

Maintain Compliance to Petrochemical (EMACT) and Organic Chemical Sector (MON) Flare Gas Rules with Rapid Online Analysis by Prima PRO Mass Spectrometers

Author: Daniel Merriman, Thermo Fisher Scientific, United Kingdom

Keywords

- Lower Heating Value (LHV)
- Net Heating Value (NHV)
- Higher Heating Value (HHV)
- Gross Heating Value (GHV)
- Environmental Protection Agency (EPA)
- EPA Refinery Sector Rule (RSR) 40 CFR 63
- National Emission Standards for Hazardous Air Pollutants (NESHAP)
- Generic Maximum Achievable Control Technology Standards for Ethylene Production (EMACT)
- Miscellaneous Organic Chemical Manufacturing (MON)
- Total Sulfur

Introduction

Increasingly, national and local government bodies are requiring processing companies to monitor the various emissions from their plant stacks and flares to reduce the amount of pollution entering the atmosphere. Initially the focus was on oil refinery flares; more recently petrochemical and chemical plant flares are receiving attention as potential sources of hazardous air pollutants.

Petrochemical plants

In March 2020 EPA signed several Risk and Technology Review (RTR) rules, including National Emission Standards for Hazardous Air Pollutants (NESHAP): Generic Maximum Achievable Control Technology Standards for Ethylene Production (EMACT). EPA decided that current requirements for EMACT flares are not adequate to ensure 98% destruction efficiency needed to meet standards. As a result EMACT flares are subject to the same flare definitions and requirements as refineries and must be continuously



monitored. Existing ethylene crackers must comply 3 years after publication of the final rule in the Federal Register, new crackers, or facilities that started construction after October 9, 2019, must comply on initial start-up or date of publication of final rule, whichever is later.

Organic chemicals manufacturer

In May 2020 EPA finalized amendments to the 2003 Miscellaneous Organic Chemical Manufacturing National Emission Standards for Hazardous Air Pollutants (NESHAP), known as MON. This adds monitoring and operational requirements for flares that control ethylene oxide emissions and flares used to control emissions from processes that produce olefins and polyolefins. It also allows facilities outside of this subset to opt into these flare requirements in lieu of complying with the current flare standards.

EPA estimates these finalized amendments will reduce hazardous air pollutant (HAP) emission by 107 tons per year,

with reductions in ethylene oxide emissions of ~0.76 tons per year. EPA also estimates that emissions of HAP from flares will be reduced by ~ another 260 tons per year.

Oil refineries

The above referenced rules follow those of November 2018 when the US Environmental Protection Agency (EPA) 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 period¹. 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 has to be added. This may then require the addition of steam to the flare, to avoid the production of visible emissions.

Measurement of flare gas streams by Process Mass Spectrometry

Analysis of flare gases presents a series of challenges, whatever process they originate from. 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. Although many regulations simply require 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. Speed of analysis speed is also crucial, as the heating value of the flare can change quickly. Analysis times measured in minutes increase the risk of failing to meet emission standards.

Process Mass Spectrometry 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 C_6 . Analysis of these 19 components will typically be performed in under 30 seconds, allowing one mass spectrometer to monitor more than one flare, depending on the distances involved.

Advantages of Prima PRO Process Mass Spectrometer

At the heart of the Thermo Scientific™ Prima PRO Process Mass Spectrometer is a magnetic sector analyzer (Figure 1), which offers unrivalled precision and accuracy compared with other mass spectrometers. Thermo Fisher Scientific™ manufactures both quadrupole and magnetic

Component	Molecular Weight	Flare Gas Typical Composition %mol
Hydrogen	2	0-40
Methane	16	15-95
Water	18	0-8
Carbon Monoxide	28	0-1
Nitrogen	28	0-40
Ethylene	28	0-12
Ethane	30	2-15
Oxygen	32	0-5
Hydrogen Sulfide	34	0-10
Propylene	42	0-20
Carbon Dioxide	44	0-10
Propane	44	0-5
1-3, Butadiene	54	0-0.2
Butenes	56	0-15
i-Butane	58	0-10
n-Butane	58	0-5
C_5 and C_6	70+	0-15
Carbonyl Sulfide	60	0-10ppm
Carbon Disulfide	76	0-1ppm

Table 1 Example of flare gas stream composition

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.

