DEVELOPMENT OF A SURFACE IONIZATION DETECTOR FOR HYDROGEN UNDER ATMOSPHERIC CONDITIONS

by

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ABSTRACT

The design parameters for a surface ionization detector for hydrogen in air are determined, and a description of the detector is presented.

A possible theoretical model of the ionization process is given. The experimental procedure is explained and performance curves in hydrogen/air and hydrogen/nitrogen are shown.

Suggestions for detectors for gases other than hydrogen have been included. These detectors, operating on the surface ionization principle, should exhibit many of the same characteristics as the detector for hydrogen, and will probably exhibit similar sensitivities.

I. INTRODUCTION

As a result of the explosive nature of small amounts of hydrogen in air[1], an accurate hydrogen detection device is badly needed. This detector must meet the requirements of being selective in its measurements, reliable in operation and sensitive to very dilute mixtures of hydrogen.

Of the detectors now in use, one[2] operates by burning the hydrogen with air on a palladium filament and measuring the resultant rise in the filament temperature. Another detector, developed by the Bendix Company[3], measures the change in the resistance of a palladium film when exposed to hydrogen.

Each of the above detectors has certain disadvantages. The first detector has limited sensitivity becuase of the large heat capacity of the filament. It also requires the presence of an oxidizing gas. The second detector is sensitive to oxygen, therefore all oxygen must be excluded from the system. Its response is dependent upon the rate of hydrogen diffusion in and out of the palladium film and this may result in a long response time at low hydrogen pressures.

This thesis will discuss the development of a surface ionization detector for hydrogen. This detector provides a reproducible current of positive ions when exposed to hydrogen. The ion current is linearly proportional to the hydrogen content of the carrier gas from 0.5 to 4% hydrogen by volume.

This detector has the important advantage that it can operate when diluent gases (i.e. nitrogen) are interfering with the use of combustion detectors. It operates equally well in the presence of inert gases or in the presence of air. It is rapid in response (3-10 seconds) to mixtures as low as 0.5 per cent hydrogen in air by volume. It is selective in that, with the exception of carbon monoxide and Freon, it responds only to the presence of hydrogen. Thus, the selectivity, reliability and sensitivity give this detector particular advantage over other systems currently used for similar purposes.

II. SURFACE IONIZATION OF HYDROGEN

The ionization of hydrogen when it is brought into contact with heated palladium is not clearly understood. The experiments of Finch and his associates[4] showed that various metals acquired an electrical charge when heated in the presence of certain gases. This charging process could be explained in terms of positive ions leaving the metal surface, which thereby acquired a negative charge.

The rate of charging was different for each metal-gas combination, indicating that the reaction was specific and unquestionably related to the chemisorption of the gas on the metallic surface. Of all reactions, that of platinum with hydrogen was most energetic in terms of charging. Because of the similarities in the electron structure of platinum and palladium, it was believed that palladium would also have an energetic reaction and this reaction was studied for use as a hydrogen detector.

In trying to explain the phenomenon of the production of this charging, Finch et. al. proposed that two processes might take place one after the other on the surface. In the first process the gas molecule would be physically bound to the surface in an electrically neutral condition in the form of a condensed layer of at least monomolecular thickness. According to Langmuir[5], this layer consists of the gas molecule which is physically adsorbed on the surface without exchange of charge or dissociation. In the second process the gas would be dissociated and

the resultant atoms would be ionized by donation of an electron to the Fermi level of the metal. These positive ions would then evaporate from the surface leaving it negatively charged.

It should be noted here that Finch loc. cit. does not explain the process in exactly this way since the details of dissociation and ionization on surfaces had not been clarified at that time[6]. However, reading between the lines, it is clear that Finch was being led to the proper conclusions.

Finch was led astray to some extent by the idea that the porosity of the surface was an important factor in the ionization process. The early studies of surface porosity by Taylor[7] may have been responsible for this. In any case the diffusion data of Smith[8] indicates that the surface ionization process cannot be dependent upon diffusion since it occurs within seconds of the time the hydrogen contacts the palladium.

The present explanation in terms of electron donation is supported by experiments on the effect of absorbed hydrogen on the paramagnetic susceptibility of palladium[9]. From this work it is clear that the hydrogen is ionized, with the electrons making a contribution to the reduction in susceptibility, and some of the protons diffusing around in the metal. Proton resonance experiments by Norberg[10] substantiate this theory. Assuming that this mechanism operates during hydrogen adsorption, a layer of positively charged H^+ ions would exist on the surface of the palladium. A fraction of these ions would evaporate as either H^+ or H_2^+ and the palladium would acquire a negative charge. This is in exact agreement with the work of Reference 4 and the results reported here.

