FIRST Newsletter

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Product Spotlight: G8 GALILEO ON/H

Rapid Assessment of Oxygen, Nitrogen and Hydrogen in Steels, Alloys and Other Materials

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Introduction

The physical properties of many materials are impacted, both positively and negatively, by elemental composition. The careful control of these elemental concentrations, from raw material to finished product, is critical to producing the highest quality material. For example, oxygen and nitrogen content is normally monitored during the fabrication of steel because both have a significant impact on the strength. Likewise, hydrogen is also of importance because it has a severe negative influence on the mechanical properties of steel. In addition to steel mill applications, automotive companies, contract laboratories and many other entities must have a reliable and rapid means of measuring the oxygen, nitrogen and hydrogen content in an assortment of sample shapes and compositions. Fortunately, the Bruker **G8 GALILEO ON/H** gas analyzer is fully equipped to provide this vital information.

The **G8 GALILEO ON/H** (Figure 1) is a modern analytical instrument designed for the rapid and automatic determination of oxygen, nitrogen and hydrogen in solid materials. This analyzer is based on the inert gas fusion (IGF) principle, which involves fusion of the sample material in a graphite crucible at temperatures that can exceed 2500°C. The gas fusion analysis (GFA) principle is also commonly termed a melt extraction (ME) since the total oxygen, nitrogen and hydrogen composition is extracted via sample melting.

Electrode Furnace

The electrode furnace, along with the advanced detection system, comprises the heart of the **G8 GALILEO**. The furnace consists of two electrodes, an upper and lower, which serve as electrical conduits for passing current through a graphite crucible that retains the sample of interest. Inert carrier gas is flowed across the crucible and an electrical current sufficient enough to melt the sample is passed through the electrodes causing the crucible to resistively heat and the sample to melt. Achieving a thoroughly fluid melt is critical to completely liberating the three primary elements of interest in IGF: oxygen, nitrogen and hydrogen. Because of the high-temperatures necessary for most IGF applications, water cooling of the electrodes is required.

*Figure 1: Bruker **G8 GALILEO ON/H** analyzer for rapid assessment of the oxygen, nitrogen and hydrogen content in a variety of sample matrices and configurations.*

Melting the sample releases oxygen, if originally present, which will react with available carbon from the graphite crucible to form carbon monoxide

(CO). Likewise, hydrogen gas (H_2) and nitrides, the latter of which decompose into molecular nitrogen (N_2), also liberate if present in the sample. Once released from the sample, these constituents (CO, H_2, and N_2) are transported by the carrier gas through the furnace and travel through the **G8 GALILEO** as represented in the gas flow diagram found in Figure 2.

Gas Flow Design

The **G8 GALILEO** is an open system, meaning that a membrane pump is used to transport the gases through the system. After the CO, H_2, and N_2 products are formed the pump, which is located adjacent to the downstream exhaust, pulls the gases through a quartz wool filter and micron paper filter to remove particulates (e.g., carbon dust) that may have been generated during the analysis.

Oxygen Detection

After the gas stream is purified the oxygen content is measured with a dual-range CO infrared (IR) detector arrangement, as shown in Figure 2. Carbon monoxide will absorb IR at specific wavelengths corresponding to specific vibrational and rotational levels of the CO molecule. This attenuation of the infrared light is detected by appropriate sensors equipped with specific narrow-band optical filters. Since N_2 and H_2 do not absorb IR radiation, they pass through the IR cell undetected. The CO response, which is proportional to the oxygen content in the original sample, is quantified with an analog-to-digital (A/D) converter and displayed as an oxygen intensity vs. time plot on the screen in real-time.