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 Process

Mass Spectrometer 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. The Prima PRO Process Mass Spectrometer 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.

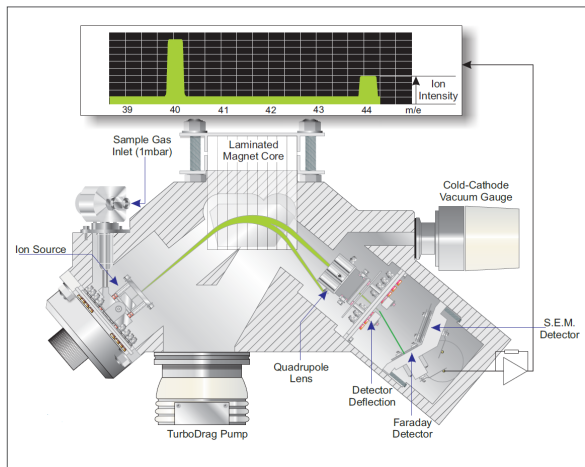


Figure 1 Prima PRO Process Mass Spectrometer magnetic sector analyzer

The ability of the Prima PRO Process Mass Spectrometer 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 Process Mass Spectrometer has been independently evaluated by EffectTech 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 recognised ISO/IEC 17025:2005 standards; this specifies the general requirements for the competence to carry out tests and/or calibrations, including sampling.

Rapid Multistream Sampling

If the Mass Spectrometer 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 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 the Prima PRO Process Mass Spectrometer's 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 other multistream sampling device offers the same level of guaranteed reliability.

Measuring fuel properties with Prima PRO Process Mass Spectrometer

The following fuel properties can routinely be derived by the Prima PRO Process Mass Spectrometer.

Lower Heating Value is calculated using the value of 1212 BTU/scf for Hydrogen as recommended by EPA

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)	$\frac{\text{Air Requirement}}{\sqrt{(\text{Specific Gravity})}}$

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 Process Mass Spectrometer's magnetic sector analyzer is ideally suited to hydrogen analysis because it does not suffer from the 'zero blast' that 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 the Prima PRO Process Mass Spectrometer is normally better than 0.1% relative.

Figure 2 shows how the Ideal LHV of the flare gas stream is calculated by Thermo Scientific™ GasWorks software Derived Values, based on the individual components' Ideal LHVs.

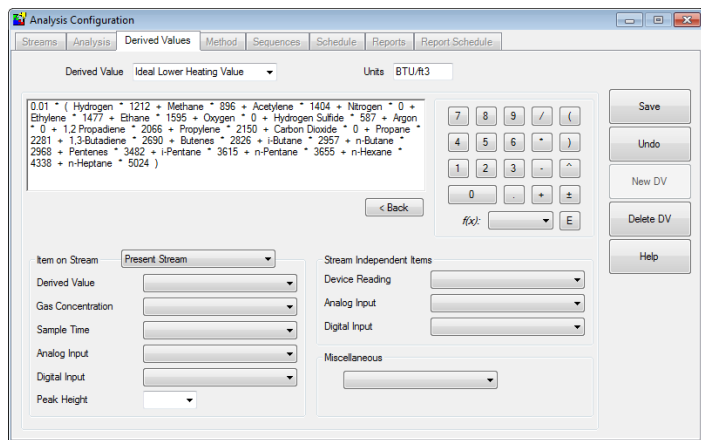


Figure 2 GasWorks Derived Value for Ideal Lower Heating Value

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 3 and 4. Figure 3

shows an example of the analytical method for a flare gas stream, Figure 4 shows that for a process stream. Both methods, along with additional process methods, are being utilized on a single Prima PRO Process Mass Spectrometer measuring a combination of process streams and flare gas.

