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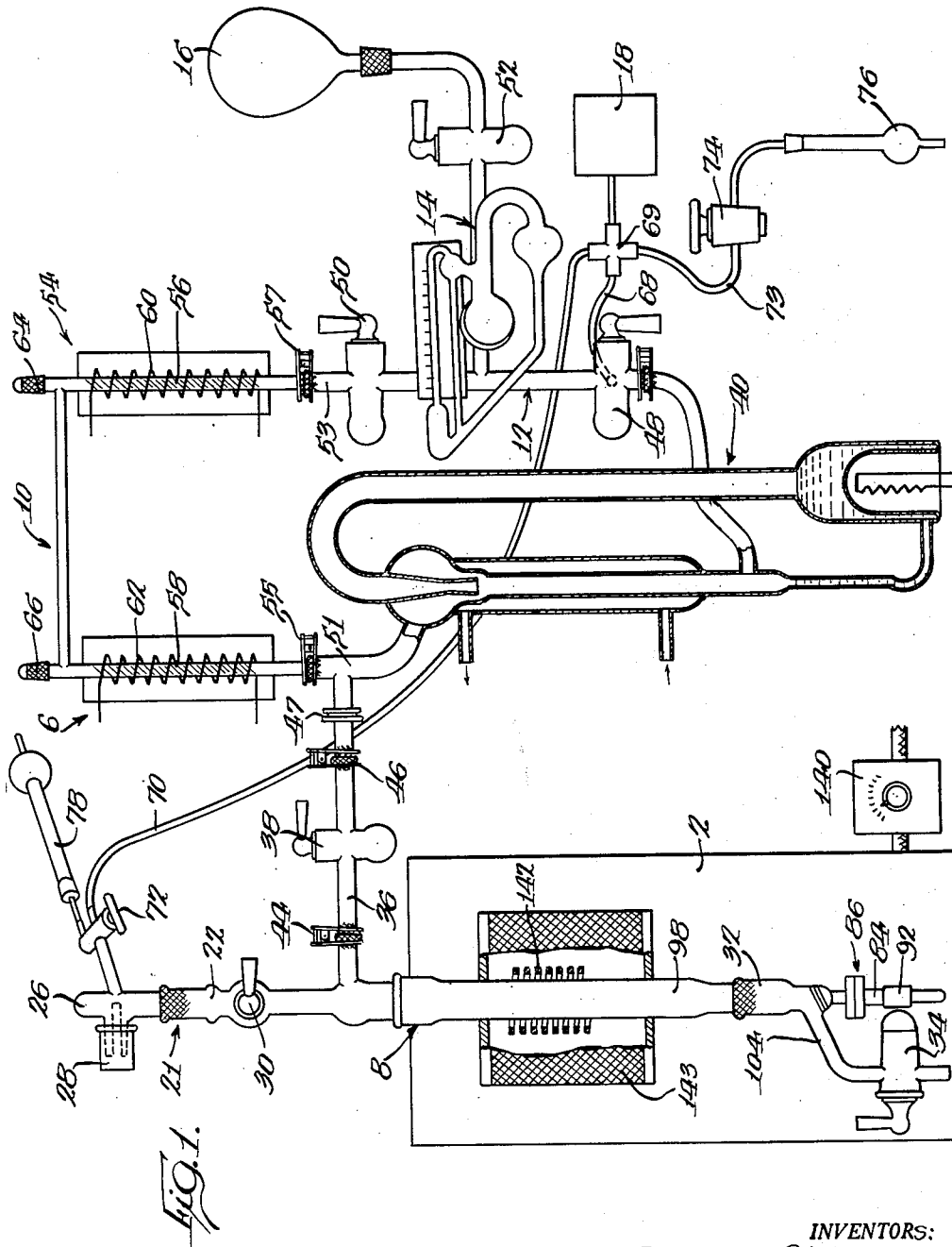
E. L. BENNET ET AL

