Talanta 125 (2014) 257–264

Contents lists available at ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

An electrochemical calibration unit for hydrogen analysers

Sergiy V. Merzlikin [a,b], Andrea M. Mingers [a], Daniel Kurz [a], Achim Walter Hassel [b,*]

[a] Max Planck Institute for Iron Research, Max Planck Str. 1, 40625 Düsseldorf, Germany
[b] Institute for Chemical Technology of Inorganic Materials, Johannes Kepler University Linz, Altenberger Str. 69, 4040 Linz, Austria

ARTICLE INFO

Article history:
Received 22 July 2013
Received in revised form
30 January 2014
Accepted 4 February 2014
Available online 12 February 2014

Keywords:
Hydrogen
Deuterium
Analysis
Electrochemical calibration
Melt extraction

ABSTRACT

Determination of hydrogen in solids such as high strength steels or other metals in the ppb or ppm range requires hot-extraction or melt-extraction. Calibration of commercially available hydrogen analysers is performed either by certified reference materials CRMs, often having limited availability and reliability or by gas dosing for which the determined value significantly depends on atmospheric pressure and the construction of the gas dosing valve. The sharp and sudden appearance of very high gas concentrations from gas dosing is very different from real effusion transients and is therefore another source of errors. To overcome these limitations, an electrochemical calibration method for hydrogen analysers was developed and employed in this work. Exactly quantifiable, faradaic amounts of hydrogen can be produced in an electrochemical reaction and detected by the hydrogen analyser. The amount of hydrogen is exactly known from the transferred charge in the reaction following Faradays law; and the current time program determines the apparent hydrogen effusion transient. Random effusion transient shaping becomes possible to fully comply with real samples. Evolution time and current were varied for determining a quantitative relationship. The device was used to produce either diprotium (H_2) or dideuterium (D_2) from the corresponding electrolytes. The functional principle is electrochemical in nature and thus an automation is straightforward, can be easily implemented at an affordable price of 1–5% of the hydrogen analysers price.

1. Introduction

High strength steels [1–3] and steels for critical applications, such as pipe lines [4–6], or parts in aggressive aqueous environments [7–9] are highly susceptible to hydrogen embrittlement. The sources of hydrogen are different in nature, some being uptake during acid pickling and electroplating [10,11], welding [12,13], corrosion [14], galvanic coupling [15,16], cathodic protection [17], tribochemical reactions [18], and others more. Higher hydrogen concentrations enhance the risk of hydrogen embrittlement resulting in the continuous or sometimes sudden degradation of the mechanical properties, such as strength and ductility. This leads to a shorter lifespan of steel products and possible critical failures of the material. Quantification of hydrogen in metals for industrial applications and in laboratory tests is one the key parameters to predict the risk or probability of hydrogen induced embrittlement. Reliable analysis of the hydrogen concentration inside the steel is therefore of great importance.

The melt extraction technique is being widely used for the analysis of total hydrogen contents of steels [19,20]. In this method a sample is heated up to 2500–3000 °C inside pyrocoated graphite crucible using an electrical impulse furnace. Released gases such as hydrogen and oxygen are fed into the thermal conductivity detector or infrared detector [19] by means of a carrier gas (usually nitrogen). The melt extraction with carrier gas has found widespread industrial application due to the uncomplicated design making routine hydrogen analysis at ambient pressure fast and cheap as compared to (ultra high vacuum) UHV-based techniques, like TDA (thermal desorption analysis) [21–23]. Most steel plants have some kind of online analysis system in which hot samples from the production process can be analysed during production.

Typically the sample is put into the inner one-way crucible situated inside the outer reusable crucible, placed between two dc electrodes. The sample is being molten during the analysis and analytes are transported by the carrier gas into the detector. This determination technique can be also employed in analysing coated steel sheets. A large number of influencing factors such as sample preparation, cleaning, treatment, coating removal and others more were thoroughly investigated and compared using various Round Robin tests in a European multi partner project that was recently concluded [24]. Parts of this work have been made public in the course of this comprehensive project [25,26].

The instruments used in melt extraction analysis are usually being calibrated either by gas calibration or with certified reference

---

* Corresponding author. Tel.: +43 73 224688700.
E-mail address: talanta@elchem.de (A.W. Hassel).

http://dx.doi.org/10.1016/j.talanta.2014.02.008
0039-9140

materials (CRM's) of stable and precisely known hydrogen concentrations. To perform the gas calibration, a gas dosage valve adjusted to some fixed volume and filled with helium is used. Helium, having a very similar thermal conductivity as hydrogen, is normally used due to the cost reasons to save CRM's and security restrictions and explosion danger attributed to the work with hydrogen gas. Certified reference materials, usually titanium alloys pre-charged with known amounts of hydrogen, which are stable over long periods of time, are being proposed on the market from different companies. A number of certified hydrogen concentrations are available. Both calibration methods have their pros and cons.

Disadvantages are

- difficulties with an exact measurement of the calibration gas' volume
- coefficients are needed to correct the differences in the thermoconductivity
- wide ranges of possible hydrogen concentrations are not covered with the CRM's
- time stability of CRM's
- high purchasing costs of CRM's
- irregularities with their charging
- strongly pronounced tailing of hydrogen transients from metallic samples to name only a few

To overcome these limitations an electrochemical calibration method for hydrogen analysers was developed and employed in this work. Exactly quantifiable amounts of hydrogen can be produced in an electrochemical reaction and detected by the hydrogen analyser. The amount of hydrogen is exactly known from the transferred charge in the reaction following Faradays law; and the current time program determines the apparent hydrogen effusion transient.

