



The Hydrogen Analysis of Solid Samples

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Abstract

Each year the marketplace sees increasing demands for the analysis of hydrogen contained in various sample materials. It is now recognized that hydrogen analysis is crucial not only in the steel industry but also in the manufacture of such high purity metals as aluminum, copper, titanium and in the development of new alloys and new materials. To meet these demands, Horiba has developed and marketed two models of a new type of hydrogen analyzer with a flexible power control function, the EMGA-521 and the EMGA-621.

This report discusses the design and principle of measurement of the new hydrogen analyzer, using data from actual measurements. Also introduced here is the behavior of the hydrogen content of the sample when the flexible power control function of the analyzer is used and the importance of sample pre-treatment in hydrogen analysis.

1 Introduction

Marketplace needs for analyzing hydrogen in solid samples are increasing year by year. It would be no exaggeration to say that the attention is being focused on hydrogen (H) atomic number 1 in almost all solid samples from ferrous metals, non-ferrous metals, ceramic materials, and superconductive materials. Horiba has developed the EMGA-521/621 hydrogen analyzer in solid samples that incorporates a temperature increase analysis function for not only analyzing the total hydrogen content in materials but also for learning more about the behavior of hydrogen.

Besides analyzing the total hydrogen content, two new mechanisms, a column bypass mechanism and a coexisting gas compensation mechanism have been incorporated in this analyzer in

order to analyze temperature increase suited to the development of various materials. In this paper, we report the basic principle of measurement, characteristics, and analytical accuracy of this analyzer, an example of analysis of an actual sample using the temperature increase analysis function, and the reaction of hydrogen with a graphite crucible or Sn flux, as well as the getter effect.

2 Properties of Hydrogen in Metal

Hydrogen in metal samples demonstrates the following typical behaviours:

- It easily diffuses even at low temperatures,
- It causes grain boundary corrosion,
- It causes brittle rupture, and
- It causes the properties of non-ferrous metals to deteriorate.

Though all of these behaviours adversely effect the properties of materials, there have been reports recently to the effect that increasing the content of hydrogen in ceramic or superconductive materials alternatively improves their properties. Subsequently, the importance of hydrogen is being reviewed.

The generation of hydrogen from materials can be broken down into three diffuse forms

- 1) Generation during cooling to room temperature from the melt phase: diffuse hydrogen,
 - 2) Generation in a solid state until it reaches solidus line from room temperature: diffuse hydrogen, and
 - 3) Generation after melting: residual hydrogen.
- Of these three forms of hydrogen, the EMGA-521/621 can measure (2) diffuse hydrogen and (3) residual hydrogen.





3 Principles of Measurement

This analyzer uses inert gas fusion in impulse furnace-column separation-thermal conductivity detection that conforms to JIS Z 2614. Current flowing in a graphite crucible causes Joule heat ($Q = I^2R$) to be generated, and this heat causes the sample to be heated and fused in inert gas (in this example argon (Ar) was used).

The oxide in the sample reacts with the graphite crucible, and is extracted as carbon monoxide (CO), and the hydrogen and nitrogen are extracted as

hydrogen gas (H_2) and nitrogen gas (N_2), and are carried together with the inert gas (carrier gas).

On the other hand, as thermal conductivity detectors detect the specific heat of gas, there is no gas selectivity. For this reason, after oxidization to carbon dioxide (CO_2) by a gas selective oxidant, CO is adsorbed in a decarburizer, and water content is adsorbed by a dehydrator. The resulting hydrogen and nitrogen are separated in a separation column, and measured at a thermal conductivity detector.

Figure 1 shows an overview of the analyzer. Figure 2 shows the gas flow. Table 1 shows the main specifications.



