

Prima PRO process mass spectrometer

Accurate multi-component blast furnace gas analysis maximizes iron production and minimizes coke consumption

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Key words

- Top gas analysis
- Gas efficiency
- Mass balance
- Heat balance
- Above burden probe
- Below burden probe
- Coke rate
- Calorific value
- Magnetic sector

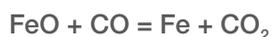
Introduction

Over a billion tonnes of iron a year are produced in blast furnaces, representing around 94% of global iron production¹. The blast furnace consists of a large steel stack, lined with refractory brick. Iron ore, coke and limestone are dropped into the top of the furnace and preheated air blown into the bottom through nozzles called 'Tuyeres'. Iron oxides are reduced in the melting zone, or 'Bosh', forming liquid iron (called 'hot metal') and liquid slag. These liquid products are drained from the furnace at regular intervals, and the blast furnace will run continuously for several years, until the refractory lining needs replacing.

A wide variety of chemical reactions take place in the blast furnace. At the elevated temperatures towards the bottom of the furnace, a series of direct reduction reactions take place; these can be simplified to:



At lower temperatures higher up in the furnace, a series of indirect reduction reactions take place, simplified to:



These reduction zones are shown in Figure 1.

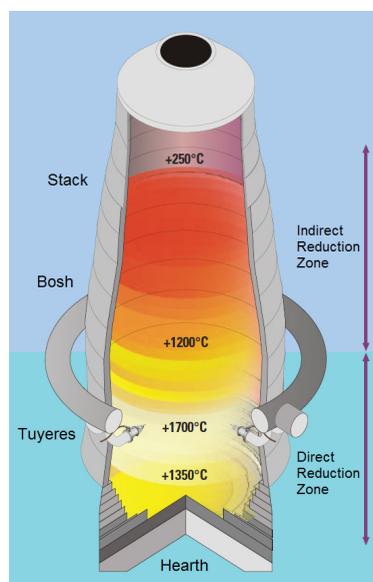


Figure 1
Reduction
profile in the
blast furnace

Analysis of carbon monoxide (CO) and carbon dioxide (CO₂) give vital information on the efficiency of the reduction processes. Historically, two Non-Dispersive Infra-Red (NDIR) analyzers were used, one to measure CO, the other CO₂. Additional discrete analyzers were required to monitor oxygen and hydrogen – typically paramagnetic O₂ analyzers and thermal conductivity analyzers for H₂.

Thermo Scientific process mass spectrometers have been widely used for many years on many important gas analysis applications on iron and steel plants, including blast furnace, basic oxygen steelmaking, coke oven gas analysis, secondary steel process control, fuel gas analysis and direct reduction iron processes².

Process control requirements

The advantages of process MS over conventional analysis techniques have been proven over many years in the iron and steel industry. The ability to measure a wide range of components on a single analyzer, coupled with advanced calibration, data transmission, and self-diagnostic software, makes the modern mass spectrometer ideal for integration into the modern plant. On blast furnaces, superior gas analysis is being used to calculate gas efficiency, mass & heat balances, and heat profiles through probe analysis, as well as being an essential tool in the early detection of cooling water leaks and sample system failures.

Figure 2 shows 64 hours' data from a Thermo Scientific™ Prima PRO Process MS monitoring the six gases in the blast furnace top gas every 10 seconds. The pulse every 12 hours is generated by an automatic nitrogen blowback from the sample conditioning system, to keep the sample probe clear of particulates.

