Thermo Fisher
S C I E N T I F I C

Improving low carbon steel production in specialty steel processes

Prima PRO Process Mass Spectrometer

Keywords
- Low Carbon Steel
- Stainless Steel
- Argon Oxygen Decarburization (AOD)
- Vacuum Degassing
- Vacuum Oxygen Decarburization (VOD)
- Ruhrstahl Heraeus (RH)
- Hit Ratio
- Variable Pressure Inlet

Introduction
World crude steel production reached 1,691 million tonnes in 2017, up by 5.3% compared to 2016.[1] While much of this capacity is still produced in primary steel processes such as basic oxygen furnaces and electric arc furnaces, the need for refined steel with greater durability and resistance to heat and corrosion has led to the increased use of vacuum degassing processes, such as VOD and RH, in secondary steel production. These processes are able to achieve ultra-low levels of residual carbon, while at the same time retaining desired levels of other alloy materials. If these processes are to achieve the required level of steel product quality, they need fast, continuous gas analysis of the furnace exhaust gas. Without accurate information on the composition of the gas leaving the furnace, any variations in the decarburization process are only detected after the event, resulting in the production of out-of-specification steel.

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Specialty steel production

Conventional steelmaking processes are ideally suited to the production of standard grade mild steels. However, to meet increasing demand for high quality specialty steels for industries such as construction, automotive, and aerospace, a further processing stage called secondary steelmaking is required. A range of different processes is available, including stirring with inert gases such as argon, adding alloys, vacuum degassing, and powder injection. Approximately 75% of modern steel types have been developed in the past 20 years. For example, modern cars are built with new steels that are stronger but up to 35% lighter than in the past.[2]

Blowing oxygen into molten steel under vacuum conditions saves time and money over that of conventional steelmaking methods. It also produces high-chrome steels with very low levels of residual carbon, hydrogen, and nitrogen, yielding a wide range of stainless, heat-, and corrosion-resistant steels. Stainless steel contains percentage levels of chromium; as chromium is easily oxidised it is important to decarburize stainless steel to a low carbon level while avoiding loss of chromium.

This is achieved by decreasing the partial pressure of carbon monoxide to ensure preferential removal of carbon over chromium from the melt. In practice, this is done in the Argon Oxygen Decarburization (AOD) furnace by dilution using argon or in the Vacuum Oxygen Decarburization (VOD) or Ruhrstahl Heraeus (RH) processes by reducing the pressure over the molten metal. Figure 1 shows a typical VOD stainless steel production furnace.
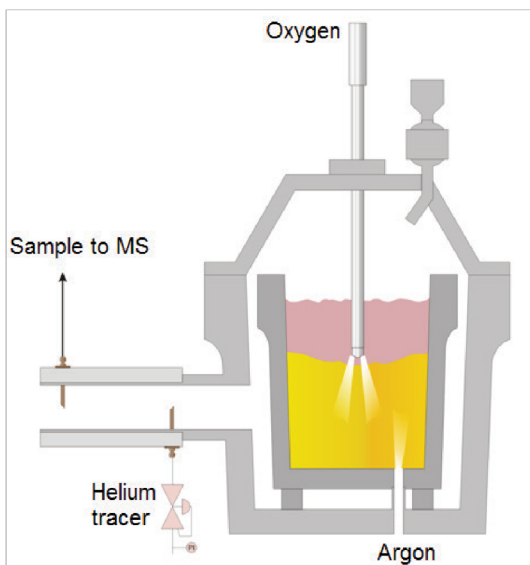

Figure 1. Vacuum Oxygen Decarburization Furnace

Dynamic monitoring of furnace exhaust gas

The various specialty processes mentioned above differ in various operational aspects, but they all need to produce consistent product quality to demanding specifications. It is also important to minimize plant operating costs. Analyzing the composition of the furnace exhaust gas provides vital process information:

- **CO & CO_2:** Decarburization rate, residual carbon content, slag development

- **O_2:** Lance position, slopping prediction, slag development

- **N_2:** Residual carbon, phosphorus and manganese content, slopping prediction

- **H_2:** Early detection of cooling leaks, water content in flux additions

If this information is to be used as part of a dynamic process control model, it needs to be fast, accurate, and reliable.

Advantages of mass spectrometry

Traditional Non-Dispersive Infra-Red (NDIR) analyzers are used in many conventional steelmaking processes to measure CO and CO_2, but they can only sample at atmospheric pressure. In vacuum steelmaking the process pressure changes dramatically, typically from atmospheric pressure down to less than 1 mbar, over the 20-30 minutes of the melt. So NDIR analyzers have to sample some distance downstream from the process. Analytical data is updated several minutes after the gas leaves the melt and the control system is forced to operate on historic rather than real-time data.

