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# DETERMINATION OF HYDROGEN IN MILLIGRAM QUANTITIES OF TITANIUM AND ITS ALLOYS

*by Dumas A. Otterson and Robert J. Smith*

*Lewis Research Center*
*Cleveland, Ohio 44135*

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16. Abstract

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# DETERMINATION OF HYDROGEN IN MILLIGRAM QUANTITIES OF TITANIUM AND ITS ALLOYS

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## SUMMARY

An accurate, versatile, and sensitive method for the determination of hydrogen in milligram-size titanium samples is presented. It involves extraction of hydrogen at 1070 K while a mercury diffusion pump transfers the evolved gases into the inlet of a mass spectrometer. All the evolved gases may then be positively identified and determined. This method can be readily adapted for use with other metals and alloys and for the study of the slow evolution of hydrogen. Reduction of interferences due to the evolution of hydrogen by reactions involving vapors such as those of water, acteone, and vacuum grease is discussed.

## INTRODUCTION

In our study of the tensile properties of the titanium (Ti) - hydrogen system, an accurate method for the determination of hydrogen in Ti was needed. Also desirable was sensitivity to nanogram quantities of hydrogen.

Many methods are available for the determination of hydrogen in metals. Guldner indicates that the most satisfactory method involves hot extraction of hydrogen with the sample being added to the extraction system through a vacuum lock (ref. 1). The National Bureau of Standards (NBS) used hot extraction at 1670 K to establish the certified values for hydrogen in Ti (ref. 2). Generally, a McLeod gage is used to measure the extracted hydrogen. Even though this measurement can be accurate in the nanogram range for pure gases, the problems associated with the separation of gases in this range are not known at this time. Aspinal (ref. 3) avoids these problems by using a mass spectrometer to determine the gases evolved during vacuum fusion. However, there appears to be little discussion of the interfering reactions which liberate hydrogen in the nanogram range in the presence of reactive metals such as Ti.

This report describes a hot-extraction method which utilizes a mass spectrometer to determine the extracted hydrogen. The hydrogen is extracted from small samples (milligram quantities) at 1070 K by using a mercury diffusion pump to maintain a low pressure over the specimen during extraction and to help define the volume of the extracted gases in the mass spectrometer. Because of the desired accuracy, the effect of hydrogen pressure on the volume so defined is studied and reported. This extraction temperature is lower than those usually used. It results in the formation of less extraneous hydrogen than higher temperatures.

This reduced interference also contributes to the success of this method for small samples. Greater control of the interferences is required for these small samples than for the much larger samples which are often used in other methods. This control was developed and tested by using the method to measure the hydrogen found when using hydrogen-free Ti (<0.5 ppm hydrogen). The substances which react with Ti to yield nanogram amounts of hydrogen are also discussed. The discussion may well aid in the improvement of other methods for the determination of hydrogen in other reactive metals as well as in Ti. Moreover, improved control of the interferences is needed to achieve higher precision in the determination of the ratio of hydrogen isotopes; this control is readily obtained by this method.

The accuracy of the method was evaluated by determining the hydrogen in Ti NBS Standard Reference Material 354. Statistical data from our results using thin slices of this material are compared with those reported for this material in reference 2.

## EXPERIMENT

### Sample Preparation

One should note that the dimensions of the individual pieces of the sample and its cleanliness are of utmost importance in this method for the determination of hydrogen in Ti.

In order to extract the hydrogen quantitatively from Ti in 1/4 hour at 1070 K, at least one dimension of each piece of the sample should not be much greater than 0.25 millimeter. If all the dimensions are significantly larger, the specimen may be cut so that it has a dimension near this size, or a longer extraction period may be used. The NBS Standard Reference Material 354 was supplied in the form of pieces with 1-centimeter sides and a 1.4-millimeter thickness (ref. 2). Thin slices were removed from these pieces by cutting them perpendicular to the large surface with a water-cooled diamond cutoff wheel. Samples slices to thicknesses between 0.4 and 0.7 millimeter were analyzed. They weighed between 14 and 28 milligrams. The 0.25-millimeter

wires which were analyzed by us generally weighed about 1 milligram.

Water and organic contaminants were removed from the surface by rinsing with suitable solvents. If solvents other than chloroform were used, the sample was subsequently rinsed twice with reagent grade chloroform. The final chloroform rinse was made immediately prior to the analysis in order to prevent any other organic contaminant from accompanying the sample into the desorption chamber.

## Apparatus

The apparatus consists of a desorption chamber, a manifold, a cold trap, a three-stage mercury diffusion pump, and a mass spectrometer; these items are joined together, in the sequence listed, to form a unified vacuum system. Figure 1 is a schematic drawing of the apparatus up to the inlet of the mass spectrometer. Borosilicate glass is used throughout except for the desorption chamber; this is made from quartz.