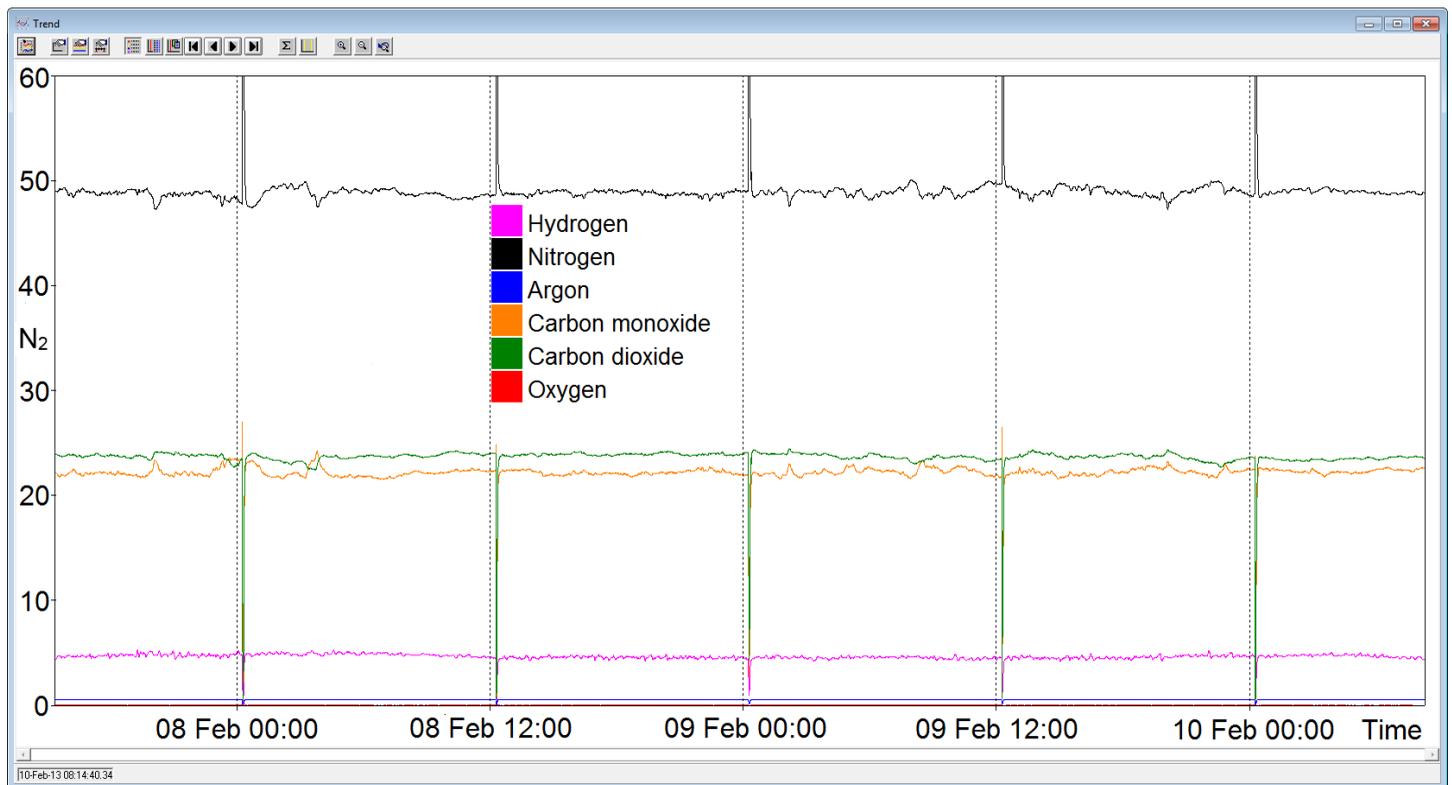


Figure 2 Prima PRO Blast Furnace Top Gas data over 64 hours

Gas efficiency

Efficient control of the blast furnace process relies on fast, accurate analysis of the CO & CO₂ concentration in the top gas. MS has a distinct advantage over traditional infrared analyzers, offering reduced response time, increased accuracy and better long term stability.

If the CO₂ level is too high, heat leaves the furnace by the exothermic reaction:



If the CO level is too high, then chemical heat leaves the furnace as coke is consumed as fuel.

Gas Efficiency η is calculated as:

$$\eta = \frac{100 \times [CO_2]}{[CO] + [CO_2]}$$

A 1% increase in Gas Efficiency can result in a decreased coke consumption of 5 Kg/tonne of hot metal, and an increased yield of 3.5% of hot metal at constant direct reduction.

Figure 3 demonstrates both the accuracy and the stability of the Thermo Scientific process mass spectrometer. The MS was set to analyze a calibration cylinder nominally containing 22.99% CO and 20.99% CO₂ every 20 minutes over 64 hours. RSDs for CO and CO₂ were respectively just 0.059% and 0.042%, and mean values were virtually identical to the cylinder certificate values.

