Fast on-line monitoring of flare gases

Process mass spectrometry

Introduction

Government organizations often require processing companies to monitor various emissions from their plant stacks and flares to reduce the amount of pollution entering the atmosphere. For example, the US Environmental Protection Agency (EPA) has published amendments to Refinery Sector Rule (RSR) 40 CFR Part 63 affecting flares; refineries had to bring flares into compliance with new §63.670 'Requirements for Flare Control Devices' by January 30, 2019. The new requirements define five flare operating limits—combustion zone net heating value (NHV_{CZ}), dilution net heating value (NHV_{dil}), flare tip exit velocity, pilot flame presence, and visible emissions—and specifies an NHV_{CZ} minimum operating limit of 270 BTU/scf, based on a 15 minute block period[1].

NHV_{CZ} can be calculated by measuring the net heating value of the vent gas (NHV_{VG}), making flare gas analysis a vital part of any compliance strategy. If the NHV_{CZ} approaches 270 BTU/scf, additional fuel gas such as propane or natural gas have to be added. This may then require the addition of steam to the flare, to avoid the production of visible emissions.

The analysis of flare gases presents a series of challenges to the processing industries. Firstly, the emissions are typically made up of complex mixtures of inorganic and organic species, and compositions and concentrations vary dramatically over time as process conditions change. And although many regulations require just the total heating value, total sulfur, or total hydrocarbon values to be recorded, measuring the concentrations of individual components helps identify the source of the emission, locating the problem to a specific part of the plant. Finally, the analysis speed is crucial as the heating value of the flare can quickly change. Analysis times measured in minutes increase the risk of failing to meet emission standards.

Measurement of flare gas streams by process mass spectrometry

Process mass spectrometry (MS) is particularly suited to the measurement of flare gas streams because it offers accurate, fast, multicomponent analysis. Table 1 shows an example of a flare gas stream containing hydrogen, nitrogen and hydrocarbons up to C6. Analysis of these eleven components will typically be performed in just 20 seconds, allowing one mass spectrometer to monitor more than one flare, depending on the distances involved. Alternatively, one MS can be used to measure process streams and flare streams, even though the composition and concentrations may be very different.

Table 1. Example of flare gas stream composition

Component			Flare gas typical composition %mol
Name	Formula	Molecular weight	
Hydrogen	H_2	2	1 – 3
Nitrogen	N_2	28	40 – 85
Ethylene	C_2H_4	28	5 – 20
Ethane	C_2H_6	30	5 – 20
1-Butene	C_4H_8	56	0.5 – 1.5
i-Butane	$i\text{-}C_4H_{10}$	58	0.1 – 0.5
n-Butane	$i\text{-}C_4H_{10}$	58	0.1 – 0.3
1-Hexene	C_6H_{12}	84	2.5 – 7.5
n-Hexane	$n\text{-}C_6H_{14}$	86	0 – 1

Advantages of magnetic sector MS

Thermo Fisher Scientific manufactures both quadrupole and magnetic sector mass spectrometers. Over thirty years of industrial experience have shown the magnetic sector based analyzer offers the best performance for industrial online gas analysis. Thermo Scientific™ Prima PRO process mass spectrometers (Figure 1) offer ideal capabilities for industrial gas analysis.

Key advantages of magnetic sector analyzers include improved precision, accuracy, long intervals between calibrations and resistance to contamination. Typically, analytical precision is between 2 and 10 times better than a quadrupole analyzer, depending on the gases analyzed and complexity of the mixture.

Neutral gas atoms and molecules are first converted into positively charged ions in the Prima PRO MS ion source. This is an enclosed type for high sensitivity, minimum background interference and maximum contamination resistance. It is a high-energy (1000 eV) analyzer that offers extremely rugged performance in the presence of gases and vapors that have the potential for contaminating the internal vacuum components. Prima PRO MS has a proven track record of monitoring high percent level concentrations of organic compounds without experiencing drift or contamination.