Paramagnetic analyzers can be used to measure O_2, while thermal conductivity analyzers can be used to measure H_2. These analyzers also suffer from slow response, while the need to operate three different types of analyzers adds to the plant maintenance burden. Moreover, the three analyzers cannot analyze inert gases, so N_2 is calculated by difference, a result that suffers from the sum of the errors of the three analytical techniques.

Mass spectrometry operates at high vacuum so it is ideal for monitoring vacuum processes. It is also able to monitor all seven components in Table 1 in seconds rather than minutes, ensuring the plant control model is frequently updated with accurate compositional data.

Key control parameters

Figure 2 shows an example of VOD process data. The rapid changes in composition can clearly be seen, indicating the benefits of fast analysis provided by the MS. Process pressure is also shown, dropping from 380 mBar to 5 mbar over the duration of the melt.
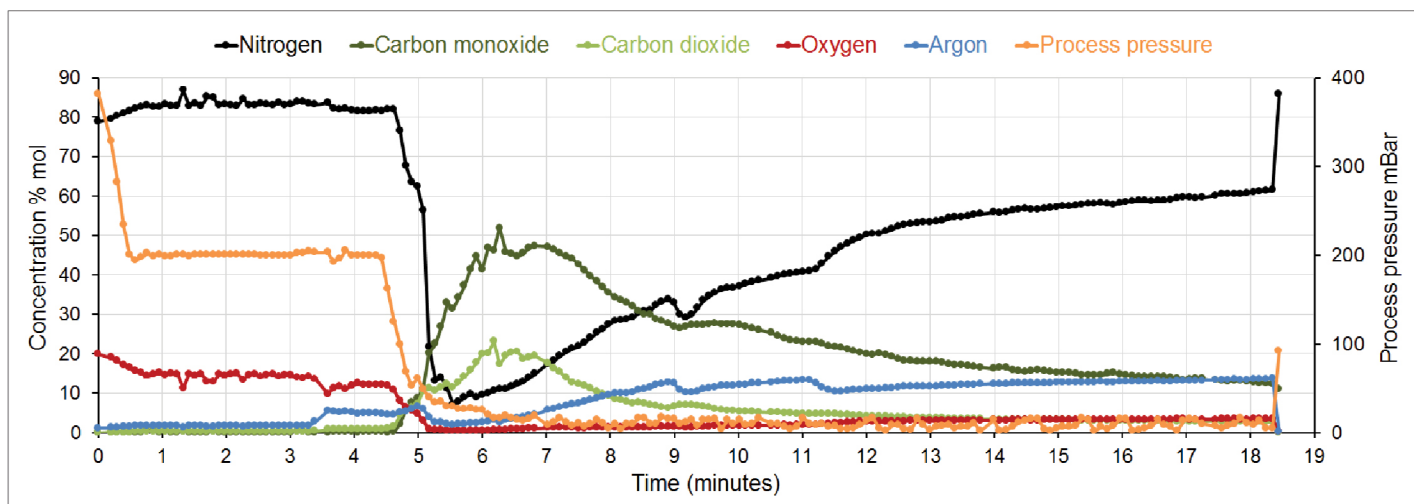

Figure 2. Trend display of typical VOD process data

Precision of analysis

At the heart of the Thermo Scientific™ Prima PRO Mass Spectrometer (MS) 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 on-line 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. Its analysis times are similar to a quadrupole analyzer, 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.

The ion source is an enclosed type for high sensitivity, minimum background interference, and maximum contamination resistance. This 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 analyzer. Typical performance specifications for the Prima PRO MS are shown in Table 1. Analytical performance is demonstrated by analyzing the calibration bottle over 1 hour following calibration, with an analysis time of just 6 seconds. Standard deviations measured on the calibration cylinder will be equal to or better than the stated values.

Table 1. Typical Prima PRO MS performance for VOD and RH processes

Gas	Typical concentration range % mol	Calibration cylinder concentration % mol	Standard deviation % mol
H_2	0 – 15	2	≤ 0.002
CO	0 – 90	40	≤ 0.03
N_2	0 – 100	10	≤ 0.03
O_2	0 – 25	1	≤ 0.002
Ar	0 – 50	41	≤ 0.03
CO_2	0 – 70	5	≤ 0.01
He	0 – 10	1	≤ 0.002

Prima PRO variable pressure inlet

In principle, a mass spectrometer is ideal for monitoring vacuum processes as the MS analyzer itself is operating at high vacuum. However, it is vitally important that the pressure in the MS remains constant as the process pressure changes.

