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**THE GRAVIMETRIC DETERMINATION OF
HYDROGEN IN MOLYBDENUM METAL**

by

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ABSTRACT

The combustion-gravimetric method for the determination of hydrogen has been modified and adapted to the measurement of hydrogen in molybdenum metal. The sample is burned in oxygen at 1100° C. Fused magnesium oxide sand is used to absorb the molybdic oxide produced and prevent its sublimation in the combustion tube. The water produced by oxidation of the hydrogen present is absorbed in anhydrous magnesium perchlorate and weighed. An average recovery of 99.1% with a standard deviation of 8 ppm was obtained for the analysis of 62 samples containing known amounts of hydrogen in the 10 to 500 ppm range.

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INTRODUCTION

The classical combustion-gravimetric method⁽¹⁾ for the determination of hydrogen still has some advantages over newer methods in terms of simplicity, accuracy, and wide range of applicability. In this Laboratory, modifications of the method are used for the determination of hydrogen in a variety of materials including many metals. The analysis of molybdenum by this method, however, is complicated by the fact that the molybdic oxide produced sublimes into the cooler parts of the combustion tube and eventually plugs it up completely. Walter and Offner⁽³⁾ determined hydrogen in niobium by heating the sample in argon which subsequently flowed through hot copper oxide to convert any hydrogen to water. This technique, applied to molybdenum metal would eliminate the problem of the molybdic oxide, but the complete evolution of hydrogen under these conditions could be proved only by the use of proper standards that were not available. The quantitative release of hydrogen under conditions of complete oxidation of a sample seems obvious, making possible the use of any stable hydrogen compound as a standard.

Start
2/1/5 → The purpose of this study, ~~was~~ therefore, to find a way to prevent the

→ 8

sublimation of molybdic oxide at high temperatures, and under these conditions to determine the accuracy and precision which could be expected in determining hydrogen over a wide range of concentrations.

EXPERIMENTAL

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Copper oxide and magnesium oxide were tried as absorbing materials to prevent the sublimation of molybdic oxide. The copper oxide was very effective in preventing sublimation, but the resulting copper molybdate was so fluid that it could penetrate unglazed ceramic boats and accumulated in the combustion tube. It could not penetrate a glazed boat, but if the boat happened to break or tip over in the combustion tube the resulting mess was worse than molybdic oxide alone. Magnesium oxide effectively retained the molybdic oxide in the combustion boat and remained as a porous solid, permitting an easy access of oxygen and escape of water vapor.

Fused magnesium oxide is also used in this Laboratory to hold back fluorine in the determination of carbon in uranium tetrafluoride.⁽²⁾ It could probably be used in the determination of hydrogen or carbon in the presence of other volatile acid-forming substances.

High purity molybdenum metal for this study was obtained in the form of a rod, and turnings were taken on a lathe. No hydrogen could be detected in this metal. Known samples were prepared by adding a weighed amount of zirconium hydride to the molybdenum turnings for each

determination. Five grams of turnings was used in each case, while the zirconium hydride varied from 5 to 100 milligrams. The hydrogen added is expressed in parts per million of the sample taken. The results, summarized in groups, are shown in Table I. The blank for the determination, which becomes very significant in the lower ranges, was found to be lower when glazed porcelain boats were used than when unglazed boats were used.

APPARATUS AND REAGENTS

Apparatus, See Figure 1.

Preheater furnace, an electric furnace approximately 13 inches long and capable of taking a tube 1 inch in diameter is used. The Type 70 furnace manufactured by Hevi-Duty Electric Co. has been found satisfactory.

Preheater tube, this is a length of 1-inch O.D. nickel tubing about 19 inches long. It is threaded at both ends to fit standard copper flare-fitting adapters. At each end there is a plug of rolled copper gauze, and the space between is filled with wire-form copper oxide. The tube is maintained at a temperature of 750° C.

Purifying train, this is a series of three tubes following the preheater. There is a sulfuric acid bubbler, an Ascarite tube for removing carbon dioxide, and an anhydrous magnesium perchlorate tube for the removal of water. All are connected by 12/5 semi-ball joints.