Unfortunately the complete thermodynamics of the process are not clear and there is no theoretical analysis with which our data can be compared. However there seems to be no question that the ionization process occurs and can be used as a detector for hydrogen.

III. DESIGN OF THE EXPERIMENTAL SYSTEM

A. Physical Layout

A schematic diagram of the experimental set-up is shown in Figure 2. A picture depicting the construction is shown in Figure 6. All the conduit from the mixing chamber to the evacuator fan was copper tubing or copper pipe. The inlets into the mixing chamber from the source gases were surgical rubber tubing. The window was one-quarter inch plexiglas. All copper connections were soldered and all connections were checked for leaks before operation. The volume of the ionization chamber was 7.07 cubic inches. The mixing chamber was one and one-half inch diameter copper tubing packed with copper screening.

B. Gas Input System

The primary or carrier gas was either bottled nitrogen or air taken from the University lines. The flow rate was 10 cubic feet per hour as measured by a flow meter manufactured by the Victor Equipment Company of San Francisco, California. The gases to be examined (secondary gases) were standard bottled gases except for methane (city gas) which was taken from the University lines.

C. Metering Devices

Because of the small flow rate of the secondary gas (generally hydrogen), a means of calibrating the flow meter was needed. For this purpose the bubble meter method for gas flow measurements described by

Levy was most practical[11]. Figure 2 shows schematically how Levy's method was modified to take advantage of the available equipment.

By allowing the gas under investigation to flow through the flow meter at a particular setting and averaging the time it took for soap bubbles to travel 11.2 inches up the calibrated tube, it was possible to determine the rate of flow for each setting of the flow meter. Typical results for this calibration of meter settings to flow rate are shown in Figure 3. A simple conversion factor converted the flow rate of the secondary gas into per cent of the entire flow on a volume basis. After the calibration was completed, the bubble apparatus was disconnected from the system.

D. Detection System

99.995% palladium wire, 0.01 inch in diameter, was used for the ionizer. The apparent surface area of the palladium filament was 0.0472 square inches. The collector was 0.032 inch diameter nickel wire coiled around the filament. The alternating current for heating the filament was controlled by a Variac through an isolation transformer. A voltmeter was used to insure that the proper voltage was maintained. The collector was negatively biased by a standard 67.5 volt dry cell enclosed in a Faraday cage. The ion currents were measured by a Model 204-A KIN TEL Electronic Galvanometer whose sensitivity was $\pm$ 0.001 microamperes full scale to $\pm$ 1 miliampere full scale in seven ranges. The pyrometer used to measure the filament temperature was a Model #95 Pyro Micro-Optical Pyrometer manufactured by the Pyrometer Instrument Company of Bergenfield, New Jersey. The evacuator fan was a 110 volt squirrel cage blower exhausting to the atmosphere.

IV. EXPERIMENTAL PROCEDURE

A. Initial Activation of Equipment

In order to insure the accuracy of the data and to prevent the burnout of the palladium filament, the apparatus was always put into operation by following certain steps. The primary flow (nitrogen or air) was turned on and the evacuator fan was turned on. This started the flow of gas through the system. The next step was to heat the palladium filament. This was accomplished by adjusting the Variac so that a 12.8 volt potential existed across the filament. A visual check with the optical pyrometer after the filament was heated insured that a temperature close to 850 ^{o}C was attained. The final step was to negatively charge the nickel collector by connecting the ion current circuit.

B. Introduction of Gas

After waiting fifteen minutes to insure the stability of the base current, the secondary gas to be examined was metered into the mixing chamber. For each run the gas was allowed to flow for sixty seconds and then turned off. While the gas was flowing, the change in ionic current was measured. This procedure was repeated three times for each setting of the flow meter and the average ionic current change recorded. After each influx of gas, the system was allowed to return to the original base current reading before introducing more gas. After the three readings were taken at one meter setting, the secondary flow meter was adjusted to a new value.

V. RESULTS

A. Determination of Optimum Filament Temperature

The first series of experiments was run to determine the proper filament temperature for maximum signal to noise ratio. This was accomplished by using a constant mixture of 0.98 per cent hydrogen in nitrogen by volume. With this mixture running through the apparatus the temperature of the filament was varied by changing the supply voltage. With each change in voltage the signal to noise ratio also changed. Figure 4 clearly indicates that a temperature of about 850 °C is best in terms of signal to noise ratio. This is in good agreement with the results of Finch[4] on platinum.