The unique VP inlet of the Prima PRO MS contains two control valves working in opposition—as one valve opens, the other closes. This ensures a wide dynamic range and fast, precise control. The inlet controls the analyzer pressure at just 0.1 mbar and can therefore handle sample pressures down to 0.3 mbar. The VP inlet is shown in schematic form in Figure 3.
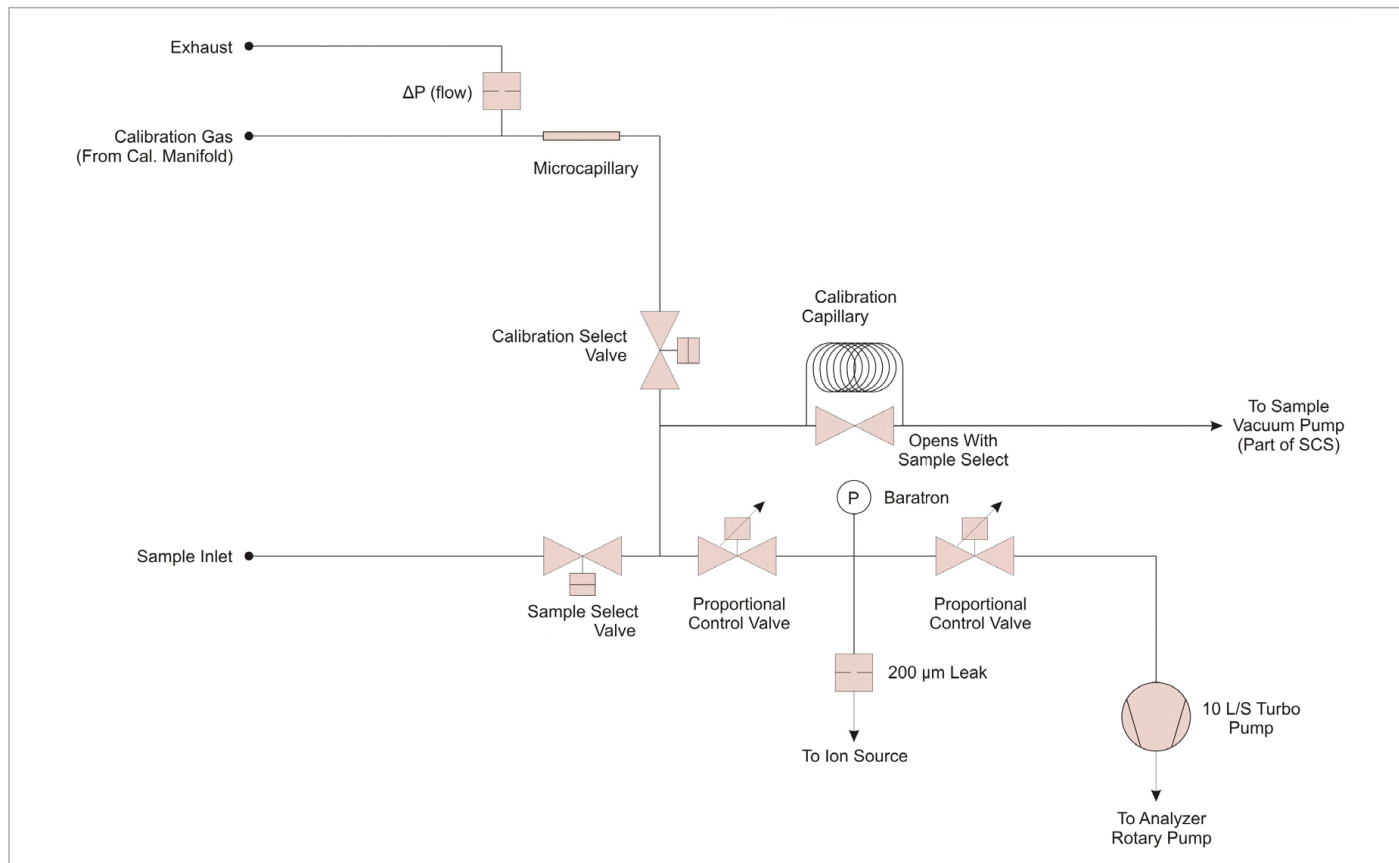

Figure 2. Schematic of Prima PRO VP variable pressure inlet

Gas sampling system

Getting a reliable, representative gas sample from the vacuum process to the Prima PRO MS is vitally important if the MS is to provide accurate, reliable data to the plant control system. Thermo Fisher has worked with an experienced system integrator, Thyson Technology Ltd., to develop a sample system specifically designed for VOD/RH gas sampling.

