



## Process Mass Spectrometry in Iron and Steel

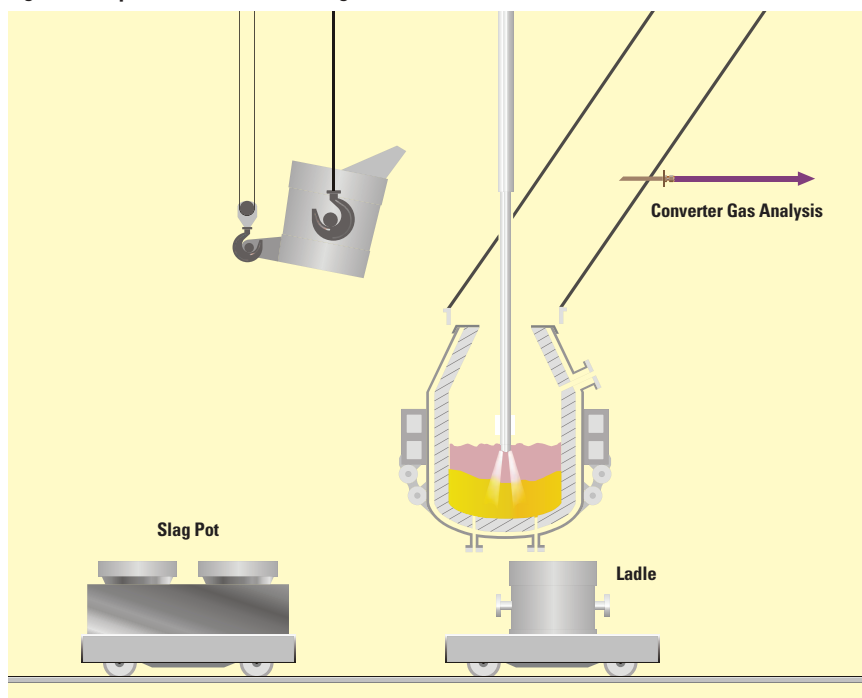


# Plant Optimization at the Speed of Mass Spectrometry.

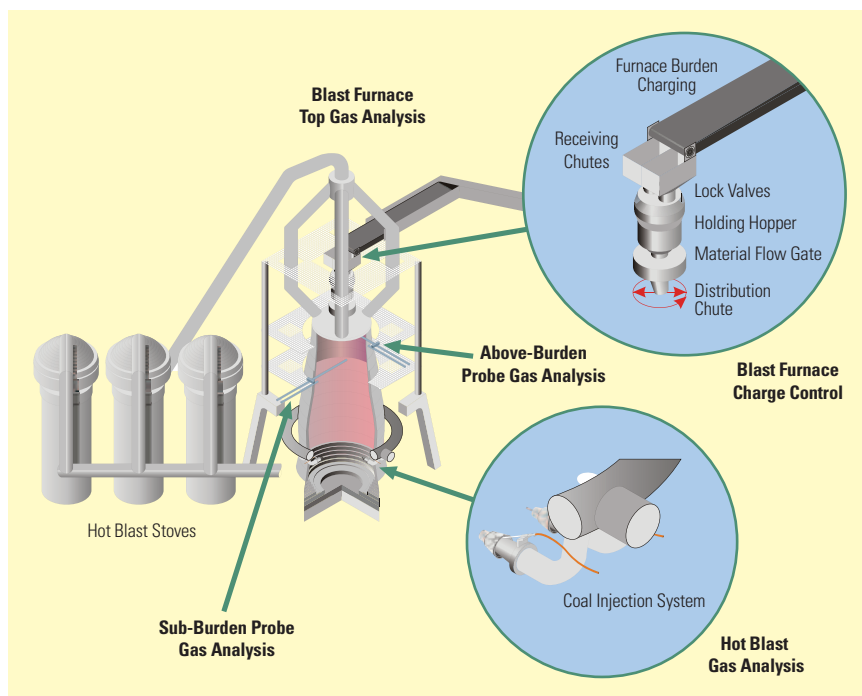
## Field-Proven Technology with a Worldwide Installation Base

From the blast furnace to the galvanizing line, Thermo Scientific process mass spectrometers have proven to optimize a diverse range of hot metal production processes. These reliable, online instruments provide fast, accurate, comprehensive gas analysis, enabling integrated steel mills and mini-mills around the world to efficiently monitor primary and secondary conversion methods. Whether you need to determine the endpoint of a batch process or to rapidly update control parameters on continuous processes, the new Thermo Scientific Prima PRO mass spectrometer is built to meet the application-specific needs of today's modern steel mills.

**Figure 1: Endpoint determination during steel conversion**



**Figure 2: Charge control in the blast furnace**



## Thermo Scientific Prima PRO: The Next Generation Begins

Backed by more than 30 years of process mass spectrometry success, the next-generation Thermo Scientific Prima PRO has been engineered to meet a number of challenging iron and steel applications, including:

- Blast furnace optimization
- Primary steel production
- Secondary steel production
- Direct reduced iron processing
- Electric arc furnace control
- Coke oven gas optimization.

The Prima PRO decreases coke consumption and increases yields via precise analysis of a wide range of process gases. Highly reliable and easy-to-own, this modern process mass spectrometer (MS) delivers faster, more complete, lab-quality online gas composition analysis, enabling real-time optimization of many hot metal processes. Gas concentration and derived value measurements include higher and lower calorific value (CV), density, specific gravity (SG), Wobbe Index (WI), Stoichiometric air requirement (SAR) and combustion air requirement index (CARI) as well as complete and precise compositional analysis. Rapid payback, superior measurement quality and minimal maintenance requirements make the Prima PRO the analytical technology of choice for gas analysis within the iron and steel industry.

### Principles of Operation

The cornerstone of the Prima PRO, and the preferred technology for highly stable, rapid gas analysis, is the scanning magnetic sector MS. Using this technology, gas is continuously drawn from the sample conditioning system via a multi-stream inlet into the ion source where the gas molecules are ionized and fragmented. The ions are accelerated at high energy into the electromagnetic mass filter before selected ions are counted at the detector. The fragmented molecules produce a very repeatable 'fingerprint' spectrum, allowing gases with similar molecular weights to be measured with high accuracy and without interference. The onboard controller presents gas concentration data and derived values, such as CV and WI, directly to the process control system using a variety of industry standard protocols. A rugged, fault-tolerant design ensures availability, typically exceeding 99.7%, while maintenance requirements are significantly minimized.