Nitrogen Detection

After CO is measured the carrier gas, still containing CO, N_2 and H_2, flows through a three-way solenoid valve, routing the gas stream through one of two paths depending on the previously-defined configuration properties (i.e., software settings) before the remaining measuring gases are detected by the downstream thermal conductivity detector

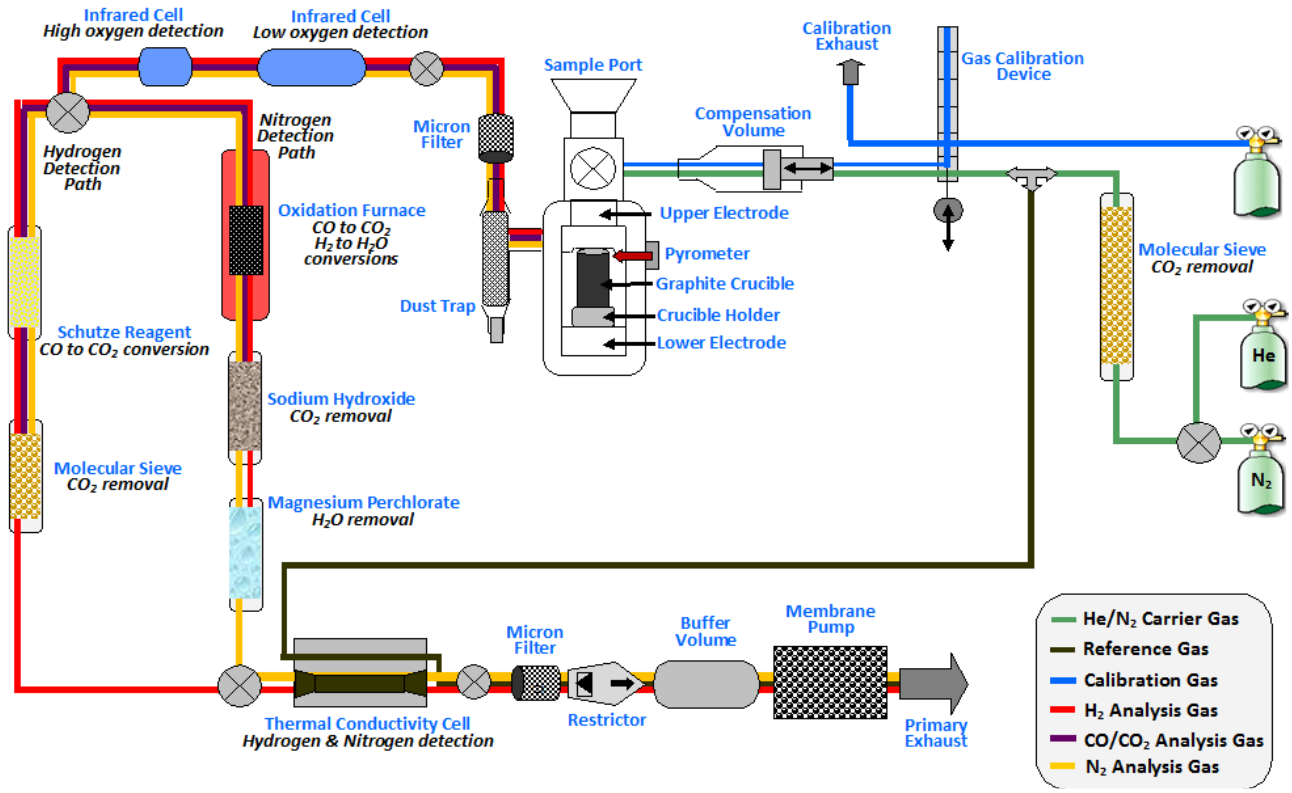

*Figure 2. Flow diagram of the **G8 GALILEO** representing the gas flow path and major components.*

featuring outstanding stability and linearity. Unlike the aforementioned IR cell, which responds exclusively to CO molecules, the TCD is inherently a non-selective, "universal" detector. It will respond to any molecule(s) having a thermal conductivity different than that of the carrier gas. For this reason both N_2 and H_2 are detected independently and other potentially interfering molecules with different thermal conductivities must be removed prior to detection.

