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HYDROGEN CONTAMINATION IN TITANIUM AND TITANIUM ALLOYS

Part II. Comparison of Various Methods for Hydrogen Analysis

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FOREWORD

This report was prepared by the Metals Branch and the Analysis and Measurement Branch and was initiated under Metals Branch Project No. 7351, "Metallic Materials", Task No. 73510, "Titanium Metals and Alloys", and Analysis and Measurement Branch Project No. 7360, "Materials Analysis and Evaluation Techniques", and Task No. 73600, "Procedures for the Composition Analysis of Aircraft Materials". It was administered under the direction of the Materials Laboratory, Directorate of Research, Wright Air Development Center, with Lt. John W. Seeger and Lt. J. A. Winstead acting as project engineers.

The assistance of the Applied Mathematics Branch of the Aeronautical Research Laboratory, Dr. H. Leon Harter and Mrs. Mary D. Lum, on the statistical comparisons is gratefully acknowledged.

Many laboratories contributed to this report. Their recognition of the importance of the problem and their cooperativeness in furnishing information and in performing analytical work is appreciated.

The actual hydrogen contents of material supplied by the titanium producers for this investigation should not be taken as representative of mill capability since producers were asked to provide a range of hydrogen levels. Laboratory comparisons should not be taken as necessarily indicative of present analytical capabilities since titanium technology is moving rapidly and improvements in analytical equipment and techniques can be expected.

This report covers work conducted from January 1955 to May 1956.

ABSTRACT

Descriptions of various analytical methods for hydrogen determination in titanium and its alloys are presented, with information on operating procedures and costs.

Laboratories using these methods in general are in disagreement, and vary considerably in analytical reproducibility. Material non-uniformity in hydrogen distribution from position-to-position in a sheet examined in relation to experimental error is found to be a significant factor. A suggested experiment for a single sheet disputed between two laboratories is given as a model by which appropriate experiments can be devised to incorporate the sources for disagreement found in this investigation.

PUBLICATION REVIEW

This report has been reviewed and is approved.

FOR THE COMMANDER:

M. R. WHITMORE
Technical Director
Materials Laboratory
Directorate of Research

SUMMARY

The various methods for hydrogen determination can be grouped in two main categories: extraction of hydrogen under vacuum from a solid or fused specimen, and combustion of a specimen with gas sweep and oxidation of hydrogen to water.

The need for a vacuum system imposes considerably more elaborate apparatus, subject to occasional breakdown and consequent delay. Generally, however, the vacuum methods are capable of performing more analyses per day than the essentially single specimen per set-up combustion methods. The combustion methods have the advantage that they are normally less expensive, and perhaps can be fabricated within the laboratory.

Choice of a method will in part depend upon the volume of work anticipated, the availability of skilled construction or maintenance personnel, and the need for analysis of other interstitial elements.

Laboratories, even those using the same method, do not in general agree. It cannot be established from this investigation how much may be due to the methods; however, it does appear that the method is a less influential factor than laboratory differences themselves. Experience may show that a bias may hold for a number of laboratories, as suggested by this experiment, and adjusting individual hydrogen determinations may be appropriate.

Laboratories differ in their analytical reproducibility, which is difficult to separate from heterogeneity of the material being analyzed. Certainly, within the usual size bars or sheets or forgings, the differences from position-to-position can be significant.

It is apparent that acceptance inspection of material must be designed to sample as many individual sheets or bars within an order as can be accomplished, since differences between sheets can be large. Sampling from several locations within the sheet is suggested to adequately rule on disputed sheets.

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I. INTRODUCTION

In July 1954 the Materials Laboratory, Directorate of Research, Wright Air Development Center initiated an intensive research program on the effects of hydrogen contamination in titanium and titanium alloys. The results of this program were presented at a technical meeting held at Wright Air Development Center on 29 October 1954, and in WADC Technical Report 54-616, Part I.

With the growing appreciation of the need for control of hydrogen content in mill products, attention was directed to the various analytical methods available for hydrogen determination. Adoption of hydrogen analysis for routine acceptance of material required analytical methods which not only yielded acceptable values but which were not prohibitively costly or difficult to operate.

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II. METHODS FOR HYDROGEN DETERMINATION

METHOD I. VACUUM FUSION AT 1900°C

Principle

The vacuum fusion gas analysis apparatus was designed for use as a tool in analyzing for minute gaseous impurities in highly purified metals. Under proper melting conditions and under high vacuum, metals may be made to give up their gases quantitatively. The combined oxides react with the graphite crucible in which the melting is conducted and the oxygen is released in the form of carbon monoxide. The hydrogen and nitrogen are liberated directly.

The mixture of hydrogen, nitrogen and carbon monoxide is pumped by a mercury diffusion pump into a vacuum chamber of known volume. The pressure of the gas collected is measured by a McLeod gauge which is simply a device used to measure very low gas pressures.

At low pressures Dalton's Law applies. The total pressure P_T of the gases present is equal to the sum of the pressures which each gas would exert if it alone were present in the given volume.

$$P_T = P_{N_2} + P_{CO} + P_{H_2}$$

After the total pressure of the gases is determined, they are circulated through a tube containing copper oxide and through a tube containing magnesium perchlorate. The hydrogen and carbon monoxide take oxygen from the copper oxide and are converted to water vapor and carbon dioxide respectively. The magnesium perchlorate absorbs all of the water vapor and the remaining gases are then allowed to circulate through a cold trap cooled to -196°C by liquid nitrogen. Here the carbon dioxide is frozen out while the nitrogen remains gaseous. The nitrogen is then returned to the McLeod gauge where its pressure is determined.

The cold trap is then allowed to rise to room temperature and this releases the CO_2 whose pressure plus the pressure of nitrogen is then measured. Knowing the pressure of the nitrogen and the pressure of the nitrogen plus carbon dioxide and the total pressure of the gases, all the necessary data for computation of the weight of each gas can be obtained.

$$P_{(N_2 + CO_2)} - P_{N_2} = P_{(CO_2)}$$

$$P_T - P_{(N_2 + CO_2)} = P_{(H_2)}$$

Since the volume in which the gas was compressed is known, the respective weights of each gas can be determined.

Description of Apparatus

At the extreme left of the apparatus is the furnace (Figure 1). This consists of a Pyrex shell closed at the bottom with a ground glass stopper. The entire shell is air cooled with a suitable blower. Inside the furnace, suspended by platinum wires, is a quartz test tube. The test tube is partially filled with very fine graphite. This in turn supports a graphite crucible.

The graphite crucible is equipped with a funnel to insure that the samples will fall into the crucible. For use in specific instances where vapor pressure of the metal is very high, or the reaction very violent a graphite plug is also provided. This graphite plug is actuated by a external magnetic device. Gases are led into the apparatus through a tube of approximately one inch ID. At the upper end of the furnace is a sample tube. The small pusher for non-magnetic samples is used by catching the sample between the jaws and pushing it along. This precludes a premature introduction of the sample into the furnace.

At the extreme upper end of the furnace is a right angle prism equipped with a cobalt glass filter. Through this prism the operator may accurately observe the temperature of the furnace and, under certain conditions, may even follow the reactions which are taking place. The cobalt glass is removed from the optical path when reading temperatures.

Immediately to the right of the furnace is the transfer pump, (refer to Figure 1). This is an all-glass, two-stage, high speed mercury diffusion pump. Gas enters this pump through the 25 mm. tube from the furnace and is driven out the foreline by the mercury jet.

At the upper end of the foreline of the transfer pump will be observed two "U" tubes. These "U" tubes are mercury cut-off type valves. It will be noted that one of them (the first one) when open conducts the gas through a 20 mm. tube to the main H-2-P diffusion pump and then through the mechanical pump and into the atmosphere. The second "U" tube, when open, introduces the gas into a three stage mercury diffusion pump which drives the gas into the analytical system. This pump is heated and controlled in the same way as the transfer pump and is referred to as the circulating pump.

The foreline of the circulating pump is connected through a Tee to either a Toepler pump or a mercury cut-off (operated by stopcock No. 4). Gases directed into the Toepler (operated by stopcock No. 3) may be quantitatively transferred to the McLeod gauge (operated by stopcock No. 5) and its accessory expansion bulbs by raising the mercury in the Toepler until a little runs over into the McLeod. This mercury must be returned from time to time (end of each analysis) by raising the level of the mercury in the McLeod until it runs into the Toepler.

Gases which are led through the "U" tubes (operated by stopcock No. 4) may be stopped at the Toepler by closing this "U" or allowed to pass through the two heated traps. The first of these contains copper oxide and is heated by a Glas-Col heater. The temperature is controlled by a variable resistor on the console marked CuO Heater. The temperature is measured by an iron-constantan thermocouple connected to a low resistance microammeter. Throwing the thermocouple switch to the left will give the temperature of the CuO. This should be approximately 325°C. Throwing the same switch to the right gives the temperature of the second trap which contains $Mg(ClO_4)_2$.

Gases pass from the $Mg(ClO_4)_2$ to a double trap. Under this trap is a sliding shelf to hold the DeWar flask of liquid nitrogen. At the beginning of an analysis this flask is cautiously raised into position and the trap is thereby maintained at a temperature of about -196°C. This will freeze out all the CO_2 and any water not picked up by the $Mg(ClO_4)_2$. Gases may go in either of two directions from this trap. By opening cut-off No. 11, they may be pumped by the circulating pump back into the Toepler to be subsequently measured, or they may be pumped into the atmosphere by closing No. 11 and opening No. 12, which connects directly with the main exhaust line.

Return now to the measuring system controlled by the stopcocks Nos. 5 to 10, inclusive. The McLeod gauge and five "U" tubes are attached on one leg to a manifold. Stopcock No. 6 controls a special leak-proof mercury stopcock. In the course of ordinary analysis this is not used. This special "U" tube may be used to introduce gases into the system, or conversely, to remove them for further examination without breaking vacuum in the system. After the system has been evacuated, mercury is allowed to rise in this "U" tube until it will go no further. This should be done with care so as not to damage the grinding. The stopcock on the mercury feed tube is then closed. The ground glass cap at the rear of the apparatus can then be removed and additional apparatus of the operator's choosing attached.

The next "U" tube, operated by the stopcock No. 7, connects the measuring system with the remainder of the analytical system. When this is open, gas is pumped from the measuring system by the circulating pump and may be circulated or returned to the Toepler.

The "U" tubes controlled by stopcocks Nos. 8 and 9, respectively, connect McLeod gauge through the manifold to the expansion bulbs of 500 ml. and 2000 ml. capacity, respectively. In operation, if the quantity of gas collected is too great to be measured in the McLeod alone, the McLeod is opened and the gas allowed to expand into either or both of the bulbs and a new reading is then taken.

The last "U" tube on the manifold connects the measuring system to the main exhaust line and is used to evacuate the measuring system at the end of each analysis.

This is the description of National Research's Vacuum Fusion Gas Analysis Apparatus. This particular model is available commercially. Other models have been designed and built by various laboratories for their use.

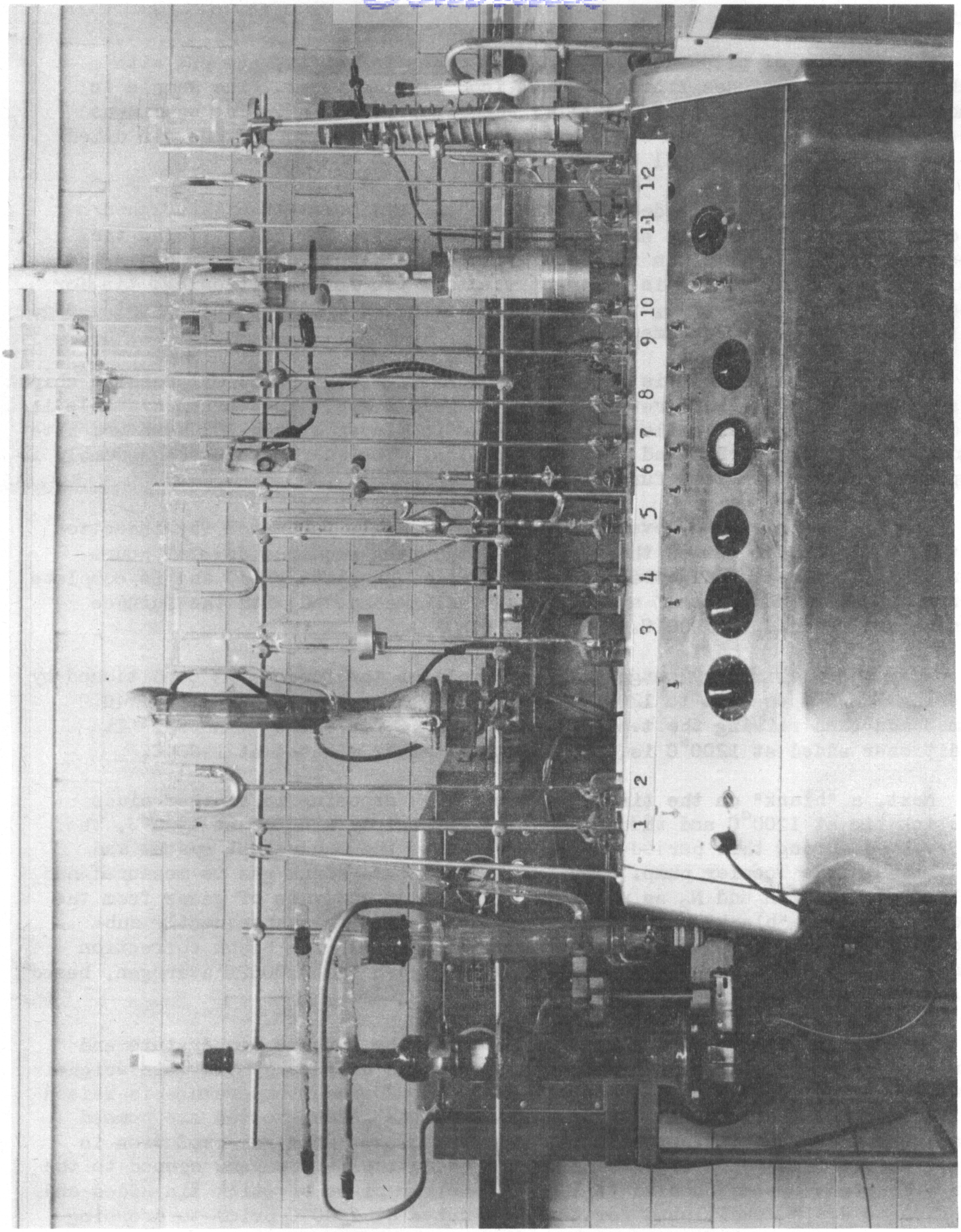

Figure 1 - Apparatus for Method I, Vacuum Fusion at 1900°C.

Procedure

Small cubes of titanium, 0.15 to 0.25 grams in weight, are cut with a hacksaw and the surfaces finished on silicon carbide paper. The sample is handled with tweezers during and after the final polishing. The specimens receive a final cleaning in C. P. ether (or other solvent) and are air dried and weighed on an analytical balance.

Five specimens are loaded into the loading arm together with weighed pieces of stick tin as well as scrap titanium and tin for conditioning the apparatus and a tin specimen for determining the "blank" due to gases in the tin. The order of loading is: scrap titanium, tin for conditioning, tin for blank determination, sample, tin for sample, tin for conditioning, sample, etc., up to a total of five specimens.

The reaction crucible is of carbon containing about 5 ml. of graphite chips of size such that they are retained on a 20-mesh sieve. The carbon crucible is held inside a quartz crucible with an insulating layer of sub-200 mesh graphite powder between the carbon and quartz crucibles. The quartz crucible assembly is suspended inside the glass furnace shell.

The system is closed, evacuated and the crucible is heated (by induction heater) to 2400°C to outgas the system. Outgassing requires several hours (varies greatly between laboratories and type of graphite used) and is complete when a predetermined rate of evolution of gas is achieved with the furnace temperature reduced to 1900°C.

When the preliminary outgassing is complete, the furnace is conditioned by lowering the temperature to 1200°C, dropping in the scrap titanium (0.1-0.2 grams) and then raising the temperature to 1900°C for thirty minutes. Tin conditioner added at 1200°C is outgassed for thirty minutes at 1900°C.

Next, a "blank" on the tin is determined by dropping in another piece of stick tin at 1200°C and then outgassing for thirty minutes at 1900°C, the gas evolved during this period being pumped into the analytical system and collected in the Toepler pump. The quantity of this blank gas is measured and analyzed for CO_2, $H_2$and N_2 as will describe under analysis of gases from the specimen. These "blank" values for CO_2, H_2, and N_2 are subsequently subtracted from the gas values determined on the sample. The blank correction normally corresponds to approximately 0.008% oxygen and 0.0002% hydrogen, based on a 0.25 gram titanium sample.

The specimens are now analyzed by lowering the furnace temperature and simultaneously dropping in a titanium specimen and a piece of tin (tin weighed about twice that of the titanium specimen). The furnace temperature is raised to 1900°C for thirty minutes during which time the gases evolved are pumped from the furnace and collected in the Toepler pump. After gas evolution is complete, the furnace is isolated from the analytical system and opened to the main evacuation system, cooled to 1200°C, another piece of stick tin added and the furnace again conditioned for thirty minutes at 1900°C prior to dropping the next specimen.

The collected gas is then transferred to the McLeod gauge where the pv (pressure-volume) product is measured by compressing the gas into the calibrated capillary of the McLeod gauge. This pv product gives a measure of the combined carbon monoxide, hydrogen and nitrogen.

The gas is then analyzed for these three components. The carbon monoxide is oxidized to carbon dioxide and the hydrogen to water by passing the gases over hot copper oxide. No change in number of moles of gas occurs during this reaction. The oxidized gases then pass through a tube filled with magnesium perchlorate which permanently removes the water vapor from the gas stream and then through a trap cooled to the temperature of liquid nitrogen to freeze out and temporarily remove the CO_2. Thus, only nitrogen remains; this is pumped back into the Toepler pump, transferred to the McLeod gauge and its pv product measured. The CO_2 is then released by removing the liquid nitrogen from the trap and allowing the trap to warm to room temperature. The carbon dioxide is then pumped into the Toepler pump, transferred to the McLeod gauge, and the pv product of the combined carbon dioxide and nitrogen determined.

The pv products of carbon dioxide and of hydrogen are then calculated from these three readings as follows:

$$pv_{CO_2} = pv(CO_2 + N_2) - pv_{N_2}$$

$$pv_{H_2} = pv_{total} - pv(CO_2 + N_2)$$

The percentages of oxygen and hydrogen may then be calculated by using the pv products of carbon dioxide, hydrogen and the proper conversion factors. The conversion factors vary with the volume of the system.

Comments

Hydrogen determination by vacuum fusion at 1900°C is a slow procedure but oxygen determination can be performed at the same operation. Usually five samples can be analyzed for hydrogen and oxygen during one run which requires two to three eight hour days. This includes sample preparations, pumping down of apparatus, outgassing graphite, and making the oxygen and hydrogen determinations.

An experienced technician can make accurate determinations of oxygen and hydrogen by this method.

The cost of the described equipment is approximately $8,000. Supplies of graphite crucibles and funnels, graphite, high vacuum wax, and stopcock greases, mercury, and pump oils must be kept in supply.

METHOD II. VACUUM EXTRACTION AT 1600°C.(1)

Principle

Hydrogen is extracted from titanium when it dissolves in a carbon-saturated iron bath at 1600°C. Hydrogen can be extracted at lower temperatures but Battelle chose this procedure to assure complete extraction. Oxygen determinations can be made by the tin-bath technique operated at a higher temperature. At 1600°C only partial removal of O_2 is accomplished. The evolved gases are collected and the pressure measured in a known volume, and analyzed for hydrogen by the fractional-freezing method.

Description of Apparatus

Vacuum fusion apparatus built by Battelle.(2) Principle of equipment is essentially the same as described in Method I.

Procedure

One gram analytical samples are cut from specimen, abraded with a clean, degreased file. About eighteen cleaned samples are loaded into the storage arm of the vacuum-fusion apparatus. The graphite crucible is packed with 200 mesh graphite. Enough iron is stored in storage arm so that maximum concentration of titanium in the bath will not exceed 30 weight percent. The system is then closed with high vacuum wax and pumped down to low vacuum. The furnace is evacuated and outgassed at 2300 to 2500°C for 1-1/2 to 2-1/2 hours. The temperature is then lowered to 1600°C and a blank collected for five minutes. If blank is equivalent to 0.006 cc. per hour, the iron bath is dropped into the graphite crucible and outgassed for about one hour and a blank collected. If a reproducible blank is obtained, it is analyzed and then a sample is dropped into the bath at 1600°C and evolved gases are collected for 20 minutes. The gas is measured and then pumped through a CuO trap which oxidizes the H_2 to H_2O and CO to CO_2. The water is frozen out with dry ice-acetone trap (-90°C) and CO_2 and N_2 pumped back into the gauge and pressure measured. The amount of hydrogen can be determined from differences as indicated in following equation:

$$P_{H_2} = (P_{\text{Total}} - P_{CO_2 + N_2}) - P_{\text{Blank}}$$

When pressure of H_2 in a known volume is measured the determination can be calculated readily. Twelve determinations per 8 hour day can be made by this method.

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(1) Battelle Memorial Institute, analysis performed at 1600°C; temperatures of 1450 and 1500°C are used by other laboratories.

(2) Mallett, M. W., and Griffith, C. B., Trans. ASM (1954) 46, 375.

METHOD III. VACUUM EXTRACTION FROM 1200° TO 1450°C

Principle

Titanium and titanium alloys will release hydrogen gas quantitatively at temperatures from 1000° to 1450°C. At this temperature hydrogen is the only gas released and can be pumped into the analytical system of apparatus and pressure measured. Calculations can be made directly from total pressure.

Description of Apparatus

The apparatus of Method I is also used for this method. The gas is not circulated through the analytical system as gas separation is unnecessary.

Procedure

Small cubes of titanium, 0.15 - 0.30 grams in weight, are cut with a hacksaw and the surfaces finished on silicon carbide paper or a grease-free file. The sample is handled with tweezers during and after final polishing. The specimens receive a final cleaning in C. P. ether (or other solvent) and are air-dried and weighed on an analytical balance. Approximately thirty samples are then loaded into the loading arms.

The quartz crucible assembly is suspended inside the glass furnace shell. The graphite chips and graphite plug are not used as described in Method I. The system is closed, evacuated and the crucible is heated (by induction) to 2400°C to outgas the system. Outgassing requires approximately three to four hours (varies with laboratories and types of graphite used) and is complete when a predetermined rate of evolution of gas is achieved with the furnace temperature reduced to 1400°C.

When the outgassing is complete, and a negligible blank is determined, the system is ready to make hydrogen determinations.

The specimens are analyzed by dropping into the furnace at 1400°C and collecting gas for ten minutes during which time the gases evolved are pumped from the furnace and collected in the Toepler pump. (More than 10 minutes are required if temperature is below 1400°C). After the gas evolution is complete the furnace is isolated from the analytical system and opened to the main evacuation system.

The collected gas is then transferred to the McLeod gauge where the pv (pressure-volume) product is measured by compressing the gas into the calibrated capillary of the McLeod gauge. This pv gives a measurement of the hydrogen gas, as only hydrogen is released at this temperature. Calculations are made from the total pressure. The gas is pumped out of the system and the system is ready for the following determination.

Comments

Various laboratories have different vacuum fusion apparatus with various modifications for increasing the number of hydrogen determinations per run. Some laboratories are using a larger graphite crucible thus increasing their capacity to forty or fifty samples per run. Thirty samples can be analyzed in approximately two to two and one-half eight hour days. The average time per sample is decreased when more samples are analyzed per run.

The cost of equipment and training of personnel are equivalent to the vacuum fusion Method I.

METHOD IV. VACUUM EXTRACTION AT 1400°C, USING MOLYBDENUM CRUCIBLE(1)

Principle

The apparatus works on the principle of hot extraction of hydrogen in a vacuum. Titanium and titanium alloys release hydrogen quantitatively at temperatures below the melting point.