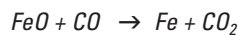
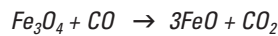
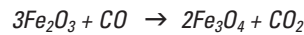
### New Models Deliver Strong ROI

- Fast (1 to 20 seconds per point) online gas analysis for accurate tracking of process dynamics
- Comprehensive compositional gas analysis results in more data supplied to advanced process control (APC) models
- Stable with a 30- to 90-day calibration interval (automated)
- Reliable, fault-tolerant design for availability of >99.7%
- Small footprint with no large shelter required; standard A/C sufficient
- Minimal maintenance requirements reduce operating costs

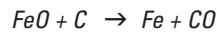
# Imagine a Gas Analyzer that Can Pay You Back in Days.

## Blast Furnace Optimization

The blast furnace is charged with iron oxide bearing sinter pellets (FeO), flux and coke which are loaded into the furnace through a rotating distributor or chute. To achieve correct distribution of these materials, the feed rate and the order that the materials are fed into the top must be controlled. Indirect reduction of the iron ore by carbon monoxide takes place inside the top of the blast furnace stack between +300°C to +1400°C (+570°F to +2550°F):



At higher temperatures, direct reduction takes place:



The optimum coke rate is achieved when direct reduction is maximized.

## Top Gas Analysis Using the Prima PRO

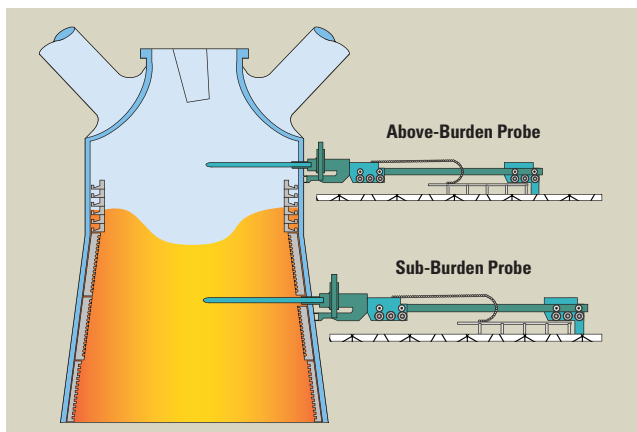
The Prima PRO provides accurate measurement of CO, CO<sub>2</sub>, N<sub>2</sub> and H<sub>2</sub>. If there is too much CO in the top gas, chemical heat will leave the furnace and coke consumption will be too high. If the CO<sub>2</sub> is too high, heat will be carried from the furnace by the exothermic reaction  $2\text{CO} > \text{C} + \text{CO}_2$ .

The N<sub>2</sub> measurement is an important parameter for the online kinetic process models that are used for deriving mass balance, heat balance, fuel capacity and hot metal production.

H<sub>2</sub> is measured for safety reasons. If the reading is too high, it indicates water is leaking into the furnace, creating a dangerous situation that can result in explosions. 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.

Burden probes are often used to collect periodic temperature and gas composition profiles. These data points are used to monitor burden distribution.

Figure 3: Above-burden and sub-burden probes



**For a blast furnace producing 5,000 tons of pig iron, a reduction in coke consumption of just 10 kg per ton of iron produced provides a payback of approximately \$13,000 per day. Upgrading to a Prima PRO can result in complete installation payback within 30 days.**

Precision is the standard deviation observed over 24 hours and assumes an analysis time of 15 seconds. For shorter analysis time (n seconds), down to three seconds minimum, the precision specification data are modified according to:

*Precision for n seconds analysis time equals  $(12/(n-3))^{0.5}$  x (precision for 15 s analysis time). For five and 10 second analysis times, the precision will be worse by factors of 2.4 and 1.3 respectively.*

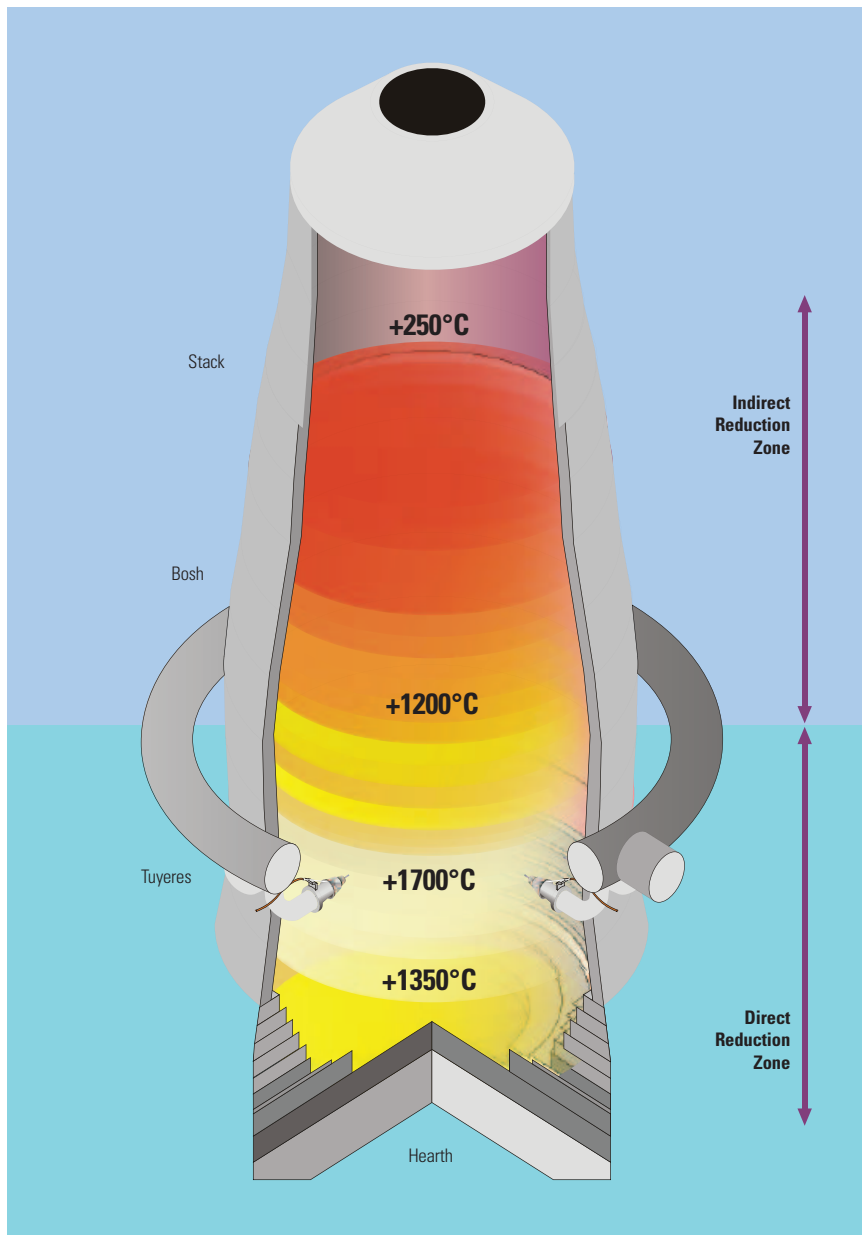
Table 1: Typical mass spectrometer performance specification