It should be noted here that the optical pyrometer was close to the end of its effective range at 850 °C. For this reason the above value of 850 °C can only be accepted as accurate to $\pm$ 15 °C. In the later experimental work the filament temperature was reproduced each time by using the same current and voltage. Occasional checks with the pyrometer gave the $\pm$ 15 °C spread indicated above. In future experiments we hope to make use of an infrared pyrometer to measure filament temperatures more accurately.

B. Hydrogen in Nitrogen and in Air

The experimental curve in Figure 5 shows the results of runs at 850 °C for various ratios of hydrogen in nitrogen. A series of points for hydrogen in air mixtures are also shown and it is clear that the

reaction is essentially independent of the presence of oxygen.

C. Other Gases

Test runs in pure air, carbon dioxide, nitrogen and methane (city gas) gave no response. There was some sensitivity to carbon monoxide in nitrogen, but the mixtures needed to produce a response were quite rich in carbon monoxide (4 or 5%) and this should not be important in most cases where hydrogen is to be detected. Freon-12 also showed a response when a mixture above 12 per cent Freon in air was used. Such a mixture would also be unlikely under the conditions where hydrogen is to be detected.

VI. DISCUSSION AND CONCLUSIONS

It is clear from Figure 5 that the system has ample sensitivity and signal to noise ratio. The sensitivity can be extended to well below 0.1 per cent hydrogen in air by use of a larger ionizing surface.

Nitrogen was used as a primary or carrier gas for most of the testing because of its inherent safety. Operation at hydrogen in air ratios above 10 per cent is feasible, but calibration must be done in a protective enclosure because the lower explosive limit is 4.00 per cent hydrogen in air[1].

The detector is quite specific for hydrogen, however, the exact process by which hydrogen is ionized by palladium is difficult to understand. A careful search of the literature[12,13,14] reveals conflicting opinions and some authors question that the surface ionization process even exists[14]. Further investigations are needed to settle the debate. One means of investigation would be to direct the ions from the heated filament into a mass-spectrometer for analysis and this will be done in a future experiment.

From the data presented, the results of this experimental device may be extrapolated to include other, similar devices. The work of Finch and Stimson loc. cit. indicates that specific metals may be used as ionizers for various gases. This might permit the development of new detectors that could operate at atmospheric conditions without the burnout problems attendant upon the hot filaments used for chemisorption detectors[15].

APPENDIX

The calibration of the Dohrmann flow meters was effected by use of a modified bubble meter method[11]. The device consists of a 1 liter glass beaker, a three-holed rubber stopper, two glass inlet pipes, a twenty-four inch piece of glass tubing, a rubber ear syringe and some liquid soap solution.

The set-up is shown schematically in Figure 2. A particular setting of the flow meter is chosen and the secondary gas is allowed to flow through the apparatus. By squeezing the ear syringe, the level of the liquid soap is raised until it touches the bottom of the glass tubing. After touching the bottom of the glass tubing, the level is allowed to go down and a bubble forms on the bottom of the tube. Because of the gas pressure, the bubble rises up the tube. After thoroughly wetting the sides of the tubing by allowing several bubbles to rise up the tube, the effect of any friction on the sides of the tube is nearly negligible.

The time the bubble takes to pass the graduations on the glass tube is proportional to the rate of flow of the secondary gas. The distance between graduations was 11.2 inches. The internal diameter of the tube was 0.35 inch. The volume displaced by the bubble passing was 0.000625 cubic feet. The rate of flow of the secondary gas is the volume divided by the time required for the bubble to travel between the graduations. The per cent of the entire flow is equal to the rate of

flow of the secondary gas divided by the rate of flow of the combined primary and secondary gases.

The accuracy of this method is influenced by two factors. The first is the ability of the observer to maintain the flow meter at the proper setting. The second is the ability of the observer to accurately time the movement of the bubble. The variations in the flow meter were minimized by maintaining a constant pressure from the bottled nitrogen gas supply. The variations in the timing were minimized by taking the average of repeated runs. The maximum deviation from the average was only one second.

A typical recording for hydrogen is shown in the table below:

Meter Reading (glass ball)	Average Time (sec)	Flow Rate (ft^3/hr)	Base Flow (ft^3/hr)	% Gas
1.5	69	0.0326	10	0.325
2.0	42.5	0.0529	10	0.527
3.0	23	0.0977	10	0.968
3.5	17	0.1322	10	1.305
5.0	10	0.2250	10	2.200
7.0	6	0.3750	10	3.620

Using these figures, a calibration graph as shown in Figure 3 was constructed.