Ions are then accelerated through a flight tube, where they are separated by their mass to charge ratios in a magnetic field of variable strength. Since the magnetic sector mass spectrometer produces a focused ion beam at the detector, the peak shape obtained is ‘flat-topped’ and uniform response is observed over a finite mass width. As the height of the peak is directly proportional to the number of ions striking the detector it is also directly proportional to the concentration of the component being measured. As long as the measurement is taken anywhere on the peak’s flat top, high precision analysis will be observed.

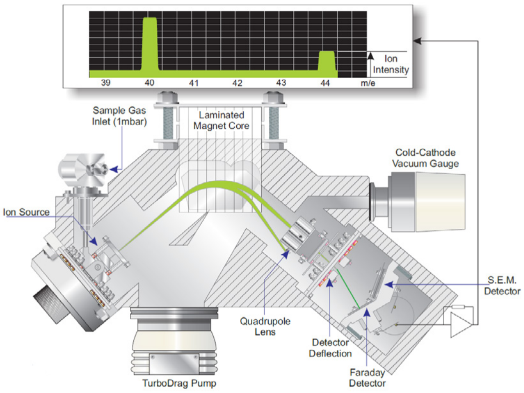


Figure 1. Prima PRO magnetic sector analyzer

The Prima PRO MS’ ability to measure over a wide dynamic range is critically important if the varying composition levels in flare gas are to be measured accurately. The Prima PRO MS has been independently evaluated by EffecTech UK, an independent specialist company providing accredited calibration and testing services to the energy and power industries for gas quality, flow and total energy metering. It is accredited to internationally recognized ISO/IEC 17025:2005 standards; this specifies the general requirements for the competence to carry out tests and/ or calibrations, including sampling.

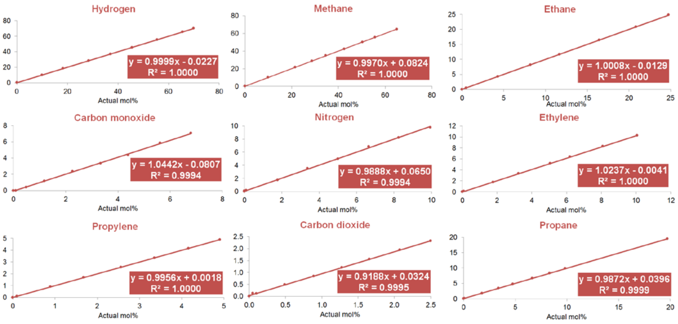


Figure 2. Prima PRO MS linearity data

Effectech linearity tests

The Prima PRO MS was calibrated for sensitivity using just one gas mixture, and then tested with a set of nine reference gases covering a wide range of compositions. Figure 2 shows the linearity plots generated by EffecTech. They demonstrate significantly better linearity than that achieved by a thermal conductivity detector fitted to a gas chromatograph, and prove that Prima PRO MS is capable of generating accurate, reliable composition data from complex gas mixtures.

Table 2. Statistical report on Prima PRO MS 30 day run analyzing 13-component calibration cylinder without calibration

Name	Average	Standard deviation	Relative standard deviation
Hydrogen	18.98	0.106	0.56%
Methane	15.65	0.068	0.44%
Acetylene	1.19	0.007	0.58%
Ethylene	33.77	0.072	0.21%
Ethane	10.09	0.054	0.53%
Methyl acetylene	0.39	0.008	2.12%
Propylene	5.73	0.014	0.24%
Carbon dioxide	0.44	0.017	3.72%
Propane	5.87	0.012	0.21%
Butadiene	0.99	0.006	0.59%
n-Butene	0.56	0.004	0.69%
i-Butene	0.50	0.012	2.50%
n-Butane	5.83	0.022	0.37%

Long-term stability

Prima PRO MS' long-term stability means the system can run for long periods without recalibration, significantly longer than quadrupole MS systems. Table 2 shows standard deviations achieved on a 30-day run without recalibration on a gas cylinder containing 13 different compounds, including 11 hydrocarbons.