Gas Component	% Molar Concentration	Precision % Absolute
N <sub>2</sub>	46.00	0.02
CO <sub>2</sub>	26.00	0.02
CO	24.00	0.03
H <sub>2</sub>	4.00	0.02
O <sub>2</sub>	<0.01	0.001
Ar	<0.01	0.001

## Benefits of Prima PRO Gas Analysis

- Minimizes coke usage
- Maximizes iron production
- Produces more consistent quality iron
- Improves thermal control of furnace
- Enables safer operation

Figure 4: Reduction profile within the blast furnace



# Increase Throughput Without Sacrificing Ease-of-Use or Simple Maintenance.

## Primary Steel Production

### Basic Oxygen Steel Making

Molten iron from the blast furnace is decarburized at the steel plant when pure oxygen is blown at supersonic speeds through a water-cooled retractable lance. This process reduces the carbon content by oxidation. Furnaces used for this process are often referred to as converters, basic oxygen furnaces (BOF), or the basic oxygen process (BOP) or Linz Donawitz (LD) converters. A typical vessel holds 280 tons of steel with the carbon content reduced on average from 4% to 0.3 to 0.6%, depending on the target chemistry.

During this process, the ladle is charged with 20% scrap. Molten iron is added to achieve the required charge balance. Before the lance is lowered, the typical chemistry is 4% carbon, 0.5% silicon, 0.1% phosphorous and 0.02% sulfur. Once the lance is lowered, the carbon is burned to form CO and CO<sub>2</sub>. The temperature rises to +1700°C (+3000°F), melting the scrap and lowering the carbon content. At this point, fluxes are fed into the vessel to form slag which absorbs impurities. In addition, the CO helps to purge N<sub>2</sub> from the steel. Variations to the converter include bottom-blowing Tuyeres which enable efficient stirring via a mixture of oxygen and inert gases, including N<sub>2</sub> and/or Ar.

### Cryogenic Air Separations

Air separation plants generate pure O<sub>2</sub>, pure Ar and pure N<sub>2</sub> which are required for primary steel conversion. A molecular sieve in the pre-purification unit (PPU) removes water, CO<sub>2</sub> and oxides of N<sub>2</sub>. The dry air entering the cold box consists of 78.11% N<sub>2</sub>, 20.95% O<sub>2</sub> and 0.94% Ar. Distillation columns cryogenically separate the three gases, and the residual O<sub>2</sub> is removed from the Ar in a second distillation stage. With Ar costs approximately 80 times those for nitrogen, N<sub>2</sub> is the preferred inert stirring gas. Unfortunately, low carbon sheet steels intended for special applications (i.e., automobile body panels) require very low N<sub>2</sub> contents (20 to 50 ppm), making it necessary to use Ar once the N<sub>2</sub> limit has been reached.

### Furnace Effluent Gas Analysis Using the Prima PRO

Analysis of CO and CO<sub>2</sub> using the Prima PRO enables detection of the process endpoint to minimize oxygen use, ensure a faster process and avoid slopping which damages the furnace. Where a process uses both N<sub>2</sub> and Ar to reduce chromium oxidation, the Prima PRO's gas composition data helps to minimize consumption of expensive Ar by accurately controlling the optimum switchover point. However, reducing the number of reblows is the primary goal. Fast, accurate gas analysis reduces the need for intermediate hot metal at-line sampling which adds up to six minutes to the heat time or up to 6% of tap-to-tap time. Furthermore, a reblow adds 5 to 10 ppm of N<sub>2</sub> to the steel when air is added to the furnace during the sampling rotation.