2. Experimental

2.1. Setup

All of the measurements were carried out using either an *Eltra* OH 900 gas analyzer (Fig. 1) or a *Leco* RH 402 gas analyzer both equipped with a thermal conductivity detector. The samples are molten inside the graphite crucible at approximately 2200 °C. Hydrogen and oxygen diffusing out from the melt are transported to the detector with a nitrogen carrier gas. Carrier gas is pre-cleaned using a packed bed of sodium hydroxide and with magnesium perchlorate, respectively, to remove CO_2 and any moisture correspondingly, prior to entering the furnace. Potentially transported dust particles are removed by quartz wool in the dust trap. Oxygen reacts to form CO on the surface of the hot crucible and further reacts to form CO_2 in the presence of a catalyst (I_2O_5 on silica). In this way oxygen is detected as its reaction product CO_2 in the IR-cell. Afterwards it is being absorbed by NaOH to prevent it from entering the thermal conductivity detector. The carrier gas then again passes CO_2- and H_2O-traps on its way to the detector, where hydrogen containing in the carrier gas is detected.

The instrument was calibrated to hydrogen using one point calibration with helium and, additionally, this calibration was tested with standard hydrogen-impregnated material from *Leco*. CRM's with certified hydrogen mass fractions $c_{(H2)}=(1.8\pm0.4)$ $\mu g\ g^{-1}$ and $c_{(H2)}=(6.0\pm0.2)\ \mu g\ g^{-1}$ were used. After that the instrument was reconnected so that the carrier gas was sucked from the electrochemical cell. The normal operational parameters of the analyser were used.

The scheme of the electrochemical setup attached to the Eltra analyser is shown in Fig. 2.

The electrochemical cell is a U-shaped glass tube (see Fig. 2) with its two compartments being separated by a frit. As a non-deuterated electrolyte 0.5 M H_2SO_4 (*Merck, 96%, p.A.*) was used. The 0.5 mol l^{-1} deuterated electrolyte was prepared from D_2O (*Merck, 99.9%*) and D_2SO_4 (*Merck, 96% acid content in D_2O*). Counter and working electrodes with an area of 0.1 cm^2 were made of Pt-wire (99.999%). CompactStat potentiostat (*Ivium technologies*) with integrated power booster was used to control the galvano- and potentiostatic experiments, integrated *IviumSoft* software was used for data management and analysis. Nitrogen gas enters both compartments of the cell at a constant flow rate of 10 l h^{-1} through two glass capillaries connected to the flow meter. In the left cell compartment, where oxygen evolution takes place at the counter electrode, the nitrogen gas flushes the oxygen out of the cell through the opening. In the right compartment, where the hydrogen evolves at the working electrode, the nitrogen is used as carrier gas to transfer the hydrogen into the hydrogen analyser.

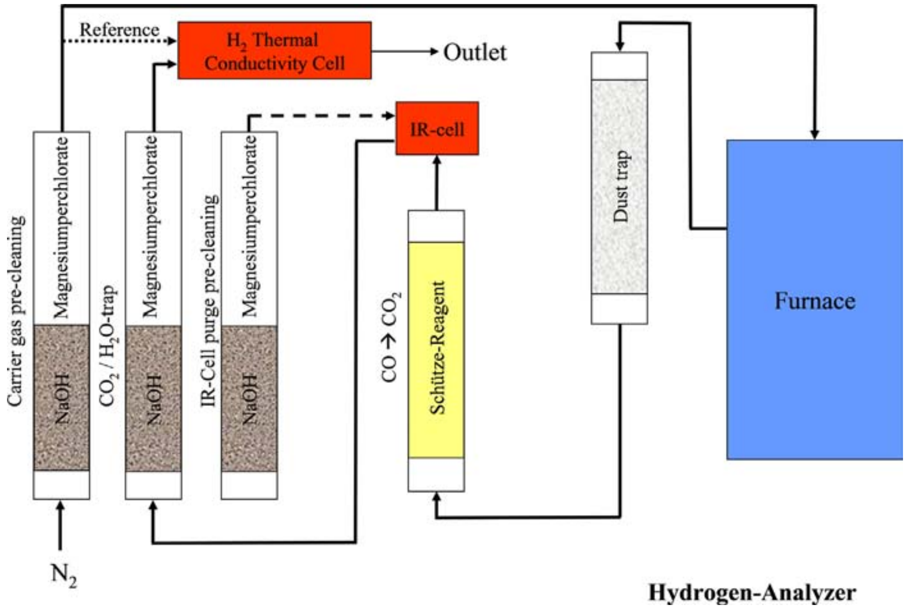

Fig. 1. Flow scheme of Melt extraction hydrogen analyser Eltra OH900 adapted from producers documents.

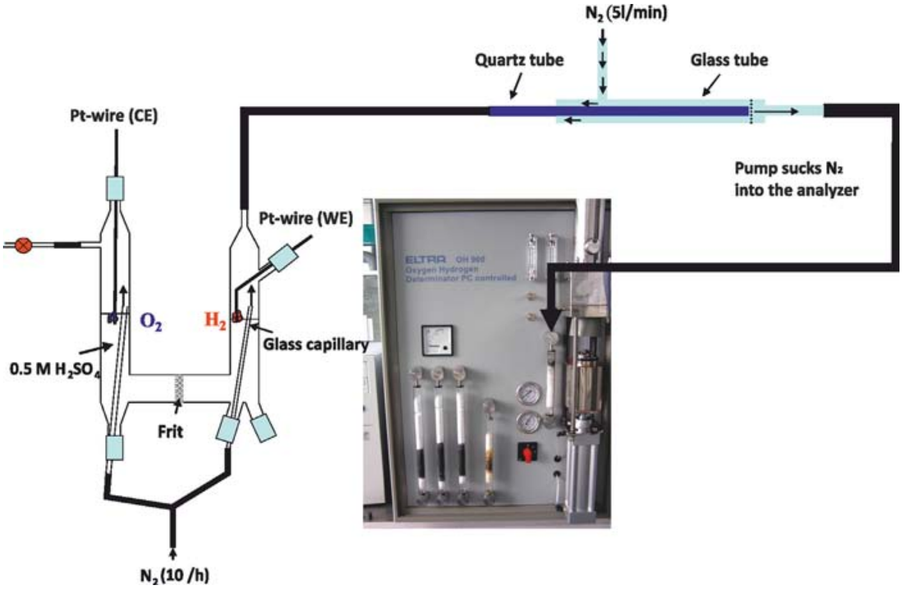

Fig. 2. Scheme of the electrochemical calibration cell connected to the hydrogen analyser.