Pre-selecting nitrogen detection in the software configuration allows the gas stream to flow through the "Nitrogen Detection Path" segment labeled in Figure 2. The first component encountered is an oxidation furnace consisting of copper oxide (CuO) in a quartz reagent tube heated to approximately 550°C. The heated CuO oxidizes the CO and H_2 to carbon dioxide (CO_2) and water (H_2O), respectively. Nitrogen (N_2), however, is unaffected by the presence of heated CuO. Passing the gas stream, now consisting of CO_2, H_2O and N_2, through sodium hydroxide (NaOH) provides a reaction that will remove CO_2. Likewise, the drying reagent magnesium perchlorate ($MgClO_4$) removes H_2O from the gas stream. With the interfering species removed and the gas stream consisting only of N_2 and carrier gas, the nitrogen content can be accurately measured with the aforementioned TCD. The signal is converted and quantified with an A/D converter and the peak profile corresponding to N_2 content in the sample is displayed in real-time.

The gases then flow through a micron filter and a series of components (e.g., membrane pump) that transfer the gases at a constant flow rate and pressure within the detector region. The gases then exit the analyzer via the primary exhaust.

Hydrogen Detection

Instead of following the "Nitrogen Detection Path" (Figure 2) subsequent to CO detection, the gas stream can alternatively be directed to the "Hydrogen Detection Path" shown in Figure 2. The flow path is specified within the software settings and the appropriate carrier gas is automatically selected by the software based on the element selection (i.e., N_2 or H_2).

The original gas stream, consisting of carrier gas, CO, N_2 and H_2 initially passes through Schutze reagent (iodine pentoxide, I_2O_5 carrier). This selective oxidizing agent converts CO to CO_2 and does not affect the species of interest - H_2. A reagent tube containing molecular sieve is encountered next. The small 'beads' of this sieve contain countless small pores that are the proper size (at room temperature) to trap CO_2 molecules. Fortunately, H_2 molecules are far too small to become trapped in the pores of the sieve and are free to pass unaffected.

Now that the gas composition is exclusively H_2 and carrier gas, the gas stream can be directed to the aforementioned TCD for measurement of the hydrogen content.

Carrier Gases

The carrier gases used in IGF, being both inert and highly pure, are used to facilitate the sample fusion and to assist in transporting and detecting the elements of interest. The purity and pressure requirements for the most common carrier gases are listed in the *Instrument Specifications* section.

As indicated in the flow diagram of Figure 2, the **G8 GALILEO** features a special molecular sieve trap for purifying the incoming carrier gas. The principle of trapping unwanted species with this molecular sieve material is the same as described previously. Any CO_2 or H_2O impurities within the incoming gas stream, if not removed, could bias the oxygen and nitrogen results.

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Any of the common IGF carrier gases (helium, nitrogen or argon) can be used for applications involving the assessment of oxygen in the sample. The choice of carrier gas for the detection of N_2 and H_2, however, is more critical. To achieve the highest possible sensitivity with a TCD the carrier gas must have a significantly different thermal conductivity than the species of interest. For example, the detection of N_2 typically uses helium as a carrier gas since both have very different thermal conductivities. Conversely, a nitrogen carrier is commonly used for H_2 assessment.

Crucible Outgassing

Removing contaminants from the graphite crucible prior to the measurement is crucial to attaining accurate measurements. With a simple button press on the **G8 GALILEO** software the crucible can be outgassed (i.e., purified) by passing a current through it and resistively heating it up. This process is done just prior to the gas fusion process and takes less than a minute.

Furnace Control

To achieve accurate and reproducible measurements the furnace must be controlled during the gas fusion process. The **G8 GALILEO** provides a distinct advantage by featuring three means of controlling the analysis: power, current and temperature.

