components of reporting compliance and effective flare control. Direct measurements of vent gas composition can be used to calculate NHV_{VG} and high precision gas analysis ensures accurate, actionable NHV_{VG} data (Table 1). When regulated material is sent to the flare, NHV_{VG} changes dramatically as hydrogen and hydrocarbon concentrations in the stream spike and recede. Regardless of the BTU content of the sample, the MAX300-RTG maintains constant, high precision on the NHV parameter due to the inherent repeatability of the gas analysis (Fig. 2).

Table 1. A speciated MAX300-RTG analysis of refinery vent gas containing hydrocarbons, hydrogen, and air compounds. The high precision of the concentration data transfers through the calculation to produce a highly repeatable Net Heating Value (NHV). The equation used to calculate NHV is included below. Recent RSR updates permit the use of 1212 Btu/scf for calculating hydrogen's NHV contribution. This makes hydrogen speciation a critical component of accurate NHV reporting.

Component	Concentration (%)	STD (ppm)
Hydrogen	16.36	850
Methane	78.99	840
Nitrogen	0.38	62.7
Propane	0.811	61.2
Ethane	0.016	49.5
Propylene	0.126	19.7
Isobutane	0.276	30.7
Carbon Dioxide	0.751	25.98
Butene	0.097	19.9
N-Butane	0.437	37.4
Heptane	0.018	3.47
N-Pentane	0.148	19.5
Hexane	0.014	11.1
NHV:	**958.3 Btu/scf**	**1.3 Btu/scf (0.13 % RSD)**

$$NHV_{vg} = \sum_{i=1}^{n} (x_i . NHV_i)$$

$$\begin{aligned} = ((\%H_2 \times 1212) &+ (\%CH_4 \times 896) + (\%C_2H_4 \times 1477) \\ &+ (\%C_2H_6 \times 1595) + (\%C_3H_6 \times 2150) \\ &+ (\%C_3H_8 \times 2281) + (\%C_4H_8 \times 2826) \\ &+ (\%IsoC_4H_{10} \times 2957) + (\%NC_4H_{10} \times 2968) \\ &+ (\%C_5H_{12} \times 3655) + (\%C_6H_{14} \times 4404) \\ &+ (\%C_7H_{16} \times 5100))/100 \end{aligned}$$

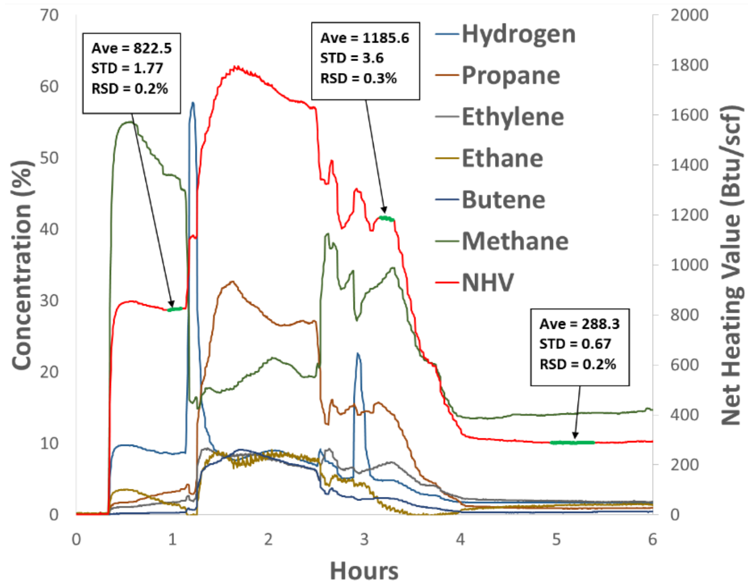


Figure 2. NHV changes rapidly as regulated material is sent to a refinery flare. Of the 14 hydrocarbons being measured, the 5 primary contributors to NHV are shown along with hydrogen. Increases in propane and other C3+ compounds drove the high heating value to over 1780 Btu/scf at the same time that the sulfur compounds reached their highest levels in the stream. As the NHV value changes, the MAX300-RTG maintains a fixed, high precision, ± <0.4%, as demonstrated by the Relative Standard Deviation (RSD) calculated for three sections of the trend.

Penalties for noncompliance may result in fines per violation. In addition, transparency rules make these records open to the public. To remain in compliance when NHV_{CZ} drops toward the 270 Btu/scf limit, refineries must add supplemental gas in the form of natural gas or propane. Simultaneously, the addition of steam may be required to eliminate smoking. Flare control is a complex process and, in order to maintain a sufficient NHV_{CZ}, the refinery will need many vent gas composition updates within the fixed cycle mandated by the RSR. Slower analytical technologies, historically used for flare gas analysis, will be insufficient for control, giving only one or two NHV updates within the 15 minute block. Real-time data is necessary to avoid noncompliance penalties and wasteful over-application of supplemental gas and steam. The MAX300-RTG can measure over 30 components and report full composition updates in >20 seconds, providing the speed of response essential for effective flare control.