Description of Apparatus

Figure 2 shows the apparatus. The vacuum pumping system provides the necessary capacity to ensure the rapid outgassing of the system which is accomplished by a mechanical pump and a H-2-P high vacuum oil diffusion pump.

The furnace assembly includes the following features:

1. Induction heating for rapid attainment of 1400°C.

2. Quartz furnace tube, which eliminates the need for packed insulation and permits rapid outgassing of furnace.

3. Magnetically operated crucible assembly, which allows the sample to be dumped into a cool receptacle after the completion of an analysis to ensure that it will not evolve further gases.

4. Large capacity loading arms, which permit operation for at least eight hours without opening to atmosphere.

Principal components of the furnace assembly include:

1. Quartz furnace tube approximately 3/4" inside diameter by 7" high.
2. Molybdenum crucible approximately 5/8" X 3/4".
3. Centering tubes approximately 5/8" X 3/4".

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(1) Description of National Research Corporation's Method

4. Magnets for manipulation of crucible.

5. Quartz spent - specimen receptacle approximately 5/8" in diameter by 3-1/2" high.

6. Prism mounted at top of furnace to allow use of optical pyrometer for measuring furnace temperatures.

7. Two loading arms with capacity of 15 to 20 samples each.

8. Magnetically operated pushers for moving samples through loading arms.

9. Industion coils and oscillator power supply of adequate size to bring crucible and sample rapidly to 1400°C.

10. Blower to cool quartz furnace tube.

The analytical system need measure only the total amount of gas given off, since at 1400°C hydrogen is the only gas evolved in significant quantities. Measurements are made in terms of pressure rise in a known volume. A three stage mercury diffusion transfer pump with extremely high fore pressure tolerance moves the evolved gas from the furnace into the analytical train. To control the mercury better in case of glass breakage and to keep it as clean as possible, regulated low pressure carbon dioxide from a tank is used to actuate the mercury cut-off. These cut-offs isolate the H-2-P from the train, and the train from a supplementary volume. This supplementary volume is connected to the train when so much hydrogen is evolved from a sample that the pressure rises to the point where the McLeod gauge goes off scale. By use of the two calibrated volumes, it is possible to get "on scale" reading over the whole range of the apparatus.

A special Pirani gauge calibrated for hydrogen, and a strip chart recorder can be attached to the analytical system.

The stainless steel cabinet is 28" X 40" X 35" high. Mounted on it are aluminum rods to support the furnace and analytical assemblies. It houses the oil diffusion pump, the mechanical pump and the mercury reservoirs. The controls for the mercury cut-offs and the McLeod vernier are conveniently located on top.

Procedure

Samples may be one solid piece of titanium, compacted pellets, chips, sponge, or drillings, and weigh about a quarter gram. Chips or drillings are placed in special re-useable tantalum capsules. Cleaned samples are charged into horizontal loading arms near the top of the furnace. When charging is complete, the outer end of each loading arm is sealed off with a glass cap.

The apparatus is then pumped down and the molybdenum crucible heated to about 1500°C to outgas the system and obtain a suitable blank. The blank is the background reading of the system when operated without a sample in the furnace.

It is a measure of gas coming from the crucible and the walls of the apparatus. For a clean system, it usually takes about forty minutes to get a blank of about 0.5 parts per million.

After a satisfactory blank has been obtained, one sample is moved by a magnetically operated pusher along the loading arm until it drops into the crucible, where it is heated by induction to approximately 1400°C. It is held at this temperature until the gauge indicates no further gas is being evolved. This usually takes three to five minutes. At 1400°C alloy composition has little effect on the rate of hydrogen evaluation.

The exact pressure of the gas is then read. The volume of the system is so chosen that the pressure develcped from a quarter gram sample containing less than 125 parts per million of hydrogen falls within the linear response region of the Pirani gauge. The standard model is furnished with both a McLeod gauge and an indicating Pirani gauge calibrated for hydrogen. The Pirani gauge is equipped both with an indicating meter and with an expanded scale strip-chart recorder. The recorder not only provides a permanent record, but substantially reduces analytical time by indicating clearly when the hydrogen evaluation is complete. For hydrogen concentrations less than 125 ppm, accurate pressures can be read directly from the recorder. Between 125 and 625 ppm the non-linear recorder reading may be used in conjunction with a calibration curve. The McLeod gauge can be used over the full range of the apparatus, but is slower to operate. It gives more precise readings, especially in the upper levels of hydrogen concentration.

When readings on a sample have been completed, the furnace is cooled (5-10 seconds) and the crucible is lowered magnetically to dump the sample into a cold container below the furnace. Since the samples are not permitted to accumulate in the hot zone of the furnace, there is no danger of incomplete hydrogen evolution of one sample affecting the analysis of a subsequent sample. The analytical cycle is completed by pumping out the gas until the blank is obtained. For a standard unit the whole operation takes from four to ten minutes.

Comments

The equipment described is a commercial item, National Research Corporation Model 917 Hydrogen Determinator-Titanium. The equipment complete with McLeod gauge, indicating Pirani gauge, recorder, and stand list for approximately $6,000.00.

The method described is rapid method for hydrogen determinations of titanium and can be operated by a competent laboratory technician.

The other laboratory in the report using this method was Brush Development Laboratory. Their equipment consists of a vacuum fusion apparatus with an additional horizontal furnace for induction heating of a molybdenum boat. Although equipment is considerably different the method is essentially the same as one described.

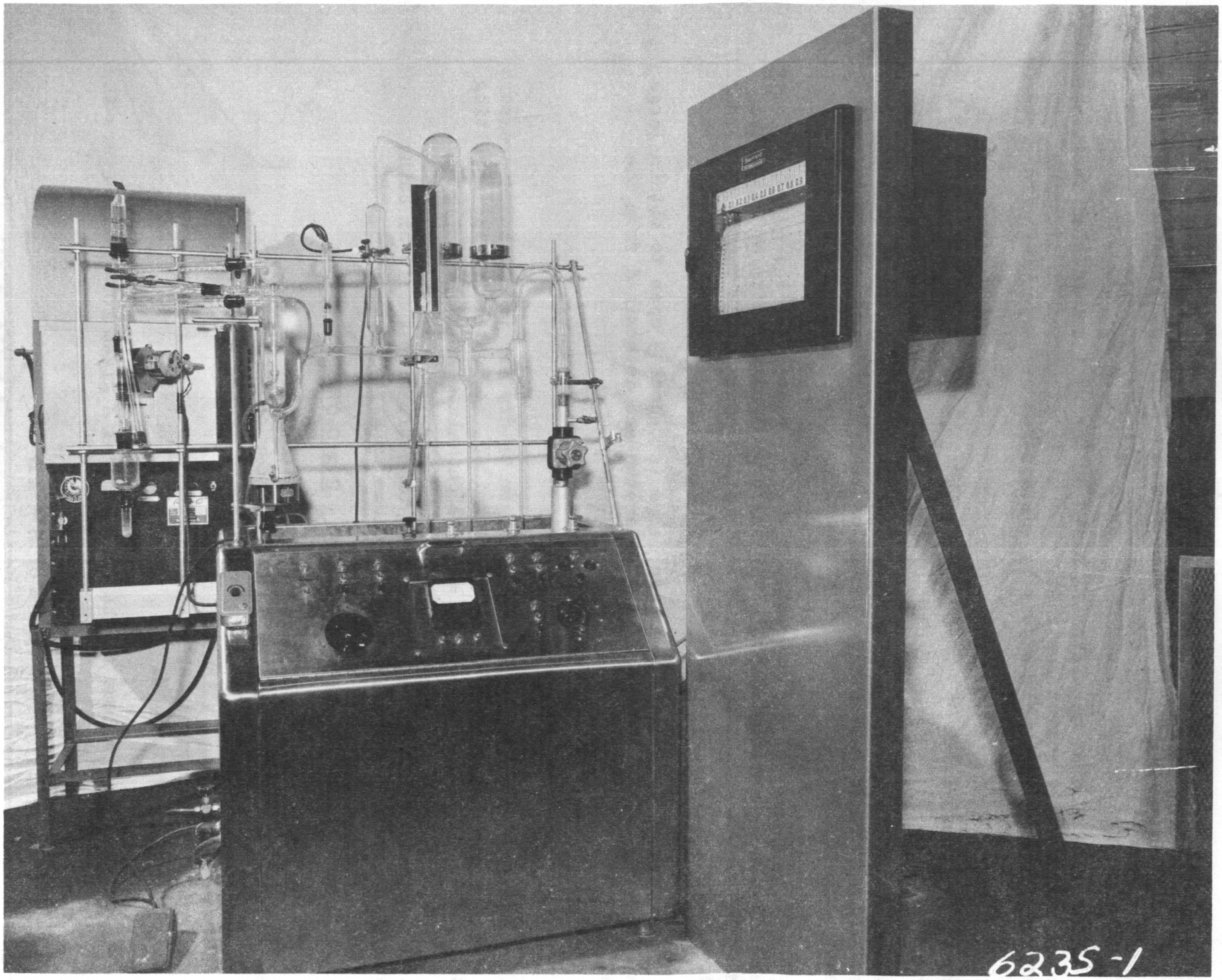

Figure 2 - Apparatus for Method IV, Vacuum Extraction at 1400°C, Using Molybdenum Crucible.

METHOD V. VACUUM EXTRACTION AT 1000°C, USING QUARTZ CRUCIBLE(1)

Principle

The design of this apparatus is based on the well established fact that hydrogen is the only common gas that, once it is dissolved in titanium, can be extracted to a measurable extent by the control of temperature and pressure of the sample environment.

Description of Apparatus

Figure 3 shows the major points in the construction of the apparatus except for details of instrumentation, electrical wiring, and mechanical arrangements. These latter details can be readily made to conform to the plans of the builder.

The vacuum system is constructed of Pyrex, except for the quartz furnace tubes. The whole unit is assembled in and rigidly clamped to an angle iron framework. The breaks shown in the schematic sketch of the vacuum system are to be ignored.

The volume of both the small and large (stopcock 9 open to obtain large volume) gas measuring volumes of the apparatus are determined from the relation;

$$PV = pv$$

by introducing a measured volume of hydrogen or dry air (v) at known pressure (p) into the system volume (V) being determined, and obtaining the resulting system pressure reading (P) on the dibutyl phthalate manometer.

The mass of hydrogen gas extracted from a titanium sample on being measured in either the small or large volume is given by,

$$\text{mass of H in grams} = \frac{PV}{RT} \times \frac{2 \times 0.077}{76}$$

where p = system pressure in cm. of dibutyl phthalate.
V = capacity in liters of particular system measuring volume in use.
R = gas constant (0.08207).
T = temperature °K.

For a given measuring volume of the apparatus at a given room temperature the above reduced to,

$$\text{mass of H} = kP$$

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(1) The apparatus to be described was designed and built at Allegheny Ludlum Steel Corporation's Research Laboratory at Brackenridge, Pennsylvania.

The percent of hydrogen by weight in the sample is readily calculated from the following.

$$H\% = \frac{k(\text{P-blanks}) \times 100\%}{\text{Sample weight in grams}} + \begin{pmatrix}\text{H\%} \\ \text{residual in} \\ \text{sample}\end{pmatrix}$$

Residual hydrogen in the sample is fairly constant for a given apparatus but must be determined for the equipment by some independent means, such as vacuum fusion. The residual is dependent, for one thing on the speed at which the furnace tube is pumped.

The following list gives additional details on the components shown in the schematic sketch:

A	Cap of sample loading port combined with air leak.
B	Sample storage arm.
C	Window for observation and optical temperature readings.
D	Furnace heads, marked #1 and #2 for left and right furnace tubes respectively.
E	Clear fused quartz tubes.
K	Double tube resistance wound furnace with temperature automatically controlled at 1000°C.
M	Three stage mercury diffusion pump - speed of 20 liters/sec.
P1 P2	Pirani type vacuum gauges.
S,T3	Cooling trap at about -80°C, (dry ice-acetone mixture).
T1 T2	Traps for manometer fluid in case of blow-over.
TC1 TC2	Chromel-alumel thermocouples.
U	Auxiliary volume (5000 ml.) for sample of high hydrogen content.
V	Dibutyl phthalate manometer with adjustable scale.
W	Mechanical pump - speed of 58 liters/min.

Procedure

The operation of the apparatus will be described step-wise through a complete cycle of operation:

1. Both furnace assemblies are isolated from vacuum system by closing stopcocks 1 and 2 (abbreviated Sc 1 and Sc 2) and turning up Sc 5. Scs 6 and 7 are closed and scs 8 and 9 are open.

2. Both pumps, vacuum gauges and furnace are turned on.

3. Either liquid nitrogen, or dry ice-acetone mixture is placed around trap (T4). Dry ice-acetone goes on T3.

4. Up to 20 samples are loaded into arm (b) of #1 tube and cap (A) replaced with Sc 3 closed.

5. Furnace assembly #1 is evacuated through mechanical pump for about 5 minutes by turning down Sc 5, then #1 furnace assembly is evacuated through diffusion pump by turning up Sc 5 and opening Sc 1. Furnace blank is taken 1/2 to 1 hour later.

6. In the meanwhile the preparation of samples and the loading of them into right tube #2 can begin and will be completed during the analysis of those in the first tube.

7. By now gauge (P1) should be reading less than 1.0 micron and (P2) about the same or slightly higher (1 to 2 microns max.) which indicates it's time to take a blank on the first tube already loaded with samples.

8. Blank gas from furnace is collected for 30 minutes by closing Scs 8 and 9 and reading pressure on manometer (V) after which collected blank, if any, is pumped from system through Sc 8. Blank reading is generally zero or not more than 0.02 cm. per 30 minutes.

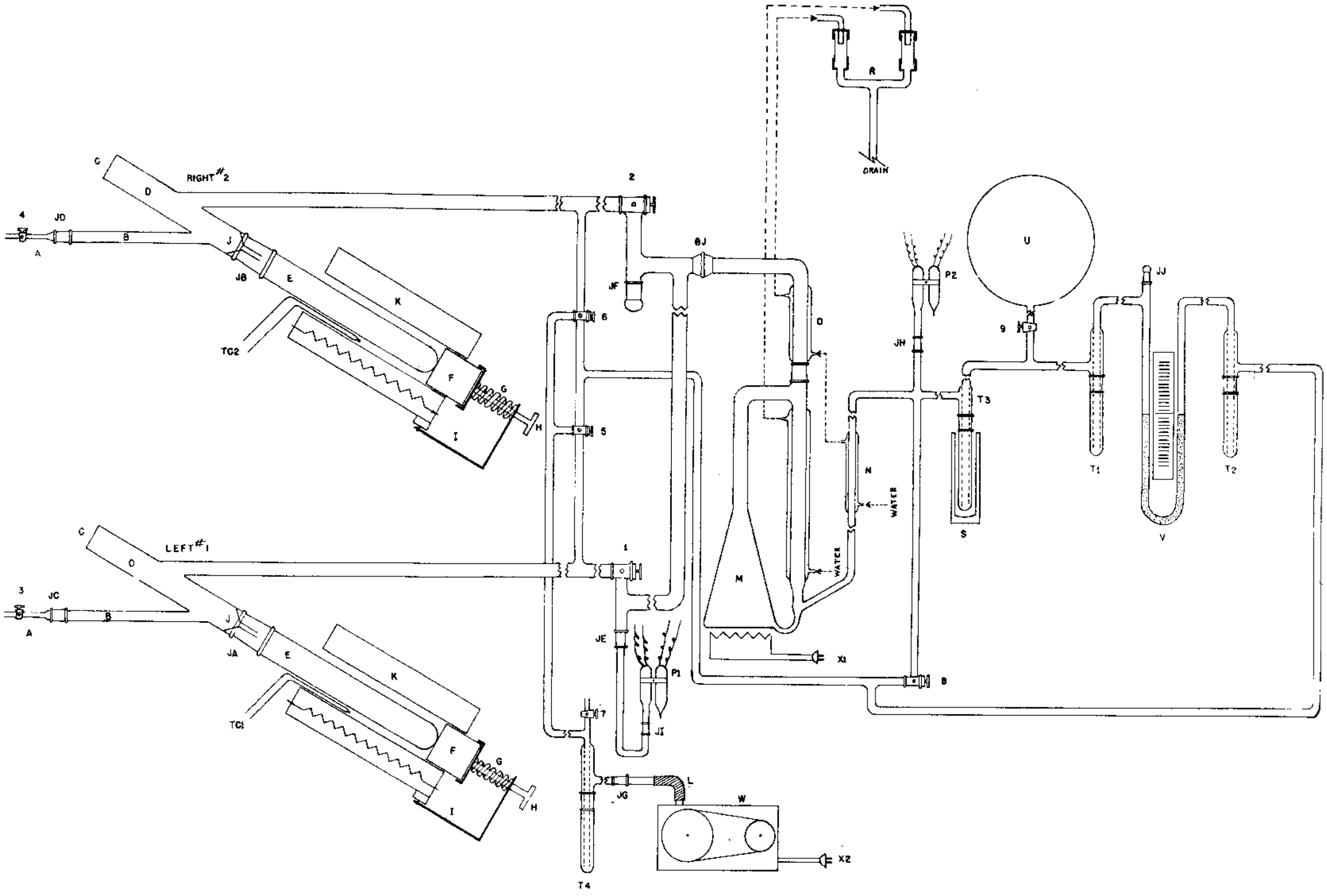
9. Samples in tube #1 are now run in a manner similar to the taking of the blank, that is, by closing Sc 8 (Sc 9 is still closed from step 8) just before pushing sample into furnace tube (E). The sample is moved by a magnetic pusher activated by an external magnet. Degassing of sample continues, with pressure readings being recorded every five minutes, until rate of gas evolution returns to base or blank rate. If manometer reading exceeds 4 cm. auxiliary volume, (U) is opened to the system through Sc 9. Final pressure on manometer is used in calculating the analysis after correcting for blanks. The extracted gas is then rejected from the system through Sc 8 by pumping until pressure on P2 returns to the value originally registered for the evacuated system.

Time required to run samples depends on the sample thickness, and, of course, increases with it. Turnings and sheet require from 20 to 30 minutes to degas. Material one-quarter inch thick would require about 60 minutes.

Sample Preparation

Sheet, rods, etc. are cut or sawed to size and all surfaces filed or carefully ground to remove all scale or oxidized layer. The sample is then washed in reagent grade carbon tetrachloride using forceps to manipulate the samples and taking care not to touch with fingers or otherwise picking up contamination. Sample is weighed and loaded into apparatus. Sample weight used depends on amount of hydrogen expected - we use about 3 grams for a hydrogen content of about 0.005 weight percent. Proportionately smaller weights are used with samples of higher gas content.

Drillings or millings are weighed and wrapped in pure sheet tin. Turnings are not washed if it is certain they haven't been touched with hands or otherwise contaminated. Tin is pre-cut into standard size sheets of about two inches square and washed before using. A blank is determined on each lot of tin sheet to determine the necessary correction to be applied to each sample. The correction is small (about 0.09 cm.) being less than 5% of the sample pressure reading, usually obtained by proper adjustment of sample weight.



ALLEGHENY LUDLUM HOT EXTRACTION APPARATUS FOR HYDROGEN IN TITANIUM

Figure 3 - Apparatus for Method V, Vacuum Extraction at 1000°C, Using Quartz Crucible

Comments

The total cost of constructing the equipment including labor was about $2,500 per apparatus.

METHOD VI. EQUILIBRIUM PRESSURES AT 1000°C(1)

Principle

McQuillan's data indicate that in single phase titanium under equilibrium conditions dissolved hydrogen behaves as an ideal liquid, i.e., a linear relationship exists between the logarithm of the equilibrium pressure and reciprocal absolute temperature when the hydrogen concentration in the metal is held constant. Likewise, a plot of the logarithm of equilibrium pressure vs. the logarithm of concentration of hydrogen in the metal is linear under isothermal conditions. In regions where alpha and beta titanium co-exist, equilibrium pressure is independent of the hydrogen concentration in the metal, as would be predicted from phase rule considerations. It has been established that hydrogen is the only common gas that once dissolved in the metal can be extracted to any measurable extent by temperature and pressure manipulation alone. Thus, determination of the equilibrium hydrogen pressure over a specimen of single phase titanium at a predetermined temperature for which the pressure-concentration relationship is known and in an apparatus of known volume affords data from which the hydrogen content of the metal can be readily calculated.

From a practical standpoint it is highly desirable to make these determinations in the beta region, as equilibrium is established very rapidly with commercially pure titanium above the transition point (882°C). The temperature at the transition point of alloys depends on composition and contaminants.

Description of Apparatus

All parts of the apparatus (Figure 4) other than the sample tubes and heating sleeves are fabricated from borosilicate glass. Pressure is measured by means of the Todd Universal Gauge (A), a three-scale mercury gauge with a range of 0.0001 to 25 mm. mercury. Bulb (B) is of approximately 250 ml. capacity and is carefully calibrated for volume between stopcocks before attachment to the manifold. Tapered joint (C) permits attachment of other equipment to the bulb. Silica sample tubes (D) are connected to the manifold through 4 mm. high vacuum stopcocks. Heating sleeve (E) is supplied with power by a 500 watt combination of a constant voltage transformer and variable transformer in tandem (F). Temperature is measured by a 20 gauge chromel-alumel thermocouple (G) and potentiometer (H). Evacuation is effected by means of a single stage mercury diffusion pump (I) with conventional mechanical forepump. Power to the heater of the diffusion pump is controlled by a 5 amp variable transformer (J); 4 mm. stopcocks (K) and (L) permit isolation of the manifold from the gauge and from the pumping system. All stopcocks and tapered joints are hand-lapped to a fine finish. Stopcocks are lubricated with a highly refined vacuum grease with low thermal coefficient of viscosity, such as

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(1) Method of E. I. duPont de Nemours as described in Journal of the Electrochemical Society, Vol. 102, No. 3, March, 1955

Apiexon N. and joints sealed with nongassing hard wax. Removable asbestos paper shields (M) protect the stopcocks from heat of the gas flame used in sealing and unsealing the hard waxed joints.

Details of a silica sample tube and heating sleeve are shown in Figure 5. Sample tubes are fabricated entirely from transparent silica. The titanium sample rests on the bottom of the sample tube chamber (N). Sleeve (O) acts as a guide for the thermocouple, the hot junction of which touches the bottom of the furnace chamber. Thus the sample is separated from the thermocouple by only about 1 mm. of silica. Chamber (P) provides for water cooling so that joint (Q) is kept at approximately room temperature. The water-cooled chambers of adjacent sample tubes are connected by short lengths of rubber tubing permitting in-line flow of cooling water. The heating sleeve consists of a silica shell (R) covered with thin asbestos paper and wound with 6 feet of 1/32 x 0.0035 inch nichrome ribbon. The ends of the heating ribbon are joined to short lengths of heavy nichrome ribbon (S) which protrude from the shell to form lugs for connection to the power source through small battery clamps. A small opening (T) at the bottom of the sleeve provides access for the thermocouple. The wound sleeve is covered with a thermal insulating layer of macerated asbestos paper (U) 3/16 inch in thickness. After bakeout, the exterior of the sleeve is painted with heat resistant aluminum paint. The inner diameter of the silica shell of the sleeve is approximately 1 mm. greater than the outer diameter of the sample tubes. A sample tube with heating sleeve in place is shown in Figure 4. Approximately 2 ml. of the sample tube volume is heated by the sleeve.

Calibration

The purpose of the calibrated bulb (B) in Figure 4 is to provide a means for determining the volume of the equipment. The procedure consists of partial evacuation of the system with the lower stopcock of the bulb closed, the upper stopcock open, and the stopcock to one sample tube open. Stopcock (L) is then closed and pressure measured by the gauge. The upper stopcock of the bulb is then closed, stopcock (L) is opened, and the system evacuated to a low pressure. This leaves a known volume of gas under a known pressure in the bulb. Stopcock (L) is then closed and the gas in the bulb is expanded to the evacuated system. Pressure is again determined. The volume of the apparatus (with the bulb) is then:

$$V_a = V_b \frac{P_1 - P_2}{P_2}$$

where V_a = volume of apparatus, V_b = volume of bulb, P_1 = initial pressure, and P_2 = final pressure (temperature assumed constant).

