Technical Note

Hydrogen Analysis in steel and metals: Solid Extraction or Fusion

Jérôme Barraqué
Jobin Yvon S.A.S., 16-18 rue du Canal, 91 165 Longjumeau, France

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1 Introduction

The JY HORIBA EMGA 621W Hydrogen analyzer has been designed for accurate measurements of hydrogen content in different sample types such as ferrous metals, non-ferrous metals, semiconductors or electronic materials. The hydrogen content is extracted by fusion of the sample in inert gas and analyzed by a high sensitivity thermal conductivity detector. It is also possible to avoid fusion and extract hydrogen content in the sample by heating below the melting point. The purpose of this note is to explain when to use fusion or solid extraction, the benefits, the applications and samples.

2 Principle of the EMGA 621W

The sample is placed in a graphite crucible. The crucible is maintained between the higher and the lower electrode of the impulse furnace. A high current passes through the crucible creating an increase of the temperature. The gas generated in the furnace is analyzed by the thermal conductivity detector after dust and moisture removal.

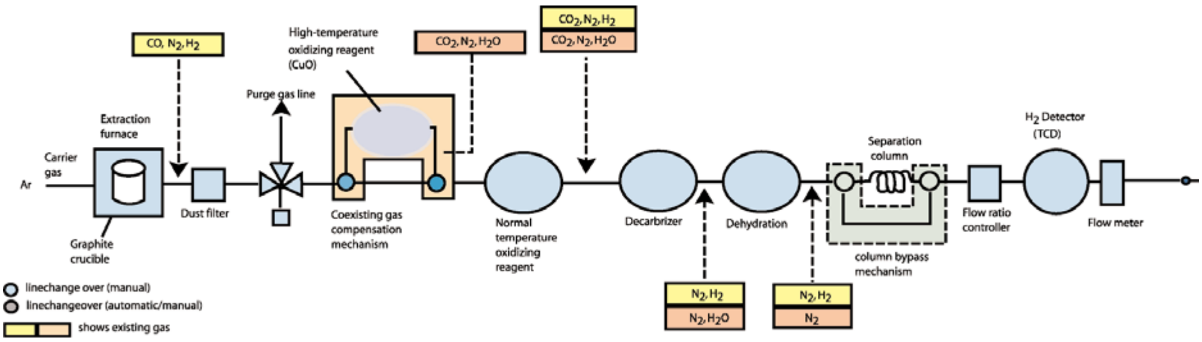

Figure 1: Principle of the EMGA 621 W

3 Graphite crucibles

For Hydrogen analysis two different kind of graphite crucible can be used: small and long crucibles.

3.1 Small crucible

The small crucible (figure 2) is used for high hydrogen concentration. A small sample quantity can be used with this crucible.

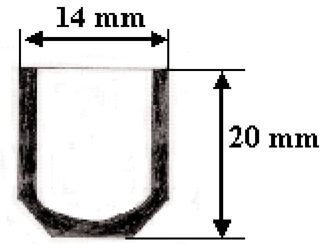

Figure 2: Small crucible

3.2 Long shape crucible

The long shape crucible (figure 3) is for low sample hydrogen concentration. In this kind of crucible a higher amount of sample is analyzed.

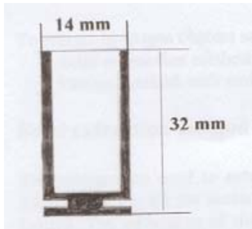

Figure 3: Long crucible

3.3 Inner crucible

Another small graphite crucible, called the inner crucible (figure 4), can be added to improve temperature homogeneity. This cricible can be added inside both of the previous crucibles.

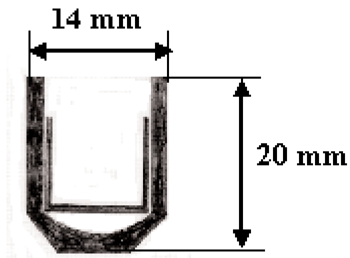

Figure 4: Inner crucible

The graph below shows the correlation between the power applied in the EMGA 621W furnace and the temperature obtained at different positions of the crucibles.