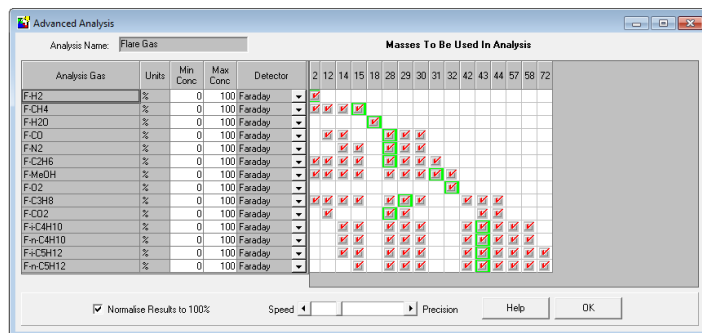


Figure 3 Example of flare stream method

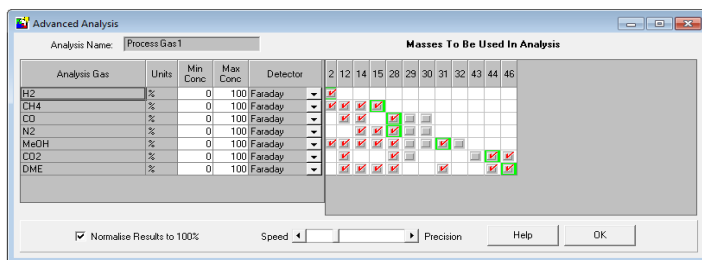


Figure 4 Example of process stream method

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.

Flare gas test data

To verify performance on a refinery flare gas application, the Prima PRO Process Mass Spectrometer was subjected to a factory test on a gravimetric cylinder containing 21 components, including inorganics and hydrocarbons from C₁ to C₆. Table 2 shows the cylinder composition, the Prima PRO Process Mass Spectrometer's quoted performance (standard deviation over 8 hours) and the results obtained from the test. The measured standard deviations for all 21 components were lower than the specified standard deviations over 8 hours.

As well as the composition data, the Prima PRO Process Mass Spectrometer calculated the Net Heating Value over the 8 hours of the test; as with the component concentrations, the measured NHV standard deviations are well below the specified 8-hour standard deviations.

Component	Concentration %mol	Prima PRO Specification for Standard Deviation %mol (8 hours)	FAT test Ave %mol (8 hours)	FAT Test Actual Standard Deviation %mol (8 hours)
Hydrogen	10	≤0.02	9.8835	0.0077
Methane	64.53	≤0.05	64.6662	0.0125
Carbon Monoxide	5	≤0.05	5.0829	0.0264
Nitrogen	10	≤0.05	9.8557	0.0469
Ethylene	2	≤0.02	1.9867	0.0010
Ethane	2	≤0.02	2.0367	0.0012
Oxygen	1	≤0.001	0.9941	0.0006
Hydrogen Sulfide	0.05	≤0.0005	0.0484	0.0003
Propylene	1	≤0.001	0.9961	0.0011
Carbon Dioxide	1	≤0.001	0.9597	0.0007
Propane	1	≤0.001	1.0910	0.0007
1,3 Butadiene	0.1	≤0.005	0.0992	0.0003
Butenes	0.5	≤0.005	0.5023	0.0005
i-Butane	0.5	≤0.005	0.4892	0.0011
n-Butane	0.5	≤0.005	0.5059	0.0026
Carbonyl Sulfide	100 ppm	≤1 ppm	100.5319	0.4470
Pentenes	0.1	≤0.005	0.0992	0.0004
i-Pentane	0.3	≤0.005	0.3083	0.0012
n-Pentane	0.3	≤0.005	0.2792	0.0042
Carbon Disulfide	100 ppm	≤1 ppm	100.4589	0.2733
n-Hexane	0.1	≤0.005	0.0957	0.0010
NHV (BTU/scf)		≤0.1 % relative	899.5394	0.07%

Table 2 Factory test on gravimetric cylinder containing 21 inorganic and hydrocarbon compounds, analyzed over 18 hours

Figures 5a to 5d show trend data for major components, minor components, sulfur components and NHV over the 8 hours of the test.

