# Fast On-Line Monitoring of Flare Gases with the Prima PRO Process Mass Spectrometer

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Application Note

**Key Words**

- EPA 40 CFR Part 60, Subpart Ja
- Higher Heating Value (HHV)
- Magnetic Sector
- Rapid Multistream Sampler
- Total Sulfur

## Introduction

Many industries such as oil refineries and chemical & petrochemical plants use flare stacks to burn waste gases, either process by-products or gases produced during unplanned plant operations. They are vital to the safe operation of plants, providing a way to burn safely excess flammable gases. Increasingly, national or local government bodies are requiring the flare gas composition to be monitored, to reduce the amount of pollution entering the atmosphere.

For example, in the USA, the US Environmental Protection Agency issued regulation 40 CFR 60, Subpart Ja, coming into force in 2015, requiring refineries to analyze flare gases for Higher Heating Value (HHV), sulfur concentration, and gas flow.

A flare gas stream is a mixture of waste gases from the various processes on the plant, so the list of components present, and their concentrations, will vary dramatically over time. Although regulations generally require just the total heating value 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.

## Measurement of Flare Gas Streams by Process Mass Spectrometry

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 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 compositions and concentrations may be very different.

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**Table 1:** Example of flare gas stream composition.

| Component | | | Typical Reactor Outlet Concentration %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 | 0.5 - 1.5 |
| **1-Butene** | $C_4H_8$ | 56 | 0.1 - 0.3 |
| **i-Butane** | $i\text{-}C_4H_{10}$ | 58 | 2.5 - 7.5 |
| **n-Butane** | $i\text{-}C_4H_{10}$ | 58 | 0 – 1 |
| **1-Hexene** | $C_6H_{12}$ | 84 | 0.1 – 0.3 |
| **n-Hexane** | $n\text{-}C_6H_{14}$ | 86 | 0 - 1 |
| **Methane** | $CH_4$ | 16 | 5 - 20 |
| **Propane** | $C_3H_8$ | 44 | 0.1 - 0.5 |

## Advantages of Thermo Scientific™ Prima PRO Process MS

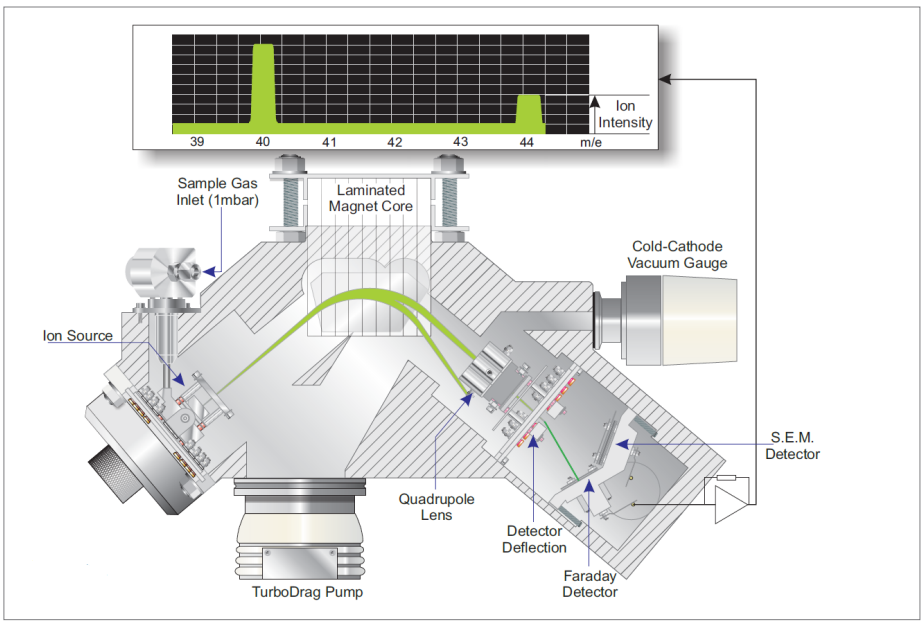
At the heart of the Prima PRO is a magnetic sector analyzer (Figure 1) which offers unrivalled precision and accuracy compared with other mass spectrometers. Thermo Fisher Scientific manufactures both quadrupole and magnetic sector mass spectrometers; over thirty years of industrial experience have shown 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 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 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's magnetic sector analyzer.