3,148,032

APPARATUS FOR HYDROGEN ANALYSIS

Filed Oct. 11, 1960

3 Sheets-Sheet 1



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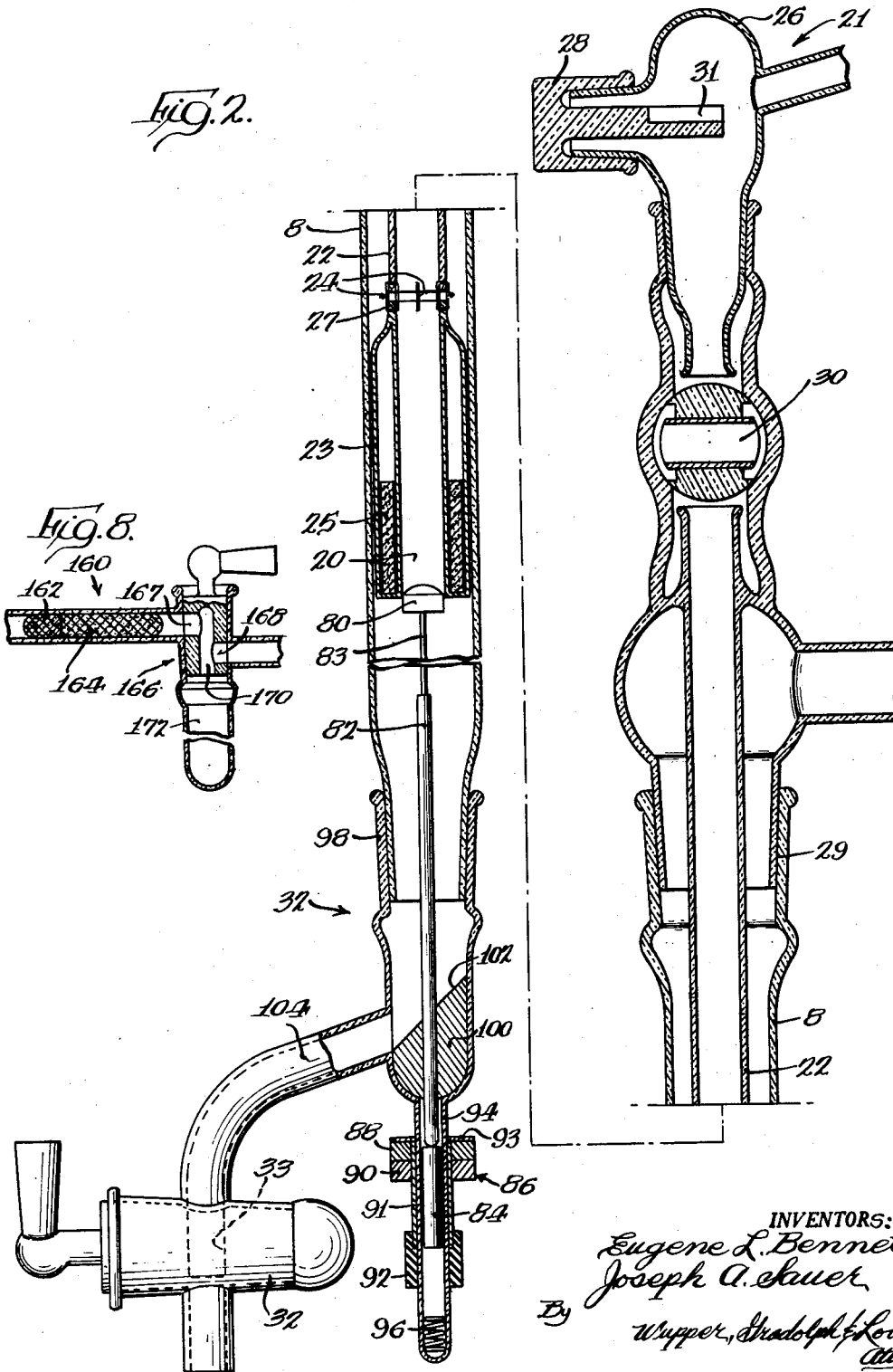
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APPARATUS FOR HYDROGEN ANALYSIS

Filed Oct. 11, 1960

3 Sheets-Sheet 2

FIG. 2.



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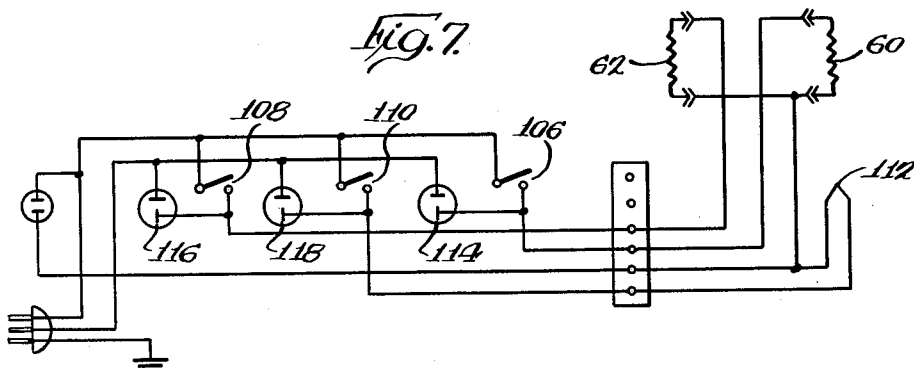
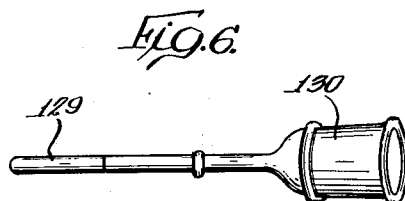
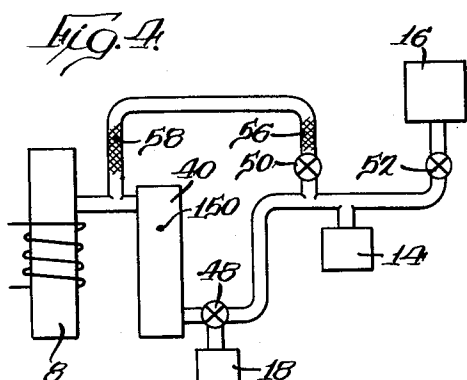
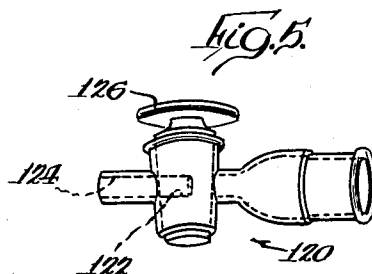
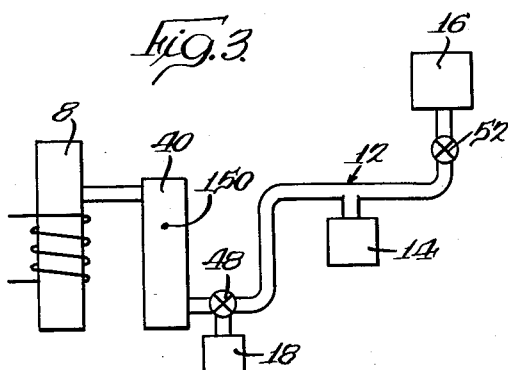
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**3,148,032**

