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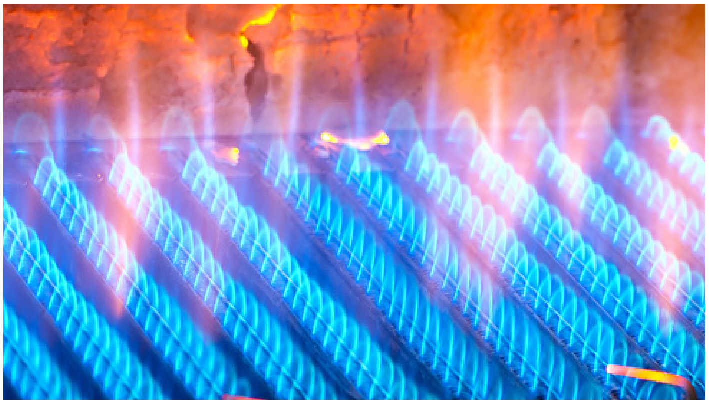
APPLICATION NOTE

Prima PRO Process Mass Spectrometer

Fast On-Line Monitoring of Fuel Gases

Authors: Daniel Merriman & Graham Lewis, Thermo Fisher Scientific, Winsford, Cheshire, United Kingdom



Key Words

- Calorific Value
- Heating Value
- Wobbe Index
- Stoichiometric Air Requirement
- Combustion Air Requirement Index
- ISO 6976:2016
- ISO 10723:2012
- Magnetic Sector
- Rapid Multistream Sampler

Introduction

Furnace or power plant fuel gases which have variable composition pose particular challenges for process engineers who need to achieve optimum efficiency and product yield. As the gas composition changes, the heating (calorific) value changes and the burner temperature can therefore change. So too can the amount of air that is required for combustion. Unless these properties are monitored and compensated for, the furnace or power plant will not be properly controlled, causing significant inefficiency, wastage and even burner damage.

Normally furnaces are operated at constant temperature; to achieve this, a gas-fired furnace would ideally burn a gas of constant composition, delivered at a constant rate and using a constant intake of air at the correct rate for complete combustion. In practice, the gas supply is of varying composition, especially on a petrochemical complex or integrated iron and steel works, where fuel gases from a variety of processes are utilized. Thus in order to maintain a constant temperature, either the rate of the gas supply needs to be varied or, in the case of a mixing station mixing various gas streams, the relative flow rates of the different gases need to be varied. Also, the air supply rate needs to be varied, since there will be energy wasted if either too little air or too much air is used. If there is too little air, some of the fuel gas will be unburned and wasted. If too much air is added then heat will be wasted. In metallurgy processes, excess air can also cause surface defects on metal surfaces due to oxidation, and poor temperature control can have an adverse effect on product quality.

The typical components of fuel gases have a wide range of energy values; for example ISO 6976:2016 states a gross calorific value for methane at 15.55 °C (60 °F) of 891 kJ/mol, while n-hexane's is 4198 kJ/mol at the same temperature[1]. This wide range means that relatively low concentrations of some components can have a significant impact on the energy value of the gas stream. It is therefore imperative to provide a comprehensive analysis of the gas stream, not just measure the major components. Process Mass Spectrometry is the ideal technique for determining the properties of fuel gases, by virtue of its speed and accuracy. It is therefore becoming widely adopted as the preferred technique

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Fuel gas energy parameters

By analyzing the composition of the fuel gas, the precise heating properties can be predicted. This enables a 'feed-forward' method of control (rather than 'feed-back'). The calorific value (also known as the heating value) is calculated from the analyzed composition according to the sum of the pure component calorific values weighted on a mole fraction basis[1], as below.

