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, pharmaceuticals and biotechnology and iron and steel manufacture. They offer fast, flexible analysis of a wide range of inorganic and organic gases, over an extremely wide range of concentrations.

An example of the mass spectrometer's capabilities is shown in Table 1. This details the performance of a 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 concentration levels, with typical Relative Standard Deviations 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.
Mass Spectrometer Components

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

- Sample selection: to present the appropriate stream to the analyser
- 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
- Detection: to measure the number of ions at each mass to charge ratio, to enable quantitative composition data on the sample being analyzed.

These 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. We are unique in that we offer all of the available technologies.

### Sample Selection

The two main types of sample selector used for gas analysis are:

- **Continuous inlet**: this is used when a relatively large amount of sample is available to flow to the MS. Sample selection is under software control and RMS rapid multi-stream samplers, 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. Also, it is important that there is no cross-contamination in the multi-stream inlet. Because of the speed of MS 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 contaminated with non-selected samples caused by internal leaks in the sample selector. Solenoid valves and rotary valves are more likely to suffer from internal leaks than RMS rapid
multi-stream samplers designed specifically for gas analysis mass spectrometers. Continuous inlets have been used in the plant for process applications, and in 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 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 & leak inlet is the membrane inlet. 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, thereby ensuring 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 eject electrons 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, it is 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 Molecular Weight 28 but give different fragment patterns, Nitrogen producing 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.](image)

Electron Impact technology is relatively simple and extremely well proven. It offers a wide dynamic range and relatively consistent sensitivities for a wide range of compounds. Filaments will typically last a year or more but must be regarded as consumables. EI operates at vacuum and typically ionizes just 1 in 100000 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. These include:

**Atmospheric Pressure Ionization:** This involves a two-stage ionization, a corona discharge followed by collision & charge transfer between ionized and neutral species. API is used to analyze trace (part per trillion) impurities such as H₂, CO, CO₂, H₂O, O₂, CH₄, Kr and Xe in UHP gases N₂, Ar, He, and H₂.

**Chemical Ionization** produces ions by collisions with reagent gas ions. It is a ‘softer’, lower energy process than EI, producing much less fragmentation and simpler spectra. The reagent gas must be present in large excess compared to the compounds of interest. CI offers advantages over EI in applications where fragmentation makes trace analysis difficult or even impossible, such as analysis of NOₓ, COₓ and SOₓ emissions in automotive exhaust gas.

**Proton Affinity Ionization** uses gas phase hydronium ions (H₃O⁺) as ion source reagents. Like CI it produces less fragmentation and simpler spectra than EI. It can be used to monitor Volatile Organic Compounds (VOCs) down to ppt levels.

**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 6cm. 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 at the mass of interest is on the peak’s flat top, high precision analysis will be observed. If masses are aligned within the central \( 1/3 \) 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 N₂⁺ and O₂⁺ shown at masses 28 and 32 respectively. The flat top peak profile is seen clearly.
Quadrupole MS
The Quadrupole MS consists of four cylindrical rods, aligned parallel to each other. 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 blue 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 ‘round top peak’. So it is ‘fault sensitive’ – any drift in the mass scale will produce an error in the peak height measurement. This has to be corrected 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 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 build up. In the early stages, this can be corrected by recalibration, but over time the contamination will need to be removed by cleaning. The intervals between cleaning can be relatively short if the sample streams contain high levels of hydrocarbons.

We manufacture 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 on line gas analysis.

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 what 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 also 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.
**Mass spectra: fingerprints**

Figure 5 shows examples of mass spectra from Thermo Scientific™ GasWorks process MS software. These were produced in our Prima range of magnetic sector mass spectrometers, using Electron Impact ionization. Each molecule (N₂, O₂ and CO₂ in this case) and atom (Ar in this case) produces a unique fingerprint, a combination of molecular ions and fragment ions in the case of molecules, a combination of singly- and doubly-charged ions in the case of atoms such as argon.

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, the geometry of the ion source, mass spectrometer lens voltages, and pressure. The fragmentation pattern also may change with time due to ageing of the filament. The possibilities for different fragmented ions can be considerable, especially for hydrocarbons.

**Quantitative Analysis & Calibration**

The first step in setting up a method to perform an analysis on a given gas mixture is to identify suitable mass peaks to monitor. It is advisable to avoid or minimize overlaps between the spectra, such as mass peaks which correspond to more than one gas. For example, consider the analysis of air gases nitrogen, oxygen, argon and carbon dioxide plus the alcohols methanol and ethanol. Table 2 below 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 CH₃O⁺ fragment at 31 AMU and the C₂H₅OH⁺ 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 above. 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. An important assumption is made (and generally obeyed) that the overlapping peaks when combined obey the principle of linear peak superposition. The principle of linear peak superposition is that the composite peak height at a particular mass is simply equal to the sum of the peak heights which correspond linearly to the individual concentrations of the contributing components in the complex mixture. This may be represented as:

\[ i_1 = s_{11} f_{11} c_1 + s_{21} f_{21} c_2 + s_{31} f_{31} c_3 + \ldots + s_{n1} f_{n1} c_n \]

where \( i_1 \) is a composite peak height, and for \( 1 \) to \( n \) components contributing to this peak, \( s \) is the base peak sensitivity, \( f \) is its cracking pattern and \( c \) is its concentration. Values of \( s \) and \( f \) are determined for each component during calibration. During analysis the peak heights \( i \) are measured for \( 1 \) to \( n \) (or \( >n \) ) masses so that there are at least \( n \) simultaneous equations to determine the \( n \) unknown values of \( c \). Matrix inversion is used to solve these sets of simultaneous equations. These calculations are normally executed easily and rapidly by the MS computer within a fraction of a second, and typically the complete analysis going from sample introduction to giving a reading of gas concentrations takes only seconds.