Rapid multistream sampling

If the MS is to monitor multiple flare streams, or flare streams and process streams, then a fast, reliable means of switching between streams is required. Solenoid valve manifolds have too much dead volume and rotary valves suffer from poor reliability so we developed the unique Rapid Multistream Sampler (RMS). It offers an unmatched combination of sampling speed and reliability, and it allows sample selection from 1 of 32 or 1 of 64 streams. Stream settling times are application dependent and completely user configurable. The RMS includes digital sample flow recording for every selected stream. This can be used to trigger an alarm if the sample flow drops—if a filter in the sample conditioning system becomes blocked, for example.

The RMS can be heated to 120°C and the position of the stream selector is optically encoded for reliable, software controlled stream selection. Temperature and position control signals are communicated via Prima PRO MS' internal network.

The RMS has a proven track record of carrying out 10 million operations between maintenance and has a three year warranty as standard. No othermultistream sampling device offers the same level of guaranteed reliability.

Measuring fuel properties with Prima PRO MS

The following fuel properties can routinely be derived by the Prima PRO mass spectrometer:

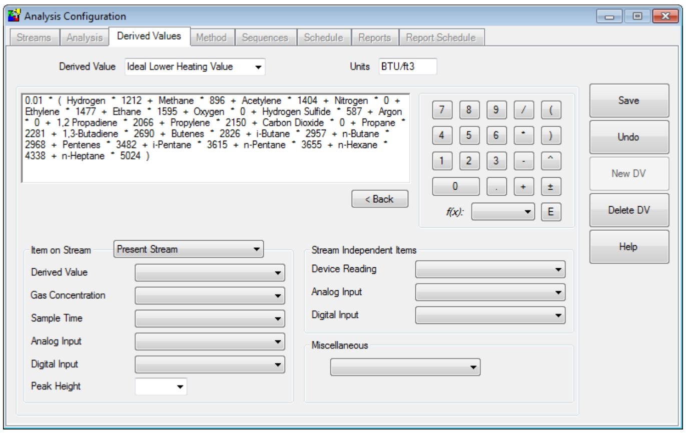
Lower heating value (LHV)	Also known as net heating value or lower calorific value
Higher heating value (HHV)	Also known as gross heating value or higher calorific value
Compressibility	
Actual lower heating value	$\frac{\text{Ideal lower heating value}}{\text{Compressibility}}$
Density	
Specific gravity	
Lower wobbe index	$\frac{\text{Lower heating value}}{\sqrt{\text{(Specific gravity)}}}$
Higher Wobbe Index	$\frac{\text{Higher heating value}}{\sqrt{\text{(Specific gravity)}}}$
Air Requirement	
Combustion Air Requirement Index (CARI)	$\frac{\text{Air requirement}}{\sqrt{\text{(Specific gravity)}}}$

Lower Heating Value is calculated using the value of 1212 BTU/scf for hydrogen as recommended by EPA 40 CFR Parts 60 and 63, instead of the theoretical value of 274 BTU/scf. This provides a better indication of flare performance (e.g., meeting the minimum operating limit of 270 BTU/scf). Accurate analysis of hydrogen over a wide dynamic range is critical because of its high combustion potential; The Prima PRO magnetic sector analyzer is ideally suited to hydrogen analysis because it does not suffer from the 'zero blast' which makes analysis of light molecules problematic on many quadrupole analyzers.

HHV differs from LHV in that it takes into account the latent heat of vaporization of water in the combustion products.

The precision of these measurements with Prima PRO MS is normally better than 0.1% relative.

Figure 3 shows how the Ideal LHV of the flare gas stream is calculated by Thermo Scientific™ GasWorks Derived Values, based on the individual components' Ideal LHVs.



Derived Value: Ideal Lower Heating Value

Units: BTU/ft3

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0.01 * ( Hydrogen * 1212 + Methane * 896 + Acetylene * 1404 + Nitrogen * 0 +
Ethylene * 1477 + Ethane * 1595 + Oxygen * 0 + Hydrogen Sulfide * 587 + Argon
* 0 + 1,2 Propadiene * 2066 + Propylene * 2150 + Carbon Dioxide * 0 + Propane *
2281 + 1,3-Butadiene * 2690 + Butenes * 2826 + i-Butane * 2957 + n-Butane *
2968 + Pentenes * 3482 + i-Pentane * 3615 + n-Pentane * 3655 + n-Hexane *
4338 + n-Heptane * 5024 )
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Item on Stream: Present Stream

