Article

Analysis of Samples Cleaning Methods Prior to Hydrogen Content Determination in Steel

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Abstract: There are multiple references to sample cleaning methods prior to hydrogen content determination, or hydrogen spectroscopy analysis, but there is still no unified criteria; different authors use their own "know-how" to perform this task. The aim of this paper is to solve, or at least clarify, this issue. In this work, the most commonly used sample cleaning methods are compared. Then, five different methodologies are applied on certified hydrogen content calibration pins and on high strength steel concrete-prestressing strands and the three main situations regarding hydrogen content in the microstructural net (non-charged, charged, and charged and uncharged) are studied. It was concluded that the HCl solution C-3.5 cleaning method recommended by ASTM G1 introduces large amounts of hydrogen in the samples; but can be useful for eliminating superficial oxides if necessary. The rest of the methods had similar results; but the more complete ones that involve ultrasounds and last longer than 8 min are not appropriated when important diffusion may occur on the samples during their application. Simple methods that involve acetone or trichloroethylene and last around 1 min are preferable for almost all situations as these are faster, easier, and cheaper. As a final recommendation, as trichloroethylene is toxic, the simple acetone method is, in general, the most convenient one for regular hydrogen content analysis.

Keywords: hydrogen analysis; steel embrittlement; cleaning method; pattern pins; acetone; trichloroethylene; ultrasounds; aggressive environment; cathodic polarization

1. Introduction

Hydrogen is a very common element in the earth; it is present in both the atmosphere and the crust. The main forms in which it appears are in gaseous compounds or as part of water and geological compounds. It is, thus, an element that will coexist with materials in their structural applications. It is especially critical for high strength steels, because of the effects that hydrogen has on their mechanical properties. hydrogen presence in this type of steels mainly comes from two sources: the manufacturing process (i.e., casting, refining) and from the environmental conditions that can take place in its structural applications (i.e., transportation of petroleum products, aqueous corrosion processes, cathodic protection systems).

The behavior of steels in environments where hydrogen is present gives rise to embrittlement phenomena that depend on the material's microstructure as well as on the hydrogen content in its atomic network. For this reason, it is of the utmost importance to determine the content of hydrogen trapped in the materials and its interaction with the microstructure. This aspect must be regarded as a decisive factor, prior to any modelling, in the design of new alloys for the manufacture of tanks for gas storage at high pressures, which could be employed in new energy sources based on pressurized hydrogen cells. In view of it, the choice of non-invasive cleaning methods prior to the determination of

the hydrogen content in structural steels has been addressed in this work. There are numerous works evaluating the effect of hydrogen on high strength steels considering the acting mechanisms, especially the synergistic action of hydrogen together with local stress states. Some of the most unanimously accepted nowadays for medium and high strength steels are collected in [1,2]:

- HEDE (hydrogen-enhanced decohesion mechanism): It is based on the reduction of the cohesive forces in the area close to the crack tip when a critical stress or deformation is reached due to the introduction of hydrogen atoms in the area; hence failure by cleavages takes place [3,4].
- HELP (hydrogen-enhanced local plasticity): Accumulated hydrogen close to the crack tip eases dislocation movement under low stress levels because of the reduction in mechanical properties caused by hydrogen. The failure is due to a subcritical crack growth by microvoid coalescence [5].
- AIDE (adsorption-induced dislocation emission): It is a combination of HEDE and HELP. Atomic hydrogen is absorbed in the most stressed areas (crack tip), which causes cohesive force weakening by HEDE mechanisms, and consequently subcritical crack propagation by HELP mechanisms. Failure occurs by the combined effects of cleavages and dislocations together with microvoid coalescence [6].
- HEMP (hydrogen-enhanced macroscopic plasticity): A reduction in the yield stress, together with an early plasticization (known as HEMP), that takes place when hydrogen content is large enough to affect the mechanical properties [1,2].
- HAM (hydrogen-assisted microfracture): There is a failure micromechanism change from ductile to brittle when a certain material is getting charged with hydrogen; ductility is gradually reduced modifying the macroscopic failure mechanism [1,2].
- DHF (decohesive hydrogen fracture): Takes place when a brittle fracture, initiated by decohesion effects caused by hydrogen, produces the material's final fracture [1,2].

It must also be pointed out that hydrogen failures are usually caused by a combination of several of the above mechanisms, this being called mixed fracture (MF). In all of them the effects are shown in the crack tip, where subcritical damages are found for nominal stresses lower than the yield stress.

The behavior depends on the stress at the crack tip, the hydrogen content in the fracture process zone, the load rate, the stress intensity factor, the temperature, the material strength, the composition of the grain boundary, the plastic deformation, the dislocation density profile at the crack tip, the stress distribution, and the distribution of the hydrogen traps [7].

The behavior of high strength steels facing aggressive environments is affected by the aforementioned issues. Some good examples of HIC can be found in gas transport pipes made out of low alloy steels, which can often show micro cracks because of the action of hydrogen on the dislocations that causes a change in their mechanical properties [8]. Another effect that is difficult to control and has caused some off-shore platform failures in the North Sea [9], is produced by the potential levels used in the cathodic protection systems against corrosion which produce large amounts of hydrogen. For all these reasons, it is essential to analyze the hydrogen content in steel, or carry out hydrogen spectroscopy analysis, both in the design and construction phases as well as during the infrastructures operation, in order to verify its behavior throughout its service life and to be able to control the grade of embrittlement of the steel and avoid catastrophic failures.

The hydrogen content is normally determined by means of analyzers that use the hot extraction technique. This process consists of heating the sample up to a temperature so that the hydrogen contained in it is able to diffuse out. After that, the hydrogen content is determined by a thermoconductivity cell which measures the gradient of thermic conductivity in the environment passing through it. Before this process, a precise calibration/verification is necessary in order to ensure accuracy. Apart from providing the samples with a precise geometry, their storage prior to the analysis is decisive in order to avoid hydrogen diffusion; the samples must be immediately tested, and if this is impossible they should be stored at the lowest possible temperature (i.e., in liquid nitrogen). After this,

and just prior to the analysis, the most important task for this process is their cleaning in order to free them of any impurity, which could lead to a wrong result.

