Flare Emissions Monitoring

APPLICATION NOTE

A Safe-to-Validate, Single-Analyzer Solution for Refinery Flare Emissions Monitoring

New environmental regulations have recently prompted many oil refineries and chemical manufacturers to adopt methods for measuring the composition of the waste gas streams headed to the flare. In November of 2015, the US EPA's implementation of 40 CFR 60 subpart Ja mandated the analysis of hydrogen sulfide, and Total Sulfur in refinery flare gas, with similar requirements being administered in markets worldwide. The EPA has since increased regulation to include the reporting of the BTU content by the start of 2019.

Flare streams consist of a mixture of waste gas from various plant processes, and the composition can change dramatically from one minute to the next. The dynamic nature of these samples, and the potential for a high-level release of sulfurs and hydrocarbons makes real-time mass spectrometry particularly well suited for flare monitoring. The MAX300-AIR, industrial mass spectrometer, measures the full, speciated composition of the flare gas stream and delivers continuous, automated H_2S, Total Sulfur and NHV (BTU) data.

The MAX300-AIR is a single-analyzer solution for the entire flare CEMS application. In addition, the mass spectrometer is linear over the entire detection range for all components (typically, <1 ppm to 100%). This has led to EPA approval of validation methods using ppm-level H_2S bottles at sites with a history of high sulfur concentrations in their flare gas streams. Percent-level sulfur standards are dangerous to plant personnel, and expensive to maintain. Compared to the alternative, MAX300 validation gases are safe and cost-effective.

Figure 1. The MAX300-AIR is an environmental mass spectrometer capable of performing quantitative analysis on a wide variety of compounds at concentrations ranging from 10 ppt* to 100%. The system is optimized for fully-automated, continuous analysis in hazardous industrial settings.

* Documented on benzene in air

Fully Speciated Flare Composition and Root Cause Analysis

Since the implementation of NSPS Ja in November of 2015, the MAX300-AIR has been measuring full composition flare data at refineries across the United States. In addition to the H_2S, Total Sulfur and BTU values, refineries are required to report on root cause analysis when H_2S exceeds 162 ppmv. MAX300 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.

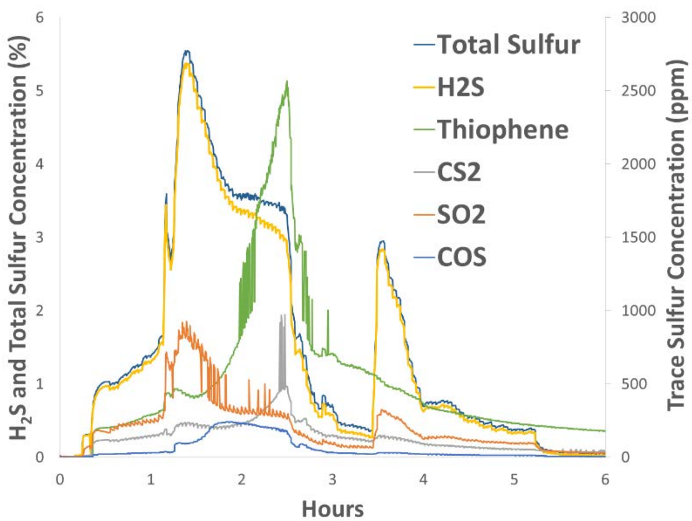


Figure 2. Total Sulfur is shown with the top 5 sulfur compounds measured during the flare event. Total Sulfur is calculated from the sum of the speciated sulfur analysis. Hydrogen sulfide was the most prevalent, reaching 5.4%, but several other sulfurs were present at ppm levels, at times contributing significantly to the Total Sulfur number.

Figures 2, 3 and 4 show the MAX300 analysis of a high sulfur event in a refinery flare stream. At this site, the mass spectrometer was performing the simultaneous measurement of 31 components, including 10 sulfur compounds and 14 hydrocarbons. It gives the refinery the data needed for compliance, and a deeper understanding of what material is being vented by the operating units. As the flare gas is pumped from the probe and through the sample handling cabinet, a small portion continuously flows into the MAX300'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 BTU are calculated automatically and sent to the refinery's data system. The full list of compounds measured by the MAX300 is determined by the needs of the user, and several trace contaminants are often included in the flare application (Figure 4). Additional components can easily be added in the future, if necessary.