The desorption chamber is 15 centimeters long; it has a closed bottom and an inner joint (standard taper $\overline{\S}$, 19/38) at the top to connect it with the manifold. The 5-centimeter length nearest the closed end of the extraction chamber has a reduced diameter (4 mm). Only this part of the desorption chamber is heated. The Ti sample is held in a gold thimble in the lower part of this chamber during the desorption of hydrogen. The gold thimble is closed at its lower end. It has a small enough diameter to slide into the 4-millimeter section of the quartz tube, but is 6 centimeters long so as to extend into the unheated part of the desorption chamber. A hook at its open end facilitates its removal from the desorption chamber.

An external movable tube furnace, 10 centimeters long, is used to heat the 4-millimeter section of the desorption chamber containing the Ti sample. This furnace is thermostatically controlled. Heat shields are located between the heated portion of the desorption chamber and its connecting tapered joint. A stream of air is also used to help keep the joint near room temperature.

The manifold consists of two standard-taper outer joints (19/38 and 24/40) and three vacuum stopcocks. The manifold facilitates venting, evacuation, and changing of samples. It is attached to the cold trap by means of the 24/40 standard-taper joint. This joint permits direct access to the center part of the cold trap when cleaning is required. The trap is cooled with liquid nitrogen. Several strips of copper rest on the bottom of the cold trap and extend up the center part to a point slightly above the highest level of the liquid nitrogen. This use of the copper is intended to minimize any temperature effects due to changes in the liquid-nitrogen level.

The three-stage mercury diffusion pump has a pumping speed of about $60 \times 10^3$ cubic centimeters per second after a forepressure of $10^{-3}$ torr (0.13 $N/m^2$) is reached. Its

rated attainable vacuum is $10^{-8}$ torr ($1.3\times10^{-6}$ $N/m^2$).

Any mass spectrometer which is designed to do simple gas analysis should be suitable for this work. We used a Consolidated Electrodynamics Corporation model 621 spectrometer and were able to achieve 1 percent precision in the determination of hydrogen by careful maintenance of the mass spectrometer and by determining its response to known amounts of hydrogen each day it is used.

The vacuum system is carefully cleaned. All surfaces which are rinsed with acetone or other solvents are subsequently rinsed with chloroform. Only a small amount of vacuum grease (Spectrovac Stopcock Grease, Type 2) is used in the joint of the desorption chamber. Any grease that extends beyond the areas of contact of the joint is removed with chloroform.

## Calibration of Apparent Volume of Hydrogen

In this apparatus, the hydrogen which is desorbed from the specimen is pumped into the inlet system of the mass spectrometer by the diffusion pump. Obviously, this hydrogen occupies a volume larger than that of the inlet system. The volume of hydrogen also includes that part of the vacuum system between the inlet of the mass spectrometer and the pumping interface of the diffusion pump. The apparent volume is determined by use of Boyle's law because of the difficulty in locating precisely the pumping interface, which is one of the boundaries of this volume.

The pressure of hydrogen in the known volume of the inlet of the mass spectrometer is measured before and after expanding to the pumping interface of the diffusion pump. From these data the apparent volume is readily calculated. By varying the initial pressure, the effect of pressure (after expansion) on the apparent volume is obtained.

## Analytical Method

The desorption system was conditioned and tested every day before it was used for the determination of hydrogen in Ti. To condition the system, the narrow end of the desorption chamber containing the gold thimble and hydrogen-free Ti was heated to 1070 K. The gases obtained during the first 5 or 10 minutes are discarded. After that, the hydrogen collected in 15 minutes is determined. Collections are repeated until a constant value is obtained; two collections are usually sufficient. This system is considered to be suitable for use if the amount of hydrogen (the blank) collected is small compared with the amount expected in the analysis. When the blank is too large, it can be reduced to as little as 10 nanograms of hydrogen by careful cleaning of the extraction chamber.

Generally, this can be accomplished by removal of extraneous vacuum grease with chloroform. Occasionally metal deposits should be removed either by rinsing with dilute hydrofluoric acid or by heating the chamber to 1070 K while exposed to air.