## APPARATUS FOR HYDROGEN ANALYSIS

Filed Oct. 11, 1960

3 Sheets-Sheet 3

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3,148,032

## APPARATUS FOR HYDROGEN ANALYSIS

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Joseph, Mich., a corporation of Michigan  
Filed Oct. 11, 1960, Ser. No. 61,917  
3 Claims. (Cl. 23—253)

This invention relates to an improved method and apparatus for analyzing for the hydrogen content of various materials.

Practically all metals contain elements other than those given in the usual chemical analysis, and among them are the gases, hydrogen, oxygen, and nitrogen. Although usually present in only a few parts per million (p.p.m.), they may have physical effects which seem considerably out of proportion to the small amount present. As an indication that the industry recognizes the important effects of these gases, it is merely necessary to witness the increase in installations of vacuum melting and vacuum degassing equipment in the last decade.

Each of the above mentioned gases has its own effect. The major phenomenon associated with hydrogen content is strain rate sensitivity, whereby the ductility of a metal which varies with the rate that stress is applied is markedly affected by the amount of hydrogen present. This may result in unforeseen failure of parts such as steam turbine rotors and perhaps rocket fuel engines. Additional effects of hydrogen are hydrogen embrittlement, flaking, blow holes in castings, and poor quality of enameled surfaces on cast iron products.

The gas which is most frequently absorbed by metals is hydrogen. Liquid copper, iron, and nickel will dissolve hydrogen in large quantities. Even in the solid state, tantalum is capable of absorbing enormous quantities of hydrogen.

This hydrogen becomes available to the metal from dissociation of water vapor during fabrication processes, by decomposition of the water vapor by the metal from electrodeposition process, and from acid or caustic pickling procedures.

Thus a rapid and convenient means of analyzing for hydrogen is important for checking incoming materials, controlling the processing of materials, determining the causes of failure of elements, and correlating effects of hydrogen content with physical properties.

One type of hydrogen analyzer is shown in United States Patent No. 2,932,558, issued April 12, 1960. Other known methods and apparatus are universally characterized by substantially more cost and longer periods of time required for analysis.

There is an ever present need for a lower priced, faster operating hydrogen analyzer for analysis of metal samples. The improved apparatus of the present application is capable of determining the hydrogen content of samples within three to ten minutes, a substantial departure from known techniques and apparatus. In addition, the improved apparatus is substantially less expensive.

It is therefore a primary object of the present invention to provide an improved method and means for analyzing for the hydrogen content of samples.

A more specific object of the present invention is the more rapid and more economical nondestructive removal of hydrogen from a sample by the combination of heat and a vacuum, and the analysis for the hydrogen content of the sample by measurement of the pressure change which it produces in the apparatus.

It is a further object of the present invention to provide improved apparatus for analyzing for hydrogen in a sample in which the samples may be added to and re-

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moved from the equipment without breaking the vacuum of the entire system.

Other objects and the various features of the invention will be evident upon a perusal of the following description taken in connection with the accompanying drawings, in which:

FIG. 1 is a diagrammatic view of the improved apparatus;

FIG. 2 is an elevational view, partially in section, showing the sample introduction, extraction, and ejector assembly;

FIGS. 3 and 4 diagrammatically illustrate the two methods by which the equipment is operated for determining the hydrogen content;

FIGS. 5 and 6 show certain of the accessories used with the improved apparatus;

FIG. 7 is a circuit diagram showing certain of the electrical details of the improved apparatus; and

FIG. 8 is a longitudinal vertical sectional view of an accessory which is useful under certain circumstances.

The improved method is one of "hot extraction" in which the so-called dissolved or interstitial hydrogen is removed from the sample by a combination of heat and vacuum. The sample is not melted, and pressure is measured both before and after the evolution of the hydrogen. The difference in pressure indicates the amount of hydrogen present. Some samples, as zirconium and many of its alloys, give off only hydrogen under these conditions, and the determination is a direct one. For samples giving off various quantities of carbon monoxide and nitrogen with the hydrogen, a simple separation step is employed in the analysis procedure.

The glass elements of my improved apparatus may be made of any suitable high temperature material.