Derived Value

Gas Concentration

Sample Time

Analog Input

Digital Input

Peak Height

Stream Independent Items

Device Reading

Analog Input

Digital Input

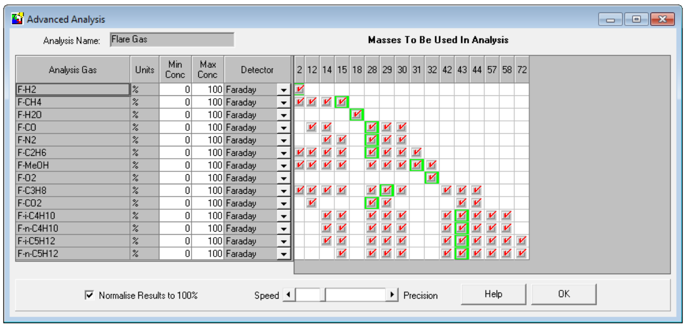
Miscellaneous

Figure 3. GasWorks derived value for ideal lower heating value

Analysis times are typically 30 seconds or less, including settling time. Data are communicated to the plant host computer as they are measured, by one or more of a number of available methods, e.g., 4-20 mA or 0-10V analog outputs, Modbus, Profibus, or OPC.

Analytical set-up

GasWorks software supports an unlimited number of analysis methods, enabling the analysis to be optimized on a per-stream basis. The most efficient peak measurements and the most appropriate speed versus precision settings can be selected for each gas stream, depending on process control requirements. Examples of different analysis methods are shown in Figures 4 and 5. Figure 4 shows an example of the analytical method for a flare gas stream; Figure 5 shows that for a process stream. Both methods, along with additional process methods, are utilized on a single Prima PRO process MS measuring a combination of process streams and flare gas.



Analysis Name: Flare Gas

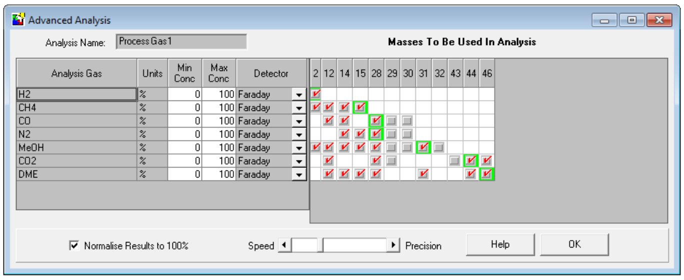
Masses To Be Used In Analysis

Analysis Gas	Units	Min Conc	Max Conc	Detector	2	12	14	15	18	28	29	30	31	32	42	43	44	57	58	72
F-H2	%	0	100	Faraday	☑															
F-CH4	%	0	100	Faraday	☑	☑	☑	☑												
F-H2O	%	0	100	Faraday					☑											
F-CO	%	0	100	Faraday		☑	☑			☑	☑	☑								
F-N2	%	0	100	Faraday			☑	☑		☑	☑	☑								
F-C2H6	%	0	100	Faraday	☑	☑	☑	☑		☑	☑	☑	☑							
F-MeOH	%	0	100	Faraday	☑	☑	☑	☑		☑	☑	☑	☑	☑						
F-O2	%	0	100	Faraday										☑						
F-C3H8	%	0	100	Faraday	☑	☑	☑	☑		☑	☑	☑			☑	☑	☑			
F-CO2	%	0	100	Faraday		☑				☑	☑					☑	☑			
F-i-C4H10	%	0	100	Faraday			☑	☑		☑	☑	☑			☑	☑	☑	☑	☑	
F-n-C4H10	%	0	100	Faraday			☑	☑		☑	☑	☑			☑	☑	☑	☑	☑	
F-i-C5H12	%	0	100	Faraday			☑	☑		☑	☑	☑			☑	☑	☑	☑	☑	☑
F-n-C5H12	%	0	100	Faraday				☑		☑	☑	☑			☑	☑	☑	☑	☑	☑

