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The Inert Gas Extraction-Gas Chromatographic Determination of Hydrogen in Ferrous Metals

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The inert gas extraction-gas chromatographic technique has been applied for the determination of hydrogen in ferrous metals. As this method was dependent on gas chromatography, the simplification was performed on the apparatus and the analytical operation. A procedure was evolved, according to which the extracged hydrogen was measured by means of gas chromatography using the precolumn technique, *viz.*, (1) the hydrogen was rapidly transferred from the metal into an argon stream by means of H-F induction furnace, (2) this was concentrated into the cold precolumn for 4 min to collect the total amount of hydrogen from the extraction tube, (3) this was measured by gas chromatography. Analytical results obtained on 3 iron base metals suggest that the method can be widely used for the determination of hydrogen in ferrous metals.

Several methods for the determination of hydrogen in metals have recently been reviewed.[1] These include vacuum or inert gas extraction by heating or by melting and chemical methods. Among them, *viz.*, gas chromatography,[2,3] emission spectrometry[4] and isotope methods,[5,6] have recently been proposed for the determination of hydrogen in metals. Although hydrogen is generally determined by the hot-extraction method with fair accuracy, the vacuum fusion method[7] is usually employed to extract hydrogen completely in ferrous metals. Marincek and Feichtinger,[8] using a procedure based on the vacuum fusion method, found that some of hydrogen still remained in the metals over a range of temperature from 1300 to 2100°C. Bennek and Klotzbach[9] have proposed a reliable method based on tin-bath technique at 1100—1150°C using quartz crucible instead of graphite one being difficult to degass sufficiently. Bennek's method is widely used to de termine hydrogen in metals. The present paper deals with a procedure for the determination of hydrogen in ferrous metals by means of gas chromatography. The apparatus now in use consists of a compact and convenient unit. One hundred determinations of hydrogen have been carried out, and a reliable results for the extraction of hydrogen in steel and cast iron were obtained.

Experimental

Preparation of Samples. Steel and chill cast iron plate samples approximately 2 mm in thickness and lump ferro silicon samples were used for the test. Steel samples were prepared by cutting or breaking to an appropriate weight. Samples (1 to 1.5 g) were used after treatment of the surface. The treatment was as follows: (1) abrase with grinding paper (with exception of ferro silicon samples which break in pieces); (2) wash with carbon tetrachloride; (3) dry in hot stream of argon. It is advisable to dry the sample in the extraction tube every time just before the experiment, because the gas adsorbed on the surface of the treated sample is considerably increased during storage in a desiccator and then the removal of the gas dependent on sweeping gas is very troublesome.

Apparatus. The apparatus used for the determination of hydrogen in metals which is simplified by attaching a precolumn and is, therefore, different from usual gas collection methods, as shown in Fig. 1.

Purified argon (99.9%) was used as the carrier gas. The moisture contained in the carrier gas was removed by passing it through the desiccant tube.

Procedure. Prior to the analytical experiment, the carrier gas was passed continuously through an extraction system consisting of transparent quartz and glass tubes at 200°C for a few hours until the blank value of hydrogen could be maintained below 10^{-4} m*l*/min. A sample was introduced into a quartz crucible from upper part of the quartz tube under an argon flow (the flow rate is 60 m*l*/min) and was dried at 150°C for several minutes. After the flow rate was

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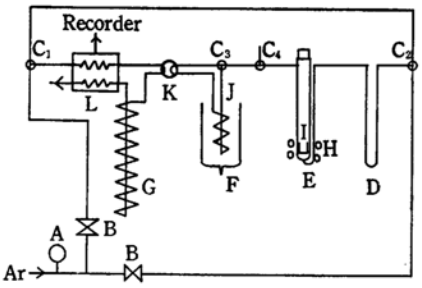

Fig. 1. Apparatus.

A: Pressure regulator
B: Needle valves
C_1—C_4: Three ways cocks
D: P_2O_5 desiccant tube
E: Transparent quartz tube (volume of about 15 m*l*)
F: Dry ice - acetone bath
G: GC column
H: H-F coil (commercially available combustion unit)
I: Quartz crucible
J: Precolumn (packed with silica-gel)
K: Gas sampling cock
L: Thermal conductivity cell of gas chromatograph

controlled to 10 m*l*/min, the system was connected with the precolumn being held below −70°C. The sample was heated to 1400°C for 4 min, and the hydrogen, collected in this precolumn, was determined by gas chromatography.