When the desorption chamber is suitably conditioned, the furnace is moved away, and both it and the desorption chamber are cooled. The chamber is opened without allowing air to enter the cold trap, and the quartz tube is removed from the rest of the system. Excess vacuum grease is wiped from its open end with lens tissue. A small funnel is inserted into the quartz tube without contaminating it with grease by sliding it through a cylinder made of clean weighing paper that is inserted in the open end of the desorption tube. The gold thimble is removed from the desorption chamber by being pulled through the funnel. The analyzed sample is dumped out of the gold thimble, and the next sample to be analyzed is dipped in chloroform, dried in air, and added to the gold thimble. The thimble and its contents are then added to the extraction chamber through the funnel. Only grease-free surfaces are permitted to touch the gold thimble or the sample after it has been rinsed with chloroform. The desorption chamber is reassembled, and most of the air is removed by an auxiliary pumping system. The desorption chamber is then evacuated through the mass spectrometer pumping system. The small end of the quartz tube is heated to 570 K and evacuated for at least 5 minutes. The collection of gases is started. The temperature is increased to 1070 K. After 15 minutes, both the desorption chamber and the analytical system of the mass spectrometer are sealed off from the rest of the system. The gases in the tubing between the desorption chamber and the analytical system of the mass spectrometer are discarded. The pressure of the hydrogen in the analytical system is determined mass spectrometrically, and this hydrogen is then discarded. The amount of hydrogen desorbed is calculated from the gas laws by using the pressure so determined and the apparent volume of hydrogen. The hydrogen desorbed in the next 15 minutes is determined in the same manner. Collections and analyses are repeated until the amount found is the same as that obtained from hydrogen-free Ti. Generally, this level is reached by the second collection with 0.25-millimeter-diameter Ti wire specimens. With thicker samples, more time is required for quantitative hydrogen desorption.

## RESULTS

Table I contains data obtained in the analysis of nine thin slices of NBS Standard Reference Material 354. Presented in this table are the thicknesss of the slices, their weight, and the hydrogen content as determined by this method corrected for the blank. The corrections amounted to 2 or 3 ppm hydrogen, and in these cases, the blanks are equal to the amount of hydrogen obtained when consecutive collections were low and con-

stant. Such blanks generally equal those obtained when hydrogen-free Ti (less than 0.5 ppm hydrogen) samples are analyzed. The statistical analysis data are presented in table I in the same form as that used to evaluate the results for the certification of the NBS samples (ref. 2). Virtually all the hydrogen was extracted from these specimens in 45 minutes.

Figure 2 shows how the change in hydrogen pressure affects the apparent volume of the hydrogen (i.e., the volume of the expansion volume of the mass spectrometer, its inlet system, and that portion of the desorption system to the pumping interface of the diffusion pump). The pressures studied cover the pressure range that can be used in the mass spectrometer. At 0.01 torr (1.33 $N/m^2$) of hydrogen, the apparent volume is about 1328 square centimeters. Between 0.046 and 0.400 torr (6.1 and 53 $N/m^2$), the volume varies between 1344 and 1348 cubic centimeters.

Figure 3 shows typical data obtained from 0.25-millimeter-diameter Ti wires (7700 ppm hydrogen) that had been charged with hydrogen electrolytically. Each data point shows the amount of hydrogen which was desorbed from the specimen in 15 minutes as the temperature was raised from that of the previous data point to the temperature indicated. The specimen was at the indicated temperature for about three-fourths of the collection period. These data are plotted as the logarithm of the number of nanograms of the hydrogen as a function of the temperature. The amount collected at 300 and 570 K and the second collection at 1070 K was the same as the blank for those temperatures. Hence, the maximum amount that could have desorbed is equal to the uncertainty of the blank. The actual amount of hydrogen that would be expected to desorb at the two lower temperatures might be estimated by extrapolation from the data points at 670 and 770 K (short-dash line in fig. 3). The values obtained in this manner for 300 and 570 K are far less than the uncertainty of the measurement.

The data above 570 K show that hydrogen desorption is first detected at 670 K. Most of it is desorbed at 870 K. Some is still desorbed at 970 and 1070 K. However, the amount desorbed in the second collection at 1070 K is negligibly small.

## VALIDITY OF METHOD

The results presented in table I for NBS Standard Reference Material 354 show that the method is essentially as accurate as and has as good precision as the method used to establish the certified value of the hydrogen content. The average value obtained by our method from the nine slices which were cut from three pieces was 216 ppm hydrogen. The standard deviation for these results is 4.9 ppm, and the coefficient of variation is 2.3 percent. The 95-percent confidence level for our method is 216±4 ppm. The certified value for this standard sample is 215±6 ppm hydrogen with a 95-percent confidence

level of 214.9±5.2 ppm (ref. 2). These values are based on results obtained from six laboratories that reported standard deviations as great as 5.9 ppm and as low as 3 ppm and coefficients of variation ranging between 2.9 and 1.4 percent. Our average value is slightly greater than the certified value, which was obtained by desorption at temperatures ranging from 1620 to 2170 K; this indicates that the lower desorption temperature is adequate for the desorption of hydrogen from 15- to 30-milligram samples. Our standard deviation and coefficient of variation are within the range of those samples used to establish the certified value. Hence, the method presented in this report can be said to be essentially as accurate and precise for these small slices as the method used to certify the much larger NBS specimens.