Determination of the equilibrium pressure-concentration curve must also be determined. A few grams of titanium hydride was placed in a silica sample tube and surmounted by a small plug of glass wool to prevent dusting. The tube was attached to the apparatus at joint (C) by hard wax. The hydride was thoroughly outgassed at room temperature, followed by heating to a moderate temperature where evolution of a minor amount of hydrogen helped to sweep out any remaining gases. After outgassing, the tube was never exposed to air during the equilibrium determinations. A 0.500 gram sample of commercially pure titanium sponge was placed in a sample tube which was hard waxed to the manifold. The titanium specimen was outgassed by heating at 1000°C and a pressure of approximately 10^{-5} mm. Outgassing under these conditions reduces the hydrogen content of the titanium to less than 3 ppm in 60 minutes. After outgassing, the sample tube was allowed to return to room temperature. Stopcock (L) was closed, isolating the system from the pumps and, with both stopcocks on bulb (B) open, the hydride tube was heated to generate hydrogen. When the desired hydrogen pressure had been attained, the upper stopcock on the bulb was closed and the heating discontinued. Hydrogen pressure and room temperature were observed. The titanium specimen was then heated to 1000°C and, when the system had attained equilibrium (less than 10 minutes over-all), room temperature and hydrogen pressure were again observed. From these observations and the known volume of the apparatus, one point of the equilibrium curve can be calculated:

$$H_o = 2.02 \times \frac{P_1}{760} \times \frac{273}{T_1} \times \frac{V}{22{,}400} = 3.23 \times 10^{-5} \frac{P_1 V}{T_1}$$

$$H_G = 2.02 \times \frac{P_E}{760} \times \frac{273}{T_E} \times \frac{V}{22{,}400} = 3.23 \times 10^{-5} \frac{P_E V}{T_E}$$

$$H_T = H_o - H_G$$

$$C_E = \frac{H_T}{S} \times 100$$

where: H_o = hydrogen introduced, grams; H_G = gaseous hydrogen at equilibrium, grams; H_T = hydrogen in the titanium at equilibrium, grams; C_E = concentration of hydrogen in titanium at equilibrium, weight percent; P_1 = initial hydrogen pressure, mm Hg; T_1 = room temperature, °K, at P_1; P_E = equilibrium hydrogen pressure, mm Hg; T_E = room temperature, °K, at P_E; V = volume of apparatus, ml; and S = weight of titanium specimen, grams.

The titanium was then outgassed and the cycle repeated at 12 levels of equilibrium hydrogen pressure in the range 0.001 - 10 mm Hg. A plot of the equilibrium pressure vs. concentration at 1000°C is shown in Figure 6. The mean deviation of points from the curves is less than 2%. Repeat measurements with ingot and sheet of commercial purity showed that equilibrium values for these materials fell on the same curve.

Procedure

Specimens to be analyzed should be in the range 0.4-0.6 gram and are weighed to ±0.01 gram. The physical form of samples is relatively immaterial; samples may be in the form of sponge, solid pieces of ingot or sheet, drillings, turnings, shavings, or finely divided metal. Samples are placed in individual sample tubes which are attached to the manifold with hard wax. If less than a full complement of sample tubes is attached to the manifold, it is advisable to cap off the remaining joints to minimize the possibility of leaks. The system is evacuated at room temperature to an ultimate pressure of about 10^{-4} mm. The pressure in the system is observed and, with all stopcocks to sample tube open, stopcock (L) is closed. After 10 minutes the pressure is again observed. If the final pressure is 5×10^{-4} mm. or lower, the error introduced by leaks will be negligible if the hydrogen content of samples is above 20 ppm. All stopcocks to the sample tubes are then closed with the exception of #1 tube. With heater and thermocouple in place, the tube is heated to 1000°C in 6-7 minutes and held to $\pm 2^\circ$C to the end of 10 minutes from start of heating. Room temperature and hydrogen pressure are then observed. Heating is discontinued, the stopcock of #1 tube closed and #2 opened. The system is evacuated to about 10^{-4} and the analytical cycle repeated for the second specimen. Successive samples are treated in the same fashion. Equilibrium pressures can be determined in a single apparatus at the rate of four per hour.

Calculation of the hydrogen content of a specimen involves, for the general case: (a) estimation of equilibrium hydrogen concentration, C_E, from the curve (Figure 6); (b) calculation of the hydrogen in the gas phase at equilibrium from observed pressure and room temperature and known volume of the apparatus; (c) summation of the hydrogen in the gaseous and condensed phases and conversion to percent hydrogen in the original specimen:

$$\%H = C_E + 2.02 \times \frac{P_E}{760} \times \frac{273}{T_E} \times \frac{V}{22{,}400} \times \frac{100}{S}$$

$$= C_E + 3.23 \times 10^{-3} V \frac{P_E}{T_E S}$$

$$= C_E + K \frac{P_E}{T_E S}, \text{ where } K = 3.23 \times 10^{-3} V$$

Nominal values used in the calculations are $V = 400$ ml, $T_E = 300^\circ$K, and $S = 0.50$ gram.

If the sample weight and room temperature are held constant, the percent hydrogen in the sample will be a function of the equilibrium pressure alone. Small variations in T_E introduce negligible error. Therefore, if S is held constant, T_E varies only a few degrees, and V is known, it is possible to draw a curve interrelating percent H with P_E. A plot of percent H vs. P_E is shown in Figure 7 in which nominal values of $T_E = 300^\circ$K and $S = 0.50$ gram were used.

After analyses have been completed, sample tubes are removed from the manifold, the titanium specimen discarded, and the tubes cleaned by digestion in warm 10% HCl. After rinsing with water and methanol and oven drying, the tubes are ready for re-use.

This method can be applied to the determination of hydrogen rich alloys provided the proper C_E curves are established for the particular alloy.

Comments

The equilibrium method is rapid for hydrogen determinations in titanium, and with low hydrogen titanium, such as sponge, the sample need not be weighed as the weight percent hydrogen can be read from the graph (Figure 6). Equilibrium curves must be established for each alloy of titanium. If some alloying element raises the beta transition point above 1000°C, results may be unreliable.

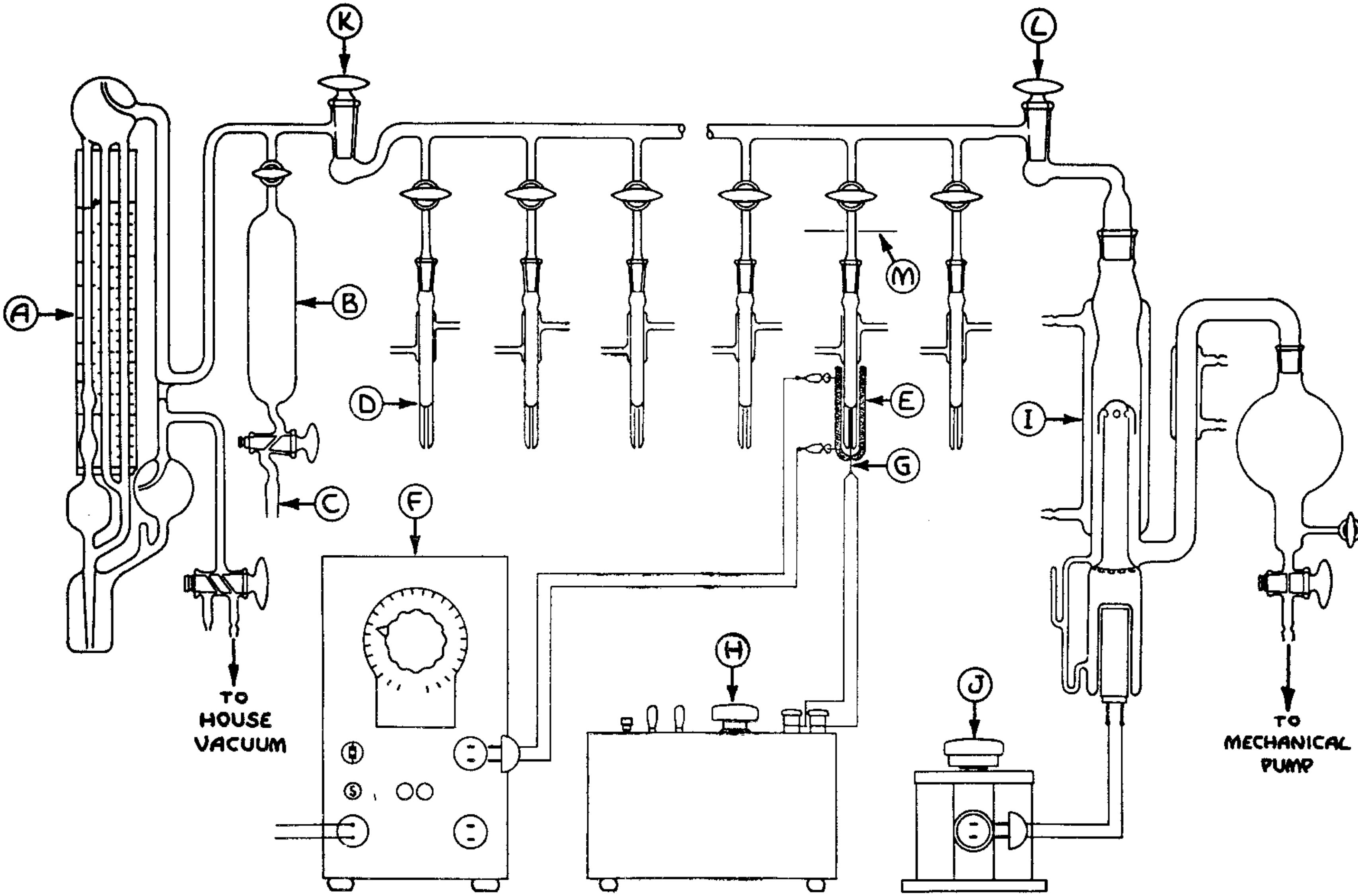

Figure 4 - Apparatus for Method VI, Equilibrium Pressures at 1000°C

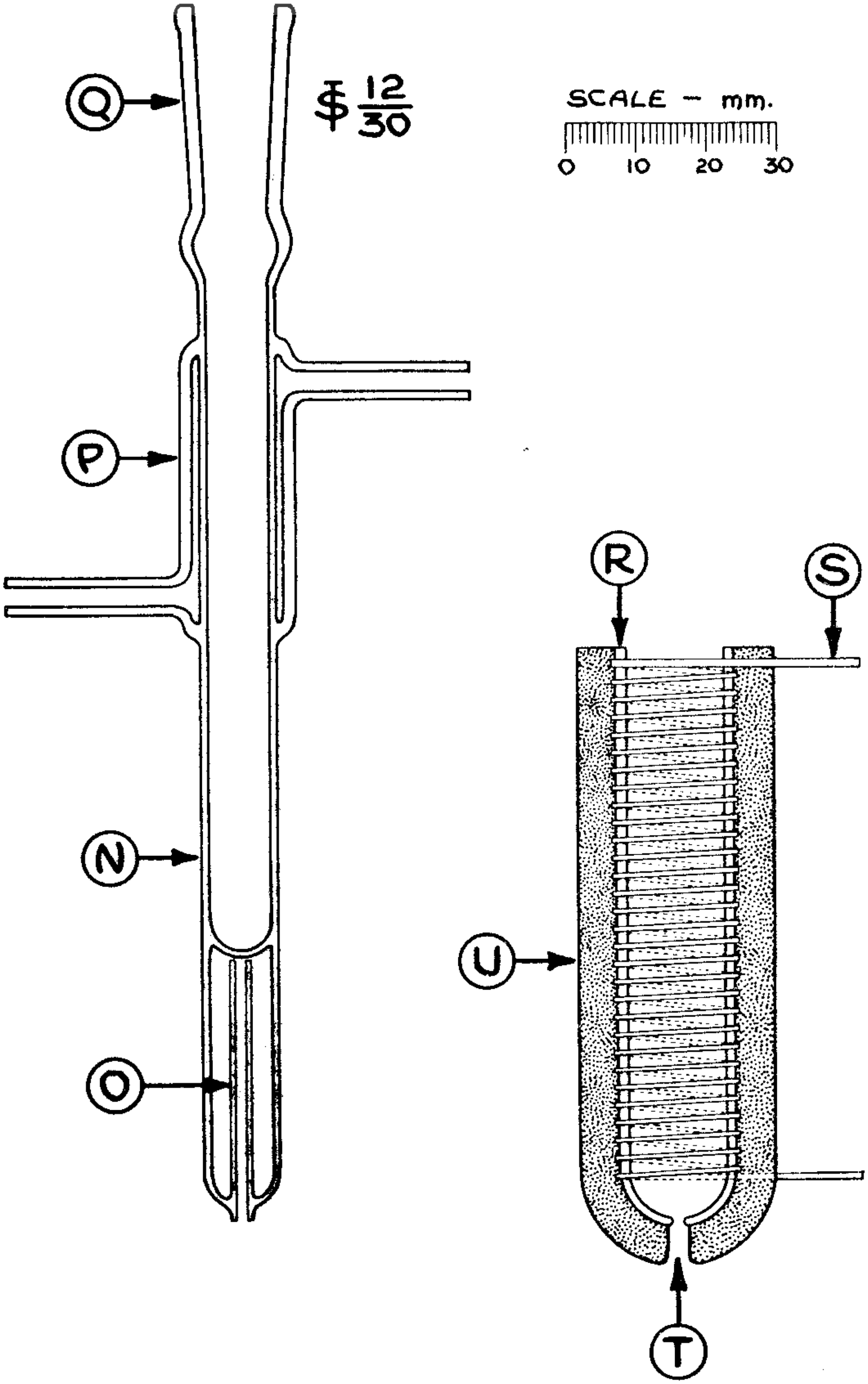

Figure 5 - Details of Sample Tube and Heating Sleeve.

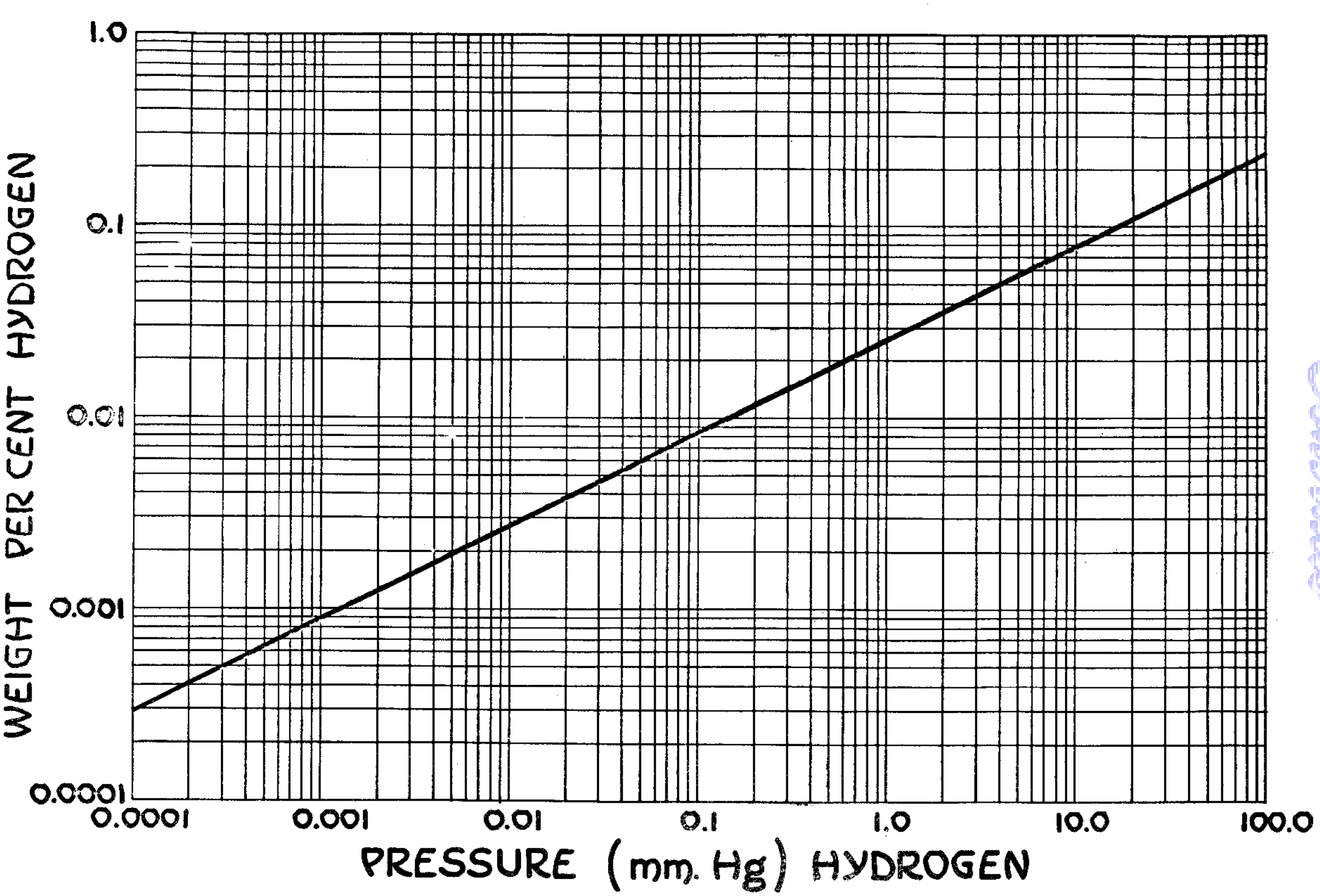

Figure 6 - Equilibrium Curve for Titanium - Hydrogen at 1000°C.

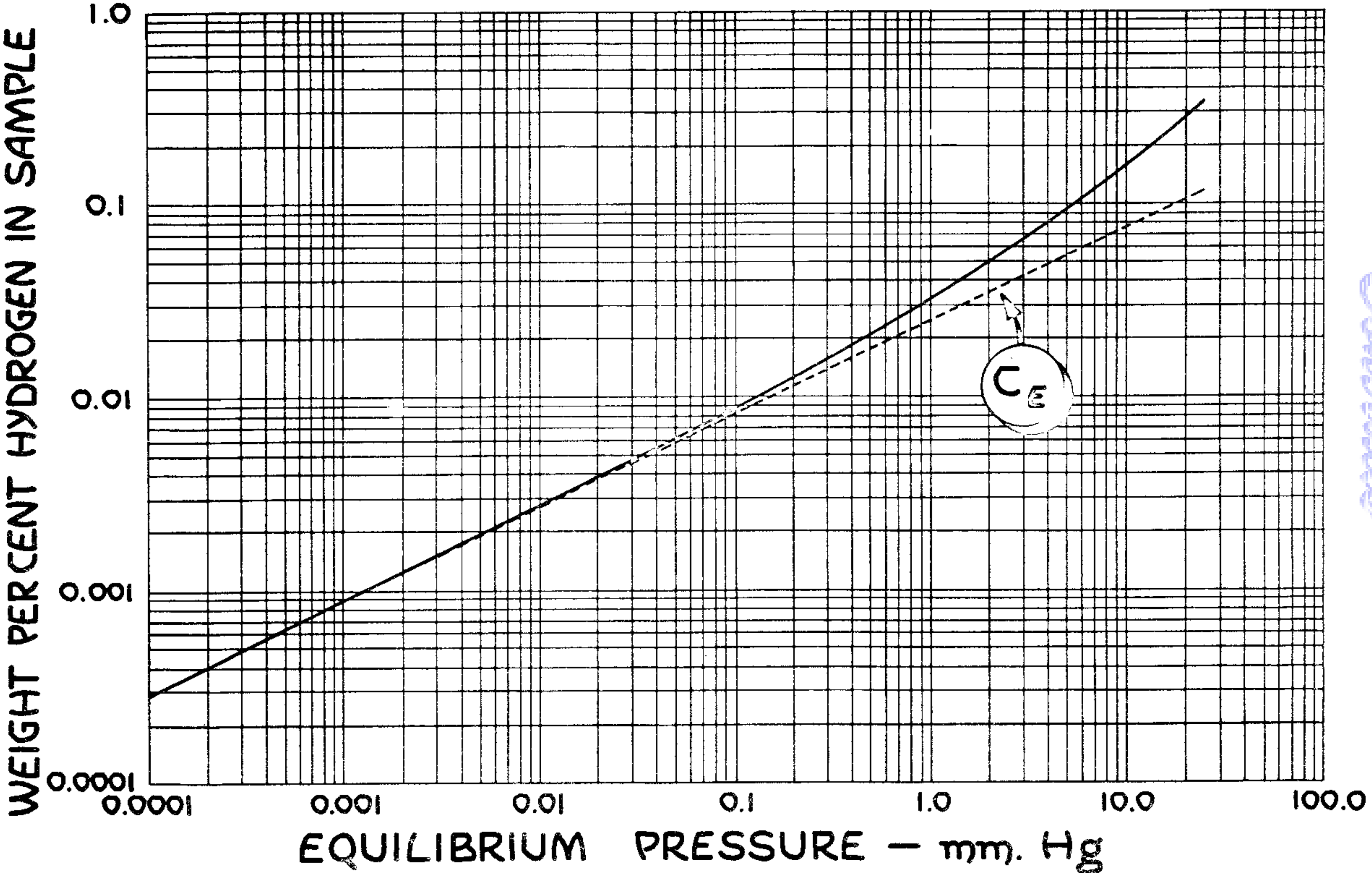

Figure 7 - Percent H vs. P_E at 1000°C. V = 400 ml; T_E = 300°K; and S = 0.50 gram

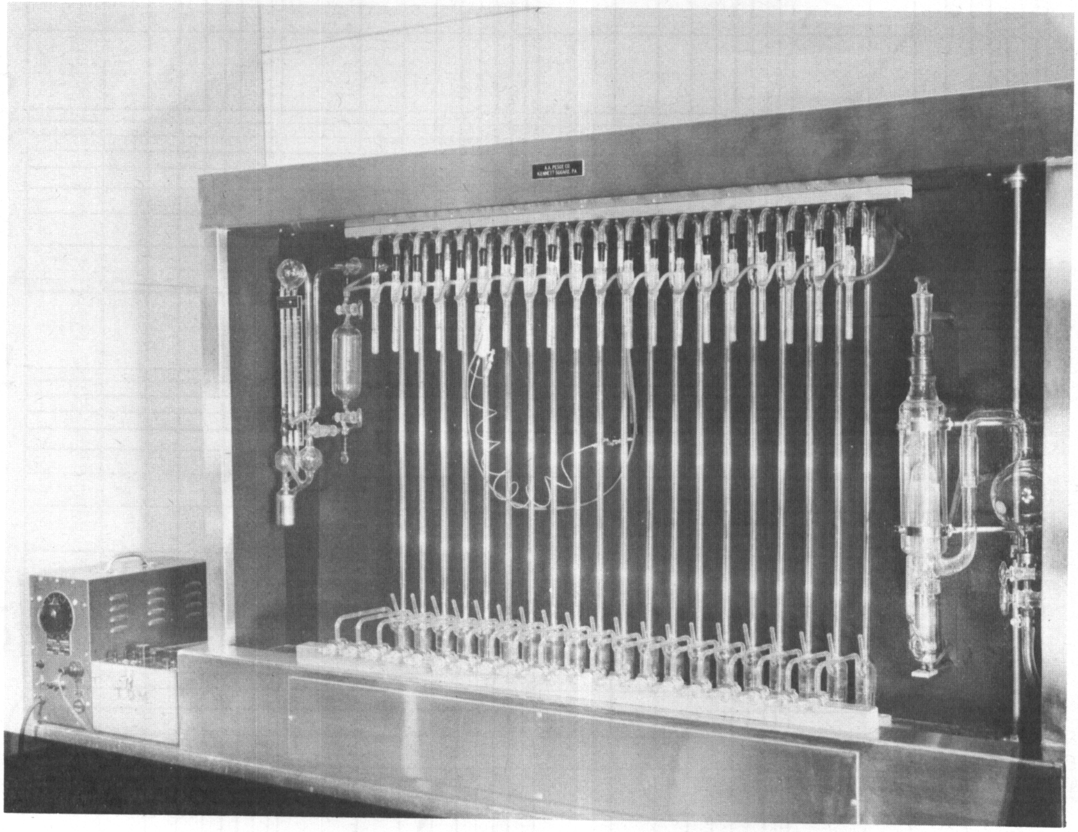

Figure 8 - Commercial Model of Equilibrium Equipment

The equipment described was built by duPont for the development of the method. Equilibrium equipment as being built by A. A. Pesce is shown in Figure 8. A twenty unit apparatus, less sample tubes and sample tube heater, lists for approximately $1,850.00. Quartz sample tubes are $20.00 each and sample tube heater is $8.00.