Combustion assembly, the combustion tube is a 1-inch diameter quartz tube 40 inches long, reduced at one end to terminate in a 12/5 semi-ball joint. The last 12-inch section of the tube is packed with wire-form copper oxide held in place with metallic copper turnings. This packed section is maintained at 750° C by a furnace similar to that used in the preheater. The middle section of the tube is maintained at 1100° C by another similar furnace, for the combustion of the sample. The oxygen inlet is about 2 inches from the open end of the combustion tube. The tube is closed with a rubber stopper which is protected from the heat by a stainless steel baffle. The stem of the baffle extends through the stopper about 20 inches so that the baffle can be used to push the sample

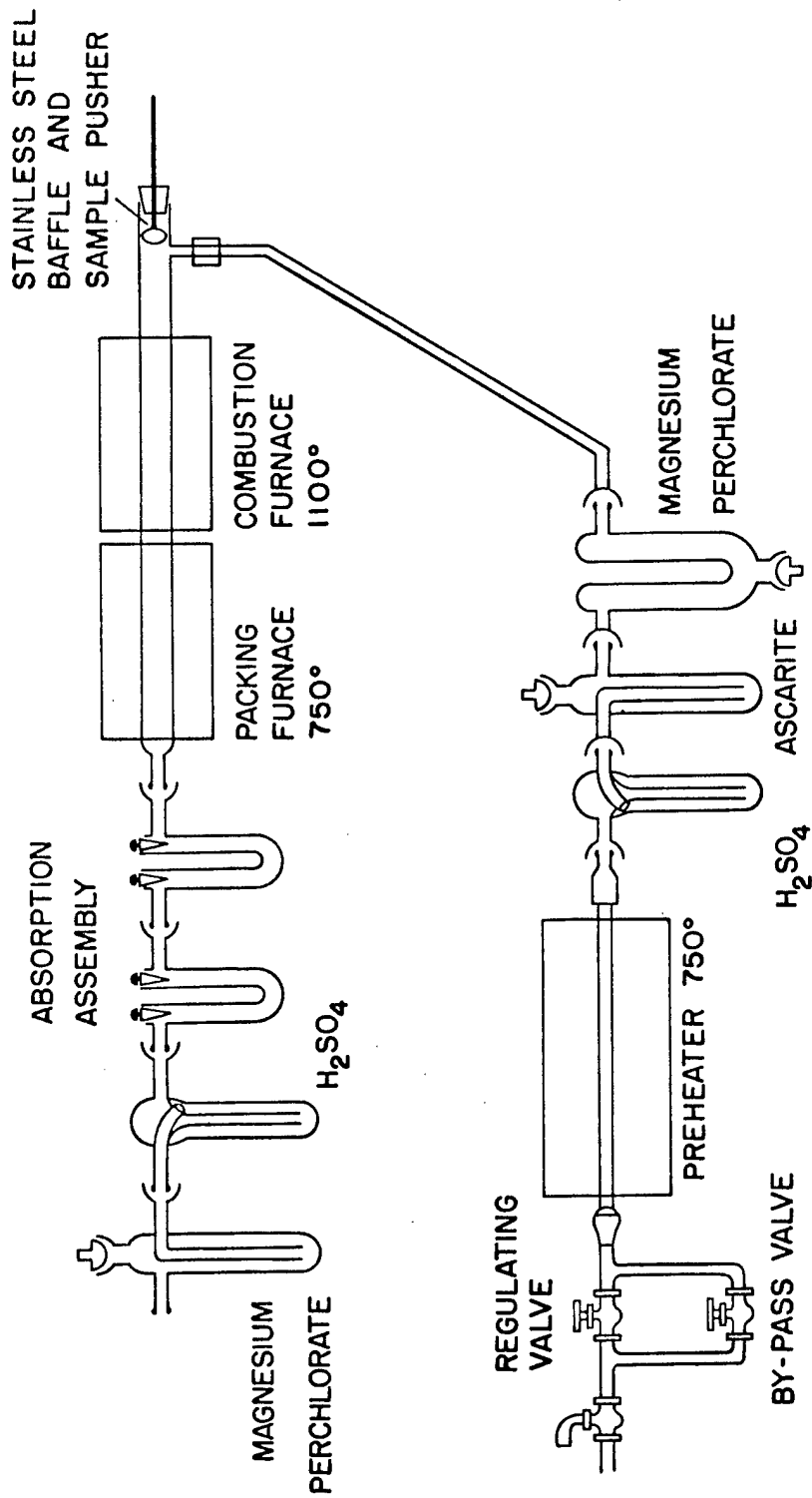


Figure 1. Combustion train for hydrogen.

into the hot part of the combustion tube after the tube has been closed and flushed.