However, the precision and accuracy may not be as good for the milligram samples of the tensile specimens that were of interest to us. This can readily be seen when one notes that a variation in the blank of 4 to 6 nanograms of hydrogen corresponds to an error of 4 to 6 ppm for milligram samples but not over 0.6 ppm for a 10-milligram sample.

## DISCUSSION OF METHOD

This method for the determination of hydrogen in Ti has several unusual featues. The sample should be thin and may weigh as little as 1 milligram, the extraction temperature is only 1070 K, and a mercury diffusion pump is used to help contain the gases during the determination of hydrogen.

The thinness of the specimen permits the extraction of hydrogen to be carried out in a reasonably short time at 1070 K. Thus, gold may be used to hold the Ti at 1070 K instead of graphite or molybdenum, which is generally used. Gold does not react with interfering agents, and only a little treatment is required to eliminate adsorbed substances which may interfere. The daily conditioning for the desorption system is most likely required because of the water which is adsorbed on the quartz and glass in the desorption chamber. Studies have shown that water is apparently adsorbed only on the quartz and glass in the desorption chamber and that water is apparently adsorbed on the quartz only at sites which contain chemisorbed hydroxyl groups. These sites can be removed by heating. If the chamber is heated above 670 K, rehydration does not readily occur (ref. 4). The high blanks that were observed occasionally when the desorption chamber was not conditioned by being heated to 1070 K probably resulted from rehydration of the quartz by water which desorbed from the unheated parts of the desorption chamber.

Our use of the mercury diffusion pump removes the gases as they are formed in the extraction chamber. Hydrogen extraction is faster, and smaller amounts of other gases remain in the extraction chamber to react with Ti to liberate hydrogen. Some of these

improvements will be discussed in more detail in the section Desorption of Hydrogen From Titanium.

## Volume Variation With Hydrogen Pressure

The data of figure 2 show that the apparent volume of hydrogen does vary a little with its pressure, so we must infer that the pumping interface of the diffusion pump is affected by the pressure. This inference is in accord with Alexander's data (ref. 5). His data show that the pumping interface (the layer in which the pressure increases from that of the pump inlet to that of its exit) moves toward the gas exit of the pump as the pressure decreases. Our data indicate that in general the error is small enough to be ignored in the present work. Between 0.05 and 0.400 torr (6.5 and 53 $N/m^2$) of hydrogen the variation is less than 5 cubic centimeters in a volume greater than 1300 cubic centimeters. Thus, the error due to this source is less than 0.5 percent. Below 0.05 torr (6.5 $N/m^2$), the volume decreases by about 20 cubic centimeters, or less than 2 percent. If this error cannot be tolerated, a correction can readily be made for this decrease in apparent volume. Inasmuch as mercury diffusion pumps are often not as effective with hydrogen as with heavier gases (ref. 5, p. 195), one should find less variation in the apparent volume of other gases because of differences in their pressure.

## Desorption of Hydrogen From Titanium

In this work, desorption can be considered to be quantitative when the hydrogen content is reduced to about 1 ppm. In addition, no other reaction should occur that could either add an appreciable amount of hydrogen to that extracted from the specimen or remove an appreciable amount of hydrogen.

Desorption temperature. - The contention that hydrogen can be quantitatively extracted from small specimens at 1070 K is supported by calculations of hydrogen solubility and by much experimental evidence.

The solubility of hydrogen in Ti under the conditions of this determination can be estimated by using the following equation

$$\log_{10} \frac{S}{p^{1/2}} = \frac{2020}{T} - 0.285 \qquad \text{for SI units}$$

or

$$\log_{10} \frac{S}{p^{1/2}} = \frac{2020}{T} - 0.723 \quad \text{for the units of reference 6}$$

where S is the solubility in ppm, p is the hydrogen pressure, and T is the absolute temperature. Inasmuch as the attainable vacuum of the diffusion pump is $10^{-8}$ torr ($1.3\times10^{-6}$ N/m$^2$), the hydrogen pressure should not be over $10^{-6}$ torr ($1.3\times10^{-4}$ N/m$^2$) at the end of the collection. Hence, the amount of hydrogen in Ti at 1070 K should not be over 0.5 ppm when the desorption stops.