Figure 5: BOF gas analysis data

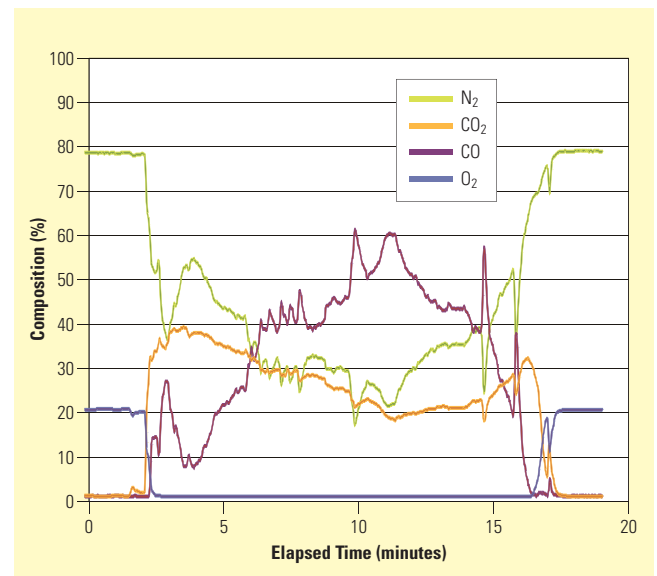
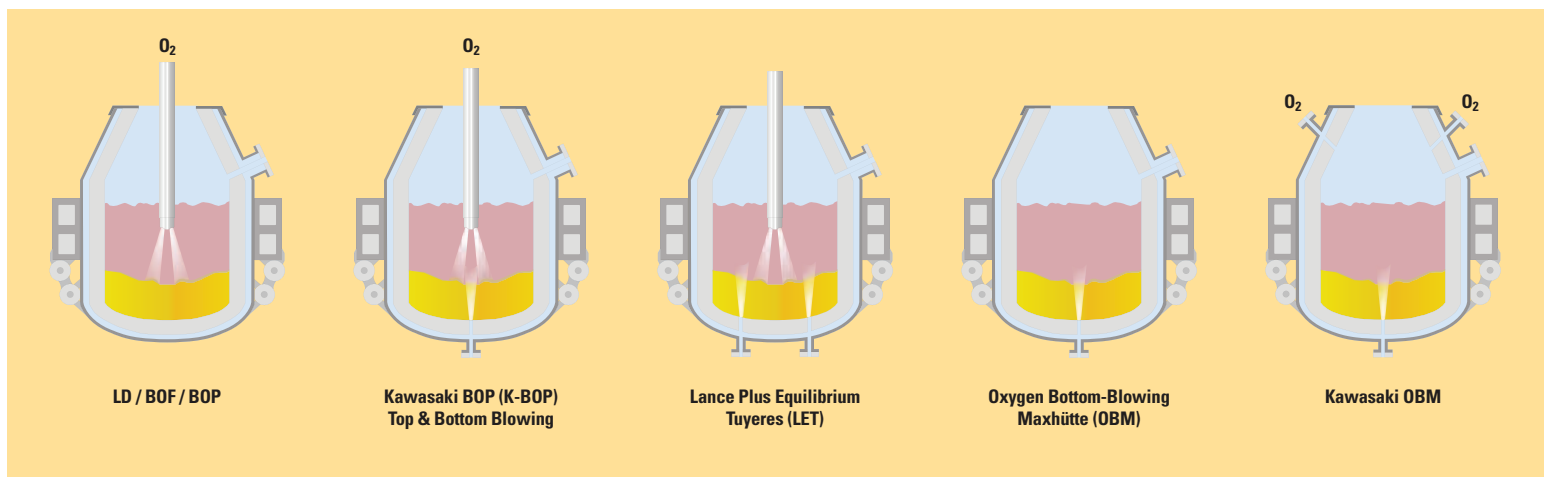


Figure 6: Steel converter variations



## Secondary Steel Production

### Recirculation Degassing (R-H Process)

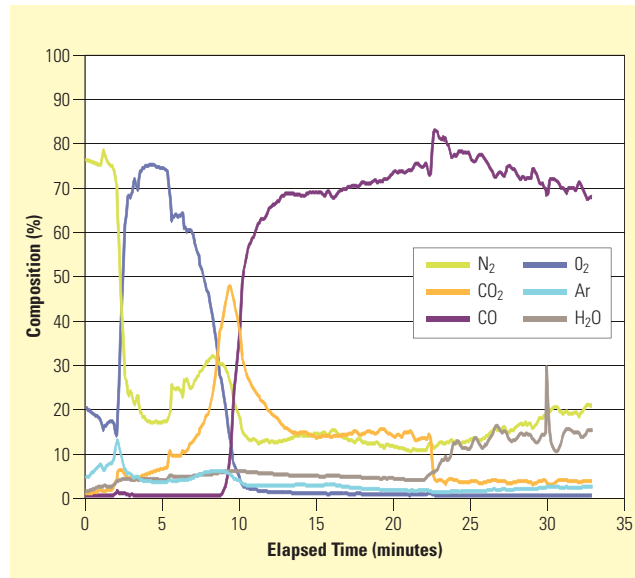
Degassing removes the  $H_2$ ,  $N_2$ ,  $O_2$  and C that react with the  $O_2$  when the vacuum is applied. This process reduces the number of inclusions, improving toughness, fatigue strength and machinability of the final product. Better control of the steel's cleanliness is also a prime degassing benefit. Alumina, inherent in all steel making processes, is a major source of poor steel cleanliness. The use of slags with an affinity for alumina enables production of very clean steel products. In the R-H version of this process, an evacuated vessel is lowered into the ladle and hot metal is drawn up through one of a pair of snorkel tubes into the degassing vacuum chamber. Ar is injected into one tube in order to initiate vigorous recirculation as well as boiling of the hot metal.

### Vacuum-Oxygen Decarburization (VOD) Using the Prima PRO

The VOD process is used to convert unrefined steel into stainless steel or other high quality, ultra-low carbon steel. Once the ladle is charged, the converter top, consisting of a vacuum hood with an oxygen lance and a hopper for desulfurizing slag treatments and alloying elements, is closed. The pressure in the vessel is lowered from atmosphere (1000 mbar) to 1 mbar or less using large multi-stage steam ejectors or three-stage dry pumping systems. The lance blows  $O_2$  over the melt while Ar is bubbled up from the bottom in order to purge the carbon oxidation products and remove impurities. Incorporating the Prima PRO's sample tap into the vacuum system enables direct monitoring of decarburization and degassing for optimum process control. The Prima PRO can also be used to calculate total gas flow from the vessel via an accurately metered helium injection, an arrangement that provides comprehensive data to the kinetic control models. In the production of ultra-low carbon steel (less than or equal to 30 ppm), a mean error of 1 ppm in the carbon content is achievable when the Prima PRO's unique magnetic sector MS provides data to the APC system.

