White paper

Tools for high performance gas analysis

Process mass spectrometers

Author

Sam Evans, Thermo Fisher Scientific, Winsford, Cheshire, United Kingdom

Keywords

Multi-component, on-line process gas analyzer, ultra-fast analysis, multi-stream, high performance mass spectrometer, industrial or laboratory installation, reliable and low maintenance

Introduction

Although traditionally regarded as a powerful but delicate laboratory tool, gas analysis mass spectrometers have been used for many years in a wide variety of industrial process applications, including petrochemicals and chemicals,[1] pharmaceuticals and biotechnology[2] and iron and steel manufacture.[3] They offer fast, flexible analysis of a wide range of inorganic and organic gases, over an extremely wide range of concentrations, and have been shown to be very robust and reliable.

An example of the mass spectrometer's capabilities is shown in Table 1. This details the performance of a Thermo Scientific™ Prima™ PRO Magnetic Sector Mass Spectrometer (MS) analyzing natural gas with a cycle time of 30 seconds (including stream switching time) over an eight hour period. The MS is analyzing major and minor components, from tens of percent down to parts-per-million (ppm) concentration levels, with typical relative standard deviation (RSD) ranging from 0.02% for the major components, to 2–5% for the trace components.

Unlike many other gas analyzers whose analytical capabilities are defined in hardware, mass spectrometers' analytical capabilities are mainly defined in software. This allows the same MS to analyze a wide range of sample streams with widely different compositions. For example, in the chemical and ironmaking industries, the MS can analyze natural gas with methane concentrations over 90% as shown in Table 1 as a feedstock, then later in the process measure streams containing methane at less than 0.5% concentration.

thermo scientific

Component	Typical concentration %mol	Precision of measurement (standard deviation) %mol
Methane	93.0	0.020
Nitrogen	1.0	0.005
Ethane	3.0	0.005
Carbon dioxide	1.0	0.002
Propane	1.0	0.002
Isobutane	0.2	0.002
n-Butane	0.2	0.002
Isopentane	0.1	0.002
n-Pentane	0.1	0.002
n-Hexane	0.1	0.002
Hydrogen sulfide	3.0 ppm	0.5 ppm
Methyl mercaptan	10.0 ppm	0.5 ppm
Ethyl mercaptan	10.0 ppm	0.5 ppm
n-Propyl mercaptan	10.0 ppm	0.5 ppm
n-Butyl mercaptan	10.0 ppm	0.5 ppm

Table 1. Natural gas analysis by MS.

Mass spectrometer components

All mass spectrometers share the same basic functional steps, whether they are analyzing gases, liquids or even solids. These are:

- **Sample selection** to present the appropriate stream to the analyzer
- **Pressure reduction** to drop the pressure from atmospheric pressure to the vacuum pressure (typical 10^{-5} to 10^{-6} mBar) required by the MS
- **Ionization** to convert the neutral atoms and molecules in the sample to electrically charged ions; in the case of gas analysis MS, the ions are positively charged
- **Mass separation** to separate the electrically charged ions according to their mass to charge ratio (m/z)
- **Detection** to measure the number of ions at each mass to charge ratio, and to enable quantitative composition data on the sample being analyzed

The 5 basic MS elements are shown in Figure 1. Although a vast array of technologies is available for each element of the MS, only a relatively small number of these technologies are suitable for process gas analysis.

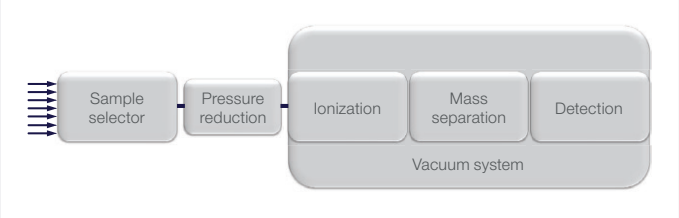

Figure 1. MS basic components.

Sample selection

The two main types of sample selector used for gas analysis are continuous and batch inlets.