The data of figure 3 indicate temperatures which may be used to remove interfering substances as well as to achieve quantitative extraction of hydrogen. From the figure we note that Ti can be heated to 570 K for almost 15 minutes without measurable loss of hydrogen. This fact permits us to heat the specimen prior to the collection of desorbed hydrogen so as to remove as much as possible other adsorbed substances that might interfere. Indeed, our subsequent experience shows that this preheating of the desorption system permits us to open the desorption chamber prior to the determination of hydrogen in each specimen without the loss of much time. Thus, analyses can be carried out as the samples are prepared rather than only when a number are ready to be analyzed.

The fact that virtually no hydrogen is desorbed in the second collection at 1070 K (see fig. 3) indicates that hydrogen can be quantitatively desorbed from electrolytically charged Ti samples in 15 minutes at 1070 K in our system. This is confirmed upon examination of the results obtained from over 50 electrolytically charged specimens (some with and some without thermal homogenization). That is, over 99 percent of the extractable hydrogen is found to be in the first 15-minute collection, in which the temperature is raised to and kept at 1070 K. A small error in the blank could account for most of the cases in which this is not so. In addition, data obtained with NBS specimens also indicate that virtually all the hydrogen can be extracted at 1070 K in a relatively short time. However, these specimens are larger, so more than 15 minutes are required for quantitative desorption.

Effect of sample dimensions. - The need for longer desorption times by larger specimens is consistent with the work of Albrecht and Mallett (ref. 6), who found that the rate of hydrogen desorption from Ti was affected by specimen size and the presence of oxide films. In the present work, the dependence of time needed for complete desorption is observed with 0.25-, 0.50-, and 1.25-millimeter-diameter wires and with NBS samples. As noted in the previous section, over 99 percent of the hydrogen is desorbed from most of the smallest specimens during the first desorption period at 1070 K. The 0.50-millimeter Ti specimen requires 30 minutes and the 1.25-millimeter Ti specimen 45 minutes for extraction of 99 percent of the hydrogen.

Complete extraction is generally accomplished in 45 minutes with slices of the NBS pieces ranging in thickness from about 0.40 to 0.78 millimeter. Extraction from un-

sliced specimens (14 mm thick) which were sandpapered to remove the dark surface layer also appears to be complete in 45 minutes. However, for these unsliced pieces no result is over 209 ppm. These apparently low results might be due to either incomplete desorption or loss of hydrogen-rich material when the dark surface layer was removed If the dark surface layer is not removed from this type of sample, hydrogen extraction is still incomplete after 2 hours. Presumably this layer acts as a barrier (ref. 6). In view of the difficulties and the limited amount of work with the large specimens, we can not recommend this method for specimens without at least one dimension that is less than 0.7 millimeter.

## Interfering Reactions

Many substances can react with hydrogen to cause low results. One example of such a substance which might be added to the system under normal circumstances is a Ti film. The evaporation of Ti must be avoided because freshly formed Ti films can absorb hydrogen even at room temperature (ref. 7). One reason to select as low an extraction temperature as practical is to minimize Ti evaporation. The gold thimble is longer than the heated portion of the desorption chamber so that, if Ti does evaporate, it will not contact hot quartz. A black film has been formed several times during the development of the method. This film yields high blanks in ensuing work. Presumably hydrogen is absorbed when the film is formed and is slowly lost later.

It is difficult to exclude all the substances that yield hydrogen under these conditions. Not all are known, and water, the best known of these substances, is almost omnipresent. A good example of a substance that is not generally known to yield hydrogen under these conditions is acetone. Our experience shows that acetone can cause high blanks. Yet acetone has been recommended as a degreasing agent for Ti specimens prior to the determination of hydrogen (ref. 4). We believe that the large samples which are analyzed by this method yield so much hydrogen that any error due to acetone would not readily be observed.

In our work, high blanks were noted when acetone was detected in the mass spectrometer. They were obtained when only acetone had been used to clean the specimen or the vacuum system near the extraction chamber. These problems were avoided by using chloroform as a final rinse for the glassware and the specimens.

Other organic compounds also yield hydrogen by a reaction with hot Ti. High blanks may be caused by such varied things as vapors from vacuum grease and lint from paper towels. Large blanks are noted when certain vacuum greases are used in the joint and the stopcocks nearest the desorption chamber, when the joint becomes warm, and when any of the greases moves into the vacuum system from the area of contact between the

inner and outer portion of the joint. Low blanks are generally attained by keeping the temperature of the joint as low as possible by the use of heat shields and a stream of cool air and by the use of Spectrovac Stopcock Grease, Type 2. When paper towels or lens tissues that could lose fibers easily are used to clean the joint, high blanks may occasionally be observed. When microscope slide lens tissue is used, this type of blank is not noted.