☑ Normalise Results to 100%

Speed … Precision

Figure 4. Example of flare stream method



Analysis Name: Process Gas1

Masses To Be Used In Analysis

Analysis Gas	Units	Min Conc	Max Conc	Detector	2	12	14	15	28	29	30	31	32	43	44	46
H2	%	0	100	Faraday	☑											
CH4	%	0	100	Faraday	☑	☑	☑	☑								
CO	%	0	100	Faraday		☑	☑		☑	☐	☐					
N2	%	0	100	Faraday			☑	☑	☑	☐	☐					
MeOH	%	0	100	Faraday	☑	☑	☑	☑	☑	☐	☐	☑	☐			
CO2	%	0	100	Faraday		☑			☑	☐				☐	☑	☑
DME	%	0	100	Faraday		☑	☑	☑	☑			☑			☑	☑

☑ Normalise Results to 100%

Speed … Precision

Figure 5. Example of process stream method

These two methods clearly show the amount of spectral overlap in the MS fragmentation patterns. It is extremely important to measure these fragmentation patterns from the actual components of interest—the use of surrogate compounds may simplify the calibration process but will inevitably lead to a reduction in accuracy.

Test data and process data

Table 3 shows the Prima PRO MS' analytical performance on the two different stream types displayed in Figures 4 and 5. Stream analysis cycle time was 30 seconds. If multiple sample streams are measured the stream switching time and settling time is 10 seconds, so n streams can be analyzed with a cycle time of n x 40 seconds. Analytical performance was demonstrated during commissioning by analyzing two calibration gases periodically over 8 hours and observing the standard deviation values detailed in the table.

Table 3. Example of Prima PRO MS performance specification for flare gas and process gas streams

		Flare gas		Process gas	
Component	Formula	Flare gas – concentration (%mol)	Flare gas – Prima PRO Precision (Standard deviation) %mol ≤	Process gas – concentration (%mol)	Process gas – Prima PRO Precision (Standard Deviation) %mol ≤
Hydrogen	H_2	Balance	0.1	2	0.01
Methane	CH_4	10	0.02	Balance	0.05
Carbon monoxide	CO	10	0.05		
Nitrogen	N_2	10	0.05	4	0.01
Ethane	C_2H_6	1	0.005	2	0.01
Methanol	CH_3OH	0.1	0.005		
Carbon dioxide	CO_2	1	0.005	1	0.005
Propane	C_3H_8	1	0.005	0.1	0.005
i-Butane	$i\text{-}C_4H_{10}$	1	0.005	0.1	0.005
n-Butane	$n\text{-}C_4H_{10}$	1	0.005	0.1	0.005
i-Pentane	$i\text{-}C_5H_{12}$	0.5	0.005	0.1	0.005
n-Pentane	$n\text{-}C_5H_{12}$	0.5	0.005	0.1	0.005
n-Hexane	$n\text{-}C_6H_{14}$			0.1	0.005
n-Heptane	$n\text{-}C_7H_{16}$			0.1	0.005
HHV			0.3% relative		

Table 4 shows data from a Prima PRO MS factory test on a gravimetric cylinder containing 20 components, including in organics and hydrocarbons from C1 to C6. The test was carried out over 18 hours, and the measured standard deviations for all 20 components were lower than the specified standard deviations over 8 hours.

As well as the composition data, Prima PRO MS calculated the Compressibility, Ideal Lower Heating Value and Actual Lower Heating Value for the stream. Figure 6 shows these three parameters over the 18 hours of the test; as with the component concentrations, the measured LHV 18 hour standard deviations are well below the specified 8 hour standard deviations.