The improved apparatus includes an induction furnace 2 as a source of heat with a variable manually controlled transformer 140 for adjusting the sample temperature. Connected with this is the hydrogen analyzer proper 6 consisting of an artificial fused quartz (such as Vycor glass, for instance) reaction tube 8, extraction glassware 10, a glass analytical section 12, a McLeod vacuum gauge 14, and a glass expansion volume 16. In operation, the analyzer is attached to a mechanical vacuum pump 18.

The reaction tube encloses an inert blank-free crucible 20 which is heated in the induction field and supplies the necessary temperature conditions for the sample. Samples are introduced singly into the reaction tube by a loading section 21 and are dropped into the crucible without breaking the vacuum in the reaction tube. When the hydrogen is extracted from the sample, the sample is removed from the apparatus by a glass sample ejector 32, again without substantially breaking the vacuum.

The crucible 20 embodies the basic features disclosed and claimed in Patent No. 2,779,581, issued January 29, 1957, to Eugene L. Bennet for "Combustion Analysis Crucible." It consists of a closed and evacuated annular envelope 23 formed of fused quartz or similar material containing a graphite ring 25. The enclosure in the specific embodiment illustrated is about two and one-half inches long and has an external diameter of about  $\frac{7}{8}$ " and a passage through the center with a diameter of about  $\frac{1}{16}$ ". The graphite ring is about one inch long and fits loosely within the envelope 23. At its upper end the envelope 23 has a short extension 27 which is pierced at four places to provide holes which are connected to similar holes at the lower end of a sample guide tube 22 by small wire loops 24. As thus suspended, there is a space between the sample guide 22 and the crucible of about  $\frac{1}{16}$ " to  $\frac{1}{8}$ ". The glass sample guide and the quartz crucible are thus free to expand and contract relative to each other.

The crucible suspended below the sample guide is in-

serted into the top of the reaction tube 8 until interfitting ground glass joint elements at 29 between the sample guide and the reaction tube come together. When the elements are in this position, the graphite ring 25 is at about the center of the field of the induction furnace coil.

By a means to be explained presently, the sample to be heated is temporarily located within the graphite ring. The ring absorbs energy from the induction field and becomes heated to the desired temperature. Heat is thus transferred to the sample by radiation from the ring, and since the ring largely shields the sample from the induction field, the temperature of the sample is not greatly influenced by its ability, or lack of it, to become heated directly in an induction field. The temperature from sample to sample is therefore quite uniform regardless of the sample material or condition.

The upper end of the sample guide 22 is provided with a head 26 having a lateral extension with an opening therethrough. This extension is connected by a ground glass joint to a sample holder 28 which can be loaded and attached to the extension. When desired, the sample can be dropped from a pocket 31 in the sample holder so as to fall down the sample guide while maintaining the vacuum in the system simply by rotating the sample holder at the ground glass joint a matter of less than 90°.

Below the sample holder, the sample guide tube is provided with a stopcock 30 which can be closed to isolate the loading section 21 from the reaction tube, or which, when opened, permits a sample to fall therethrough. For this application, it is preferred to use the stopcock forming the subject matter of the copending patent application of Eugene Bennet, Serial No. 15,768, filed March 17, 1960, now U.S. Patent 3,019,808, since a stopcock of this type may be used for long periods without danger of contaminating the samples with stopcock grease.

The lower end of the reaction tube is connected to the sample ejector 32 which is provided with a glass stopcock 34.

A connector 36 having a central stopcock 38 connects a mercury diffusion pump assembly 40 to the sample guide at an intermediate point. The connector 36 is secured at either end to the sample guide 22 and the diffusion pump intake by means of ground ball and socket joints and clamps 44 and 46. A grommet 47 is provided for resiliently mounting the glass tubing.

The analytical section 12 extends from the diffusion pump outlet through a stopcock 48 to the stopcocks 50 and 52. The diffusion pump inlet 51 and the upper end 53 of the analytical section are connected to the ends of an inverted U tube 54 by ball and socket joints retained by clamps 55 and 57. The U tube includes a copper oxide cartridge 56 in one leg, and in the other leg a cartridge 58 of washer-absorbent material such as magnesium perchlorate. The cartridges are enclosed within electric heaters 60 and 62. The upper ends of the U tube branches are sealed with caps 64 and 66.

The mechanical vacuum pump 13 is connected to the stopcock 48 by means of a line 68 and a glass cross 69. The pump is also connected to the head 26 by way of line 70 and stopcock 72 and to atmosphere by way of a line 73, a glass stopcock 74, and a moisture trap 76. The stopcock 72 is also connected to atmosphere by way of a moisture trap 78.

Each of the connections between the fluid lines is preferably sealed with a wax (such as that sold under the trademark Apiezon "W") by means of a torch. All other joints are preferably made with a high-vacuum grease such as that sold by Dow-Corning under the name "High Vacuum Silicone."

The various stopcocks will now be described in more detail. The stopcock 30 is operable into two positions, one for sealing off the fluid connection between the upper and lower ends of the sample guide and the other for permitting transfer of a sample into the crucible.

The stopcock 34 is operable to one of two positions for receiving and ejecting a tested sample from the sample ejector 32.

The stopcock 72 is operable to three positions. In one position, it connects atmosphere through the moisture trap 78 into the head 26 to permit removal and loading of the sample holder. In a second position, it connects the mechanical vacuum pump to the head for evacuation of the head, the sample holder, and the sample guide. In a third position, it closes off the head from both the moisture trap and the vacuum pump for transfer of a sample from the holder to the reaction tube.

