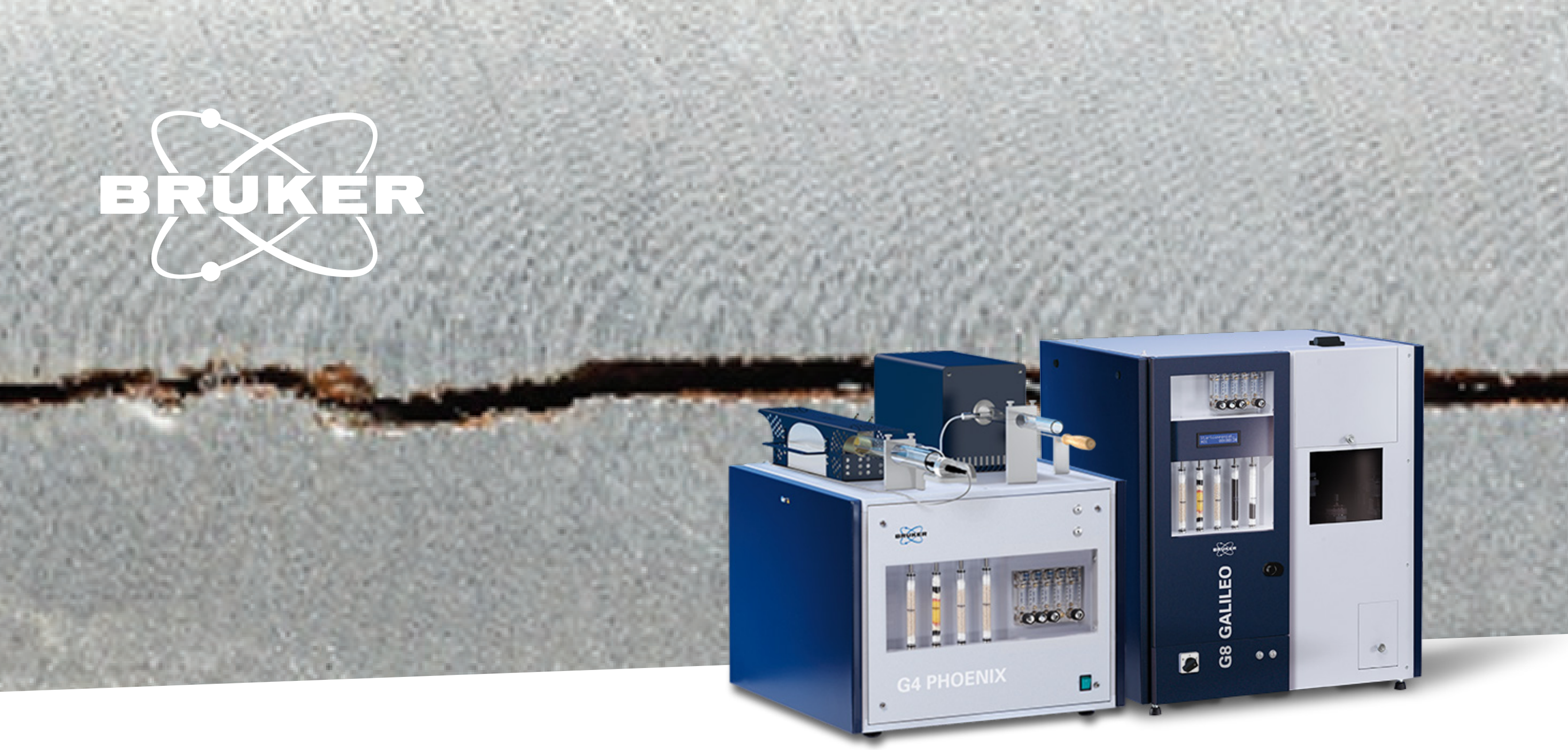


CS/ONH

Diffusible Hydrogen in Steel – addressing the analytical challenges

Application Note 002

Introduction

Hydrogen embrittlement is a widespread and dreaded phenomenon in the metal industry, especially affecting high-strength steels. Even without a visible indication of corrosion, it can lead to material failure.

There are three forms of hydrogen that can be present in a metal lattice:

1) diffusible hydrogen, which can freely move through the lattice,
2) reversibly trapped/weakly bonded hydrogen, or
3) irreversibly trapped hydrogen present in form of hydrides or within dislocation cores.