METHOD VII. MACRO-COMBUSTION AT 900°C(1)

Principle

The titanium sample is heated to 900°C in an oxygen atmosphere with lead as a catalyst to control the rate of reaction. The hydrogen liberated is oxidized to water by copper and collected in a magnesium perchlorate weighing tube and weighed.

Description of Apparatus

The diagram of the apparatus used is shown in Figure 9. (The copper oxide tube for oxygen purification has been lengthened and an electric furnace has replaced the Meker burner). The weighed sample plus lead is placed in a piece of Vycor Tubing, 15 mm in diameter and 7 inches long, and this tube is supported in the reaction tube upon clay supports (3 rounded clay covers for combustion boats). The reaction tube is made of quartz. The furnace is the hinge type (Multiple Unit, Hevi Duty Electric Company) because the furnace should be removable. The copper oxide (wire form) which is used to insure oxidation of the hydrogen is held in place by crumpled balls of fine copper wire and is heated by a Meker burner. The water is collected in a small magnesium perchlorate weighing tube with stopcocks at its ends. A protective tower containing magnesium perchlorate and Ascarite is placed after the weighing tube. The oxygen used in the determination is purified by passing it through hot copper oxide and then through Ascarite and magnesium perchlorate. A blank must be deducted. The method is applied to the determination of hydrogen over the range 0.005 to 1 percent. The time required for a single analysis is about 1-1/2 hours. By the use of 3 or more parallel systems a considerable number of analyses can be run daily. The apparatus is not expensive and is not subject to long breakdowns.

Procedure

Prepare the apparatus as shown in Figure 9. Ignite several pieces of Vycor tubing 15 mm in diameter and 7 inches long, and several clay supports in a muffle at 1000°C for 2 hours, remove and store in a desiccator.

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(1) Method of Frankford Arsenal

Turn on the furnace and the Meker burner to preheat the copper oxide and adjust the flow of oxygen to a rapid rate. Place a piece of the 15 mm Vycor tubing on three of the clay supports and push the tubing and supports to the center of the reaction tube by means of a stout wire bent at the end. Place the furnace which has been previously heated to 900°C in place, and heat for 30 minutes. Remove the furnace but allow oxygen to flow. Turn the stopcocks of the collection tube and quickly disconnect the collection tube. Open momentarily to the atmosphere to equalize the pressure and weigh. Maintain the furnace at high temperature while permitting the reaction tube to cool to approximately room temperature.

The sample can be in any form so long as the volume is small enough to allow the lead to flux with the entire sample. Thin strips of sample are preferred. The sample should be cleaned with carbon tetrachloride and dried in an oven at 100°C for several minutes. Use a 5 gram sample and 10 grams of lead. With the oxygen flowing detach the copper oxide tube and place it in a desiccator. Quickly remove the 15 mm tubing from the reaction tube and place the weighed sample, mixed with lead, into this tubing. Push the tubing and sample to the center of the reaction tube, taking care that the tubing rests on the clay supports and does not come in contact with the sides of the reaction tube. Attach the copper oxide tube, heat it for 5 minutes with the Meker burner, then attach the collection tube and the protective tower. Place the furnace, previously heated, to about 900°C, in position and heat for 30 minutes. The sample should ignite within 5 to 10 minutes after the furnace is put in position. Disconnect the collection tube and weigh. The gain in weight is water. Find the blank by carrying an empty tube through the determination. Calculate the hydrogen in the sample by the following formula:

$$\%\ \text{Hydrogen} = \frac{11.2 \times (H-B)}{W}$$

where H = Weight of water (grams) obtained for run.
B = Weight of water (grams) obtained for blank.
W = Weight of sample (grams)

To prepare for the next run, detach the copper oxide tube and place it in a desiccator. Remove the 15 mm tubing from the reaction tube. If this tubing is not cracked, the titanium oxide may be pushed out and the same tubing used again.

To shut down the apparatus, detach the copper oxide tube and store it in a desiccator. Attach to the reaction tube a protective tube containing magnesium perchlorate which is held in place by glass wool. This protective tube is made of a piece of pyrex tubing about 6 inches long with a 29/42 male ground glass joint at one end.

Comments

Macro-combustion units can be built for approximately $400 each, but an accurate analytical balance is necessary to weigh the water produced.

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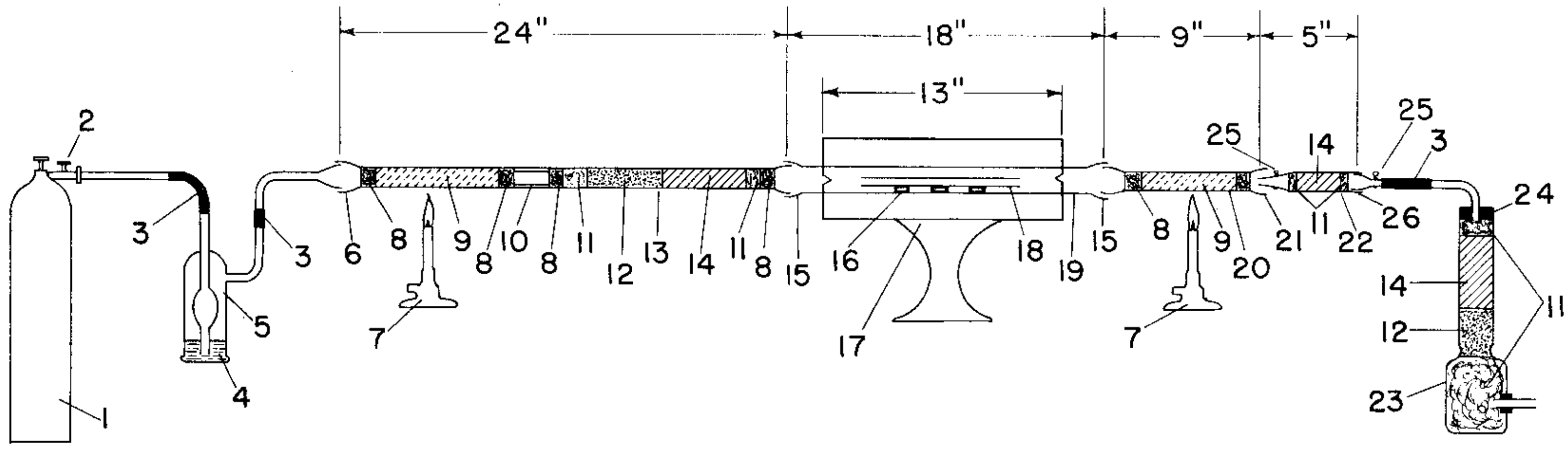

1. TANK OF OXYGEN
2. NEEDLE VALVE
3. TYGON TUBING
4. SULFURIC ACID
5. SMALL GAS WASHING BOTTLE
6. GROUND GLASS JOINT (24/40)
7. MEKER BURNER
8. CRUMPLED BALL OF FINE COPPER WIRE
9. COPPER OXIDE
10. SMALL GLASS TUBE INSERTED TO SEPARATE COPPER OXIDE FROM ASCARITE
11. GLASS WOOL
12. ASCARITE
13. PURIFICATION TUBE (VYCOR, 25 MM IN DIA.)
14. ANHYDRONE
15. GROUND GLASS JOINT (29/42)
16. CLAY SUPPORTS
17. ELECTRIC FURNACE (HINGE TYPE)
18. SAMPLE TUBE (VYCOR, 15 MM IN DIA. AND 7 INCHES LONG)
19. REACTION TUBE (QUARTZ, 25 MM IN DIA.)
20. COPPER OXIDE TUBE (VYCOR, 15 MM IN DIA.)
21. GROUND GLASS JOINT (10/30)
22. COLLECTION TUBE (PYREX, 15 MM IN DIA.)
23. CALCIUM CHLORIDE TOWER (10 INCHES IN HEIGHT)
24. RUBBER STOPPER
25. MICRO STOPCOCK
26. GROUND GLASS JOINT (18/35)

Figure 9 - Apparatus for Method VII, Macro-Combustion at 900°C.

METHOD VIII. MICRO-COMBUSTION AT 1200°C(1)

Principle

The titanium metal is burned in pure oxygen to titanium oxide. The water and carbon dioxide liberated are absorbed in micro absorption tubes filled with magnesium perchlorate and Ascarite, respectively. The carbon and hydrogen are calculated from the increase in weight of the tubes.

Description of Apparatus

(a) Oxygen Purification Train (Figure 10).

(1) Oxygen reservoir bottle, 1 gallon, filled about two thirds full of concentrated sulfuric acid.

(2) Absorption tower containing a layer of glass wool, a layer of sodium hydroxide pellets and another layer of glass wool.

(3) Two sidearm Vycor combustion tubes. The tubes are packed as follows: 7 cm of silver wool or wire screen is placed in the far end of the tube, followed by 3 mm of ignited asbestos, 7.5 cm of copper oxide, 3 mm of platinized asbestos, 7.5 cm of copper oxide and then 3 mm of platinized asbestos to hold the copper oxide in place. The tubes are placed in two electric tube furnaces so that all of the copper oxide and 3.5 cm of the silver are within the heated zone.

(4) Four U-tubes, two filled with Ascarite and two filled with magnesium perchlorate.

(b) Combustion Tube.

(1) The combustion tube for burning the titanium metal is made of Vycor tubing as follows: a 520 mm length of 25 mm i.d. tubing is sealed to a 300 ml length of micro carbon and hydrogen tubing. The latter should be 10 mm i.d. and have a 30 mm length of 3 mm o.d. tubing on the exit end. The large tube has two side arms of 3-5 mm o.d. tubing opposite from one another and 25 mm from the open end, through which oxygen is admitted.

(2) The combustion tube is filled (beginning at the small end) with 100 mm of silver wool or screen, 2 mm of ignited asbestos plug, 90 mm of copper oxide, 2 mm platinized asbestos plug, 90 mm of copper oxide and 2 mm platinized asbestos plug. This filling is different from the usual micro carbon hydrogen filling in that no lead dioxide is used. The copper oxide is heated to 650°C in a electric tube furnace. The first 20 to 30 mm of silver is also located within the furnace and is heated to 500-600°C. The remainder of the silver is heated in a constant temperature mortar at 175°C.

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(1) Method of Dow Chemical Company. Reproduction in whole or in part not authorized without the written permission of The Dow Chemical Company.

(c) Micro Stopcock. This is attached to the 3 mm section of the combustion tube protruding from the constant temperature mortar.

(d) Absorption Tubes. The standard micro carbon and hydrogen absorption tubes are used for collecting the water and carbon dioxide. These tubes are filled with magnesium perchlorate and Ascarite in the usual manner.

(e) Aspirator System.

(1) A U-tube filled with magnesium perchlorate and Ascarite is inserted between the absorption tubes and the aspirator bottle. This prevents any water or water vapor from backing up into the absorption tubes.

(2) A 4-liter aspirator bottle filled about two-thirds full of water.

(f) Alundum Shields. These tubes or shields, which should just fit the larger part of the combustion tube, can be purchased from the Fisher Scientific Company as No. 7-685, Size No. 2 (5.5 inches long). These tubes are then cut along their length so that an arc of about 2 cm is cut out. The combustion boat can then rest on the Vycor tube and the upper port of the tube be protected from spattering of the sample.

(g) High temperature furnace (1200°C) equipped with thermocouple and pyrometer. This is a split furnace that can be pulled over the combustion tube to fire the sample. This furnace was constructed in the laboratory.

(h) Two oxygen cylinders with reducing gauges.

(i) Micro balance.

(j) Combustion boats, Leco HF-B, 3-3/4 inches long, 5/8 inch wide and 1/2 inch high. For protection of the boats during combustion, they should be lined with 60-mesh alundum.

Procedure

Conditioning of the Combustion Tube and Absorption Tubes

(a) With the entire train set up as in the diagram, open the aspirator bottle and pass oxygen through the train at a rate of approximately 30-50 ml per minute. The water is measured in a graduate and the stopcock on the last U-tube is adjusted to obtain the correct rate of flow. When this adjustment is complete a 1500 ml beaker is used to catch the water during a complete analysis.

(b) With oxygen passing through the train, move the high temperature furnace, which has been brought up to 900°C, over the combustion tube (which contains the alundum shield and boat). Turn the pyrometer up to 1200°C and heat for about 10-15 minutes or until about 500 ml water has been collected. Turn the pyrometer back to 1000°C and continue heating until 750-800 ml of water has been collected. Remove the furnace and allow the combustion tube and contents to cool, meanwhile continuing the sweeping until a liter of water has been collected. Place a pinch clamp on the aspirator bottle and close the stopcock on the U-tube. Disconnect the absorption tubes and take them to the micro balance. Wipe the tubes with a chamois, place them on the rack holder and remove any static charges. Allow the tubes to stand 15 minutes before weighing.

Preparation of the Sample

The titanium metal should preferably be in the form of fine turnings, or shavings. It was found that approximately 0.5 gm of iron chip accelerator plus 0.3-0.5 gm of tinned copper (Dualaccelerator) burns 0.5 gram of sample completely and forms a homogenous melt. Weigh the sample in a boat smaller than the one used for the combustion, which can be inserted into the combustion tube and emptied into the large boat by means of a long pair of forceps. Spread 0.5 gm of iron chip accelerator on top of the sample. Place tinned copper strips (Dualaccelerator) in the large combustion boat.

Combustion of the Metal

(a) Close the micro stopcock and step up the supply of oxygen. Remove the large aluminum foil-covered rubber stopper from the large end of the combustion tube. The fast rate of oxygen coming out the side arms of the combustion tube prevents any air from entering the tube. By means of a glass rod with a platinum wire attached pull the boat just out of the shield but do not remove from the combustion tube. With the long pair of forceps place 1 strip of tinned copper in the boat. Next transfer the sample which contains the iron chip accelerator to the boat. Transfer as completely as possible. Finally place another strip of tinned copper on top of the sample in the combustion boat. Push the combustion boat back into the middle of the shield and replace the rubber stopper. Open the micro stopcock and let the oxygen pass through the combustion tube for 10 minutes. Connect the tared absorption tubes in the proper place in the train (between the micro stopcock and the protective U-tube). Close the micro stopcock. With the oxygen turned on at a fast rate, move the high temperature furnace which is at 900°C over the sample. Turn the pyrometer up to 1200°C.

(b) When the combustion of the titanium has ceased (approximately 1-2 minutes) the micro stopcock and the aspirator bottle are opened. The oxygen rate is reduced so that just an excess is indicated in the reservoir bottles. Sweep at 1200°C till about 500 ml of oxygen has been passed through, then turn the pyrometer back to 1000°C. Hold this temperature for another 250-300 ml of water. Remove the furnace from the combustion tube and continue sweeping till 1 liter of water (total) has been collected. Shut off the aspirator bottle and the protective U-tube. Disconnect the absorption tubes and take them to the micro balance. Wipe the tubes with a chamois, discharge them, and place on the rack holder for 15 minutes before weighing. Weigh the tubes and reserve them for the next determination.

(c) Run a blank determination under identical conditions without the sample.

Calculations

$$\% \text{ Carbon} = \frac{0.2729 \text{ x wt. of carbon dioxide in milligrams x } 100}{\text{wt. of sample in milligrams}}$$

$$\% \text{ Hydrogen} = \frac{0.1119 \text{ x wt. of water in milligrams x } 100}{\text{wt. of sample in milligrams}}$$

Comments

(a) A complete determination can be run in approximately 1 hour according to the following schedule:

5 minutes to ignite sample
30 minutes to heat and sweep entire train
15 minutes to wipe, discharge and prepare absorption tubes for weighing
5 minutes to weigh absorption tubes
5 minutes to load sample and connect absorption tubes
60 minutes total

(b) A new combustion tube should be conditioned by actually firing three or four 0.5 gm samples of titanium according to the procedure and also by heating and cooling the combustion tube for 15 minute periods until on running a blank determination the hydrogen absorption tube will show an increase of not over 0.2 mg and the carbon tube not over 0.1 mg.

Once a new combustion tube has been conditioned it is not necessary to run a blank every day unless different amounts of flux are added. The blanks on a 0.5 gm of iron chip accelerator plus two strips of tinned copper (0.3 gm) usually are quite consistant.

(c) The micro-combustion train can be constructed for approximately $900 but a micro-analytical balance is necessary for weighing the water and carbon dioxide produced. If a micro-balance is not presently available, this will make a considerable increase in the cost of micro-equipment.

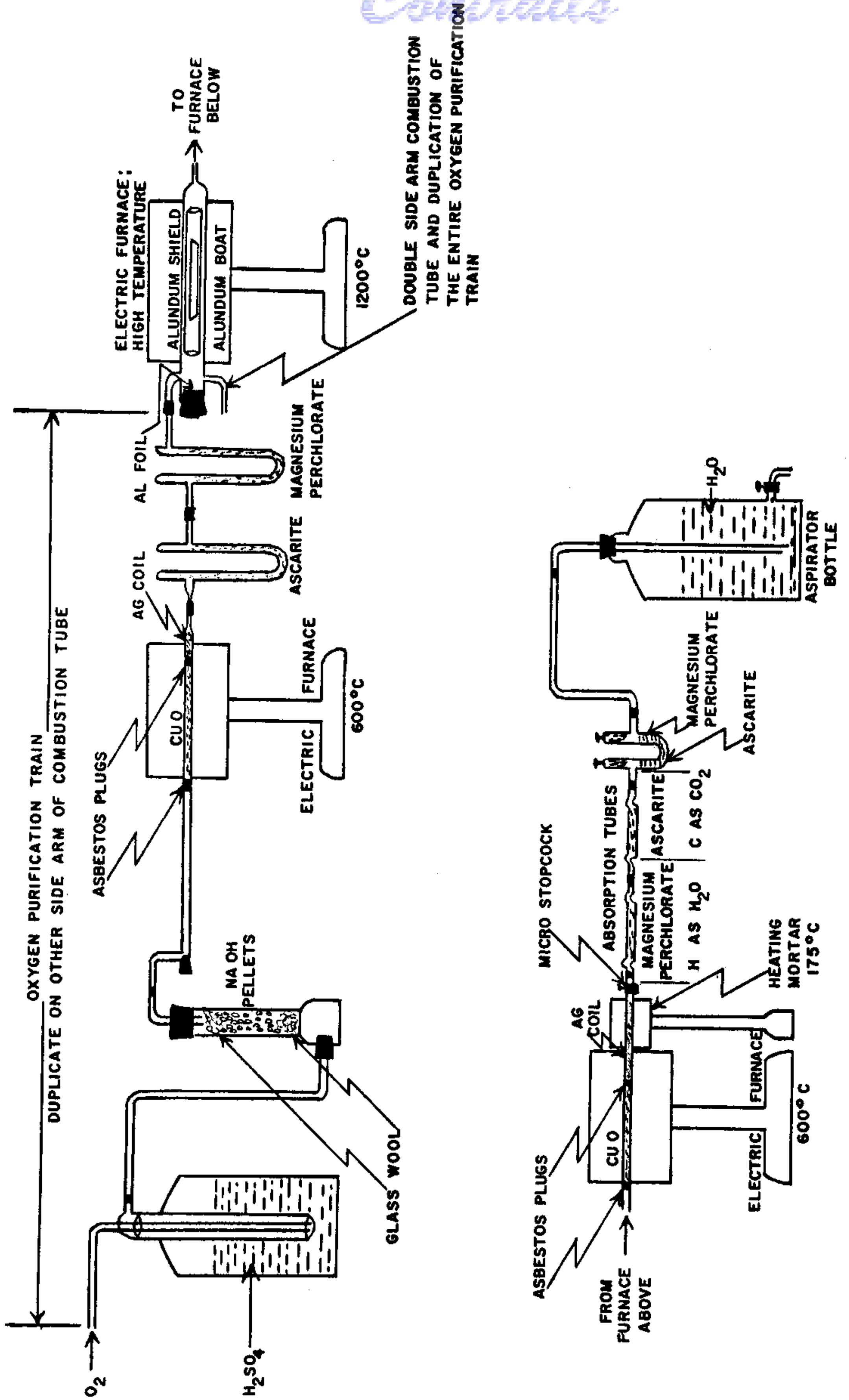

Figure 10 - Apparatus for Method VIII, Micro-Combustion at 1200°C

METHOD IX. HOT EXTRACTION IN HELIUM ATMOSPHERE[1]

Principle

Hydrogen may be determined by thermally decomposing the sample in a helium atmosphere with a high frequency combustion unit, the evolved hydrogen oxidized to water with hot copper oxide, and the resulting water vapor absorbed in magnesium perchlorate.

Description of Apparatus

The apparatus is assembled in the following manner: A cylinder of Grade A helium (National Cylinder Gas Company) is fitted with an Oxweld valve and a float type helium flow meter. A glass-stoppered drying jar (Fisher) filled with anhydrous Magnesium perchlorate is connected to the flow meter with tygon tubing. Additional tubing is used to connect the drying jar to the incoming gas port on the Lindberg ("H-F") High Frequency Combustion Unit (1/2 to 1 KW). The two gas flow control valves on the front panel of the combustion unit are opened completely and the gas flow controlled by the flow meter on the helium cylinder. Another drying jar is connected by tygon tubing to the out-going gas port of the combustion unit. The drying jar is joined to a quartz combustion tube (35 cm length x 1 cm diameter) by additional tygon tubing. The quartz tube is filled to within 5 cm from both ends with wire form cupric oxide, which is held in place with quartz wool plugs. The tube is heated by a Fisher Micro Combustion Furnace and the combustion tube temperature measured with a Hoskins "Chromel Alumel" pyrometer. The outgoing end of the combustion tube is fitted with a glass socket which connects to a ball joint on a "Nesbitt absorption bulb. A ball joint clamp is used to hold the quartz tube and Nesbitt absorption bulb together. The first absorption bulb is connected with tygon tubing to a second absorption bulb. Both bulbs are filled with anhydrous magnesium perchlorate. The second bulb is used only to keep water vapor from coming into the system. The exhaust helium is passed through tygon tubing into an Erlenmeyer flask containing water in order that the rate of flow may be observed visually.

Procedure	Comments
1. Test the entire apparatus for leaks manometrically.	
2. Sweep the system with helium gas (2.5 cu. ft per hour) for at least 30 minutes.	2. The purpose of this operation is to free the apparatus from absorbed moisture and to equalize the entire system. It need only be repeated at the start of each series of analysis. The first determination may be slightly high for this reason. The quartz tube containing the cupric oxide is also heated (650°C) during this period.