The sampling system is based on many years of experience with the application and comprises three major components: the control system, the sample conditioning system panel, and a pair of heated sampling probes. The first two units are mounted on a single floor-standing frame connected directly to the Prima PRO MS, and the sample probes are mounted on the process duct. Due to the high dust loading in the process, the two heated sampling probes each have a built-in filter which is automatically cleaned by the system. It carries out a brief pre-clean before each run to remove any dust that might have collected on the probes since they were last used.

Once the pre-clean is complete, it signals to the Prima PRO system that a good sample is available and the unit is now sampling VOD/RH process gas. Then the MS starts analyzing. At the end of each run it carries out a complete cleaning process, back purging the sample system filter, sample lines, and probes with nitrogen in sequence. Figure 4 shows the Prima PRO MS and the Thyson Technology sample conditioning system.

Figure 4. Prima PRO with VP variable pressure inlet and Thyson Technology sampling system

Using MS data to control the process

The unique combination of magnetic sector stability, precise inlet pressure control, and quantitative software helps ensure that the process data produced by the Prima PRO MS is accurate and reliable. A range of industry standard communication protocols can transfer this data to process control systems to optimize the steelmaking process.

Analysis of trace helium to improve decarburization control

Aside from measuring the six standard gases, the Prima PRO MS can provide accurate analysis of helium at ppm levels. This is introduced as a tracer gas at a known flow rate; combining this with the concentration values of carbon monoxide and carbon dioxide measured by the Prima PRO MS provides an extremely accurate method for calculating the decarburization rate. This is continuously updated with the high speed data from the MS. Table 2 shows how GasWorks software's Derived Value function can calculate decarburization rate using a metered helium introduction, and Figure 5 shows the stability of the Prima PRO MS measuring helium at 1% concentration over one hour.

Table 2. Derived Value calculation for decarburization rate using metered helium introduction

Decarburization rate (kg/min) =

$$\frac{dC}{dt} = 0.012 \times ([CO] + [CO_2]) \times F \times \frac{1}{[He]} \times \frac{1}{22.4}$$

Where:

Rate of introduction of helium into off-gas stream = F (l/min STP)
Molar gas volume at STP = 22.4 litres

Concentrations of Helium (He), Carbon Monoxide (CO) and Carbon Dioxide (CO_2) as [He] mol%, [CO] mol% and [CO_2] mol% respectively
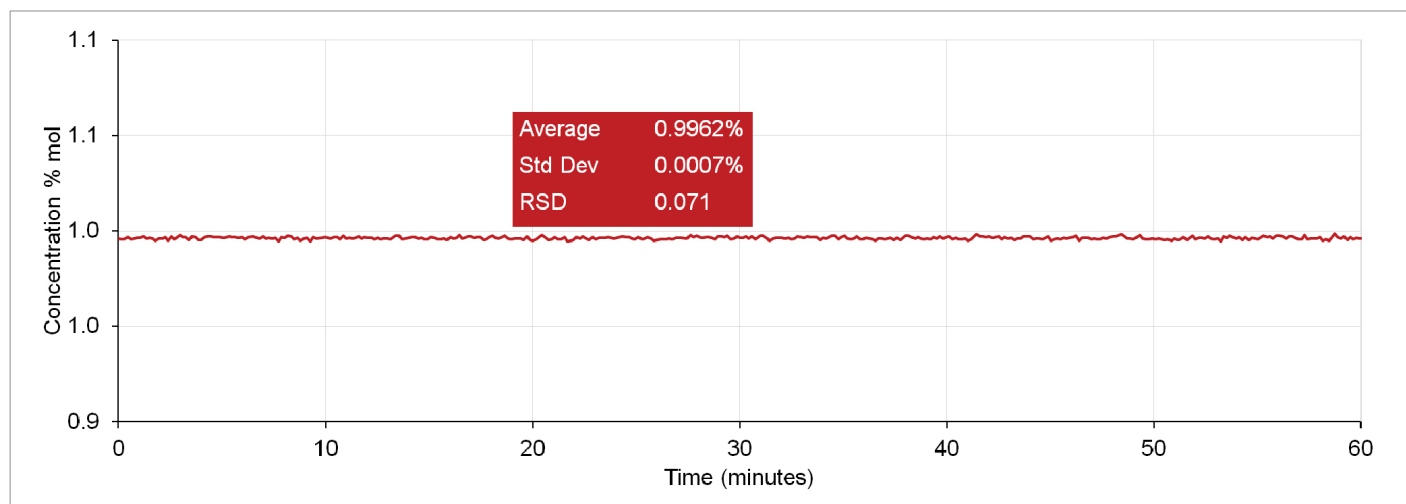
STP = 0 °C and 101.3 kPa