Figure 1: Model EMGA-621 hydrogen analyzer for analysis of hydrogen concentration in solids

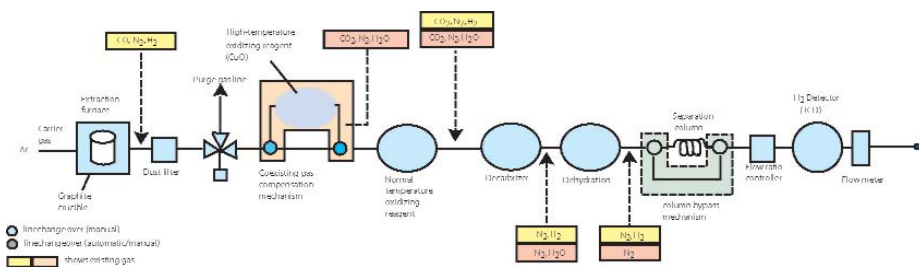


Figure 2: Gas flow in the EMGA-621



**Table 1: EMGA-521 and EMGA-621 Specifications**

Product Name	Hydrogen analyzer
Model	EMGA 521/621
Principle	Inert gas fusion in impulse furnace-column separation-thermal conductivity detection
Applications	Hydrogen in ferrous and non ferrous metals, semiconductors and electronic materials
Range	0 to 0.02wt% (0 to 200wtppm) Range may be expanded to 0 to 100% -by reducing the sample amount.
Sensitivity (minimum reading)	0.000001 wt%. (0.01 wtppm) Select either wt% or W\ppm at installation.
Accuracy (repeatability)	$s_{n-1} = 0.04wtppm$ or $CV = 1\%$ whichever is larger wit hydrogen reference gas
Sample Required	1,0g for regular analysis (for ferrous metals)
Weight Compensation	0.00001 to 99.999999 g
Input Range	Automatic input from optional electronic balance or manual input
Analysis time	About 100 sec from gas extraction to measurement
Display Devices	1) Analysis results: CRT and printer, (2) Message: CRT (3) Preset conditions: CRT and printer
Analysis Conditions	1) Extraction conditions: Furnace control: Electrical power control Wattage setting Temperature setting 2) Integration conditions: Preset time integration or integration up to reach comparator level, whichever is shorter (3) Graphite crucible Large or small one can be used
Calibration	(1) 1 .point or multi-point calibration using standard sample or gas, (2) Approximation by least squares method, (3) Gas calibration function, (4) Calibration mode compensation function, (5) Calibration mode memory (manual input, 5 calibration modes), (6) Calibration data, discard function, (7) Measurement data copy function, (8) Graphic output of calibration results function
Data Storage	Pre-programmed sample data up to 100 Analysis results up to 10 100

4. Description of Main Features

4.1 Hydrogen/Nitrogen Separation Column

The hydrogen/nitrogen separation column used on this analyzer is filled with synthetic zeolite. Generally, the separation capability increases as the particle diameter of the filler decreases, however pressure increases. The amount of adsorption (V) of the filler is expressed as $V = f(P, T)$ where T is temperature and P is gas concentration (partial pressure). When gas concentration is constant, the

amount of adsorption is a function for temperature only. Also, as adsorption is accompanied by heat generation at all times, the separation capability improves as the temperature becomes lower. Figure 3 shows the relationship between column temperature and the separation capability. From this figure, it can be seen that the separation capability of the column improves as the temperature becomes lower. At this analyzer, an electronic cooler is used to maintain the column temperature at about 20°C. This reduces pressure loss, and moreover improves the separation capability for nitrogen.

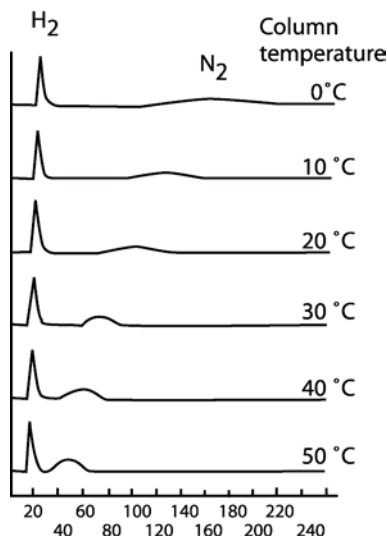


Figure 3: Column temperature vs. N_2/H_2 separation column

4.2 Carrier Gas

Argon (Ar) is used as the carrier gas for this analyzer. Nitrogen gas is considered to be ideal as a carrier gas for eliminating the effect of nitrogen contained in a sample. Also, there is no need to separate capability gases in a column. However, when heating and out-gassing graphite crucibles in nitrogen gas at high temperatures in excess of $3,000^\circ\text{C}$ for the analysis of high melting point materials, the hydrogen gas that is generated from the graphite crucible reacts with nitrogen, the carrier gas. Ammonia (NH_3) and hydrogen cyanide (HCN) are generated. HCN is extremely poisonous for the human body. This is the reason why Ar is used instead of N_2 .