The reaction between water and Ti to produce hydrogen is well known. Low- and constant-hydrogen blanks can be attained only by the proper control of the water in the vacuum system. Water from the walls of the vacuum system and from the cold trap can contribute to the hydrogen blank. The conditions that yield a negligibly small contribution from the quartz were established in an early modification of this method (ref. 8). They are

(1) Heating as little of the quartz as possible

(2) Heating the same amount of quartz during each analysis

(3) Daily heating of the quartz to 1070 K while the system is evacuated prior to doing any analysis

(4) Evacuating and heating the desorption chamber and its contents to 570 K for 5 minutes after the introduction of a sample

(5) Preventing direct contact between Ti and hot quartz by use of a gold thimble

Several observations show that water from the cold trap contributes to the blank. First, the blank is much greater if a dry ice (195 K) bath is used in the cold trap instead of liquid nitrogen (78 K). Second, the magnitude of the blank increases as the level of liquid nitrogen drops. Third, if a lot of air passes through the cold trap, ensuing blanks are high. To achieve low and constant blanks, several things may be done. After the sample is added to the desorption chamber, most of the air should be removed by a pumping system which bypasses the liquid-nitrogen-cooled cold trap. Fluctuations in the blank due to changes in the level of liquid nitrogen can be controlled by the use of strips of a nonreactive metal such as copper. These strips are placed in the center of the cold trap. They extend from the bottom to a point slightly above the highest possible level of the liquid nitrogen. Thus, water is trapped on a surface that is always close to 78 K rather than on the walls, whose temperature increases as the level of the liquid nitrogen drops.

## Application of Method to Other Systems

The general method and special techniques described in this report are applicable to the determination of hydrogen and/or deuterium in many materials. These include metals, alloys, and even nonmetallic solids. For some systems, modification may be

needed to achieve accurate results. To show that the method does yield accurate results, one merely needs to demonstrate that the extraction of hydrogen is quantitative under the conditions (temperature, pressure, etc.) used for the material being analyzed. Temperatures up to the softening point of quartz (about 1450 K) may be used if the interfering reactions are controlled. Data such as those presented in figure 2 (hydrogen loss as a function of temperature) are a great aid in establishing the proper conditions for quantitative extraction. Knowledge of the diffusion constants and solubility of hydrogen in the material involved are helpful but not essential. Of course, the accuracy of the method should be evaluated by using it to analyze similar materials of known hydrogen content if at all possible.

Experience at the Lewis Research Center shows that our method or a modification of it can be used to determine deuterium or hydrogen in palladium (Pd) (refs. 9 and 10), Pd-silver (Ag) alloys, titanium - 8-percent-aluminum - 1-percent-molybdenum - 1-percent-vanadium (Ti-8Al-1Mo-1V) alloy, niobium (Nb), and X-irradiated hypophosphites. In some cases, specific properties of the system require modifications of the method. For instance, Pd with 7000 ppm hydrogen tends to lose hydrogen even at room temperature. Thus, Pd specimens must be stored in liquid nitrogen, and the evacuation of air from the extraction chamber prior to gas collection should be done in as short a period of time as possible. Fortunately, enough air can be removed in a few minutes for our purpose inasmuch as complete removal of all components is not required. Palladium does not react with any component of the air to yield hydrogen at its extraction temperature (570 K) (ref. 10). In contrast, the Ti alloy and Nb behave more like Ti in their extraction and reactivity characteristics. Our tests show that the method requires no modification for these materials.

Hydrogen-producing reactions that occur at room temperature or below may also be studied. For example, we have found that amalgamated Al can react with water near liquid-nitrogen temperatures. About 4 nanograms of hydrogen is liberated in 15 minutes from an Al surface of which less than 12 square centimeters appears to be amalgamated. Prior to amalgamation none was detected. Experience also shows that the hydrogen can be extracted from X-irradiated granules of hypophosphites in about 8 hours at room temperature. Elevated temperatures cannot be used because of the chemical instability of the salts.

Furthermore, one should note that this use of the mass spectrometer permits the simultaneous determination of several gases, even inert ones, that can be extracted from a solid by a modification of the method. Indeed, the method is especially suitable for the determination of hydrogen-deuterium ratios. We have applied the method to determining hydrogen contamination of deuterated Pd (ref. 9) and Ti. In the latter case, careful attention to the control of interfering agents is required to prevent high results for the degree of hydrogen contamination.