In common 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 the 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 supplier of gas analysis mass spectrometers 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.

Independent Tests on Magnetic Sector MS
A Thermo Scientific™ Prima PRO magnetic sector MS was tested in accordance with ISO10723 in Effectech UK’s ISO17025 accredited laboratory. The MS was tested for fuel gas quality metering, analyzing inorganic gases (N₂, H₂, CO, CO₂) and organics (C₁ to C₃, C₂=, C₃=).

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.

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

The Coefficients of Determination (R²) for the nine components are shown in Table 5.

<table>
<thead>
<tr>
<th>Component</th>
<th>Concentration %mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrogen</td>
<td>9.00 ± 0.015</td>
</tr>
<tr>
<td>Carbon dioxide</td>
<td>5.00 ± 0.015</td>
</tr>
<tr>
<td>Methane</td>
<td>9.00 ± 0.02</td>
</tr>
<tr>
<td>Ethane</td>
<td>5.00 ± 0.013</td>
</tr>
<tr>
<td>Propane</td>
<td>10.0% 0.025</td>
</tr>
<tr>
<td>Ethylene</td>
<td>5.00 ± 0.0015</td>
</tr>
<tr>
<td>Propene</td>
<td>5.00 ± 0.0130</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>43.00 ± 0.0700</td>
</tr>
<tr>
<td>Carbon monoxide</td>
<td>9.00 ± 0.0150</td>
</tr>
</tbody>
</table>

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

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

Figure 6: Linearity data for nine fuel gas components
Examples of Laboratory and Process MS

It is often necessary to develop new analytical methods in the laboratory which are then transferred to the industrial plant as a new process is ‘scaled up’. It is therefore vital that the results from the laboratory gas analysis MS correlate directly with those obtained from the Process MS. Although the external packaging of the two 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.

### Table 5: Coefficients of Determination for nine components shown in Figure 6.

<table>
<thead>
<tr>
<th>Component</th>
<th>Coefficients of Determination ($R^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$H_2$, CH$_4$, C$_2$H$_6$, C$_3$H$_8$, C$<em>6$H$</em>{12}$</td>
<td>1.0000</td>
</tr>
<tr>
<td>C$_3$H$_6$</td>
<td>0.9999</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>0.9995</td>
</tr>
<tr>
<td>CO, N$_2$</td>
<td>0.9994</td>
</tr>
</tbody>
</table>

Figure 7 shows the magnetic sector’s excellent long term stability, the analysis of a hydrocarbon process calibration cylinder over 30 days without recalibration.

### Figure 8: Example of laboratory gas analysis MS – Prima BT

### Figure 9: Example of process gas analysis MS for hazardous area installation – Prima PRO Ex
Example Applications

Thermo Scientific gas analysis mass spectrometers have been used to monitor process streams in many different industrial processes:

Petrochemicals & Chemical Processes
- Olefins & Polyolefins
- Ethylene Oxide
- Ammonia & Methanol
- Flare Gas Analysis
- Workplace monitoring of VOCs

Iron & Steel Processes
- Ironmaking: Blast Furnace, Direct Reduction Iron, Coke Oven
- Steelmaking: Basic Oxygen Steelmaking, Electric Arc Furnace, Secondary Steelmaking (AOD, VOD, RH)

Biotechnology & Pharmaceutical Processes
- Fermentation off-gas analysis
- Product Drying/Solvent removal

In Process Research & Development, they have been used for a wide variety of applications:
- Catalysis Research
- Pilot Plant gas analysis
- Nuclear Research
- Research Fermentation
- 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 Coke Oven gas stream has great value as fuel, so the MS software should be 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 reduce dramatically their fuel usage, providing rapid payback for the MS installation. In some cases payback periods are measured in days rather than weeks or months.

<table>
<thead>
<tr>
<th>Measurement</th>
<th>Concentration (%mol)</th>
<th>Standard Deviation (%mol) ≤</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen</td>
<td>Balance</td>
<td>0.08</td>
</tr>
<tr>
<td>Methane</td>
<td>24</td>
<td>0.05</td>
</tr>
<tr>
<td>Ammonia</td>
<td>0</td>
<td>0.001</td>
</tr>
<tr>
<td>Carbon Monoxide</td>
<td>6</td>
<td>0.05</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>3</td>
<td>0.05</td>
</tr>
<tr>
<td>Ethylene</td>
<td>2</td>
<td>0.01</td>
</tr>
<tr>
<td>Ethane</td>
<td>1</td>
<td>0.01</td>
</tr>
<tr>
<td>Oxygen</td>
<td>0.3</td>
<td>0.002</td>
</tr>
<tr>
<td>Hydrogen Sulfide</td>
<td>0.4</td>
<td>0.002</td>
</tr>
<tr>
<td>Argon</td>
<td>0.1</td>
<td>0.002</td>
</tr>
<tr>
<td>Carbon Dioxide</td>
<td>1</td>
<td>0.005</td>
</tr>
<tr>
<td>Benzene</td>
<td>0.1</td>
<td>0.001</td>
</tr>
<tr>
<td>Toluene</td>
<td>0.05</td>
<td>0.001</td>
</tr>
</tbody>
</table>
Summary

Thermo Scientific 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

Although various ionization techniques are available, Electron Impact (EI) is the most widely used because of its simplicity and wide dynamic range. Various technologies are also available for separating the ions generated in the ion source. 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.

References