Calorific Value of Mixture = [Calorific Value of Pure Component A × Mole Fraction of Component A]
+ [Calorific Value of Pure Component B × Mole Fraction of Component B]
+ [Calorific Value of Pure Component C × Mole Fraction of Component C]
+ etc

In practice the fuel gas will flow through a restriction such as an orifice or valve and the actual flow is inversely proportional to the square root of the density of the gas, so the property known as the Wobbe Index is more useful than the Calorific Value. The Wobbe Index is defined as follows:

$$\text{Wobbe Index} = \frac{\text{Calorific Value}}{\sqrt{(\text{Specific Gravity})}}$$

The Wobbe Index indicates the effective heating value of the fuel gas.
The specific gravity is equal to the density of the gas divided by the density of the reference gas (normally air).

Density is calculated according to:

Density of Mixture = [Density of Pure Component A × Mole Fraction of Component A]
+ [Density of Pure Component B × Mole Fraction of Component B]
+ [Density of Pure Component C × Mole Fraction of Component C]
+ etc

To predict the required ratio of air/fuel required for complete combustion the property known as Stoichiometric Air Requirement is calculated as:

Stoichiometric Air Requirement (SAR) = [SAR of Pure Component A × Mole Fraction of Component A]
+ [SAR of Pure Component B × Mole Fraction of Component B]
+ [SAR of Pure Component C × Mole Fraction of Component C]
+ etc

square root of the density of the gas, so the property known as CARI (Combustion Air Requirement Index) is more useful than the Stoichiometric Air Requirement. The CARI is defined as follows:

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

Measurement of Fuel Gases by Process Mass Spectrometry

Process Mass Spectrometry is particularly suited to the measurement of fuel gas because the analysis is comprehensive, accurate and fast. The analysis of all the components present in fuel gas which typically contains many components (e.g. H_2, CH_4, CO, N_2, O_2, C_2H_4, Ar, C_3H_6, CO_2, C_3H_8, C_4H_{10} and C_6H_6) is completed in less than 30 seconds, with a precision of typically better than 0.1% relative or 0.01 mol% absolute. Mass spectrometers function by ionizing the sample gas molecules and atoms, then using magnetic or electric fields to separate the resulting characteristic ions according to their mass to charge ratio.
The various ion currents are measured with a detector[3].

An example of such an instrument designed for process measurements is the Thermo Scientific™ Prima PRO which is a compact and rugged unit using a scanning magnetic sector MS analyzer. This instrument, shown in Figure 1, provides exceptional reproducibility and linearity.

Advantages of Prima PRO Process MS

At the heart of the Prima PRO is a magnetic sector analyzer 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.

A unique feature of the Prima PRO magnet is that it is laminated. Our analyzer scans at speeds equivalent to that of quadrupole analyzers, offering the unique combination of rapid analysis and high stability. This allows the rapid and extremely stable analysis of an unlimited number of user-defined gases. The scanning magnetic sector is controlled with 24-bit precision using a magnetic flux measuring device for extremely stable mass alignment.

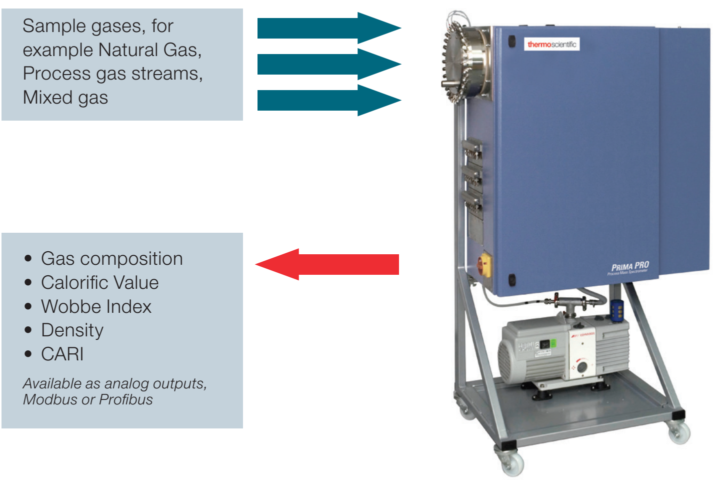

Figure 1: Thermo Scientific™ Prima PRO magnetic sector mass spectrometer used for on-line analysis of fuel gases