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(1) Method of ANP Division, General Electric Company

3. Turn the filament switch of the Lindberg ("H-F") High Frequency Combustion Unit to "ON".	3. With the helium gas flowing at the rate of about 2.5 cu. ft. per hour and the temperature of the quartz combustion tube controlled at 650°C, the apparatus is now ready to use.
4. Remove the first Nesbitt absorption bulb from the hydrogen train and weight it.	4. While weighing the bulb, allow helium to continue passing through the remaining apparatus.
5. Reconnect the bulb, allowing helium to pass through for about 10 minutes.	
6. Disconnect and reweigh.	6. Repeat this operation until constant weight is obtained.
7. Replace the absorption bulb in the hydrogen train.	
8. Weigh rapidly a 1.0 to 2.0 gram sample into the cupelet.	8. Cupelets are previously heated at 800°C for 30 minutes and stored in a desiccator before use.
9. Cover the weighed sample with about two grams of tungsten powder (30-mesh).	9. The tungsten powder is commercial grade and prepared by heating in helium for 15 minutes at 2200°C.
10. Place the prepared cupelet on the pedestal hearth and insert into the Lindberg ("H-F") High Frequency Combustion Unit.	
11. Fire the sample by turning the high voltage switch of the Lindberg ("H-F") High Frequency Combustion Unit to "ON".	
12. Allow helium to pass for 10 to 15 minutes.	

13. Move the Micro Combustion furnace to all parts of the quartz combustion tube in order to vaporize any condensed water present.	
14. Remove the first Nesbitt absorption bulb and weigh.	14. Allow five minutes for the bulb to come to equilibrium before weighing. After removing spent cupelet and turning "HV" switch to "OFF", the apparatus is ready for the next determination.

Calculations

$$\text{Wt } H_2O = \text{Final wt. bulb} - \text{Initial wt. bulb}$$

$$\% \text{ H} = \frac{\text{Wt. } H_2O \times 11.19}{\text{Wt. of sample}}$$

III. COMPARISON OF HYDROGEN DETERMINATIONS BY THE VARIOUS METHODS

SELECTION OF SAMPLES

Materials from which samples were taken were supplied by the four producers of titanium mill products and represented a range of hydrogen contents, of alloying elements, and of sheet and bar sizes. The nominal composition and form of these materials is shown in Table I.

TABLE I. NOMINAL COMPOSITION AND FORM OF MATERIALS

Designation	Nominal Composition	Form
RR 1	Commercially pure	Sheet, approx. 0.080"
RR 2	5 Al, 2-1/2 Sn	Sheet, approx. 0.080"
RR 3	8 Mn	Sheet, approx. 0.080"
RR 4	Commercially pure	Bar, approx. 2" diameter
RR 5	4 Al, 4 Mn	Bar, approx. 2" diameter
RR 6	5 Al, 1 Fe, 2 Cr, 2 Mo	Bar, approx. 3/4" diameter
RR 7	2 Fe, 2 Cr, 2 Mo	Bar, approx. 3/4" diameter
RR 8	3 Al, 5 Cr	Bar, approx. 2" diameter
RR 9	6 Al, 4 V	Bar, approx. 2" diameter
RR 10	3 Mn, 1 Cr, 1 Fe, 1 Mo, 1 V	Sheet, approx. 0.080"
RR 11	3 Mn, 1 Cr, 1 Fe, 1 Mo, 1 V	Sheet, approx. 0.080"
RR 12	8 Mn	Sheet, approx. 0.080"
RR 13	3 Mn, 1-1/2 Al	Sheet, approx. 0.125"
RR 14	Same as RR 4	Bar, approx. 2" diameter
RR 15	8 Mn	Sheet, approx. 0.035"

Specimens were milled with coolant to avoid overheating and possible change in hydrogen content. Sheet specimens except the thin RR 15 were also milled to avoid fine laminar shear cracks which might for some methods have influenced results. Specimens for Frankford Arsenal were prepared as fine chips by light cuts with a shaper, and specimens for other laboratories using a combustion method were furnished as solid pieces from which chips could be taken.

To avoid confusion, the materials sampled for this experiment will be referred to as alloys, such as Alloy RR 1, even though some are commercially pure grades. The specific piece on which triplicate hydrogen determinations were made will be referred to as a specimen.

No thermal treatments were performed on the specimens to promote uniformity in hydrogen distribution. Such non-uniformity is encountered in routine analyses of titanium mill products, and it was of interest to observe the extent of this non-uniformity and its influence in combination with other factors in the experiment. Also, assurance that true homogeniety had been achieved would be questionable. By assigning specimens to laboratories in random fashion, the effect of differences between specimens can be handled statistically.

HYDROGEN DETERMINATIONS AS REPORTED

Hydrogen determinations as reported by the participating laboratories are presented in Table II. Several features are not apparent by inspection of the data:

a. The determinations by WADC Materials Laboratory for both Methods I and III were all obtained from the same Alloy specimen (e.g. RR 3).

b. Two sets of specimens were analyzed by duPont, each set by both Method I and Method VI. The determinations for a given set were all obtained from a single Alloy specimen.

c. Some laboratories purposely performed the individual determinations which comprise the triplicate determinations on different days, thereby reflecting in their results a source of error from day-to-day differences not reflected in results from all laboratories. Although the variation in triplicate determinations is likely to be larger, this affords the best estimate of laboratory reproducibility.

d. Specimens were distributed to the participating laboratories at intervals rather than all at one time. Some laboratories performed the analytical work as specimens were received; others waited until all specimens were accumulated. Results from some laboratories may have been influenced by a change in analytical technique or a difference in operators during the elapsed time between groups of specimens. The difference between Alloys RR 4 and RR 14, the same commercially pure bar reintroduced into the experiment, may in some cases be partly attributed to this.

TABLE II

HYDROGEN DETERMINATIONS (in ppm) AS REPORTED BY PARTICIPATING LABORATORIES

Laboratory	Alloy														
	RR 1	RR 2	RR 3	RR 4	RR 5	RR 6	RR 7	RR 8	RR 9	RR 10	RR 11	RR 12	RR 13	RR 14	RR 15
	Method I - Vacuum extraction at 1900°C, samples in tin bath, analysis from differential pressures.														
WADC Materials Laboratory	109	128	129	170	83	38	87	110	67	124	193	267	156	111	254
	113	139	140	159	82	26	78	107	71	121	193	267	157	111	246
	122	131	138	152	80	30	80	115	78	129	200	269	164	112	256
Ladish Company	106	142	122	134	86	46	90	118	85	155	198	242	158	133	266
	102	142	132	137	86	52	71	96	85	150	198	252	162	133	273
	118	136	122	-	91	37	78	94	80	147	207	241	152	149	271
Republic Steel Corporation	123	151	147	157	103	49	96	119	75	175	202	318	210	192	251
	156	141	141	134	72	43	81	108	74	133	192	329	183	191	264
	124	155	130	161	84	39	125	133	104	143	191	280	182	202	272
duPont (1st set)	104	134	121	100	70	34	75	99	65	124	186	232	155	121	271
	102	145	119	89	69	30	78	98	66	135	197	255	155	119	270
	100	138	122	-	73	29	83	104	74	134	189	255	156	127	271
duPont (2nd set)	107	120	128	130	59	44	85	102	66	105	193	249	140	94	278
	106	117	126	128	61	36	95	96	69	106	193	244	140	93	260
	107	129	123	131	60	40	93	102	71	106	192	247	130	89	279
Watertown Arsenal	106	118	131	109	67.4										
	93	113	124	109	66.7	Not Reported									
	110	121	129	120	66.7										
	106		128	111											
	Method II - Vacuum extraction at from 1450 to 1600°C, sample in graphite crucible, analysis from differential pressures.														
Electro Metallurgical Company	112	152	127	124	76	34	86	114	78	149	190	275	161	120	290
	85	117	136	112	66	34	83	102	76	131	190	273	159	111	285
	112	130	130	171	66	42	84	106	71	154	201	277	169	94	295
				120	61										
	Method III - Vacuum extraction at from 1200 to 1450°C, sample in graphite crucible, analysis from total pressure.														
WADC Materials Laboratory	120	154	140	170	78	28	82	110	82	131	188	276	159	117	257
	119	136	135	170	80	33	79	113	82	130	196	268	159	114	252
	111	144	138	164	74	30	86	114	82	136	197	270	156	112	258
Republic Steel Corporation	119	152	140	152	81	39	104	117	86	143	215	280	164	152	270
	117	169	130	146	75	38	96	114	79	133	206	248	164	152	285
	127	163	133	141	81	40	90	112	-	146	215	275	172	154	272
Mallory-Sharon Titanium, Corp.	130	130	140	163	72	45	89	118	79	119	205	286	173	147	309
	148	131	136	159	86	40	87	114	80	121	195	285	174	148	304
	130	130	141	164	75	45	87	114	79	118	199	296	180	148	307
Wyman-Gordon Company	111	143	131	141	76.4	34.7	78.0	95.3	75.3	107	198	261	151	126	250
	113	133	138	144	75.9	32.8	78.8	95.1	76.4	107	205	267	153	121	255
	110	136	130	148	77.2	32.9	78.2	97.7	78.0	115	194	267	152	122	258
Westinghouse Electric Corporation	129	168	145	114	81.4	26.0	66.5	121	77.0	138	198	281	166	174	260
	127	163	155	105	79.5	25.7	78.0	124	76.2	134	198	282	166	176	279
	133	175	143	109	81.7	23.5	78.0	122	71.7	132	196	280	182	183	265
Pratt & Whitney Aircraft	115	129	144	121	82	36	113	114	79	131	214	276	163	163	298
	113	171	146	120	84	35	98	113	87	132	203	266	158	162	292
	114	125	137	118	79	33	87	109	82	151	197	269	156	164	295
Rem-Cru Titanium, Inc.	111	157	124	142	84.3	35.6	80.8	108	72.6	124	194	213	162	110	262
	111	157	125	142	74.2	32.4	81.0	109	73.6	127	196	211	159	111	261
	112	152	125	139	83.4	31.5	84.5	111	72.5	128	194	218	159	109	252
						37.1	86.6	109	70.9	129	197				
Watertown Arsenal	123	122	104	116	57.9	28.9	66.8	108	62.3	143	185	246	141	104	247
	146	103	107	112	61.5	29.2	72.7	104	75.1	131	191	250	147	105	244
	108	-	127	113	56.3	20.5	76.4	94	56.2	133	183	246	149	100	-
	96					24.0	70.0	93	79.7						
						24.2									
Armour Research Foundation	107	164	122	161	52	8.8	71	87	79	152	183	261	130	142	231
	115	168	126	151	65	15	77	86	80	151	182	255	130	137	234
	118	163	131	161	60	*41	65	91	71	153	189	249	129	140	250
						*23									
	* Armour notes 30 minutes gas collection time for these analyses contrasted to 20 minutes time for others.														
National Research Corporation	113	-	-	114	81.4	-	80.8	108	69.0	144	184				
	118	-	-	116	77.4	-	80.9	110	70.0	143	187	Not Reported			
	118	-	-	120	79.1	-	82.3	109	73.4	137	183				
	Method IV - Vacuum extraction at from 1300 to 1400°C, sample in molybdenum crucible or boat, analysis from total pressure.														
Brush Laboratories	103	125	121	118	78.8	33.6	82.5	98.1	81.2	113	173	246	144	114	264
	112	127	125	127	78.3	34.2	84.3	102	82.4	98.3	180	252	147	111	258
	103	128	127	121	70.7	32.7	82.2	98.0	81.1	99.1	164	248	141	113	269
					71.9					111					
					74.2					112					
					78.7					121					
National Research Corporation	118	143	147	115	80.7	33.0	84.5	115	74.2	157	186	275	169	129	287
	117	134	146	111	79.0	30.7	~~84.3~~	~~110~~	~~72.8~~	~~153~~	~~188~~	~~274~~	~~172~~	~~129~~	~~291~~
	119	135	149	112	80.0	31.1	88.1	111	73.8	152	188	276	172	126	296
	Method V - Vacuum extraction at from 100 to 1075°C, sample in resistance heated quartz tube, analysis from total pressure.														
Allegheny-Ludlum Steel	128	142	139	154	72	42	83	105	74	136	180	280	164	129	294
	124	149	141	156	74	43	84	107	78	142	187	275	162	126	294
	-	-	-	-	-	-	-	-	-	-	-	284	164	126	295
Titanium Metals Corporation	134	155	151	161	66	33	88	101	78	128	200	298	172	172	314
	131	141	148	146	77	32	87	110	83	135	202	298	160	172	292
	135	173	136	153	74	32	85	101	78	157	-	295	170	169	305
National Research Corporation	-	125	144	-	-	33.0									
	-	137	146	-	-	34.4	Not Reported								
	-	135	150	-	-	32.2									
	Method VI - Equilibrium at 1000°C, analysis from equilibrium pressure.														
duPont (1st set)	105	121	121	88	76	26	77	108	71	132	194	232	176	114	249
	107	139	125	103	77	29	84	99	68	129	197	251	149	122	273
	-	145	131	96	58	27	83	109	70	127	191	247	150	125	255
duPont (2nd set)	110	124	127	130	70	45	88	99	65	108	192	258	135	101	282
	108	116	134	135	69	45	87	97	64	112	185	243	137	99	264
	-	109	125	139	68	46	92	-	-	-	198	251	139	103	276
	Method VII - Macro-combustion using 5 or 10 gram sample at 800 to 900°C with oxygen sweep, hydrogen oxidized to water and weighed.														
Frankford Arsenal	-	-	121	160	102	44	97	120	69	177	231	274	199	150	311
	-	-	135	140	108	51	93	109	88	149	206	274	184	155	327
	-	-	120	124	86	51	109	111	96	160	215	231	175	143	307
	Method VIII - Micro-combustion method, using 1/2 gram sample at 800 to 1200°C, hydrogen oxidized to water and weighed.														
Dow Chemical Company	114	125	110	163	39	31	86	109	67	142	184	250	148	105	287
	121	135	125	172	43	16	82	123	59	134	190	280	148	122	304
	126	130	117	162	47	13	72	101	70	149	192	255	152	105	296
	123				44	19			74						
	Method IX - Hot extraction in helium atmosphere, hydrogen oxidized to water and weighed.														
General Electric (ANP Division)	277	305	271	197	220	166	179	88	118	157	321	388	184	207	386
	243	310	246	244	223	109	188	83	129	142	352	381	238	198	373
	214	284	268	214	298	186	155	*88	144	165	311	*333	247	*133	*275
														*134	*277
	* General Electric notes determinations indicated by asterisks were obtained on duplicate specimens, and that specimen RR 2 (5 Al - 2-1/2 Sn) did not melt.														

OBSERVATIONS FROM THE DATA

Several observations can be made from cursory inspection of the data:

a. Reproducibility for most laboratories, judged by variation within triplicate determinations, is neither surprisingly good or bad.

b. Real differences appear to exist between specimens of some of the Alloys, exceeding the variation within triplicate determinations. Values for RR 4 and for RR 14 show this most strikingly.

c. The volume of data makes further observations difficult, although the values for Method IX seem to be significantly different from those for other Methods.

STATISTICAL ANALYSIS OF THE DATA

Statistical analysis offers substantially more information from a volume of data than is usually possible by inspection alone, relating observed differences to the probability they might have occurred by chance effects of unrecognized factors rather than by real effects of experimental factors. An analogy to a quality control problem will illustrate operation of chance effects. For an assembly, the dimensions of the whole are a function of the dimensional tolerances of the components, and a tolerance for the whole assembly is far less than the sum of tolerances for its components since a "canceling out" of plus and minus tolerances is experienced. Use of a close tolerance for the assembly is thereby possible, and the frequency with which the assembly tolerance will be exceeded can be predicted if component dimensions are "in control". The effects are real, but the action is by chance.

A frequent consequence of collecting a volume of data generated by a number of observers is that precise control over all elements of an experiment is sacrificed. Some of the loss has already been mentioned. It becomes necessary to adapt the resulting data to statistical analysis and to recognize whatever restrictions this imposes.

Missing data are a frequent experience. Techniques have been developed for laboriously supplying values which will restore the desired condition of equal subgroup numbers without biasing observations to be made from the experiment. The difficulty increases tremendously, however, where subgroup size varies considerably or where values for entire samples are missing.

Simpler steps are taken to adapt the raw data of Table II to statistical treatment:

a. Only laboratories reporting results for all fifteen Alloys are used for statistical comparisons, with one exception. Frankford Arsenal, using Method VII, reported no values for Alloys RR 1 and RR 2 so these Alloys are excluded for other laboratories to permit comparison with Frankford Arsenal.

b. All determinations have been rounded off to units of parts per million hydrogen (0.0001%).

c. Where one determination for a specimen is missing, the arithmetic mean of the other two values is supplied. The specimen mean is not biased by this, but better analytical reproducibility is claimed. Therefore, a degree of freedom for the error term and total is lost for each missing value supplied.

d. Where determinations in excess of three are reported for a specimen, these are rejected by using a table of random numbers 1/. All values thereby have an equal chance of being retained, and no degrees of freedom are lost.

e. Where an apparently valid cause exists for a difference between determinations for a given specimen, and this reason is stated by the particular laboratory, the questioned value is replaced by a substitute as though it were a missing value. This was necessary only for data of Method IX.

Data thus prepared for statistical analysis are presented in Table III.

Analysis of Variance

Persons unfamiliar with statistical methods nevertheless recognize that each individual value reflects in some way the effect of the various experimental factors, and in some way it should be possible to separate variation among values into components due to the factors, in this case due to the method of analysis, to the laboratory and operator, to location of the specimen within the original sheet or bar, to the material and its hydrogen level, to analytical precision, and possibly to influence of these factors one upon the other.

Comparisons of averages and ranges determined arithmetically would furnish only a part of this information. If a statistical term called the variance, related to the familiar sigma or standard deviation, is calculated

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1/ Snedecor, G. W., Statistical Methods. Table 1.2, pp 10-13

TABLE III

HYDROGEN DETERMINATIONS (in ppm) FOR STATISTICAL ANALYSIS

Laboratory	Alloys														
	RR 1	RR 2	RR 3	RR 4	RR 5	RR 6	RR 7	RR 8	RR 9	RR 10	RR 11	RR 12	RR 13	RR 14	RR 15
Method I - Vacuum Fusion at 1900°C, samples in tin bath, analysis from differential pressures.															
WADC Materials Laboratory	109	128	129	170	83	38	87	110	67	124	193	267	156	111	254
	113	139	140	159	82	26	78	107	71	121	193	267	157	111	246
	122	131	138	152	80	30	80	115	78	129	200	269	164	112	256
Ladish Company	106	142	122	134	86	46	90	118	85	155	198	242	158	133	266
	102	142	132	137	86	52	71	96	85	150	198	252	162	133	273
	118	136	122	136	91	37	78	94	80	147	207	241	152	149	271
Republic Steel Corporation	123	151	147	157	103	49	96	119	75	175	202	318	210	192	251
	156	141	141	134	72	43	81	108	74	133	192	329	183	191	264
	124	155	130	161	84	39	125	133	104	143	191	280	182	202	272
duPont (1st set)	104	134	121	100	70	34	75	99	65	124	186	232	155	121	271
	102	145	119	89	69	30	78	98	66	135	197	255	155	119	270
	100	138	122	94	73	29	83	104	74	134	189	255	156	127	271
Method II - Vacuum extraction at from 1450 to 1600°C, sample in graphite crucible, analysis from differential pressures.															
Battelle Memorial Institute	105	136	128	153	76	29	80	106	76	109	179	255	152	138	253
	113	156	131	151	76	32	80	102	76	122	180	262	151	138	251
	108	124	125	153	76	32	79	98	77	142	191	262	151	135	250
Naval Research Laboratory	104	140	123	143	78	31	75	112	65	139	186	267	151	145	290
	104	144	123	146	78	30	81	106	72	143	183	267	156	138	273
	102	142	125	140	77	32	82	112	74	137	175	276	162	137	278
Electro Metallurgical Co.	112	152	127	124	76	34	86	114	78	149	190	275	161	120	290
	85	117	136	112	66	34	83	102	76	131	190	273	159	111	285
	112	130	130	171	61	42	84	106	71	154	201	277	169	94	295
Method III - Vacuum extraction at from 1350 to 1450°C, sample in graphite crucible, analysis from total pressure.															
WADC Materials Laboratory	120	154	140	170	78	28	82	110	82	131	188	276	159	117	257
	119	136	135	170	80	33	79	113	82	130	196	268	159	114	252
	111	144	138	164	74	30	86	114	82	136	197	270	156	112	258
Republic Steel Corporation	119	152	140	152	81	39	104	117	86	143	215	280	164	152	270
	117	169	130	146	75	38	96	114	79	133	206	248	164	152	285
	127	163	133	141	81	40	90	112	82	146	215	275	172	154	272
Mallory-Sharon Titanium Corp.	130	130	140	163	72	45	89	118	79	119	205	286	173	147	309
	148	131	136	159	86	40	87	114	80	121	195	285	174	148	304
	130	130	141	164	75	45	87	114	79	118	199	296	180	148	307
Wyman-Gordon Company	[illegible]	143	132	141	76	35	[illegible]	[illegible]	75	[illegible]	[illegible]	251	152	126	250
	113	133	138	144	76	33	79	95	76	107	[illegible]	267	153	121	255
	110	136	130	148	77	33	78	98	78	115	194	267	152	122	258
Westinghouse Electric Corp.	129	168	145	114	81	26	66	121	77	138	198	281	166	174	260
	127	163	155	105	80	26	78	124	76	134	198	282	166	176	279
	133	175	143	109	82	24	78	122	72	132	196	280	182	183	265
Pratt & Whitney Aircraft	115	129	144	121	82	36	113	114	79	131	214	276	163	163	298
	113	171	146	120	84	35	98	113	87	132	203	266	158	162	292
	114	125	137	118	79	33	87	109	82	151	197	269	156	164	295
Rem-Cru Titanium, Inc.	111	157	124	142	84	36	81	108	73	127	194	213	162	110	262
	111	157	125	142	74	32	84	109	74	128	196	211	159	111	261
	112	152	125	139	83	37	87	111	72	129	197	218	159	109	252
Watertown Arsenal	123	122	104	116	58	29	67	108	75	143	185	246	141	104	247
	146	103	107	112	62	20	73	104	56	131	191	250	147	105	244
	96	112	127	113	56	24	76	93	80	133	183	246	149	100	246
Armour Research Foundation	107	164	122	161	52	9	71	87	79	152	183	261	130	142	231
	115	168	126	151	65	15	77	86	80	151	182	255	130	137	234
	118	163	131	161	60	12	65	91	71	153	189	249	129	140	250
Method IV - Vacuum extraction at from 1300 to 1400°C, sample in molybdenum crucible or boat, analysis from total pressure.															
Brush Laboratories	103	125	121	118	78	34	83	98	81	99	173	246	144	114	264
	~~112~~	~~127~~	~~125~~	~~127~~	~~72~~	~~34~~	~~84~~	~~102~~	~~82~~	~~111~~	~~180~~	~~252~~	~~147~~	~~111~~	~~258~~
	103	128	127	121	74	33	82	98	81	121	164	248	141	113	269
National Research Corp.	118	143	147	115	81	33	84	115	74	157	186	275	169	129	287
	117	134	146	111	79	31	84	110	73	153	188	274	172	129	291
	119	135	149	112	80	31	88	111	74	152	188	276	172	126	296
Method V - Vacuum extraction at 1000°C, sample in resistance heated quartz tube, analysis from total pressure.															
Allegheny-Ludlum Steel	128	142	139	154	72	42	83	105	74	136	180	280	164	129	294
	124	149	141	156	74	43	84	107	78	142	187	275	162	126	294
	126	146	140	155	73	42	84	106	76	139	184	284	164	126	295
Titanium Metals Corporation	134	155	151	161	66	33	88	101	78	128	200	298	172	172	314
	131	141	148	146	77	32	87	110	83	135	202	298	160	172	292
	135	173	136	153	74	32	85	101	78	157	201	295	170	169	305
Method VI - Equilibrium at 1000°C, analysis from equilibrium pressure.															
duPont (1st set)	105	121	121	88	76	26	77	108	71	132	194	232	176	114	249
	107	139	125	103	77	29	84	99	68	129	197	251	149	122	273
	106	145	131	96	58	27	83	109	70	127	191	247	150	125	255
Method VII - Macro-combustion using 5 or 10 gram sample at 900°C with oxygen sweep, hydrogen oxidized to water and weighed.															
Frankford Arsenal	-	-	121	160	102	44	97	120	69	177	231	274	199	150	311
	-	-	135	140	108	51	93	109	88	149	206	274	184	155	327
	-	-	120	124	86	51	109	111	96	160	215	231	175	143	307
Method VIII - Micro-combustion method, using 1/2 gram sample at 1200°C, hydrogen oxidized to water and weighed.															
Dow Chemical Company	114	125	110	163	39	31	86	109	59	142	184	250	148	105	287
	121	135	125	172	47	16	82	123	70	134	190	280	148	122	304
	126	130	117	162	44	19	72	101	74	149	192	255	152	105	296
Method IX - Hot extraction in helium atmosphere, hydrogen oxidized to water and weighed.															
General Electric (ANP Division)	277	305	271	197	220	166	179	88	118	157	321	388	184	207	386
	243	310	246	244	223	109	188	83	129	142	352	381	238	198	373
	214	284	268	214	298	186	155	86	144	165	311	384	247	202	380

this can be separated into components to furnish the desired information if proper experimental design is provided. The Analysis of Variance technique is used for this report, as described below. References to the statistical methods will be found in the Bibliography.