Proper positioning of the capillary is highly important to allow for a timely transport of the hydrogen. This aspect is of particular importance if an artificial shaping of the hydrogen effusion is required. The hydrogen-nitrogen outlet is connected to the electrochemical device at the inlet where usually the furnace gas input is connected. The hydrogen analyser constantly transports nitrogen into the device with the help of a pump. The difference between the experiment and normal operation of a hydrogen analyser such as the Eltra OH900 is that the gas, which is sucked in, is not coming from the furnace but from the electrochemical cell. The evolved hydrogen is led through a flexible Viton feeding to a quartz tube, which is placed inside a glass tube that is open on one side. The latter glass tube enables to operate the whole set-up at atmospheric pressure, using the flux of nitrogen at 5 l min^{-1} as a barrier to prevent the inflow of ambient air. The open tip of the quartz tube is placed in the outer glass tube deep enough beyond the barrier gas region to assure produced hydrogen is being sucked quantitatively into the analyser and not flushed out.

3. Results and discussion

A typical sample weight in hydrogen determination in metallic samples is 1 g. Calibration standards are often used to cover a range of up to e.g. 10.0 ppm, which is equal to 10.0 μg g^{-1} of hydrogen. For calculating the amount of electrical charge required to evolve 10 μg of hydrogen, Eq. 1 can be used:

$$Q = \frac{m(H_2) \times z \times F}{M(H_2)} \quad (1)$$

where: Q is electrical charge, z is the stoichiometric equivalent number and F is the Faraday constant, $m(H_2)$ is the weight of hydrogen formed and $M(H_2)$ is the molar mass. Computing these values yields a charge of 0.96 C to produce 10.0 μg of hydrogen (diprotium). At this point it does not matter whether the charge is transferred under galvanostatic or potentiostatic conditions and during which time or current density. The same amount of charge is required to produce either H_2 (diprotium) or D_2 (dideuterium) from hydrogenated or fully deuterated electrolyte solutions. The term “amount” refers to the molarity therefore the mass of D_2 formed from the same amount of charge is twice as large as that of diprotium because of the doubled atomic weight.

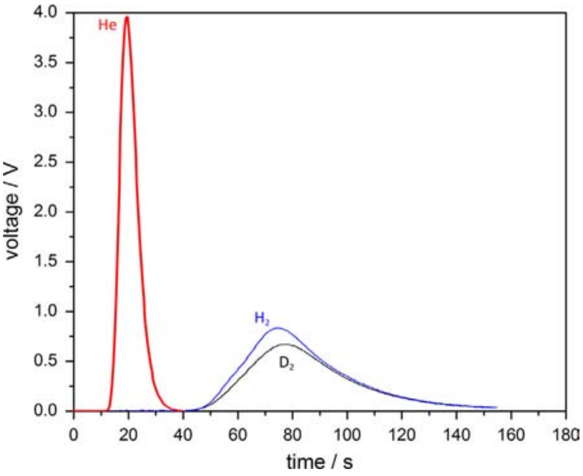

Fig. 3. Gas signal intensity as a function of time for calibration helium (injected), deuterium and hydrogen peaks (galvanostatic electrochemical hydrogen production −30 mA during 32 s).

Fig. 3 shows the gas signal as a function of time. As compared to the relatively sharp and short helium signal that results from the almost instant injection of helium the signals from electrolysis are retarded and smeared out. An extrapolation of the rising edge of the 3 peaks yields delay times of 12 s for He and 44 s for H_2 and D_2. This delay time is the time required for the gas to reach the detector and involves the entire series of dead volumes such as tubes, pipes, packed beds etc. This time is already longer for the electrolytically produced gases as they have to pass through densely packed dust trap and approximately one meter long gas tube, whereas the He gas inlet is situated after that section directly at the entrance to the catalyst packed bed. Such a short entrance can also be used for hydrogen determination from material that is held at elevated temperatures over longer periods in time for a smooth and selective out gassing of diffusible hydrogen [27]. The second effect observed for the hydrogen species is that the signal is smeared out. Obviously the retardation would be at least as long as the electrolysis time itself, which is 32 s in this experiment. Furthermore a tailing is observed for the signals which are comparable for H_2 and D_2.

This is an interesting effect that can be of use to simulate various kinetics of hydrogen effusion from different types of samples by changing the duration of the electrolysis or to intentionally shape the electrolysis program. In some cases the time of hydrogen appearance in the transient results from the particular source. Residuals on the surface such as oil, lubricants, water, but even traces of hydrogen containing solvents may yield hydrogen immediately after heating, bulk hydrogen on the other hand may take a bit longer to appear in the gas stream as it has to first diffuse out from the solid [28].

3.1. Determination of the standard deviation

3.1.1. Electrochemical experiments with non-deuterated sulphuric acid

The standard deviation of hydrogen and deuterium amount detected during potentiostatic and galvanostatic modes of electrochemical cell operation was measured with reference to the helium calibration. The results and the experimental conditions for hydrogen are shown in Table 1.

