

# A Brief Review on Methods for Diffusible Hydrogen Measurement in Welds

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## ABSTRACT

Hydrogen is obnoxious in high strength steels because it poses the risk of causing failure of material well below its yield strength. Failures triggered by hydrogen in weld joints are generally known as cold cracking or hydrogen assisted cracking. Cracks are not permitted in the welds and any undetected cracks can severely affect the performance of welded components and this is a serious safety concern. Hydrogen enters in steel weldment during welding and remains in the weld joint either as Diffusible Hydrogen or as residual hydrogen. While the residual hydrogen is immobile and has no role in cold cracking, diffusible hydrogen is free to diffuse at or near ambient temperatures. Diffusible hydrogen is accumulated in the regions of stress and produces a tensile stress field that expands the crystal lattice leading to microcracks. Therefore, diffusible hydrogen content in welds should be reduced to levels that do not cause cracking. This brings forth the need for measurement of diffusible hydrogen content in welds. However, the diffusivity of hydrogen in steel is very high and hydrogen starts effusing out even before the start of the measurement. Therefore, development of standard procedure for diffusible hydrogen measurement is difficult. In spite of the intricacy, several methods were developed in the past few decades for the measurement diffusible hydrogen because of the growing interests in the still not so clear role of hydrogen causing HAC and the increasing demand for batch production of welding consumables. This paper presents a brief yet a systematic review of the methods for diffusible hydrogen measurement in steel welds.

**KEY WORDS:** (Diffusible hydrogen), (Standard method), (Mercury method), (Hot extraction), (Gas chromatography), (PEMHS)

## 1.0 INTRODUCTION : NEED FOR DIFFUSIBLE HYDROGEN MEASUREMENT

It is well documented that diffusible hydrogen ( $H_d$ ), which is mobile in steel lattice at or near room temperature is mainly responsible for hydrogen assisted cracking (HAC) or cold cracking of in steel weld joints [1-3]. HAC has received considerable attention owing to its prevalence in steel welds [4]. Regardless of the extensive research and developments, HAC is still experienced regularly by fabricators, particularly during the welding of high-strength structural steels [2, 5]. Therefore, heavy responsibilities are placed on the fabricator

to employ appropriate safeguards in the welding procedures to prevent HAC. In this approach, the fabricators generally rely on preheating, interpass temperature control, post heating and post weld heat treatment, combined with the use of low-hydrogen basic-type welding consumables to reduce the risk of HAC. In this process, the choice of a safe preheat temperature requires a knowledge of the diffusible hydrogen content in a weldment [3]. The knowledge of hydrogen content also helps in classifying welding consumables based on their hydrogen contents. This paper presents a brief review of different methods available for the measurement of  $H_d$  in weldments.

## 2.0 PREPARATION OF SPECIMEN FOR H<sub>b</sub> MEASUREMENT IN WELDMENTS

There are several methods available for the determination of H<sub>b</sub> in weldments. Among these, four methods are currently recommended by various standards such as IIW/ISO [6], AWS [7], BS [8], JIS [9, 10], DIN [11], AS/NZ [12], GOST [13] and BIS IS [14]. These include glycerin method, mercury methods in which collection and measurement of hydrogen is carried out at room temperature, and gas chromatography method and/or carrier gas-hot extraction method and vacuum hot extraction methods for the rapid determination of H<sub>b</sub>. The determination of HD involves three steps.

1. Preparation of weld specimen
2. Collection of H<sub>b</sub> from the weld
3. Measurement of H<sub>b</sub>

Generally in all the methods, a standard weld specimen is used for H<sub>b</sub> measurement. A test assembly, used for preparing the weld specimen, consists of a specimen piece of dimension 30×15×10mm and run-on and run-off pieces of dimensions 45×15×10 mm (except in the case of glycerin method). The test assembly is degassed at 650°C for 1 h to remove any bulk hydrogen and cooled in a furnace. Their surfaces are ground to remove the oxide scale formed during degassing treatment. These are finished at right angles to ensure good contact between the adjacent pieces, cleaned with acetone followed by warm air and stored in desiccators until they were used for welding. During welding, the specimen is placed in between the run on and run off pieces. The run-on piece is used for arc striking and run-off piece for arc extinction during welding so that a stable arc and uniform shape of the deposit can be obtained on the specimen. The specimen is welded using prebaked welding consumables as discussed in the earlier sections. The welding is carried out by placing the test assembly on a welding fixture, a copper jig. The dimensions of the jig are such that during welding, the heat is immediately conducted away from the test assembly to the copper jig. More details regarding the preparation of weld specimen for H<sub>b</sub> measurement is available in the standards mentioned earlier [6-14]. A photograph of copper jig holding the test assembly is shown in **Fig.1**. The schematic of a test assembly after deposition of the bead is shown in **Fig. 2**. Immediately after the welding, the test assembly is quenched and stored at sub-zero temperatures. Dry ice or liquid nitrogen is used for storing the specimens till it is taken out for H<sub>b</sub> measurement. The run-on and run-off prices are broken off and only the specimen is used for measurement.

In the methods which use fluids like mercury or glycerin, H<sub>b</sub> is collected at or near room temperature. In hot extraction method like gas chromatography, vacuum extraction and PEMHS, H<sub>b</sub> collection is carried out at elevated temperatures which enable quick measurement. Details about the different methods available for collection and measurement of H<sub>b</sub> are given in the following sections.