Figure 5. One hour stability plot for helium trace gas (1% concentration)

Improving hit ratio

The Prima PRO system allows the carbon content of molten steel to be controlled very accurately. Figure 6 shows the improvement in hit ratio of the carbon content in two grades of steel, using Thermo Scientific™ process MS compared with traditional gas analysis methods. For steel with 30 ppm carbon content, the hit ratio increased from 90.4% to 100% without over-blowing.
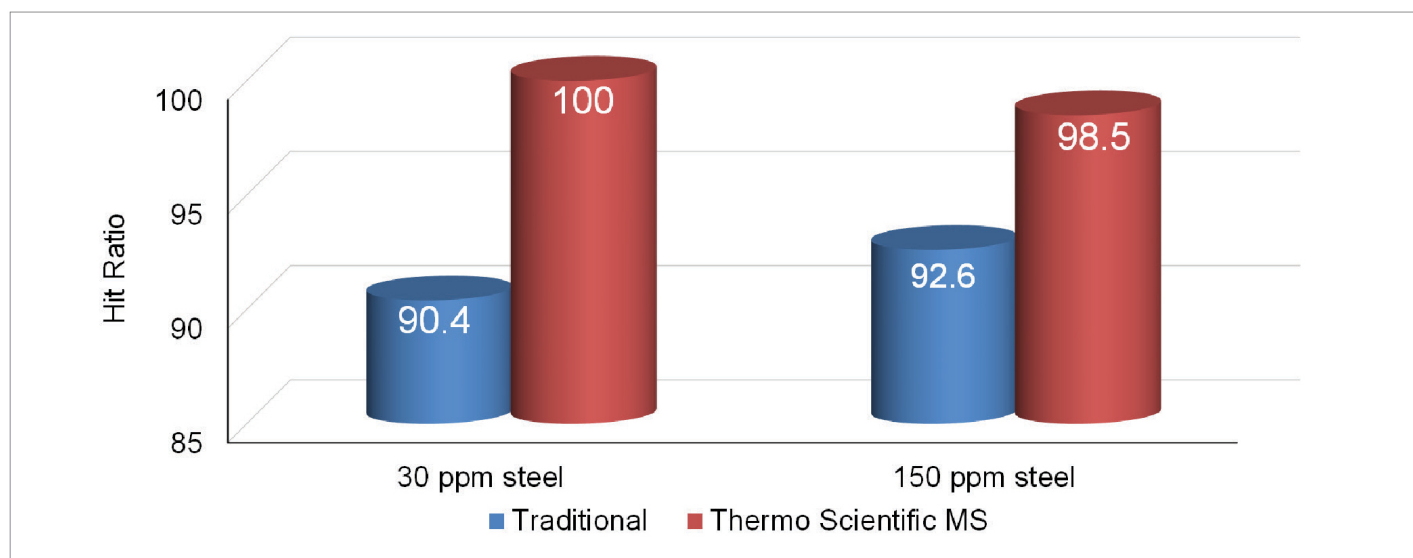

Figure 6. Improved hit ratio for low carbon steel with Thermo Scientific process MS

Summary

The Thermo Scientific™ Prima PRO Process Mass Spectrometer offers optimal on-line measurement precision and stability for vacuum degassing process monitoring and control. Its fault tolerant design combined with extended intervals between maintenance and simplified maintenance procedures helps ensure maximum availability.

Prima PRO benefits

- Improved yields and quality of steel produced

- Reduced cost of ownership

- Direct on-line analysis over the complete pressure range, from 1000 mbar to 0.3 mbar

- Monitors all gases – N_2, O_2, CO, CO_2, H_2, Ar, He

- Continuous high-speed monitoring enables more accurate kinetic model performance

- Fast payback of installation costs—a 1% increase in throughput is worth around $20,000 per day for a furnace producing 10,000 tons of steel per day, meaning the costs of installing a Prima PRO system can often be paid back in less than 30 days

References

- World Steel In Figures 2017, World Steel Association

- World Steel Association Media Centre, "About Steel"

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