The measured mean value of the consumed charge in the galvanostatic experiment corresponds exactly to the calculated value, since galvanostatic operation means constant current for a predefined duration. There is a small deviation between these values in the potentiostatic experiment, because the current (i.e. consumed charge) may vary during the experiment. The theoretical hydrogen content was calculated from the transferred charge and was compared with the measured mean value. The deviation in charge may be overcome if an electronic integrator is used so that the electrolysis is halted as soon as the target value is reached, alternatively the potentiostat could be used to make a real time numerical integration with the same halt condition.

3.1.2. Electrochemical experiments with deuterated sulphuric acid

The standard deviation was determined under the same test conditions used for hydrogenated electrolyte. From Eq. (1), the mass of deuterium produced by the charge consumption to produce 10 μg hydrogen is equal to 20.03 μg (or 4.97×10^{-6} mol) with respect to the molar mass. The volume of deuterium formed under these experiment's conditions can be calculated from the ideal gas law and is equal to $V(D_2)=1.21\times10^{-4}$ l.

The volume of D_2 is equal to the volume of H_2 for the same amount of charge, which is 0.96 C in this case; however the mass is twice that of hydrogen. The calculation of the theoretical hydrogen content determined by the detector in case of deuterium should be done in a different way, because of the different thermal conductivity of hydrogen and deuterium. As the detection principle of the *Eltra* analyser is based on the detection of the gas with respect to its thermal conductivity, a correction factor *f* must be introduced into the calculations for the detected signal, i.e. the sensitivity of the analyser for deuterium equals to that of hydrogen multiplied by the factor *f*. This factor is calculated from Eq. (2) for the voltage response of the TCD detector described below in Section 3.3 and is equal to approx. 0.67. Thus, when the gas volume of 121 μl which has a weight of 20.03 μg for deuterium and 10 μg for hydrogen, is introduced into the analyzer, it is being detected as approximately 6.70 μg of hydrogen.

The experimental results and the experimental conditions are listed in Table 2.

In all experiments the mean value of deuterium (recalculated in hydrogen) detected is 20–30% higher than the theoretical value, similar to the results (32–40%) of the hydrogen experiments in Table 1. This discrepancy is constant and persistent throughout all electrochemical experiments performed. This phenomenon is addressed in Section 3.3.

Table 1
Determination of the standard deviation of charge and analysed hydrogen.

Experiment	Galvanostatic	Potentiostatic
Test conditions	−30 mA, 32 s	−3 V, 32 s
Mean value of charge/C	0.957	0.952
Standard deviation of charge/C	±0.0	±0.04
Calculated H_2 mass/μg	10	9.96
Measured mean value H_2/μg	14.05	13.37
Standard deviation of H_2/μg	±0.45	±0.49
No. of analyses	10	10

*Calculated from charge consumed in the experiment.

3.2. Analysis of the linearity of the detected hydrogen as a function of current and time in galvanostatic mode

Variation of the hydrogen/deuterium signals detected as a function of time and current when the electrochemical cell was operated in a galvanostatic mode was also investigated.

3.2.1. Variation of charging time

The time of charge passing through the electrolyte was varied from 40 s down to 2 s in steps of 2 s. For both, deuterated and non-deuterated electrolytes the peaks of hydrogen/deuterium detected in the experiments as shown in Fig. 4 and the values of total concentration as shown in Fig. 5 demonstrate a convincing linear correlation between time of the electrolysis and amount of hydrogen and deuterium evolved.

Extrapolation of the linear fits for detected hydrogen amounts in Fig. 5 with a good accuracy yields no dead time for the evolution

Table 2
Determination of the standard deviation of charge and analysed hydrogen (deuterium); calculated values are derived from the consumed charge; deuterium amounts are presented as equivalent of hydrogen.

Experiment	Galvanostatic	Potentiostatic
Test conditions	−30 mA, 32 s	−3 V, 32 s
Mean value of charge*/C	0.960	0.545
Standard deviation of charge/C	$\pm3.1\times10^{-5}$	±0.016
Calculated amount H_2 (D_2)/μg	7.04 (H), 14.1 (D)	4.11 (H), 8.22 (D)
Measured mean value H_2/μg	9.32 (H)	5.58 (H)
Standard deviation of H_2/μg	±0.37	±0.16
No. of analyses	10	10

* Calculated from the charge consumed in the experiment.

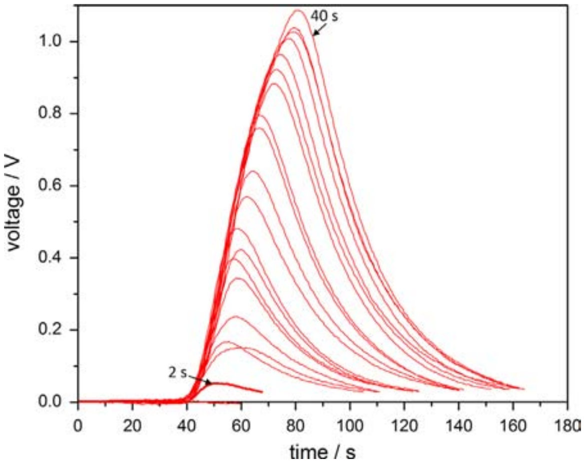

Fig. 4. Peaks of detected hydrogen as a function of electrolysis time for 0.5 M H_2SO_4 electrolyte.