The stopcock 38 is operable to two positions for opening and closing a fluid path between either end of the connector 36. This path is closed only when the system sections are being isolated to clean the reaction tube, locate a leak, etc. The large bulb on the bottom of this stopcock may be used as a "freeze-out" trap by surrounding it with Dry Ice in acetone.

The stopcock 52 is operable to two positions for connecting or disconnecting the expansion volume 16 and the analytical section. This adds the capacity of the volume 16 to the analytical section when the amount of hydrogen (and carbon monoxide and nitrogen) evolved from the sample is sufficient to cause the pressure in the analytical section alone to be off-scale on the McLeod gauge.

The stopcock 50 is operable to two positions for connecting or disconnecting the U tube and the analytical section. When the extracted gas contains carbon monoxide and nitrogen as well as hydrogen, the pressure is read on the McLeod gauge. Next, stopcock 50 is opened, and the gas is circulated by means of the diffusion pump through the heated copper oxide and water absorbent. The hydrogen is converted by the copper oxide to water which is absorbed in the magnesium perchlorate, leaving a new pressure due to carbon dioxide and nitrogen only. Although the carbon monoxide is converted to carbon dioxide by the copper oxide, this is on a molecule-for-molecule basis and does not change the volume of gas in the system. The difference in pressure gives the pressure due to hydrogen only.

The stopcock 74 is operable to two positions for connecting or disconnecting atmosphere and the vacuum pump. When it is desired to turn the pump off electrically, stopcock 48 closes the connection with line 68 and stopcock 74 is opened before the electrical connection is broken. This provides a supply of dry air to the mechanical pump through trap 76, thus preventing sucking oil from the pump into the analytical system.

By the use of these stopcocks, it is possible to compartmentalize the entire system for the purpose of controlling its operation and also for the purpose of determining the location of any leaks which may occur in the system.

With particular reference to FIG. 2, it will be seen that the preferred crucible 20 is bottomless. A false or removable bottom 80 is provided for the crucible so that samples may be retained therein. The false bottom in turn is supported at the upper end of a push rod 82 made up of a glass rod sealed at its upper end to a tungsten extension 83. The push rod 82 rests on the upper end of an armature 84 of a magnet assembly 86. The assembly includes an iron plate 93 secured to the upper end of a non-magnetic mounting sleeve 91, and a pair of magnets 88 and 90 attracted to the bottom surface of the plate. A resilient plastic bushing 92 is connected to the sleeve 91 and frictionally maintains the magnet assembly in fixed position at a desired location at the lower end of the sample ejector 32.

The ejector includes a lower portion 94 of reduced diameter which receives both the armature 84 and the push rod 82. A spring 96 rests at the bottom of the portion 94 to prevent damage to the ejector. The upper end of the ejector is expanded outwardly at 98. The lower end of the expanded section includes an insert 100, preferably of aluminum, with a diagonal upper surface

102. The ejector also includes a downwardly extending arm 104 which supports the stopcock 34.

The magnets 88 and 90 retain the armature 84 in the relative position shown in FIG. 2; that is, the upper end of the armature is slightly below the upper end of the magnet 88. When the magnets 88 and 90 are raised and lowered, the bushing 92 retains the assembly in set position. The armature follows the magnet assembly to permit the push rod and the false bottom 80 to lower a corresponding distance. This will permit a sample in the crucible to fall from the crucible into the ejector. The sample will strike the aluminum insert 100 for deflection into the arm 104 and into a small pocket 33 in the stopcock 34 for ejection.

As seen in FIG. 7, the electric heaters 60 and 62 are energized respectively by the actuation of switches 106 and 108 for heating and activating the copper oxide and heating and reactivating the water absorbing material. Switch 110 is actuated to energize a diffusion pump heater 112. Pilot lamps 114, 116, and 118 indicate the energized or deenergized conditions of the heaters 60, 62, and 112 respectively.

A stopcock 120 (FIG. 5) is used for "dosing" or admitting a known volume of air to the hydrogen analyzer for determination of the analysis volumes with and without the expansion volume 16 connected. It will be noted that there is a partial bore 122 in the stopcock, and when the stopcock is attached to the apparatus in place of sample holder, the stopcock bore is turned from the atmosphere to the vacuum side, thus admitting a volume of air equivalent to the volume of the bore.

The volume of the bore must be determined accurately before use by admitting mercury through the small end 124, filling the tubulature almost completely. Pressure must be applied with a finger to be certain the mercury fills all voids, and at the same time the stopcock plug 126 is turned at right angles. The surplus mercury in the tubulature is then allowed to drain. The stopcock plug is carefully removed and the mercury in the bore is then transferred to a watch glass and carefully weighed. By reference to a handbook table, density of the mercury is found for the room temperature at which it was weighed, and the bore volume is calculated in milliliters. This should be repeated several times and the average figure should be recorded on a label. The stopcock is then greased. A preferred volume is in the order of .05 milliliter.