## 3.0 METHODS BASED ON COLLECTION OF H<sub>b</sub> OVER A FLUID

### 3.1 Glycerin Method

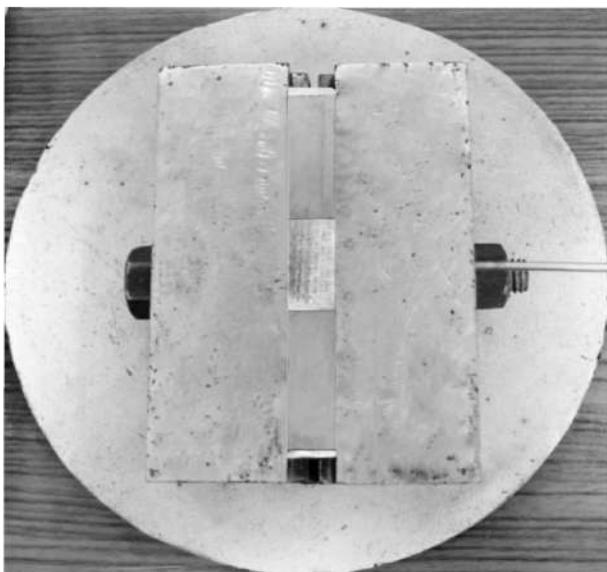
Glycerin method is the oldest method used for the determination of H<sub>b</sub> in welds. This method was first introduced in the AWS Specification A5.5-48T (ASTM A316-48T) in 1948 [15-18]. In this method, hydrogen is collected over glycerin in a graduated apparatus designed for this purpose (**Fig. 3a**). In this method, four test specimen blanks (each one of dimensions 125×25×12mm<sup>3</sup>) were deposited with a single bead using a prebaked 4mm diameter and 150mm long electrode [19]. The bead is deposited along the width of the specimens (along 25 mm each with a total of 100mm for four specimens). The welding conditions are a short arc and a welding current of 150A. After the deposition, the specimens are quenched in ice cold water, separated and stored under dry ice or liquid nitrogen until measurement. For the collection and measurement of H<sub>b</sub>, each of the four specimens is introduced in an apparatus containing glycerin as shown in **Fig.3b**. Temperature of glycerin is maintained at 45°C and hydrogen is collected from the weld sample for 48 hours. Hydrogen evolved from all the four specimens is collected simultaneously in four different apparatus. The amount of gas collected over glycerin is measured to the nearest 0.05 ml and the average estimated is corrected for standard temperature and pressure using equation 1. The H<sub>b</sub> content is expressed in ml of hydrogen per 100g of deposited metal.

$$H_{GLYCERIN} = \left( V_t \right) \left( \frac{273}{273+T} \right) \left( \frac{P}{760} \right) \left( \frac{100}{W_f - W_i} \right) \frac{ml}{100g} \quad ....1$$

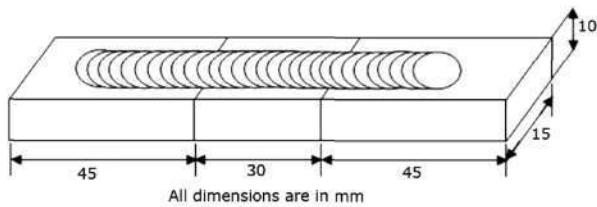
Where,  $H_{GLYCERIN}$  = H<sub>b</sub> measured using glycerin method,  $V_t$  = Volume of hydrogen measured at temperature  $T$  and pressure  $P$ ,  $W_i$  = Weight specimen before welding and  $W_f$  = Weight of specimen after welding.

Glycerin method was inexpensive and user friendly. This method showed wide scatter in results (50-90%) [18, 20, 21]

and was removed from the AWS A5.5 specification due to several other serious limitations. It was found that the  $H_2$  contents obtained over glycerin are consistently lower than those obtained over fluids such as mercury [22] because hydrogen is partially soluble in glycerin. Later, investigations revealed that the gas collected over glycerin is not entirely



**Fig. 1 : Copper jig holding test assembly**



**Fig. 2 : Schematic of test assembly**

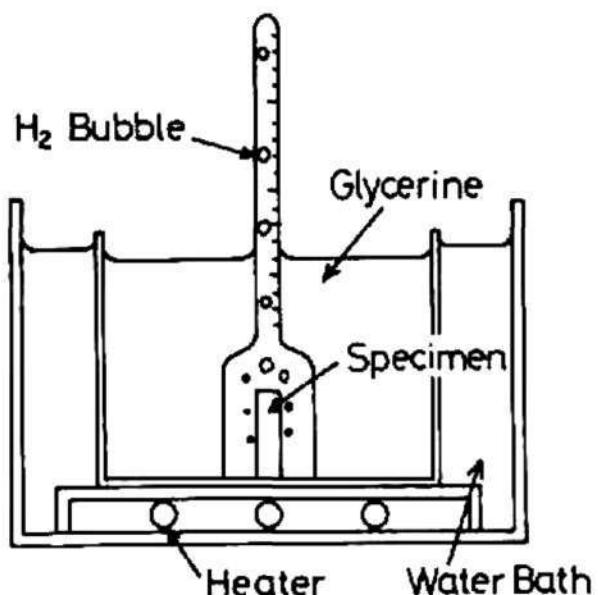


(a) Photograph

hydrogen but is a mixture of several other gases soluble in glycerin such as oxygen and nitrogen.  $H_2$  contents obtained using this method changed with change in the purity and viscosity of glycerin and with variation in glass shape and size shapes of glassware [23]. Also, this method was not suitable for measurement of very low levels of  $H_2$  (<2ml/100g) because of significant solubility of hydrogen in glycerin. Despite the limitations, this method is in use by American bureau of shipping [24, 25].