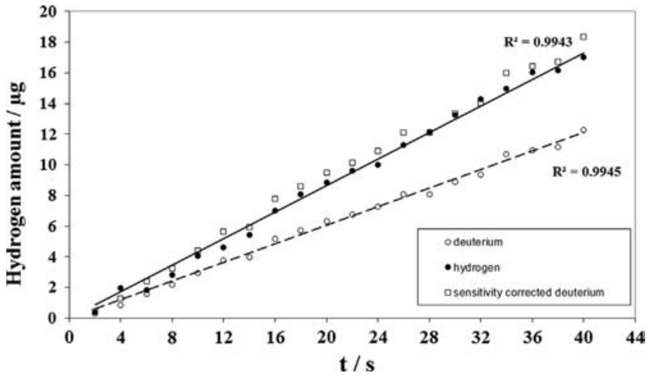

Fig. 5. Hydrogen amount versus electrolysis time at $I = -30$ mA for 0.5 M H_2SO_4 and 0.5 M D_2SO_4 electrolytes. Linear fits: H_2—solid line; D_2—dashed line.

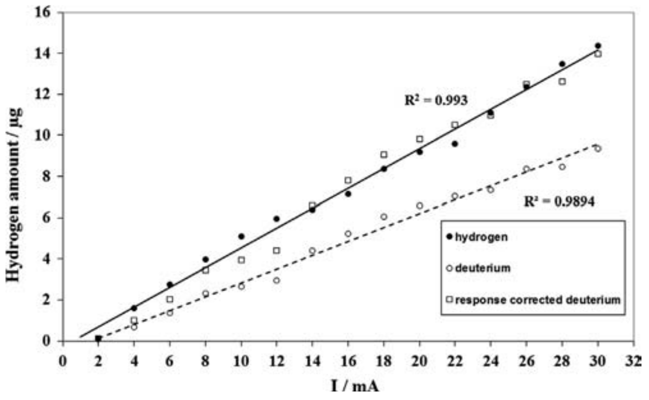

Fig. 7. Hydrogen amount as a function of current for 0.5 M H_2SO_4 and 0.5 M D_2SO_4 electrolytes. Linear fits: H_2—solid line; D_2—dashed line.

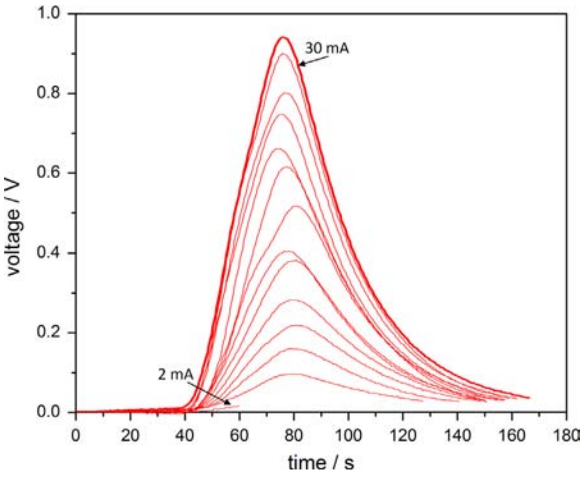

Fig. 6. Peaks of detected hydrogen as a function of current for 0.5 M H_2SO_4 electrolyte.

of both hydrogen (solid line) and deuterium (dashed line). Thus, almost no hydrogen/deuterium dissolution takes place in the electrolyte. The deuterium signal was corrected for the H_2–D_2 difference in thermal conductivity with the factor $f = 0.67$. A very good correspondence with the theoretically expected *hydrogen response values* for deuterium detected during the experiments can be seen, noted as “corrected deuterium” in Fig. 5. One should keep in mind that the detector analyses the difference in thermal conductivity of the gas volume with respect to the reference gas, and not the mass. Therefore, the actual *concentration* of deuterium in the sample can be obtained by multiplication of these apparently detected *hydrogen response values* by 1.99, which is the molar mass ration of deuterium and protium.

3.2.2. Variation of current

The current was varied in 2 mA steps between 2 mA and 30 mA for both electrolytes. Fig. 6 shows the peaks of detected hydrogen which are increasing with increasing current. As it can be seen from the fits for hydrogen (solid line) and deuterium amounts (dashed line) on concentration vs. current plot in Fig. 7, the behaviour is linear even in the small currents region, similar to the results of variation of the charging time. It is nicely seen that the peak maxima coincide, demonstrating that a higher hydrogen amount does not cause an additional dead time. This is clearly different from Fig. 4 which had a constant onset with a delay as it is expected for a variation in time. It is known that high cathodic polarisation will instantaneously lead to hydrogen formation, even in cases where the electrode is covered by an oxide, the breakdown of the oxide film will cause immediate activation and thus only a negligible delay [29].

The results of the measurements with the deuterated electrolyte correspond to those with non-deuterated ones concerning the linearity and reproducibility. Extrapolation of the lines for linear fit of detected gas concentrations (dashed line for D_2 signal; solid line —experimental H_2 values) in Fig. 7 to zero gas production yield higher dead currents for deuterated solution (2 mA compared to 1 mA for 0.5 M H_2SO_4), if compared to the non-deuterated one. It is a detection problem at low concentrations attributed to the limitations of the detector. Looking at the H-signal for 2 mA galvanostatic experiment in Fig. 6, it can be seen that the signal is cut off after 1 min of the measurement. This happens because the H-signal level reaches the threshold limit of 1% of the signal's maximum [30]. If this point is excluded from the extrapolation, the extrapolation line intercepts x-axis at zero with a good accuracy of chi-squared equal to 0.98. A very good correspondence with the theoretically expected *hydrogen values* for deuterium detected during the experiments with 0.5 M D_2SO_4 was found (Fig. 7). As described previously for the variation-of-time experiments, the difference between the actual *concentration* of deuterium and the *hydrogen values* remains the same. Corrections with the molar mass of deuterium to protium are required to reach the mass concentration of deuterium.