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 2. It has a three year warranty as standard; no other multistream sampling device offers the same level of guaranteed reliability

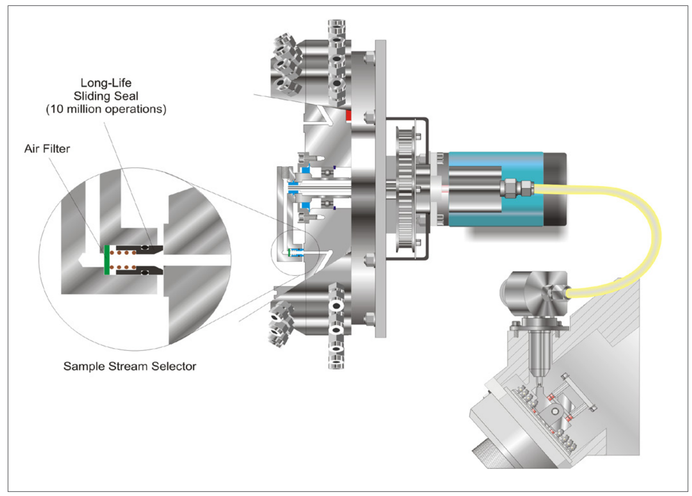

Figure 2. 64-port Rapid Multistream Sampler

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
Compressibility	
Actual Lower Calorific Value	$\frac{\text{Ideal Lower Calorific Value}}{\sqrt{\text{(Specific Gravity)}}}$
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	
Combustion Air Requirement Index (CARI)	$\frac{\text{Air Requirement}}{\sqrt{\text{(Specific Gravity)}}}$

The precision of these measurements with Prima PRO is normally better than 0.1% relative. Higher Calorific Value differs from Lower Calorific Value in that it takes into account the latent heat of vaporization of water in the combustion products.

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.

Independent Evaluation of Prima PRO on Fuel Gas Analysis

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 recognized ISO/IEC 17025:2005 standards; this specifies the general requirements for the competence to carry out tests and/or calibrations, including sampling. It covers testing and calibration performed using standard methods, non-standard methods, and laboratory-developed methods. It is applicable to all organizations performing tests and/or calibrations.

The conventional method for assessing the performance of an on-line process gas analyser is in accordance with the international standard ISO 10723[2]. EffecTech used this method to assess the performance of the Prima PRO for the nine components listed in Table 2. It contains a wide range of inorganic and organic components including hydrogen, nitrogen, carbon monoxide, carbon dioxide and saturated and un-saturated hydrocarbons.

Prima PRO was calibrated for sensitivity using just one mixture, detailed in Table 2. As the process analyzer needs to measure these compounds over a wide dynamic range of concentrations, Prima PRO was tested with a set of nine reference gases covering the range of compositions shown in Table 2. These cover a range of amount fractions for each component greater than that expected through a typical fuel gas metering point. The nine reference gases were manufactured to EffecTech's requirements by a gravimetric method using mass pieces traceable by weight to the UK National Physical Laboratory (NPL).

Table 2. EffecTech calibration gas and reference gas ranges

Component	Calibration gas (% mol/mol)	Sample composition range (% mol/mol)	
		Minimum	Maximim
Nitrogen	9.000 ± 0.015	0.10	9.94
Carbon Dioxide	5.000 ± 0.015	0.05	2.50
Methane	9.000 ± 0.020	9.84	65.03
Ethane	5.000 ± 0.013	0.50	24.75
Propane	10.000 ± 0.025	0.11	19.74
Ethene	5.000 ± 0.0015	0.099	10.06
Propene	5.000 ± 0.013	0.098	4.91
Hydrogen	43.000 ± 0.070	10.005	69.88
Carbon Monoxide	9.000 ± 0.015	0.098	6.79

Each gas was analyzed for 30 cycles over 5 minutes (10 second cycle time).