4.3 Graphite Crucible

Even when Ar is used as the carrier gas, the graphite crucible and hydrogen are considered to react at about 2000°C and release methane (CH_4). The influence of CH_4 was confirmed by holding graphite crucibles at room temperature and at 2000°C and dosing hydrogen. Also, tin (Sn) is used as the flux for lowering the melting point of the sample, reducing the generation of hydrogen and reducing corrosion of the sample on the crucible. We also confirmed the getter effect (adsorption of

hydrogen) by the flux. Table 2 shows the measurement results. Though the getter effect caused by generation of CH_4 and flux is recognized slightly, if we assume that a sample which contains 1 ppm concentration hydrogen was analyzed, it can then be judged that the influence would be equivalent to about 0.001 ppm and is within a range that can be ignored in practice.

Table 2: Effects on measurements using graphite crucible and Sn flux

Measurement conditions			
Crucible	Room temp.	2000°C	2000°C
temp	Without	With	With
Sn flux	Without	With	With
Measured result			
Mean value	159.9	157.9	159.0
(ppm)			
Standard	0.099	0.057	0.141
deviation (ppm)			
Repeatability	0.062	0.036	0.088
(%)			

5 Temperature Increase Analysis Function

An optional temperature increase analysis function is available in order to find out more about the behavior of hydrogen. The temperature increase analysis function is a function for gradually increasing the power applied to the graphite crucible to slow its temperature.

The temperature increase analysis function enables hydrogen of differing extraction to be classified and quantified. The analyzer is also provided with a hold function for holding the extraction temperature when the extraction peak has been detected in the temperature increase process.

There are three hold functions, which can be freely selected by the operator.

(1) **Auto:** Extraction peak is automatically distinguished, and temperature is held at extraction temperature.

(2) **Manual:** The operator judges the extraction peak, and the temperature is held at the desired temperature.



(3) Memory: Hold conditions are stored to memory, and extraction is carried out at the same temperature increase conditions.

The following two new technologies have been developed in order to effectively demonstrate this temperature increase analysis function.

5.1 Column-bypass Mechanism

The column-bypass mechanism has been developed to shorten the extraction gas time lag, which is a problem during temperature increase analysis. During fixed temperature analysis, the extraction peaks of hydrogen and nitrogen are extracted via an H_2/N_2 separation column. However, during temperature increase analysis, if hydrogen and nitrogen are passed through a column, they will be continuously separated, and gas generated at the initial stages of temperature increase will mix with gas generated in the latter stages thus making it difficult to distinguish their extraction peaks. For this reason, we linked the entrance and exit of the column so that extracted gas could be directly introduced to a thermal conductivity detector during temperature increase analysis. This is the column-bypass mechanism.

Though this mechanism operates automatically during temperature increase analysis, it is also provided with a switch to set the bypass to manual. This function can also be used to measure samples whose hydrogen content is very low, such as copper, in which there is no need to separate H_2 and N_2 with a separation column.

5.2 Coexisting-gas Compensation Mechanism

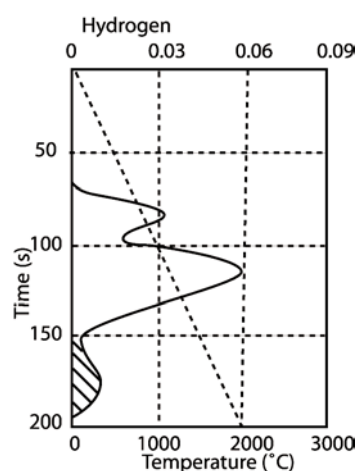
During temperature increases such as mentioned above, all gas components extracted from the sample must be measured separately from gas components other than hydrogen as the column-bypass mechanism is used. The "coexisting-gas compensation mechanism" was developed for this purpose.