For high-hydrogen flares, the speciated measurement of hydrogen is vital. With a net heating value of 274 Btu/scf, increasing hydrogen in the vent gas can drive a flare dangerously close to the allowable limit (270 Btu/scf). However, in recognition of hydrogen's high combustion potential, the EPA has allowed 1212 Btu/scf to be applied as hydrogen's NHV for the purposes of determining NHV_{VG} (Table 1). Vent gas monitors that speciate hydrogen will report a higher NHV_{VG} than a calorimeter alone, keeping the refinery in compliance and saving supplemental gas.

Fully Speciated Flare Composition: Sulfur and Trace Components

Since the implementation of NSPS Ja in 2015, the MAX300-RTG has been measuring full composition flare data at refineries across the United States. In addition to H_2S, Total Sulfur and NHV_{VG}, refineries are required to report on root cause analysis in cases of noncompliance. MAX300-RTG users have the information necessary to identify which process units are the primary contributors to the flare stream at any given time. Real-time, speciated gas analysis ensures that root cause analysis and corrective action planning are fast and accurate.

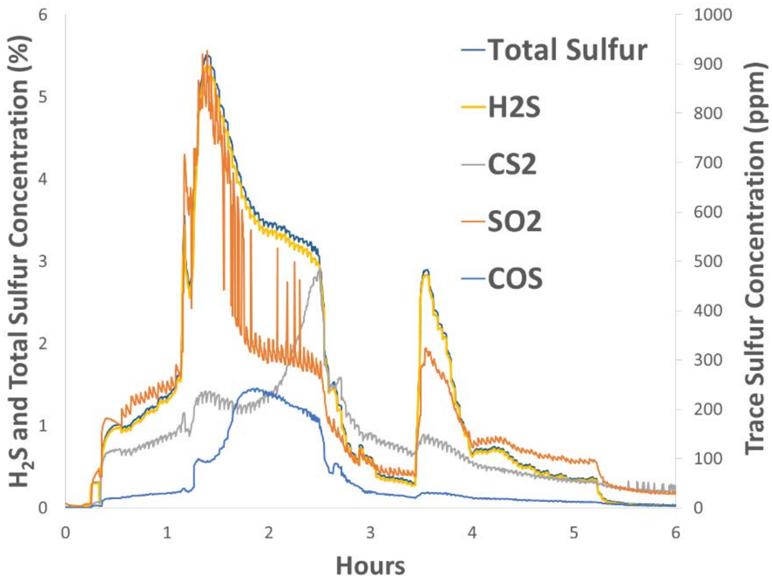


Figure 3. Total Sulfur was calculated from the sum of 10 speciated sulfur concentrations. Of the primary contributors, hydrogen sulfide was the most prevalent, reaching 5.4% during the event, but several others were present at ppm levels, at times contributing significantly to the Total Sulfur number.