3.3. Discussion on the discrepancy between the electrochemically produced and detected amounts of hydrogen

Two series of the galvanostatic/potentiostatic electrochemical experiments, each consisting of 10 individual measurements, for both deuterated and non-deuterated electrolytes were carried out. The results are summarized in Table 3. The calculations of the manufacturer concerning the conversion of helium values to hydrogen values by the thermal conductivities were the basis for creating a similar factor for the conversion of deuterium to hydrogen in Table 3.

3.3.1. Direct comparison of helium gas and electrochemical unit analyser calibration.

The analyser was calibrated with (a) the electrochemical unit with 0.5 M H_2SO_4 operated galvanostatically to produce 10 $\mu g\ g^{-1}$ of hydrogen (-30 mA during 32 s) and (b) with helium gas calibration. Afterwards, CRM’s from Leco Corporation certified for 1.8 ± 0.4 and 6.0 ± 0.2 $\mu g\ g^{-1}$ of hydrogen (3 individual measurements of each CRM type) were measured as samples. With calibration (a) the amount of hydrogen detected during the melt

Table 3
Summary of all experimental series with the electrochemical cell. Calculated values are derived from the consumed charge; deuterium amounts are presented as equivalent of hydrogen.

	Hydrogen				**Deuterium**			
	Galvanostatic		Potentiostatic		Galvanostatic		Potentiostatic	
Measured mean value/μg	**14.05**	**13.45**	**13.37**	**12.27**	**9.32**	**9.51**	**5.58**	**7.70**
Standard deviation/μg	± 0.45	± 0.14	± 0.49	± 0.11	± 0.37	± 0.17	± 0.16	± 0.26
Theoretic mass of H_2 (D_2) from charge/μg	**10.03**	**10.03**	**9.95**	**9.23**	**10.03** (20.03)	**10.03** (20.03)	**5.70** (11.38)	**7.87** (15.73)
Sensitivity normalised mass of H_2 (D_2)/μg					**6.72** (13.42)	**6.72** (13.42)	**3.82** (7.62)	**5.27** (10.54)
Mean value of charge/C	0.960	0.960	0.952	0.883	0.960	0.960	0.545	0.754
Std. deviation/C	0.000	0.000	± 0.042	± 0.005	$\pm 3.16 \times 10^{-5}$	$\pm 3.16 \times 10^{-5}$	± 0.016	± 0.021
Test conditions	−30 mA, 32 s	−30 mA, 32 s	−2.8 V, 32 s	−2.8 V, 32 s*	−30 mA, 32 s	−30 mA, 32 s	−3 V, 32 s	−3 V, 32 s
Systematical error	+40%	+34%	+34%	+32%	+26%	+28%	+19%	+26%

extraction of both types of CRM's was always 31 ± 3% lower than certified value. With calibration (b) the concentration of hydrogen detected during the melt extraction of CRM's corresponded to certified hydrogen values.

One of the thing needed to be mentioned here is the fact, that the initial factory calibration of the thermal conductivity detector have been made using the hydrogen amounts from the melt extraction of Leco CRM's to find a correlation between the TCD voltage output and an amount of the hydrogen, passing the thermal conductivity cell during the analysis. Afterwards, basing on this correlation, a corresponding volume of helium gas has been empirically found and tailored to match the area A found from the melt extraction of CRM's. The area for helium gas A_{He} is different from the area for hydrogen A_{H2}. A physical nature of this difference becomes clear when one takes a look Eq. (2) for TCD voltage output as a response on the mixture of two gases passing along the filaments of the TCD:

$$E = \text{const} \times \left[\frac{(\lambda - A_{12}A_{21}) + (\lambda A_{12} - A_{21})(x/1-x)}{(\lambda+1) + A_{21}(1-x/x) + \lambda(x/1-x)} \right] \qquad (2)$$

where A_{12} and A_{21} are constants and are calculated in a following way:

$$A_{12} = \frac{1}{\sqrt{2}} \left[\frac{d_1 + d_2}{2d_1} \right]^2 \sqrt{\frac{m_1 + m_2}{m_2}} \qquad (2')$$

$$A_{21} = \frac{1}{\sqrt{2}} \left[\frac{d_1 + d_2}{2d_2} \right]^2 \sqrt{\frac{m_1 + m_2}{m_1}} \qquad (2'')$$

d_1 and d_2 are molecular diameters; m_1 and m_2—molecular masses of reference gas 2 (nitrogen) and measured gas 1 (helium, hydrogen and deuterium). Eq. (2) is a derivate from the voltaic output of a Wheatstone bridge inside the TCD and Wassiljewa equation [31] for a relative thermal conductivity of a binary gas mixture; using it the A_{He}/A_{H2} ratio was calculated to be 0.626 within concentration interval from 1 to 1000 μg g^{-1} for gases at room temperature, atmospheric pressure and constant gas flow rate.

In order to crosscheck the results, an additional test was made with a *Leco* RH 402 hydrogen analyser, which is also equipped with a thermal conductivity detector and a gas dose valve. The latter can be filled up with helium or optionally with pure hydrogen gas. This test enables a direct comparison of a signal from equal helium and hydrogen volumes detected by the thermal conductivity detector.

The analyser was calibrated with a Leco CRM's and then the same micro volumes of He and H_2 were analysed. In each case the analysis was repeated ten times and the standard deviation is presented in Table 4. The ratio of the measured counts between helium and hydrogen is equal to 0.63. This ratio measured with the *Leco* RH 402 analyser corresponds very well to that calculated from Eq. (2). It was not possible to compare deuterium gas to helium directly in *Leco* RH 402.

Table 4
Results of gas analysis with a Leco hydrogen analyser.

	Helium	**Hydrogen**
Measured mean value/counts (of 10 analyses)	982	1563
Standard deviation/μg	0.03	0.03
Ratio of He/H	0.63	

From this results it is clear that a 1.6 times higher quantity of helium gas is needed to reach the signal level in the thermal conductivity detector corresponding to that of hydrogen gas. This ratio does not correlate to the ratio of the gases' thermal conductivities ($f\,1 = 0.837$) used as correction factor in the *Eltra* instrument software.