To activate or test the effectiveness of the copper oxide, it is convenient to admit some hydrogen into the system and circulate it through the copper oxide-water absorbing system to determine how fast the hydrogen is removed. This is done by substituting a palladium tube 129 sealed to a capsule 130 (FIG. 6) in place of the sample holder, and applying heat to the palladium tube using a Bunsen burner. Some hydrogen from the flame passes through the palladium and can be detected by the apparatus if it is operating properly. Similar results can be obtained by heating a metal hydride in a side tube of Vycor substituted in place of the sample holder.

The preparation and operation of the improved apparatus will now be described. Prior to conducting actual tests, the apparatus is calibrated for temperature, the determination of the analysis volumes with and without the volume 16 connected, and the optimum extraction time for differing materials.

After the pressure in the system has been reduced, the induction furnace is energized and the temperature of the crucible is adjusted by manual adjustment of the dial 140 on the variable temperature control transformer. The temperature is measured by an optical pyrometer (not shown) sighted on the crucible, thus enabling one to correlate temperature against the dial reading on the variable transformer, assuming temperature equilibrium has been reached, and that the line voltage is constant. There is

also a correlation between the plate current ammeter reading on the induction furnace and temperature.

The unit is preferably calibrated for a maximum temperature of 1200° C. and whatever lower temperatures are desired. Calibrations at increments of 100° C. are desirable. It is unnecessary and undesirable to go above 1200° C. since the crucible is inert and does not need blanking at 1400° C. as with other crucibles. Calibration will be facilitated by removal of the screen guard 143 for the high frequency coil 142 to make optical pyrometer sightings easier.

The apparatus is then left under vacuum for several hours, or preferably overnight in order to eliminate blank that may be contributed from various portions of the apparatus with the sample holder in place, the stopcocks 30, 38, 48, 50, and 52 open, the stopcocks 34, 72, and 74 closed, and the heaters 62 and 60 energized. The setting of the transformer allows moisture to be removed from the reaction tube in about an hour.

After several hours, or an overnight period, a reading on the McLeod gauge should indicate no pressure. If this is not the case a leak or a source of gas evolution from somewhere in the system is indicated. A test to determine if all moisture is removed from the water absorbing cartridge 58 is to adjust stopcock 48, so that the diffusion pump outlet is connected to the analytical section, and determine whether or not the vacuum holds for ten minutes. If this test proves satisfactory, the heater 62 is de-energized to allow it to cool to room temperature. During this period the stopcock 48 is adjusted to connect the pump 18 to the analytical section. The instrument is now ready for calibration of the two analysis volumes.

Refer to FIG. 4 for a definition of two volumes  $V_S$  and  $V_L$ . Volume  $V_S$  extends from point 150—the effective output of the diffusion pump where the mercury condenses on the wall—to stopcocks 50 and 52, and to gauge 14. Volume  $V_L$ , in addition, includes the expansion volume 16. Determination of these volumes (in milliliters) is necessary for final calculation of hydrogen analysis results. The procedure is one of starting with a zero reading on the McLeod gauge, then admitting known volumes of air by means of the dosing stopcock 120. The new pressure is read and the volume is determined by substitution in the formula:

$$V_T = \frac{P_A V_1}{P_T}$$

where

$V_T$ —total volume, including the McLeod gauge, in milliliters,

$P_A$ —pressure of the air in the dosing stopcock (atmospheric in this case) in microns (1 millimeter mercury=1000 microns),

$V_1$ —precalibrated volume of dosing stopcock in milliliters, and

$P_T$ —pressure, in microns, in total volume after expansion from the dosing stopcock volume.

The first step is to close stopcock 30, open stopcock 72 to the atmosphere through moisture trap 78, remove sample holder 28, and attach the dosing stopcock. The dosing stopcock is turned so the calibrated bore 122 is turned toward the apparatus. Stopcock 48 disconnects the pump 18, stopcock 72 is turned to connect the mechanical vacuum pump until change in the sound of the pump indicates the volume above stopcock 30 is exhausted. Stopcock 72 is turned to close off both atmosphere and pump 18. Moisture trap 78 is removed temporarily from stopcock 72 and put on the small end of the dosing stopcock 120. Stopcock 50 is opened, stopcock 48 connects the pump 18 to back up the diffusion pump, and after about one minute stopcock 30 is opened. The McLeod gauge should indicate no pressure. Then 50 is closed and 48 turned to isolate the pump 18.

The stopcock handle 126 is then rotated so the bore

122 receives dry air at atmospheric pressure through the moisture trap. It is further rotated to let this calibrated volume of air into the apparatus, and after a few seconds the McLeod gauge is read in microns. This is value  $P_T$ . The volume of the dosing stopcock bore was determined previously in milliliters, using mercury for the calibration. This is  $V_1$ .  $P_A$  is the atmospheric pressure as determined by a barometer. These are substituted into the formula above to determine the small volume,  $V_S$ . Several results should be obtained. The unit can be evacuated after each "dose" by connecting pump 18 through stopcock 48 and by opening stopcock 50. The diffusion pump evacuates the analytical chamber by way of the hydrogen removing section 10. The only error is the imperfect mechanical pump 18 vacuum (less than 20 microns) in the small volume between the diffusion pump cutoff point 150 and stopcock 48 which, when subsequently expanded into the analytical section, is insignificant (no more than three microns) in relation to the pressures of 300–800 microns normally present after the hydrogen has been removed from an average test sample.