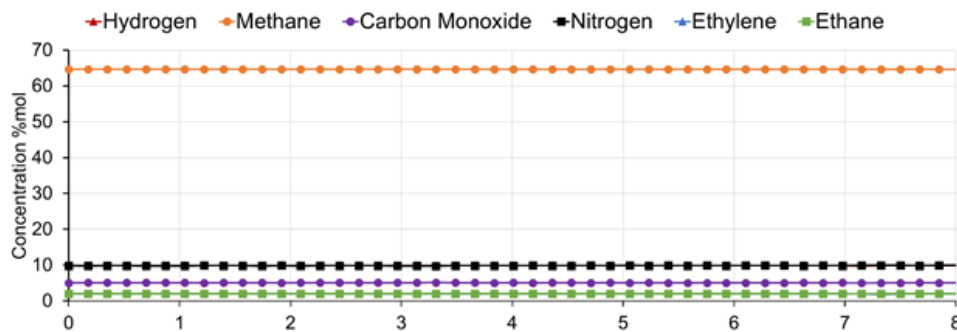


Figure 5a Major component concentrations obtained during factory test on gravimetric cylinder containing 21 inorganic and hydrocarbon compounds, analyzed over 8 hours

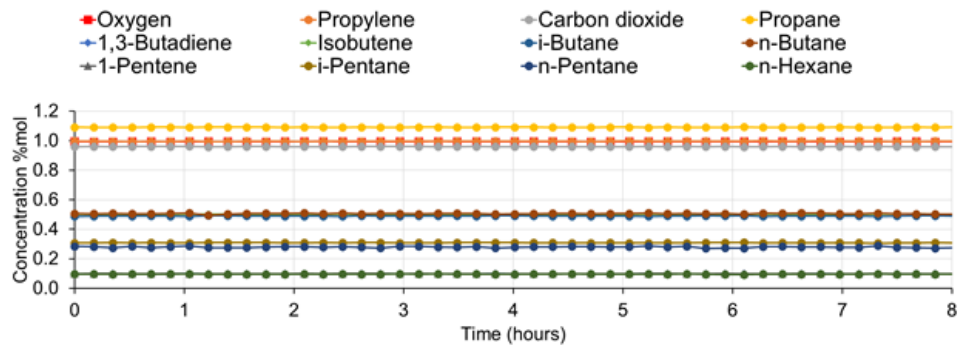


Figure 5b Major component concentrations obtained during factory test on gravimetric cylinder containing 21 inorganic & hydrocarbon compounds, analyzed over 8 hours

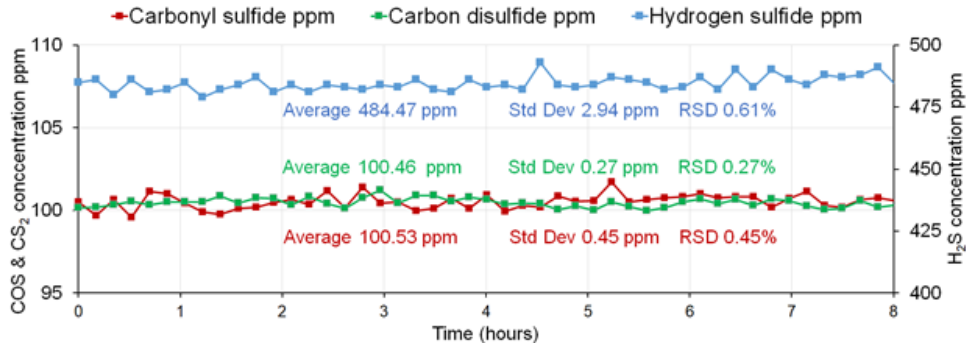


Figure 5c Sulfur component concentrations obtained during factory test on gravimetric cylinder containing 21 inorganic & hydrocarbon compounds, analyzed over 8 hours