### 3.2 Mercury Method

Collection of  $H_2$  over mercury is widely accepted and is by far the most reliable method. With the removal of glycerin method from the standard, mercury was the obvious choice as a hydrogen collection medium [18, 26]. This method was adopted as a standard method for the first time in the standard ISO 3690:1977 [17]. In mercury method, weld specimens are prepared as discussed in section 2. The materials, apparatus, procedures for specimen preparation,  $H_2$  collection and its measurement using this method are detailed in many standards mentioned above [6, 7, 12]. For measurement, the weld specimen, after quenching and cleaning, is admitted into a Y-tube eudiometer of mercury apparatus and the limb is closed. The weld specimen is moved to the graduated closed limb of the Y-tube with the help of a magnet. The Y-tube along with the weld specimen is evacuated. The weld specimen is allowed to evolve hydrogen until complete evolution of hydrogen from weld specimen [6]. The gas collected in the Y-



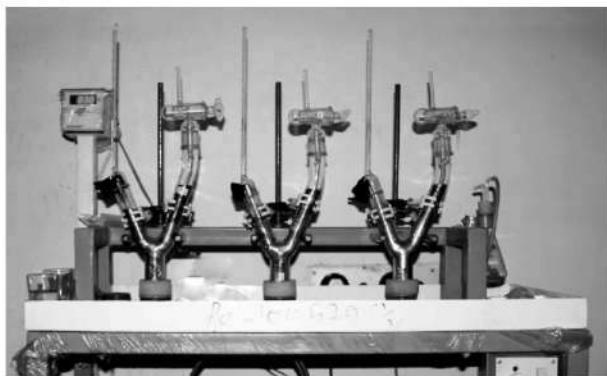
(b) Schematic

**Fig. 3 Glycerin apparatus for  $H_2$  measurement**

tube was normalized to standard conditions of temperature and pressure using equation 2 and was expressed in ml of hydrogen per 100 grams of deposited metal. Three such measurements are carried out simultaneously in three Y-tubes

$$H_{MERCURY} = \left( V_F - V_I \right) \left( \frac{273}{273+T} \right) \left( \frac{B-H}{760} \right) \left( \frac{100}{W_F - W_I} \right) \quad ..... 2$$

Where,  $H_{MERCURY}$  =  $H_0$  measured by the mercury method at STP (ml/100g of deposited metal),  $V_i$  = Initial volume of gas in the burette of Y-tube,  $V_f$  = Final volume of gas in the burette of Y-tube,  $T$  = Temperature at which measurement is carried out,  $W_f - W_i$  = Weight of the deposited metal,  $B$  = Ambient pressure reading in the Barometer,  $H$  = Mercury head, i.e., Difference in the heights of mercury levels in the two limbs of Y-tube at the end of measurement.



**Fig. 4 : Mercury apparatus used for HD measurement**

Results obtained using mercury method are found to be reproducible and reliable. This method is recommended as the primary standard/reference for  $H_b$  measurement. Any new method to be used for  $H_b$  measurement must show good correlation with the mercury method [6]. This method is retained in the recent revision of IIW, ISO 3690:2012 along with a couple of emerging hot extraction methods and is recommended by several other standards like AWS A4.3, AS/NZ S3572. The major difference in the mercury method in ISO 3690:1977 and ISO 3690:2012 is the increase in the time of hydrogen collection from 72 h to the complete evolution of hydrogen which is about 12-21 days (It is recommended in ISO 3690:2012 that the collection of hydrogen must be continued until there is no increase in the calculated volume of hydrogen for  $H_b$  measurements on successive days). The change in collection time was based on a study by Jenkins et al [27] who found that the  $H_b$  contents obtained from 72 h measurements show poor reproducibility. Also, the results obtained from 72 h

measurements were consistently lower than those obtained for 21 day measurements at room temperature. Though this method resolved all the issues associated with glycerin method, fear of possible health hazards associated with the handling of mercury and long time required for completion of measurements introduced new concerns on H<sub>2</sub> measurements. Recently, it was suggested that hydrogen collection from weldment in mercury can be carried out at temperatures up to 180°C with reduced safety concerns by incorporating some modifications to the mercury eudiometer design and sealing [28]. However, no further developments are reported in the literature regarding the implementation or consideration of these modifications. Due to safety concerns, this method is not allowed in many countries.

### **3.3 Other methods based on collection of H<sub>2</sub> over fluids**

Apart from the above mentioned methods, there are many other methods which are neither included in any standard nor are in wide practice either because of serious drawbacks or because of limited investigation and availability. Most of these methods are similar to mercury or glycerin methods in principle which is based on volumetric displacement of a liquid/fluid by the  $H_2$  evolved from the weld specimen and subsequent volume measurement. These differ only with respect to the type of fluids over which  $H_2$  is collected. The liquids which are employed in these methods include silicone oil [29], water [30], 10N  $K_2CO_3$  [31], ethyl alcohol, ethylene glycol, paraffin and carbon tetrachloride [23]. The percentage of  $H_2$  collection over these fluids in comparison to mercury is given in **Table 1**.

**Table 1 : Efficiency of H<sub>2</sub> collection over different collecting fluids [23]**

Collecting mediums	Efficiency of H <sub>b</sub> collection (%)	Remark
Mercury	100	Widely Accepted
‡ 10N K <sub>2</sub> CO <sub>3</sub>	100	Insufficient investigation
*Water	100	Insufficient investigation
Silicone oil	100†, 5-32	Insufficient investigation
Glycerin	79-88	Poor accuracy
Ethyl alcohol	23-39	Poor accuracy
Distilled water	58-72	Poor accuracy
Ethylene glycol	18-32	Poor accuracy
Paraffin	10-19	Poor accuracy
Carbon tetrachloride	10-20	Poor accuracy

<sup>†</sup>[29], \* [30], # [31]

Except for the collection over mercury, all the other volume displacement methods mentioned above are not used for  $H_b$  measurement because of their poor accuracy. However, the collection over glycerin is still in use following some modifications [24].

#### 4.0 METHODS BASED ON THE COLLECTION OF $H_b$ AT AN ELEVATED TEMPERATURE

With the increasing demand for batch production of welding consumables, there was an urgent need for the quality control to reduce the minimum 72 h requirement for  $H_b$  collection to reasonably lower collection time. It was almost certain that collection times cannot be lowered by adopting collection of hydrogen over fluids. This required adoption of techniques with provisions of heating the weld to accelerate the evolution of hydrogen. Methods developed over the past three decades for the rapid determination of  $H_b$  are discussed below.