Continuous inlet this is used when a relatively large amount of sample is available to flow to the MS. Sample selection is controlled by software and rapid multi-stream samplers (RMS). Rotary valves or banks of solenoid valves are used to switch between gas samples. It is important that the multi-stream inlet has minimal dead volume to ensure fast switching between sample streams; otherwise the speed of the MS is compromised by the time taken to flush the inlet with new sample.

It is also important that there is no cross-contamination in the multi-stream inlet. Because of the speed of MS analysis, it is not uncommon to have up to 60 sample streams being analyzed by one MS. It is vital that the selected sample is presented to the MS for analysis without being cross-contaminated with sample from other streams, which could be caused by internal leaks in the sample selector. Solenoid valves and rotary valves are more likely to suffer from internal leaks than rapid multi stream (RMS) samplers designed specifically for gas analysis mass spectrometers. Continuous inlets have been used both in the plant for process applications and the laboratory for research applications.

Batch inlet this is used when a limited amount of sample is available, usually at low pressure. The sample is expanded into a fixed volume to reduce its pressure and then drawn into the MS. Batch inlets can also include a capillary inlet for continuous sampling and are suitable for laboratory research applications.

Pressure reduction

Gas analysis mass spectrometers operate at vacuum, typically 10^{-5} to 10^{-6} mBar. In most applications it is preferable to ensure that the original sample composition at the original sample pressure (usually atmospheric or slightly above atmosphere) is maintained at the vacuum pressure in the MS. The pressure reduction system should not discriminate between lighter and heavier atoms and molecules.

The most common inlet is a combined capillary and molecular leak. In the early days of process MS, long capillaries up to 2 metres in length were used. Nowadays, short micro-capillaries are preferred; they are easier to heat uniformly, and easier to replace if blocked by particulates.

An alternative to the capillary and leak inlet is the membrane inlet used in the Thermo Scientific™ Sentinel™ PRO system. This is suitable for monitoring trace levels of volatile organic compounds (VOCs) in air; these permeate through the membrane preferentially compared to the major inorganic components of air. The membrane inlet has been widely used to monitor ppb and ppm levels of harmful VOCs such as vinyl chloride, benzene and acrylonitrile around chemical and petrochemical plants and refineries. This helps ensure that workers are not exposed to harmful levels of toxic and carcinogenic compounds.

Ionization

The most common technology for ionizing gas samples is electron impact (EI), also known as electron ionization. In EI, streams of high energy electrons are emitted from a hot filament and focused to collide with the sample gas. These collisions cause electrons to be ejected from the outer shells of the sample atoms and molecules, producing positively charged ions which are directed into the mass separator by electrodes. This process has to take place under vacuum to protect the filament and prevent collisions between the ions formed in the ion source. Even under high vacuum, the filament will gradually wear out, requiring replacement. In a process MS there should therefore be a standby filament so the MS does not stop analyzing when a filament fails. In modern process MS systems the ion source can be replaced quickly and easily, avoiding the more complex task of replacing the filaments inside the source.

The electron energy is usually set at 70 eV; this not only ionizes the sample with maximum efficiency, but it is also powerful enough to break molecular bonds in the sample molecules. The resulting fragmentation is used to differentiate between compounds with the same molecular weight. An example is shown in Figure 2, the fragmentation of nitrogen and carbon monoxide. Both have a molecular weight of 28 amu but give different fragmentation patterns, Nitrogen producing an N atom fragment with mass to charge ratio 14, and Carbon Monoxide producing C and O atom fragments with mass to charge ratio 12 and 16 respectively.

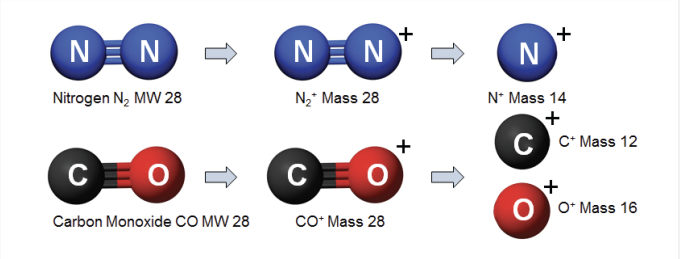

Figure 2. EI fragmentation for nitrogen and carbon monoxide.