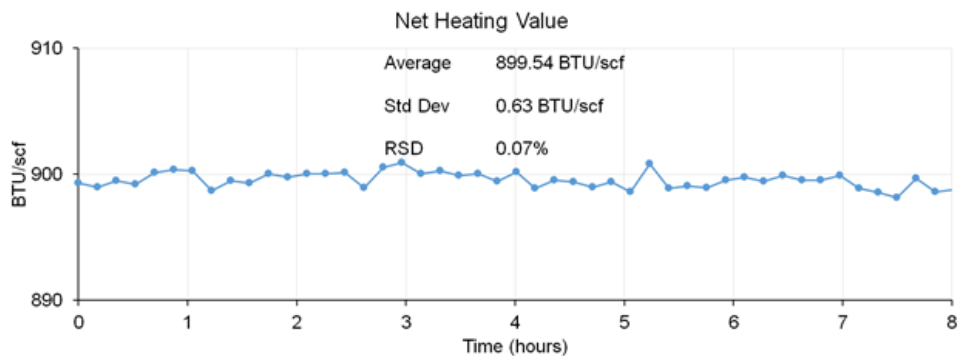


Figure 5d NHV obtained during factory test on gravimetric cylinder containing 21 inorganic & hydrocarbon compounds, analyzed over 8 hours

Analysis of total sulfur

In general, refinery regulators are interested in values for hydrogen sulfide (H₂S) and Total Reduced Sulfur (TRS). However there is some divergence on what constitutes TRS. In some cases it is defined as H₂S together with carbonyl sulfide (COS) and carbon disulfide (CS₂). It can also be defined as a mixture of compounds which contain a sulfur component in the reduced form, most commonly H₂S, methanethiol (methyl mercaptan, CH₃SH), dimethyl sulfide (DMS, (CH₃)₂S) and dimethyl disulfide (DMDS, CH₃S₂CH₃).

Mass spectrometers can measure a number of sulfur compounds down to ppm levels; typical Prima PRO Process Mass Spectrometer performance figures are shown in Table 3. Analysis time is less than 30 seconds, including stream switching time and standard deviations are measured over 8 hours.

Component	Typical Composition %mol	Precision of analysis by Prima PRO Process MS (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

Table 3 Typical Prima PRO Process Mass Spectrometer performance specification for sulfur compounds

To demonstrate the Prima PRO Process Mass Spectrometer's excellent linearity when analyzing sulfur species, a unit was calibrated for hydrogen sulfide, carbonyl sulfide and carbon disulfide at a single concentration using three cylinders, then used to analyze a series of cylinders containing the three sulfur species.

- H₂S was calibrated at 0.0506%, then MS analyzed H₂S concentrations from 0% to 89.88%
- COS was calibrated at 0.2006%, then MS analyzed COS concentrations from 0% to 0.2006%
- CS₂ was calibrated at 0.198%, then MS analyzed COS concentrations from 0% to 0.198%

Table 4 shows the test gases used to demonstrate system linearity, with the calibration gases shown in red. Figure 6 shows the linearity achieved for the three sulfur species.

This data shows that the Prima PRO Process Mass Spectrometer can be safely calibrated for hydrogen sulfide at trace levels (0.05% in this case) and yet measure up to 100% concentrations.