All these forms can contribute to hydrogen embrittlement, which in return can lead to material failure. However, in high-strength steels, diffusible hydrogen is considered to be mainly responsible for the loss of ductility and/or tensile strength, i.e., by hydrogen-induced cracking of the material. It can enter the material during production, post-production treatment, or environmental exposure and can freely move within the metal lattice. Therefore, it can diffuse out of the sample within a few hours or sometimes days, leaving space for hydrogen to re-enter the metal lattice at any given time. This makes it crucial to either determine the correct amount of diffusible hydrogen immediately after production or to properly store/seal samples (i.e., galvanization with zinc, storage in liquid nitrogen, or dry ice) until they can be analyzed.

Depending on the tensile strength of the steel, different hydrogen concentrations can be critical: at ≥800 MPa, hydrogen concentrations of <1 ppm can already result in hydrogen embrittlement, whereas at 300 MPa the material might be able to take in up to 100 ppm of hydrogen without failure. Hence, determining the amount of diffusible hydrogen is essential for process and quality control to avoid the consequences of hydrogen embrittlement. Both the **G8 GALILEO** combined with the external infrared furnace IR07, and the **G4 PHOENIX** provide an efficient and reliable means of determining the amount of diffusible hydrogen.

However, to develop a proper experimental setup to truly evaluate the effect of diffusible hydrogen, preparation techniques and storage must be accurately planned.

Objectives

This study investigates the effect of galvanization with zinc on storing the hydrogen content within the sample, by measuring galvanized and non-galvanized charged samples two and seven days after charging. The second part of the report focuses on the capability of absorbing hydrogen by simply "charging" blank samples with concentrated hydrochloric acid. In this report, we show that measurable differences can be resolved for different charging intervals.

Measuring Principle

The diffusible (<300°C) and/or reversibly trapped hydrogen (>300°C) content in solid samples can be determined by either the **G8 GALILEO** with IR07 or the **G4 PHOENIX**. They are both equipped with a quartz tube that is encased by an infrared furnace.

This infrared furnace is able to heat up the sample to max. 900°C either isothermally, in ramps, or in steps. The 30 mm in diameter quartz tube can hold samples of up to 28 × 200 mm. The detection system consists of a highly sensitive thermal conductivity detector (TCD) that can measure down to 0.05 ppm at 1 g sample mass. An optional mass spectrometer can be added, which increases sensitivity and can measure down to low ppb levels of hydrogen.

Chemical composition C45 Element	Range (%)
C	0.42-0.50
Mn	0.50-0.80
P	max. 0.045
S	max. 0.045
Si	max. 0.400
Ni	max. 0.400
Cr	max. 0.400
Mo	max. 0.100
Cr+Mo+Ni	max. 0.630

Sample Information

Provided and charged by: Ruhr-Universität Bochum (RUB), Fakultät für Maschinenbau, Institut für Werkstoffe, AG Werkstoffprüfung Prof. Pohl, Bochum, Germany.

Material: Heat-treated steel C45 (low-alloyed heat treatable steel with 0.42-0.5% carbon as the defining alloying element, used in i.e., automotive and mechanical engineering).

Treatment: The samples were heat treated to create a high-strength martensitic steel (approx. 1 300 MPa) with a good ductility. This is achieved by heat treatment at 850°C, subsequent quenching (in oil or water), and followed by tempering at 500°C (Q&T = Quenching and Tempering).

Shape and size: Cylinders with a diameter of 8 mm and a length of 30 mm, ~10-11 g sample weight.

Further preparation (RUB): 10 samples were charged with hydrogen in 18.5% HCl for 4 h. Charging of the samples was carried out without a promotor using corrosive charging. During charging the acid is stirred using a magnetic stirrer with a stirring bar to constantly supply fresh acid to the sample and to continuously remove corrosion products emerging from the reaction of the sample with the acid. After two hours h, the acid is renewed to ensure that a constant level of hydrogen is provided during the whole charging process.