To determine large volume  $V_L$ , exactly the same procedure is used, but stopcock 52 is opened to add the expansion volume 16. In this case several "doses" are added to the system until the McLeod gauge gives a reading of about half scale. The pressure should not approach that at which the diffusion pump slips, however.  $V_L$  then becomes the accumulated volume of all the "doses."

The stopcock 30 is then closed and the moisture trap 78 is returned to stopcock 72 to admit dry air above stopcock 30. The dosing stopcock is next replaced by the sample holder, the space above stopcock 30 is again evacuated, and the stopcock 30 is reopened. The apparatus is now ready for hydrogen "blank" checking. When the crucible is energized, some gas may be liberated into the system since heat from the crucible will cause adsorbed gas to be released from the glassware walls. After a few minutes of pumping and an indication that the McLeod pressure is at zero, the stopcock 48 is turned to the analysis position disconnecting the pump 18, and stopcock 50 is closed. A McLeod gauge reading is then taken and recorded at an interval of four minutes, after which the furnace is turned off. Stopcock 50 is opened and the collected gas is circulated through the copper oxide and water absorbent, as shown in FIG. 4, for another four minutes and the McLeod gauge pressure is read. The difference in pressure, if any, is the hydrogen "blank" for a four minute period. Blanks may be obtained similarly for three and five minutes or other periods.

Usually the blank is so extremely small that it may be ignored without introducing an error of any practical consequence, since the adsorbed gases appear, in practice, to include almost no hydrogen.

The minimum safe extraction time and optimum temperature is determined by experience, and can be accomplished by analyzing a series of samples of approximately the same composition. Extraction time and separation time are conveniently kept at 15 minutes each, and the temperature is changed in increments as each sample is analyzed. The lowest temperature above which there is no increase in the amount of liberated hydrogen can then be used. Employing this temperature, shorter extraction and separation times can be tried, remembering in such case that a new blank correction is used if the hydrogen blank is appreciable.

The procedure for sample analysis is similar to that for determining blank in the apparatus. The gauge 14 is first checked to make certain pressure is zero. The sample is admitted to the holder 28 while stopcock 30 is closed and atmospheric pressure exists in the head 26. The sample holder is secured to the head and the head is evacuated through stopcock 72. Stopcock 72 is closed and stopcock 30 opened. Stopcock 48 is turned to connect pump

18 to the diffusion pump, and after a few seconds stopcock 50 is closed. Stopcock 48 is turned to disconnect pump 18.

The sample is then dropped into the crucible by rotating the holder. The sample is extracted for the predetermined time, at the end of which the gauge pressure is read. The furnace is then turned off, stopcock 50 is opened, the gas is circulated for four minutes through the U tube 54, and the new McLeod pressure is read. The pressure difference is then determined and is corrected by deducting the "four minute blank" as determined previously.

If the amount of gas is too large to be read, stopcock 52 is opened to the expansion volume 16, making the total volume of the system  $V_L$ . If the expansion volume is not used, the precalibrated volume is  $V_S$ . The amount of hydrogen is then readily calculated by

$$\text{Hydrogen, p.p.m.} = \frac{PVM \times 1000}{RTW \times 760}$$

where

$P$ =corrected pressure difference from the McLeod gauge in microns or the pressure if only hydrogen is given off,  
 $V$ =either  $V_S$  or  $V_L$ , the precalibrated volumes, whichever is used,  
 $M$ =molecular weight of hydrogen, 2.016,  
 $R$ =gas constant (82.05 milliliter atmos. per deg. Kelvin mole),  
 $T$ =temperature of the calibrated volume, in degrees Kelvin,  
 $W$ =grams of sample used.

With some samples the amount of carbon monoxide evolved from the heated sample may be so great as to make it difficult to correctly read the hydrogen quantity present. If this is a problem, the interfering carbon monoxide can be removed in the manner shown in FIG. 8. Here a section 160 is illustrated which may be substituted in place of that at 36. Although not shown, this section has ball and socket joints at its ends as has the section 36. Included in the section 160 is a wire mesh container filled in the direction of flow with a portion 162 of Hopcalite (an intimate mixture of copper oxide and manganese dioxide), followed by a portion 164 of sodium hydroxide.

The Hopcalite converts any carbon monoxide to carbon dioxide which is absorbed in the sodium hydroxide, thus preventing the carbon monoxide from getting to the diffusion pump inlet. In the process of making this conversion, water vapor is liberated, but this can be trapped at the stopcock 166. Stopcock 166 is essentially similar to the one at 38, in that it is of the vacuum type with vertically offset inlet and outlet passages 167 and 168 in the plug which communicate with a vertical bore 170 which, in turn, leads to a closed bulb 172 beneath the plug's lower end. Ordinarily this arrangement is used so that the vacuum space beneath the plug end aids in holding the plug in place, thus preventing leakage.

In the present structure, the bulb 172 is about three inches or so long, and this bulb is submerged in a Dry Ice, acetone bath, as is a well known expedient for condensing and freezing the water vapor out of the system. The evolved gas which reaches the diffusion pump inlet, therefore, has substantially all of the carbon monoxide, carbon dioxide and water vapor removed therefrom, thus making the system more sensitive to the quantity of hydrogen to be measured and subsequently removed in the section 10.