A question arises why the amounts of hydrogen detected after melting of the CRM's (H_{solid}) and hydrogen produced electrochemically (H_{gas}) obviously give different peak areas or voltage response. One of the reasons could be the difference in thermal conductivities λ between H_{solid} and H_{gas}, as λ is a function of the temperature. H_{solid} is being released at 2200 °C during the melt extraction and enters the TCD still hot, whereas H_{gas} enters it at room temperature. Using the existing data for dependence of a thermal conductivity λ of hydrogen and nitrogen [32] on the temperature, the corresponding voltaic response of the TCD was calculated for gases at 1300 °C and 2200 °C. In Table 5 the comparison of the corresponding ratios of the TCD voltage response for two physically relevant situations: (1) ["hot-H_2-in-cold-N_2" vs. "cold-H_2-in-cold-N_2"] and (2) ["hot-H_2-in-hot-N_2 vs. "cold-H_2-in-cold-N_2"] is shown.

As it can be seen, neither at 1300 °C nor at 2200 °C these ratios cannot explain the 31 ± 3% discrepancy between H_{solid} and H_{gas}.

Since the analyser operates at atmospheric pressure, there should not be any effects related to the pressure difference between H_{solid} and H_{gas}.

Another possible source of the constant difference in measured vs. theoretical hydrogen concentration (or H_{solid} vs. H_{gas}) could be the gas flow rates inside the analyser and TCD detector. To test the influence of a carrier gas flow on the detected hydrogen amount a number of experiments were carried out. The analyser was calibrated with helium, 10 μg g^{-1} of hydrogen were produced galvanostatically (−30 mA, 32 s) with the electrochemical unit and analysed at 20 l h^{-1} carrier gas flow rate (instead of 10 l h^{-1} used in all previous experiments). The average concentration of the H_{gas} over 5 consecutive measurements was found to be 9.5 ± 0.2 μg g^{-1}. The peak form though was wide, smeared out and non-reproducible, with 2 or more concentration maxima as it can be seen from an example in Fig. 8.

Decreasing of the carrier gas flow rates to 10–15 l h^{-1} leads again to the reproducible peak forms with constant discrepancy between helium gas calibration (and H_{solid}) and H_{gas}. It seems that the gas flow rates, playing a distinctive role in the TCD detector response, cause the reported 31 ± 3% discrepancy between the

Table 5
Correction values (ratios) for the voltage output of TCD for hydrogen in nitrogen as a function of thermal conductivity changes at high temperature.

Temperature/°C	Combination	
	1)	**2**)
1300	1.01	1.06
2200	1.02	1.06

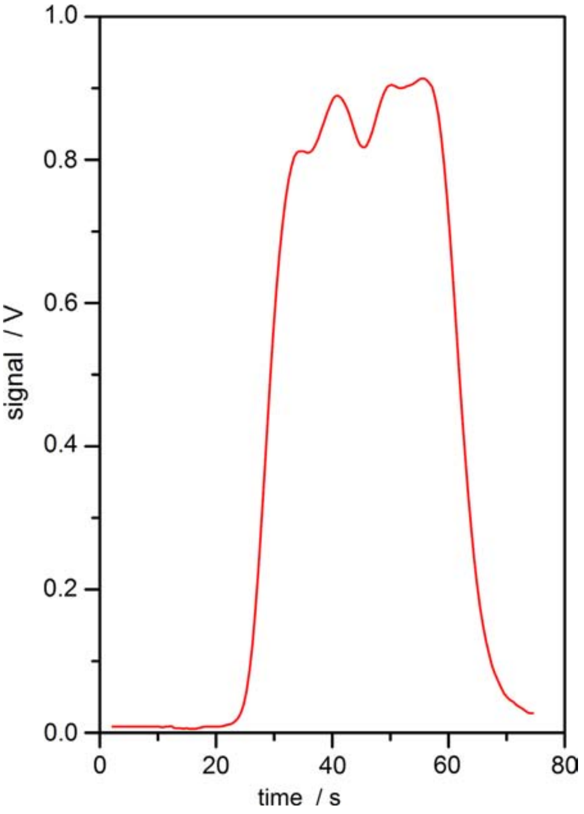

Fig. 8. Peak of hydrogen produced using electrochemical unit galvanostatically (−30 mA, 32 s) with carrier gas flow rate of 20 l h^{-1}.

values expected from the electrolysis charges, and those actually measured by the analyzer (or between H_{solid} and H_{gas}).

Since a very nice reproducibility and linearity together with a reproducible peak form at a carrier gas flow rate of 10 l h^{-1} has been demonstrated, it is advisable to use these conditions for calibration, only introducing the correction factor H_{solid} to H_{gas} a factory basic factor depending on the type of the hydrogen analyser.

Thus, the one point gas calibration with helium of the hydrogen analyser with the detector based on thermal conductivity is not fully reliable. Due to the fact that the adjustment of the valves for gas calibration is done manually by the manufacturer for each analyser device, there might be a variance in accuracy of this procedure for various devices in different laboratories. Finally it has to be taken into account that the results for helium calibration are empirically derived from the measurements of the solid CRM's.

4. Conclusions

Accurately defined quantities of hydrogen and deuterium were produced by consumed charge control using an electrochemical setup connected to the hydrogen analyser. These amounts of gas can be used for the direct calibration of the detector. The electrochemical calibration is superior to the gas calibration, being precisely controllable, multipoint, linear calibration method. Among the major advantages is also the shape of the signal which is similar to that obtained during melt extraction of metals. The peak is broadened and spans over a wider timescale and not as short and sharp as a gas peak from a dosing valve. This is due to the fact that both electrolysis time and the height of the applied current influence the peak shape. In this way systematically different detector response time during the gas calibration and the actual measurement can be eliminated.