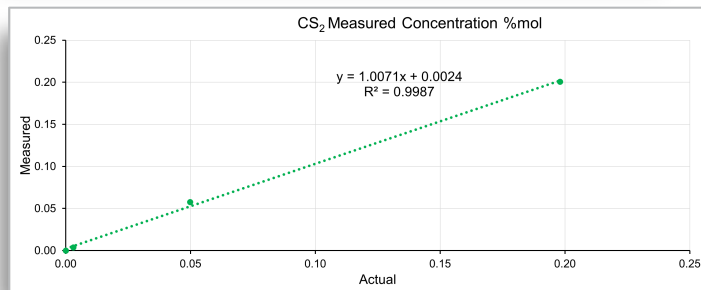
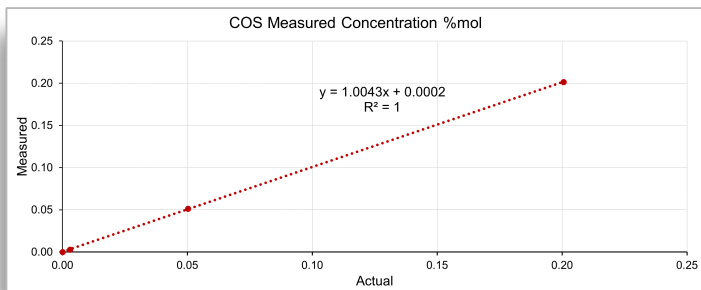
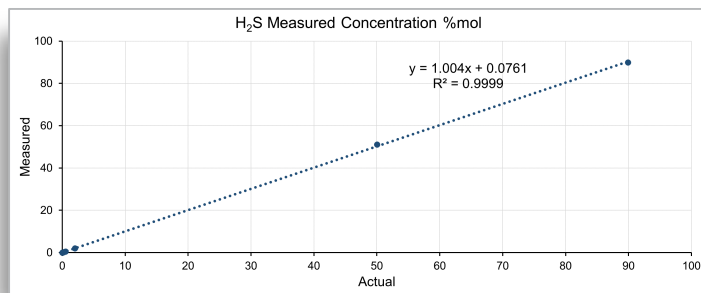
H ₂ S Actual Concentration %mol	H ₂ S Measured Concentration %mol	COS Actual Concentration %mol	COS Measured Concentration %mol	CS ₂ Actual Concentration %mol	CS ₂ Measured Concentration %mol
0	0.0001	0	0	0	0.0002
0.003	0.0028	0.003	0.0029	0.003	0.0039
0.0506	0.0503	0.0502	0.0513	0.0498	0.0576
0.2505	0.261	0.2006	0.2015	0.198	0.2006
0.4997	0.526				
2	2.08				
50.03	51.1				
89.88	89.88				

Table 4 Sulfur test gases used to demonstrate Prima PRO Process Mass Spectrometer linearity

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 iQ Flare System which provides a solution for continuous and accurate determination of total sulfur in flare gas streams². SOLA iQ Flare uses PUVF (pulsed ultra-violet fluorescence) spectrometry to determine total sulfur. All organically bound sulfur is first converted to sulfur dioxide (SO₂) by sample combustion. Irradiation of SO₂ with ultraviolet light at a specific wavelength forms an excited form of SO₂. The excited SO₂ relaxes to its ground state by the emission of light or fluorescence. The intensity of the emitted light is directly proportional to the SO₂ concentration and thus the flare stack's total sulfur concentration.

Figure 6 Prima PRO Process Mass Spectrometer linearity for hydrogen sulfide, carbonyl sulfide and carbon disulfide



Summary

The Prima PRO Process Mass Spectrometer provides fast on-line accurate analysis of flare gas and process gas composition. In recent years the Prima PRO Process Mass Spectrometer has achieved great success monitoring refinery flare gases. It already has a proven track record over many years monitoring ethylene furnaces³ and ethylene oxide processes⁴ and is ideally suited to monitor flare gas streams from these same processes as they increasingly fall under the spotlight of concerns over hazardous emissions. The inherent power of mass spectrometry, combined with the flexibility of GasWorks software, enables one Prima PRO Process Mass Spectrometer 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, the Prima PRO Process Mass Spectrometer 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.

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USA

27 Forge Parkway
Franklin, MA 02038
Ph: (713) 272-0404
Fax: (713) 272-2273
orders.process.us@thermofisher.com

Europe

Ion Path, Road Three,
Winsford, Cheshire CW73GA UK
Ph: +44 1606 548700
Fax: +44 1606 548711
sales.epm.uk@thermofisher.com

Find out more at thermofisher.com/flaregases