Figure 3 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. More information on EffecTech is available at http://www.effectech.co.uk.

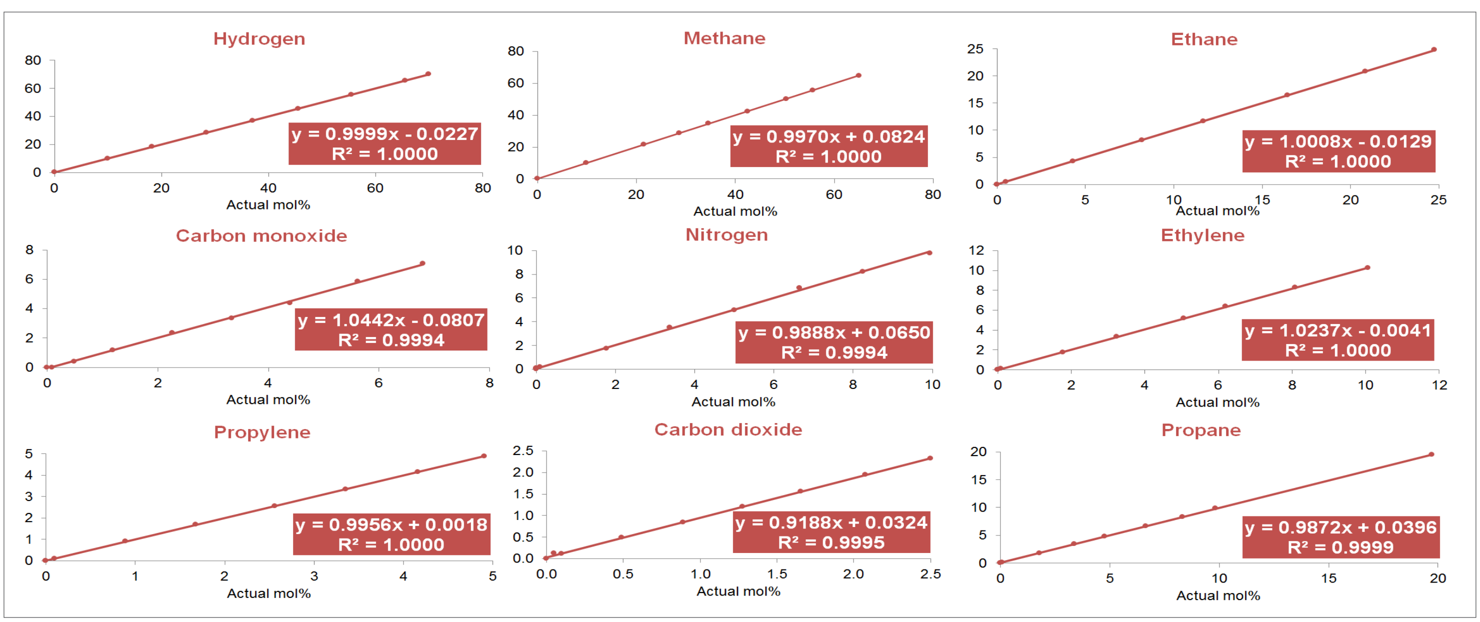

Figure 3 Prima PRO linearity data

Precision & stability

A key requirement of a good fuel gas analyzer is to operate with high levels of precision for long periods without recalibration the analyzer is effectively 'down' when it is calibrating. Prima PRO's magnetic sector analyzer produces characteristic flat-topped peaks, shown in Figure 4. As the height of the peak is directly proportional to component concentration, the peak shape gives inherently stable concentration data, which means Prima PRO's typical calibration interval is one month and normally takes place automatically.

Figure 5 shows example data from test runs on cylinders representing two different types of fuel gas. They show the reproducibility of the calorific value measurements over 24 hrs.