Although scarce, there are a few standards [10,11], report references, and other documentation [12, 13] that provide some basic indications on selecting, preparing, and cleaning samples for their analysis. The cleaning is usually performed by immersion of the samples in chemicals such as acetone or trichloroethylene, helped sometimes by ultrasounds, for a time that can vary from seconds to a few minutes. The influence of these solvents, which have hydrogen in their chemical composition, and the cleaning methods durations on the hydrogen content results has not yet been studied in depth. Therefore, it is not known whether hydrogen content can be modified or distorted by introducing a sufficiently large amount of hydrogen, especially when the contents to be evaluated are relatively low.

The cleaning methods presented in this work, are mainly based on the learning by doing know-how acquired over decades; each technician in each lab uses slightly different techniques which have been continuously optimized, including also the recommendations of manufacturers of the measurement equipment. In this paper, the main sample cleaning methods prior to hydrogen content analysis are reviewed, in order to evaluate their accuracy and define their validity with respect to the situation considered.

The main objective of this paper is to compare the different cleaning techniques in each one of the aforementioned hydrogen content situations, to clarify their advantages and disadvantages, as well as their accuracy, and to determine the most suitable method for situations where hydrogen embrittlement due to the environmental conditions plays an important role.

2. Background about Sample Types and Cleaning Methodologies

Currently, the normative regarding sample preparation is not very extensive, the most important standards being ASTM E1806 [10] or ISO 14284:1996 [11], which make limited references to sample cleaning methods. The main procedures to follow are shown below.

2.1. Main Samples Geometries

There are different types of samples to analyze hydrogen content, covered by the three types currently used by the manufacturers of hydrogen analysis equipment to calibrate their equipment; the melting pots and the ovens in the equipment are manufactured accordingly [12,13]:

- Pins: The most commonly used, generally of a mass of between 0.5 and 2 g and cylindrical shape (generally twice or three times longer than its diameter).
- Cylindrical bars: Having a much greater length than its diameter and a mass of between 5 and 10 g generally.
- Metal powder: Normally used in cases of very high hydrogen contents, or when small amounts need to be used (price, toxicity, ...).

In the literature, some authors use cylindrical geometries such as the aforementioned ones [14]. Others point out parallelepipeds of $5 \times 5 \times 5$ mm^3 and approximately 1 g [13], or of $7 \times 6 \times 6$ mm^3 and 2 g approx., for some research works [12]. Small plates of $10 \times 10 \times 0.5$ mm^3 and 0.4 to 0.5 g have been used to study diffusion conditions under certain geometries [15].

In some experimental works, to avoid machining samples or to analyze complete small components, it is also common to use samples of irregular shapes where all three dimensions have a similar length, and a mass of around 0.5 to 2 g. The aforementioned differences in shape do not have any influence on the hydrogen content results, normally expressed in ppm (parts per million). The weight and total hydrogen mass trapped the sample introduced are the only variables needed to define the content. As the equipment has its own precision scales incorporated to weigh the sample prior to the analysis, and the hydrogen mass is automatically obtained by the analyzer, then the ratio between them is directly expressed in ppm in the display [12,13,16].

2.2. Recommendations for Sampling Performance

When the sample is taken from a melted product, the appropriate size can be obtained with a trepanation tool, but when it is taken from a forged product a saw or an abrasive cutting disc must be used to obtain it from the central line of the product and then machine it.

The method must ensure that the hydrogen diffusion, which can take place at room temperature, is controlled and minimized during sampling, storing, and test preparation. To avoid this, samples must be kept at a temperature as low as possible during all the steps of the sampling process, storing, and preparation. Therefore, the samples should be kept in a refrigerant liquid, like liquid nitrogen, an acetone suspension, or solid carbon dioxide, in order to avoid diffusion, especially in thin samples.

In order to eliminate some oxidized products and surface defects, samples can be subjected to abrasion of the sample surface until these are all eliminated without heating the sample.

In order to prepare the final sample geometry, a piece of material with an adequate mass should be cut minimizing the heating, by cooling it down with frequent intervals or by means of a refrigerated cutting machine. The final surface of the sample can be obtained by filing, shot blasting, or light grinding.

If samples cannot be immediately submitted to degreasing, cleaning, and hydrogen content determination, the samples must be stored at the lower possible temperature to avoid hydrogen diffusion. The cooling must be as fast as possible, and the storage temperature as low as possible, in order to impeach a noticeable diffusion. This is usually done by liquid nitrogen immersion, which assures a proper storage during several days if the nitrogen covers the samples completely and its evaporation is minimized and/or compensated. All those samples inadequately cooled or stored should be removed from the experimental program.

The samples should be degreased, cleaned, and analyzed immediately after preparing them. If liquid refrigerant is employed, samples can be stored before analyzing, in which case the cleaning must be done just prior to the analysis. For degreasing, it is recommended to dip the samples in acetone, dry them with a sudden vacuum for some seconds and then directly analyzing them. Alternatively, dipping in 2-propanol (isopropyl alcohol) and afterwards drying with diethyl ether can be considered.

2.3. Main Sample Cleaning Methods

The methods used to clean the samples are divided into three groups depending on their nature: mechanical, chemical, and electrolytic processes [10,11].

- The mechanical processes include scraping, blasting, and brushing, among others. These methods must be carefully performed and used only when chemical and electrolytic methods are not enough, or in combination with them. Appropriated grits or sand blast material must be carefully chosen in order not to introduce further contamination that can modify the results.
- The chemical methods have been specified through "try and failure" (testing different solvents and different dipping times); the solvents most commonly employed are acetone, trichloroethylene, or hydrochloric acid (HCl). It is normally recommended to combine them with slight brushing, without metallic bristles (mechanical method), or ultrasounds alternatively repeating the chemical procedure and the brushing or ultrasounds. These methods can last for times regularly between seconds and a few minutes, and are usually applied at room temperature. It must be taken into account that the longer the method takes and the higher the cleaning temperature is, the more important the diffusion and inaccurate the result, for this reason shorter cleaning methods (around 1 min) tend to be preferred.
- The electrolytic methods, often used when corrosion or strong superficial oxidation is present on the samples, do not apply to the case under study, as this paper focuses on the sample cleaning without any observable superficial corrosion or oxidation. The electrolytic methods, as the chemical ones, also include the use of brushing or ultrasounds before and after the electrolytic cleaning. To correct the metal loss caused by its use, the standard ASTM G1 [17] recommends

using a simple graphic method to differentiate the metal loss due to the cleaning process, or using control samples without corrosion to be able to measure afterwards the mass taken away by the cleaning process.