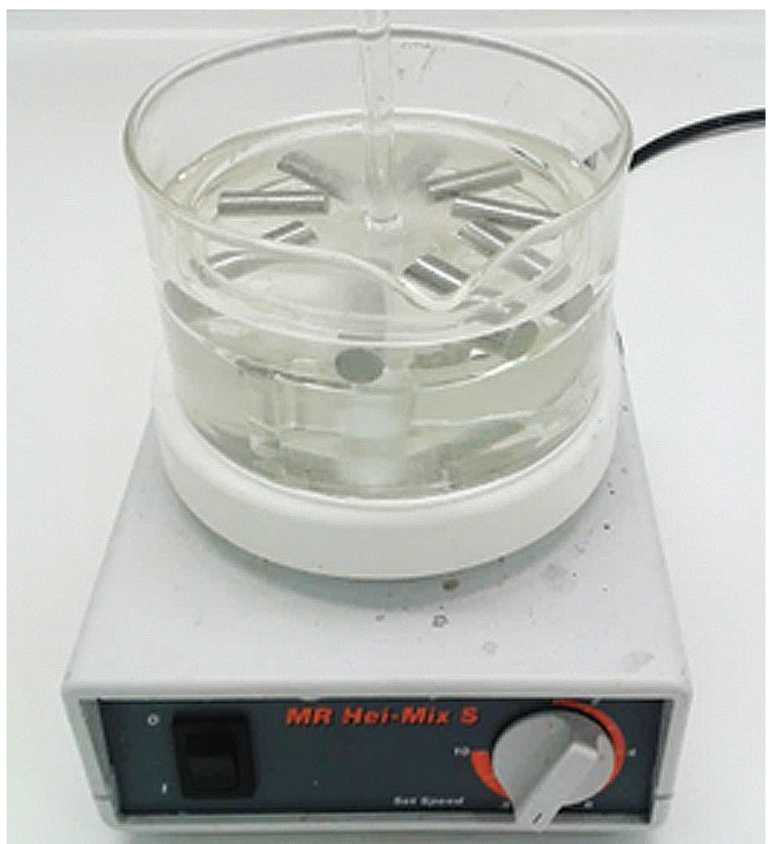


Fig. 1
Charging of nine samples in 18.5% HCl underuse of a magnetic stirrer (Source: Ruhr-Universität Bochum, Institut für Werkstoffe, Werkstoffprüfung).

Five of the ten charged samples were zinc-coated by galvanization, while the remaining five samples were left blank after charging. Eighteen samples were left uncharged (see Figure 2).

Figure 3 shows the experimental setup for galvanization as performed by Ruhr-Universität Bochum for this study. The sample is cathodically switched, while two zinc plates (99.99% Zn) are switched as sacrificial anodes. The sample and both zinc plates are covered in a zinc-bearing electrolyte (Zylite® HT Plus). The applied current density of the power supply was set to 20 mA/cm² and samples were left in this setup for 12-15 minutes each.

Zinc has a low hydrogen solubility, is easy to apply to the sample, and can also be easily removed. It is most commonly used as a corrosion protective coating, either being applied through galvanization (small parts like screws) or by hot-dip galvanizing (larger parts like railings or lampposts).

However, as an analytical tool to prevent diffusible hydrogen from degassing from the sample, only galvanization is sufficient. This can simply be explained by the microstructure of a galvanized vs. a hot-dipped galvanized sample. While galvanization creates an impermeable layer, hot-dip galvanizing results in the growth of longer crystals, creating a higher permeability (Figure 4). Thus, hydrogen can still diffuse out of a hot-dipped sample, while it can be preserved when galvanizing the sample.

Method parameters

Hot Extraction IR07		
Start delay	120 s	0°C
Max. of Startcomp.	10 s	
Analysis time	1500 s	300°C
Endcompensation	300 s	300°C
Max. of endcomp.	600 s	
Sample mass	10-11 g	

Fig. 2
Simplified illustration of the preparation procedure at Ruhr Universität Bochum.