Experimental Model

Alloys for this experiment include nearly all commercially important titanium alloys and represent a range of hydrogen contents from low to high as well. The factor "Alloys" is therefore considered a fixed factor 1/.

Similarly, nearly all known methods for hydrogen analysis are included, so that the factor "Methods" is considered a fixed factor.

Laboratories are naturally associated with some one or more methods of analysis available to them, so that agreement of laboratories using the same method is an observation of interest. The term "Laboratories within Methods" is a nested or hierarchal classification, and the experimental model looks like this

$$\underline{A,\ B,\ c|B}$$

where capital letters designate fixed factors and lower case letters designate random factors.

Here a complication arises. To properly achieve randomness for a nested factor it must represent a random sample of a large population and must be assigned to the factor in which it nests in a random fashion. Lacking this mathematically ideal condition, a restriction is placed on the observation drawn from the "B" factor as will be discussed 2/.

For the ideal condition with random nested factor "c", test ratios are determined as follows:

1/ A fixed factor is one whose levels comprise a finite population. A random factor is one whose levels constitute a random sample from a large population.

2/ Harter, H. L. & Lum, M. D., Partially Hierarchal Models in the Analysis of Variance. WADC Technical Report 55-33, March 1955, pp 3-4.

A, B, c|B

Source	Expected Value of Mean Square	Test Ratio
A	$n_B n_c n_e \sigma^{*2}_A + n_e \sigma^{*2}_{Ac} + \sigma^2_e$	S_A/S_{Ac}
B	$n_A n_c n_e \sigma^{*2}_B + n_A n_e \sigma^2_c + \sigma^2_e$	S_B/S_c
c|B	$n_A n_e \sigma^2_c + \sigma^2_e$	S_c/S_e
AB	$n_c n_e \sigma^{*2}_{AB} + n_e \sigma^{*2}_{Ac} + \sigma^2_e$	S_{AB}/S_{Ac}
Ac|B	$n_e \sigma^{*2}_{Ac} + \sigma^2_e$	S_{Ac}/S_e
e|ABc	σ^2_e	--

where n = the number of levels of the subscript effect and σ^2 = the variance.

If the nesting factor does not meet all of the requirements for randomness, then the mean square for factor "B", Methods, represents a combination of effects. One is the desired effect of Methods and the other is a meaningless effect Laboratories between Methods, which may be large and acting either to inflate or partly cancel the effect of Methods, leading to a wrong conclusion.

For this experiment, the nested factor Laboratories within Methods would have to meet these requirements for randomness:

a. That for each Method there are a great number of Laboratories who may participate

b. That each Laboratory may be directed to use any of the Methods

c. That selection of the Laboratories and assignment to a Method is done in a random fashion.

These requirements cannot be fully met in practice. The resulting weakness in comparing Methods will be examined.

Comparison of Methods for Hydrogen Determination

Table IV presents the analysis of variance for all data except that of Method VII, where results for the first two Alloys were not reported.

The statistically highly significant difference among Alloys is a result of the intentionally provided range of hydrogen contents. (Significance is denoted by an F value larger than that expected for a 5% or a 1% probability that the effect would appear significant by chance alone. The F value is a ratio of the appropriate mean squares, and is determined by the experimental design. Each F value is a test of an hypothesis that the numerator and denominator yield a ratio of 1.0 and a real effect does not exist.)

From the experimental design, a test ratio for Methods is

$$F = S_B / S_c = \frac{\text{mean square for Methods}}{\text{mean square for Laboratories within Methods}}$$

where the denominator is for a <u>random</u> nested factor. Neglecting this restriction, Table IV shows the F value obtained:

$$F = \frac{57,536.5}{3,086.0} = 18.64^{***} \qquad \text{Highly significant.}$$

A mean square can be calculated contrasting Method IX with Other Methods, and tested in the same way:

$$F = \frac{389,393.1}{3,086.0} = 126.18^{***} \qquad \text{Highly significant}$$

And similarly, Method IX can be excluded and a mean square for Other Methods tested:

$$F = \frac{2,227.1}{3,086.0} = 0.72 \qquad \text{Not significant at 5\% level.}$$

Without the knowledge that interpretation of the F value is restricted, Table IV would indicate that once Method IX is excluded the remaining Methods are in agreement. Exclusion of Method IX is supported by inspection of the raw data; the further inference that remaining Methods are in agreement is uncertain.

WADC Materials Laboratory analyzed the same Alloy specimen by both Methods I and III (vacuum fusion operated at 1900°C and 1400°C). If the data are used for a separate analysis of variance, Table V, a significant difference between the two Methods is seen:

$$F = \frac{\text{mean square for Method I vs. Method III}}{\text{mean square for triplicate observations (error)}}$$

$$F = \frac{211.6}{20.4} = 10.4^{**} \qquad \text{Significant at the 1\% level.}$$

TABLE IV

COMPARISON OF METHODS FOR HYDROGEN DETERMINATION, EXCLUDING METHOD VII WHERE DATA IS INCOMPLETE

STATISTICAL ANALYSIS OF VARIANCE

Source of Variation	D.F.	Sum of Squares	Mean Square	Test by	F	Req'd for Significance 5% 1% levels
(1) Among Alloys	14	4,249,560.5	303,540.0	(6)	665.07***	1.74/2.17
(2) Among all Methods	7	402,755.7	57,536.5	(3)	18.64***	2.70/4.14
Method IX vs. others	1	389,393.1	389,393.1	(3)	126.18***	4.54/8.68
Among other Methods	6	13,362.6	2,227.1	(3)	0.72	2.79/4.32
(3) Labs within Methods	15	46,289.8	3,086.0	(7)	62.34***	1.69/2.08
(4) Alloys x Methods	98	144,626.0	1,475.8	(5)	3.23**	1.32/1.48
Alloys x Method IX vs. Others	14	109,758.1	7,839.9	(5)	17.18***	1.74/2.17
Alloys x Other Methods	84	34,867.9	415.1	(5)	0.91	1.34/1.52
(5) Alloys x Labs within Methods	210	95,852.6	456.4	(7)	9.22***	1.21/1.31
(6) Among triplicate observations	663	47,102.1	71.0	---	---	
for Method IX	26	15,567.3	598.7	(7)	12.09***	1.52/1.79
(7) for other Methods	637	31,534.8	49.5	---	---	
Total	1007	4,986,186.6				

Data: Method I through IX, excluding that of Method VII. 23 Laboratories, 15 Alloys, 3 Observations per specimen. 27 degrees of freedom lost when missing values supplied as shown in Appendix, reducing error term from 690 to 663 and total from 1037 to 1007.

* denotes significance at 5% level, ** at 1% level, *** very highly significant.

TABLE V

COMPARISON OF METHODS I AND III USED BY WADC MATERIALS LABORATORY FOR HYDROGEN DETERMINATIONS ON THE SAME SPECIMEN

STATISTICAL ANALYSIS OF VARIANCE

Source of Variation	D.F.	Sum of Squares	Mean Square	Test by	F	Req'd for Significance 5% 1% levels
(1) Among Alloys	14	352,079.0	25,148.5	(3)	1237.7***	1.86/2.40
(2) Between Methods	1	211.6	211.6	(3)	10.4**	4.00/7.08
Alloys x Methods	14	436.7	31.2	(3)	1.5	1.86/2.40
(3) Among triplicate observations	60	1,224.0	20.4	-		
Total	89	353,951.3				

* denotes significance at 5% level, ** at 1% level, *** very highly significant.

This gives an idea of the weakness of the Table IV comparison of Other Methods, imposed by deviations from randomness of the Laboratories within Methods term by which Methods were tested.

The conclusions from comparison of Methods, then:

a. One Method is readily seen to differ from the rest

b. The analysis of variance suggests that non-agreement due to the remaining Methods is less than non-agreement among Laboratories themselves

c. No inference about agreement among the remaining Methods is really justified

d. To establish an exact test for agreement among Methods, a much more elaborate experiment would be required with replication for each Laboratory to provide the necessary randomness.

Comparison of Laboratories within Methods

While non-randomness of the nested factor Laboratories weakens the comparison of Methods since this is the yardstick by which Methods are judged, the non-randomness does not jeopardize comparison of Laboratories themselves.

The straightforward test would be to disregard the classification by Methods and to test the factor Laboratories by an error term derived from all triplicate observations. Doing this, non-agreement is readily seen. The next question is whether Laboratories using any one Method might agree among themselves. The error term is derived for only the Laboratories being tested.

Method	Laboratories M.S.	Error S.S.	(triplicate obs.) D.F.	M.S.	F	Req'd for Significance
I	5399.9	9862.7	118	83.58	64.61***	2.68/3.95
II	156.8	6020.0	90	66.89	2.34	3.10/4.85
III	3065.3	9196.0	266	34.57	88.67***	1.98/2.58
IV	4080.4	790.7	60	13.18	309.59***	4.00/7.08
V	1173.7	1844.7	48	38.43	30.54**	4.04/7.19

The three Laboratories using Method II appear to be in agreement; elsewhere, Laboratories using the same Method do not all agree. Undoubtedly it would be possible to select pairs or groups of Laboratories which agree, and might agree also with the Laboratories of Method II, but this grouping would not correspond to a classification by the Method used.

Agreement does not imply accuracy, for no absolute standards exist by which accuracy can be judged. It would be sufficient for the present if Laboratory agreement could be achieved, or at least if Laboratories were known to differ by a constant and predictable bias.

To see if a fixed bias exists for any of the Laboratories, a regression line (the best fitting straight line for all of the hydrogen values) for each Laboratory is shown in Figures 11 through 15. Calculations are similar to the familiar method of least squares for curve fitting.

It is to be expected that the slopes of these regression lines will vary from unity (which would represent perfect agreement with calculated mean hydrogen values), but the lines should be clustered fairly closely about the dashed unity-slope line. Only the regression line is shown. "Goodness of Fit" of actual points to the regression line is indicated by the term sum of deviations from regression, $\sum d^2_{y \cdot x}$.

A regression line paralleling the dashed line and separated from it by an appreciable distance would be an indication of a fixed bias. Several of the Laboratories show such a bias; most, however, show regression lines skewed to the dashed line so that an average bias determined at the center would not hold over the entire range of hydrogen values.

Agreement among Laboratories can be forced by using as a correction factor the average of the bias at 0 ppm hydrogen and the bias at 300 ppm hydrogen, applying this to each hydrogen value for the Laboratory. To obtain agreement, it is necessary to adjust every Laboratory having a bias of 4 ppm or greater. The adjustment will naturally be most effective near the center of skewed lines, but this range of hydrogen values around 150 ppm is the one of most practical importance.

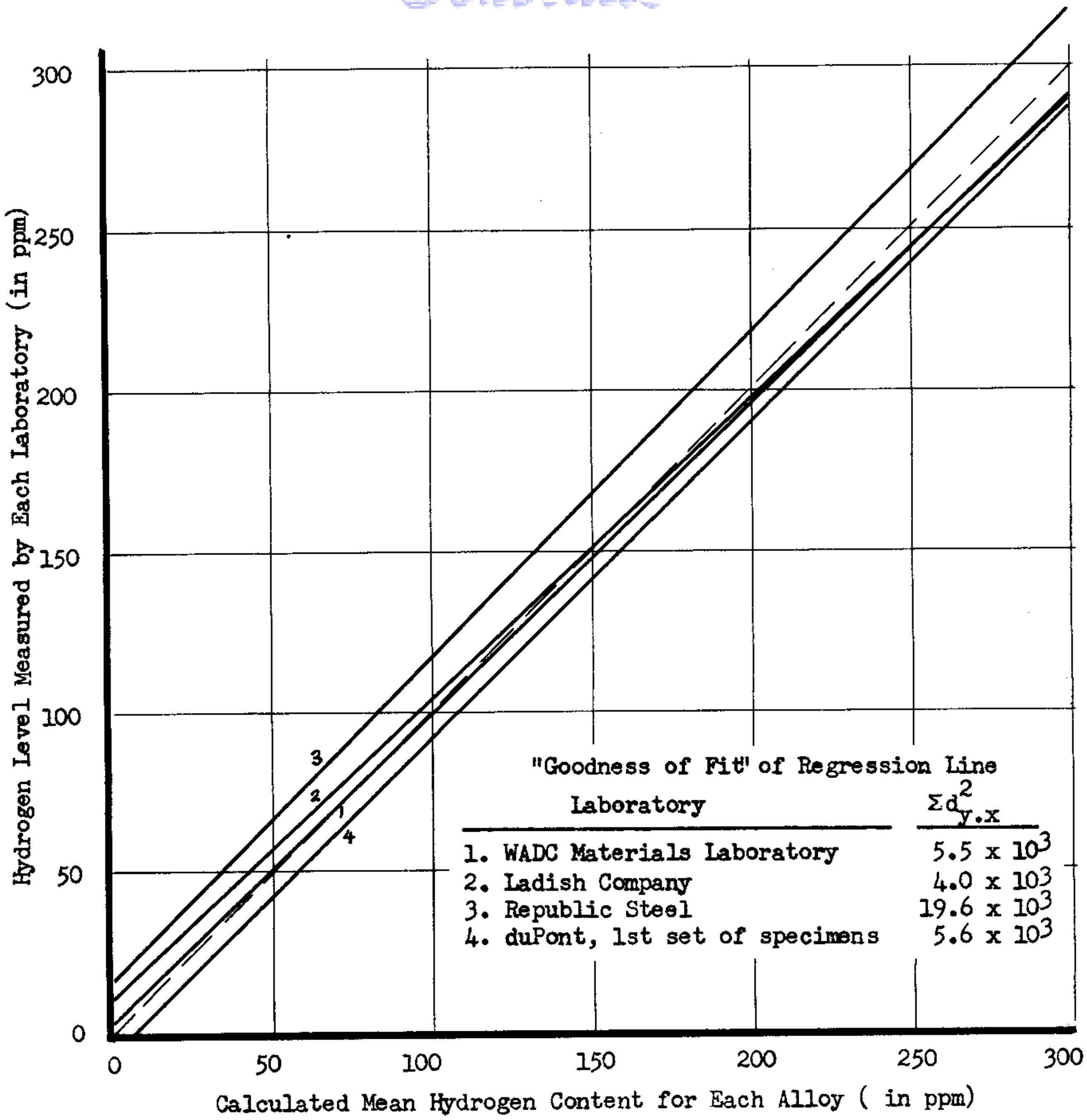
Table VI shows the average bias determined for each Laboratory. It is not recommended that these correction factors be adopted by the individual Laboratories without further confirmation.

Specimen Non-Uniformity

Just by inspection, there is reason to suspect that specimens of the same alloy differed in hydrogen content. In the statistical analysis of Table IV, the effect appears in the term Alloys by Laboratories within Methods. Three other sources possibly contribute to the interaction significance:

a. The alloying elements by which Alloys differed may influence a Laboratory's ability to determine hydrogen.

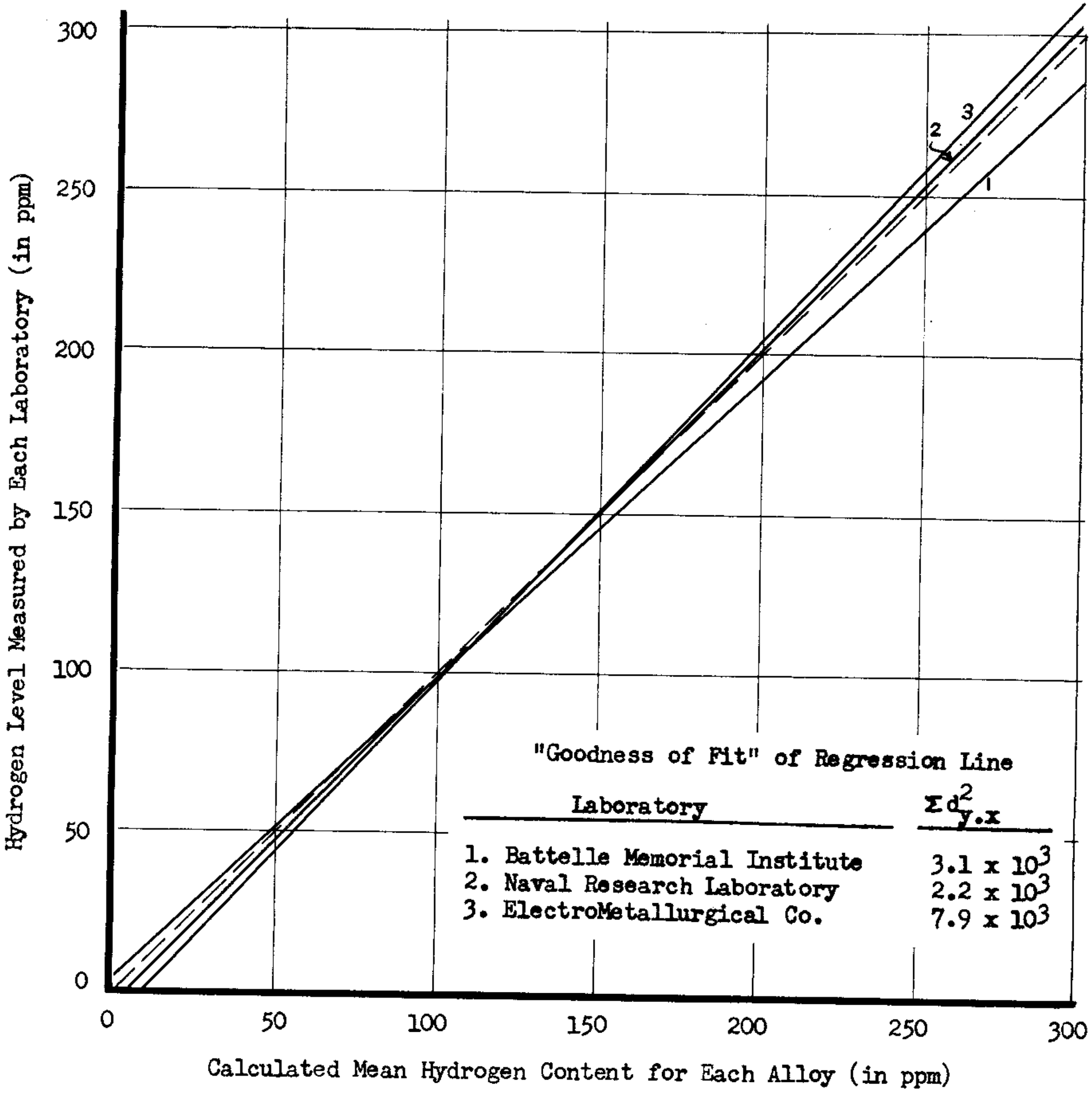
b. A Laboratory's accuracy may not be consistent over the range of hydrogen contents provided.



"Goodness of Fit" of Regression Line

Laboratory	$\Sigma d^2_{y.x}$
1. WADC Materials Laboratory	5.5×10^3
2. Ladish Company	4.0×10^3
3. Republic Steel	19.6×10^3
4. duPont, 1st set of specimens	5.6×10^3

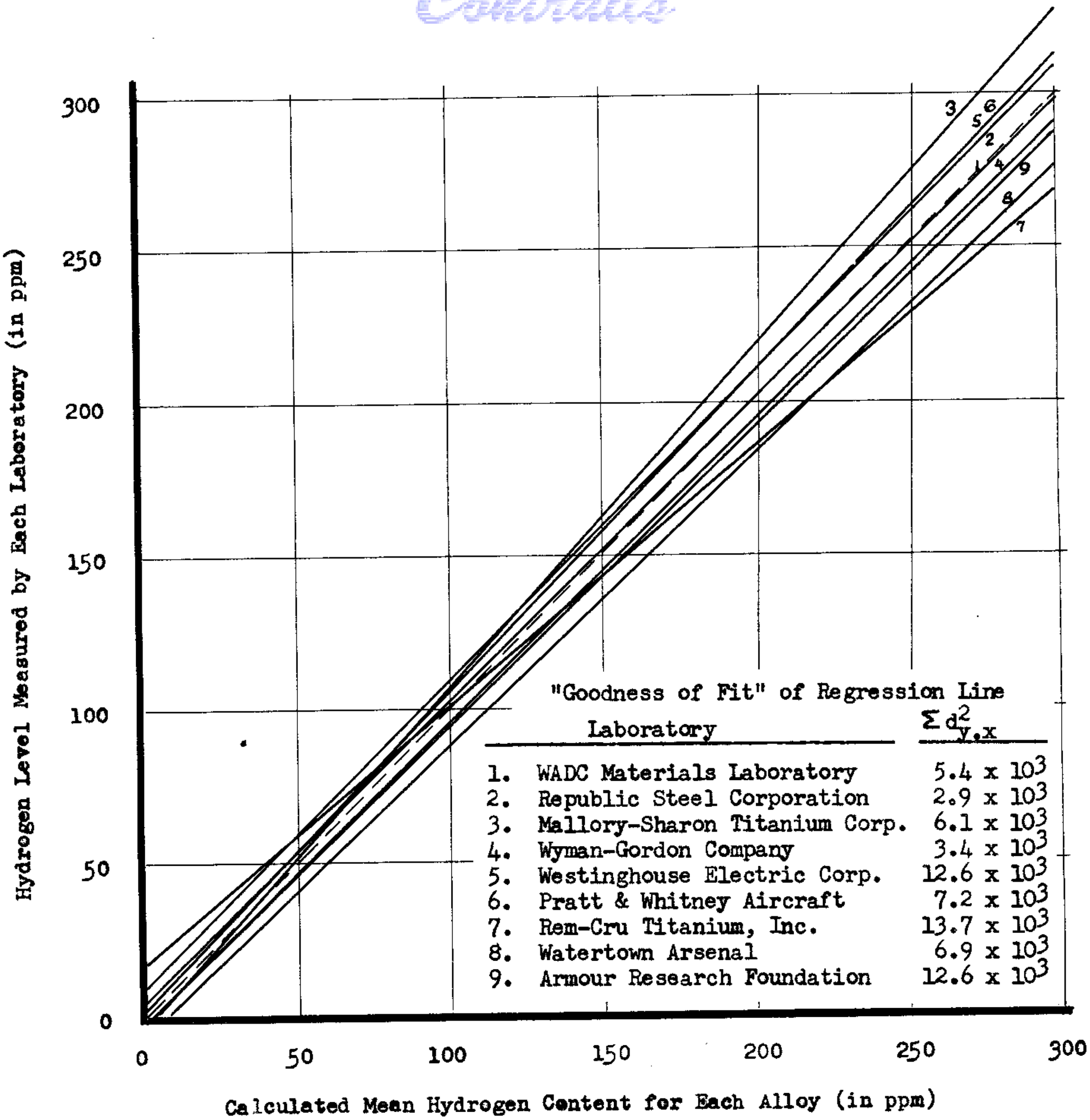
Figure 11 - Regression Lines for Laboratories Using Method I.