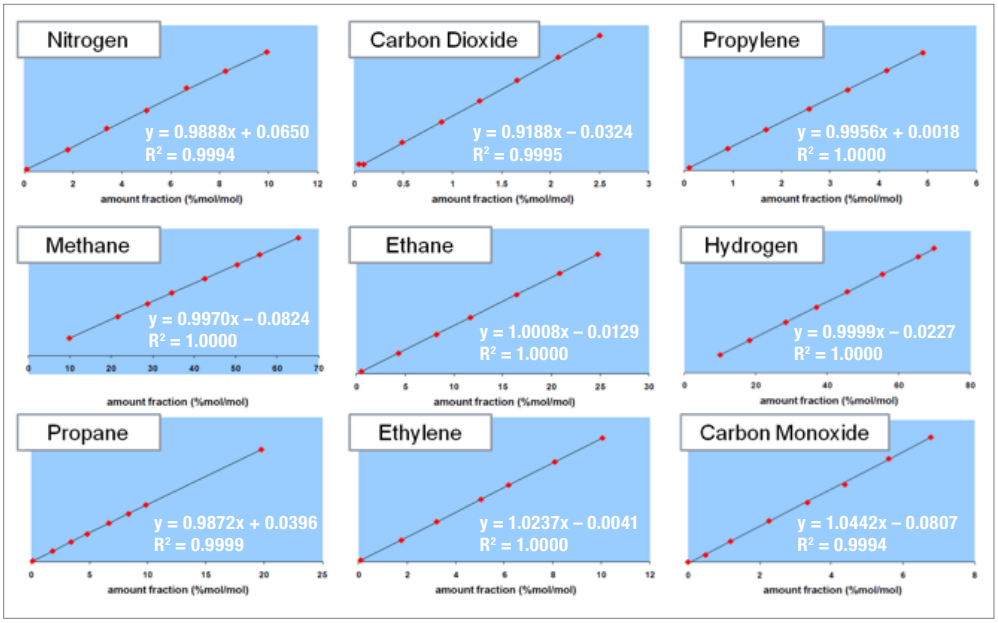


Prima PRO's ability to measure over a wide dynamic range is critically important if the varying composition levels in flare gas are to be measured accurately. Prima PRO has been independently evaluated by EffecTech UK, an independent specialist company providing accredited calibration and testing services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

## Linearity

Prima PRO 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 is capable of generating accurate, reliable composition data from complex gas mixtures.

**Figure 2:** Prima PRO linearity data.




## Long-term Stability

Prima PRO's 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.

**Table 2:** Statistical report on 30 day run with Prima PRO analyzing 13-component calibration blend.

| | Average Balance | 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% |

## Rapid Multistream Sampling

If the MS is to monitor all 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 RMS Rapid Multistream Sampler. 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 Prima PRO's internal network.

The RMS is shown in schematic form in Figure 3. It 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.

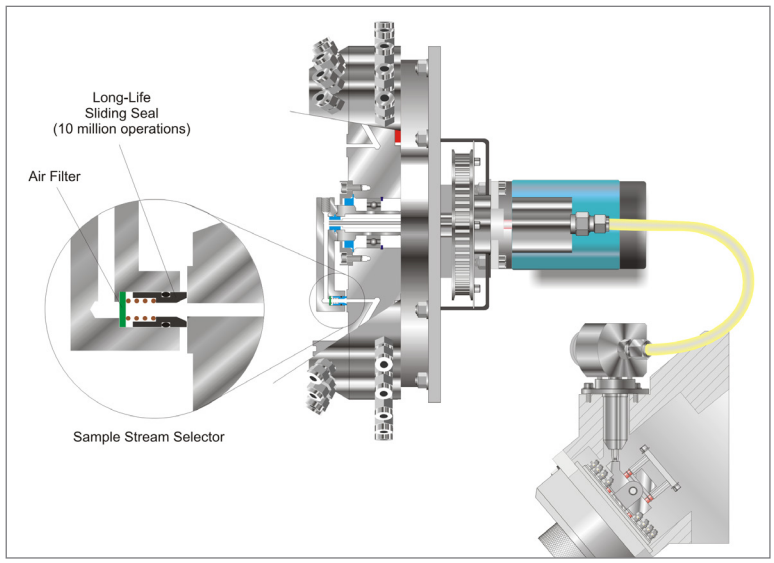



**Figure 3:** 64-port Rapid Multistream Sampler.

## Measuring Fuel Properties with Prima PRO

The following fuel properties are normally derived by the Prima PRO mass spectrometer:

| | |
|---|---|
| Lower Calorific Value | Also known as Lower Heating Value |
| Higher Calorific Value | Also known as Higher Heating Value |
| Density | |
| Specific Gravity | |
| Lower Wobbe Index | $\frac{\text{Lower Calorific Value}}{\sqrt{(\text{Specific Gravity})}}$ |
| Higher Wobbe Index | $\frac{\text{Higher Calorific Value}}{\sqrt{(\text{Specific Gravity})}}$ |
| Air Requirement | |
| CARI | $\frac{\text{Air Requirement}}{\sqrt{(\text{Specific Gravity})}}$ |

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

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

Prima PRO's 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 being utilized on a single Prima PRO process MS measuring a combination of process streams and flare gas.

