FIRST ● Newsletter

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# Product Spotlight: G4 PHOENIX DH

## Assessing Diffusible Hydrogen to Avoid Embrittlement and Other Costly Failures

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### Introduction

Much like pesky termites attacking your home, hydrogen, being the smallest and lightest element on the periodic table, has very destructive capabilities. The result can range from a costly failure to a tragic, catastrophic event.

Hydroelectric power stations are commonly supplied with water from a nearby dam using sophisticated delivery systems. One such infrastructure is located in the Swiss Alps, routing water from the Grande Dixence Dam to the Bieurdron power station. Shortly after being brought online, a rupture occurred in the penstock compromising a 60-ft$^2$ section of the pipe. The massive surge of water, flowing at roughly 5,300 ft$^3$/s, devastated everything downstream of its path within a square kilometer – even claiming the life of three people.[1] The failure was linked to faulty weld seams with probable cause being delayed hydrogen-induced cold cracking as a result of diffusible hydrogen.

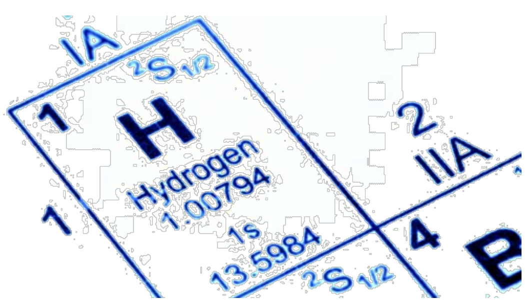


*Figure 1: Hydrogen properties as found on the periodic table.*

Source: Internet

Luckily most hydrogen-induced failures aren't this catastrophic. But even "minor" ones can prove problematic and costly. And fortunately steps can be taken to help prevent failures, such as assessing the material composition (e.g., hydrogen content) prior to distribution and eventual implementation.

### General Theory

#### Hydrogen

There are essentially two forms of hydrogen in metals, diffusible and residual, which together account for the total hydrogen content in a sample. Both forms are detrimental to physical properties of a material.

Diffusible hydrogen (DH) is "mobile" hydrogen that is released from the material at room temperature or even below over a period of time. The liberation process begins immediately upon fabricating the work piece and can continue for years. The release rate can be accelerated by heating the sample though a process termed "hot" extraction, which constitutes the principle for the G4 PHOENIX DH.

The remaining hydrogen in the sample, termed residual hydrogen (RH), is immobile "fixed" hydrogen that is bound to the metal lattice. This form of hydrogen is only released by melting the sample, such as through a "melt" extraction process, at temperatures sufficient to dissociate any hydrides present.

#### Diffusible Hydrogen

How can the lightest element on the periodic table have so much impact on material integrity? Because its diminutive size actually improves a hydrogen atom's ability to diffuse into the metal lattice through interstitial diffusion. Exposure of the material to air and moisture during casting, forging, welding and heat treatment are a few avenues for hydrogen to penetrate. Upon entering the lattice hydrogen atoms can combine in lattice dislocations, micro-voids, grain boundaries, etc. to form pockets of molecular hydrogen that can be extremely detrimental to the material. Since molecular hydrogen has a volume that is 26 times that of its atomic species an enormous internal pressure (up to 14,500 psi) is built up in the material, leading to premature formation of cracks and other imperfections already present in the material. These premature damages remain even after the hydrogen diffuses and the residual voids can lead to hydrogen-induced embrittlement, hydrogen-assisted cracking, flake formation, or pickling if the sample is put under sufficient stress (Figure 2).

*Figure 2: Crack formation as a result of diffusible hydrogen.*
Source: SLV (Duisburg, Germany)

**Preventing Failure**

How can the aforementioned hydrogen-induced failures be prevented? By controlling the sample fabrication process and subsequently quantifying the DH prior to distribution. Historically, DH has been assessed through a mercury-displacement technique where the sample is stored in a eudiometer at room temperature for approximately 72 hours. Liberated diffusible hydrogen displaces the medium (mercury) and the volume of displacement is used to estimate the amount of DH originally in the sample. The toxic nature of mercury combined with the long analysis times pushed the industry to seek a better alternative.

## G4 PHOENIX DH

Existing mercury displacement techniques are being replaced by a superior mercury-free alternative offered by Bruker. The G4 PHOENIX DH (Figure 3) is an analytical instrument capable of rapidly analyzing samples by using the hot extraction principle in combination with sophisticated detector technology.