3. Materials and Methodology

For this study, two different materials were used: certified hydrogen content calibration pins (calibration pins), and high strength steel pins obtained from concrete prestressing wires (wire pins). With the aim of studying the three possible hydrogen scenarios, wire pins were analyzed under three different hydrogen charging conditions: without any charging, just after hydrogen charging, and charged and uncharged by diffusion to air during exposition for 24 h. The hydrogen charging was performed in a liquid solution by applying a cathodic polarization condition, which reproduces situations of high aggressive environments present in the petrochemical and off-shore industry [15,16]. This technique has been used by the authors of the paper during three decades, so their know-how assures a uniform hydrogen charge throughout each sample and consistent across samples.
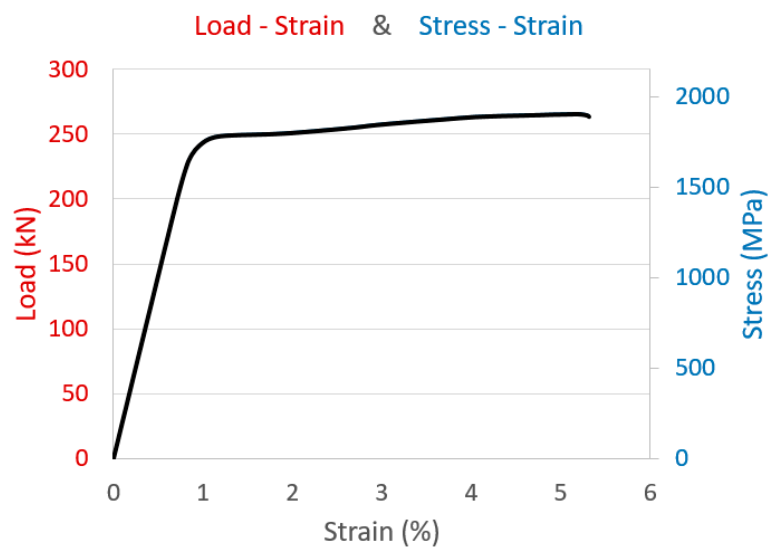
3.1. Materials Employed

Two different materials were used for this study:

- Certified hydrogen content calibration pins (calibration pins). This material was supplied by the company LECO^R under the reference "502-061" (which is equivalent to Eltra 91400-1002 and to ALPHA AR555) [18], and consisted of the electroplated cylindrical 1 g (0.989 ± 0.009 g) steel pins (10 mm long and 4 mm of diameter), which have a hydrogen content of 1.91 ± 0.41 ppm certified by the manufacturer. The diffusivity of this material is considered negligible as the pins are electroplated [12,13]. The calibration pins did not require any other previous preparation before application of the cleaning method prior to the hydrogen content tests. A total of 50 samples were employed.
- High strength steel pins obtained from the central wire of a 5 mm of diameter 7 wire concrete prestressing strand (wire pins). A total of 90 cylindrical wire pins of around 2 g (12 mm long and 5 mm of diameter) were obtained, ergo 10 samples for testing each possibility to be studied (combination of cleaning methods and hydrogen charging conditions). To obtain the wire pins, it was first necessary to separate the central wire from the rest, and then clean it with lab paper and acetone to remove the dust and superficial remains of soap and grease from the manufacturing processes. The samples were visually checked and did not present any superficial corrosion products on them as, on the one side were manufactured the week prior to the tests performance, and on the other side the grease covering them prevented any corrosion. Nonetheless, in order to guarantee any corrosion at all, after degreased, the central wire was slightly sanded with #2000 sandpaper and cleaned again with lab paper and acetone and dried with air. Finally, the samples were cut in a precision metallographic cutter, removing the edges, which had suffered heating while being sampled by non-refrigerated means from the strand roll at the factory.

As stated by the manufacturer, this steel has the chemical composition shown in Table 1 and the microstructure presented in Figure 1: pearlitic eutectoid microstructure with cementite sheets not specially located in the core of the wire; it did not undergo any heat treatment, two weeks after the fabrication was drawn and braided. The hydrogen content, prior to drawn and after braid, was measured by the manufacturer in an independent laboratory and was equal to 2.0 ppm approximately, which was found to be consistent with its microstructure and chemical composition from the manufacturer's point of view. The strands were manufactured and characterized according to UNE 26094 [19], obtaining the results shown in Figure 2 and Table 2.

Table 1. Chemical composition of the wire pins steel; % weight provided by the manufacturer.

C	Mn	Si	P	S	Cr	Ni	Cu	Mo
0.795	0.665	0.214	0.011	0.016	0.193	0.126	0.268	0.023
Sn	**V**	**N**	**Al**	**B**	**Ti**	**Pb**	**Zn**	**Fe**
0.014	0.002	0.0095	0.002	0.0004	0.001	0.001	0.001	Rest
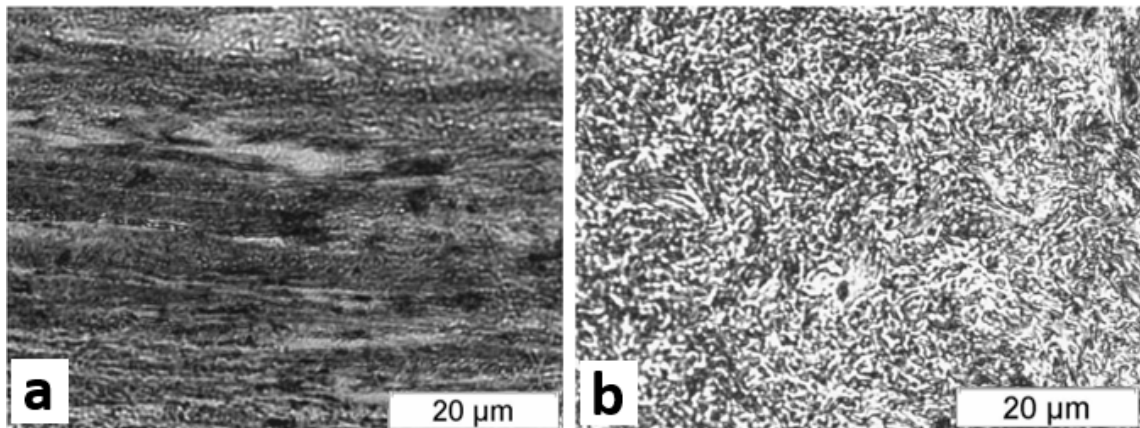
Figure 1. Microstructure of the wire pins steel; provided by the manufacturer. (**a**) Longitudinal section; (**b**) cross section.