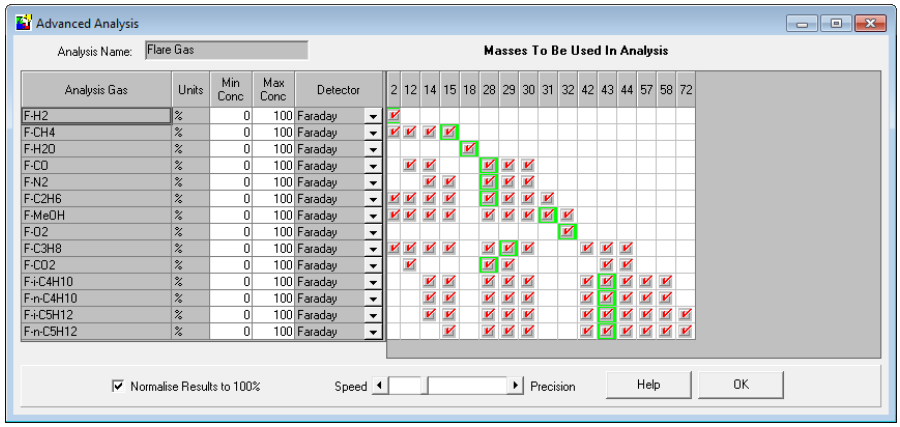



**Figure 4:** Example of flare stream method.

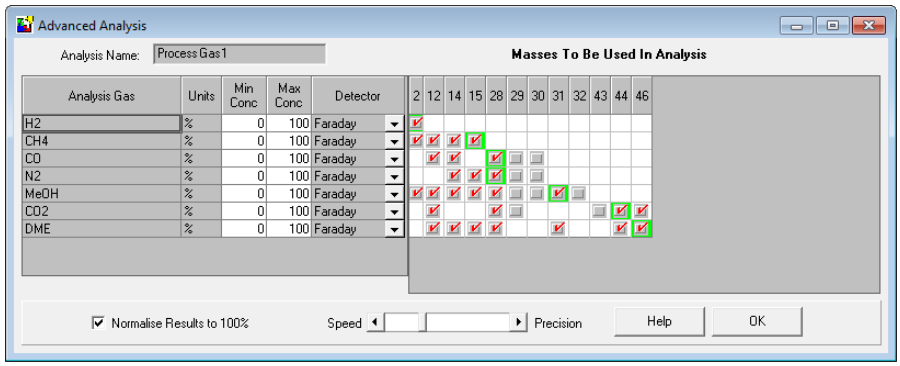



**Figure 5:** Example of process stream method.

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.

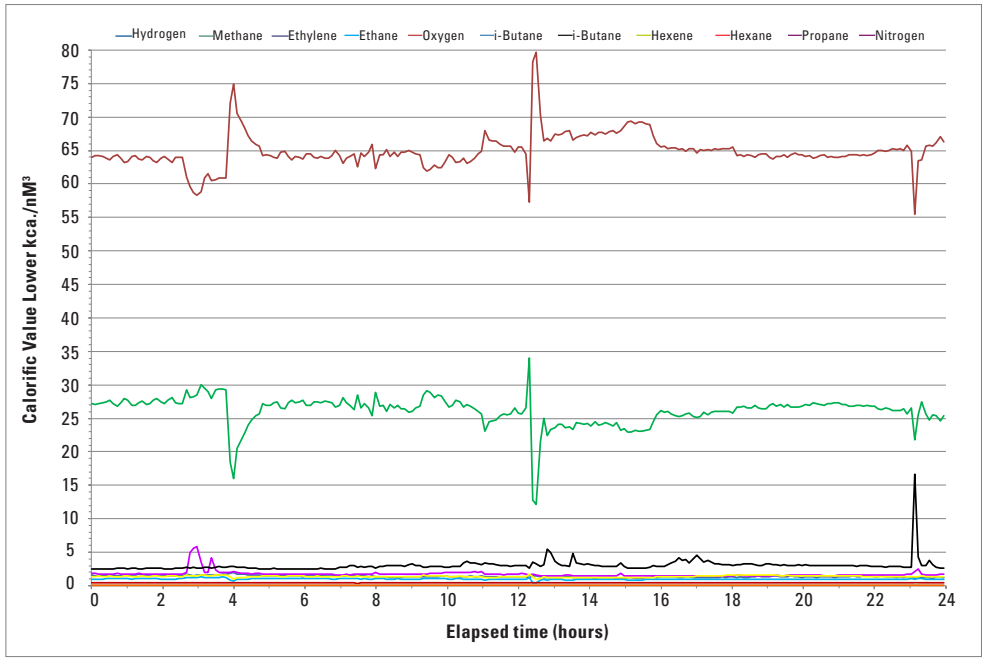
Table 3 shows Prima PRO's analytical performance on these two different stream types. Stream analysis cycle time is 30 seconds. If multiple sample streams are measured the stream switching time and settling time is 10 seconds, so n streams can all be analyzed with a cycle time of n × 40 seconds. Analytical 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 performance specification for flare gas and process gas streams.