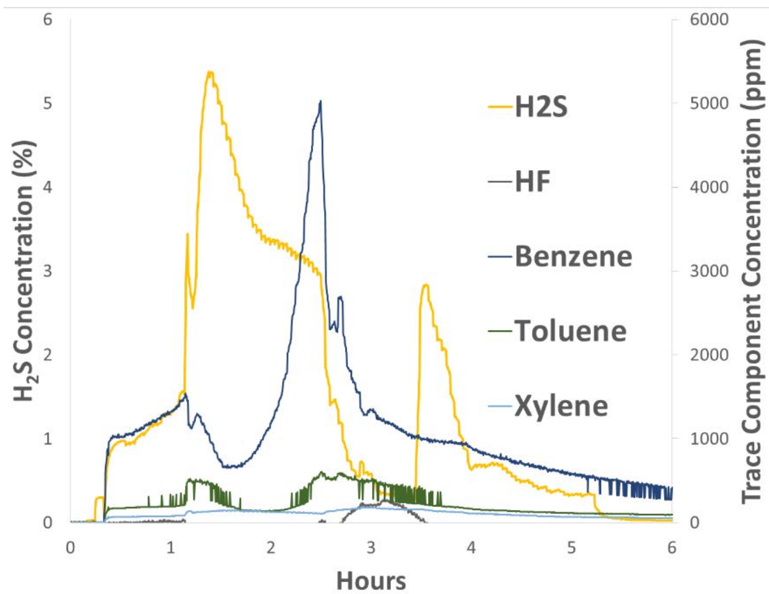
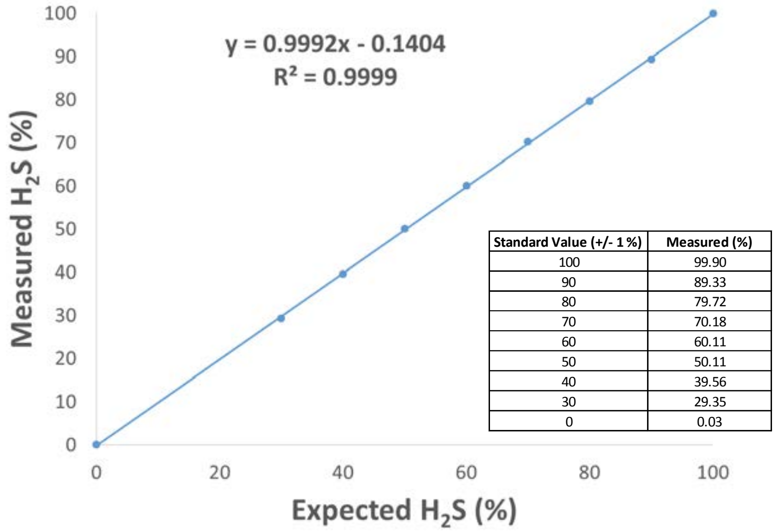


Figure 4. Trace components are shown along with the H_2S trend, indicating the progression of the flaring event. In addition to the compounds above, the MAX300-RTG was measuring nitrogen, oxygen, carbon dioxide, and water.

As the flare gas is pulled from the probe, through the sample handling cabinet, a small portion continuously flows into the MAX300-RTG's vacuum chamber, where it is ionized and electrically scanned by the mass filter. The analysis occurs at rate of 0.4 seconds per component, and Total Sulfur and NHV are calculated automatically and sent to the refinery's data system. Measurements of individual, speciated sulfur component concentrations are combined to report Total Sulfur, but the refinery has full access to the complete composition data (Fig. 3). This provides the parameters needed for compliance, as well as a deeper understanding of what material is being vented by the process units. The full list of compounds measured by the MAX300-RTG is determined by the needs of the user, and several trace contaminants are often included in the flare application (Fig. 4). Additional components can easily be added to the analysis by selecting them in the control software.

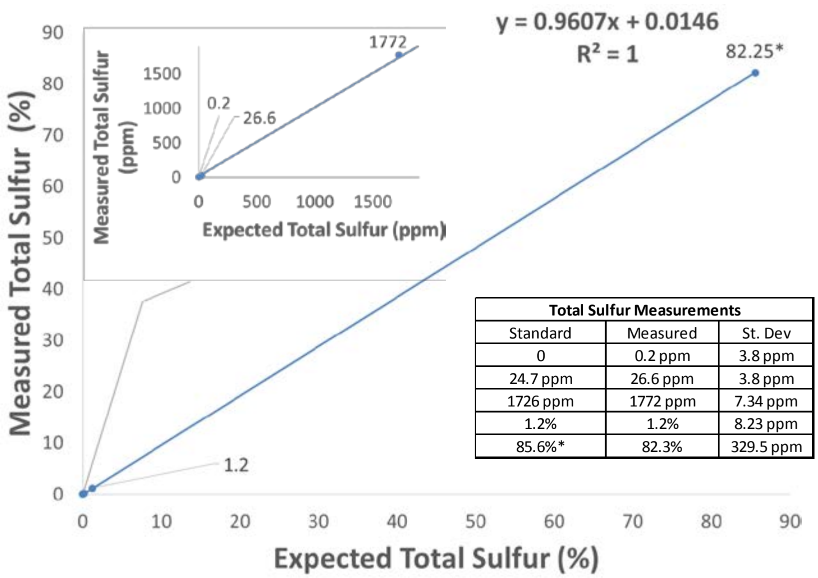
Figure 5. The MAX300-RTG, real-time mass spectrometer. For refinery flare compliance, the analyzer is often configured with a Hazardous Area Certification and corrosive-resistant materials that perform well with high-level H_2S and HF acid, according to site requirements.

Linear Analysis and Safe Sulfur Validation Using <300 ppm H_2S



Standard Value (+/- 1 %)	Measured (%)
100	99.90
90	89.33
80	79.72
70	70.18
60	60.11
50	50.11
40	39.56
30	29.35
0	0.03

Figure 6. Full-scale linearity of hydrogen sulfide. The dynamic range for H_2S in a flare gas sample is 1 ppm – 100%. The sensitivity and linearity of the MAX300-RTG is constant across that entire range based on a single-point calibration. Daily and quarterly validations using only <300 ppm H_2S standards are safe for refinery personnel and EPA approved.