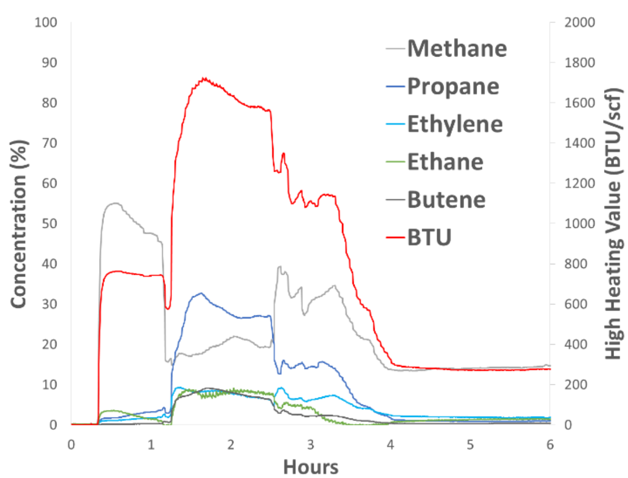


Figure 3. Flare stream BTU and the top 5 contributing hydrocarbons. Increases in propane and other C3+ compounds drove the high heating value to over 1720 BTU/scf at the same time that the sulfur compounds reached their highest levels.

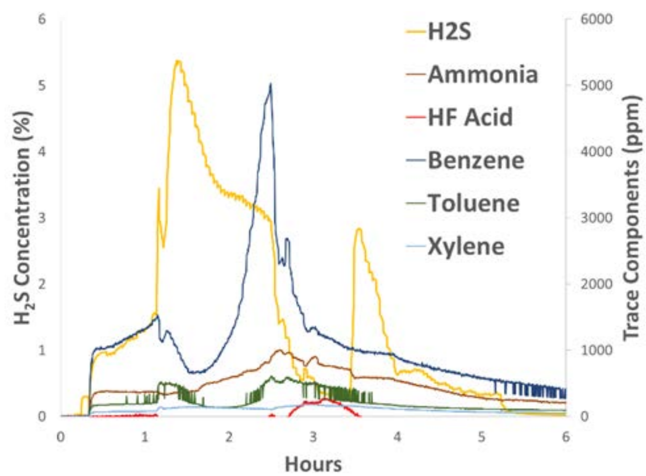
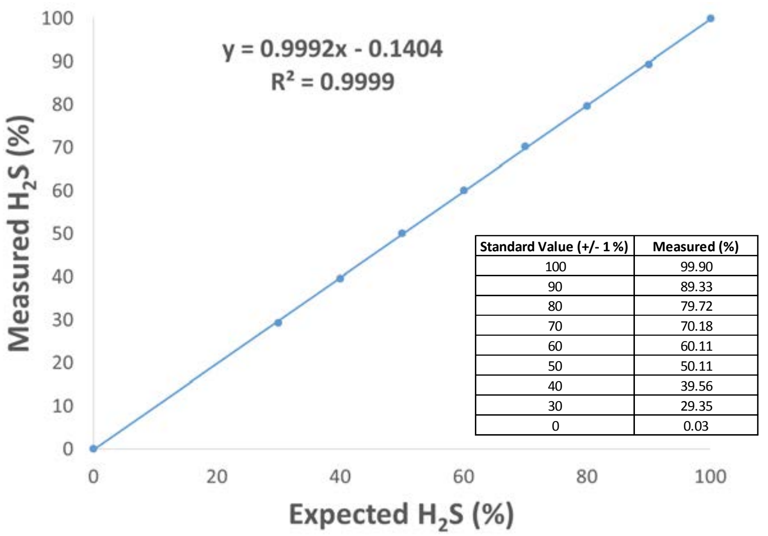