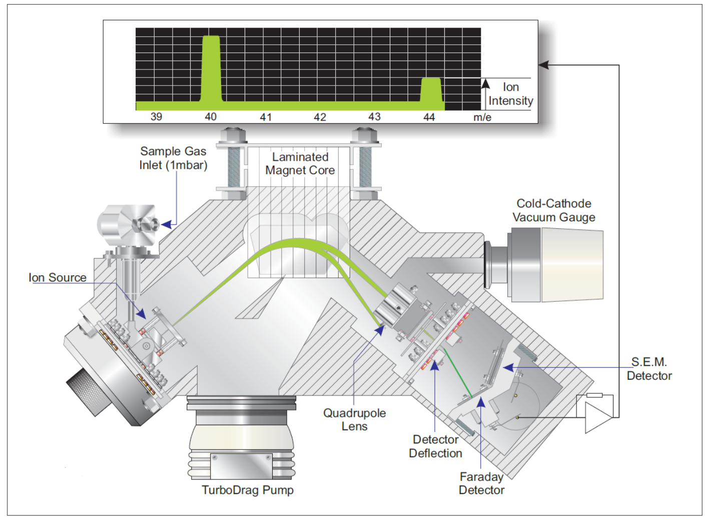

Figure 4. Prima PRO's magnetic sector analyzer

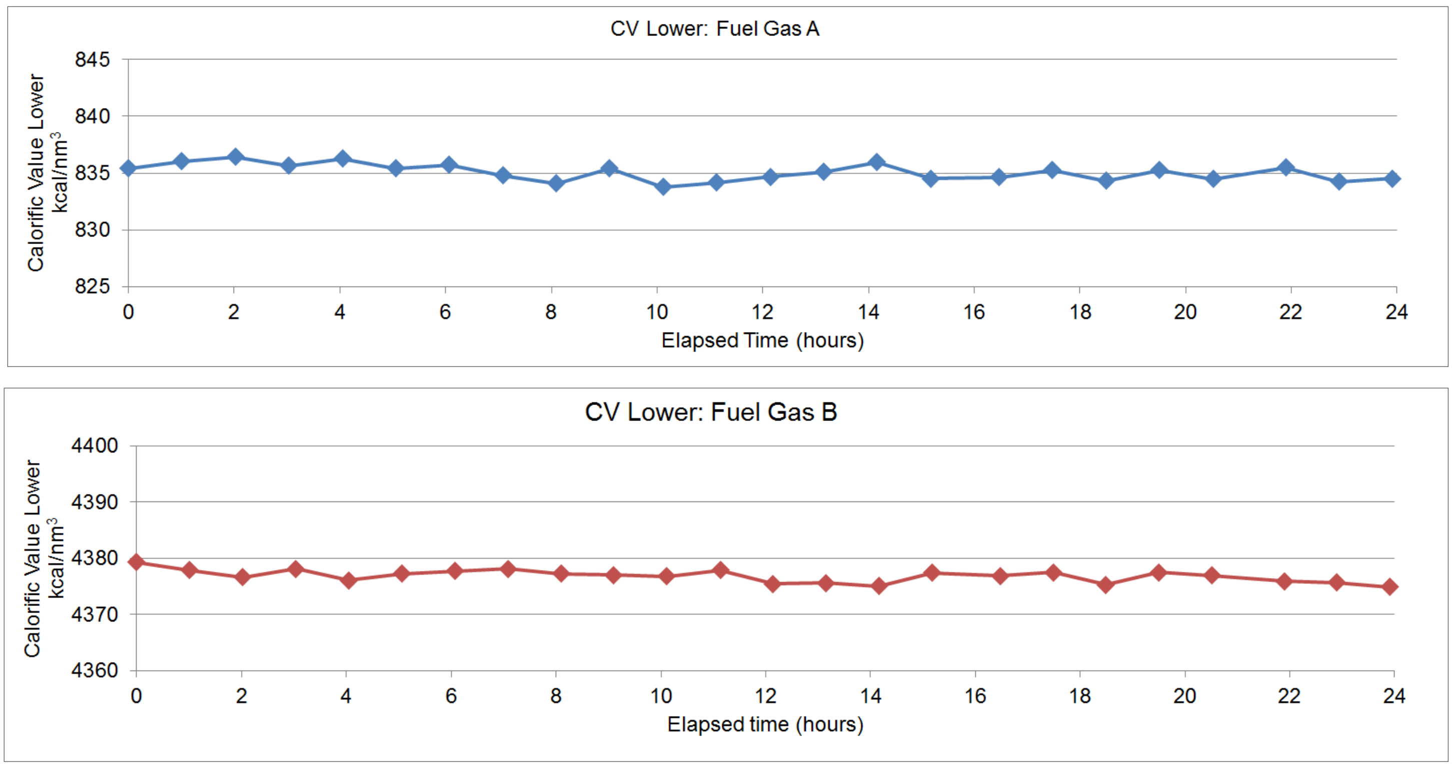

Figure 5. 24 hour calorific value data from two different types of fuel gas

Statistical reports for the two cylinders are shown in Tables 3 and 4. Measured standard deviations are well within Prima Prima PRO's long-term stability is also excellent. Figure 6 shows a 30-day run without recalibration on a hydrocarbon blend calibration cylinder; standard deviations for the eleven components in the cylinder are shown in Table 5.

Table 3. 24 hour statistical report for Fuel Gas A

	Fuel Gas A										
	H_2	CO	N_2	O_2	Ar	CO_2	CV Lower	CV Upper	SG	WI	Density
Certificate	4.03	24.08	43.74	1.01	1.01	26.13	831.8	850.7	1.083	799.3	1.4007