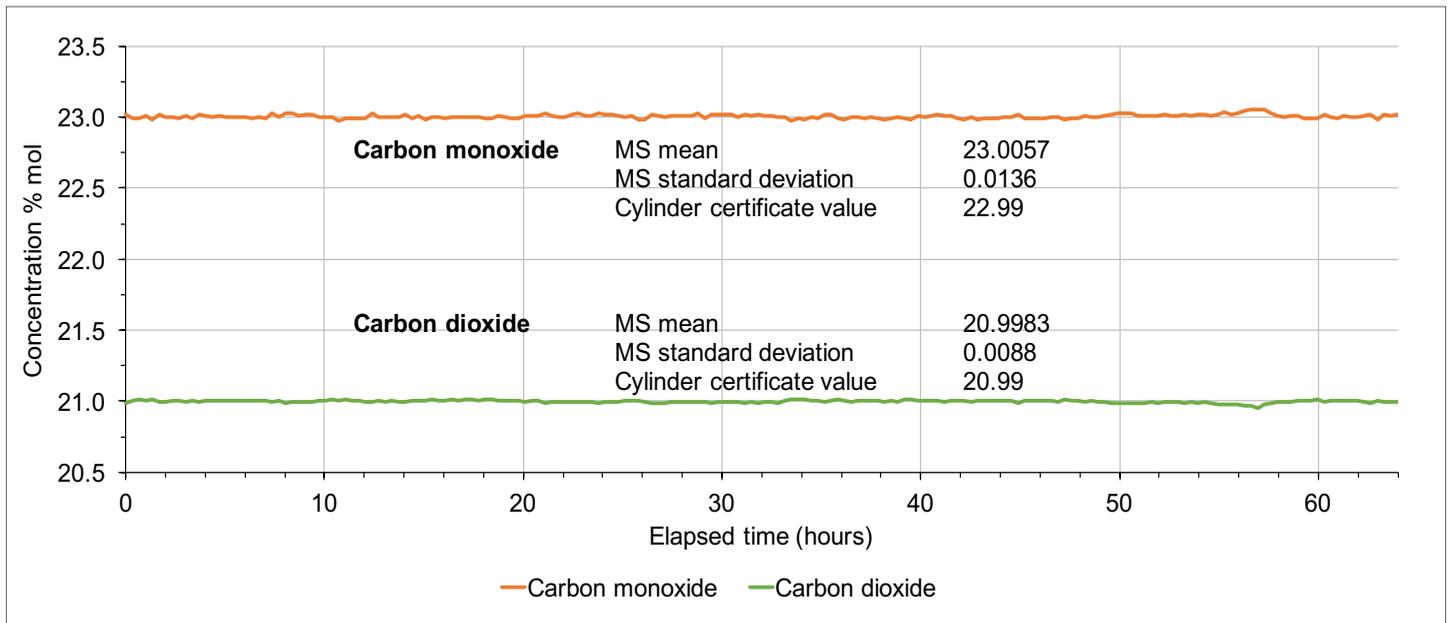


Figure 3 Stability and accuracy of CO & CO₂ MS measurement

Mass balance

Consistent iron quality can only be maintained through close control of the furnace temperatures, and top gas composition and flow are essential in achieving this control. The nitrogen concentration in the top gas is fundamental to the flow calculation; if discrete analyzers are used, then the nitrogen concentration has to be inferred by the calculation:

$$[N_2] = 1 - ([CO] + [CO_2] + [H_2])$$

Nitrogen concentration is subject therefore to the sum of three errors if discrete analyzers are used. In contrast, MS is able to measure all the critical components, and the accuracy of this instrument is constantly maintained by comparison with a certified gas standard. The material and heat balances are an essential input to the mathematical models developed by many steel-making companies, to calculate excess heat in lower regions of the furnace.

A 1% error in the nitrogen analysis can result in a 3% error in the mass balance prediction. Similarly, a 1% nitrogen error can cause errors of up to 5 kg/therm in the coke rate (1 therm = 100,000 BTU), and up to 10,000 m³/hour in the blast volume.