##### 4.1 Gas Chromatography Method

Gas chromatography (GC) was the first method which provided scope for the rapid determination of  $H_b$ . In this method, the weld specimen is enclosed in an isolated collection chamber (**Fig. 5**) and heated to 150°C [17, 32-34]. Either argon gas is filled inside the chamber to keep the specimen in an inert atmosphere or the chamber is evacuated after keeping the specimen in it. An aluminium or steel chamber is used for  $H_b$  collection [31]. After the collection of  $H_b$ , its analysis is carried out using a GC. Since the weld specimen was heated at high temperature, evolution of diffusible hydrogen from the weld specimen is completed in 6 h. Therefore, in the GC method, the time duration of  $H_b$  measurement is reduced to 6 h [35].

In the GC method hydrogen analysis is based on the change in thermal conductivity. Details about the  $H_b$  measurement using this method are given elsewhere [36-38]. In general, gas chromatography involves the separation of a mixture of gases in its column. It detects the individual gases in a gas mixture. The separation of individual gases is achieved on the basis of their retention time in the stationary phase of the GC column. Retention time is the time for which a gas is retained in the column. For a given column, different gases have different retention times. Therefore In a gas mixture, different gases reach the thermal conductivity detector (TCD), at different times. In the  $H_b$  measurement, a carrier gas such as pure argon accompanies the hydrogen collected in the collection chamber to the TCD. TCD setup has four Tungsten-Rhenium alloy filaments connected in two channels in a Wheatstone bridge

configuration. During the analysis, these filaments are heated to a particular temperature. When different gases are passed across the channels, heat is lost and each channel will experience a temperature drop depending upon the thermal conductivity of the gases. The temperature gradient across the channels induces a change in the filament resistance. The principle of gas analysis using the TCD is the measurement of the change in resistance. For  $H_b$  measurement, initially a baseline is set by passing the same gas (reference gas) across both the channels. Later,  $H_b$  collected in the chamber is injected through the GC column. In this situation, gas mixture containing hydrogen flows across one of the channels and the reference gas across the other. This produces a change in resistance and a net output voltage ( $V_{out}$ ) which is displayed as a peak. The area under the peak is proportional to the volume of hydrogen in the gas mixture. A typical hydrogen peak from GC is shown in **Fig. 6**. Before carrying out actual measurement the GC is calibrated using known volume of hydrogen injected into the GC.

$H_b$  contents obtained with GC agreed well with those obtained with the standard mercury method. This method is recommended by various standards such as ISO 3690: 2012,

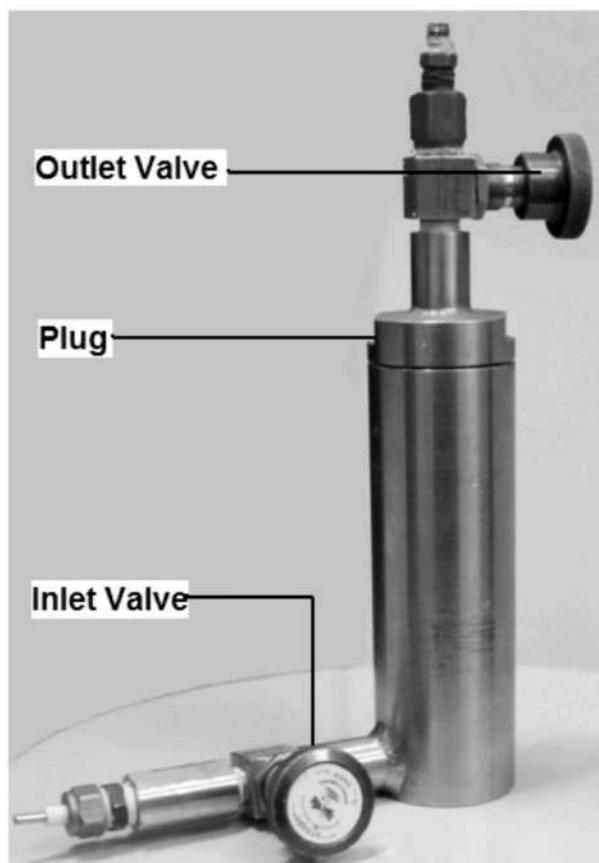


Fig. 5 : Chamber for  $H_b$  collection

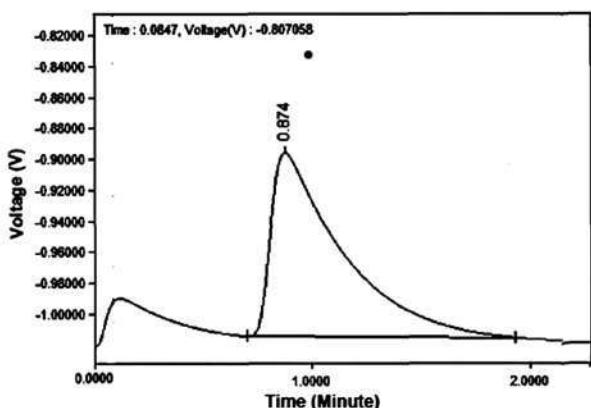


Fig. 6 : Response of GC for a hydrogen injection

AWS A4.3-93, AS/NZ S3752, JIS Z 3118, etc. In the mid 90's, Oerliken-Yanaco marketed a GC based H<sub>2</sub> analyzer (**Fig.7**) which was widely used by welding consumable manufacturers. At that point, temperature higher than 150°C was not

considered for H<sub>2</sub> collection because of two reasons. First, a slight possibility of oxidation of specimen surface at higher temperatures. Surface oxidation is known to slow down hydrogen evolution from the weld specimen [21, 39, 40]. Second issue was overestimation of H<sub>2</sub> due to the release of residual hydrogen at higher temperatures [41]. Though this method is comparatively faster than the mercury method and the results obtained using this method agrees well with mercury method, there are still several limitations. The results obtained using this method are affected significantly by factors such as the incomplete purging of the collection chamber, traces of moisture in the carrier gas and moisture contamination in the dehumidifier or in the GC column [35, 37, 42]. Also, this method demands calibration before each analysis [35, 37]. Although the H<sub>2</sub> measurement using this method is completed within 6 h, with the increased demand for