The detection of electrochemically produced hydrogen and deuterium by the *Eltra* analyser (calibrated to helium) systematically tends to overestimate measured values if compared to the nominal (theoretical) ones. The helium dosing procedure became suspicious and was investigated in more detail. A direct comparison test was carried out using *Leco* RH 402 analyser, in which hydrogen and helium gases were directly introduced to the dosing valve. It was found that quantity of helium gas should be approximately 1.6 times higher to reach the level of the signal corresponding to that of hydrogen gas. This does not correlate with the correction factor in the *Eltra* instrument software, which is the ratio of the corresponding thermal conductivities. The accuracy of the one point gas calibration with helium is therefore, questionable. Nominal to detected hydrogen ratios, normalized with the volume of the gas dosage valve used for the gas calibration and hydrogen density (mean value—0.63) fit with the ratios nominal-to-raw from the electrochemical measurements (mean value—0.63) and the ones for He/H (0.63) from the direct gases' comparison test.

Due to the aforementioned and to the fact that the adjustment of the valves for gas calibration is done by the manufacturer manually for each analyser device, there might be differences in accuracy for various devices in different laboratories. This source of possible errors can be avoided by using the flexible linear multipoint electrochemical calibration method introduced in this study.

Acknowledgment

The financial support of the European Commission within the Framework Research Fund for Coal and Steel through the project Hppm is gratefully acknowledged.

References

[1] M. Nagumo, ISIJ Int. 41 (2001) 590–598.
[2] K. Takai, R. Watanuki, ISIJ Int. 43 (2003) 520–526.
[3] N. Eliaz, A. Shachar, B. Tal, D. Eliezer, Eng. Fail. Anal. 9 (2002) 167–184.
[4] T. Nishimura, H. Inagaki, M. Tanimura, Hydrogen in Metals, in: Second International Congress (1977) Paper 3E9.
[5] M.Y.B. Zakaria, T.J. Davies, J. Mater. Sci. 26 (1991) 2189–2194.
[6] S.A. Shipilov, I. Le May, Eng. Fail. Anal. 13 (2006) 1159–1176.
[7] J. Ćwiek, J. Mater. Process. Technol. 164 (2005) 1007–1013.
[8] S.J. Hahn, Handbook of Case Histories in Failure Analysis (Ed.) Khlefa A Easaklul, Materials Park, OH: ASM Int.) 2, pp. 490–492.
[9] T. Fujita, Y. Yamada, SCC and HE of Iron Based Alloys, NACE-5, 1977, p. 36.
[10] E.M.K. Hillier, M.J. Robinson, Corros. Sci. 46 (2004) 715–727.
[11] M.J. Carr, M.J. Robinson, Trans. Inst. Met. Finish. 73 (1995) 58–64.
[12] S.A. Gedeon, T.W. Eagar, Weld. J. 69 (1990) S264–S271.
[13] D.M. Seeger, Hydrogen Uptake and Diffusion in Welded Microstructures of Supermartensitic Stainless Steels Final Report; Berlin 2002; 〈http://hdl.handle.net/10068/175112〉.
[14] T. Tsuru, Y. Huang, M. Rostom Ali, A. Nishikata, Corros. Sci. 47 (2005) 2431–2440.
[15] E. Symniotis, Corrosion 46 (1990) 2–12.
[16] Y.F. Cheng, Electrochim. Acta 52 (2007) 2661–2667.
[17] K. Bolton, L.L. Shreir, Corros. Sci. 3 (1963) 17–33.
[18] G.P. Shpenkov, Tribology series. 29, in: D Dowson (Ed.), Friction Surface PhenomenaElsevier, 1995.

[19] J.M. Hayashi: EMGA 621 Technical Note 27, Horiba LTD, Japan.
[20] V.S. Sastr, Talanta 34 (1987) 489–493.
[21] E. Akiyama, K. Matsukado, M. Wang, K. Tsuzaki, Corros. Sci. 52 (2010) 2758–2765.
[22] E. Akiyama, M.Q. Wang, S.J. Li, Z.G. Zhang, Y. Kimura, N. Uno, K. Tsuzaki, Metall. Mater. Trans. A 44A (2013) 1290–1300.
[23] M. Koyama, E. Akiyama, K. Tsuzaki, Corros. Sci. 54 (2012) 1–4.
[24] A.W. Hassel, S. Merzlikin, A. Mingers, C. Georges, J. Flock, K. Bergers, A. Tomandl, A. Muhr, F. Zwettler, Methodology of Hydrogen Measurements in Coated Steels (Hppm), Publications Office of the European Union, Luxembourg, ISBN 978-92-79-29712-0.
[25] N. Mabho, K. Bergers, J. Flock, U. Telgheder, Talanta 82 (2010) 1298–1305.
[26] C. Georges, T. Sturel, Eff. Hydrogen Mater. (2009) 493–500.
[27] S. Kühn, A. Luithle, F. Unterumsberger, M. Pohl. Mater. Testing 54 (2012) 222–227.
[28] S.V. Merzlikin, A.W. Hassel, K. Steinhoff, M. Wildau, Pract. Metallogr 48 (2011) 365–375.
[29] A.W. Hassel, M.M. Lohrengel, Electrochim. Acta 40 (1995) 433–437.
[30] Eltra OH 900 manual, 〈http://www.eltragmbh.com/pdf/on900op%20from%20sn%201550.pdf〉.
[31] A. Wassiljewa, Phys. Z. 5 (1904) 737.
[32] S.C. Saxena, High Temp. Sci. 3 (1971) 168–188.