These errors arise because the mass balances are closed on the assumption that the measured nitrogen in the top gas is representative of the total nitrogen input to the furnace, nitrogen not having any part in the furnace reactions. The final accuracy of the mass balances depends on which of the other gas species is interchanged with nitrogen in the form of errors. The improved nitrogen analysis afforded by the MS significantly reduces mass balance errors.

Heat balance

The heat capacity of the gas is related to its composition, and gives an indication of the temperature conditions within the high temperature, direct reduction, zone of the furnace. This affects the final quality of the iron; for example, too high a temperature will reduce carbon and sulfur levels but increase silicon levels. Conversely, if the temperature is too low then both carbon and sulfur levels will be too high, which increases downstream processing costs. For example, an increase of 100 ppm in sulfur content increases desulfurization costs by over 30%.

Hydrogen analysis

An increase in the hydrogen level in the furnace can indicate a leak from the furnace cooling system, as water dissociates into hydrogen and oxygen in the furnace. This has implications both for plant efficiency and plant safety. Water leaks will lower the furnace temperature, causing heat loss and a consequent increase in fuel consumption. In extreme cases, damage to plant and personnel can be caused by ignition of these hazardous mixtures of explosive gases.

Figure 4 shows a plot of top gas hydrogen concentration measured by Thermo Scientific process MS over a 24 hour period, with the departure of the measured H_2 value from that predicted by the mass balance model indicating a water leak. This leak was caused by the failure of a cooling member, and the furnace was taken off-blast for repair. The mass spectrometer's ability to provide fast, accurate hydrogen analysis removes the need for an additional discrete analyzer.