"Goodness of Fit" of Regression Line

Laboratory	$\Sigma d^2_{y.x}$
1. Battelle Memorial Institute	3.1×10^3
2. Naval Research Laboratory	2.2×10^3
3. ElectroMetallurgical Co.	7.9×10^3

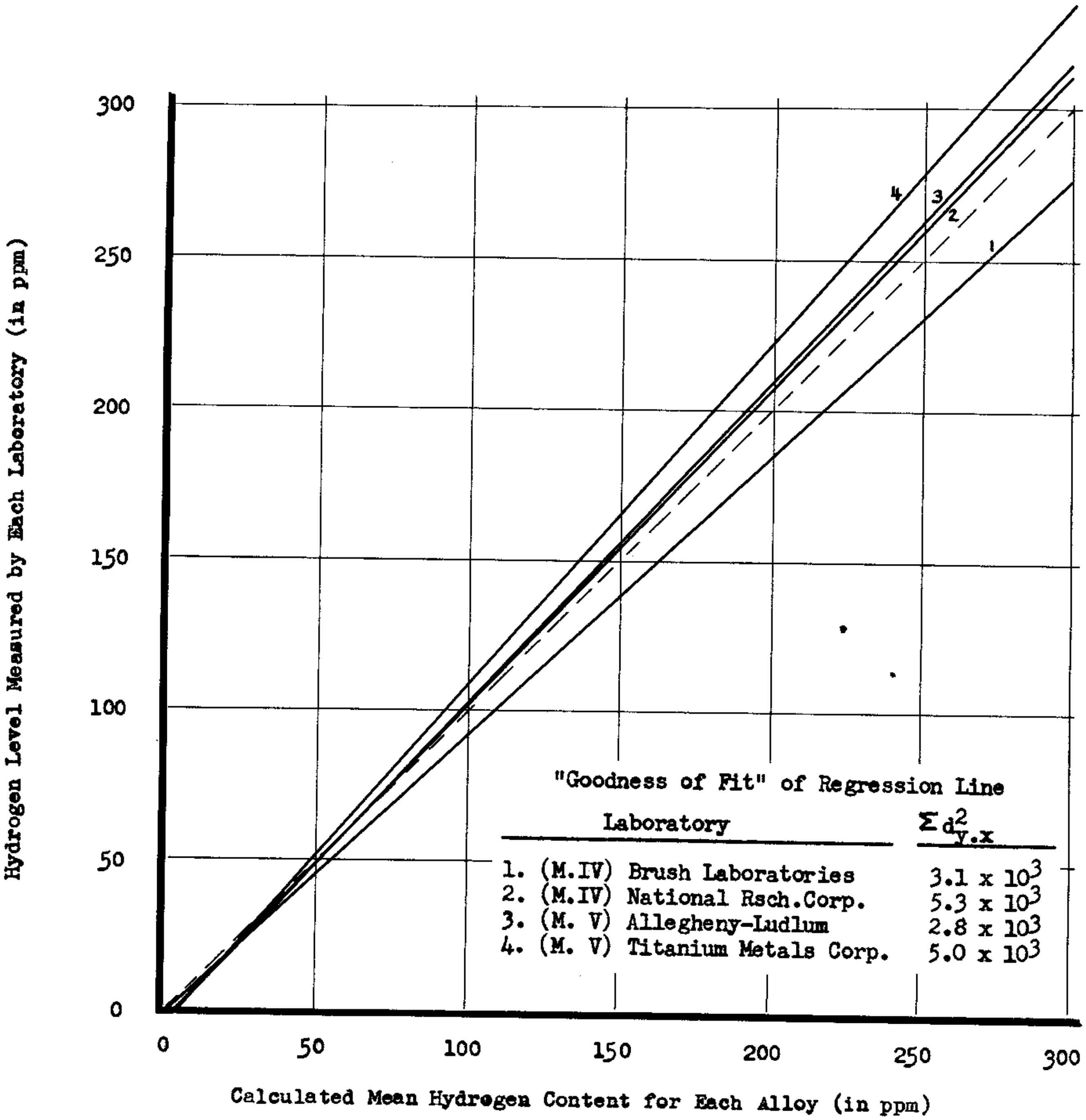
Figure 12 - Regression Lines for Laboratories Using Method II.



"Goodness of Fit" of Regression Line

Laboratory	$\Sigma d^2_{y.x}$
1. WADC Materials Laboratory	5.4 x 10^3
2. Republic Steel Corporation	2.9 x 10^3
3. Mallory-Sharon Titanium Corp.	6.1 x 10^3
4. Wyman-Gordon Company	3.4 x 10^3
5. Westinghouse Electric Corp.	12.6 x 10^3
6. Pratt & Whitney Aircraft	7.2 x 10^3
7. Rem-Cru Titanium, Inc.	13.7 x 10^3
8. Watertown Arsenal	6.9 x 10^3
9. Armour Research Foundation	12.6 x 10^3

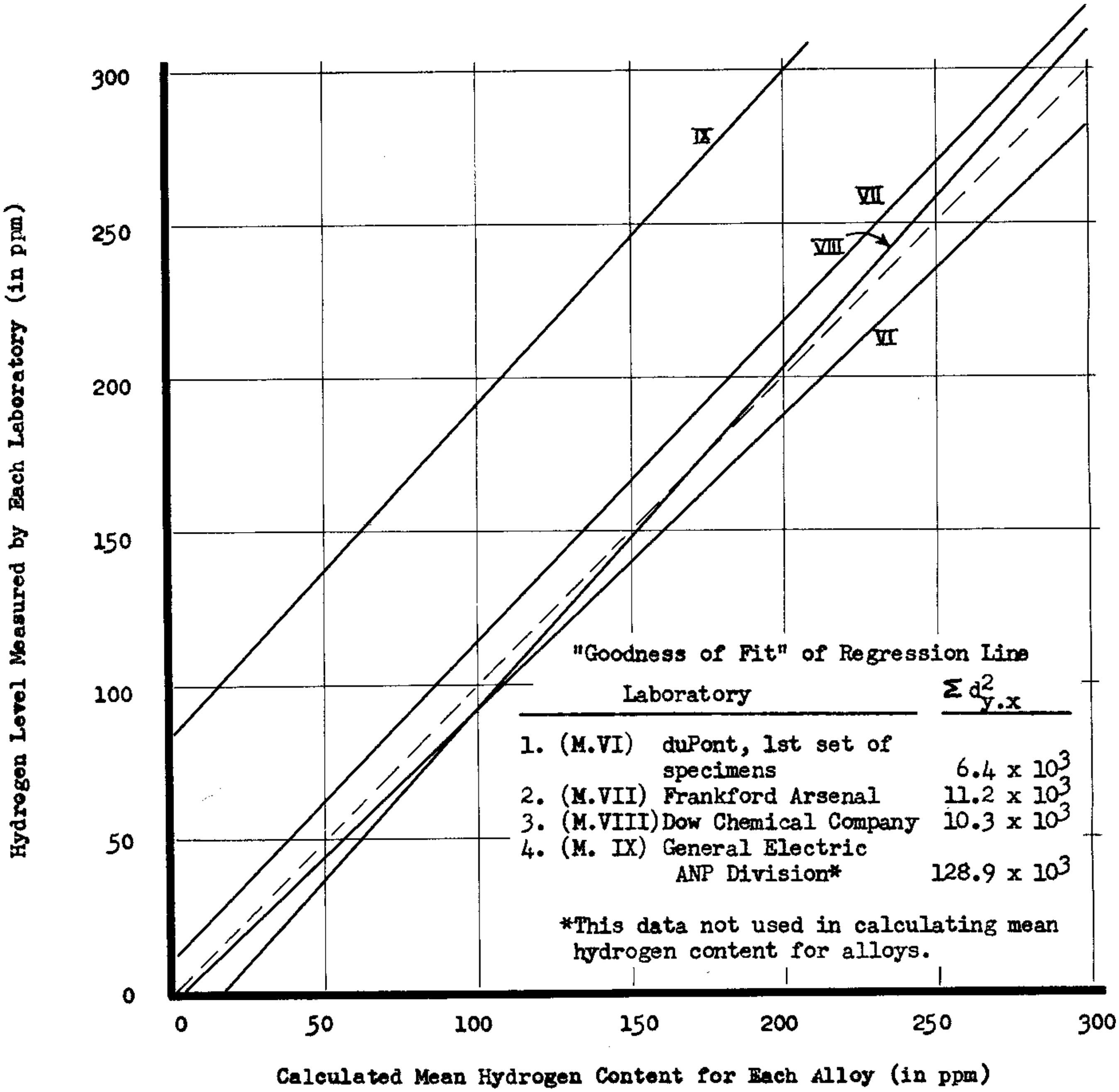
Figure 13 - Regression Lines for Laboratories Using Method III.



"Goodness of Fit" of Regression Line

Laboratory	$\Sigma d^2_{y.x}$
1. (M.IV) Brush Laboratories	3.1×10^3
2. (M.IV) National Rsch.Corp.	5.3×10^3
3. (M. V) Allegheny-Ludlum	2.8×10^3
4. (M. V) Titanium Metals Corp.	5.0×10^3

Figure 14 - Regression Lines for Laboratories Using Methods IV and V.



"Goodness of Fit" of Regression Line

Laboratory	$\Sigma d^2_{y.x}$
1. (M.VI) duPont, 1st set of specimens	6.4×10^3
2. (M.VII) Frankford Arsenal	11.2×10^3
3. (M.VIII) Dow Chemical Company	10.3×10^3
4. (M. IX) General Electric ANP Division*	128.9×10^3

*This data not used in calculating mean hydrogen content for alloys.

Figure 15 - Regression Lines for Laboratories Using Methods VI, VII, VIII, and IX.

TABLE VI

DETERMINING AVERAGE BIAS FOR LABORATORIES FROM REGRESSION LINES, FOR ADJUSTING HYDROGEN VALUES TO FORCE LABORATORY AGREEMENT

Method and Laboratory		Slope b	y intercept (x = 0 ppm) a	Bias at x = 300 ppm	Average Bias
I	WADC Materials Lab.	0.9631	+ 3	- 8	- 2
	Ladish Company	0.9527	+ 11	- 11	0
	Republic Steel Corp.	1.0125	+ 15	+ 19	+ 17
	duPont	0.9842	- 7	- 12	- 9
II	Battelle Mem. Inst.	0.9412	+ 4	- 14	- 5
	Naval Research Lab.	1.0290	- 5	+ 4	0
	Electro Metallurgical Co.	1.0675	- 10	+ 10	0
III	WADC Materials Lab.	0.9715	+ 5	- 3	+ 1
	Republic Steel Corp.	0.9946	+ 9	+ 8	+ 8
	Mallory-Sharon	1.0973	- 4	+ 26	+ 11
	Wyman-Gordon Co.	0.9725	- 1	- 9	- 5
	Westinghouse	1.0335	+ 2	+ 12	+ 7
	Pratt & Whitney Acft.	1.0360	+ 2	+ 12	+ 7
	Rem-Cru Titanium	0.8393	+ 17	- 31	- 7
	Watertown Arsenal	0.9416	- 6	- 23	- 14
	Armour Research Fndn.	0.9601	- 1	- 13	- 7
IV	Brush Laboratories	0.9247	- 1	- 24	- 12
	National Research Corp.	1.0535	- 4	+ 12	+ 4
V	Allegheny-Ludlum	1.0545	- 2	+ 14	+ 6
	Titanium Metals Corp.	1.1365	- 6	+ 34	+ 14
VI	duPont	0.9527	- 3	- 17	- 10
VII	Frankford Arsenal	1.0318	+ 11	+ 20	+ 15
VIII	Dow Chemical Company	1.0976	- 17	+ 12	- 2
IX	General Electric (ANP Division)	1.0759	+ 85	+108	+ 97

c. Some Laboratories may have obtained the triplicate determinations for an Alloy specimen in one analytical run, with day-to-day differences appearing between Alloy specimens. Day-to-day differences should appear randomly among the triplicate determinations to yield the best estimate of analytical capability (the truest error term).

These three effects, along with specimen differences in hydrogen content, cannot be separated, but are represented together in the Laboratory-Alloy interaction term. It would be possible to separate them by proper replication in an experimental design if the additional information warranted the hydrogen determinations required.

Suspicions of specimen differences are confirmed by Alloys RR 4 and RR 14, where the same bar was reintroduced in the experiment with specimens machined from opposite ends. Each specimen was taken as an element of the bar, from near-center to near-surface. No difference is found between ends, but is found between elements within ends. Radial non-uniformity is far more pronounced than longitudinal non-uniformity. Several other bars were examined, Table VII, and found also to exceed the variation to be expected from chance alone.

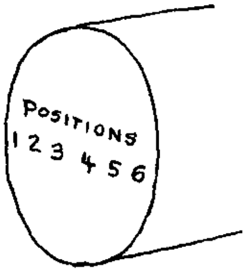
Two sets of specimens were distributed to duPont, who analyzed each set by both Method I and Method VI. This in effect provides the desired replication so that further information can be obtained from this data, as presented in Tables VIII and IX. The term Specimens of Table IX corresponds to the Laboratory classification of previous tables, and by not showing significance confirms that specimen non-uniformity does not prejudice Laboratory comparisons. The important information sought from Table IX, however, is a distinction between the effect of specimen differences and other sources which would contribute to an interaction term.

If the other sources - that is, inability to handle the alloying elements, or the extended range of hydrogen contents, or if day-to-day errors appeared between specimens of the various alloys - acted to inflate the interaction term, these would appear for either set of specimens. Differences between specimens would appear only in the interaction term when the two sets are compared. In Table IX, only the interaction term comparing the two sets of specimens is significant. Lack of significance for either set alone indicates the three other sources for an inflated interaction are not of major importance.

Without this type of experimental replication, this observation cannot be made for other Laboratories and Methods.

TABLE VII

HYDROGEN DISTRIBUTION ACROSS THE DIAMETER OF THREE BARS, RR 5, RR 8, AND RR 9



	Hydrogen Distribution (in ppm)		
	RR 5	RR 8	RR 9
Position 1	63	114	72
	63	113	72
2	84	113	77
	81	114	76
3	86	111	77
	84	109	77
4	86	108	74
	84	110	72
5	69	109	72
	73	110	71
6	66	109	66
	64	112	67

Hydrogen determinations obtained by WADC Materials Laboratory.

TABLE VIII

HYDROGEN DETERMINATIONS (in ppm) FOR STATISTICAL ANALYSIS, duPONT RESULTS FROM TWO SETS OF SPECIMENS ANALYZED BY TWO METHODS

Sample Designation

	RR 1	RR 2	RR 3	RR 4	RR 5	RR 6	RR 7	RR 8	RR 9	RR 10	RR 11	RR 12	RR 13	RR 14	RR 15
Method I - Vacuum extraction at 1900°C, samples in tin bath, analysis from differential pressures.															
duPont (1st set)	104	134	121	100	70	34	75	99	65	124	186	232	155	121	271
	102	145	119	89	69	30	78	98	66	135	197	255	155	119	270
	100	138	122	(94)	73	29	83	104	74	134	189	255	156	127	271
(2nd set)	107	120	128	130	59	44	85	102	66	105	193	249	140	94	278
	106	117	126	128	61	36	95	96	69	106	193	244	140	93	260
	107	129	123	131	60	40	93	102	71	106	192	247	130	89	279
Method VI - Equilibrium at 1000°C, analysis from equilibrium pressure.															
duPont (1st set)	105	121	121	88	76	26	77	108	71	132	194	232	176	114	249
	107	139	125	103	77	29	84	99	68	129	197	251	149	122	273
	(106)	145	131	96	58	27	83	109	70	127	191	247	150	125	255
(2nd set)	110	124	127	130	70	45	88	99	65	108	192	258	135	101	282
	108	116	134	135	69	45	87	97	64	112	185	243	137	99	264
	(109)	109	125	139	68	46	92	(98)	(64)	(110)	198	251	139	103	276

Note: Values inclosed by parentheses were supplied as shown in Appendix.

TABLE IX

COMPARISON OF duPONT HYDROGEN ANALYSES FOR TWO SETS OF SPECIMENS

STATISTICAL ANALYSIS OF VARIANCE

Source of Variation	D.F.	Sum of Squares	Mean Square	Test by	F	Req'd for Significance 5% 1% levels
(1) Among Alloys	14	696,266.6	49.733.3	(4)	1484.64***	1.78/2.24
(2) Specimens						
1st set vs. 2nd set	1	60.1	60.1	(4)	1.79	3.93/6.88
within set 1	1	0.3	0.3	(4)	0.09	3.93/6.88
within set 2	1	84.1	84.1	(4)	2.51	3.93/6.88
(3) Alloys x Specimens						
Alloys x 1st set vs. 2nd set	14	10,935.9	781.1	(4)	23.32***	1.78/2.24
Alloys x set 1	14	427.5	30.5	(4)	0.91	1.78/2.24
Alloys x set 2	14	407.0	29.1	(4)	0.87	1.78/2.24
(4) Among triplicate observations	114	3,823.3	33.5	---	---	
Total	173	712,004.9				

Data: Hydrogen determinations submitted by duPont for two sets of specimens, each set analyzed by both Method I and Method VII. 15 Alloys, 3 Observations per specimen. 6 degrees of freedom lost when missing hydrogen determinations supplied as shown in Appendix, reducing error term from 120 to 114 and total from 179 to 173.

* denotes significance at 5% level, ** at 1% level, *** very highly significant.

Analytical Reproducibility

Analytical reproducibility expressed in the triplicate hydrogen determinations for each specimen has been the basic yardstick by which experimental factors have been judged.

The mean square or variance derived from these triplicate determinations is the square of the standard deviation, sigma, which is a descriptive term for reproducibility or precision.

A standard deviation taken from the mean square for all analyses in Table IV (excluding those of Method VII & IX) is approximately 7 ppm. This says that in running repeated determinations on the same specimen, about two-thirds of them can be expected to fall within plus or minus 7 ppm of the grand mean of all determinations. This is a composite figure, based on all Laboratories.

Some Laboratories may do better, as shown by Table X. Closer agreement can be obtained by always running check analyses at the same time if day-to-day errors are appreciable, but this is a claim for better analytical capability than is justified and from time to time would cause suspicions of real differences between specimens where none actually exists. It is not known how many of the participating laboratories randomized the order between days when running the triplicate determinations for this experiment, but where known this in indicated in Table X.

Note that even when day-to-day errors were introduced by these Laboratories, the standard deviations nevertheless are lower than for many others. Analytical reproducibility or precision for some of the Laboratories is a cause for concern.

It might be speculated that this evidence of poor reproducibility is actually evidence of non-uniform hydrogen distribution even between analyses taken as close together as possible. There would be some justification for this view, as shown by the following examination of sampling from various heats of mill products.

UNIFORMITY IN DUPLICATE ANALYSES FROM SMALL SAMPLES OF MILL PRODUCTS

When duplicate specimens are taken as closely together as possible, for check analyses, it is presumed that they are identical in hydrogen content. This assumption itself may be questioned, in which case resolving a dispute between laboratories becomes difficult. The four titanium producers were asked to sample six randomly chosen sheets or bars from

TABLE X

COMPARISON OF ANALYTICAL REPRODUCIBILITY FOR LABORATORIES

Method and Laboratory		Variance, triplicate observations	Standard Deviation	
I	WADC Materials Laboratory	25.7	5.1	Includes day error
	Ladish Company	44.5	6.7	
	Republic Steel Corporation (Alloy Division)	232.7	15.2	
	duPont, 1st set of specimens	28.3	5.3	
	duPont, 2nd set of specimens	36.4	6.0	
II	Battelle Memorial Institute	43.4	6.6	Does not include day error
	Naval Research Laboratory	47.4	6.9	
	Electro Metallurgical Co.	140.0	11.8	
III	WADC Materials Laboratory	15.3	3.9	Includes day error
	Republic Steel Corporation (South Division)	47.4	6.9	
	Mallory-Sharon Titanium Corp.	18.6	4.3	
	Wyman-Gordon Company	10.4	3.2	
	Westinghouse Electric Corp.	25.6	5.1	
	Pratt & Whitney Aircraft	41.9	6.5	
	Rem-Cru Titanium, Inc.	7.5	2.7	
	Watertown Arsenal	85.5	9.2	
	Armour Research Foundation	25.6	5.1	
IV	Brush Laboratories	20.9	4.6	Includes day error
	National Research Corporation	5.5	2.3	
V	Allegheny-Ludlum Steel Corp.	7.9	2.8	
	Titanium Metals Corp.	56.8	7.5	
VI	duPont, 1st set of specimens	62.8	7.9	
	duPont, 2nd set of specimens	20.7	4.5	
VII	Frankford Arsenal	162.2	12.7	
VIII	Dow Chemical Company	64.6	8.0	
IX	General Electric Co. (ANP Div)	524.3	22.9	

three heats of one or more alloys, by which an estimate of the difficulties in obtaining satisfactory duplicate specimens could be had.

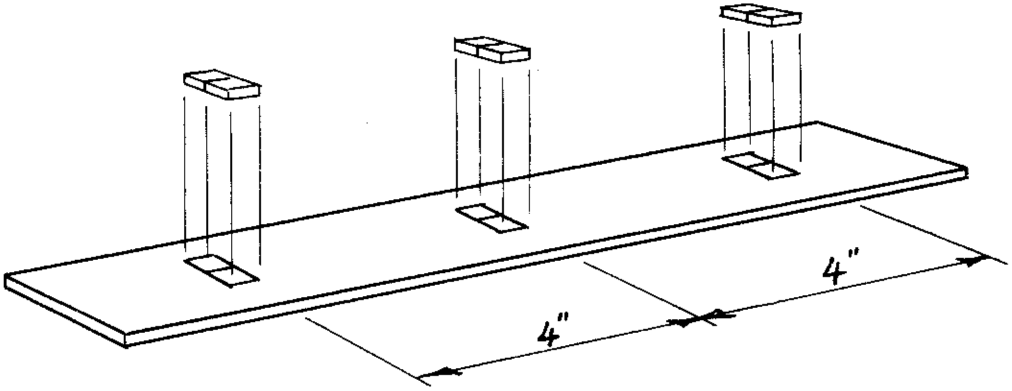
From sheet, the samples were taken as strips about 8 inches long from the perimeter and presumably at the midpoint along an edge. Bar was sampled at some convenient point, either at an end or a cut-in. Randomization of these locations was not attempted both because of its destruction of material and because this experiment did not seek to characterize the entire sheet or bar but rather to examine localized distribution of hydrogen. Figure 16 shows the manner in which positions were layed out on these samples. Designating an end as End 1 and the other as End 2 is merely a convenience and does not imply any special association in this way.

Remembering that this type of sampling is not intended to accurately portray differences between heats or sheets, nevertheless it is interesting that in some cases these differences are great. From position to position within samples, the hydrogen content is sometimes consistent, sometimes not.

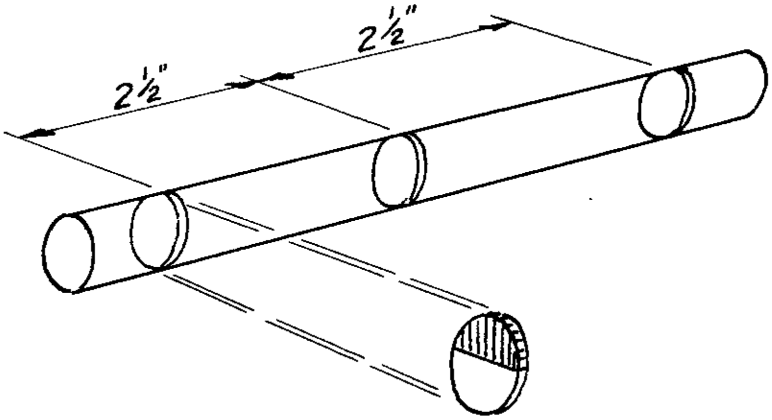
The standard deviations obtained from duplicate determinations for each heat are shown below:

	Heat 1 Std. Dev.	Heat 2 Std. Dev.	Heat 3 Std. Dev.
Ti-140A Sheet WADC Materials Laboratory	1.7	1.3	4.0
8 Mn Sheet, (Republic Steel) WADC Materials Laboratory	4.6	2.7	5.5
8 Mn Sheet, (Rem-Cru) Battelle Memorial Institute	2.1	1.7	1.7
8 Mn Sheet, (Mallory-Sharon) Battelle Memorial Institute	2.5	2.0	2.7

These standard deviations give an idea of how much variation can be expected in results on presumably identical specimens. Battelle analyses did not include day-to-day error, and hence are a more favorable estimate of very localized material non-uniformity. The WADC Materials Laboratory analyses show a possible effect from unavoidable equipment breakdown and delays and change of operators.