Figure 2. Load-strain and stress-strain graphs from the seven wire strand test.

Table 2. Main parameters obtained from seven wire strands tested and comparison with the requirements of the standard [19]; the material employed fits the requirements.

Parameter	Value	Requirement [19]
Mass density	1103 ± 1 g/m	1101 g/m
Cross section	140.5 ± 0.1 mm^2	137.2 ÷ 142.8 mm^2
$\varnothing_{Outer\ wires}$	5.00 ± 0.02 mm	–
$\varnothing_{Inner\ wire}$	5.22 ± 0.02 mm	5.1 ÷ 5.25 mm

Table 2. *Cont.*

Parameter	Value	Requirement [19]
Young's modulus, E	202 ± 3 GPa	181.4 ÷ 208.7 GPa
Yield load (stress) at 0,1%, $F_{p\,0.1}$	242 ± 3 kN (1730 ± 24 MPa)	>221 kN
Yield load (stress) at 0,2%, $F_{p\,0.2}$	248 ± 3 kN (1771 ± 21 MPa)	>229 kN
Maximum load, F_m (stress, S_m)	266 ± 3 kN (1901 ± 19 MPa)	260 ÷ 304 kN
Elongation at maximum load, A_{gt}	5.19 ± 0.05%	>3.5%
Ratio $F_{p\,0.2}/F_m$	0.93 ± 0.01	–
Environmental conditions	23.0 °C–85.9% RH	Room Temp.

3.2. Hydrogen Charging Conditions Studied

Both the calibration pins and the wire pins were studied in their as-received state, simply applying the different cleaning methods on the samples, which is explained in the next section. Hence, the hydrogen content analyzed for these cases was the as-received state for the wire pins and the certified content for the calibration pins.

Nevertheless, with the aim of studying all the possible hydrogen scenarios, the wire pins were analyzed under two more different hydrogen charging conditions: just after 24 h hydrogen charging in an aggressive environment, and charged for 24 h and uncharged by diffusion to air during exposition for another 24 h.

Hydrogen charging was performed in a liquid solution by means of an electrolytic method. After the charge, the samples were extracted one by one, dried and prepared to apply the corresponding cleaning method, accommodating this steps in a time under two minutes, in order to avoid as much as possible the diffusion effects that might take place during them. For the charged and uncharged samples, the methodology was exactly the same: samples were extracted after 24 h and dried, then were left on lab paper for another 24 h at room temperature inside a laboratory hood with permanent extraction, in order to avoid any corrosion resulting on the samples during this time. Prior to the test the lack of corrosion was checked and, finally the samples were cleaned by the corresponding method and analyzed.

The hydrogen charging was done by a cathodic polarization environment. This procedure is normally used to simulate the local effects of aggressive environments or to reproduce harsh conditions present in the cathodic protection systems on the petrochemical and off-shore industries [15,16,20]. It consists of interconnecting a noble metal acting as the anode (a grid of platinum in this case) with the steel component to be protected acting as the cathode (the samples, wire pins, in this case) when both are immersed in an acid electrolyte [21].

There must be a fixed intensity current between the anode and the cathode. In this work, a current density of 5 mA/cm^2 (of submerged sample) has been used because of its extensive references in oil and gas and offshore fields [15,22]. The resulting protection causes that the chemical reaction on the cathode (wire pins) consists of the reduction of hydrogen, which penetrates into the steel by different mechanisms in widely studied stages, leading to an increase in its concentration [23,24].

The aqueous environment employed as the electrolyte consisted of a 1N H_2SO_4 solution in distilled H_2O with 10 mg of an As_2O_3 solution and 10 drops of CS_2 per liter of dissolution. The As_2O_3 solution was prepared following the Pressouyre´s method [15,20,25]. The pH was measured in the range 0.65–0.85 during the tests, which were carried out at room temperature (20–25 °C). The solution circulation or agitation is necessary in order to remove the hydrogen bubbles on the specimen surface, to avoid pitting or other forms of corrosion and sedimentation [15,16,20,22]. Samples were charged during 24 h, an amount of time higher than the requirement calculated using an estimated diffusivity of hydrogen in this type of steels at room temperature of around 10^{-6} cm^2/s, which assured a proper and complete diffusion inside the material up to the saturation of the cylindrical wire pins of 2.5 mm of

radius. Figure 3 shows a schematic of the experimental set-up employed. The samples were machined from the wire leaving an small amount of material between one and the following to interconnect them during the charging (making it easy to separate them after embrittling by flexing with the fingers). A martyr longer part that was coming out of the electrolyte was also left in order to make the connection to the cathode outside and avoid galvanic effects; the connection to the anode was also done outside of the electrolyte.
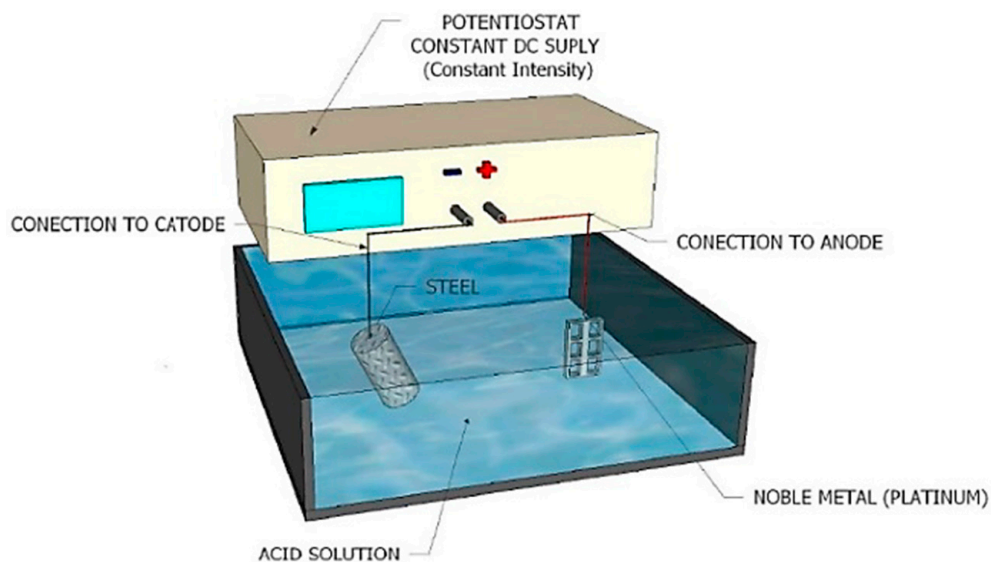

Figure 3. Schematic of the cathodic polarization experimental set-up.