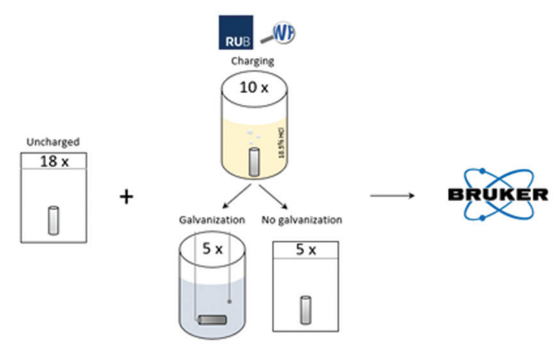
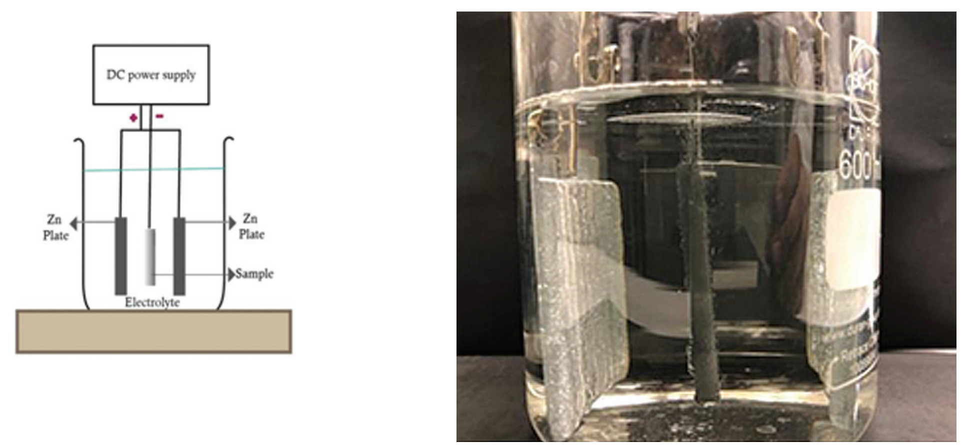


Fig. 3
Schematic illustration (left) and photograph (right) of the experimental setup for galvanization as performed for the samples analyzed in this study (Source: Ruhr-Universität Bochum, Institut für Werkstoffe, Werkstoffprüfung).



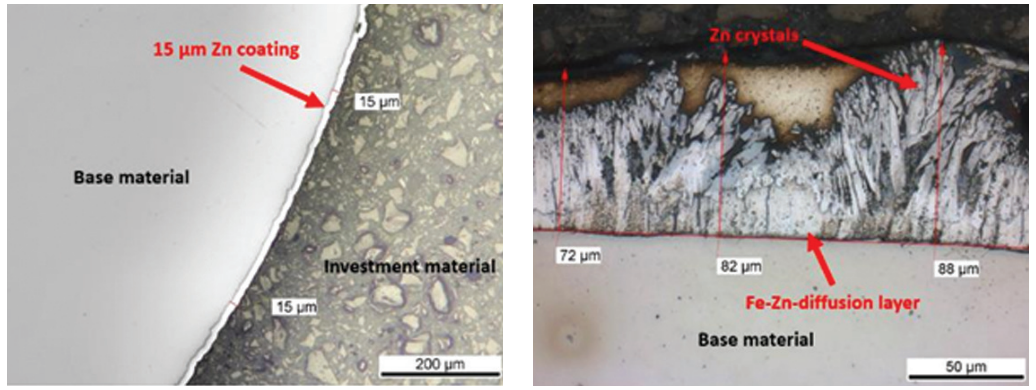


Fig. 4
Left: Base material steel with impermeable homogeneous 15 µm zinc coating resulting from galvanization as performed for the samples analyzed in this study.
Right: Base material steel with permeable inhomogeneous Fe-Zn diffusion layer and zinc crystals resulting from hot-dip galvanizing (Total thickness diffusion layer + crystals: 72-88 µm; Source: Ruhr-Universität Bochum, Institut für Werkstoffe, Werkstoffprüfung).

Calibration

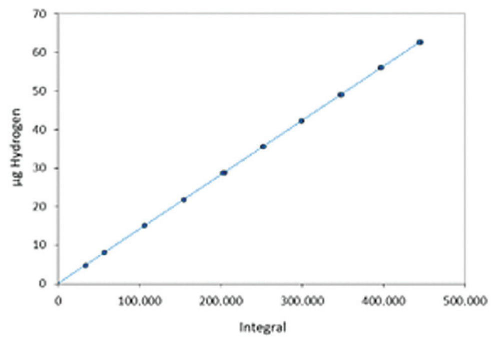


Fig. 5

Fig. 5
Plot of two cycles of ten calibration volumes with He calibration gas measured with the gas calibration unit of the G8 GALILEO with IR07, R^2 = 1.00, error bars smaller than symbols.

The system was calibrated using the onboard gas calibration. It consists of ten different volumes emerging from volume 1 to volume 10 (Figure 5), hence covering a wide calibration range that can be narrowed or extended by using different calibration gases.