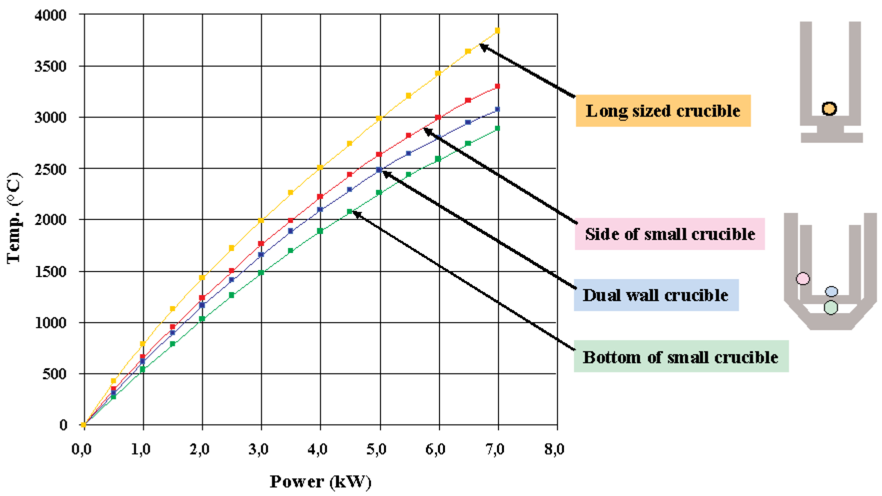

Figure 5: Power-Temperature correlation

4 Extraction methods

To extract hydrogen content in the sample two different methods are used:
- Solid extraction method without melting the sample with where the hydrogen will migrate out of the solid sample,
- Fusion method with melting of the sample.

4.1 Solid extraction method

The temperature used to extract the hydrogen content is below the melting point (500°C-1200°C) during the entire measurement (see figure 6). The sample will not be melted. The advantage of this method is that the same crucible can be re-used for several analyses, thereby reducing the cost of analysis. With this method the analysis will be longer and for some cases it is possible that some hydrogen will remain in the sample.

On the example, shown in figure 6, the extraction temperature was 900°C. It is necessary to optimize the extract temperature according to the sample type and properties, usually from 500°C to 1200°C. The programming is very easy because it is possible to enter directly the temperature in °C even if the furnace control is power (kW).

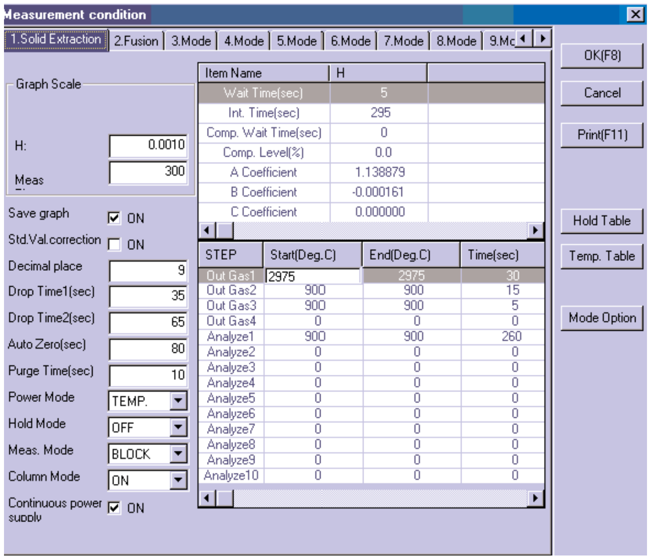

Figure 6: Solid extraction parameters

4.2 Fusion method

The temperature used to extract the hydrogen content is about 2000°C during the entire measurement (see figure 7). The sample will be totally melted. The advantage of the fusion method is that all the hydrogen content is extracted and the measurement is fast (less than 2 minutes). Each crucible is used only once during the fusion method.