Table 4. Factory test on gravimetric cylinder containing 20 inorganic & hydrocarbon compounds, analyzed

	H_2	CH_4	C_2H_2	N_2	C_2H_4	C_2H_6	O_2	H_2S (ppm)	Argon	C_3H_6
Average	30.10	36.10	0.02	10.00	2.98	9.98	2.00	503.9	0.50	2.00
Cylinder certificate	30	36.15	0.02	10	3	10	2	500	0.5	2
Actual standard deviation (18 hours)	0.023	0.015	0.0012	0.004	0.005	0.007	0.002	2.8	0.0005	0.002
Specified standard deviation (8 hours)	0.03	0.04	0.005	0.02	0.01	0.01	0.005	5	0.002	0.005
	CO_2	C_3H_8	1,3 Butadiene	Butenes	iso Butane	n Butane	Pentenes	iso Pentane	n Pentane	n Hexane
Average	0.50	2.99	0.50	0.50	0.50	0.50	0.10	0.30	0.30	0.10
Cylinder certificate	0.5	3	0.5	0.5	0.5	0.5	0.1	0.3	0.3	0.1
Actual standard deviation (18 hours)	0.003	0.002	0.004	0.0008	0.0008	0.002	0.0004	0.001	0.002	0.001
Specified standard deviation (8 hours)	0.005	0.005	0.005	0.005	0.005	0.005	0.005	0.005	0.005	0.005

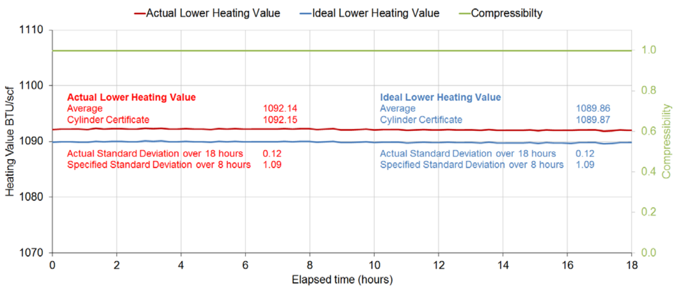


Figure 6. Heating values obtained during factory test on gravimetric cylinder containing 20 inorganic and hydrocarbon compounds, analyzed over 18 hours

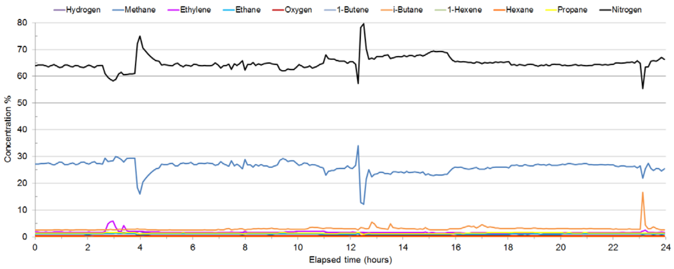


Figure 7. 24-hour trend display of flare gas stream

Figure 7 shows 24 hours' process data from a flare gas stream. Prima PRO MS shows a spike in the ethylene concentration up to 5.8% after 3 hours, then a few small spikes of i-butane up to 5.5% after 12 hours, and finally a larger spike of i-butane up to 16.6% at around 23 hours. Identifying these individual components greatly assists the root cause analysis to locate the source of these emissions.

Analysis of total sulfur

In general, regulators are interested in values for hydrogen sulfide (H_2S) and Total Reduced Sulfur (TRS). However there is some divergence on what constitutes TRS. In some cases it is defined as H_2S together with carbonyl sulfide (COS) and carbon disulfide (CS_2). It can also be defined as a mixture of compounds which contain a sulfur component in the reduced form, most commonly H_2S, methanethiol (methyl mercaptan, CH_3SH), dimethyl sulfide (DMS, $(CH_3)_2S$) and dimethyl disulfide (DMDS, $CH_3S_2CH_3$).

Mass spectrometers can measure a number of sulfur compounds down to ppm levels; typical performance figures are shown in Table 5. Analysis time is less than 30 seconds, including stream switching time and standard deviations are measured over 8 hours.

Figure 8 shows 30 consecutive measurements on a test blend of three mercaptans at ppm levels. The standard deviations for the three compounds are shown in Table 6.