GC Measurements. Hydrogen collected in the precolumn was measured by using a copper tube (4 mm in dia. ×2.5 m long) packed with Molecular Sieve 5A. The analytical conditions were as follows; column temperature, 45°C; carrier gas (argon) speed, 60 m*l*/min. The precolumn was made of a copper tube (4 mm in dia. ×70 cm long) packed with silica-gel. The operating conditions on the precolumn were as follows: column temperature, −70°C; carrier flow rate for collecting hydrogen, 10 m*l*/min. This precolumn was capable of concentrating hydrogen for 4 min at the operating conditions, as shown in Fig. 2. The hydrogen concentrated in precolumn was introduced without any warming the precolumn.

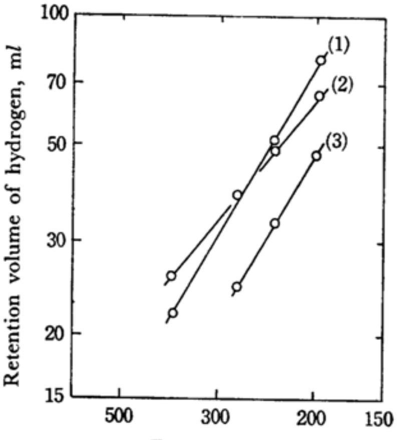

Fig. 2. Relationship between retention volume and concentration column temperature.
(1) Column: 4 mm×1 m copper, packed with silica-gel of 40—60 mesh, (2) Column: 4 mm ×1.5 m copper, packed with activated charcoal of 30—60 mesh, (3) Column: 4 mm× 70 cm copper, packed with silica-gel of 30—60 mesh

The method of the streaming of a gas was almost the same as had been reported in a previous paper.[10] A long main column was suitable for moderating the pressure change brought about by the streaming of a gas.

Results and Discussion

Reliability of the GC Measurements. The reliability of the GC measurements was tested by using each 0.5 m*l* of the mixed permanent gases kept in a gas container. The results are given in Table 1. This method was found to be convenient for the determination of hydrogen in metals because the gas sample could be concentrated into the precolumn in a short time. The precision was exceedingly good.

TABLE 1. THE PRECISION OF GC MEASUREMENTS OBTAINED BY USING THE GAS SAMPLE*

Concentration time, min	Peak areas, mm²		
	H_2×100	N_2×100	CO×10
3	566	428	1469
3	531	432	1482
3	568	442	(1530)
4	529	441	1491
4	570	438	1459
Average	553	436	1486
Without precolumn	550	430	1461

* The contents of gases in the container were 42% hydrogen, 3.4% nitrogen and 6.6% carbon monoxide.

Inert Gas Extraction. Some typical examples of the extraction of hydrogen are shown in Fig. 3. These data were obtained by heating the samples at 1400°C (black circle) and by extracting hydrogen introduced into the tube without sample (white circle). The fact that, in actual practice, the extraction rate on stell sample 4 mm in thickness is almost the same as that of hydrogen evolution from the sample, reveals the possibility of the rapid extraction of hydrogen from the sample.

The degree of degassing of the sample, which

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[10] J. Kashima and T. Yamazaki, This Bulletin, **39**, 1448 (1966).

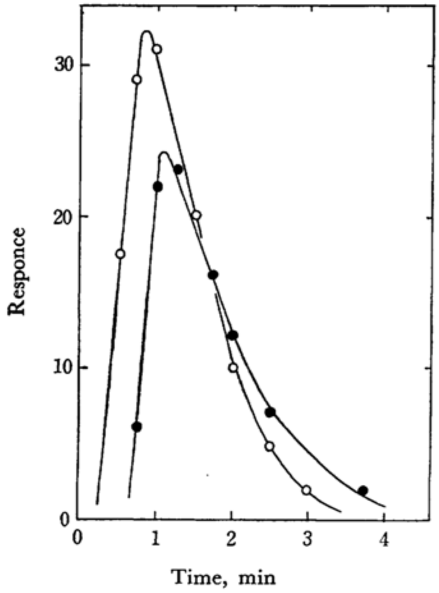

Fig. 3. Extraction curves of hydrogen.
●: Steel sample at 1400°C
○: Hydrogen introduced into the quartz tube without sample