**Each 1% increase in throughput is worth approximately \$20,000 per day for a shop producing 10,000 tons of steel per day. Upgrading to a Prima PRO can result in complete installation payback in fewer than 30 days.**

Figure 7: VOD gas analysis data



### Benefits of Prima PRO Gas Analysis

- Improves hit ratio for increased steel throughput
- Ensures more consistent steel quality
- Provides more accurate kinetic model performance for:
  - Best available speed and precision
  - Total flow calculation c/o He tracer gas analysis
- Provides rapid installation payback

Figure 8: R-H degasser

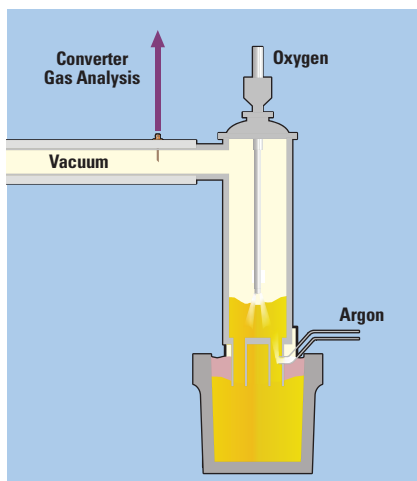


Figure 9: VOD converter

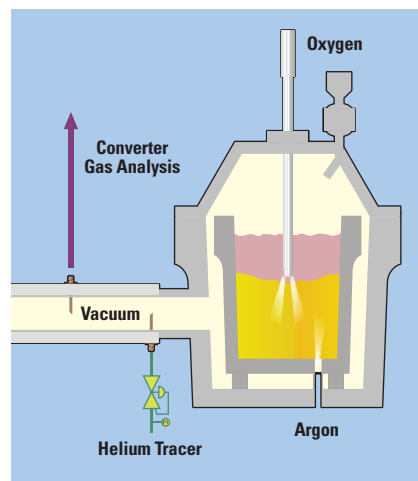


Figure 10: Hit ratio before and after

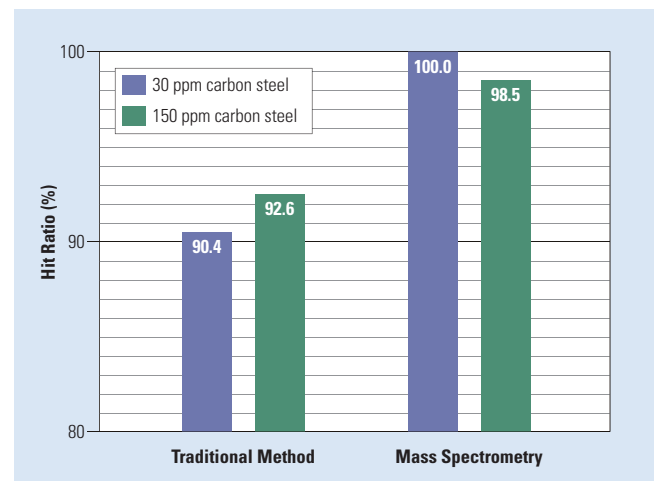
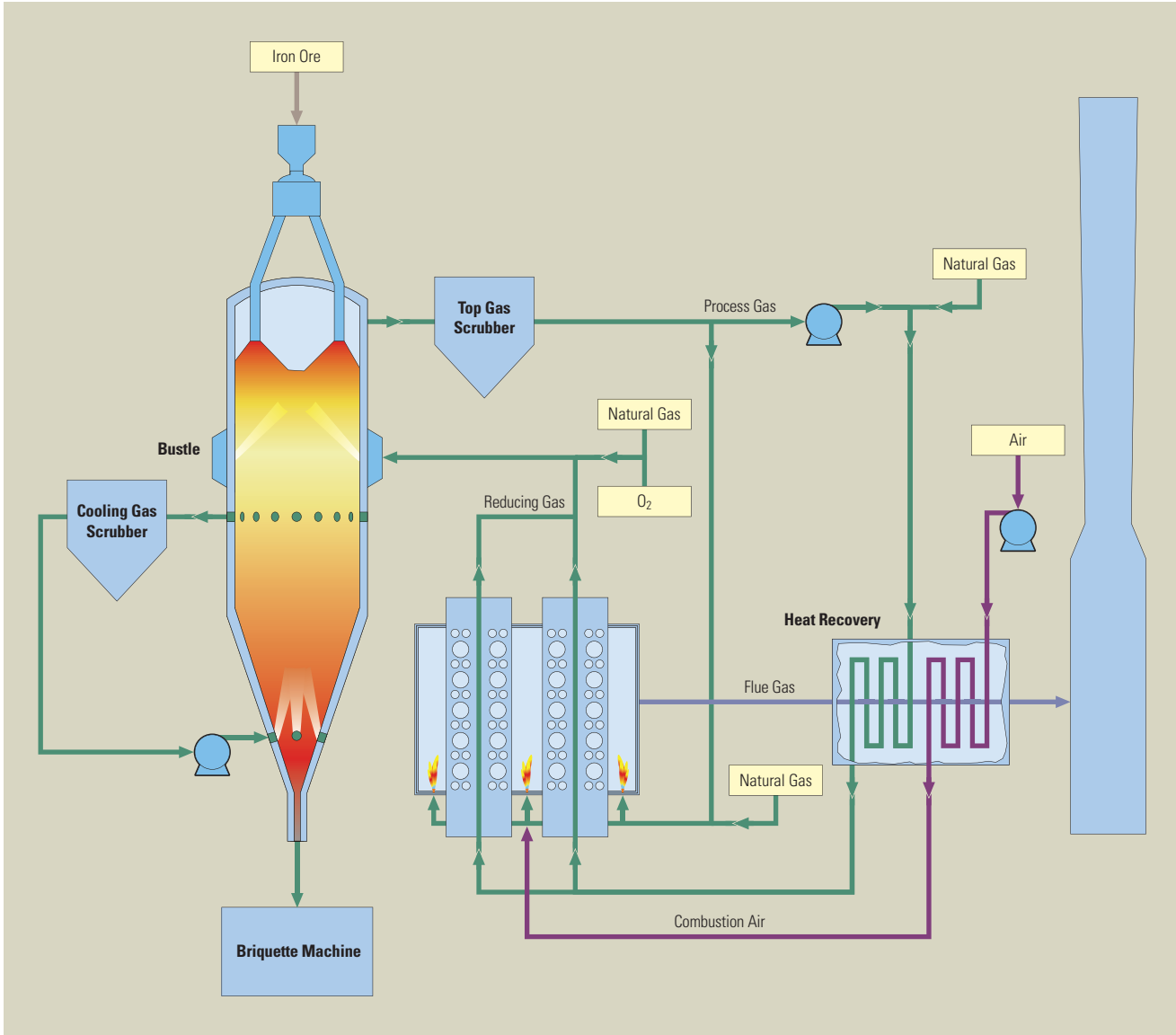