Mean	4.05	24.16	43.62	1.01	1.01	26.14	835.0	854.1	1.083	802.4	1.4002
Std Dev	0.006	0.029	0.034	0.0009	0.0004	0.003	0.7	0.7	0.0000	0.7	0.0002
RSD	0.14%	0.12%	0.08%	0.09%	0.04%	0.01%	0.09%	0.08%	0.00%	0.09%	0.02%

Table 4. 24 hour statistical report for Fuel Gas B

Fuel Gas B	H_2	CH_4	CO	N_2	C_2H_4	C_2H_6	H_2S	C_3H_6	CO_2	C_6H_6	C_7H_8	C_8H_{10}	CV Lower	CV Higher	SG	WI	Density
Certificate	63.08	24.71	5.95	1.99	1.837	0.844	0.100	0.100	1.29	0.078	0.01	0.009	4384.1	4945.5	0.3099	7875.7	0.4007
Mean	63.25	24.67	5.93	1.97	1.827	0.841	0.005	0.100	1.29	0.078	0.01	0.009	4376.8	4937.9	0.3081	7884.5	0.3985
Std Dev	0.019	0.013	0.018	0.016	0.001	0.001	0.0001	0.0002	0.0007	0.0002	0.0001	0.0002	1.2	1.2	0.0001	1.1	0.0002
RSD	0.03%	0.05%	0.30%	0.84%	0.09%	0.11%	2.37%	0.21%	0.06%	0.21%	1.16%	1.90%	0.03%	0.02%	0.04%	0.01%	0.04%