TABLE 2. REMOVAL OF HYDROGEN FROM STEEL PLATES HEATED AT 1400°C

Plate sample		$T=D_t/R^2$	Q_t/Q_0
2 mm	Cast iron	$t=20$ sec → 0.8 $t=40$ sec → 1.65	0.85 0.96
4 mm	Steel	$t=30$ sec → 0.3 $t=2.7$ min → 1.65	0.63 0.96
5 mm		$t=30$ sec → 0.19 $t=4.5$ min → 1.7	0.53 0.97
6 mm		$t=30$ sec → 0.13 $t=6.5$ sec → 1.7	0.42 0.97

Q_t/Q_0 was graphically obtained from the following equation:

$$\frac{Q_t}{Q_0}=\sum_{i=1}^{i=\infty}-\frac{2\sin^2\lambda_i}{\lambda_i^2+\lambda_i\sin\lambda_i\cos\lambda_i}\left(1-e^{-\lambda_i^2D_t/R^2}\right)$$

where Q_t is the amount of hydrogen extracted from the metal in time t, Q_0 is the initial hydrogen content of the metal and T is dimentionless time dependent on diffusion coefficient D, thickness ($2R$) and time.

was dependent on sample size, time and temperature, was calaulated according to Fick equation[11] which was obtained by Fistul' for a finite thickness, using dimensionless value. The results are summarized in Table 2. It is preferable to use a steel plate 2 mm in thickness, on the basis of the fact that, when the metal was heated to about 1400°C, the total amount of hydrogen was evolved in 50—60 sec. However, it takes about 4 min to transfer hydrogen into the precolumn. It is unsuitable to use plate samples more than 5 mm in thickness because it takes still 4 min more to extract hydrogen.

Reproducibility. The analyses of steel, cast iron and ferro silicon were carried out by this proposed method. A typical chromatogram of gases concentrated in the precolumn is shown in Fig. 4. The precision of the determinations is markedly dependent on the hydrogen content, hydrogen-pick-up by the walls of the quartz tube and the amount of the surface gas, correction of which under experimental conditions varies from 4 to 9×10^{-4} ml/cm^2. This amount was determined by rewashing an extracted sample and carring out a second extraction, as had been reported in a previous paper.[12] The reproducibility of this proposed method is represented by the following examples.

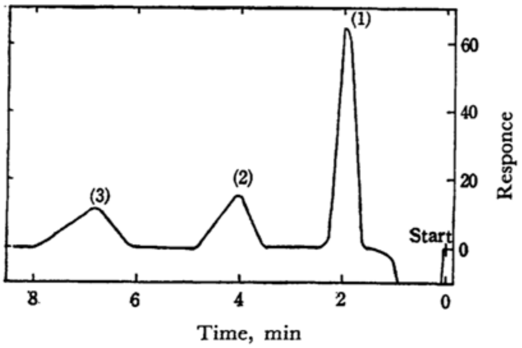

Fig. 4. Typical chromatogram of gases extracted from cast iron sample.
Hydrogen (1), nitrogen (2) and carbon monoxide (3)

(1) On a cast iron, data obtained from 8 determinations varied in the range 1.4—1.6 ppm, with a mean deviation of ±0.09 ppm.

(2) Duplicate determinations on each of 17 samples of mild steel gave results with a mean deviation of ±0.010 ppm. The hydrogen contents varied in the range 0.10—0.57 ppm.

(3) Duplicate determinations on each of 10 samples of ferro silicon gave results with a mean deviation of ±0.5 ppm. The hydrogen contents varied in the range 5.0—6.1 ppm.

Summary

A new inert gas extraction-gas chromatographic method for the determination of minute quantities of hydrogen in ferrous metals has been developed. This method was also available for trace analysis of hydrogen in the sample, because the blank value is extremely lower than that of the conventional method.

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