3.3. Proposed Cleaning Methods

From the bibliographic research outlined in Section 2, the electrolytic methods were discarded in this work, given that their nature can affect the hydrogen content results. In the case of chemical methods, the ones involving zinc powder were also discarded for safety and simplicity reasons, as spontaneous ignition could take place. Also, the ones requiring permanent agitation and long immersion times were not studied, as their time demand can give rise to a hydrogen diffusion large enough to affect the results.

Therefore, the following five chemical cleaning methods, which are the most simple, fast, economic, and widely employed ones, are finally proposed to analyze their influence on the hydrogen content analysis results. Table 3 presents a summary of the cleaning methods employed in this work.

- Simple acetone method (AC). This method starts by degreasing the samples with ethanol (C_2H_5OH v/v: 95.1–96.9%, for analysis), placing them on a paper and spraying it over them. The samples are then dried with cellulose paper and air; after this no more direct hand touching is permitted; only tweezers can be used in order to avoid any contamination (this phase is the same for all the methods used). Next, the samples are submerged in a container with acetone (C_3H_6O min. 99.8%, for analysis) at room temperature for less than one minute. Finally, the samples are placed on a lab cellulose paper to air dry them at room temperature (the drying technique is the same for all cleaning methods). The advantages of this method are based on its simplicity and fastness, and this makes the method one of the most commonly used. Another important advantage is that it is suitable for cases in which the hydrogen loss during cleaning operations needs to be minimized to be able to know the exact amount of the sample when extracted from an aggressive environment. On the other hand, it is not a very good method when the samples have a large amount of superficial oxide, as it can hardly remove it.
- Simple trichloroethylene method (TR). It consists of the same sequence as the aforementioned AC one, but substituting the acetone by trichloroethylene. After degreasing the samples in

ethanol (C_2H_5OH v/v: 95.1–96.9%, for analysis), a submersion in trichloroethylene (C_2HCl_3 min. 99.5%, stabilized with ethanol) for less than 1 min is carried out, finally the samples are dried at room temperature. This method is a simplification of the complete method (AC+U+TR), which is explained in the following paragraphs, and includes a process of submersion in acetone for 8 min which is eliminated here. The purpose of its use is to see if there are effects when reducing substantially (AC+U+TR) the duration and the possibilities of hydrogen diffusion outside and/or contamination by a longer exposition to acetone. Together with the simple acetone simple method (AC), and constituting its main alternative, these two are the most widely used in the literature. Their advantages and disadvantages are the same: they are fast and simple, ideal for situations where hydrogen loss during cleaning must be minimized, although they cannot eliminate superficial oxide when existing.

-   Compound acetone and ultrasounds method (AC+U). This method is also a simplification of the complete method explained above (AC+U+TR), eliminating the immersion in trichloroethylene and directly drying the samples instead. The main advantage of this method is the trichloroethylene elimination, as it is toxic, and also the capacity to eliminate some superficial oxides during the ultrasounds process. Nevertheless, the still longer time required than that of the simple methods can make it difficult to know the exact hydrogen content due to its diffusion out of the samples.

-   Acetone, ultrasounds, and trichloroethylene complete method (AC+U+TR). This method is outlined in [12]. First, the samples are degreased with pure ethanol (C_2H_5OH v/v: 95.1–96.9%, for analysis), and are then subjected to 8 min cleaning submerged in acetone (C_3H_6O min. 99.8%, for analysis) helped by ultrasounds at room temperature. After that, the samples are taken out and submerged in a container with trichloroethylene (C_2HCl_3 min. 99.5%, stabilized with ethanol) at room temperature for less than one minute. No rinsing was applied between solutions in this work. Finally, the samples are placed on a lab cellulose paper to air dry them at room temperature. As in (AC+U), in this case it is impossible to minimize the hydrogen loss due to the time employed, which can be substantial if the original content is low. On the other hand, given the longer immersion time and the ultrasound action, this method allows a better elimination of the superficial oxide than the simplified methods (AC) or (TR).

-   HCl solution C-3.5 method from ASTM G1 standard (HCl). As the other methods described, the first step is to degrease the samples with pure ethanol (C_2H_5OH v/v: 95.1–96.9%, for analysis). It is then followed by a 10 min immersion at room temperature in a dissolution of 500 mL of hydrochloric acid (HCl 36.5–38.0%, for analysis) plus 3.5 g of hexamethylenetetramine ($C_6H_{12}N_4$ min. 99%) and distilled water up to 1 L (or proportional quantities), after which the samples are retired and dried at room temperature and in air. This method is slower and more laborious than the rest. It also uses a more aggressive dissolution, so it is more likely to introduce hydrogen in the samples, heavily interfering with the results when the contents to be analyzed are low. Nevertheless, it must be pointed out as an advantage that it is the only one of the methods studied capable of removing superficial oxidation when this is large, cases when the oxides will have a greater influence on the results than the quantity introduced by the cleaning method if not removed.

Table 3. Summary of the cleaning methods employed in this work.

Method	Steps
Simple acetone method (AC)	Degrease the sample with ethanol.
	Immerse in acetone at room temperature for ≤1 min.
	Dry with air at room temperature.
Simple trichloroethylene method (TR)	Degrease the sample with ethanol.
	Immerse in trichloroethylene at room temperature for ≤1 min.
	Dry with air at room temperature.
Compound acetone and ultrasounds method (AC+U)	Degrease the sample with ethanol.
	Immerse in acetone at room temperature for 8 min and apply ultrasounds.
	Dry with air at room temperature.
Acetone, ultrasounds, and trichloroethylene complete method (AC+U+TR)	Degrease the sample with ethanol.
	Immerse in acetone at room temperature for 8 min and apply ultrasounds.
	Immerse in trichloroethylene at room temperature for ≤1 min.
	Dry with air at room temperature.
HCl solution C-3.5 method from ASTM G1 standard (HCl)	Degrease the sample with ethanol.
	Immerse in a solution of 500 mL of HCl, 3.5 g of hexamethylenetetramine and water up to 1 L at room temperature for 10 min.
	Dry with air at room temperature.