Electron impact technology is relatively simple and extremely well proven. It offers a wide dynamic range and relatively consistent sensitivities for a large number of compounds. Filaments will typically last a year or more but must be regarded as consumable items. EI operates at vacuum and typically ionizes just 1 in 1,000,000 analyte molecules; it is therefore excellent for analyzing percentage level concentrations, but detection of trace components can be difficult. Detection limits may also be limited by backgrounds of residual gases in the ion source and by overlapping fragmentation spectra. These limitations have led to other ionization techniques being used for specialist applications such as atomospheric pressure ionization.

Atmospheric Pressure Ionization (API): This involves a two-stage ionization, a corona discharge followed by collision and charge transfer between ionized and neutral species. **API** mass spectrometers, such as the Thermo Scientific™ APIX δQ and APIX Quattro, are used to analyze trace (parts-per-trillion) impurities such as H_2, CO, CO_2, H_2O, O_2, CH_4, Kr and Xe in ultra-high purity gases N_2, Ar, He, and H_2.

Mass separation

There are two main types of MS analyzer used for process gas analysis: magnetic sector and quadrupole.

Magnetic sector MS

In the magnetic sector MS, ions are accelerated through a flight tube, where they are separated by their mass to charge ratios in a magnetic field of variable strength. The equation describing the relationship between the ions and the magnetic sector analyzer is:

$$\frac{m}{z} = \frac{B^2 \times r^2}{2V}$$

Where m = mass of particle
z = electrical charge
B = magnetic field strength
r = radius of orbit
V = ion acceleration voltage

Typically the ion acceleration voltage is set to 1 kV and the flight tube has a radius of 6 cm. This means that a variable magnetic field of 0 to 1 Tesla will give a mass range of 1 to 150 Daltons or amu (atomic mass units). The mass range can be increased to 200 Daltons by reducing the ion energy to 750 V.

Since the magnetic sector mass spectrometer produces a focused ion beam at the detector, the peak shape obtained is 'flat-topped', i.e., uniform response is observed over a finite mass width, e.g., 0.3 amu at mass 28. 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. Provided the measurement taken is on the peak's flat top, high precision analysis will be observed. If masses are aligned within the central ⅔ of the flat top region, this is normally sufficient to guard against any drift in the mass scale. Figure 3 shows a schematic of a typical magnetic sector MS, with the molecular ion peaks for N_2^+ and O_2^+ shown at masses 28 and 32 respectively. The flat top peak profile is seen clearly.

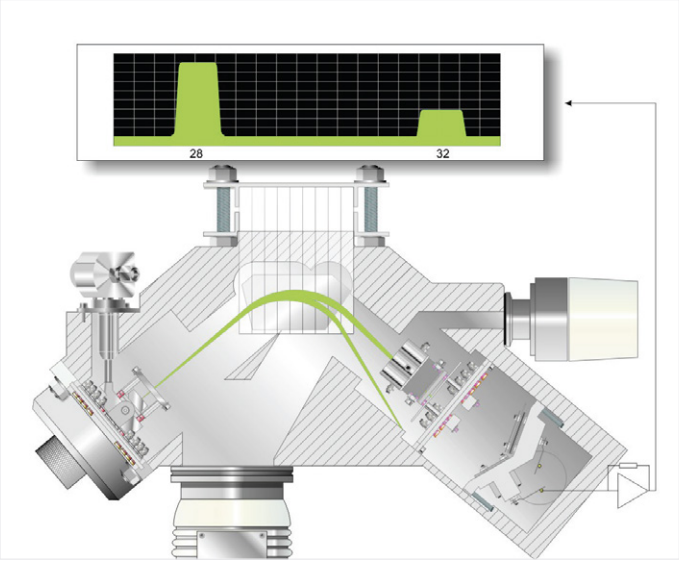

Figure 3. Thermo Scientific Magnetic Sector MS.