Combustion boats, Coor's No. 7 porcelain boats are used without covers. They are pretreated by heating at 1000° C for 1 hour and are cooled just before use.

Absorption assembly, this is composed of two pyrex U-tubes filled with anhydrous magnesium perchlorate. The stopcocks are hollow, and the sidearms terminate in 12/5 semi-ball joints. The first tube is the absorption tube, and the second is the tare. The tare tube is protected from atmospheric moisture, in case of a reverse flow of the gas during combustion of the sample, by a final sulfuric acid bubbler and magnesium perchlorate drying tube.

Miscellaneous, there will also be required such apparatus as a boat rake, pyrometer and thermocouples, a boat platform, an analytical balance, and a rack to hold the absorption tubes.

Reagents

Ascarite

Cupric oxide, wire form.

Hydrogen standard, Zirconium hydride has been found to be a satisfactory standard material, suitably stable, and containing very nearly the theoretical amount of hydrogen.

Magnesium oxide, General Electric "Magnorite," electrically fused sand. Preheat at 800° C for 1 hour and store in a desiccator.

Magnesium perchlorate, granular, anhydrous.

Oxygen, ordinary cylinder gas.

RECOMMENDED PROCEDURE

Flush the system with a stream of purified oxygen (about 80 ml./min.) for an hour and determine a blank before analyzing a sample. The blank should include everything except the sample and should be treated the same as if the sample were present. If the system is new, a series of blank determinations should be made to determine the consistency as well as the magnitude. All weighings should be made to the nearest 0.1 mg.

Weigh the absorption tubes but do not yet reconnect them to the combustion tube. Weigh 5 grams of clean molybdenum metal into a preheated and cooled boat. Cover the metal with 10 grams of preheated and cooled magnesium oxide sand. Place the boat in the cool part of the combustion tube and flush the system with purified oxygen for 20 minutes. Connect the absorption tubes into the system and push the boat into the hot part of the combustion tube by means of the sample pusher. As the sample burns, increase the flow of oxygen by means of the by-pass valve to prevent a reverse flow through the absorption tubes. When the reaction is complete return the flow to normal and continue at this rate for 30 minutes. Reweigh the absorption tubes, correct the weight of water absorbed by subtracting the blank, and calculate the hydrogen content of the sample as follows:

$$H \text{ (ppm)} = \frac{\text{grams of H}_2\text{O} \times 0.1119}{\text{grams of sample}} \times 10^6$$

RELIABILITY

Reliability data were obtained by spiking pure molybdenum metal with zirconium hydride. This material was used because molybdenum hydride was not available and it was felt that under conditions of complete oxidation of the sample there would be no difference.

A total of 62 determinations were made in groups with hydrogen concentrations of approximately 10, 50, 100, 200, and 500 parts per million. The results for each group are summarized in Table I. The overall recovery for the 62 determinations was 99.1 percent with a standard deviation of 8 parts per million. The average blank was 0.4 milligrams which was equivalent to 9 parts per million of hydrogen. However, the blank was sufficiently constant that in the lower concentration ranges the standard deviation was as low as 4 parts per million.

TABLE I
THE RECOVERY OF HYDROGEN ADDED TO MOLYBDENUM METAL

No. of determin- ations	Molybdenum present, grams	H added, average, ppm	H found, average, ppm	Standard deviation, ppm
8	5	13	17	5
6	5	49	51	4
14	5	106	107	7
20	5	200	193	.8
<u>14</u>	5	<u>457</u>	<u>452</u>	<u>10</u>
62		223	221	8

SUMMARY

The classical combustion-gravimetric method for determining hydrogen has been modified and applied to the determination of small amounts of hydrogen in molybdenum metal. By using fused magnesium oxide sand in the combustion boat with the sample, 5 grams of molybdenum can be burned without molybdic oxide subliming out into the system. The standard deviation and limit of detection of the method is about 8 parts per million.

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