*Figure 3: The G4 PHOENIX DH diffusible hydrogen analyzer featuring infrared- (top left) and resistance-based (top right) furnace options.*

**Diffusible Hydrogen Liberation**

The furnace of the G4 PHOENIX is used to rapidly heat the sample and hasten the hydrogen diffusion process. With this technique the DH can be liberated and measured in minutes instead of days.

Two furnace options (Figure 3) are available on the PHOENIX, both providing the ability to analyze solid samples without the need for boats and other accessories. The primary furnace option utilizes infrared (IR) radiation to rapidly heat the sample and is capable of reaching its maximum temperature of 900°C in a matter of seconds. Because the sample is heated rapidly and directly via IR, temperature ramping is possible; the advantage of which will be described in the

*Applications* section. The large diameter of the quartz combustion tube accommodates samples up to 30mm in diameter, conforming to AWS A4.3 and ISO 3690 requirements. The other furnace option, featuring a resistance-based heating principle, is capable of achieving higher temperatures (up to 1100°C) but with a slower response than the IR furnace.

**Diffusible Hydrogen Detection**

Once liberated from the sample the diffusible hydrogen must be quantified to provide the user a tangible result (i.e., concentration). With the G4 PHOENIX DH this is done using a sensitive thermal conductivity detector (TCD). Prior to reaching the detector the gas stream is swept through a reagent train to remove any possible contaminants, such as CO and $CO_2$, that could interfere with the detection of hydrogen and bias the results. The purified gas stream, consisting of evolved hydrogen and carrier gas (e.g., nitrogen), is then directed to the TCD where the amount of hydrogen originally present in the sample is quantified and displayed on-screen.

**Gas Calibration**

The analysis of samples with the G4 PHOENIX DH, as with most analytical equipment, requires that the instrument be calibrated to provide an accurate response (i.e., hydrogen concentration). With other Bruker gas analyzers this involves analyzing certified reference materials (CRMs) and establishing a calibration curve. But how can diffusible hydrogen CRMs exist if, as described previously, DH begins liberating immediately upon sample fabrication? In fact, they are not readily available because storage in liquid nitrogen conditions is required to prevent the hydrogen from liberating. For this reason the PHOENIX has been designed with a clever alternative to sample calibration – gas dosing. Using an integrated gas calibration device (Figure 4), consisting of 10 precisely-machined divisions (i.e.,

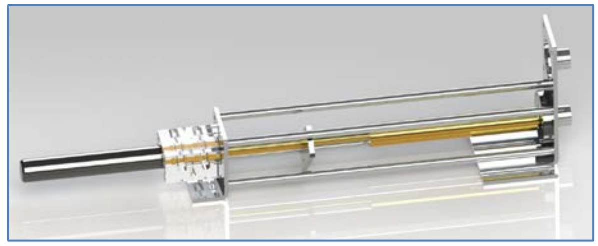

*Figure 4. Gas calibration unit for effortlessly calibrating the G4 PHOENIX.*

volume aliquots), pure gas, such as helium or hydrogen, is used to simulate the release of hydrogen from 10 individual CRMs. The resulting "dose analyses" are then used as the requisite calibration points for ensuring an accurate response.

***One-4-All*** **User Interface**

The analysis software of the G4 PHOENIX DH (Figure 5) 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. Archived results and peak profiles can also be recalled.

*Parameters.* Configurations that control sample analyses and gas calibrations 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 gas doses via single-point, two-point or multi-point calibrations.

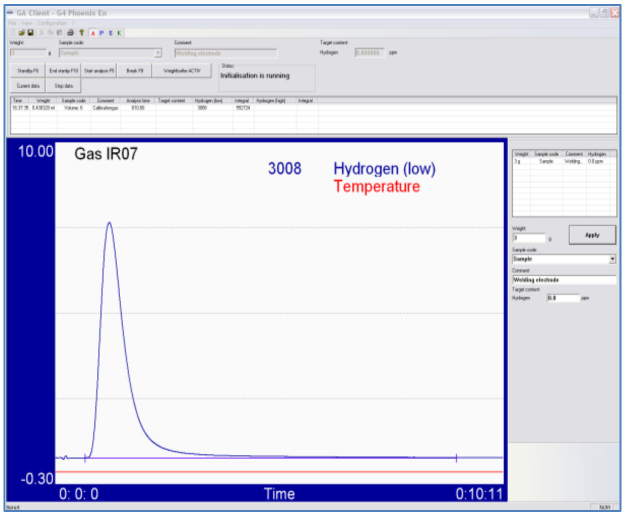


*Figure 5: Screen capture of the universal One-4-All user interface found on the G4 PHOENIX DH and all other gas analyzers manufactured by Bruker.*