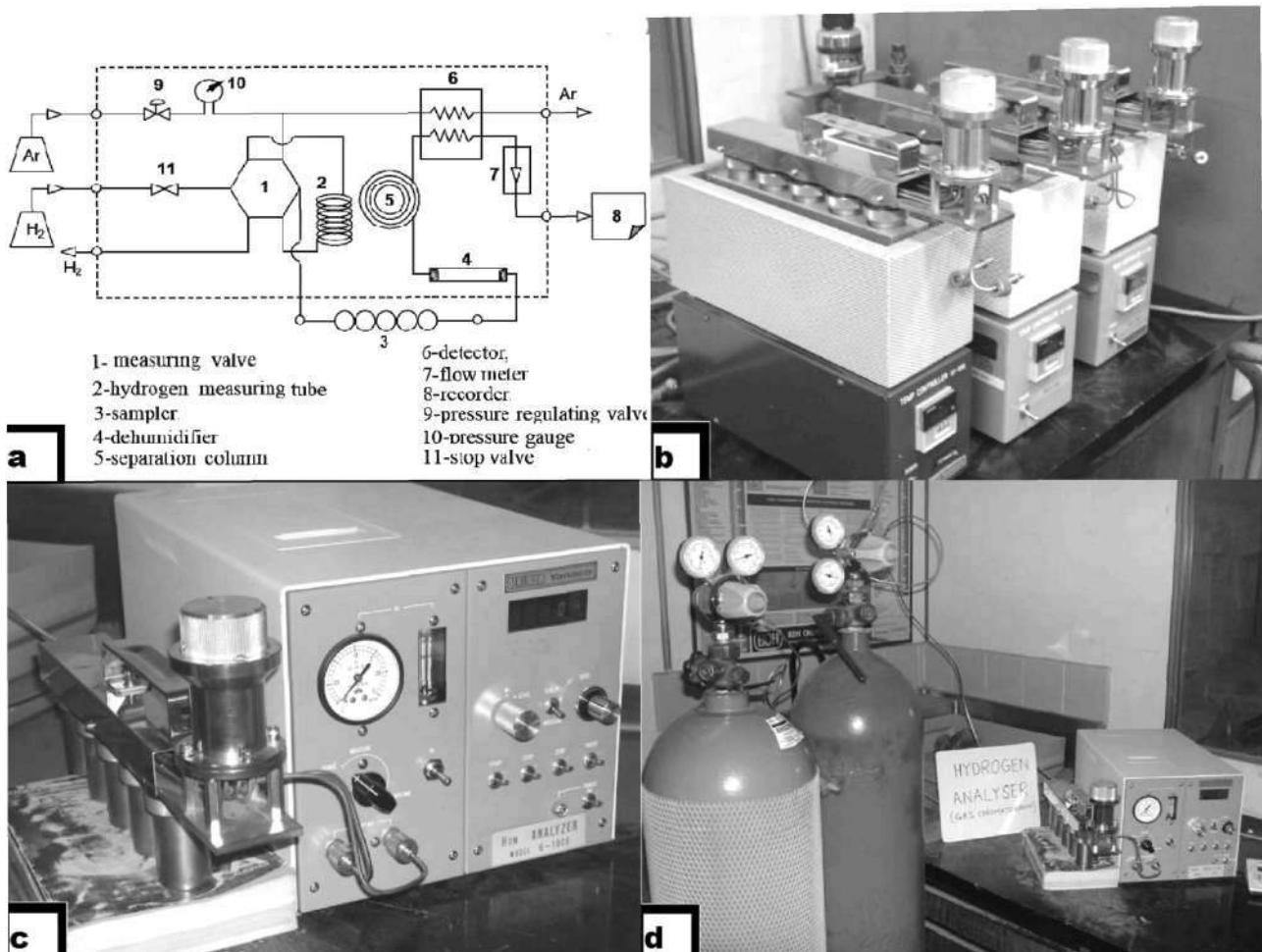


Fig. 7 Oerliken-Yanaco GC setup for HD measurement (Photo Courtesy: [54])  
 a)Flow Diagram of GC apparatus b) Electric Furnaces to heat chamber  
 c) Chambers Connected to GC analyzer d) Carrier gas connected to GC analyzer