Furnace control via percent power (%) and current (A) are commonly found with many IGF analyzers. These are suitable for analyzing common samples, such as steel and iron, for their oxygen and nitrogen content. The **G8 GALILEO**, however, offers an additional control parameter – temperature – via an optical pyrometer located adjacent to the furnace (Figure 3). This feature affords the user control of the melt process at a specific (or ramped) temperature rather than relying on power or current as an indirect, and possibly inaccurate, means of estimating the analysis temperature. Directly controlling the temperature profile is especially useful for applications involving hydrogen assessment. Additionally, the temperature profile can be displayed on-screen while operating in power or current mode as well, providing a significant benefit during application development work.

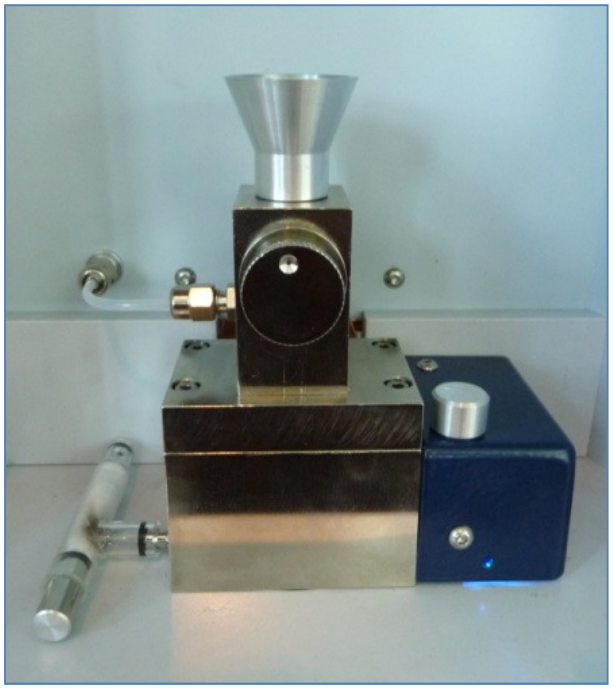

Figure 3. External view of the upper furnace assembly including the sample introduction system and optical pyrometer (blue assembly) for direct temperature control of the analysis.

Recovery and Special Applications

Some sample applications require the use of special crucibles, capsules, baskets or fluxes to promote a reliable analysis. For example, “standard” crucibles are sufficient for most applications, but attaining optimal results with specialized applications sometimes requires crucibles of different shapes and sizes (Figure 4). Refractory materials, such as

titanium for instance, require extremely high temperatures (e.g., >2800°C) to reduce oxides (e.g., TiO_2) and decompose nitrides (e.g., TiN) during the inert gas fusion process. The graphite crucibles must be able to withstand these harsh conditions so double-wall and other "high temperature" crucible designs are available to prevent the sample melt from penetrating through the crucible walls. Likewise, "tall" crucibles help prevent the sample from creeping up and over the crucible walls during analysis.

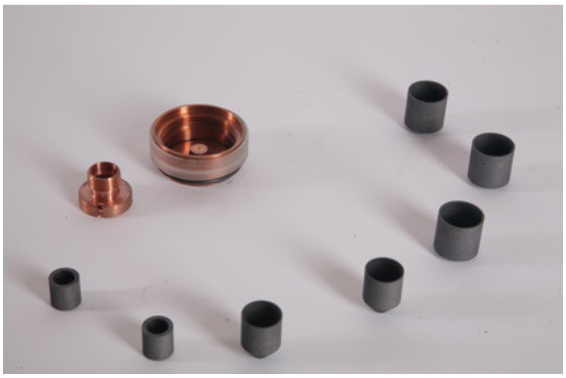

*Figure 4. **G8 GALILEO** upper (left) and lower (right) electrodes along with an array of graphite crucibles for special sample applications.*

Pins, granules, and many other sample configurations can be analyzed directly with IGF analyzers. Powder samples, however, if not contained can adhere to the interior walls of the sample introduction port. Fortunately, tin and nickel capsules are available to encapsulate the powder. These capsules also serve as a 'flux' to aid the gas fusion process by providing a thorough sample melt and improving the release of oxygen and nitrogen by lowering the melting temperature of the sample material by alloying. For refractory metal analyses the sample is embedded in a 1g nickel basket as an accelerator/flux. In general the flux should be added to the crucible in a 10:1 flux-to-sample mass ratio.