## Applications

### Welding

One of the most common applications for the G4 PHOENIX DH is the analysis of weld seams as the welding process provides a conduit for hydrogen to penetrate. Weld "coupons" can be analyzed directly with the PHOENIX if they are prepared according to AWS A4.3 requirements. The aforementioned Grand Dixence Dam tragedy is an example where the assessment of DH in weld seams may have prevented such a tragedy.

### High-strength steel

The special mechanical properties of high-strength steel make it a great candidate for use in automotive applications where maximizing strength and minimizing weight are paramount. However, the nature of these steels makes the material susceptible to hydrogen-induced cracking upon being formed for the body of the automobile. Accordingly, automotive companies are incorporating the PHOENIX into their laboratories to assess the material prior to transfer to production assembly lines.

### Temperature Ramping and Gradients

The versatile software provided with the G4 PHOENIX allows samples to be analyzed isothermally or with temperature gradients. Ramping the temperature during an analysis has

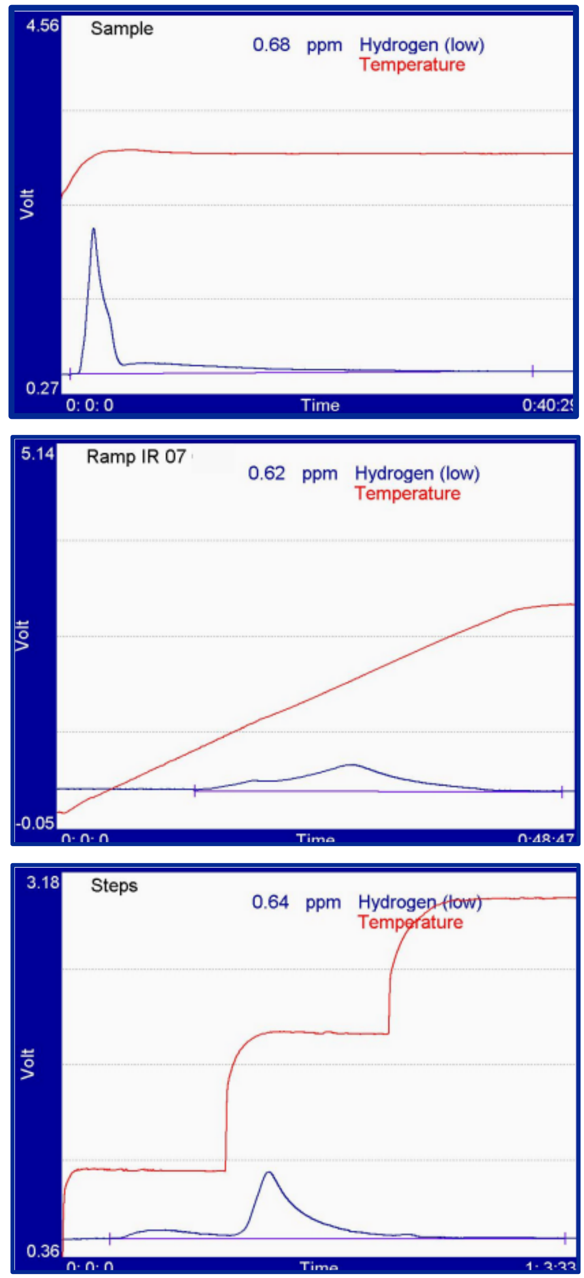


*Figure 7: Steel sample analyzed with isothermal conditions (upper), temperature ramping (middle) and temperature gradients (lower) as a function of time. Note: Red profile indicates temperature and blue profile indicates hydrogen response.*

shown that different forms of diffusible hydrogen can be sequentially liberated. Note the analysis of steel in Figure 7 in which a single hydrogen peak is discovered when a constant temperature is applied during analysis (Figure 7, upper figure). Now compare this to hydrogen profiles obtained with temperature ramping and gradients (Figure 7 middle and lower figures, respectively). Multiple forms of DH are discovered in these latter two cases as a result of differing activation energies. This ability to speciate diffusible hydrogen provides additional information about the sample composition and integrity.