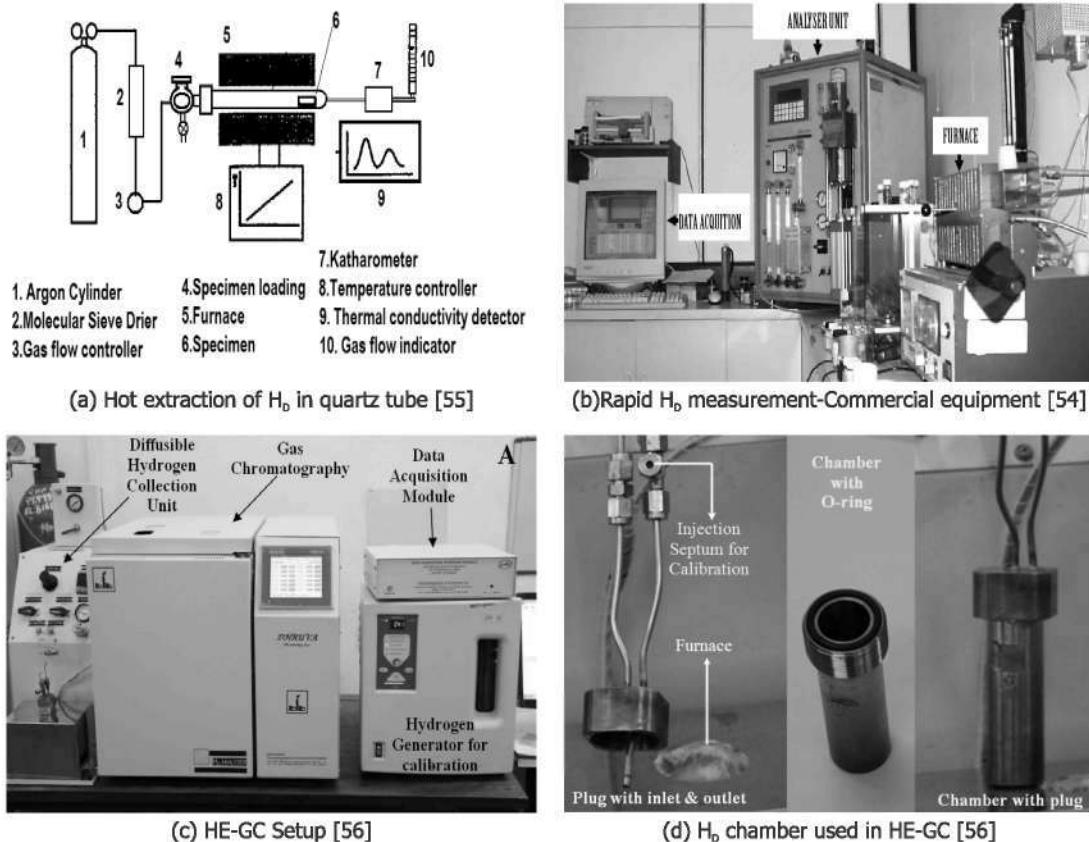


Fig. 8 : Hot extraction equipments based on GC

quality control and batch testing for product release still shorter analysis times were called for [43].

#### 4.2 Methods employing hot extraction (HE) of $H_2$ at higher temperatures

Hot extraction based methods were developed for rapid determination of diffusible hydrogen in welds [38, 39, 43]. In these methods,  $H_2$  from a weldment is extracted at very high temperatures,  $\sim 400^\circ C$ . At such higher temperatures, the collection of  $H_2$  is accomplished within 0.5 h and the total time of  $H_2$  measurement is less than 1 h. Also, it is found that the  $H_2$  contents measured using the hot extraction methods are precise, reproducible, and repeatable and are in good agreement with the primary and other alternative standard methods, therefore reliable [43-53]. At present, there are many different equipments available for the hot extraction of  $H_2$  from weldments. In general, all these equipments have two parts, a hot extraction module for the extraction and collection of hydrogen from the weld specimen at higher temperatures ( $\sim 400^\circ C$ ) and an analyzer for the detection and analysis of hydrogen extracted. Generally, a quartz tube is used for the hot extraction of  $H_2$  from weldments [55]. The commonly used

hydrogen detectors are GC and mass spectrometer. Schematics of a hot extraction method employing a quartz tube for hot extraction of  $H_2$  and a GC for hydrogen measurement is shown in Fig. 8(a). Photograph of a commercial hydrogen analyzer using hot extraction of diffusible hydrogen and measurement using a GC is shown in Fig. 8(b). Fig. 8(c) shows a GC based equipment modified for hot extraction of  $H_2$  at  $400^\circ C$  and Fig. 8(d) shows the hot extraction chamber used in this equipment. The principle of hydrogen measurement is same as discussed in the previous section.

Recently, an inexpensive and user friendly hot extraction method using a Nafion based proton exchange membrane hydrogen sensor (PEMHS) for detection and measurement of hydrogen was developed for the rapid determination of  $H_2$  [51, 52]. The hot extraction chamber used in this method (Fig. 9(a)) is slightly different from the ones discussed earlier. The present chamber has a small tubular furnace inside it. The weld specimen under investigation is kept inside the furnace, the chamber is closed and pressurized with argon to a known pressure. The specimen is heated inside the chamber as

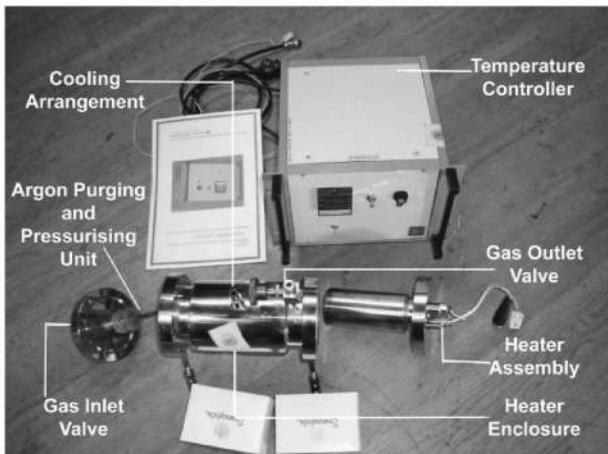
desired. After H<sub>d</sub> collection, the amount is hydrogen is determined using PEMHS. PEMHS is an electrochemical hydrogen sensor which has Nafion as its electrolyte. Nafion is a polymer and is coated with platinum black on its sides. The platinum coating works as electrodes of the electrochemical cell. The cell is calibrated by injecting known concentrations of hydrogen in Ar+H<sub>2</sub> gas mixture. When hydrogen is passed on to the sensor, it responds with a peak corresponding to the concentration of hydrogen in the Ar+H<sub>2</sub> gas mixture. From this concentration, volume of diffusible hydrogen is calculated using equation 3. Detailed principle and procedure of H<sub>d</sub> measurement using the HE-PEMHS sensor is given elsewhere [50-52, 57-59]. A crude set up of HE-PEMHS is shown in **Fig. 9(b)**.