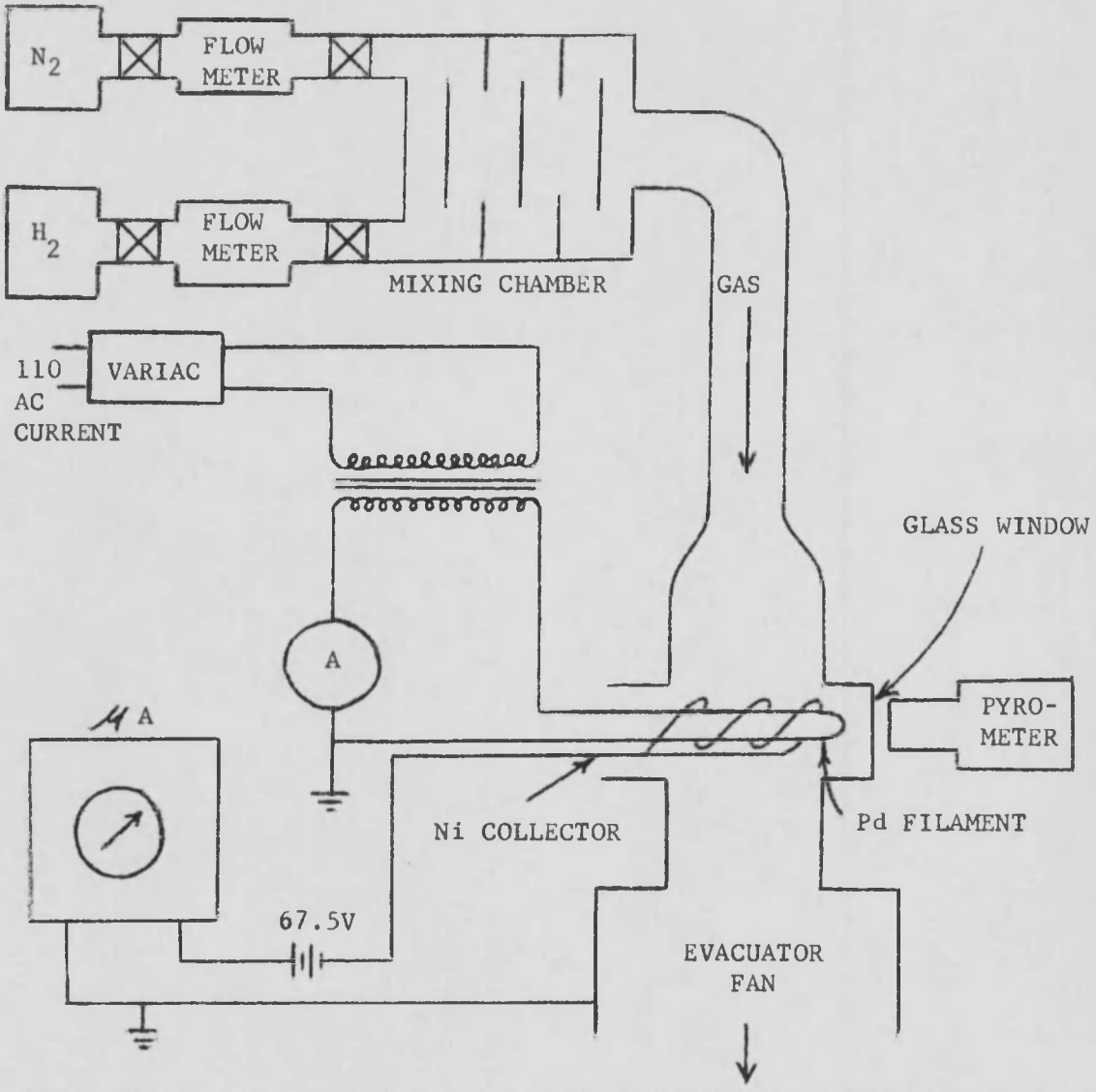

Fig. 1--Hydrogen Detector System

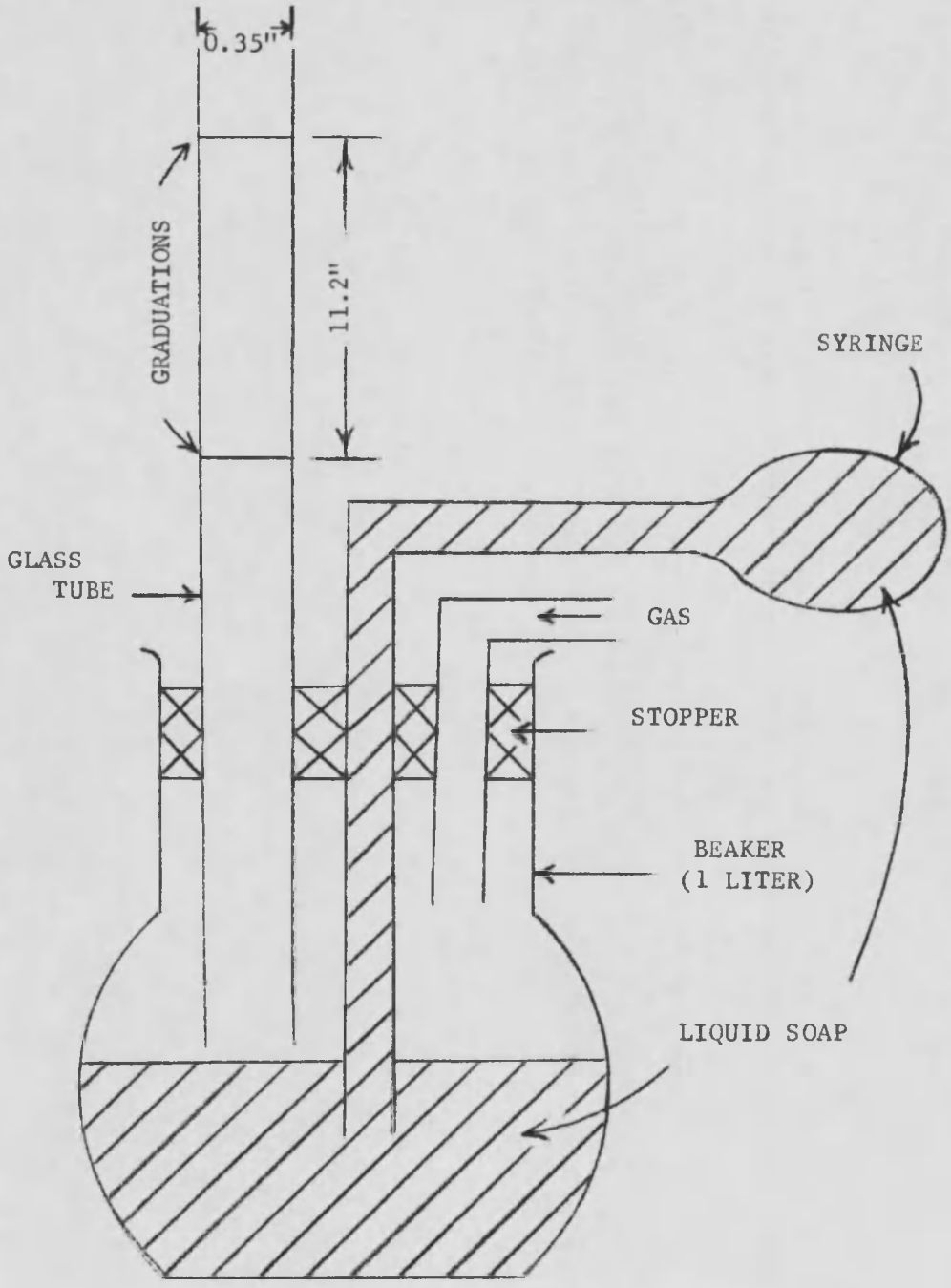