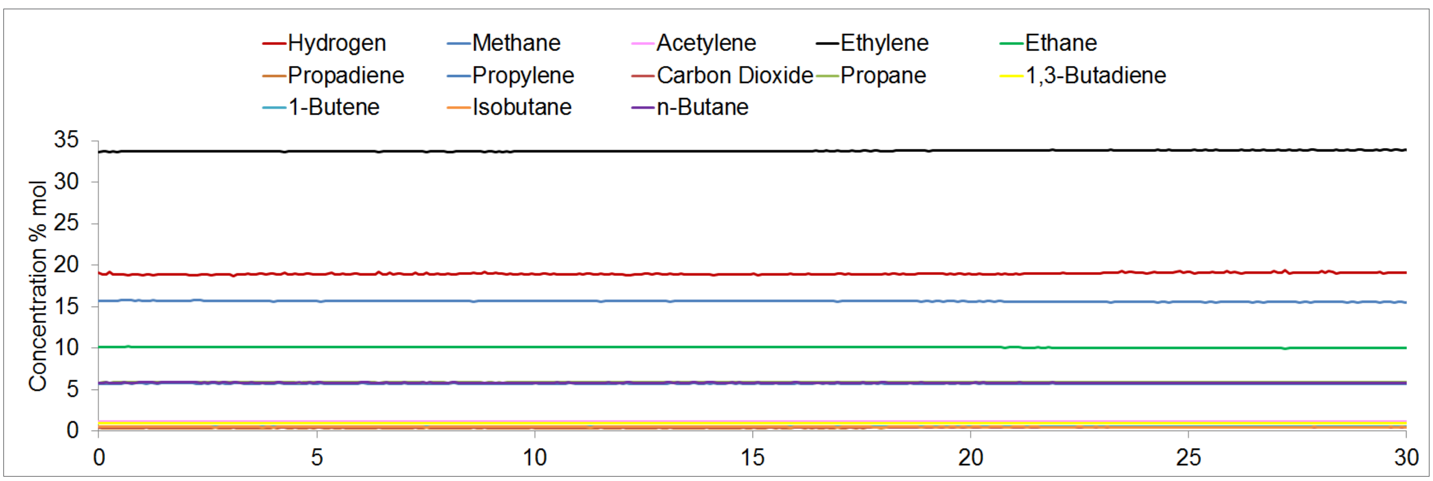

Figure 6. 30-day run with Prima PRO analyzing 13-component hydrocarbon blend

Table 5. Statistical report on 30 day run with Prima PRO analyzing 13-component hydrocarbon blend

	H_2	CH_4	C_2H_2	C_2H_4	C_2H_6	C_3H_4	C_3H_6	CO_2	C_3H_8	C_4H_6	C_4H_8	i-C_4H_{10}	n-C_4H_{10}
Ave	18.98	15.65	1.19	33.77	10.09	0.39	5.73	0.44	5.87	0.99	0.56	0.50	5.83
Std Dev	0.106	0.068	0.007	0.072	0.054	0.008	0.014	0.017	0.012	0.006	0.004	0.012	0.022
RSD	0.56%	0.44%	0.58%	0.21%	0.53%	2.12%	0.24%	3.72%	0.21%	0.59%	0.69%	2.50%	0.37%

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 fuel gas stream, depending on process control requirements. Examples of different analysis methods are shown in Figures 7 and 8: Figure 7 shows the analysis method for Fuel Gas A, Figure 8 for Fuel Gas B.