The calibration volumes are automatically injected into the carrier gas stream and can be programmed via the software. To calibrate hydrogen, either 100% hydrogen, forming gas (5% hydrogen in nitrogen), or 100% helium gas can be used. In this study, the first 5 volumes and helium calibration gas were used, to which an empirically determined gas factor of 63.7 was applied.

Sample preparation and experimental setup

To avoid the influence of contamination, the furnace was pre-heated to 900°C and left to cool before the first measurement was carried out.

The first measurements were carried out two days after the samples were originally charged by RUB. After those two days, two charged galvanized samples and two charged and not galvanized samples were analyzed. Five days later (seven days after charging), the measurements of the charged samples were repeated on two new samples of each batch to show the influence of the differently prepared samples on the diffusible hydrogen content after certain time intervals.

Part 1 – Measurement of charged and uncharged samples from RUB

Blank measurements and charged samples (no galvanization)

Uncharged and charged samples that were not previously galvanized, were washed in high purity acetone, dried with a cold blow dryer, and were immediately analyzed using the above method parameters.

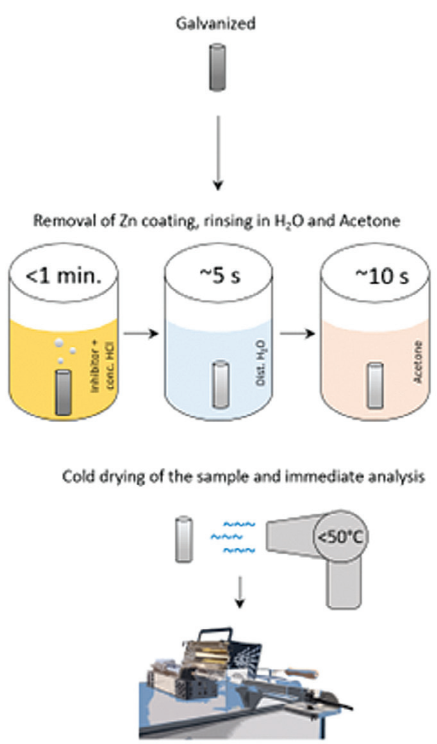


Fig. 6
Simplified illustration showing the steps from the removal of the zinc coating to the actual analysis.

Charged galvanized samples

To analyze the charged galvanized samples, the zinc coating of the samples must be removed first. If not removed, zinc can degas from the sample and contaminate the furnace during the analysis. Additionally, the zinc coating can contain hydrogen, thus making it impossible to reliably interpret the result of the diffusible hydrogen measurement. To remove the zinc coating without hampering the diffusible hydrogen content of the steel sample, one needs to use hydrochloric acid in combination with an inhibitor (i.e., hexamethylene-tetramine) that prevents hydrogen from degassing from the sample and prevents hydrogen from the acid entering the metal lattice.

200 ml of concentrated hydrochloric acid were mixed with 0.7 g of hexamethylenetetramine (=3.5 g/L). The galvanized samples were placed in the acid-inhibitor mixture until the zinc coating was completely removed. Within less than a minute, the zinc coating was visibly removed, and the reaction completed (no further degassing). After removal of the zinc coating, the sample was dropped in demineralized water (<5 s), afterward in high purity acetone (<10 s), and was dried with a cold blow dryer (Figure 8). The sample was then immediately analyzed. Removal of the zinc coating was carried out for every single sample individually and immediately before analysis.

Fig. 7
Photographs of blank samples (left) and charged not galvanized samples (right).

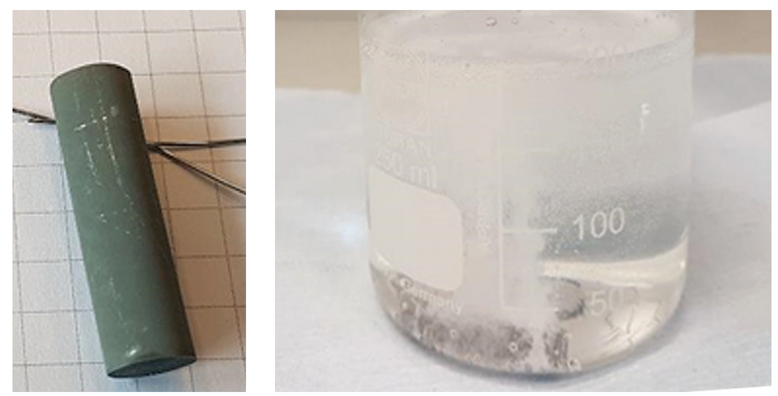


Fig. 8
Photographs of a charged galvanized sample (top) and during removal of the zinc coating in hydrochloric acid + Inhibitor (bottom).