Fig. 2--Bubble Meter Apparatus

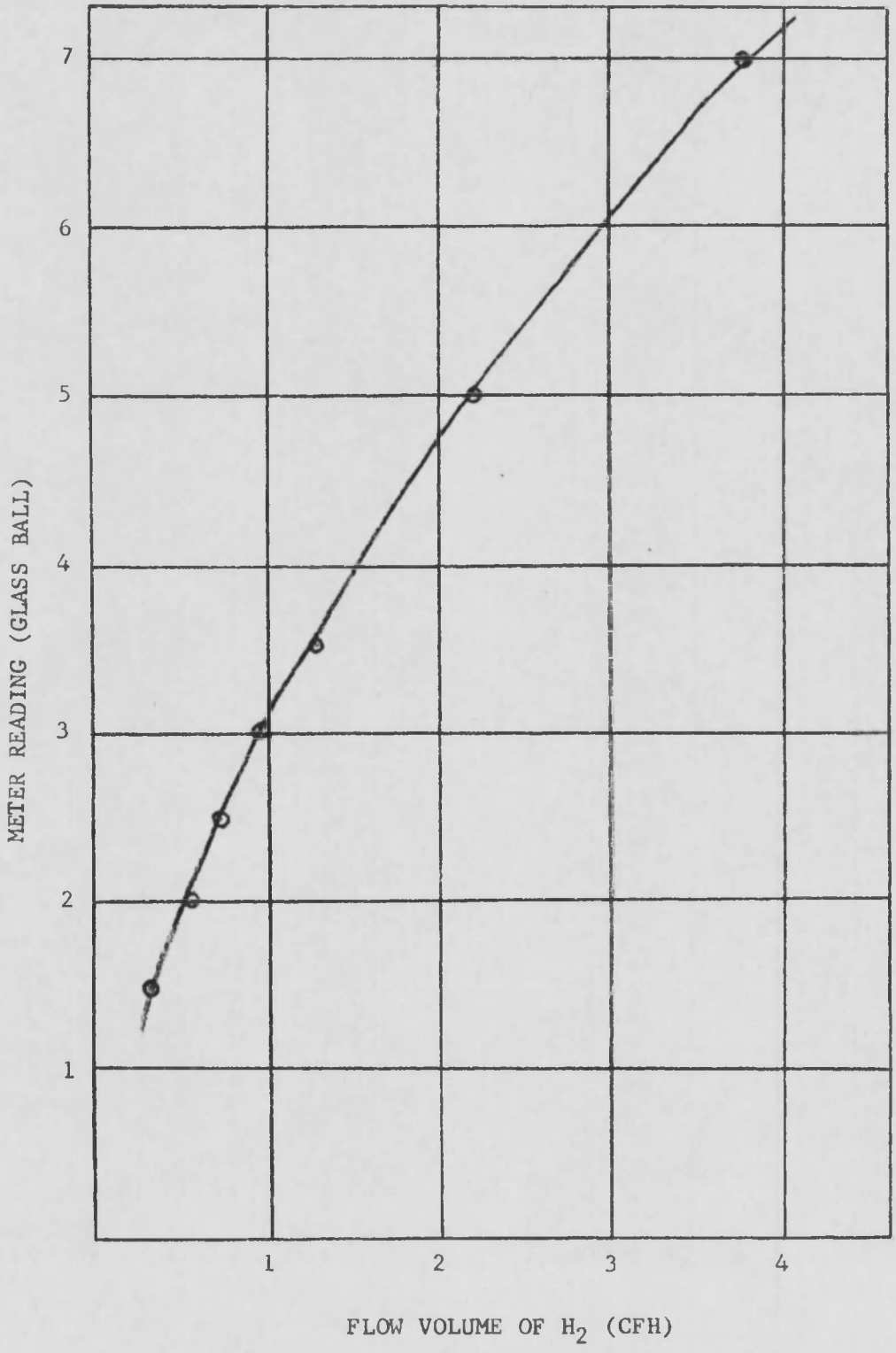

Fig. 3--Calibration Curve For The