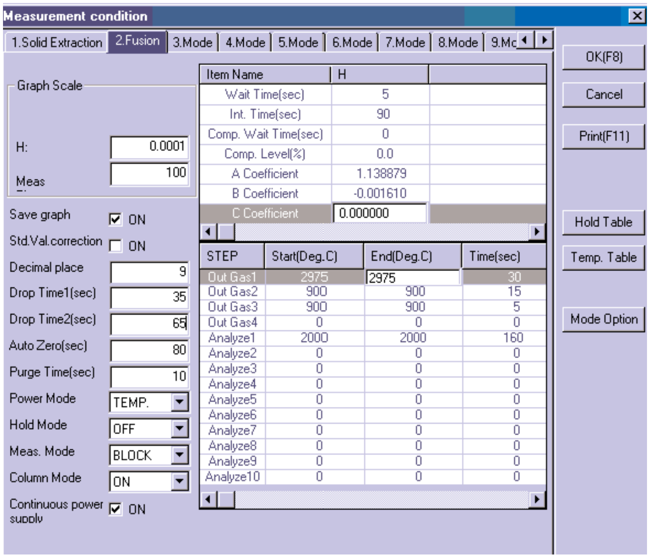

Figure 7: Fusion parameters

5 Sample preparation

To analyze steel, copper, titanium, rare-earth, aluminium rods or blocks samples the sample has to be prepared before the analysis to remove the surface contamination. They must be prepared carefully. The sample temperature should not increase because the hydrogen can diffuse out of the sample and a loss of Hydrogen can occur during the sample preparation.

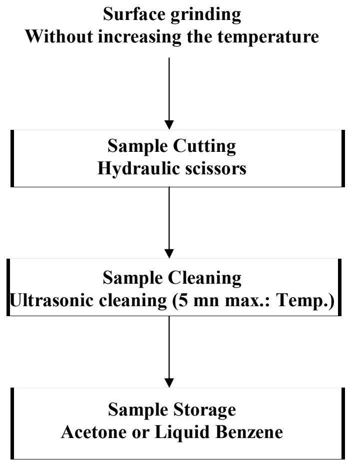

Figure 8: Sample preparation protocol

6 Calibration methods

To calibrate the EMGA 621W, two different methods can be used: a sample calibration using certified Hydrogen standard samples and a gas calibration using pure Hydrogen gas.

6.1 Sample calibration

For the sample calibration, three blanks and a Hydrogen standard sample times are measured three times. The concentration of the standard sample will be selected in order to cover all the concentration range of the samples.

6.2 Gas calibration

For the gas calibration, a fixed volume of pure Hydrogen gas is injected in the flow circuit. Based on this volume and on the pure gas concentration, the equivalent sample concentration is calculated: approximately 200 ppm for 100% Hydrogen gas).

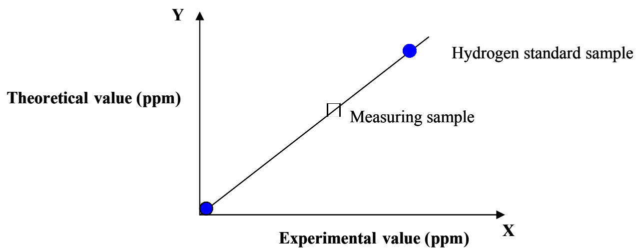

Figure 9: Calibration curve

7 Recommended method type

One of the most important advantages of the EMGA 621W is that a solid extraction and a fusion method can be done on the same instrument. On the table below you will see which method is recommended to analyze the different sample types.

Table 1: Recommended method for various applications

Applications	Solid Extraction	Fusion	Comments
Steel	Yes	Yes	No problem in both methods
Stainless steel	Yes	Yes	No diffusion at ambient temperature (diffusion 1100°C)
Steel Alloy	Yes	Yes	No problem in both methods
Nickel	Yes	Yes	Same behaviour than steel
Aluminium	No	Yes	Surface Hydrogen problem
Zirconium	No	Yes	Difficult in solid extraction
Titanium	No	Yes	Fusion recommended

8 Results

Table 2 shows that the fusion and the solid extraction provide similar results.
The only disadvantage is that the solid extraction is longer than the fusion.