Selection of Specimens from Sheet Sample



Selection of Specimens from Bar Sample

Figure 16 - Specimens from Small Samples of Mill Products for Checking Uniformity in Duplicate Analyses.

TABLE XI

HYDROGEN DETERMINATIONS (in ppm) BY WADC MATERIALS LABORATORY ON RANDOM SHEETS FROM THREE HEATS OF Ti-140A

	Heat 1			Heat 2			Heat 3		
	End 1	Center	End 2	End 1	Center	End 2	End 1	Center	End 2
Sheet 1	48 56	47 47	45 49	53 54	57 57	57 58	74 72	63 65	71 67
Sheet 2	44 43	44 43	46 45	55 56	56 56	57 56	63 64	63 81	64 64
Sheet 3	80 81	86 85	75 73	60 56	59 57	60 60	60 59	60 59	70 68
Sheet 4	68 69	62 65	65 66	54 57	51 50	50 52	62 65	62 76	70 69
Sheet 5	74 74	72 72	68 69	59 59	56 54	55 57	67 66	70 71	75 72
Sheet 6	49 49	48 48	45 46	56 53	54 53	53 53	70 69	73 74	77 75

TABLE XII

DISTRIBUTION OF HYDROGEN IN RANDOM SHEETS FROM THREE HEATS OF Ti-140A, DATA OF TABLE XI

STATISTICAL ANALYSIS OF VARIANCE

Source of Variation	D.F.	Sum of Squares	Mean Square	Test by	F	Req'd for Significance 5% 1% levels
(1) Among Heats	2	2,931.1	1,465.6	(2)	3.09	3.68/6.36
(2) Among Sheets within Heats	15	7,100.2	473.3	(3)	22.65***	1.95/2.58
within Heat 1	5	6,581.0	1,316.2	(3)	62.97***	2.48/3.58
within Heat 2	5	151.6	30.3	(3)	1.45	2.48/3.58
within Heat 3	5	367.6	73.5	(3)	3.52*	2.48/3.58
(3) Among Positions with Sheets, Heats	36	751.9	20.9	(4)	3.07**	1.63/2.02
for Heat 1:						
Center vs. Ends pooled	6	118.8	19.8	(4)	2.91*	2.27/3.15
within Ends	6	128.5	21.4	(4)	3.15**	2.27/3.15
for Heat 2:						
Center vs. Ends pooled	6	22.8	3.8	(4)	0.56	2.27/3.15
within Ends	6	52.5	8.8	(4)	1.29	2.27/3.15
for Heat 3:						
Center vs. Ends pooled	6	195.6	32.6	(4)	4.79**	2.27/3.15
within Ends	6	233.7	39.0	(4)	5.74**	2.27/3.15
(4) Among duplicate observations	54	367.5	6.8	---	---	
for Heat 1	18	50.5	2.8	Standard Deviation = 1.7		
for Heat 2	18	28.0	1.6	Standard Deviation = 1.3		
for Heat 3	18	289.0	16.0	Standard Deviation = 4.0		
Total	107	11,150.6				

* denotes significance at 5% level, ** at 1% level, *** very highly significant

TABLE XIII

HYDROGEN DETERMINATIONS (in ppm) BY WADC MATERIALS LABORATORY ON RANDOM SHEETS FROM THREE HEATS OF REPUBLIC STEEL 8 Mn

	Heat 1			Heat 2			Heat 3		
	End 1	Center	End 2	End 1	Center	End 2	End 1	Center	End 2
Sheet 1	73	70	81	70	70	65	62	65	63
	76	69	92	70	65	64	58	61	56
Sheet 2	100	115	104	56	62	64	77	65	64
	101	116	109	60	59	70	79	76	76
Sheet 3	93	104	110	62	59	60	57	69	61
	103	106	108	62	59	59	70	56	63
Sheet 4	75	71	86	81	75	78	69	72	67
	73	73	79	79	75	75	70	74	75
Sheet 5	78	71	86	56	64	51	61	82	82
	76	80	90	56	52	52	79	82	84
Sheet 6	101	84	71	61	62	63	82	78	77
	96	75	86	59	60	62	82	79	75

TABLE XIV

DISTRIBUTION OF HYDROGEN IN RANDOM SHEETS FROM THREE HEATS OF 8 Mn, DATA OF TABLE XIII

STATISTICAL ANALYSIS OF VARIANCE

	Source of Variation	D.F.	Sum of Squares	Mean Square	Test by	F	Req'd for Significance 5% 1% levels
(1)	Among Heats	2	11,529.1	5,764.5	(2)	9.31**	3.68/6.36
(2)	Among Sheets within Heats	15	9,291.1	619.4	(3)	10.96***	1.95/2.58
	within Heat 1	5	5,806.8	1,161.4	(3)	20.56***	2.48/3.58
	within Heat 2	5	1,738.1	347.6	(3)	6.15**	2.48/3.58
	within Heat 3	5	1,746.2	349.2	(3)	6.18**	2.48/3.58
(3)	Among Positions within Sheets, Heats	36	2,035.0	56.5	(4)	2.90**	1.63/2.02
	for Heat 1:						
	Center vs. Ends pooled	6	581.7	97.0	(4)	4.97**	2.27/3.15
	within Ends	6	894.3	149.0	(4)	7.64**	2.27/3.15
	for Heat 2:						
	Center vs. Ends pooled	6	47.7	8.0	(4)	0.41	2.27/3.15
	within Ends	6	156.3	26.0	(4)	1.33	2.27/3.15
	for Heat 3:						
	Center vs. Ends pooled	6	81.3	13.6	(4)	0.70	2.27/3.15
	within Ends	6	273.7	45.6	(4)	2.34*	2.27/3.15
(4)	Among duplicate observations	54	1,052.1	19.5	---	----	
	for Heat 1	18	377.5	20.9	Standard Deviation = 4.6		
	for Heat 2	18	127.5	7.1	Standard Deviation = 2.7		
	for Heat 3	18	547.0	30.4	Standard Deviation = 5.5		
	Total	107	23,907.3				

* denotes significance at 5% level, ** at 1% level, *** very highly significant.

TABLE XV

HYDROGEN DETERMINATIONS (in ppm) BY BATTELLE MEMORIAL INSTITUTE ON RANDOM SHEETS FROM THREE HEATS OF REM-CRU 8 Mn

		Heat 1			Heat 2			Heat 3	
	End 1	Center	End 2	End 1	Center	End 2	End 1	Center	End 2
Sheet 1	79 79	79 80	81 82	88 90	86 86	86 84	66 70	63 64	64 62
Sheet 2	73 82	78 77	78 76	85 85	90 86	93 95	84 84	81 82	79 81
Sheet 3	77 78	74 76	78 72	79 81	82 83	83 81	69 72	79 79	75 75
Sheet 4	74 76	80 80	78 74	78 75	74 77	76 75	72 71	64 66	66 65
Sheet 5	72 71	73 72	72 70	108 108	93 91	97 92	60 59	54 59	58 58
Sheet 6	86 84	90 92	86 84	92 94	92 94	94 97	86 82	79 83	72 74

TABLE XVI

DISTRIBUTION OF HYDROGEN IN RANDOM SHEETS FROM THREE HEATS OF 8 Mn, DATA OF TABLE XV

STATISTICAL ANALYSIS OF VARIANCE

	Source of Variation	D.F.	Sum of Squares	Mean Square	Test by	F	Req'd for Significance 5% 1% levels
(1)	Among Heats	2	4,914.4	2,457.2	(2)	6.96**	3.68/6.36
(2)	Among Sheets within Heats	15	5,292.3	352.8	(3)	15.54***	1.95/2.58
	within Heat 1	5	786.8	157.4	(3)	6.93**	2.48/3.58
	within Heat 2	5	1,973.7	387.5	(3)	17.07***	2.48/3.58
	within Heat 3	5	2,531.8	506.4	(3)	22.31***	2.48/3.58
(3)	Among Positions within Sheets, Heats	36	818.0	22.7	(4)	6.68**	1.63/2.02
	for Heat 1:						
	Center vs. Ends pooled	6	80.0	13.3	(4)	3.91**	2.27/3.15
	within Ends	6	14.0	2.3	(4)	0.68	2.27/3.15
	for Heat 2:						
	Center vs. Ends pooled	6	123.8	20.6	(4)	6.06**	2.27/3.15
	within Ends	6	290.5	48.4	(4)	14.24***	2.27/3.15
	for Heat 3:						
	Center vs. Ends pooled	6	89.2	14.9	(4)	4.38**	2.27/3.15
	within Ends	6	220.5	36.8	(4)	10.82**	2.27/3.15
(4)	Among duplicate observations	54	186.0	3.4	---	---	
	for Heat 1	18	83.5	4.6	Standard Deviation = 2.1		
	for Heat 2	18	51.0	2.8	Standard Deviation = 1.7		
	for Heat 3	18	51.5	2.9	Standard Deviation = 1.7		
	Total	107	11,210.7				

* denotes significance at 5% level, ** at 1% level, *** very highly significant.

TABLE XVII

HYDROGEN DETERMINATIONS (in ppm) BY BATTELLE MEMORIAL INSTITUTE ON RANDOM SHEETS FROM THREE HEATS OF MALLORY-SHARON 8 Mn

	Heat 1			Heat 2			Heat 3		
	End 1	Center	End 2	End 1	Center	End 2	End 1	Center	End 2
Sheet 1	183 183	188 188	187 186	146 148	156 158	156 159	146 143	134 135	134 131
Sheet 2	178 177	188 194	189 188	141 146	155 153	153 152	138 143	132 132	128 127
Sheet 3	191 192	197 195	194 191	155 157	155 156	150 151	133 133	137 136	142 141
Sheet 4	206 195	191 196	196 200	147 149	148 150	152 152	158 158	155 158	157 169
Sheet 5	191 189	192 191	198 196	155 151	156 155	145 146	152 155	148 146	146 148
Sheet 6	184 182	186 185	190 192	167 160	149 150	144 148	154 156	157 156	152 158

TABLE XVIII

DISTRIBUTION OF HYDROGEN IN RANDOM SHEETS FROM THREE HEATS OF 8 Mn, DATA OF TABLE XVII

STATISTICAL ANALYSIS OF VARIANCE

Source of Variation	D.F.	Sum of Squares	Mean Square	Test by	F	Req'd for Significance 5% 1% levels
(1) Among Heats	2	42,459.0	21,229.5	(2)	72.80***	3.68/6.36
(2) Among Sheets within Heats	15	4,372.0	291.5	(3)	6.10**	1.95/2.58
within Heat 1	5	725.6	145.1	(3)	3.04*	2.48/3.58
within Heat 2	5	109.5	21.9	(3)	0.46	2.48/3.58
within Heat 3	5	3,536.9	707.4	(3)	14.80***	2.48/3.58
(3) Among Positions within Sheets, Heats	36	1,720.0	47.8	(4)	8.10**	1.63/2.02
for Heat 1:						
Center vs. Ends pooled	6	173.2	28.9	(4)	4.90**	2.27/3.15
within Ends	6	253.5	42.3	(4)	7.17**	2.27/3.15
for Heat 2:						
Center vs. Ends pooled	6	175.0	29.2	(4)	4.95**	2.27/3.15
within Ends	6	600.0	100.0	(4)	16.95***	2.27/3.15
for Heat 3:						
Center vs. Ends pooled	6	65.8	10.9	(4)	1.85	2.27/3.15
within Ends	6	452.5	75.4	(4)	12.78**	2.27/3.15
(4) Among duplicate observations	54	318.0	5.9	---	---	
for Heat 1	18	116.5	6.5	Standard Deviation = 2.5		
for Heat 2	18	72.5	4.0	Standard Deviation = 2.0		
for Heat 3	18	129.0	7.2	Standard Deviation = 2.7		
Total	107	48,869.0				

* denotes significance at 5% level, ** at 1% level, *** very highly significant.

TABLE XIX

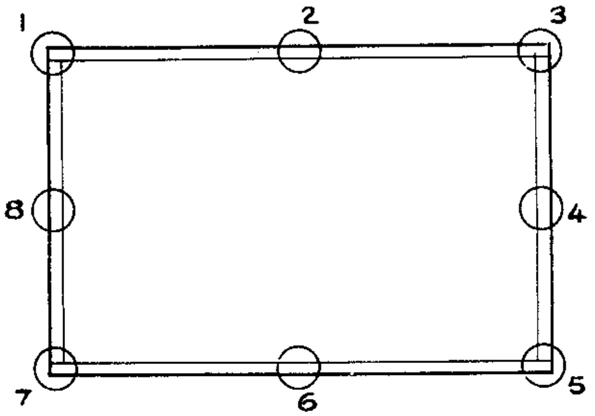
HYDROGEN DETERMINATIONS (in ppm) BY REM-CRU
ON RANDOM BARS FROM THREE HEATS OF C-130AM

	Heat 1			Heat 2			Heat 3		
	End 1	Center	End 2	End 1	Center	End 2	End 1	Center	End 2
Bar 1	121	117	112	93	90	97	101	104	100
Bar 2	118	113	108	125	130	128	104	104	99
Bar 3	84	85	84	99	98	104	97	101	87
Bar 4	87	89	87	103	103	101	92	99	93
Bar 5	86	84	84	98	92	95	96	91	96
Bar 6	97	98	102	98	101	99	89	95	85

SUGGESTED EXPERIMENTS FOR RESOLVING DISPUTES BETWEEN LABORATORIES

<u>Conditions</u>: A single sheet of material involved, with two laboratories disagreeing.

<u>Sampling</u>:



a. Six individual specimens cut at each position, three randomly assigned after cutting to each laboratory.

b. Each laboratory to perform the required twenty-four determinations in a single run if possible. If not, both laboratories must agree to randomly assign individual specimens among the alloted days.

<u>Data</u>:

	Sheet Positions							
	1	2	3	4	5	6	7	8
Lab A	x	x	x	x	x	x	x	x
	x	x	x	x	x	x	x	x
	x	x	x	x	x	x	x	x
Lab B	x	x	x	x	x	x	x	x
	x	x	x	x	x	x	x	x
	x	x	x	x	x	x	x	x

It is important that no specimens be lost during analysis.

Calculations

I. Calculate $\bar{X}$ and R, for each laboratory and for data pooled.

$\bar{X}$ = Average; R = Range

II. Analysis of variance:

Source of Variation	Degrees of Freedom	Sum of Squares	Mean Square	Test by	F	Req'd for Significance 5% 1% levels
(1) Between Labs	1			(4)		4.15/7.50
(2) Among Positions	7			(4)		2.32/3.25
(3) Labs x Positions	7			(4)		2.32/3.25
(4) Among triplicate determinations	32			---		-----
for Lab A	16					
for Lab B	16					
Total	47					

To find Sums of Squares:

S.S. Total = $\Sigma(X^2) - \frac{\Sigma X}{48}$ where X = the individual hydrogen value,

$\Sigma(X^2)$ = the sum of each value squared

S.S. Labs = $\frac{(\Sigma L_A - \Sigma L_B)^2}{48}$ where ΣL_A = the sum of values obtained by Lab A.

$$\text{S.S. Positions} = \frac{(\Sigma 1)^2 + (\Sigma 2)^2 + (\Sigma 3)^2 + (\Sigma 4)^2 + (\Sigma 5)^2 + (\Sigma 6)^2 + (\Sigma 7)^2 + (\Sigma 8)^2}{6} - \frac{\Sigma X}{48}$$

where $\Sigma 1$ = the sum of all values for Position 1

$$\text{S.S. L x P} = \frac{(\Sigma A1)^2 + (\Sigma A2)^2 + (\Sigma A3)^2 + \text{etc} + (\Sigma B1)^2 + (\Sigma B2)^2 + \text{etc}}{3}$$

$$-\frac{\Sigma X}{48} - \text{S.S. Labs} - \text{S.S. Positions}$$

$$\text{S.S. Observations} = \Sigma(X)^2 - \frac{(\Sigma A1)^2 + (\Sigma A2)^2 + (\Sigma A3)^2 + \text{etc} + (\Sigma B1)^2 + (\Sigma B2)^2 + \text{etc}}{3}$$

$$\text{The Mean Square} = \frac{\text{Sum of Squares}}{\text{Degrees of Freedom}}$$

$$\text{and F} = \frac{\text{Mean Square for factor being tested}}{\text{Mean Square for Observations (error)}}$$

This tests an hypothesis that the numerator is only another estimate of experimental error and the test ratio varies from 1.0 only by chance sampling effects. This is related to probability by a table of F values giving levels corresponding to a 1 in 20 and a 1 in 100 chance that this variation of F from unity is by sampling or chance effect alone. The converse, then, is that an F value exceeding the 5% or 1% level is the result of a real effect.

Interpretation

In the Analysis of Variance, if (1) is significant then the difference between $\bar{X}$ obtained by each laboratory is more than would be expected from experimental error. If (3) is significant, this difference is not constant from position to position and varies more than would be expected.

If (2) is significant the sheet has non-uniform hydrogen distribution judged by sampling from its edges. The Range is greater than it would be from experimental error alone. Additional information can be sought by comparisons of step III.

III. Compare from edge vs. rear edge, top edge vs. bottom edge, corners vs. midpoints. Other comparisons are possible, such as comparing one corner vs. other corners, but these can as easily be made by inspection.

Calculations

S.S. front vs. rear = Positions 1, 8, 7 vs. 3, 4, 5

$$= \frac{(\Sigma 1 + \Sigma 8 + \Sigma 7 - \Sigma 3 - \Sigma 4 - \Sigma 5)^2}{36}$$

Degrees of Freedom = 1	Req'd for significance at
	5% level, 4.15
$\text{F} = \frac{\text{M.S. front vs. rear}}{\text{M.S. observations (error)}}$	1% level, 7.50

S. S. top vs. bottom = Positions 1, 2, 3 vs. 5, 6, 7

$$= \frac{(\Sigma 1 + \Sigma 2 + \Sigma 3 - \Sigma 5 - \Sigma 4 - \Sigma 5)^2}{36}$$

Degrees of Freedom = 1

$$F = \frac{\text{M.S. top vs. bottom}}{\text{M.S. observations (error)}}$$

Req'd for significance at
5% level, 4.15
1% level, 7.50

S. S. Corners vs.
Midpoints = Positions 1, 3, 5, 7 vs. 2, 4, 6, 8

$$= \frac{(\Sigma 1 + \Sigma 3 + \Sigma 5 + \Sigma 7 - \Sigma 2 - \Sigma 4 - \Sigma 6 - \Sigma 8)^2}{48}$$

Degrees of Freedom = 1

$$F = \frac{\text{M.S. corners vs. midpoints}}{\text{M.S. observations (error)}}$$

Req'd for significance at
5% level, 4.15
1% level, 7.50

Comments

If more than one sheet is to be considered, the volume of analytical work per sheet may be reduced by obtaining hydrogen determinations in duplicate rather than in triplicate. This still gives a reasonable estimate of experimental error. Calculations for such an experiment should be outlined by a statistician.

It is important that no specimens be lost during analysis.

CONCLUSIONS

1. While one of the methods for hydrogen determination clearly differs from the rest, it cannot be established that the remaining methods do not contribute in part to differences between laboratories. It does appear that the method is a less influential factor than differences among laboratories themselves using the same method.

2. Laboratories in general are not in agreement. Certain groups could be found which agree, and one such group are the three laboratories using Method II. Some few laboratories show a constant bias, indicating a calibration error in the equipment perhaps. Most show a bias which changes over the range of hydrogen contents, but agreement can be forced <u>in this experiment</u> by adjusting individual hydrogen values where a laboratory shows a bias greater than 4 ppm in the

neighborhood of 150 ppm, the range of most practical importance. Experience may show that a correction factor for an individual laboratory is permissible, but experience alone would be the basis for such action.

3. It cannot be established that laboratories have equal analytical capabilities for all alloys, since this observation is confounded with differences in hydrogen content between specimens taken from mill products. One instance involving Methods I and VI indicates that only the specimen non-uniformity is significantly contributing to the interaction term. This is of particular interest since Method VI (Equilibrium Pressures) requires a calibration curve for each alloy making it prone to a lack of agreement with Vacuum Fusion for some alloys.

4. Not only do laboratories in general show lack of agreement, but some show poorer reproducibility than might be expected. When day-to-day error is intentionally introduced by a few of the laboratories, reproducibility is reasonably good, however.

5. It is apparent that acceptance inspection of material must be designed to sample as many individual sheets or bars within an order as can be accomplished, since differences between sheets or bars can be significant. A standard deviation of about 3 ppm can be expected just from duplicate analyses on sheet, analyzed without day-to-day error, so that the individual sheet should be considered a heterogeneous item, and sampling at a number of locations within the sheet should be practiced to adequately rule on disputed sheets.

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APPENDIX

Preparation of Reported Data for Statistical Analysis

The hydrogen determinations presented in Table II are treated in the following manner to adapt them to statistical analysis. Resulting data are given in Table III of the report.

a. Incomplete data Only data where at least two valid determinations are reported for each specimen are statistically analyzed, with the exception of results by Method VII where some comparisons are made.

b. Rounding-off values Hydrogen determinations reported to three significant figures are rounded-off to units of parts per million (0.0001%), and to the nearest even integer.

c. Missing values The arithmetic mean of the other two values is entered for a missing value. This decreases the degrees of freedom for the error term and the total by one for each such value supplied.

Method	Laboratory	Alloy	Reported values		Value Supplied
I	Ladish Company	RR 4	134	137	136
	duPont, 1st set specimens	RR 4	100	89	94
III	Republic Steel	RR 9	86	79	82
	Watertown Arsenal	RR 2	122	103	112
		RR 15	247	244	246
	Armour Research Foundation	RR 6	9	15	12
V	Allegheny-Ludlum Steel	RR 1	128	124	126
		RR 2	142	149	146
		RR 3	139	141	140
		RR 4	154	156	155
		RR 5	72	74	73
		RR 6	42	43	42
		RR 7	83	84	84
		RR 8	105	107	106
		RR 9	74	78	76
		RR 10	136	142	139
		RR 11	180	187	184
	Titanium Metals Corp.	RR 11	200	202	201

Method	Laboratory	Alloy	Reported values		Value Supplied
VI	duPont, 1st set specimens	RR 1	105	107	106
	duPont, 2nd set specimens	RR 1	110	108	109
		RR 8	99	97	98
		RR 9	65	64	64
		RR 10	108	112	110
IX	General Electric (ANP Division)	RR 8	88	83	86
		RR 12	388	381	384
		RR 14	207	198	202
		RR 15	386	373	380

d. Excess values Where determinations in excess of the three requested for the specimen are reported, these are rejected by use of a table of random numbers (Table 1.2, pp 10-13, Statistical Methods. Snedecor.)

Method	Laboratory	Alloy	Value Rejected
II	Naval Research Laboratory	RR 1	2nd, 4th
		RR 6	1st
	Electro Metallurgical Co.	RR 4	4th
		RR 5	3rd
III	Rem-Cru Titanium, Inc.	RR 6	2nd
		RR 7	1st
		RR 8	4th
		RR 9	4th
		RR 10	1st
		RR 11	3rd
	Watertown Arsenal	RR 1	3rd
		RR 6	2nd, 4th
		RR 7	4th
		RR 8	3rd
		RR 9	1st
IV	Brush Laboratories	RR 5	1st, 3rd, 6th
		RR 10	1st, 2nd, 5th
VIII	Dow Chemical Company	RR 1	4th
		RR 5	2nd
		RR 6	3rd
		RR 9	1st