Quadrupole MS

The quadrupole MS consists of four cylindrical rods which are held in strict parallel alignment. Ions are separated by their trajectories in oscillating electric fields that are applied to the rods. A radio frequency (RF) voltage is applied between one pair of rods and the other. And a direct current (DC) voltage is then added to the RF voltage. At one setting of RF, only ions of a specific mass to charge ratio will travel down the quadrupole array and reach the detector.

A schematic of a typical quadrupole is shown in Figure 4. In this example, only the green ions are travelling down the quadrupole; all heavier and lighter ions have unstable trajectories and strike the surfaces of the rods.

Comparison between magnetic sector and quadrupole MS

The magnetic sector MS provides greater stability and better precision than the quadrupole MS. Unlike the flat-topped peak generated by the magnetic sector, the quadrupole produces a Gaussian peak. So it is 'fault sensitive'—any drift in the mass scale will produce an error in the peak height measurement by measuring intensity on the shoulder of the peak rather than the peak maxima. This has to be corrected for by more frequent calibration.

The magnetic sector MS is also much more resistant to contamination than the quadrupole. The ions are accelerated into the magnetic sector MS with high energy (typically 1000 eV), so they will not be deflected by small field effects caused by contamination. The ions entering the quadrupole analyzer are accelerated with low energy (typically < 10 eV) and are therefore much more easily deflected by contamination. In the early stages, this can be corrected by recalibration, but over time the contamination will need to be removed by cleaning, and this introduces instrument downtime. The intervals between cleaning can be relatively short if the sample streams contain high levels of hydrocarbons.

Detection

The vast majority of gas analysis applications are carried out using a **Faraday Cup** (or Faraday Bucket) detector. This has a very wide dynamic range, typically measuring from parts-per-million to 100% concentration levels, is virtually indestructible and does not mass discriminate, so every singly charged ion produces the same response no matter the mass of the ion.

When greater sensitivity is required a **secondary electron multiplier (SEM)** may be used. Either a micro channel plate (MCP) or dynode tube SEM can be used to amplify the ion current through secondary emission. They can increase signal levels by several orders of magnitude to achieve part-per-billion level detection.

Unlike the Faraday detector, SEMs can be damaged by exposure to high concentration levels, and they discriminate between high- and low-mass ions.

A modern gas analysis MS may employ both detectors, with high concentration ion beams being sent to the Faraday detector and low concentration ion beams switched to the SEM under software control.

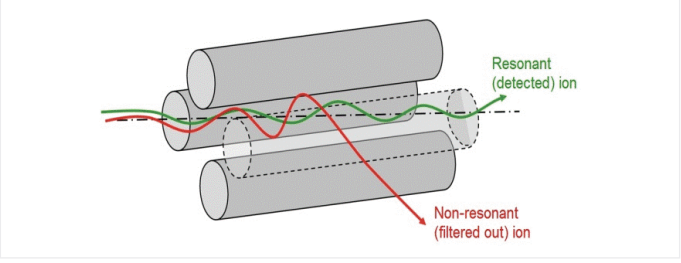

Figure 4. Illustration of a typical MS quadrupole.

Mass spectra: Fingerprints

Figure 5 shows examples of mass spectra produced in a magnetic sector MS using electron impact ionization. Each molecule (N_2, O_2 and CO_2) and atom (Ar in this case) produces a unique fingerprint, a combination of molecular ions and fragment ions of molecules, and a combination of singly and doubly charged ions in the case of atoms.

The relative numbers of ions formed from a given substance is known as the 'fragmentation pattern' or 'cracking pattern' for that substance. The fragmentation pattern can be influenced by instrument factors such as the energy of the bombarding electrons, temperature, geometry of the ion source, MS lens voltages, and pressure. The fragmentation pattern may also change with time due to ageing of the filament. The possibilities for different fragmented ions can be considerable, especially for hydrocarbons.