3.4. Equipment Used for Hydrogen Content Analysis

The equipment used for the hydrogen content measurements was a RH-402 analyzer combined with a HF-402 induction oven (LECO Corp., St. Joseph, MI, USA). This equipment uses the hot extraction technique [16]; the induction oven heats the samples over the austenization temperature, which is enough to make the hydrogen trapped in the microstructure to diffuse out completely. After this, a thrust gas (nitrogen in this case) pushes the hydrogen from the oven to the analyzer. Once in the analyzer, the gas crosses through some chemical porous filters and gets to the thermoconductivity cell, where the hydrogen content is precisely determined through the gradient of the electric resistance produced during the flow of the gas through a group of diristors associated in a Wheatstone bridge. The samples are previously weighed in an integrated scale, which allows the device to calculate the content in ppm.

All the analysis performed lasted 180 s, which proved to be enough to ensure a complete hydrogen diffusion for the type of steels and sample geometries employed. The analyzer was started 2 h before the measurements, as recommended by the manufacturer, in order to assure a temperature stability in the analysis. Also, the equipment was checked, and re-calibrated if necessary, before each working session. As advised by experts in materials characterization [12,13], the analyzer was calibrated using hydrogen gas dose, and contrasted by analyzing patterns of masses and hydrogen contents in the same range as the ones to be measured for each scenario studied before and after each analysis session. All this guarantees a resolution limitation for the described equipment of 0.2 ppm [13], reason why 10 samples are considered in each analysis condition.

4. Results and Analysis

4.1. Calibration Pins and Wire Pins in As-Received State

First, both the calibration pins and the wire pins were studied in their as-received state, in order to determine the initial hydrogen content; ergo the hydrogen introduced in its manufacturing process for wire pins, or the certified hydrogen content for calibration pins. For this purpose, each one of the five different cleaning methods proposed was applied on a set of 10 samples of each material (wire pins and calibration pins). The results are shown in Figure 4, where box and whiskers plots represent the median value, the range between first and third quartiles and the minimum and maximum values for each case. For the calibration pins, a box marking the pin calibration pattern certification range of 1.91 ± 0.41 ppm is also included.
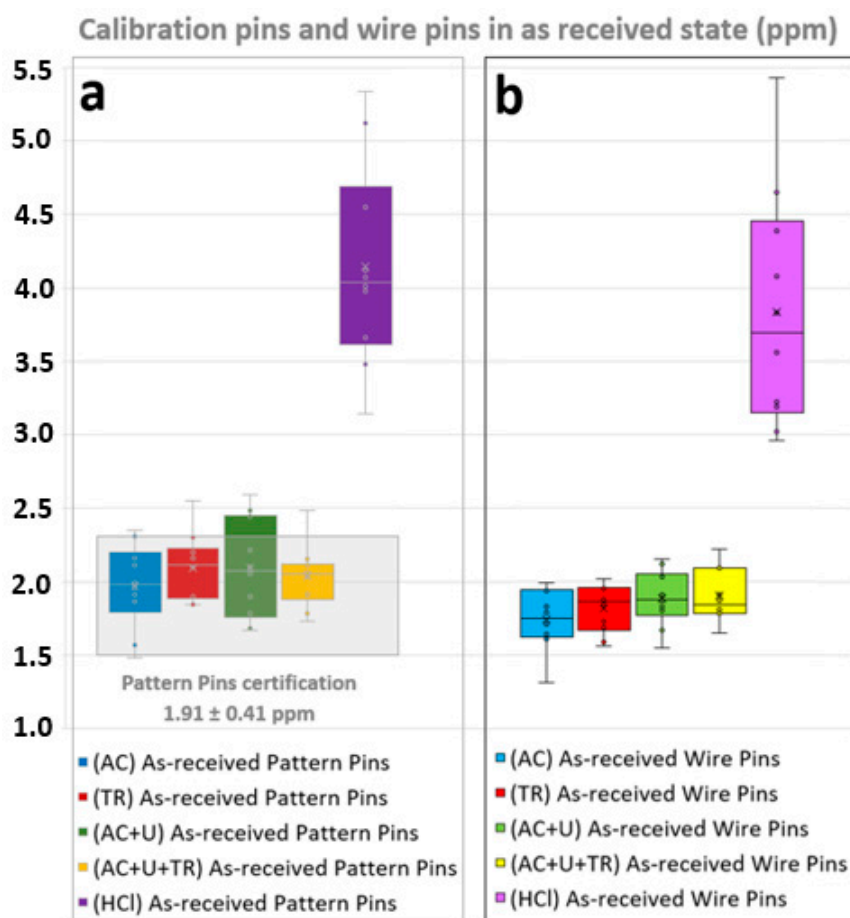

Figure 4. Hydrogen content results on calibration pins (**a**) and wire pins (**b**) after being cleaned with the 5 methods proposed. Box and whiskers plots represent the median value, the range between first and third quartiles and the minimum and maximum values for each case.

The first conclusion that should be highlighted is that the (HCl) cleaning method, proposed by ASTM G1 [17], presented for both cases, pattern pins and wire pins, is around 2 ppm higher than all the rest of the cleaning methods (comparing median values), all of which had similar results. This means that the (HCl) method introduces important amounts of hydrogen in the samples, so if it needs to be used in order to eliminate superficial oxide this consideration must be taken into account; and even more so when dealing with low hydrogen contents. However, this method should not be discarded when it comes to evaluating the hydrogen contents of samples that accumulate large amounts of corrosion products and dirt, since its excellent cleaning capacity in such cases has been proved [17]. On the other hand, mechanical methods of cleaning (see Section 2.3), whose study is not

included in this work, might be better candidates for this kind of large amounts of corrosion products and dirt elimination without modifying the hydrogen content (being careful about not using abrasive material that can affect it).

For the aforementioned reason, the (HCl) method is discarded for further analyses in this study, focusing rather on the rest of the methods involving acetone or/and trichloroethylene.