Graphite powder is another common additive, especially for the analysis of refractory materials, via IGF. Adding graphite powder to the crucible has a few benefits. It suppresses the volatility of the fusion process and inhibits the melt from boiling over the side of the crucible. The powdered graphite also provides reinforcement at the interior crucible base to prevent the hot, fluid sample melt from pooling and compromising the crucible bottom while also providing an excess of carbon.

Gas Dosing Calibration

The **G8 GALILEO**, like other IGF analyzers, primarily relies on the analysis of certified reference materials to generate a calibration curve for accurately determining the concentration of unknown samples. While a proven method, this can also prove time-consuming and expensive given the number of analyses required and the cost of reference materials. This is magnified by the fact that individual calibrations must be generated for each of the three elements: O, N and H. Fortunately the GALILEO provides a faster and cheaper alternative – automated gas calibration.

A gas calibration device (Figure 5) can be added to the **G8 GALILEO** that will generate calibration curves using only a gas supply (e.g., N_2 tank). No sample analyses are required and the furnace does not even need to be enabled. Best of all, the furnace stays clean and the need to clean after calibration is eliminated. The calibration device includes ten precisely machined divisions (i.e., volume aliquots), each sequentially larger than the previous one. By filling up an aliquot with pure gas (e.g., N_2) and transporting it to the detector the instrument effectively simulates the release of analyte (e.g., nitrogen) from an actual sample analysis. Applying this same procedure for all ten distinct volumes will simulate the analysis of ten reference materials, covering the full working range of the detector. Further, each of the elements can be calibrated with this approach: oxygen (CO supply), nitrogen (N_2 supply) and hydrogen (H_2 or He supply). Some applications, such as diffusible hydrogen that is described in the next section, actually require gas calibration because certified reference materials do not exist.

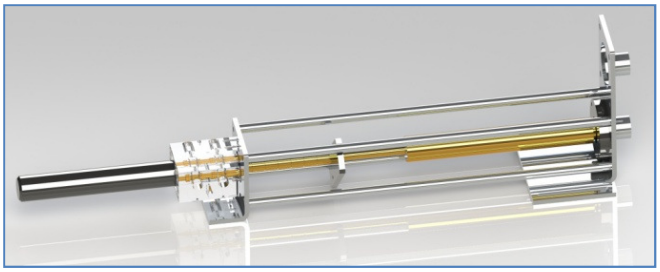

Figure 5. Gas calibration device for effortlessly calibrating the G8 GALILEO.

Diffusible Hydrogen

In addition to analyzing samples for total hydrogen content via inert gas fusion, the **G8 GALILEO** also features the unique ability to assess diffusible hydrogen content. Diffusible hydrogen (DH), which is essentially 'mobile', unbound hydrogen that can diffuse from the metal lattice at room temperature, has become an important evaluation parameter because of its direct influence on the structural integrity of materials. Because hydrogen is the smallest element it can easily penetrate into the metal lattice of materials during welding, casting, forging and other processes. The hydrogen can amass in large concentrated pockets and then leave massive voids when it diffuses from the material. Severe structural embrittlement can result through the formation of cracks and pores. The classification of these measurements, which are termed hydrogen embrittlement applications, has received considerable interest in literature and is readily tackled with the **G8 GALILEO**.

To measure DH an optional external infrared furnace (Figure 6) can be mated with the **G8 GALILEO**. The sample, such as a weld seam, is inserted into a quartz tube where it is rapidly heated with IR heating elements. The infrared heating provides direct heating of the sample material with a furnace that is fully programmable up to 900°C. The distinction with the technique provided by this external IR furnace is that the sample is rapidly heated, and not melted as with IGF, to accelerate the process of liberating DH. The liberated DH content with carrier gas is introduced into the **G8 GALILEO** and the stream flows through the aforementioned "Hydrogen Detection Path" (Figure 2) where the gases are purified and measured. Diffusible- and total-hydrogen content can be easily gleaned with this single analyzer combination rather than relying on two different instruments designed for each application.