Dohrmann Flowmeter

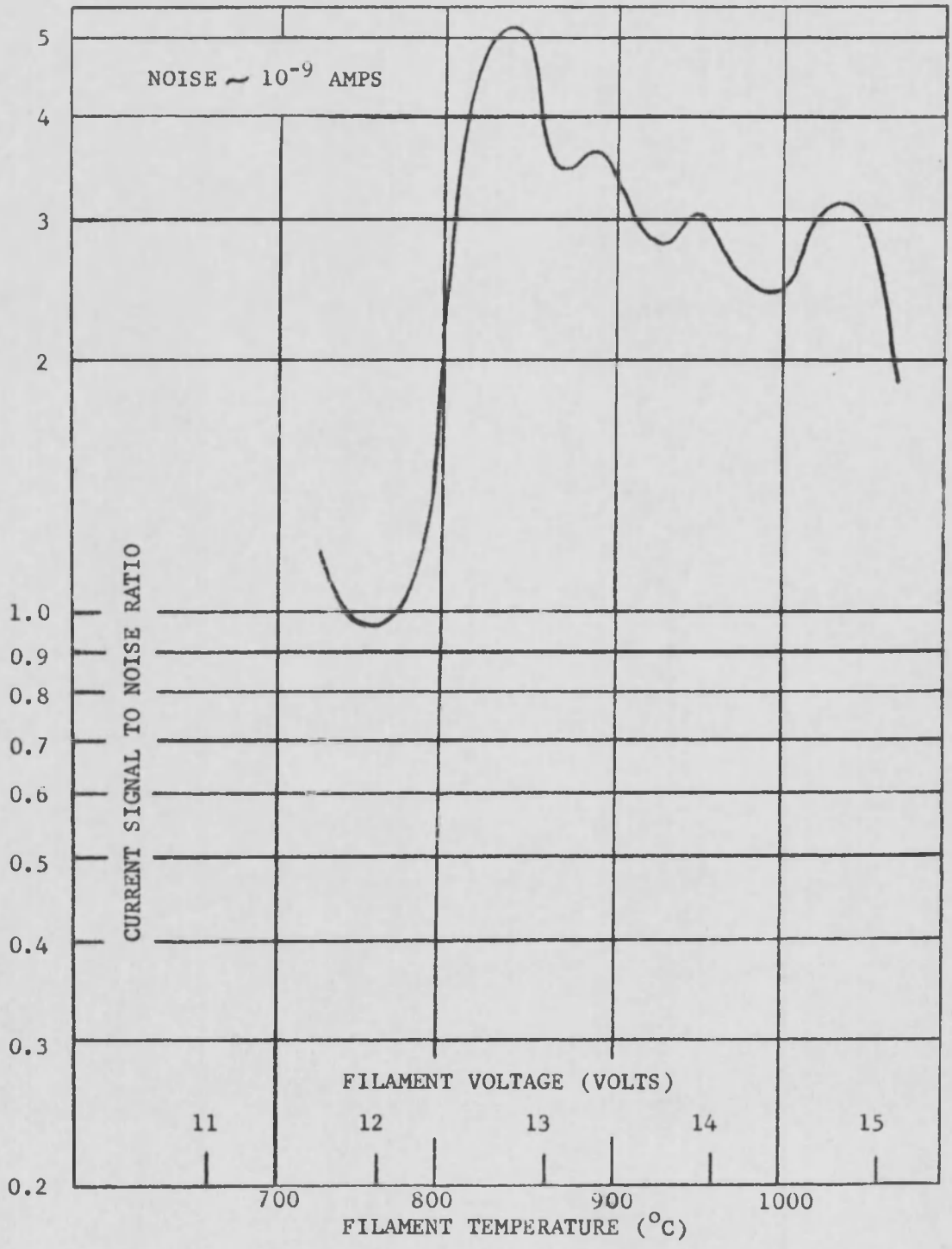

Fig. 4--Determination Of Optimum Filament Temperature