## SUMMARY OF RESULTS

An accurate and sensitive method for the determination of hydrogen in milligram quantities of titanium is presented. The method involves the extraction of hydrogen at 1070 K while it is pumped into a mass spectrometer, where virtually all extracted gases can be positively identified and determined. A mercury diffusion pump is used not only to maintain a low pressure in the extraction chamber but also to help confine the extracted gases.

The versatility and sensitivity of the method and this equipment are indicated by several observations. First, the method is applicable to virtually any metal-hydrogen system with suitable properties. Second, it may be used to determine any other gas that can be extracted. The method produces reliable results in studies of the hydrogen contamination of deuterated palladium (NASA TN D-4970) and titanium. Third, very slow reactions that produce hydrogen can be detected and studied.

The small size of the sample (1 to 30 mg) used in this method permits an accurate and fairly rapid analysis when the amount of specimen is severely limited. An obvious application is the study of the distribution of hydrogen in metals.

Lewis Research Center,
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502-01.

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TABLE I. - HYDROGEN FOUND BY METHOD OF THIS REPORT IN NBS STANDARD REFERENCE MATERIAL 354

[Certified hydrogen content, 215±6 ppm.]

| Thickness, mm | Weight, mg | Hydrogen content, ppm (a) |
|---|---|---|
| 0.77 | 26.8 | 218 |
| .44 | 16.2 | 214 |
| .46 | 17.5 | 218 |
| .41 | 13.9 | 214 |
| .42 | 14.5 | 211 |
| .48 | 16.1 | 223 |
| .45 | 17.8 | 225 |
| .48 | 16.8 | 213 |
| .46 | 16.1 | 210 |

[a] Mean = $\bar{x}$ = 216.

Value which is accepted as being correct = x = 215.

Standard deviation = $S = \sqrt{\frac{\sum_{i}^{n} \left(x_i - \bar{x}\right)^2}{n - 1}} = 4.9.$

Coefficient of variation (percent) = $\frac{S}{\bar{x}} \times 100 = \frac{4.9}{216} \times 100 = 2.3.$

Accuracy = $\frac{\bar{x} - \hat{x}}{\hat{x}} \times 100 = 0.5$ percent.