Quantitative analysis and calibration

The first step in setting up a method is to identify suitable mass peaks to monitor. It is advisable to avoid or minimize overlaps between the spectra, i.e., mass peaks which correspond to more than one gas. For example, consider the analysis of nitrogen, oxygen, argon and carbon dioxide plus the alcohols methanol and ethanol. Table 2 shows the peaks that would typically be used to quantify these six gases. It is conventional to normalize each spectrum to the base peak (that is, the most intense). For example, in the case of ethanol, the base peak is the CH_3O^+ fragment at 31 amu and the $C_2H_5OH^+$ molecular ion peak at 46 amu is 25% of the base peak.

Equal numbers of molecules of different gases in the ion source do not necessarily produce an equal ion current. This is due to differences in ionization rate and the different transmission efficiency of the analyzer for ions of different mass. Consequently a sensitivity factor, relative to the reference compound, is calculated.

This factor is known as the relative sensitivity, RS, in Table 2. For example, if the relative sensitivity of nitrogen is 1.0 and methanol is 0.5, for equal quantities of nitrogen and methanol in the ion source, the ion current measured for nitrogen will be twice that of methanol.

For some gas analysis applications considerable overlaps are unavoidable, and development of an analytical method is quite complex, involving a search for peaks which have less overlap but still have worthwhile intensity. The analysis of overlapping or 'interfering' gas mixtures involves measurement by de-convolution of the overlapping peaks by the instrument computer. This is typically performed automatically and rapidly (in fractions of a second) by an embedded processor in the MS.