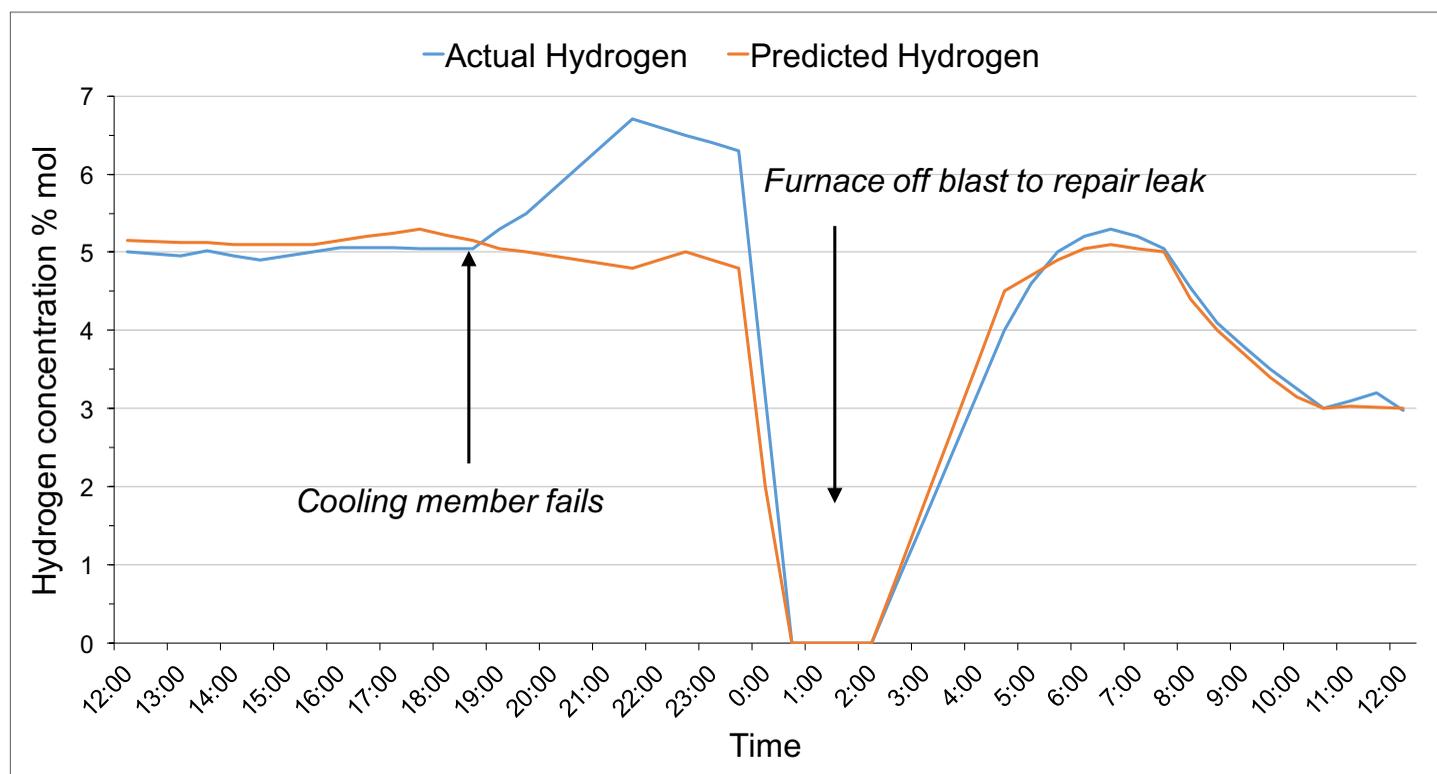


Figure 4 Actual versus predicted hydrogen concentration of top gas over 24 hours

Gas composition measurement is particularly important during the end-of-campaign blowdown that takes place prior to rebuilds and relines, because explosive gas mixtures can be generated.

Probe analysis

The fast analysis provided by MS offers another significant advantage over discrete analyzers—a number of process streams can be analyzed using a single instrument. This is achieved using a fully automated multi-inlet system, designed to switch between sample streams at high speeds with minimal sample flushing times. For example, as well as furnace top-gas, the MS can also analyze gases from probes placed above and below the Burden (the furnace charge of iron ore, coke and limestone). These are known as Above-Burden and Sub-Burden probes and provide valuable information on fuel efficiency, iron conversion and furnace charging. Figure 5 shows a schematic of these two probes; they can be moved across the furnace to build a cross-sectional profile of the furnace.

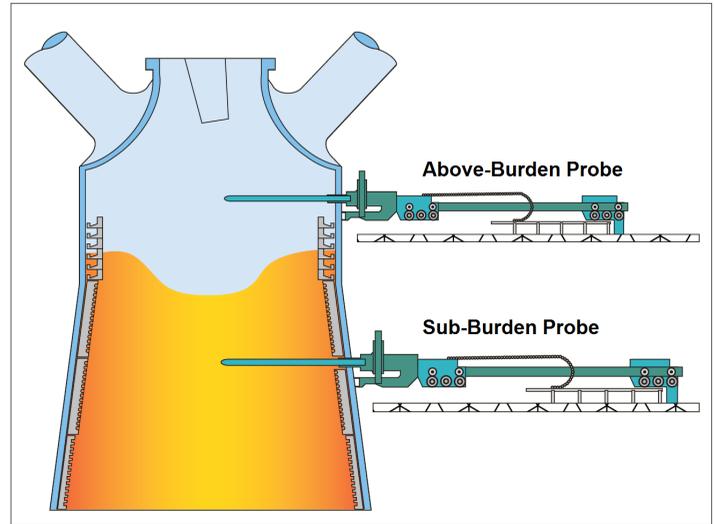


Figure 5 Above-Burden and Below-Burden probes

Figure 6 shows an example of a Sub-Burden probe profile using a Thermo Scientific process MS.