Total Sulfur Measurements		
Standard	Measured	St. Dev
0	0.2 ppm	3.8 ppm
24.7 ppm	26.6 ppm	3.8 ppm
1726 ppm	1772 ppm	7.34 ppm
1.2%	1.2%	8.23 ppm
85.6%*	82.3%	329.5 ppm

Figure 7. Total Sulfur on the MAX300-RTG, measured following a single-point calibration on a standard containing ~2000 ppm of H_2S, COS, SO_2, CS_2 and methyl mercaptan. The system records a speciated analysis of the individual sulfur components in the mixture and calculates Total Sulfur in real-time for reporting purposes. For all components, the analyzer's dynamic range is linear from <1 ppm to 100%.

* The lab GCMS did not have the detector range necessary to verify the actual concentration of the 85.6% Total Sulfur blend.

In a flare gas sample the measurement range for hydrogen sulfide on the MAX300-RTG is 1 ppm to 100%. To demonstrate the linearity of response across this range, the analyzer was connected to a sample system in which high purity H_2S and CO_2 standards were blended using a dilution system. Following a single-point calibration, the sample composition was altered and the MAX300 performed accurate, linear measurements of H_2S at several points between 0 - 100% (Fig. 6).

In addition to H_2S, flare gas streams typically contain other sulfur compounds including COS, CS_2, SO_2 and mercaptans. The MAX300-RTG uses the sum of the concentrations of all sulfur containing compounds to calculate and report the Total Sulfur value to the refinery's control system. Many sites have the potential to flare high percent-level sulfur during a release. An analyzer with the ability to accurately measure Total Sulfur across the expected dynamic range is essential for accurate reporting. The MAX300-RTG was used to measure several gas standards simulating potential flare conditions. The bottles contained H_2S, COS, CS_2, SO_2 and methyl mercaptan and were gravimetrically blended prior to being validated using a laboratory GCMS*. Using a single-point calibration the MAX300-RTG demonstrated high accuracy and repeatability across all five standards (Fig. 7).

The mass spectrometer's linearity ensures that a single-point calibration will give accurate results on both ppm sulfur readings and spikes up to 100%. It also means that the performance of the MAX300-RTG can be validated with a ppm-level H_2S standard, regardless of the refinery's maximum anticipated sulfur value. Due to the demonstrated linearity of the technique, Subpart Ja compliance users have received EPA approval to use bottles with <300 ppm H_2S for daily and quarterly validations. These sites do not need to purchase or handle dangerous percent-level sulfur standards, resulting in an overall increase in safety and reduction of cost for flare compliance.

MAX300-RTG for Refinery Flare Compliance Monitoring

The MAX300-RTG measures the total composition of flare gas and is currently employed at refineries across the US reporting NHV_{VG}, H_2S and Total Sulfur for compliance with Refinery Sector Rule (RSR) regulations, 40 CFR 60 and 63. To meet the most recent updates to RSR, a vent gas monitor must be able to measure NHV_{VG} in a highly dynamic sample stream that may contain high-level H_2S and, in some cases, HF acid. Many calorimeters do not perform well under these sample extremes and, without a speciated hydrogen measurement, they will require the integration of a separate, external hydrogen analyzer. The MAX300-RTG always measures speciated hydrogen, ensuring that NHV_{VG} is reported accurately using the 1212 Btu/scf value specified in the regulation.

In addition to monitoring, refineries will need to control the gas composition at the flare tip. When regulated material is vented, NHV_{CZ} can change rapidly but must be kept above 270 Btu/scf for each 15 minute block, according to the rule. Slow analytical techniques will not update fast enough for reliable control, increasing the risk of violation and wasting supplemental gas and steam. The MAX300-RTG has the speed necessary to update the NHV_{CV} parameter several times per minute, giving the refinery real-time information for effective flare control.

The additional information provided by the MAX300-RTG's speciated, total composition analysis is available for use by refinery operations or, in the event of a reportable noncompliance, to help make root cause analysis easy and accurate. Sites with existing flare gas sulfur analyzers can use the H_2S and Total Sulfur values from the mass spectrometer as a backup, or replacement, for those systems. For Ja compliance monitoring, the linearity of the MAX300-RTG ensures accuracy from <1 ppm to 100%, prompting EPA approval of low-sulfur validations that significantly increase the safety, and reduce the cost, of flare gas compliance.

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