Blank measurements		
Sample ID	Mass/g	Hydrogen/ppm
Blank 1	10.9342	0
Blank 2	11.5252	0
Blank 3	10.8623	0
	Mean[1)]	**0.00**
	STD[1)]	**0.00**

[1)] Mean = arithmetic average; STD = absolute standard deviation (1s)

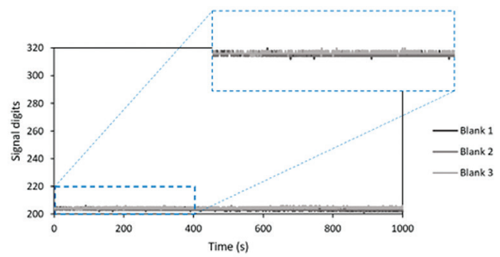


Fig. 9
Signal vs. Time plot of three blank measurements.

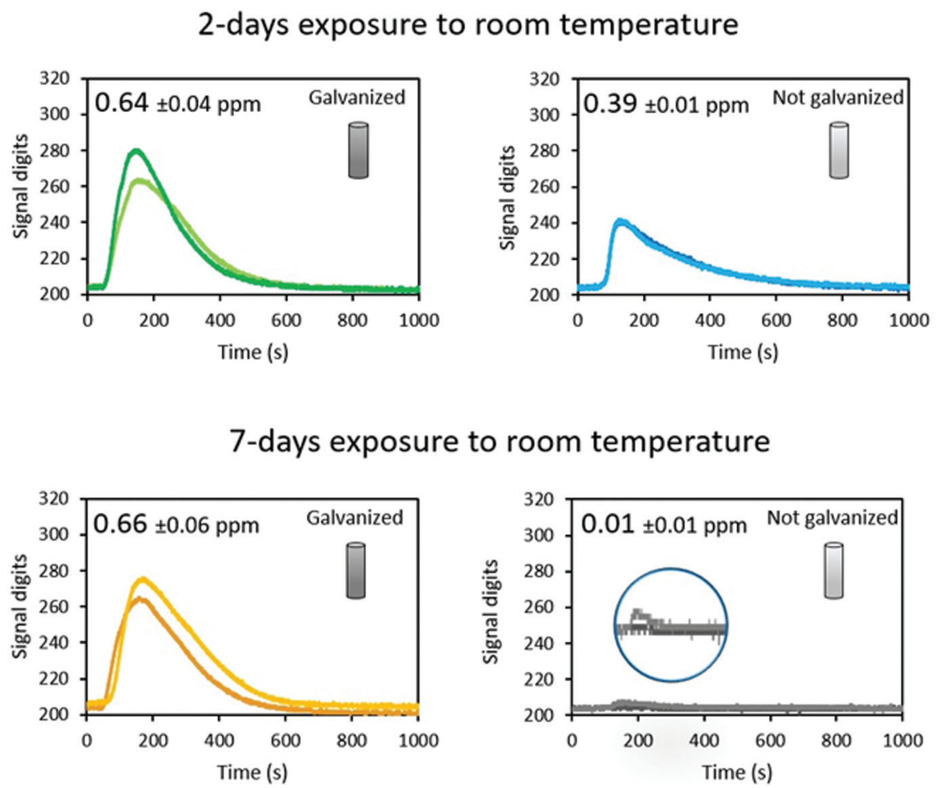


Fig. 10
Signal vs. Time plots for galvanized and not galvanized charged samples after 2- and 7-days exposure at room temperature.