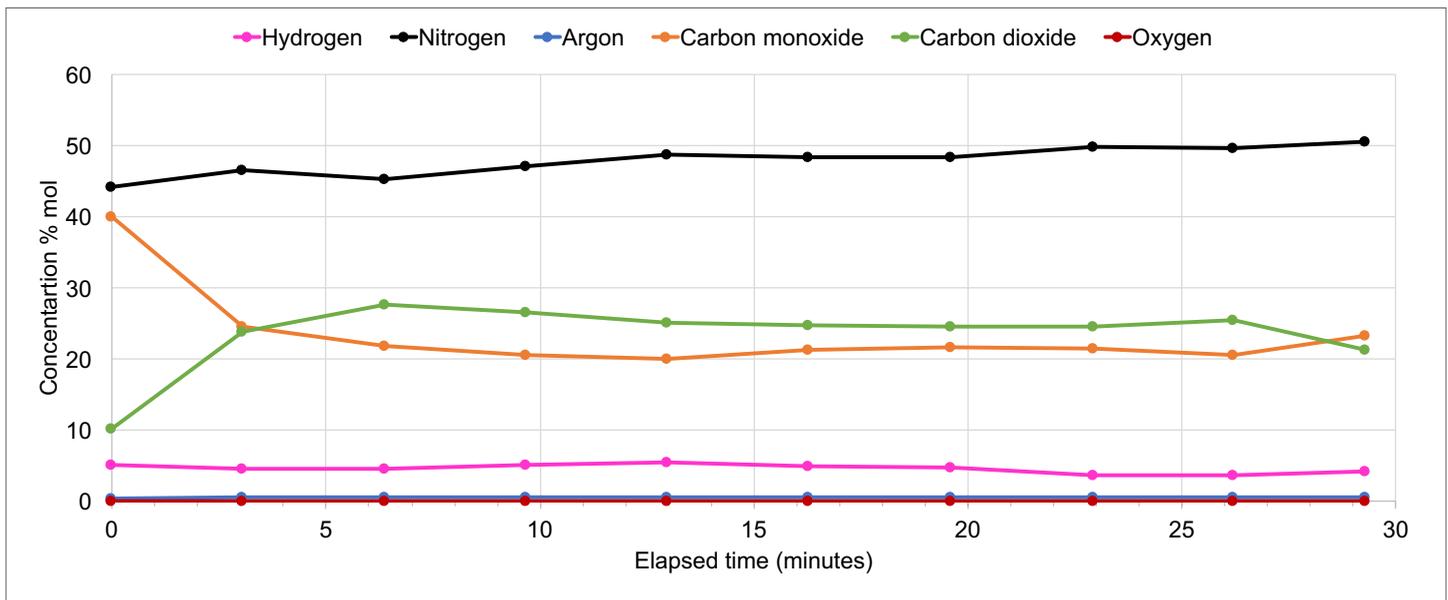


Figure 6 Sub-Burden probe profile analysis by MS

Argon analysis

If nitrogen is used as a purge gas then the analysis of argon can be very useful. The nitrogen/argon ratio in the top gas can be used to detect failures in the sampling system. Alarm levels can be set up, to alert the operator to the problem, enabling the early detection of failures and minimizing costly down time.

Fuel gas analysis

Blast furnace gas has a very low Calorific Value, between 2.9 – 3.6 MJ/m³ (700 to 850 Kcal/m³) depending on the coke rate, but it can be used as a fuel to pre-heat the air before it enters the blast furnace. It can also be mixed with other process gases (coke oven gas, steel converter gas, natural gas) and used as a fuel in the various furnaces on the integrated steel plant.

Thermo Scientific process mass spectrometers have been used to provide fast, on-line, accurate analysis of the properties of a wide range of fuel gases on integrated iron and steel works for many years³. Prima PRO can calculate and report standard energy parameters as Derived Values, including Calorific Value (Upper & Lower), Specific Gravity, Wobbe Index and Density according to ISO 6976. Table 2 shows a site acceptance test for a Prima PRO measuring

BF gas as a fuel gas; the MS measured component concentrations and also calculated Gas Efficiency, Calorific Value, Specific Gravity, and Wobbe Index. A certified calibration cylinder was analyzed periodically over 24 hours and results compared with specified values; Prima PRO passed the acceptance test easily.

Table 1 Site acceptance test for BF fuel gas analysis

| | Gas efficiency % | Calorific value MJ/m ³ | Specific gravity | Wobbe index MJ/m ³ |
|-----------------------------|---------------------|--------------------------------------|------------------|----------------------------------|
| Mean over 24 hours | 52.4001 | 3.4352 | 1.0759 | 3.3119 |
| Standard deviation | 0.0170 | 0.0013 | 0.0001 | 0.0013 |
| Relative standard deviation | 0.032% | 0.039% | 0.005% | 0.040% |
| Specified RSD | 0.10% | 0.10% | 0.10% | 0.10% |

Benefits of Prima PRO magnetic sector analyzer

Prima PRO's magnetic sector analyzer uses technology which has been proven over many years in a wide range of iron and steel applications. There are essentially two types of mass spectrometers available for continuous process gas analysis and Thermo Fisher Scientific is unique in that we offer both types of MS systems, magnetic sector and quadrupole.