In a regular gas flow, CO is selectively oxidized to CO_2 using a room-temperature oxidizing reagent. However, in the coexisting-gas compensation flow, the flow is switched to the high-temperature oxidizing reagent side manually by a cock. The extraction gas, flown from the high-temperature oxidizing

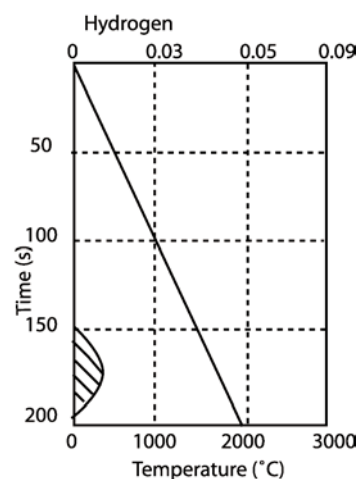
reagent, is oxidized and converted to water, and adsorbed by the dehydrator.

During temperature increase analysis, all extracted gases are measured via the regular gas flow, the high-temperature oxidizing reagent flow is then switched to where hydrogen is removed, and the resulting extracted gases are measured. The temperature increase data of hydrogen can be obtained by subtracting these two measurement results.

Figure 4 shows the results of analyzing a steel sample.

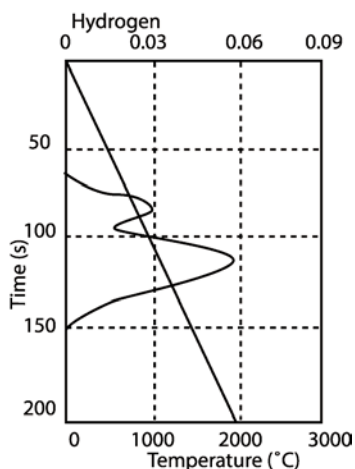


(a) Heating by the column bypass method



(b) Heating by parallel use of both the column bypass method and the coexisting gas compensation method.

Figure 4(a) and (b): Procedure for analyzing temperature increase



(c) Results after processing the extraction profile

Figure 4(c): Procedure for analyzing temperature increase

6 Measurement Accuracy of Detection System

Before analyzing the actual sample we confirmed the measurement accuracy of the detection system in this analyzer. Hydrogen gas of a known concentration was dosed and evaluated by an EMGA-621 provided with an automatic voltage regulator. Measurement was carried out for a total of 4 times over two days, once in the morning and once in the afternoon, and 10 mean values (\bar{X}) and the standard deviations (s_{n-1}) were calculated for each of the measurements. From the results, as shown in Table 3 we can judge that there was very little fluctuation in mean values, and that a quantitative limit ($5 s_{n-1}$) was at about 0.01 ppm

Table 3: Analytical accuracy using hydrogen gas dosing

	1st Day a.m.	1st Day p.m.	2nd Day a.m.	2nd Day p.m.
Mean value	0.941	0.941	0.938	0.944
Standard Deviation	0.0024	0.0020	0.0012	0.0009

7 Handling of Samples and Analytical Accuracy

7.1 Pre-treatment and storage atmosphere

Pre-treatment of samples is important when analyzing trace amounts in samples. In particular, when analyzing hydrogen, quite different analytical values may be displayed depending on the surface condition of the sample. Figure 5 shows the differences between two samples treated by two abrasing methods: chemical etching and abrasing by a metal rasp. The peak of the sample abraded by the rasp is higher. From this we can suppose that the influence of the water adsorption of sample surface is large in the case of the sample abraded by the rasp as surface area is larger than that of the sample abraded by the chemical etching.

Table 4 shows the results of analyzing a previously de-hydrogenized Cu sample after storing for six days in seven atmospheres. It can be understood from the results that a difference occurs to the storage atmosphere.