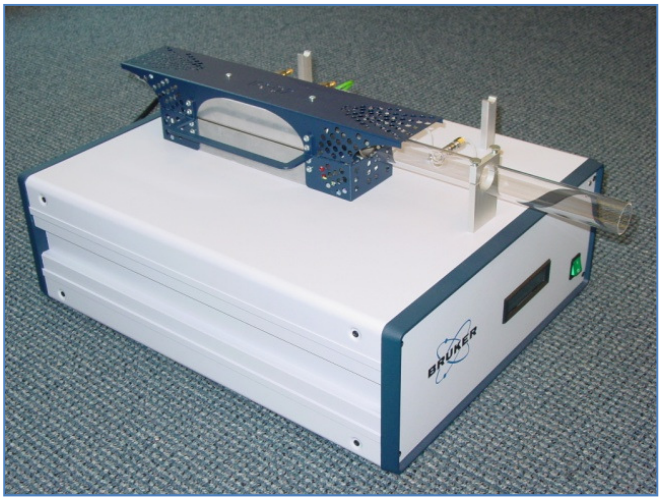

Figure 6. External infrared furnace for measuring diffusible hydrogen with the G8 GALILEO.

Automation

The **G8 GALILEO** features reliable options for automating the steps involved with analyzing samples and cleaning the furnace. For example, loading and removing graphite crucibles can be done with the "automatic crucible loader/removal" option. This features a pneumatically-driven robotic arm with small grippers (i.e., fingers) that swiftly pick up a new graphite crucible from a supply magazine and place it on the lower electrode. Once the analysis is complete the robotic arm automatically picks up the spent crucible and disposes it in a small collection bin.

The "automatic cleaning and dust extraction system" (Figure 7) is another significant time-saver that can improve sample throughput with the **G8 GALILEO**. Featuring a dual-brush system to clean the upper and lower electrodes, this cleaning device allows the user to perform other tasks around the laboratory instead of investing time in manually brushing the electrodes after analyses. An external vacuum cleaner effectively extracts the brushed, loose particulates (e.g., graphite dust) through an

integrated hose system and away from the furnace to keep the work area clean.

*Figure 7. Dual-brush system for automatically cleaning the electrodes in the **G8 GALILEO ON/H** (vacuum cleaner and integrated hose system not shown).*

When combined with the two aforementioned automated options, the additional "automatic sampler" provides a fully-automated IGF system. The autosampler dispenses samples and (if needed) flux into the sample port for up to twenty uninterrupted analyses.

While each of these automation options can be added separately, the combination of all three provides a reliable, virtually hands-free operation of the **G8 GALILEO** that can significantly improve sample throughput and provide valuable time for completing other tasks around the laboratory.

Software

The analysis software of the **G8 GALILEO ON/H** (Figure 8) shares commonality with all other gas analyzer products offered by Bruker. The primary tasks are organized into four individual screens to maximize convenience and productivity:

Analysis. This is the primary view and where samples are queued and analyzed, allowing the sample peak profiles to be viewed in real-time during each analysis.

Parameters. Configurations that control the sample combustion are defined and saved in this pane.

Statistics. This tab provides the ability to statistically evaluate the analysis results and generate sample reports.

Calibration. Screen which allows the instrument to be calibrated with results from pure substances or certified reference materials via single-point, two-point or multi-point calibrations.