## Special Configurations

### Mass Spectrometer

While the G4 PHOENIX DH provides an ideal solution for gleaning DH content in a wide array of samples, the sensitivity has been extended to extraordinary levels by combining it with a mass spectrometer (Figure 8). This technique of thermal desorption mass spectrometry (TDMS) utilizes the PHOENIX to liberate DH and then purify the gas stream prior to introduction into the MS. With this unique hybrid configuration the detection limit can be improved by an order of magnitude. Note the mass spectrum shown in Figure 9, where parts per billion (ppb) detection limits are achieved. These low detection limits are especially beneficial for the aforementioned high-strength steel applications in which even trace amounts of hydrogen can compromise the thin sheet metal.


*Figure 8: The G4 PHOENIX DH with optional mass spectrometer.*

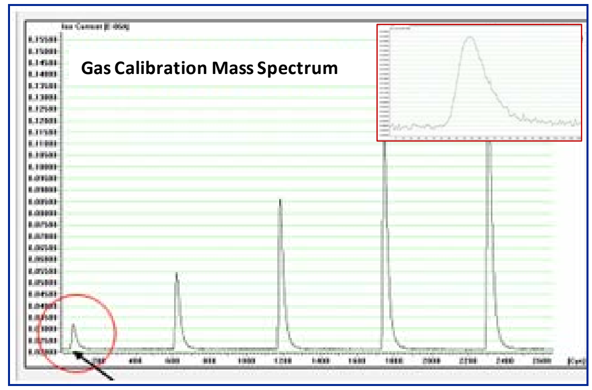


*Figure 9: Mass spectrum collected with the G4 PHOENIX-MS hybrid analyzer.*

### Complete Hydrogen Solution

As mentioned in the introduction section of this article any hydrogen trapped in a sample can negatively impact sample integrity. What if not only diffusible hydrogen, but also residual and/or total hydrogen information is desired? The G4 PHOENIX DH cannot deliver total hydrogen results but the G8 GALILEO inert gas fusion analyzer offered by Bruker certainly can. Operating on the melt extraction principle, the G8 GALILEO can melt samples at high temperatures (e.g., >2800°C) and report the total amount of hydrogen liberated. Combining the GALILEO with an external IR furnace module, similar to that found on the G4 PHOENIX, provides a complete solution for hydrogen assessment. A sample is placed in the external IR furnace and the liberated DH is introduced into the G8 GALILEO where it is quantified with a thermal conductivity detector. Or the sample can be analyzed directly with the GALILEO and the total hydrogen content quantified. This provides a single instrument solution for hydrogen assessment instead of dedicating separate analyzers for diffusible- and total-hydrogen, respectively.

The G8 GALILEO can also be combined with a mass spectrometer to provide outstanding detection limits for total hydrogen and/or diffusible hydrogen. Further, the GALILEO can be configured for oxygen and nitrogen detection capabilities as well.


*Figure 10: The G8 GALILEO ONH analyzer with external IR furnace (upper right) and mass spectrometer (lower right) with ultra-low total hydrogen assessment capabilities.*

**Instrument Specifications**

*Table 1. General instrument specifications of the G4 PHOENIX DH.*

| | |
|---|---|
| **Measuring Range*** | 0.05 – 1000 mL/100g *or* ~0.05 – 1030 ppm |
| **Can be extended by adjusting the sample mass<br>-Low measuring range with MS: ~50 ppb* | |
| | |
| **Analysis Time**** | 3 – 120 mins, nominal |
| ***Sample mass and concentration dependent* | |
| | |
| **Resolution** | 0.0001mL/100g *or* ~0.0001 ppm |
| | |
| **Reproducibility** | ±0.05 ppm or ±1% RSD, depending on sample |
| | |
| **Carrier Gas** | $N_2$, 99.999%, ~30 psi |
| | |
| **Dosing Gas** | Helium or Hydrogen |
| | |
| **Cooling Water** | 1.0 L/min minimum (IR furnace only) |
| | |
| **Dimensions and Weight** | |
| **Dimensions** (w x d x h) | 18 x 20 x 30 in |
| **Weight** | ~110 lbs |
| | |
| **Electrical Supply** | 230V ± 10%, 50/60 Hz, 16 A |

**References**


1. http://en.wikipedia.org/wiki/Bieudron_Hydroelectric_Power_Station



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