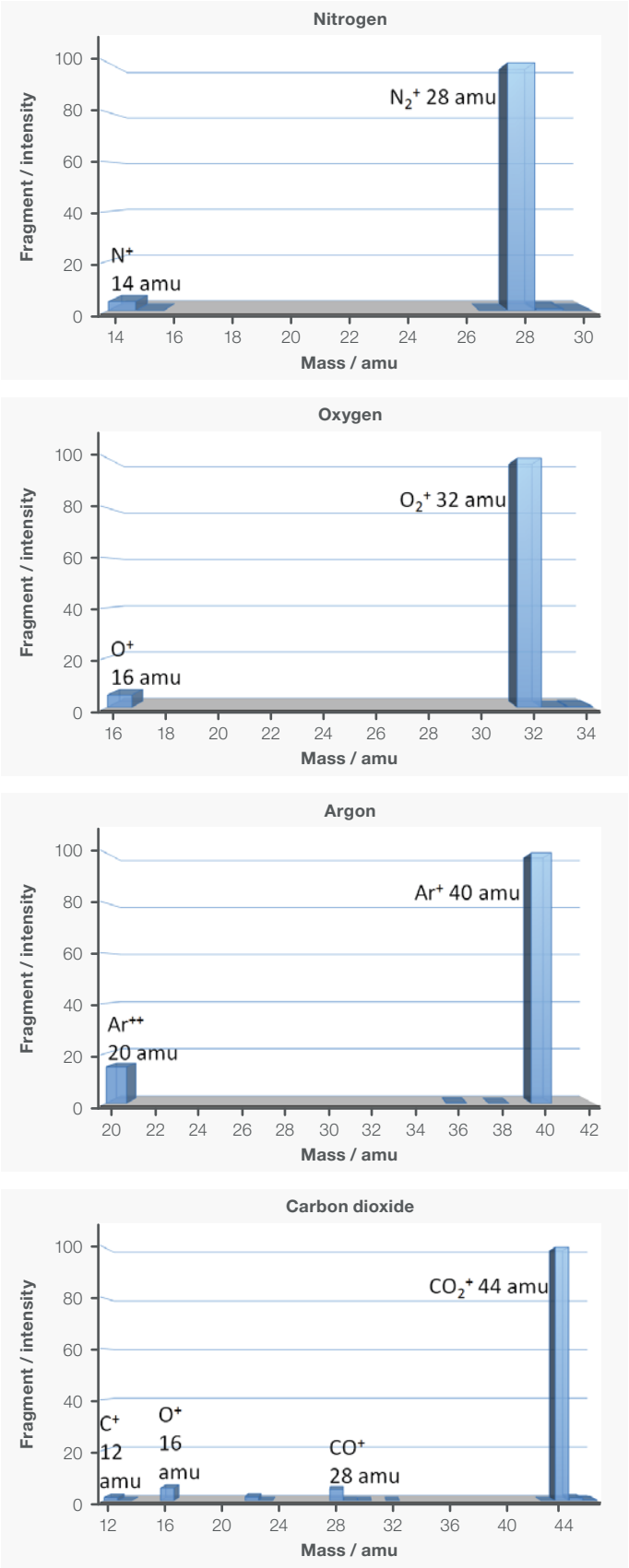

Figure 5. Mass spectra of the four main air gases, nitrogen, oxygen, argon, and carbon dioxide.

	After start-up	Nitrogen	Methanol	Oxygen	Argon	Carbon dioxide	Ethanol
Molecular weight	2.824	28	32	32	40	44	46
Relative sensitivity	0.015	1	0.5	0.83	1.45	1.2	0.8
Mass 28	0.50%	100				5	
Mass 31			100	0.01			100
Mass 32				100			
Mass 40					100		
Mass 44						100	
Mass 46						0.4	25

Table 2. Example of peak matrix used to quantify air gases plus methanol and ethanol.

As with other analytical techniques, the best analytical performance will be obtained by reference to calibrated gas mixtures whose composition is similar to that of the sample. This is straightforward if the sample composition remains fairly constant. If the gas composition varies more widely, one may need to calibrate by reference to a small number of selected gas mixtures.

As an example, consider the case of the gases required to calibrate the MS for the six gases in Table 2. Table 3 below shows the five calibration gases; the concentration levels will depend on the concentration ranges to be measured in the sample streams.

There will typically be a multi-component mixture to accurately determine relative sensitivities (cylinder 1), a 'background' gas (typically helium, cylinder 5) for measuring background signals at the various masses, and a set of cylinders to measure the fragmentation of overlapping spectra, in this case cylinder 2 (carbon dioxide), cylinder 3 (methanol) and cylinder 4 (ethanol).

A responsible MS supplier should always produce a performance specification for the customer's application, detailing the peaks to be used for the analysis, the recommended calibration gases, and a guaranteed MS performance in terms of analysis precision and speed.

Cylinder	1	2	3	4	5
Nitrogen	Balance		Balance	Balance	
Oxygen	15%				
Argon	1%	Balance			
Carbon dioxide	5%	5%			
Helium					100%
Methanol			0.04%		
Ethanol				0.04%	

Table 3. Example of calibration gases used to quantify air gases plus methanol and ethanol.

Independent tests on magnetic sector MS

A Prima PRO magnetic sector MS from Thermo Fisher Scientific has been tested in accordance with ISO10723 in Effectech UK's ISO17025 accredited laboratory. The MS was tested for fuel gas quality metering, analyzing inorganic gases (N_2, H_2, CO, CO_2) and organics too (C_2 to C_3, C_2=, C_3=).

The MS was calibrated for relative sensitivity with a single calibration gas containing the nine components shown in Table 4. Then eight different fuel mixes were prepared, containing the same nine components but over a wide range of concentrations, to test the repeatability and linearity of the MS.

Component	Concentration %mol
Nitrogen	9.00 ± 0.0150
Carbon dioxide	5.00 ± 0.0150
Methane	9.00 ± 0.0200
Ethane	5.00 ± 0.0130
Propane	10.00% 0.0250
Ethylene	5.00 ± 0.0015
Propene	5.00 ± 0.0130
Hydrogen	43.00 ± 0.0700
Carbon monoxide	9.00 ± 0.0150

Table 4. ISO 17025 accredited calibration gas used for relative sensitivities.