While there has been described what is believed to be the preferred embodiment of the present invention, it will be appreciated that various changes and modifications may be made therein; and it is contemplated to cover in the appended claims all such changes and modifications as fall within the true spirit and scope of the invention.

What is claimed as new and desired to be secured by United States Letters Patent is:

1. Hydrogen analysis apparatus comprising means providing a sample entry chamber, said chamber having a downwardly extending guide tube outlet, a stopcock in said guide tube for sealing said entry chamber and alternatively for opening said chamber at the bottom to permit a sample to drop downwardly therefrom by way of said guide tube, means providing a vertical tubular reaction chamber positioned below said entry chamber, said reaction chamber having an annular crucible therein with a vertical passage through the center thereof substantially axially aligned with said guide tube, movable platform means positioned for substantially closing the lower end of said crucible passage to support a sample at a position within said crucible passage when in one position, said platform being movable to another position to dump a sample out of said crucible passage, an induction furnace coil exteriorly of said reaction chamber and encompassing the crucible, a diffusion pump having an inlet connected to said reaction chamber, an analytical chamber structure connected to the outlet of said diffusion pump, means for determining the gas pressure in said analytical chamber, a vacuum pump, valve controlled means connecting the vacuum pump to the analytical chamber for evacuating the analytical chamber, the diffusion pump, and the reaction chamber; separate valve controlled means connecting the vacuum pump to the sample entry chamber, valve controlled means for admitting air to said sample entry chamber, means in said sample entry chamber and operable from outside the entry chamber for supporting a sample in said entry chamber when in one position and for dumping the sample through said stopcock when in another position, means operable exteriorly of said reaction chamber for moving said platform between sample supporting and dumping positions, means disposed below said platform for catching a sample dumped from said platform and for removing the sample from the apparatus, said annular crucible comprising an annular heating ring formed of a material strongly heated by an induction field, and an annular envelope formed of heat and shock resistant substantially inert material completely enclosing said heating ring.

2. Hydrogen analysis apparatus comprising means providing a sample entry chamber, said chamber having a downwardly extending guide tube outlet, a stopcock in said guide tube for sealing said entry chamber and alternatively for opening said chamber at the bottom to permit a sample to drop downwardly therefrom by way of said guide tube, means providing a vertical tubular reaction chamber positioned below said entry chamber, said reaction chamber having an annular crucible therein with a vertical passage through the center thereof substantially axially aligned with said guide tube, movable platform means positioned for substantially closing the lower end of said crucible passage to support a sample at a position within said crucible passage when in one position, said platform being movable to another position to dump a sample out of said crucible passage, means for heating said crucible, a diffusion pump hav-

ing an inlet connected to said reaction chamber, an analytical chamber structure connected to the outlet of said diffusion pump, means for determining the gas pressure in said analytical chamber, a vacuum pump, means connecting the vacuum pump to the analytical chamber for evacuating the analytical chamber, the diffusion pump, and the reaction chamber; separate valve controlled means connecting the vacuum pump to the sample entry chamber, valve controlled means for admitting air to said sample entry chamber, means in said sample entry chamber and operable from outside the entry chamber for supporting a sample in said entry chamber when in one position and for dumping the sample through said stopcock when in another position, means operable exteriorly of said reaction chamber for moving said platform between sample supporting and dumping positions, and means disposed below said platform for catching a sample dumped from said platform.

3. Hydrogen analysis apparatus comprising means providing a sample entry chamber, said chamber having a downwardly extending guide tube outlet, valve means for sealing said entry chamber and alternatively for opening said chamber at the bottom to permit a sample to drop downwardly therefrom by way of said guide tube, means providing a vertical tubular reaction chamber positioned below said entry chamber, said reaction chamber having an annular crucible therein with a vertical passage through the center thereof substantially axially aligned with said guide tube, movable support means positioned to support a sample within said crucible passage when in one position, said support means being movable to another position to dump a sample out of said crucible passage, means for heating said crucible, a diffusion pump having an inlet connected to said reaction chamber, an analytical chamber structure connected to the outlet of said diffusion pump, means for determining the gas pressure in said analytical chamber, a vacuum pump, means connecting the vacuum pump to the analytical chamber for evacuating the analytical chamber, the diffusion pump, and the reaction chamber; separate means for evacuating said entry chamber when said entry chamber is sealed from said reaction chamber, means in said sample entry chamber and operable from outside the entry chamber for holding a sample in said entry chamber when in one position and for dumping the sample into said guide tube when in another position, means operable exteriorly of said reaction chamber for moving said support means between sample supporting and dumping positions, and means disposed below said support means for catching a sample dumped from said support means.

#### References Cited in the file of this patent

##### UNITED STATES PATENTS

2,779,581	Bennet	Jan. 29, 1957
2,932,558	Bennet	Apr. 12, 1960
2,962,360	Bennet	Nov. 29, 1960

##### OTHER REFERENCES

Carson: Anal. Chem., vol. 32, #8, July 1960, pp. 936-939.