| Component | Formula | Flare gas | | Process Gas | |
|---|---|---|---|---|---|
| | | Concentration %mol | Prima PRO precision (standard deviation) %mol ≤ | Concentration %mol | 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 | – | – |

Figure 6 shows a 24-hour trend display for a flare gas stream. Prima PRO 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.

Figure 6: 24-hour trend display of flare gas stream.




## 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 in natural gas are shown in Table 4. Analysis time is less than 30 seconds, including stream switching time. Standard deviation values are measured over 8 hours.

**Table 4:** Typical Prima PRO 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 7 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 5.

**Figure 7:** Test blend of three mercaptans.

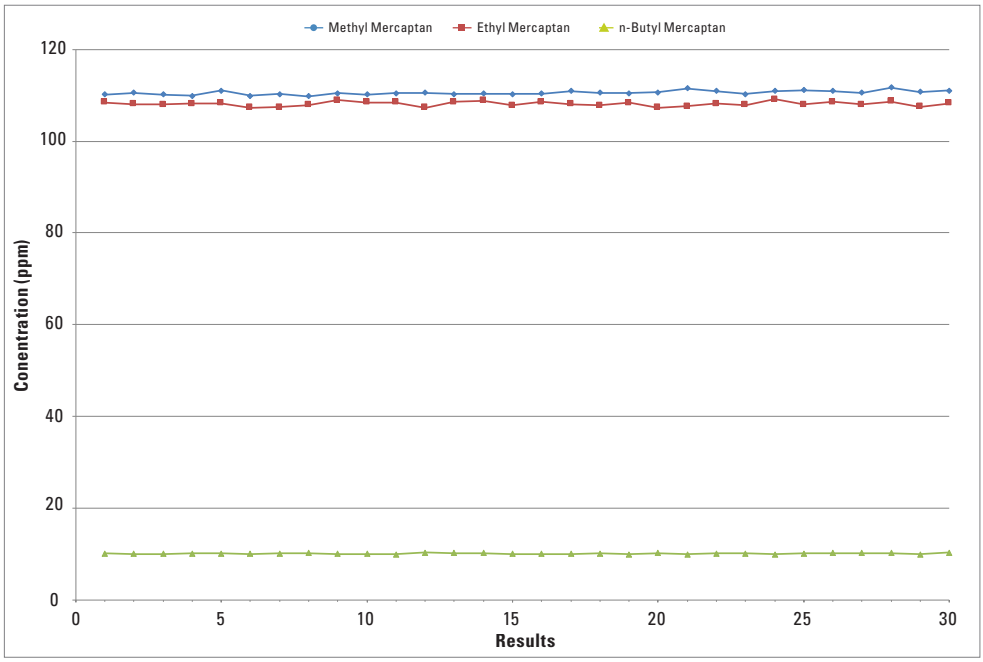



**Table 5:** Precision data for three typical sulfur compounds.

| | Mean (ppm) | Standard Deviation (ppm) | Relative Standard Deviation |
|---|---|---|---|
| **Methyl Mercaptan** | 110.603 | 0.444 | 0.4% |
| **Ethyl Mercaptan** | 108.130 | 0.468 | 0.4% |
| **n-Butyl Mercaptan** | 10.036 | 0.114 | 1.1% |

Thermo Scientific™ 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[1]. SOLA II Flare 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

Prima PRO Process MS provides fast on-line accurate analysis of flare gas composition. The inherent power of mass spectrometry, combined with the flexibility of GasWorks software, enables one Prima PRO 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 provides accurate fuel gas properties, including 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. Continuous flare stack emission monitoring using the Thermo Scientific SOLA II Flare System Thermo Fisher Scientific *Application Note,* 2014.

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