95 Percent confidence limit = $\bar{x} \pm \frac{2.306\ S}{\sqrt{n}} = 216 \pm 4.$

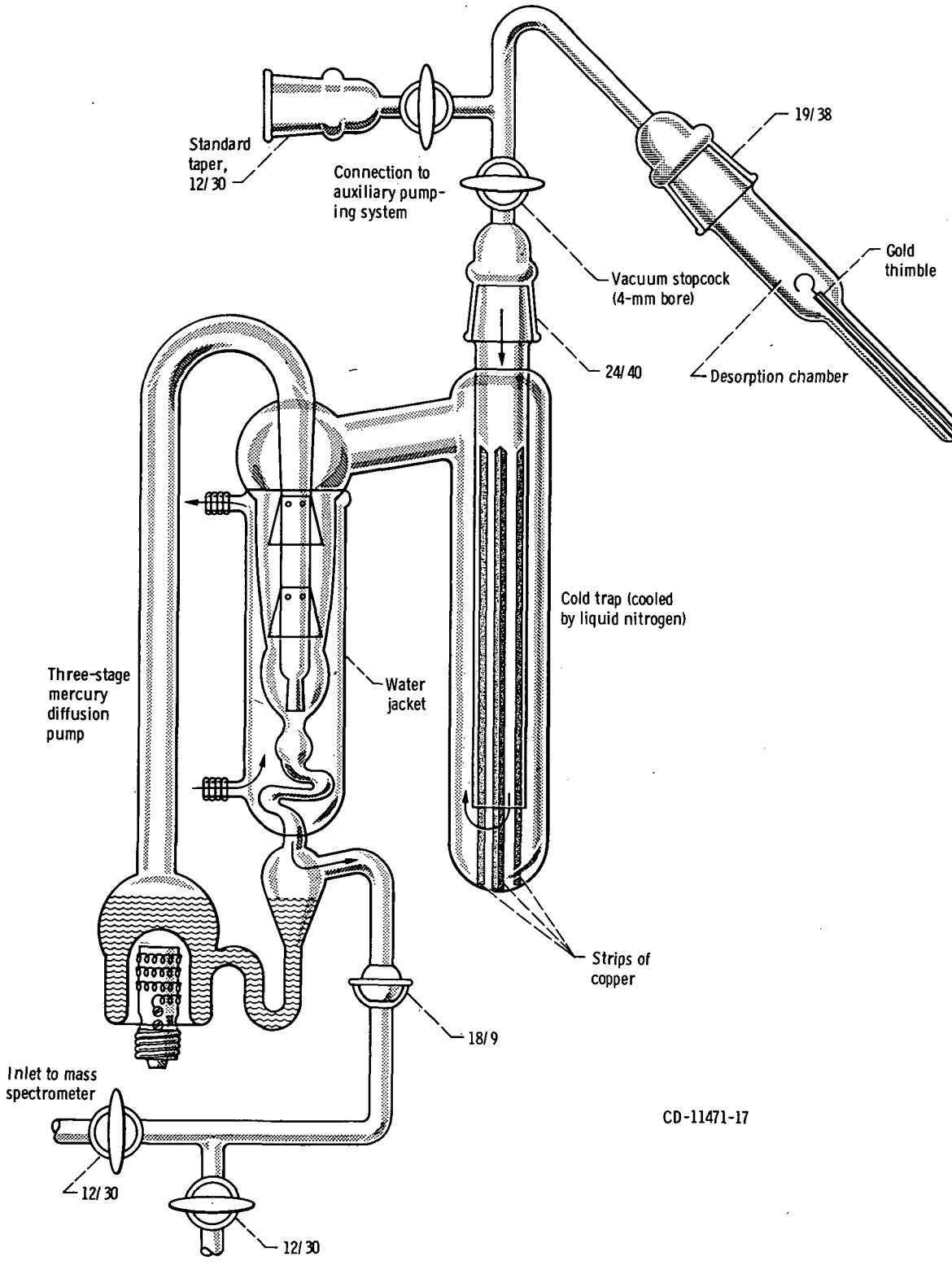


Figure 1. - Schematic drawing of desorption chamber and pumping system.

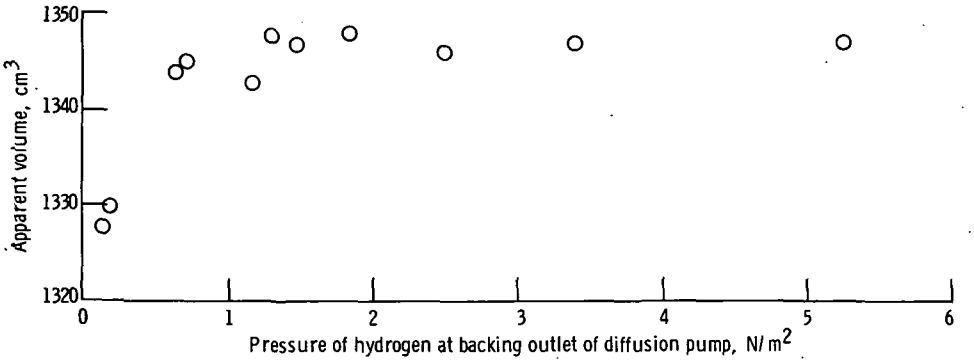


Figure 2. - Effect of pressure on apparent volume.

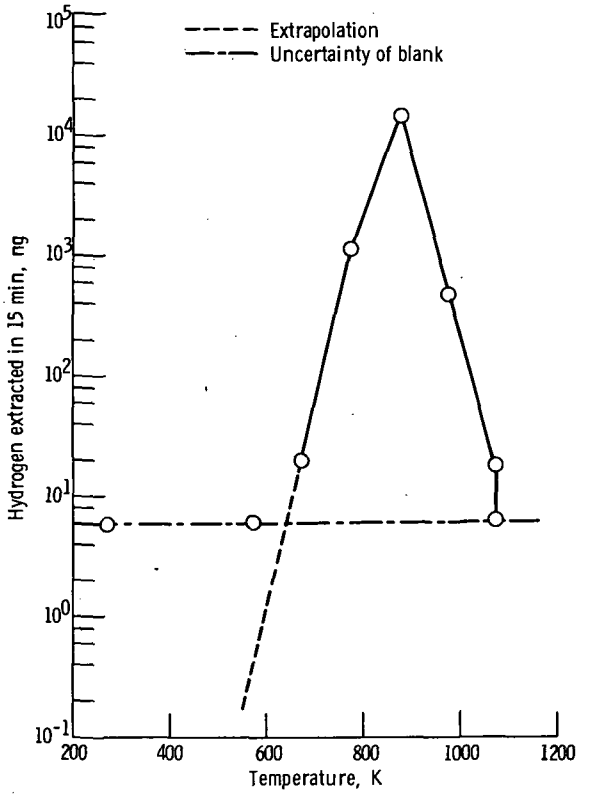


Figure 3. - Effect of temperature on extraction of hydrogen from 0.25-millimeter titanium wire. Initial hydrogen content, 7700 ppm. Quantity of hydrogen plotted includes hydrogen extracted as temperature increased from that of previous data point.

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