As it can be observed for pattern pins, the four techniques employed lead to results relatively close to the certified values (1.91 ± 0.41), the median obtained from the simple acetone method (AC) being equal to 1.97 ppm, the closest one to the certified value (1.91), while the others are around 0.2 ppm away. Regarding the dispersion between first and third quartiles, (AC) is the method showing the most centered interval, with a range of 0.4 ppm. However (TR) and (AC+U+TR) showed slightly smaller dispersion ranges (0.32 and 0.21 ppm respectively) but have higher median values: that is, they are less centered in the certified interval. Finally, (AC+U) showed the highest dispersion of all the methods, even going beyond the certified region.

Regarding the wire pins, the trends are similar to those of the pattern pins. The four techniques analyzed showed very close median values (maximum differences of 0.14 ppm). In this case, the simple acetone method (AC) also showed the lowest median value of 1.74 ppm. For as-received wire pins, dispersion between first and third quartiles was similar in the four methods analyzed, but it was more clearly centered in an upper range for (AC+U) and (AC+U+TR) than for simple (AC) and (TR) methods. This content is slightly higher than the one usually found for high strength steels in literature for cold-drawn steels, under 1.0 ppm, but consistent with the analysis performed by the manufacturer in an independent laboratory prior to drawn and after braid, which leads to values of 2.0 ppm approximately. It does not contradict the values for cold-drawn pearlitic steels employed in for hydrogen experimental works [26,27].

The higher median values and upper dispersion ranges between the first and third quartiles observed in the wire pins for the longest cleaning methodologies, (AC+U) and (AC+U+TR), mean that the slightly higher hydrogen content obtained is due to the longer time employed in these cleaning techniques. The immersion in acetone and ultrasounds for 8 min allows a small amount of hydrogen to diffuse inside the steel from the solvent. It should be taken into account that, in the case of the wire pin in the as-received condition, the effect of time could never lead to a decrease in hydrogen content since the material is in a stable condition and there is no weakly trapped hydrogen that could diffuse outside of it; nevertheless, as will be shown in Section 4.2, this effect is the opposite for the different charging conditions studied. This effect is not present in pattern pins because of their protective outside electroplating layer that prevents hydrogen from diffusing out of or inside them, as the diffusion coefficient of zinc is several orders of magnitude lower than that of steel [24]; this is the key reason why pattern pins maintain a constant content through time.

This fact does not mean that the longest methodologies introduce such a large amount of hydrogen that it affects the accuracy of the results, and evidently does not rule them out as valid methods. The aforementioned differences of (AC+U) and (AC+U+TR) with respect to (AC) and (TR) are in the range of 0.14 ppm, which is inside the usual uncertainties for a regular hydrogen analysis when testing 1 to 3 or 4 samples, as is usually done (10 pins were used for each condition in this study).

It must be pointed that, as the time and equipment demands for (AC+U) and (AC+U+TR) are higher, (AC) and (TR) will always be preferred as they are simpler, cheaper, and faster. Also for these reasons, (AC) and (TR) will be the only feasible methods when the hydrogen content determination must minimize diffusion out of the samples while being performed.

4.2. Wire Pins under Different Hydrogen Charging Conditions

With the aim of studying the three main situations regarding hydrogen content in the microstructural net of a high strength steel, three scenarios were studied. These possible scenarios are: Material without any embrittlement, where all the hydrogen present comes from its manufacturing process; material in in-service conditions in an aggressive environment; and material discharged after

being exposed to an environmentally adverse condition, where the residual content is deeply trapped in the microstructure. In order to perform this, the wire pins were analyzed under the as-received condition (studied in the previous section) and two more different hydrogen charging conditions: Just after 24 h hydrogen charging in an aggressive environment, and charged for 24 h and uncharged by diffusion to air during exposition for another 24 h. The hydrogen cathodic charging conditions have been previously described in Section 3.2.

To accurately determine the hydrogen content of the samples after the controlled charge, the exposition time outside the environment during the cleaning operations must be as short as possible, in order to prevent the weakest trapped hydrogen from diffusing out, which would lead to inaccurate results. This is based on diffusion studies that showed that hydrogen introduced by electrochemical charging processes presents significant diffusion losses in this time range (5 to 15 min), unlike the as-received condition where there is no weakly trapped hydrogen that can diffuse outside of the material [28]. Because of this, the methods involving ultrasounds, that take around 10 min, are too long; the only feasible methods are the simple acetone (AC) or trichloroethylene (TR) ones, which imply short times and give accurate results, as justified in the previous section.

Figure 5 shows the hydrogen content results for the wire pins after being cleaned by the simple acetone (AC) and trichloroethylene (TR) methods under different charging conditions: as-received, charged by cathodic polarization for 24 h and charged by cathodic polarization for 24 h and discharged in air exposition 24 h. The box and whiskers plots represent the median value, the range between first and third quartiles and the minimum and maximum values for each case, where ten samples were tested.
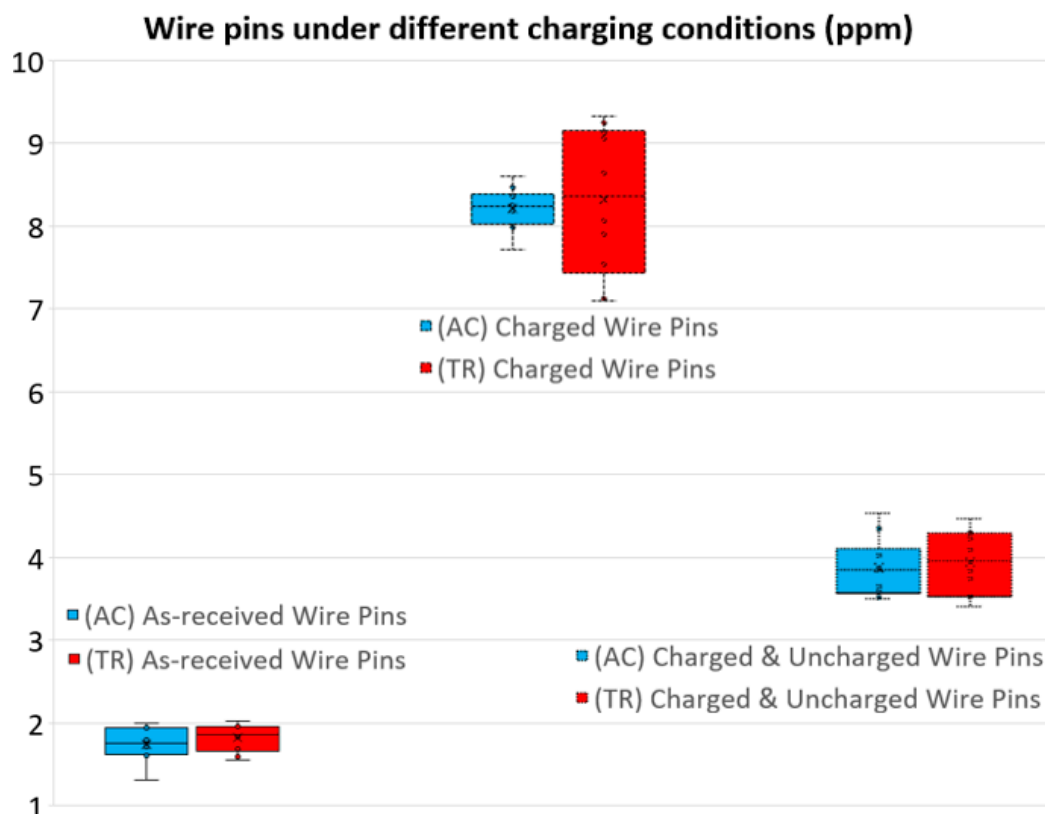