Figure 11: Midrex schematic diagram



# Improve Product Consistency and Safety with Real Time Gas Analysis.

## Electric Arc Furnace (EAF)

The EAF, together with the basic oxygen furnace, is one of two modern steelmaking techniques. Unlike the basic oxygen process, the EAF does not use hot molten metal. It is charged with solid material, normally steel scrap and DRI. The steel scrap is first tipped into the EAF from an overhead crane. Next, a retractable cover, containing electrodes that are lowered into the furnace, is swung into position over the furnace. An electric current, typically supplied by a 100 mw transformer, is passed through the electrodes to form an arc that generates enough heat to melt the scrap.  $O_2$  can also be lanced into the scrap, or wall-mounted oxygen fuel burners can be used to provide additional chemical heat. The retractable cover includes a hood that diverts gases through a post-combustion section and a dust removal system. As with other steel processes, burnt lime and dolomite are added to form a slag that blankets the molten steel and absorbs impurities. The slag also covers the arc, preventing radiant heat damage to the furnace cover and sidewalls. Carbon in the form of coke or coal is lanced into the slag, partially combusting to form CO which causes the slag to foam. Greater thermal efficiency and better arc stability result. Once the meltdown is complete, the oxygen lance is used to burn off impurities (Si, P, S, Al, Mn and Ca) and any byproduct oxides are absorbed by the slag. Finally, the C content is lowered by the  $O_2$  from the lance. Once the process is complete, the furnace is tilted and the molten steel is tapped into a preheated ladle.

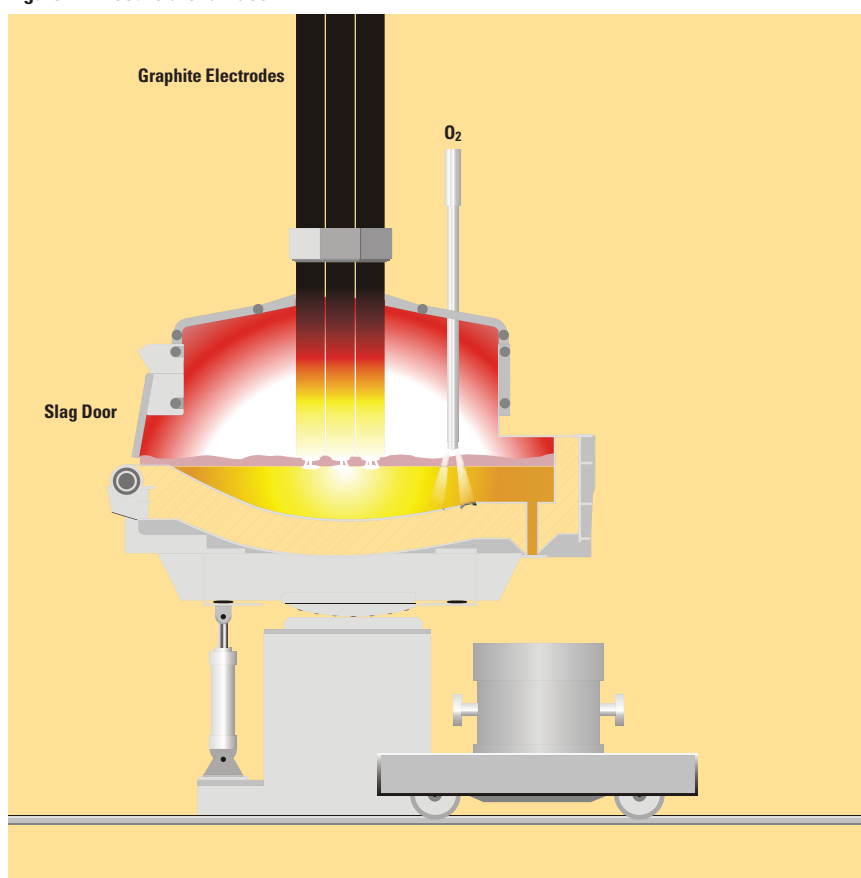
## Furnace Control Using the Prima PRO

The primary furnace control goals are to minimize energy usage, provide consistent steel specifications, achieve environmental compliance and ensure safe operation. Furnace off-gas composition, measured in real time, is used to continuously optimize chemical energy and to control post-combustion for bag house safety and environmental compliance. The gas measurement is achieved via an extractive system that employs rugged water-cooled probes and a sophisticated sample conditioning system. The output is a reliable off-gas sample for the Prima PRO which in turn provides precise gas composition measurement for dynamic, model predictive process control.

## Benefits of Prima PRO Gas Analysis

- Minimizes power consumption
- Minimizes oxygen consumption
- Minimizes tap-to-tap times
- Improves process safety

Figure 12: Electric arc furnace



## Electric Arc Furnace Gas Analysis

Figure 13a: Nitrogen & oxygen electric arc furnace gas analysis data

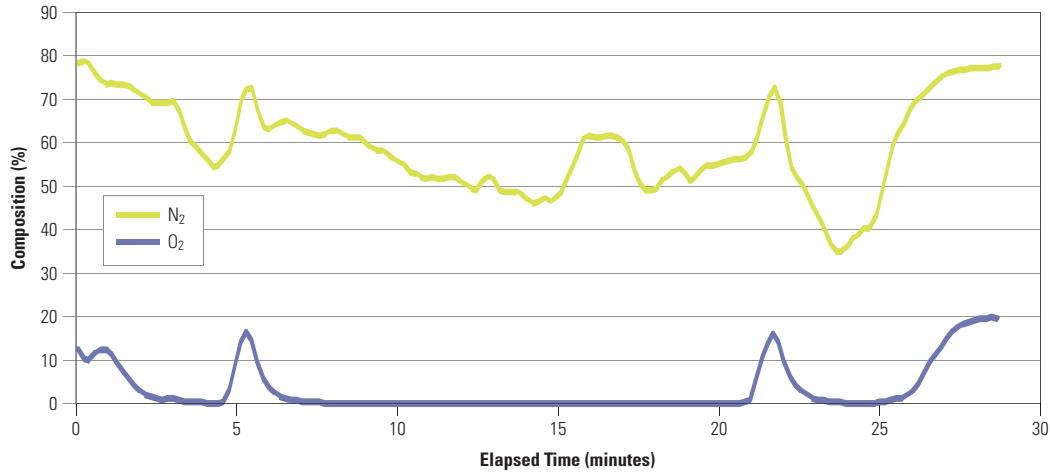


Figure 13b: Carbon monoxide & carbon dioxide electric arc furnace gas analysis data