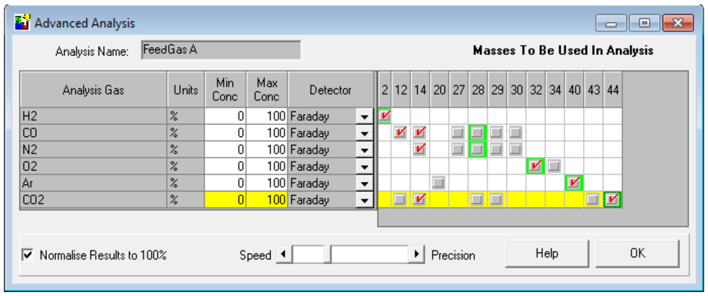

Figure 7: Analysis method for Fuel Gas A

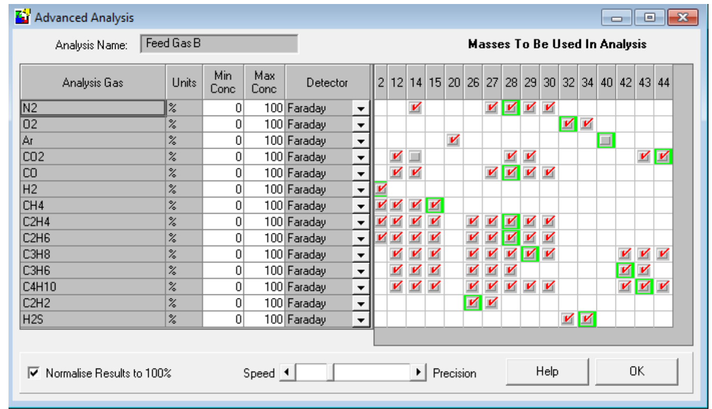

Figure 8: Analysis method for Fuel Gas B

Discussion

Although there are other simpler and lower cost instruments capable of measuring some of the properties of fuel gases, the measurements made by Prima PRO are more complete, accurate and fast.

Calorimeters, which measure the heat effect of burning fuel gas, can be used to measure Calorific Value or Wobbe Index but not both simultaneously, although they can be combined with a density meter to provide data for calculating the other property. Prima PRO's precision is typically 10 times better (0.1% relative compared with 1% relative for a calorimeter). Also, Prima PRO's response time is typically at least 10 times better (15 seconds compared with 2.5 minutes for a calorimeter).

Calorimeters cannot be used to measure the calorific value of fuel gases of widely varying composition. They also cannot be used to calculate the stoichiometric air requirement, which is essential for efficient combustion. Stoichiometric air requirement is sometimes determined by measuring excess oxygen in the furnace using a discrete oxygen analyzer. However this approach involves additional complexity and can be prone to errors if there are air leaks in the furnace.

Prior to the application of mass spectrometers to measure fuel gas, and due to the unsuitability of the calorimeter to measure multiple streams and sample types, the only solution was to use multiple calorimeters and density meters plus a discrete oxygen analyzer. The cost, complexity and maintenance requirements of a single Prima PRO are extremely favourable compared with the older multi-analyzer system option. Another of Prima PRO's advantages is flexibility—it is very easy to modify the analytical method to measure different components, so there isn't a problem if the sample gases are changed over time.

For example, the method for natural gas can be easily changed to include CO_2, C_5H_{12} and C_6H_{14}, if these components are found to be present at significant concentrations due to changes in the supplied natural gas.

The main benefits of Process Mass Spectrometry for fuel gas analysis are:-

- Reduced consumption of fuel gases
- Increase in burner lifetime
- Better furnace temperature control
- Information on environmentally significant components such as H_2S, NH_3 and naphthalene

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Summary

Prima PRO Process MS provides fast on-line accurate analysis of the properties of a wide range of fuel gases, especially on petrochemical & chemical complexes and integrated iron and steel works. These measurements include calorific value, density, specific gravity, Wobbe Index, stoichiometric air requirement and CARI as well as complete compositional analysis. These data are used to provide the most efficient use of the fuel gases.

References

1. ISO 6976:2016—Calculation of calorific values, density, relative density and Wobbe indices from composition

2. ISO 10723:2012 Natural gas - Performance evaluation for analytical systems

3. R Wright, 2004,'Mass spectrometry: gas analysis' In: P.J. Worsfold, A. Townshend and C. Poole (eds.), Encyclopaedia of Analytical Science 2nd edition, Volume 5, pp. 493-501, Elsevier.

USA
27 Forge Parkway
Franklin, MA 02038
Ph: (800) 437-7979
Fax: (713) 272-2273
orders.process.us@thermofisher.com

India
C/327, TTC Industrial Area
MIDC Pawane
New Mumbai 400 705, India
Ph: +91 22 4157 8800
india@thermofisher.com

China
+Units 702-715, 7th Floor
Tower West, Yonghe
Beijing, China 100007
Ph: +86 10 84193588
info.eid.china@thermofisher.com

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

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