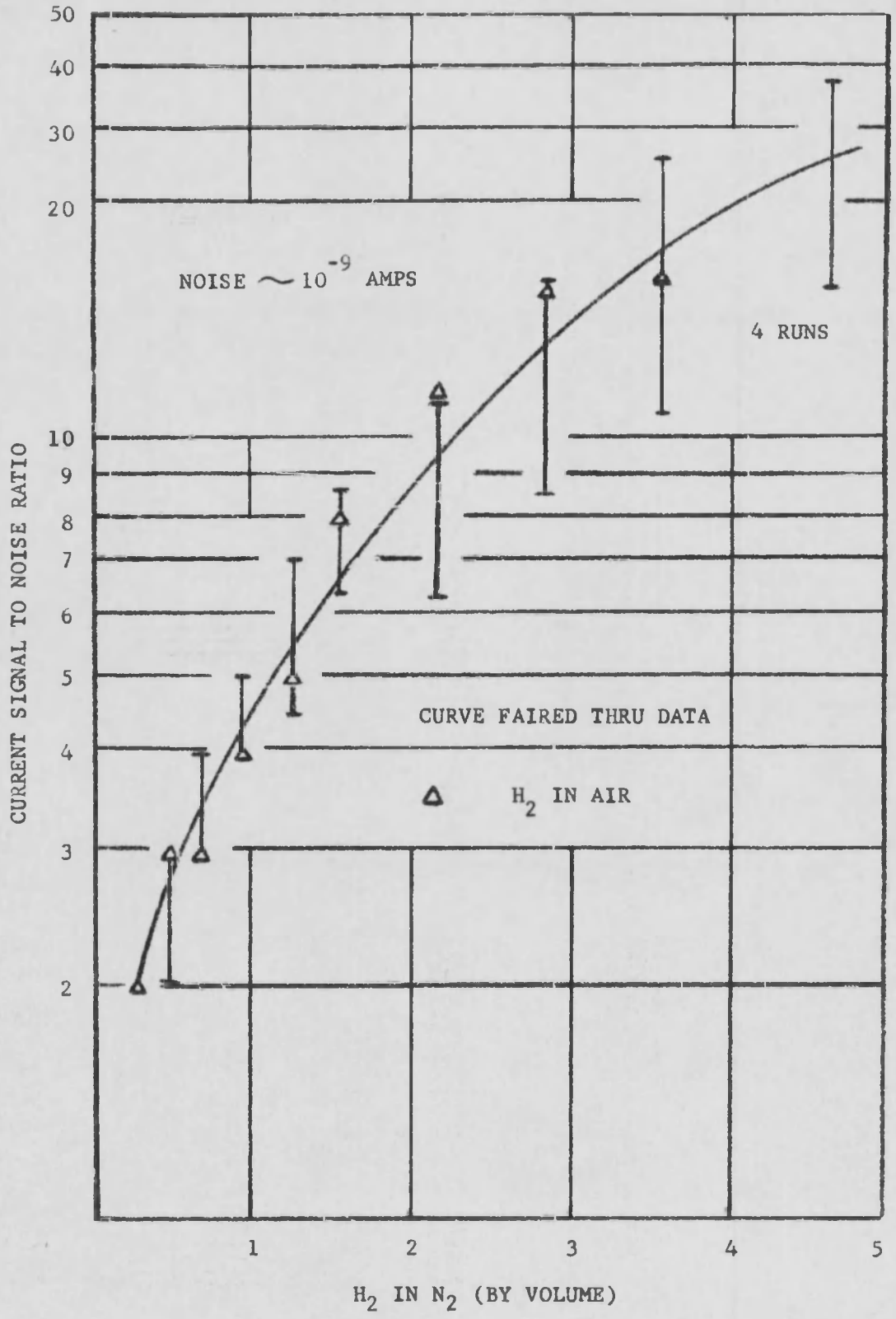

Fig. 5--Results Of The Atmospheric Hydrogen Detector