Table 2: Steel sample with 3% Chromium

Fusion (H ppm)	Extraction Time (s)	Solid Extraction (H ppm)	Extraction Time (s)
1.9	80	1.9	295
1.9	80	1.8	295
2.0	80	1.9	295

The concentrations below are close to the previous results. It shows in this case, that the hydrogen diffuses very slowly out of this kind of sample.

Table 3: Steel sample with 3% Chromium (left for a long time at ambient temperature)

Fusion (H ppm)	Extraction Time (s)	Solid Extraction (H ppm)	Extraction Time (s)
1.6	80	1.6	295
1.7	80	1.7	295
1.6	80	1.5	295

The results shown in Table 3 below between both methods are slightly different. The concentrations in solid extraction are lower than in fusion. For this kind of sample it is more difficult to extract all of the hydrogen and fusion is the recommended method.

Table 4: Stainless Steel

Fusion (H ppm)	Extraction Time (s)	Solid Extraction (H ppm)	Extraction Time (s)
1.15	80	1.02	295
1.15	80	0.94	295
1.13	80	1.02	295
1.15	80	0.91	295

8.1 Example of fusion and solid extraction curves

The graph in figure 10 below shows the fusion and the solid extraction graph for the same sample. On the graph, the red curve represents the fusion temperature (2000°C) and the solid extraction temperature (900°C). One blue line is the extraction curve of Hydrogen in fusion mode and the other for solid extraction. The extraction time is faster in the fusion mode.

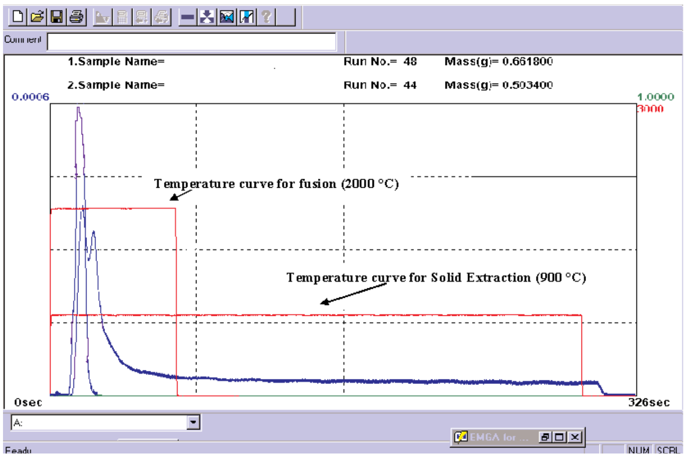

Figure 10: Fusion and solid exctraction curves

9 Conclusion

The EMGA 621W provides both fusion and solid extraction methods. According to the sample matrix (titanium, zirconium, aluminium...) and the analyst's expectations it is possible to select the proper method. Care must be taken for the sample preparation to avoid hydrogen loss due to an increase of the sample temperature.

In the USA:
Jobin Yvon Inc.
3880 Park Avenue
Edison, NJ 08820
Tel: 1-732-494-8660
Fax: 1-732-494-8796
E-mail: info@jobinyvon.com

In France:
Jobin Yvon S.A.S.
16-18, rue du Canal
91165 Longjumeau Cedex
Tel: (33) 1/64 54 13 00
Fax: (33) 1/69 09 90 88

In Japan:
Horiba Ltd.
2 Miyanohigashi, Kisshoin
Minami-ku, Kyoto 601-8510
TEL: (81) 75 313 8121
FAX: (81) 75 321 5725
www.horiba.com

Germany: (49) 89/46 23 17-0
Italy: (39) 2/57 60 56 90
U.K.: (44) 20/82 04 81 42

China: (86) 10/6836 6542
Spain: (34) 91/724 16 57

Other Countries: Contact JY S.A.S.

1-877-JYHORIBA