Table 5. Typical Prima PRO MS performance specification for sulfur compounds

Component	Typical composition (%mol)	Precision of analysis by Prima PRO (single standard deviation) ≤
Hydrogen Sulfide	3 ppm	0.5 ppm
Methyl Mercaptan	10 ppm	0.5 ppm
Ethyl Mercaptan	10 ppm	0.5 ppm
n-Propyl Mercaptan	10 ppm	0.5 ppm
n-Butyl Mercaptan	10 ppm	0.5 ppm

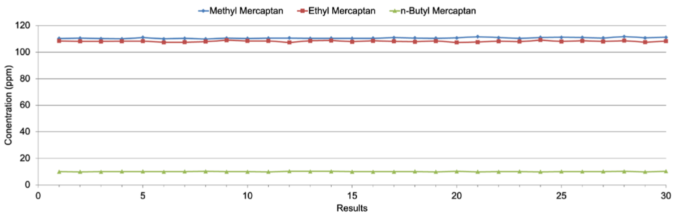


Figure 8. Test blend of three mercaptans

Table 6. Typical Prima PRO performance specification for sulfur compounds

	Methyl chloride	Vinyl chloride	Ethyl chloride	Ethylene dichloride
Mean	3.51	3.53	4.63	0.61
Standard deviation	0.04	0.06	0.16	0.05

Figure 9 demonstrates Prima PRO MS' excellent linearity for sulfur compounds. Eighteen hydrogen sulfide standards were generated by diluting a calibration cylinder using mass flow control; concentrations ranged from 4.85% down to 800 ppm.Part-per-million calibration standards can therefore be used with confidence to calibrate Prima PRO MS for sulfur compounds.

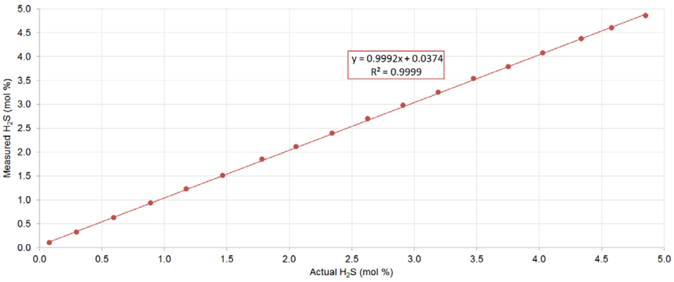


Figure 9. Linearity plot for H_2S from 800 ppm to 4.85%

GasWorks software can generate a figure for Total Sulfur using its Derived Value capability to sum the individual component concentrations. However it should be stressed that the total sulfur value only represents the sum of the sulfur compounds that the MS has analyzed—any unknown or unidentified compounds will not be reported.

For a true Total Sulfur reading we recommend the Thermo Scientific™ SOLA II™ Flare System which provides a solution for continuous and accurate determination of total sulfur in flare gas streams[2]. The SOLA II Flare system uses PUVF (pulsed ultra-violet fluorescence) spectrometry to determine total sulfur. All organically bound sulfur is first converted to sulfur dioxide (SO_2) by sample combustion. Irradiation of SO_2 with ultraviolet light at a specific wavelength forms an excited form of SO_2. The excited SO_2 relaxes to its ground state by the emission of light or fluorescence. The intensity of the emitted light is directly proportional to the SO_2 concentration and thus the flare stack's total sulfur concentration.

Summary

Magnetic sector MS, as evidenced by the Prima PRO process MS performance, provides fast, accurate on-line analysis of flare gas composition. The inherent power of magnetic sector mass spectrometry, combined with the flexibility of GasWorks software, enables one Prima PRO MS to monitor not only flare gas streams, but also multiple process streams. Root cause fault analysis is therefore greatly facilitated, by comparing the detailed composition data from the flare gas stream with that of the various process streams.

As well as complete compositional analysis, Prima PRO MS provides accurate fuel gas properties, including LHV, HHV, density, specific gravity, Wobbe Index, stoichiometric air requirement and CARI. This ensures waste gases are burnt to complete combustion and unburned pollutants are not emitted from the flare.

Reference

1. EPA 40 CFR § 63.670—Requirements for Flare Control Devices, US Government Publishing Offices.
2. Continuous flare stack emission monitoring using the Thermo Scientific SOLA II Flare System Thermo Fisher Scientific Application Note, 2014.

Learn more at **thermofisher.com/primapro**