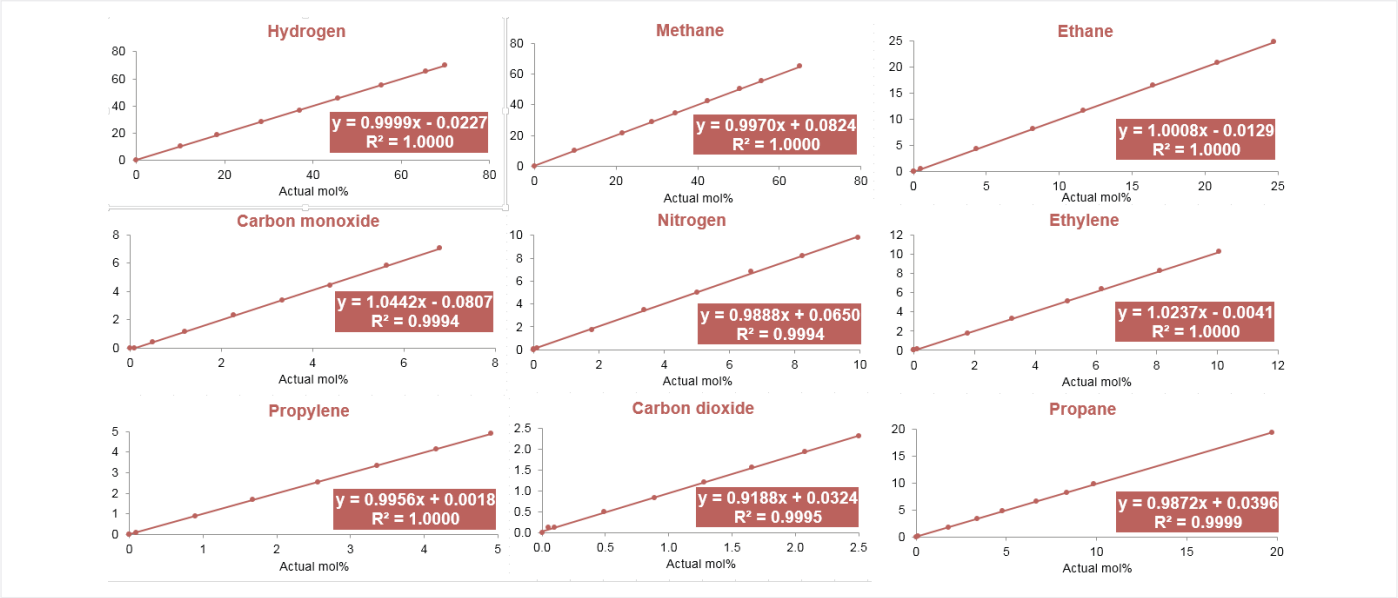

Figure 6. Linearity data for nine fuel gas components.

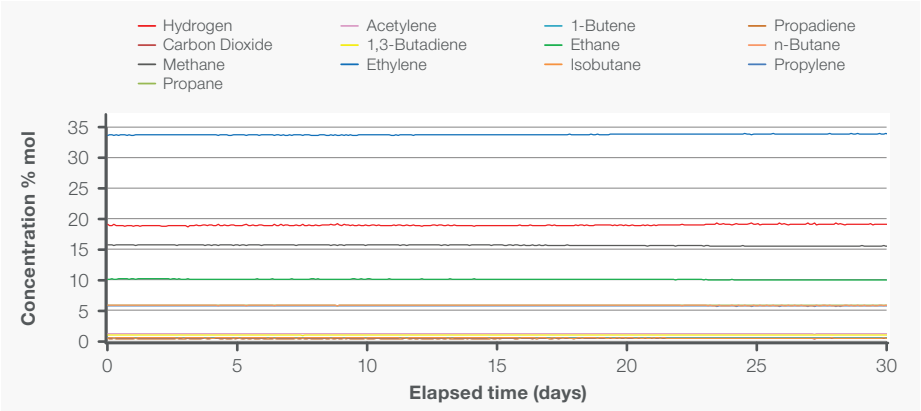

Figure 7. One month stability data for Prima PRO magnetic sector MS without recalibration.