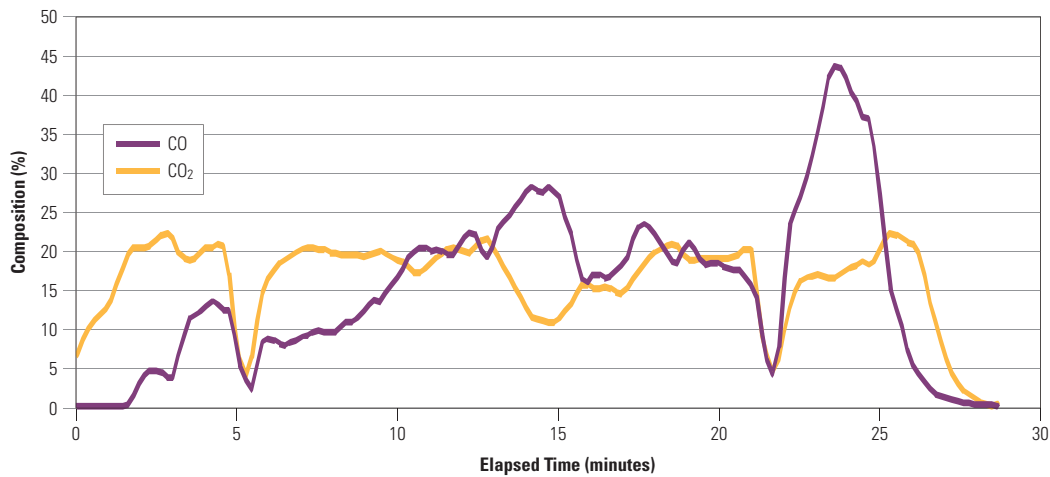
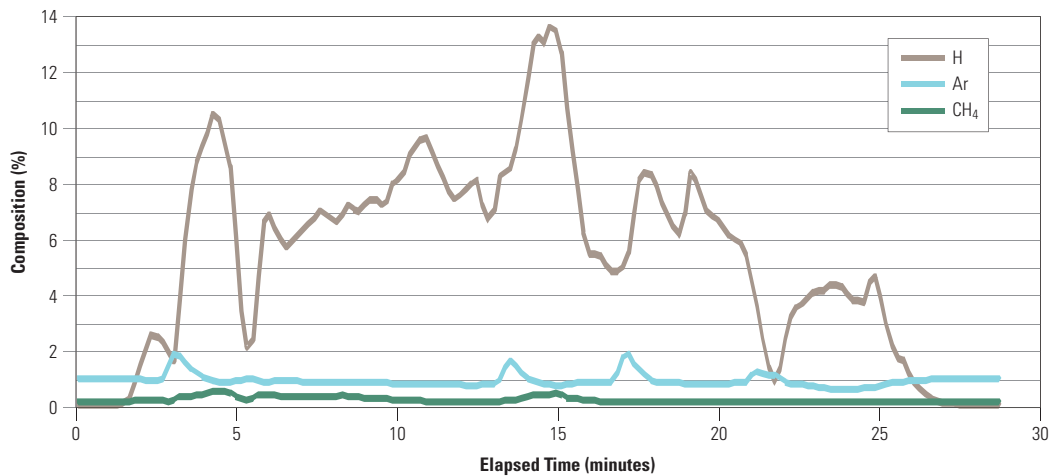


Figure 13c: Hydrogen, argon & CH<sub>4</sub> electric arc furnace gas analysis data



# Improve Precision and Response Time by a Factor of 10.

## Coke Oven Gas

In the coke oven plant, coal is converted into coke by pyrolysis. To begin the process, the coal is baked in an airless furnace or oven at +2000°C (+3600°F) or higher to extract volatile constituents, including water, coal gas and coal tar. A large quantity of gas with high CV is generated, with the oven operating largely by reusing or burning the gases emitted by the coal. There are two main aspects to analyzing the high CV gas. The first is to precisely measure its energy characteristics, enabling it to be used efficiently as fuel for the oven batteries as well as fuel for other stoves and furnaces. Properties of the gas, including CV, density, SG, WI and SAR, are simultaneously calculated by the Prima PRO. These variables enable tight combustion control to maximize energy use and to extend burner life. The second aspect to the gas analysis is the essential cleaning of the gas to prevent problems associated with gas handling and to limit harmful emissions. Rapid and complete analysis of the gas at various points, including at the secondary cooler, ammonia absorber, final cooler and benzol scrubber, allows for closed loop control of the cleaning process. One multi-stream Prima PRO optimizes both the fuel burning and gas cleaning processes for a cost-effective installation with low cost of ownership.

## Benefits of Prima PRO Gas Analysis

- Optimizes gas cleaning
- Ensures safe operation
- Enables environmental compliance

Table 3: Typical coke oven gas performance specification

Gas Component	% Molar Concentration	Precision % Absolute
H <sub>2</sub>	62 - 64	0.05
CH <sub>4</sub>	22 - 25	0.05
NH <sub>3</sub>	0.013 - 1.30	0.001
H <sub>2</sub> O	2.2 - 2.5	0.01
HCN	0.071 - 0.120	0.02
CO	5 - 6	0.05
N <sub>2</sub>	1.5 - 2.7	0.05
C <sub>2</sub> H <sub>4</sub>	1.85	0.01
C <sub>2</sub> H <sub>6</sub>	0.85	0.01
O <sub>2</sub>	0.10 - 0.15	0.002
H <sub>2</sub> S	0.23 - 0.49	0.001
C <sub>3</sub> H <sub>6</sub>	0.1	0.001
CO <sub>2</sub>	1.0 - 1.5	0.005
C <sub>6</sub> H <sub>6</sub> / C <sub>7</sub> H <sub>8</sub> / C <sub>8</sub> H <sub>10</sub>	0.17 - 0.86	0.001
C <sub>10</sub> H <sub>8</sub>	0.0007 - 0.0250	0.0002



## Fuel Gas Analysis

In general, furnaces are operated at constant temperature with a gas fired furnace ideally burning a gas of constant composition that is delivered at a constant rate and is using a constant air intake at the correct rate for complete combustion. However, gas supply in iron and steel works is of varying composition and the rate of gas supply needs to be varied to maintain a constant temperature. The rate of air supply must also be varied to minimize energy wastage if too little or too much air is used. In addition, excess air can cause metal surface defects due to oxidation. In a typical integrated iron and steel works, the gases listed in Table 4 are used either singly or in mixtures as fuel gases. The table illustrates typical CV and the corresponding SAR needed for optimum combustion.