$$H_{PEMHS} = PV \left( \frac{C}{10^6} \right) \left( \frac{100}{M} \right) \quad ..... 3$$

Where,  $H_{PEMHS}$  = H<sub>b</sub> content obtained using PEMHS method (ml/100g), C = Concentration of hydrogen collected in the chamber, P = Argon pressure in the chamber, V = Available volume of the chamber, M = Weight of deposited metal = Difference in weight of specimen before and after weld

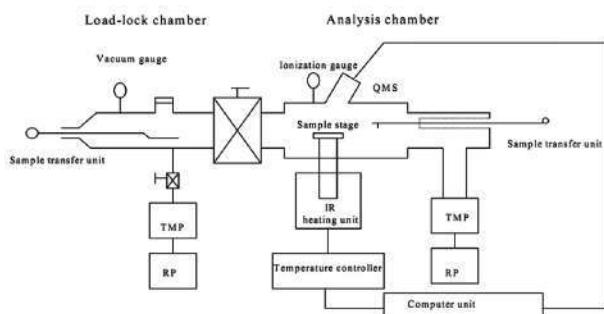
From the author's point of view, thermal desorption spectrometer (TDS) using mass spectrometers can be useful prospects for the study of diffusible hydrogen, residual hydrogen and total hydrogen of a weld specimen. The only drawback is that the instrument is very expensive in comparison with other equipments used for  $H_d$  measurement. Schematics of a TDS is shown in **Fig. 10**

ics of a TDS is shown in **Fig. 10**

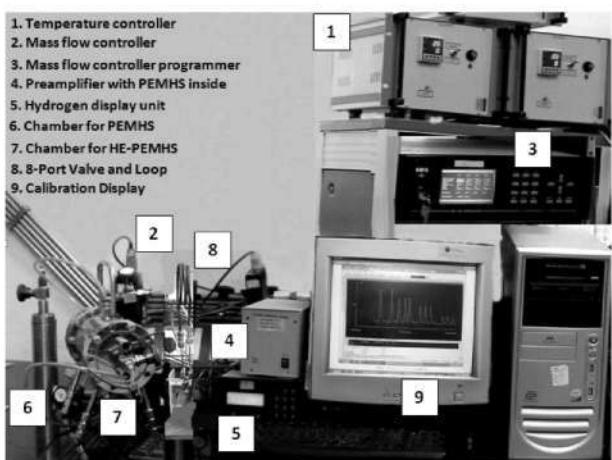


e) Hot extraction chamber of HE-PEMHS[162]

The two principal objections against hot extraction as mentioned earlier are, the potential loss of hydrogen through reactions with oxide layers present on the specimen surface [39-40] and the risk of residual hydrogen release at higher temperatures; the latter being more serious in affecting the reliability of the measurement than the former. Since an inert atmosphere is used during the hot extraction, surface oxidation of weld specimen is highly improbable. To avoid any surface oxidation, specimen cleaning by wire brushing was proposed [44]. The second issue was overestimation of H<sub>d</sub>. However, residual hydrogen release up to 400°C was either found to be insignificant or neglected in view of environmental and safety benefits associated with using this method [39, 45]. Also, the issue of residual hydrogen evolution can be neglected because diffusible hydrogen is an issue with high strength steel welds whose residual hydrogen content is almost negligible due to the absence of deep trap sites.



**Fig. 10 : Schematic of TDS used for monitoring hydrogen emission**



**Fig. 9 : Hot extraction equipment based on PEMHS**

At present, of hot extraction method seems to be the best compromise between reliability, time, and money with respect to  $H_b$  measurement in welding consumables. However, commercial hot extraction equipments for  $H_b$  measurement are available only from a few and are still very expensive.

#### 4.3 Vacuum-Extraction methods

There are reports of two types of vacuum extraction methods in the literature; one, measuring hydrogen at room temperatures [40] and the other at high temperatures [35]. Schematics of these two methods are shown in **Fig. 11**. The investigator of room temperature vacuum extraction method claims that the method measures  $H_b$  at a better accuracy than glycerin method. In the vacuum hot extraction method, the weld specimen is heated at higher temperatures in a silica furnace tube for extraction of  $H_b$ . Hydrogen along with any other gas so extracted is passed through two nitrogen cold traps into an expansion volume where condensable gases freeze out. The combined pressure of hydrogen and other gases reaching the expansion volume is monitored by a pressure gauge till the hydrogen evolution ceases. Hydrogen is removed through the palladium/silver osmosis tube and pressure of rest of the gases is measured. The difference in these two pressures is the pressure of  $H_b$ . The  $H_b$  contents obtained with this method are on the lower side as compared to that using the carrier gas hot extraction method [35].

#### 5.0 METHODS FOR DETERMINATION OF LOCAL HYDROGEN CONCENTRATION IN WELDS

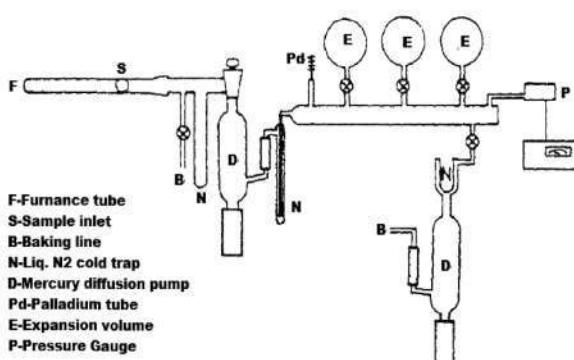
The methods discussed in the previous sections, however, are not able to determine the local hydrogen concentration in a specific area of the weld. Only the bulk hydrogen can be

measured using these methods. However, it is known that residual stress is localized in some regions of the weld. Therefore, studies on the local HAC susceptibility of a weldment require the determination of local hydrogen concentrations. For this, Olson et al and Smith have used laser ablation methods which use laser induced breakdown spectroscopy combined either with GC or with Mass spectrometry [41, 55]. Olson et al and Smith also developed a tungsten oxide based optoelectronic or fiber optic sensor [55, 60, 61] to determine the local hydrogen concentration. The sensor has a hydrogen sensing layer coated with chemochromic tungsten oxide. The sensing layer undergoes changes in physical properties, such as optical transmission properties, when it reacts with hydrogen. The changes are measured to determine the amount of hydrogen evolving from the sample area. A Seebeck hydrogen instrument based on the measurement of thermoelectric coefficient was also developed by the above researchers for the estimation of  $H_b$  content in welds [55, 62]. Recently, a non-contact hydrogen sensor based on low frequency impedance measurement was developed by Lasseigne et al [63, 64] for real time measurement of  $H_b$ . However, at present, these methods are not adopted for the  $H_b$  measurement in welds.