Charged & galvanized			
2 days after charging		7 days after charging	
Mass/g	Hydrogen/ppm	Mass/g	Hydrogen/ppm
10.9377	0.61	11.1308	0.61
10.5543	0.67	10.4440	0.70
Mean[1)]	**0.64**		**0.66**
STD[1)]	**0.04**		**0.06**

[1)] Mean = arithmetic average; STD = absolute standard deviation (1s)

Charged & not galvanized			
2 days after charging		7 days after charging	
Mass/g	Hydrogen/ppm	Mass/g	Hydrogen/ppm
10.4040	0.39	11.2672	0.00
10.5459	0.38	10.3235	0.01
Mean[1)]	**0.39**		**0.01**
STD[1)]	**0.01**		**0.01**

[1)] Mean = arithmetic average; STD = absolute standard deviation (1s)

Summary part 1

This study on diffusible hydrogen shows the importance of correct sample preparation, storage, and analysis. Samples that were charged and galvanized preserved the hydrogen content for seven days without any loss. Samples that were not galvanized already lost ~40% of hydrogen after two days at room temperature and 100% after seven days at room temperature (Figure 10). Hence, galvanic zinc plating can preserve hydrogen inside a steel sample.

Nevertheless, the zinc coating needs to be carefully applied and removed to ensure that no hydrogen is lost or added during galvanization or chemical removal, making the use of an inhibitor indispensable. An even better way of storing samples long-term is storage in liquid nitrogen.

Figure 11 shows the results of a short study carried out by Ruhr-Universität Bochum, where samples were charged, stored, and periodically analyzed over different time intervals. When storing the samples at room temperature, the samples lose most of the hydrogen within two days; when using dry ice, the first noticeable drop of hydrogen can be observed after approximately four days; whereas in liquid nitrogen, hydrogen levels stay constant over two months.

For ideal results, we thus recommend either storing samples immediately after production/charging in liquid nitrogen or galvanizing the samples, unless they can be immediately analyzed.

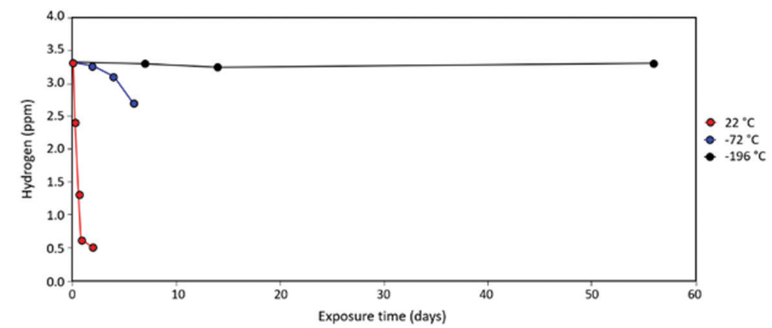


Fig. 11
Diagram showing the loss of hydrogen from the sample at different storage temperatures (22°C, -72°C, and -196°C) over several days (Source: Ruhr-Universität Bochum, Institut für Werkstoffe, Werkstoffprüfung).

Summary part 2
Charging at Bruker AXS and immediate measurement

From the original eighteen uncharged blank samples, three were analyzed as blank samples in part 1. Ten of the remaining fifteen samples were charged at Bruker AXS using concentrated hydrochloric acid. For charging, the samples were placed in acid for different time intervals.
Two samples were charged per time interval.

The first interval was 1 minute, the next two samples were charged for 5 minutes, then two for 15, 30, and 60 minutes, respectively (Figure 12). After charging, each sample was washed with distilled water, followed by high-purity acetone, and was then dried with a cold blow dryer before being analyzed. Between charging and analysis, no more than 5 minutes passed.

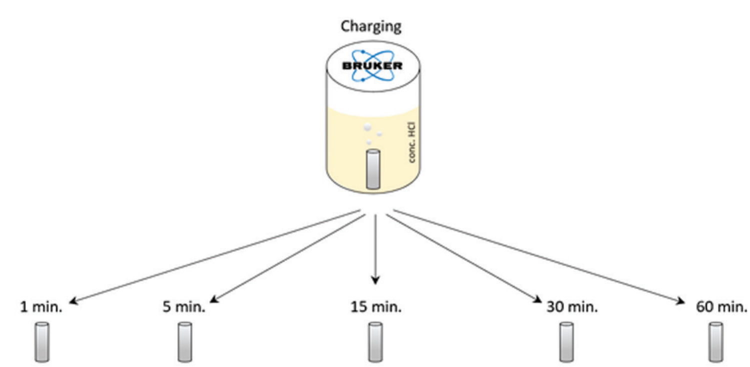


Fig. 12
Simplified illustration of charging blank samples at Bruker AXS.