Analysis of fuel gas composition enables the precise heating properties to be predicted for feed-forward control. CV is calculated from the analyzed composition according to the sum of the pure component CVs that are weighted on a mole fraction basis. However, in practice, the fuel gas flows through a restriction, such as an orifice or valve. The actual flow is inversely proportional to the square root of the density of the gas, making WI more practical than CV. The WI is defined as:

$$\text{Wobbe Index} = \frac{\text{calorific value}}{\sqrt{\text{specific gravity}}}$$

The ideal analyzer is capable of fast, online determination of both WI and CARI, enabling feed-forward control. The Prima PRO is the preferred technique for these measurements because the magnetic sector MS provides comprehensive, accurate, fast and very stable fuel gas analysis. Using the Prima PRO, analysis of all components present in fuel gas, including H<sub>2</sub>, CH<sub>4</sub>, CO, N<sub>2</sub>, O<sub>2</sub>, C<sub>2</sub>H<sub>6</sub>, CO<sub>2</sub>, C<sub>3</sub>H<sub>8</sub>, C<sub>4</sub>H<sub>10</sub> and C<sub>6</sub>H<sub>6</sub>, is completed in less than 30 seconds with a precision of typically better than 0.1% relative or 0.01 mol% absolute.

The multi-stream Prima PRO measures blast furnace gas (BFG), coke oven gas (COG), LD converter gas (LDG) and NG. It provides accurate gas compositions as well as reports precise values for lower and/or higher heating value, lower and/or higher WI, density and CARI. These data are communicated directly through one of many available data highways for feed-forward control of gas mixing and air supply.

## Alternative Technology Comparison

In principle, there are simpler, lower cost instruments capable of measuring some fuel gas properties. However, the measurements made by the Prima PRO are more complete, accurate and faster.

Calorimeters, which measure the heat effect of burning fuel gas, can be used to measure CV or WI but not both simultaneously. A calorimeter can be combined with a density meter to provide data for calculating the other property. The precision of a Prima PRO is typically a factor of 10 times better (0.1% relative compared with 1% relative for a calorimeter). Response time is also typically a factor of 10 times better (15 seconds for the Prima PRO compared with 2.5 minutes for a calorimeter). Calorimeters cannot be used to measure CV of fuel gases of widely varying composition or to calculate the SAR which is essential for efficient combustion. SAR 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 using a MS to measure fuel gas and due to the unsuitability of the calorimeter to measure multiple streams and sample types, the only solution included multiple calorimeters and density meters plus a discrete oxygen analyzer. The cost, complexity and maintenance requirements of a single Prima PRO make it an extremely favorable solution in comparison with the older multi-analyzer system. Flexibility is another advantage of the Prima PRO. It is very easy to modify the analytical method to measure different components, negating any problems if the sample gases are changed over time. For example, the analytical method for NG can be easily changed to include CO<sub>2</sub>, C<sub>5</sub>H<sub>12</sub> and C<sub>6</sub>H<sub>14</sub>, if significant concentrations of these components are present due to changes in the supplied NG.

## Benefits of Prima PRO Gas Analysis

- Reduces natural gas consumption
- Extends burner lifetime
- Reduces scab formation caused by excess O<sub>2</sub>
- Enables environmental compliance

**Table 4: Typical calorific values**

	CV kcal/m <sup>3</sup>	SAR
Coke Oven Gas	4000	4
Blast Furnace Gas	750	0.6
Steel Converter Gas	2000	1.6
Natural Gas	9000	10

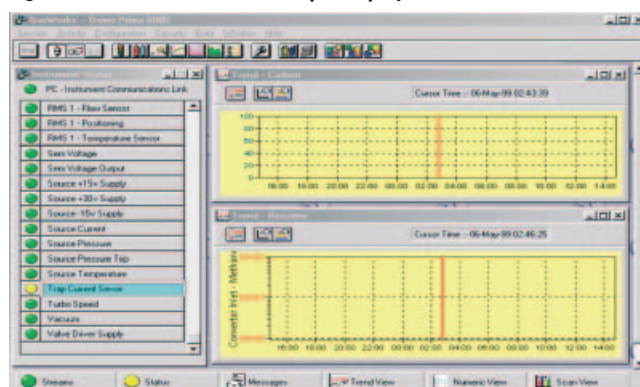
# Enhance Productivity and Increase ROI.

## Thermo Scientific GasWorks Software

The Thermo Scientific GasWorks software suite provides an intuitive, information-rich and flexible window into the operation of the Prima PRO. Produced in a certified ISO 9001 environment, GasWorks software is designed for rapid installation and to facilitate ongoing operation while providing a secure, stable platform for process analytics. It is simple to configure, operate and maintain without the need for specialist mass spectrometry knowledge.

The suite includes a wide range of functions and features, allowing it to be matched exactly to the needs of the user. Whether the requirement is for simple alarm indication in the event of a manufacturing process failure, or for complex data presentation for process understanding and control, GasWorks is well equipped to offer an effective solution. Regular updates ensure that the software takes advantage of the latest technology as it becomes available.

Figure 14: GasWorks software sample display



## World-Class Service & Support

Our service and support options are designed to ensure instrument optimization and reduce downtime. Because every customer and every instrument has different requirements, we offer a variety of services to meet your unique needs, including:

- Service agreements
- Spare parts
- Technical support
- Field installation and service
- Product training.

## Optimizing Plant Processes in Real Time

We manufacture a wide range of process instrumentation designed to meet the application-specific needs of the iron and steel industry, including:

- Process mass spectrometers
- Online moisture analyzers
- Nuclear density gauges
- Online thickness measurement gauges
- Belt scales and weightbelt feeders
- X-ray and optical emission spectrometers.

Our solutions have proven to enhance operational efficiency, ensure optimal product quality, maximize product yield and provide an ongoing return on investment.





# Process Mass Spectrometry in Iron and Steel

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