Figure 5. Hydrogen content results on wire pins after being cleaned by the simple acetone (AC) and trichloroethylene (TR) methods under different charging conditions: as-received (left), charged by cathodic polarization for 24 h (center) and charged by cathodic polarization for 24 h, and discharged in air exposition 24 h (right). Box and whiskers plots represent the median value, the range between first and third quartiles and the minimum and maximum values for each case.

A first conclusion from the results is that the three different hydrogen content situations in the microstructural net of a high strength steel were achieved, as desired. As previously exposed, a median content slightly lower than 2 ppm was obtained for the as-received samples, while the charged ones reached a value over 8 ppm, and the samples after 24 h of discharge were able to hold just 4 ppm in their microstructure. This trend is in agreement with the literature for high strength steels hydrogen discharge by air exposition after cathodic charge in this environment [28], however this must be taken into account just qualitatively, as diffusivities can vary greatly across different high strength steels, often orders of magnitude.

The values of the hydrogen content results obtained after using the simple acetone (AC) and trichloroethylene (TR) methods for each one of the charging conditions studied were very close. Nevertheless, it should be pointed that in the three cases the (TR) method showed a median value slightly higher (about 0.1 ppm) than the (AC) method.

On the other hand, the dispersion range between the first and third quartiles (Q1–Q3) obtained was similar for the as-received samples: 0.4 ppm with (AC) and 0.32 ppm with the (TR) method. But, in the cases of higher contents, the Q1-Q3 dispersion of the (TR) method was greater than the (AC) one: 1.65 ppm vs. 0.42 ppm for the charged samples and 0.6 ppm vs. 0.76 ppm for the charged and uncharged ones. The greater the Q1–Q3 dispersion in the (TR) method the higher the measured hydrogen content is, while the Q1–Q3 dispersion of (AC) seems to remain constant around 0.4–0.6 ppm. According to the bibliography, a dispersion up to 0.5 ppm between samples is usual when using the hot extraction technique and gas dose together with pattern pins to calibrate the analyzer [12,13,15], as was done in the present work.

5. Conclusions

There are multiple references to sample cleaning methods prior to hydrogen content determination, but there is still no unified criteria; different authors use their own "know-how" to perform this task.

In this paper, the most commonly used sample cleaning methodologies have been presented and compared. A wide range of five methods have been tested on certified hydrogen content calibration pins and samples obtained from a seven wire strand of high-strength steel, employing the hot extraction technique. Three different situations regarding hydrogen content in the microstructural net were studied: Samples without hydrogen charging (as-received), samples charged by a cathodic protection environment, and samples charged in the previous environment and discharged by air diffusion.

From the study carried out, the following conclusions can be drawn:

- The HCl solution C-3.5 method from ASTM G1 standard, (HCl), showed hydrogen contents around 2 ppm higher than the other methodologies (which showed close results), even for calibrated pattern pins. This proves that this method, while it can be useful for eliminating superficial oxides, corrosion deposits or dirt, introduces large amounts of hydrogen in the samples. Mechanical methods of cleaning (Section 2.3), might be also considered for this kind of tasks in order to not modify the hydrogen contents, being careful about not using abrasive that can affect it.

- The longest methodologies: The compound acetone and ultrasounds method, (AC+U), and the acetone, ultrasounds and trichloroethylene complete method, (AC+U+TR), showed slightly higher median values and dispersion ranges between first and third quartiles than the simple methods (AC) and (TR), but remain inside the usual range of uncertainties for a regular hydrogen analysis. This does not discard (AC+U) and (AC+U+TR) as valid methodologies, but the time and equipment demands are higher, so the simple methods (AC) and (TR) are generally preferred (cheaper, easier, and faster).

- The simple acetone method, (AC), and simple trichloroethylene method, (TR), are the adequate ones when the hydrogen content determination must minimize diffusion of the samples while being performed. (AC) and (TR) showed very close results for all charging conditions studied, while the greater the (TR) dispersion range between first and third quartiles the higher the hydrogen

content to be measured is; while (AC) Q1–Q3 dispersion remained constant at around 0.5 ppm. Either of these two methods can be considered adequate, taking into account the reliability of the results, their simplicity, and the speed of their execution; this last parameter is of vital importance in steel-making processes in order to not disturb the manufacturing chain.

From the abovementioned conclusions, it can be stated that all the methods tested, except for (HCl), can be applied for regular hydrogen content analysis when the samples do not have any superficial oxide, and simply need to be cleaned of common contaminants such as oil, grease, hand touching etc. Nevertheless, for economy and simplicity reasons, a general recommendation is to use the simple acetone (AC) and simple trichloroethylene (TR) methods, which were proven to be the most suitable ones.

As a final recommendation and general conclusion, taking into account that trichloroethylene is carcinogenic to humans by all routes of exposure and poses potential hazards for noncancer toxicity [29], the simple acetone method (AC) is, in general, the most suitable one to use, it being the cheapest, fastest, and safest of all.

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