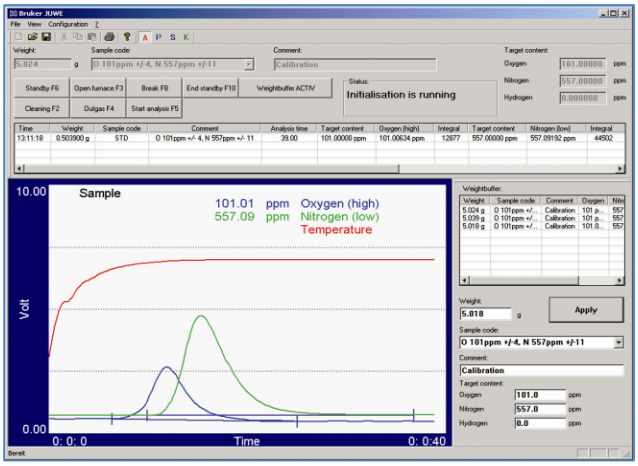

*Figure 8. Screen capture of the universal One-4-All user interface found on the **G8 GALILEO** and all other gas analyzers offered by Bruker.*

Applications

The **G8 GALILEO ON/H** can be used for numerous applications, as summarized in Table 1. The most common is steel and iron, which can be routinely analyzed with the **G8 GALILEO** in multiple configurations such as pins, granules or powder. Nickel-, iron- and cobalt-alloys are also readily analyzed with the **GALILEO.**

Recall that the **G8 GALILEO**, when combined with the external IR furnace, can measure the diffusible hydrogen content in many samples. Only the **GALILEO** and the Bruker **G4 PHOENIX DH**, the latter of which is dedicated to DH analysis, conform to the

*Table 1. Concise summary of sample applications that can be readily tackled with the **G8 GALILEO ON/H** analyzer.*

G8 GALILEO ONH - Applications		
Material	**O+N**	**H**
Metals		
Steel, Cast Iron	●	●
Pig Iron	●	●
Alloys	●	●
Non Ferrous-Metals	●	●
Aluminium	●	●
Titanium, Ti-Alloys	●	●
Zirconium, Zr-Alloys	●	●
Weld seams		●
Minerals		
Ores	●	●
Cermamics	●	
Glass	●	●
Inorganic compounds		
Salts	●	
Oxides	●	
Nitrides	●	
Other Materials		
Welding additives	●	●

requirements of the American Welding Society (AWS) 4.3 guideline. This includes the direct measurement of large sample sizes (e.g., up to 30 mm in diameter) and ability to print specially-configured post-analysis reports.

A **G8 GALILEO** and external quadrupole mass spectrometer (MS) hybrid system (Figure 9) has been developed and is commercially available for applications requiring ultra-low detection limits. The automotive industry has leveraged this advantage to assess hydrogen content in high-strength steels and alloys because of hydrogen embrittlement concerns. During the manufacturing process these thin alloy sheets can fatigue and crack as the material is contoured to fit the automotive frame. The GALILEO/MS hybrid, when combined with the external infrared furnace for DH, provides a complete hydrogen assessment at parts-per-billion (ppb) detection limits and the requisite capabilities for this automotive application.

*Figure 9. **G8 GALILEO ON/H** with external diffusible hydrogen module (upper right) and commercial mass spectrometer (lower right).*

Instrument Specifications

*Table 1. Instrument specifications of the **G8 GALILEO ON/H.***

Measuring Ranges*

Oxygen	
Low Range	0.1 – 250 ppm
High Range	200 ppm – 0.5%
Nitrogen	0.1 ppm – 0.5%
Hydrogen	0.01 – 1000 ppm

**Can be extended by adjusting the sample mass*

Analysis Time 50 s nominal**
***Sample mass and concentration dependent;*
Up to 60 mins for diffusible hydrogen measurements

Resolution 0.01 ppm

Precision/Reproducibility ±0.05 ppm / ±1% RSD**
***Sample mass and concentration dependent*

Carrier Gas

Nitrogen or Argon	99.999%, 29 psi
Helium	99.996%, 29 psi

Pneumatic Gas Air, oil & water-free, ~72.5 psi min

Water Cooling Approx. 4 LPM min.

Dimensions (w x d x h) 27.5 x 32.6 x23.6 in

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