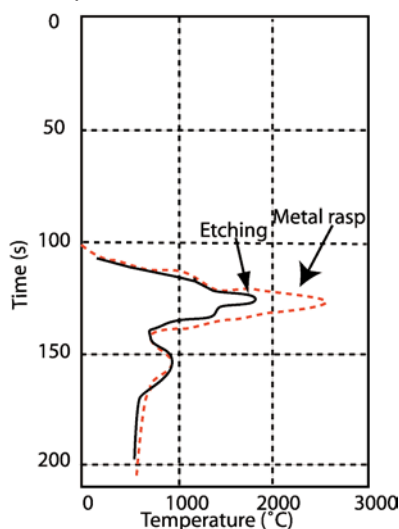


Figure 5: Effect of polishing method on extraction profile

**Table 4: The effect of the sample storage environment on analysis of hydrogen concentration**

Storage atmosphere	Hydrogen concentration (ppm)
Argon gas	0.000 ± 0.002
Dry air	0.005 ± 0.006
Petroleum benzine	0.008 ± 0.003
Acetic Acid	0.000 ± 0.003
Ethanol	0.008 ± 0.004
Wet air	0.008 ± 0.005
Water	0.011 ± 0.018

Storage term: 6 days

7.2 Analysis of actual sample

Table 5 shows the results of confirming repeatability using various samples. Temperature JSS GS-1c in the table is a set-up sample from the Iron and Steel Institute of Japan for analyzing gas in steel, and the Horiba's set-up sample is a steel sample

used for set-up in-house both of which are austenite stainless steel having stable concentrations. With JSS GS-1 c is a bar shaped sample and judged to be almost free of an oxidized layer on its surface, and was analyzed after carrying out only degreasing. On the other hand, the Horiba's set-up sample was thoroughly abraded with the metal rasp (care was taken to prevent heat being applied to the sample) as an oxidized layer was confirmed on its surface and the sample was degreased.

Bar-shaped copper (Cu) and aluminum (Al) are commercial products, and have a purity of 99.9% or more. As surface treatment, Cu was treated with acid, while Al was treated with alkali. Also, in order to improve repeatability, it is preferable to maintain the weights of the samples as constant as possible.

Table 5: Results for various types of samples

Sample	JSS GS-1c (Fe)	Set-up sample (Fe)	Cu	Al
Measuring Condition				
Sample weight	About 1.0g	About 1.0g	About 1.4 g	About 1.0g
Pre-treatment condition	None	None	Acid cleaning	Acid cleaning
Flux	Sn: 1.0g	Sn: 1.0g	None	None
Extraction Temperature	About 2000°C	About 2000°C	About 2000°C	About 2000°C
Extraction time	75s	75s	70s	70s
Measured Results n = 10				
Mean value (ppm)	1.611	5.611	0.241	0.394
Standard deviation (ppm)	0.050	0.047	0.017	0.028



7.3 Handling of Samples

The following points regarding the handling of samples must be taken in order to analyze hydrogen in solid samples with high accuracy. In particular, sample pre-treatment has an important meaning for trace hydrogen samples.

- (1) Samples must be abraded carefully so as to prevent heat being applied to the sample when there is an oxidized layer on the sample.
- (2) Chemical etching must be carried out at the same time for each sample.
- (3) After pre-treating the surface, analyze the sample as quickly as possible.
- (4) Water must be shut out from the storage atmosphere.
- (5) Weight must be as constant as possible.
- (6) Prevent heat from being applied to the samples when drying the samples taken from the solution.

8 Temperature Increase Analysis

This section introduces temperature increase analysis, an important feature of this analyzer, using the analysis results of an actual sample. Samples used were titanium hydride (TiH_2) and calcium hydride (CaH_2), hydrogen compounds and both commercial products. The temperature increase conditions were $5^\circ C/s$, and the peak hold in the Auto mode was applied.

Figure 6 shows the extraction profile of titanium hydride. The peak hold temperatures were $600^\circ C$ and $810^\circ C$. Figure 7 shows the extraction profile of calcium hydride, and indicates an extraction profile different to that of titanium hydride. The peak hold temperatures were $400^\circ C$, $700^\circ C$, and $900^\circ C$. Figure 8 shows the extraction profile when titanium hydride and calcium hydride were mixed at a proportion of 1:2.5 and temperature increase was carried out. The peak hold temperatures were $280^\circ C$, $450^\circ C$, $650^\circ C$, and $820^\circ C$.