Magnetic sector has proven more successful for a wide range of industrial process applications, because of its superior stability and lower maintenance requirements. Both types of MS use electron impact ionization to generate positive ions. These are then separated, either in a varying magnetic field (magnetic sector MS) or a varying RF/DC field between four parallel rods (quadrupole MS).

The magnetic sector MS operates with ion energies of 1000 eV, providing extremely rugged performance in the presence of gases and vapors that could contaminate the analyzer. Quadrupole analyzers operate at ion energies of typically just 5-10 volts—this can give rise to ion interactions within the MS, causing poorer short-term precision.

In a magnetic sector analyzer, the signal intensity at any specific mass position appears as a flat top peak. This means that any small drift in the mass scale will not result in a change in signal intensity. This is not the case with quadrupole mass spectrometers, which produce round top peaks.

Quadrupole analyzers also suffer from a phenomenon known as 'zero blast', making the analysis of light gases such as hydrogen problematic. Magnetic sector analyzers do not suffer from this effect, ensuring hydrogen can be analyzed with maximum accuracy for safety.

Typical Prima PRO analytical specification

Table 2 shows the typical performance specification for a Thermo Scientific Prima PRO process mass spectrometer on blast furnace top gas.

Table 2 Typical performance specification on blast furnace top gas by Prima PRO process MS with 10 second analysis time

| Component | Typical blast furnace top Gas composition %mol | Test gas concentration %mol | Prima PRO standard deviation %mol |
|-----------------|--|-----------------------------|-----------------------------------|
| Hydrogen | 2 - 4 | 4 | 0.005 |
| Carbon monoxide | 21 - 25 | 24 | 0.03 |
| Nitrogen | 48 - 53 | Balance | 0.02 |
| Oxygen | 0 - 1 | <0.01 | 0.001 |
| Argon | <0.1 | <0.01 | 0.001 |
| Carbon dioxide | 21 - 24 | 26 | 0.02 |

Analysis cycle time is 10 seconds, and precisions are demonstrated by analyzing a test gas cylinder periodically over 8 hours.

Plant integration

The Prima PRO is normally located at the base of the furnace in an analyzer shelter, taking samples from the top gas and also the Above-Burden and Sub-Burden probes as required. Prima PRO's cabinet is sealed to prevent dust ingress, cooled by a side mounted air conditioner that stabilizes the temperature within the cabinet to within $\pm 0.5^{\circ}\text{C}$, and can handle ambient temperatures between 12°C and 40°C . An on-board processor provides embedded processing power for true, stand-alone control of all mass spectrometer functions; it can connect to a local or remote PC as a GUI, and three additional configurable serial ports are provided for remote communication. Modbus RTU slave protocol communication is supplied as standard, with additional protocols such as Profibus DP and Modbus Ethernet TCP/IP available as options. 13 digital input channels and 13 digital output channels are provided as standard, additional analog and digital hardware is available as an option.

Sample conditioning is typically the same as for conventional analytical techniques, consisting of dust filtration and moisture removal. Two sample probes are typically used, one is sampling while the other is being cleaned, with automatic switchover between probes.

Summary

Thermo Scientific process mass spectrometers have been successfully monitoring blast furnace off gas at many of the world's iron and steel companies for over 30 years. For a blast furnace producing 5,000 tonnes a day, a reduction in coke consumption of just 10 kg per tonne of iron produced provides a payback of over \$10,000 a day. Users report that the combination of fast, accurate MS gas analysis for gas efficiency, heat & mass balances and hydrogen analysis, with advanced process control and mathematical modeling, has reduced coke consumption by up to 100 kg per tonne and also increased iron production. Upgrading to Prima PRO can therefore result in complete installation payback within a few weeks.

- Reduces coke consumption
- Produces consistent quality iron
- Reduces downstream processing costs
- Detects water leaks fast
- Improves thermal control of furnace
- Enables safer operation during blowdown

References

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