Figure 8. Thermo Scientific™ Prima™ BT MS.

Figure 9. The Prima PRO MS.

Each gas was analyzed for 30 cycles over 5 minutes (10 second cycle time). The results are shown in Figures 6 & 7.

The coefficients of determination (R^2) for the nine components are shown in Table 5.

Linearity test: Coefficients of determination (R^2)	
H_2, CH_4, C_2H_4, C_2H_6, C_3H_6	1
C_3H_8	0.9999
CO_2	0.9995
CO, N_2	0.9994

Table 5. Coefficients of determination for nine components shown in Figure 6.

Examples of laboratory and process MS

It is often necessary to develop new analytical methods in the laboratory which are then transferred to the plant as a new process is 'scaled up.' It is therefore vital that the results from the laboratory MS correlate directly with those obtained from the process MS. Although the external packaging of the two Prima MS analyzers may be very different (the process MS should be capable of installation in a hazardous area, for example), the analytical performance should be identical.

Figure 8 shows an example of a laboratory magnetic sector MS capable of monitoring 16 gas streams. Figure 9 shows an example of a process magnetic sector MS capable of monitoring 64 gas streams, suitable for installation in a Zone 1/Class 1 Div 1 area.

Example applications

Gas analysis mass spectrometers have been used to monitor process streams in many different industrial processes.

Petrochemicals and chemical processes

Olefins and polyolefins, ethylene oxide, ammonia, methanol, flare gas analysis, workplace monitoring of VOCs

Iron and steel processes

Ironworking: Blast furnace, direct reduction iron, coke oven
Steelmaking: Basic oxygen steelmaking, electric arc furnace, secondary steelmaking (AOD, VOD, RH), fuel gas analysis

Biotechnology and pharmaceutical processes

Fermentation off-gas analysis, product drying

In process research and development (R&D), they have been used for a wide variety of applications:

Catalysis research, pilot plant gas analysis, fermentation, nuclear research, fuel cells, biofuels

Table 6 shows a statistical report from a Prima PRO magnetic sector MS analyzing coke oven gas. Standard deviations were measured over an eight hour period with an analysis cycle time of 30 seconds. The MS is typically calibrated monthly; the calibration is fully automatic under software control.

This gas stream has great value as fuel; Thermo Scientific™ GasWorks software is able to calculate, as derived values, energy parameters such as specific gravity, calorific value, Wobbe index, air requirement and combustion air requirement index. Many companies have used the speed, precision and complete analysis provided by the magnetic sector MS to dramatically reduce their fuel usage, providing rapid payback for the MS installation. In some cases payback periods are measured in days rather than weeks or months.

Measurement	Concentration (%mol)	Standard deviation (%mol) ≤
Hydrogen	Balance	0.08
Methane	24	0.05
Ammonia	0	0.001
Carbon monoxide	6	0.05
Nitrogen	3	0.05
Ethylene	2	0.01
Ethane	1	0.01
Oxygen	0.3	0.002
Hydrogen sulfide	0.4	0.002
Argon	0.1	0.002
Carbon dioxide	1	0.005
Benzene	0.1	0.001
Toluene	0.05	0.001

Table 6. Coke oven gas analysis by MS.

Summary

Gas analysis MS has been used for process control and process research in a wide variety of industries. It offers:

- Multi-component, multi-stream analysis
- Flexible, quantitative analysis
- Speed and precision

The magnetic sector analyzer has established itself as the predominant technology for industrial gas analysis, providing the highest levels of precision, stability and resistance to contamination.

Reference

1. R. Wright, Journal of Process Analytical Chemistry 1998 Volume IV, pages 71-78.
2. J. S. Alford, Computers and Chemical Engineering 30 (2006) pages 1464–1475.
3. D. Merriman, Asia Steel, 1998, pages 71-74.

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