If we compare Figures 6, 7, and 8, the peaks of $280^\circ C$, $450^\circ C$, and $820^\circ C$ seem to be hydrogen extracted from calcium hydride, and the peak of $650^\circ C$ seems to be the peak from titanium hydride. Figure 9 shows the extraction profile of the mixed sample of titanium hydride and calcium hydride at a proportion of 1:2.5, in which an increased ratio of calcium hydride is mixed with titanium hydride, overlaid with the extraction profile of Figure 8. It appears that the peak of $820^\circ C$ has increased as

the for calcium percentage of calcium hydride has increased.

As mentioned above, temperature increase analysis is extremely important in learning about the behavior of hydrogen.

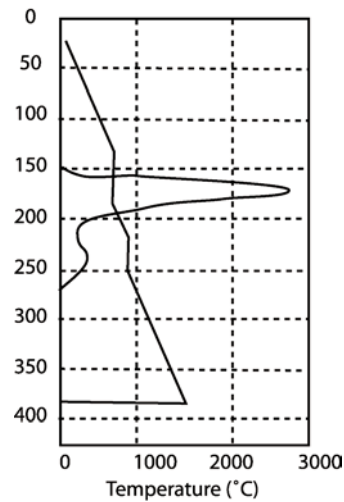


Figure 6: Extraction profile for titanium hydride

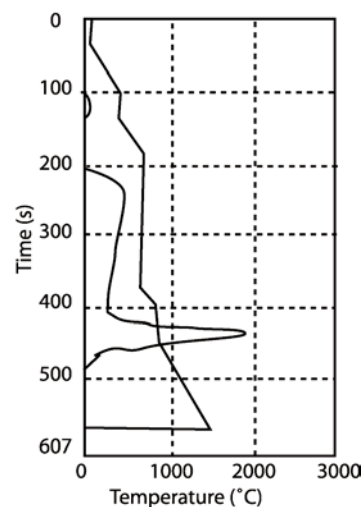


Figure 7: Extraction profile for calcium hydride

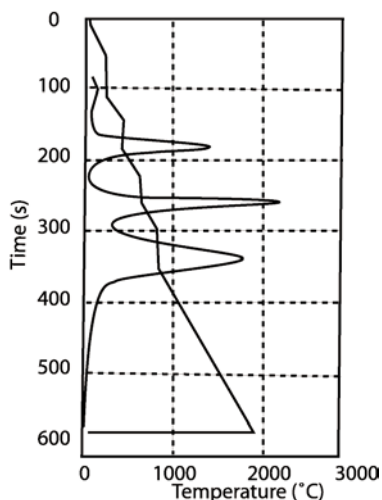


Figure 8: Extraction of profile for a 1:2 amalgam of titanium hydride and calcium hydride

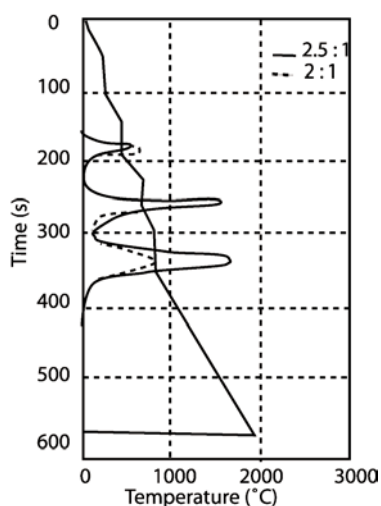


Figure 9: Extraction profiles for two different amalgams of titanium hydride and calcium hydride

9 Conclusion

The removal of absorption on the sample surface is very important for analyzing hydrogen in solid samples with high accuracy. Stable data can be obtained by reliably pre-treating samples. Also, adding a temperature increase analysis function allows the thermal behavior of hydrogen to be revealed with ease. We consider that the need for hydrogen analysis will increase even more in the future accompanying the development of new materials, so we expect that the temperature increase analysis function of this analyzer will be very useful. A future theme is the analysis of trace hydrogen (0.1 ppm or less) in light alloys (in particular, Al).

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