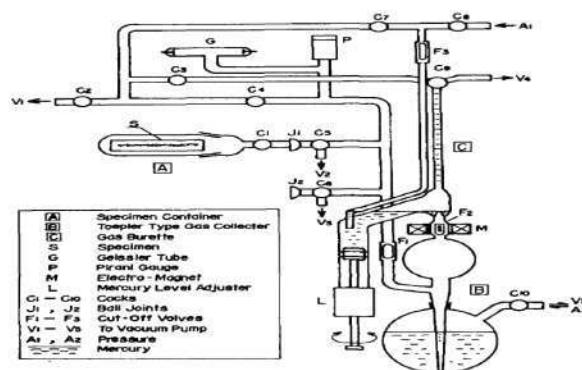
#### 6.0 COMPARISON BETWEEN DIFFERENT METHODS OF $H_b$ MEASUREMENT

##### 6.1 Glycerin method Vs Mercury method

As it was mentioned in the previous sections, glycerin method produced lower levels of hydrogen as compared to the mercury method. Kotecki [18] has summed up three studies which compared the results of the glycerin and the IIW mercury



(a)At room temperature[40]



(b)With hot extraction [35]

**Fig. 11 : Vacuum extraction apparatus for HD measurement**

methods. The correlating relationships obtained are given below.

$$H_{JS} = 0.64H_{HW} - 0.93 \quad \dots\dots\dots(4)$$

$$H_{JS} = 0.67H_{HW} - 0.80 \quad \dots\dots\dots(5)$$

$$H_{JS} = 0.79H_{HW} - 1.73 \quad \dots\dots\dots(6)$$

The above relationships show very little difference. However, it is found that results with glycerin method are consistently lower than those with mercury method.

## 6.2 Mercury method Vs GC method

Hydrogen contents obtained with GC method ( $H_{GC}$ ) at 150°C showed good correlation against those with the mercury method ( $H_{HW}$ ). A correlating relationship reported is given below [21]:

$$H_{GC} = 1.05H_{HW} \quad \dots\dots\dots(7)$$

## 6.3 Mercury method Vs HE method

Hydrogen contents obtained with hot extraction method ( $H_{HE}$ ), HE-PEMHS method ( $H_{PEMHS}$ ) and gas chromatography at 400°C ( $H_{HE-GC}$ ) showed good correlation with those from the mercury method ( $H_{HW}$ ). The correlation obtained from a round robin test is given below [46, 51, 56]:

$$H_{HE} = 0.94H_{HW} - 0.37 \quad \dots\dots\dots(8)$$

$$H_{PEMHS} = 0.998H_{HW} + 0.03 \quad \dots\dots\dots(9)$$

$$H_{HE-GC} = 1.005H_{HW} + 0.22 \quad \dots\dots\dots(10)$$

The hydrogen contents obtained with HE-PEMHS ( $H_{PEMHS}$ ) are also in good agreement with those obtained with a commercial H<sub>b</sub>-Analyzer ( $H_{ANALYSER}$ ) as given below [51]:

$$H_{PEMHS} = 0.99H_{ANALYSER} + 0.03 \quad \dots\dots\dots(11)$$

The H<sub>b</sub> contents are determined by static ( $H_{STATIC}$ ) and dynamic ( $H_{DYNAMIC}$ ) hot extraction measurements on an international round robin test [47]. Dynamic measurement stands for the hot extraction of H<sub>b</sub> and measurement at 400°C whereas static measurement stands for H<sub>b</sub> measurement at lower temperatures. The following correlations are obtained:

$$H_{DYNAMIC} = 1.14H_{STATIC}(45^\circ\text{C}) \quad \dots\dots\dots(12)$$

$$H_{DYNAMIC} = 0.78H_{STATIC}(100^\circ\text{C}) \quad \dots\dots\dots(13)$$

$$H_{DYNAMIC} = 0.76H_{STATIC}(150^\circ\text{C}) \quad \dots\dots\dots(14)$$

In equations 4 to equation 14, the subscript of H denotes the method of H<sub>b</sub> measurement.

The correlations show that the static and dynamic measurements may yield slightly different results depending upon the temperature of the static measurement. Therefore, the hot extraction methods show good accuracy, reproducibility and good correlation with the primary IIW mercury method.

## 10.0 SUMMARY

A literature review was carried out on the different methods available for the measurement of diffusible hydrogen in welds. It is understood that proper knowledge of H<sub>b</sub> content is essential to choose appropriate preheat temperatures to avoid the risk of HAC. H<sub>b</sub> measurement is an important step in achieving this objective. There are several methods available for the measurements of H<sub>b</sub> content in the weldments. Among these, the hot extraction based methods are better than the other low temperature methods with respect to accuracy, reproducibility and speed of measurement to meet the demands of batch production of welding consumables. New techniques are being developed in the pursuit of a method which would enable rapid measurement of the bulk as well as the local hydrogen concentration while being cost-effective, accurate and robust. Also, there is a need for the measurement of local hydrogen concentration in the welds for a better understanding of HAC.

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