Results part 2

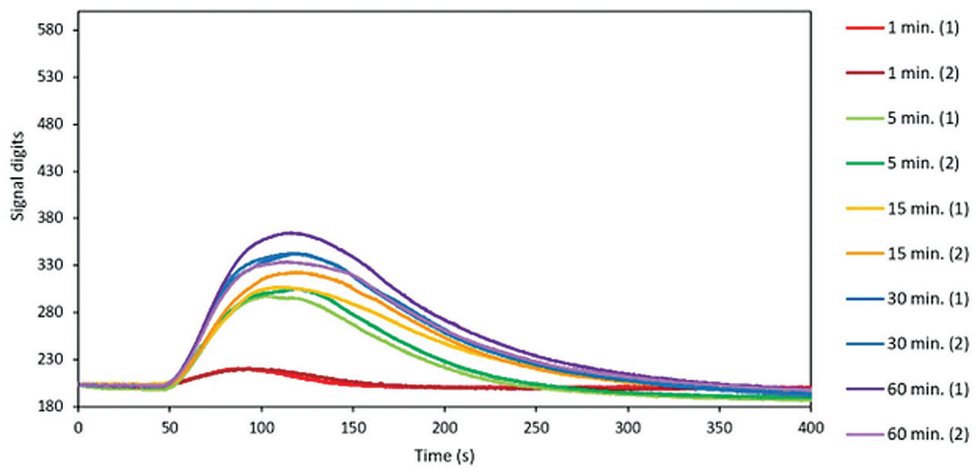


Fig. 13
Signal vs. Time plot for blank samples charged for different time intervals.

Blank samples charged at Bruker		
Charging time	Mass/g	Hydrogen/ppm
1 min.	10.2596	0.05
1 min.	11.2141	0.06
5 min.	11.2334	0.45
5 min.	11.2507	0.48
15 min.	10.7152	0.61
15 min.	10.8402	0.68
30 min.	10.7114	0.82
30 min.	11.4489	0.79
60 min.	10.5722	0.96
60 min.	10.4267	0.82

Summary part 2

Charging of samples can be carried out in many ways, the most successful being electrochemical charging underuse of a promoter. However, this study shows that a sample can also ab-/adsorb significant amounts of hydrogen by simply being placed in concentrated hydrochloric acid. Even after one minute of exposure to acid, the blank samples ab-/adsorbed ~0.05 ppm of hydrogen. A more significant increase can be observed after five minutes, where the concentration increases to ~0.45 ppm. Between 30- and 60-minute charging times, there is no significant difference or increase observed and the diffusible hydrogen concentration levels off at around 0.8-1.0 ppm (Figure 14). Reasons for this could be that the acid loses its capability of providing enough hydrogen and/or it can be due to a change in diffusion rate, as most of the hydrogen will be ab-/adsorbed surface-near while the central part of the sample remains almost free of diffusible hydrogen using this charging technique. In addition to that, corrosion products can hinder hydrogen from entering the metal lattice if no magnetic stirrer is used. Caution: samples should not be stored in concentrated hydrochloric acid for long periods of time, due to the corrosive effect of the acid which in return will influence the hydrogen intake and hence the results. Therefore, charging samples solely with hydrochloric acid is not the ideal technique to evaluate a sample's full capability of absorbing hydrogen.

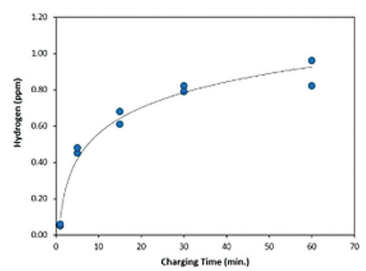


Fig. 14
Hydrogen in ppm plotted against the charging time in minutes.

This study demonstrates that the G8 GALILEO with IR07 or alternatively the G4 PHOENIX are ideal solutions for quality and process control for metal industries affected by hydrogen embrittlement caused by diffusible or reversibly trapped hydrogen. Their high precision, temperature control, and ease of use, make them vital and reliable tools for hydrogen analysis.

The G8 GALILEO further provides the possibility to measure oxygen, nitrogen, and hydrogen by inert gas fusion and allows a variety of modular system modifications. For further information, please refer to our brochure or contact Bruker directly.

Acknowledgements

Special thanks go to Mr. Jens Jürgensen and his colleagues from the AG Werkstoffprüfung Prof. Pohl of Ruhr-Universität Bochum for providing the samples and images, for many interesting discussions and new insights into the world of diffusible hydrogen.

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