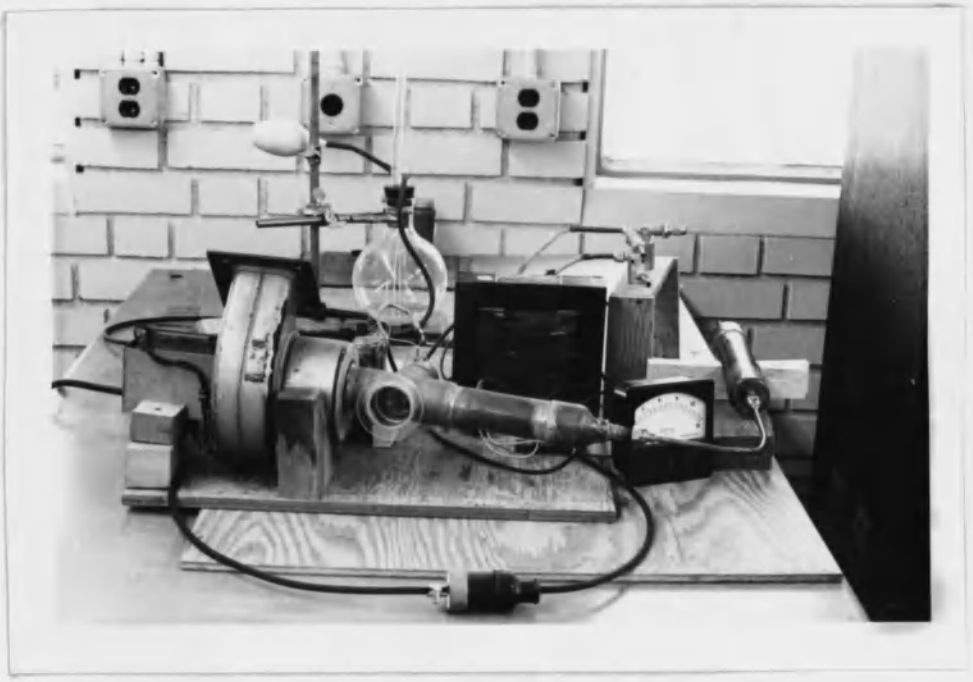

Fig. 6--Experimental System

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