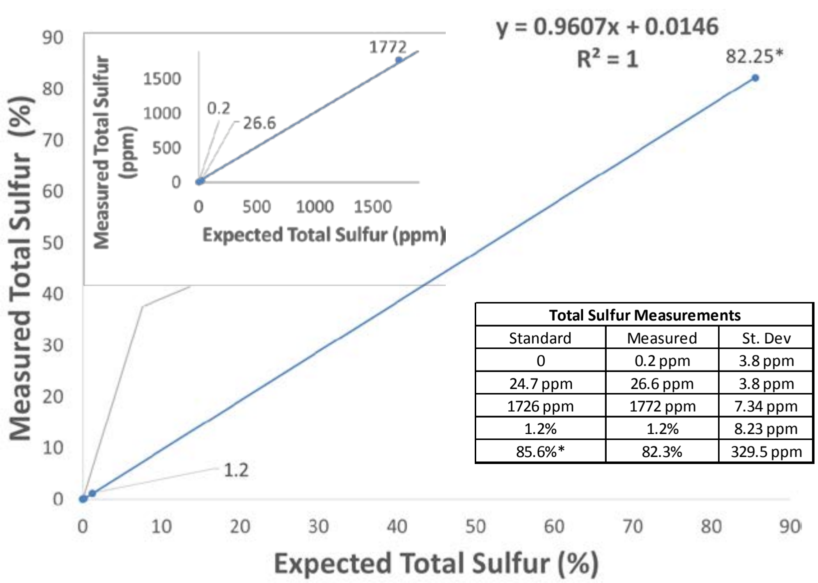
Figure 4. Trace components are shown along with the H_2S trend indicating the progression of the flaring event. In addition to the compounds above, the MAX300 was measuring hydrogen, nitrogen, oxygen, carbon dioxide, and water.

Linear Analysis and Safe 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 5. Full-scale linearity of hydrogen sulfide. The dynamic range for H_2S in the flare gas application is 1 ppm – 100%. The sensitivity and linearity of the MAX300 is constant across that entire range based on a single-point calibration. Daily validations using <300 ppm 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 6. The Total Sulfur measurement as recorded on the MAX300-AIR. This data was gathered 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 dynamic range to verify the actual concentration of the 85.6% Total Sulfur blend.

In the flare gas application, the measurement range for hydrogen sulfide on the MAX300 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% (Figure 5).

In addition to H_2S, flare gas streams typically contain other sulfur compounds including COS, CS_2, SO_2, and mercaptans. The MAX300 uses the sum of the concentration 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 Total 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 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 GCMS*. Using a single-point calibration the MAX300 demonstrated high accuracy and repeatability across all five standards (Figure 6).

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 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, MAX300 users have received EPA approval to use bottles with <300 ppm H_2S for daily validations. These sites do not need to purchase or handle highly dangerous and expensive percent-level sulfur standards, resulting in an overall increase in safety and reduction of cost for flare compliance.

High Precision Real-time BTU Calculation

The addition of the BTU requirement to the flare application has made the ability to monitor hydrocarbon and other components (hydrogen, nitrogen, water, oxygen, ammonia, BTX, etc.) essential for accurate reporting. The flexibility of the MAX300-AIR allows for site-specific customization of the gases measured, and the analysis is software editable should plant operations or regulatory requirements change over time. The high precision of the mass spectrometer guarantees high accuracy and repeatability for the reported BTU value, regardless of sample composition (Table 1).

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)**

Table 1. Speciated hydrogen and hydrocarbon measurements and calculated stream Net Heating Value (NHV). The MAX300-AIR records the concentrations of all of the compounds within the flare stream and calculates the NHV in real-time for reporting to the DCS. High precision gas analysis allows for high precision BTU values. The equation below is an example NHV calculation, designed to express the value in BTU/scf. NHV can be reported in whatever unit best fits the user's needs.

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

As with the Total Sulfur measurement, BTU is calculated and reported to the user's data control system in real-time along with the speciated concentrations of all monitored compounds. The ability to track all individual components across the entire dynamic range during a release provides an important resource for use in the root-cause analysis required by the regulation.

Conclusion

The MAX300-AIR is the only single-analyzer solution for the simultaneous measurement of H_2S, Total Sulfur, and BTU content in flare gas. The system offers the speed of analysis, dynamic range and flexible response necessary for compliance with Refinery Sector Rule (RSR) regulations, 40 CFR 60 and 63, and can even monitor multiple flare streams in an automated cycle that meets the required 15 minute reporting rate. The speciated analysis of all components provides essential information for root-cause analysis, and the linearity of the MAX300 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.

Extrel
Core Mass Spectrometers

www.extrel.com
412-963-7530

IAF101E