Jan. 20, 1970 E. L. BENNET ET AL 3,490,266

HOT EXTRACTION HYDROGEN ANALYZER

Filed June 15, 1967 2 Sheets-Sheet 1

Fig. 1.

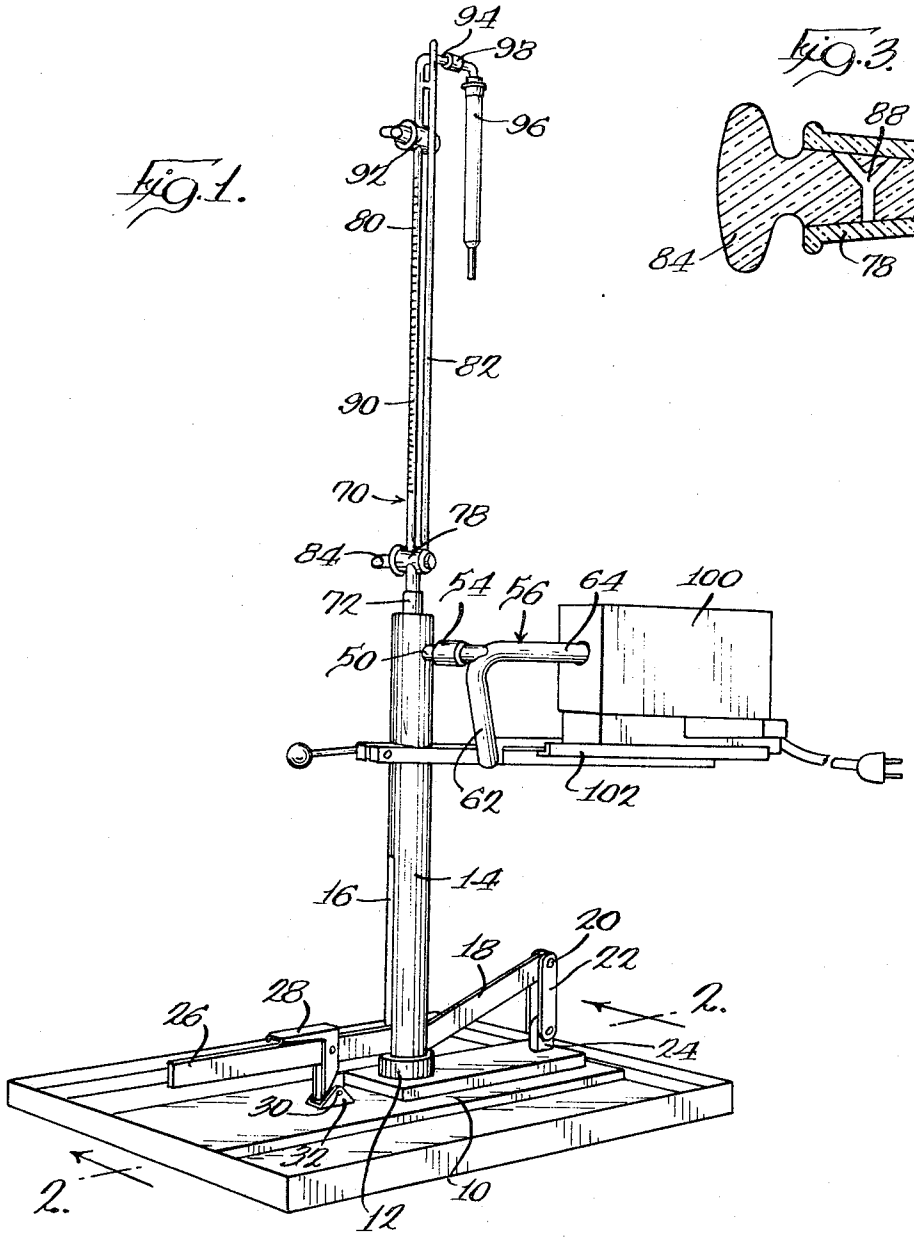


Fig. 3.

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Fig. 1.

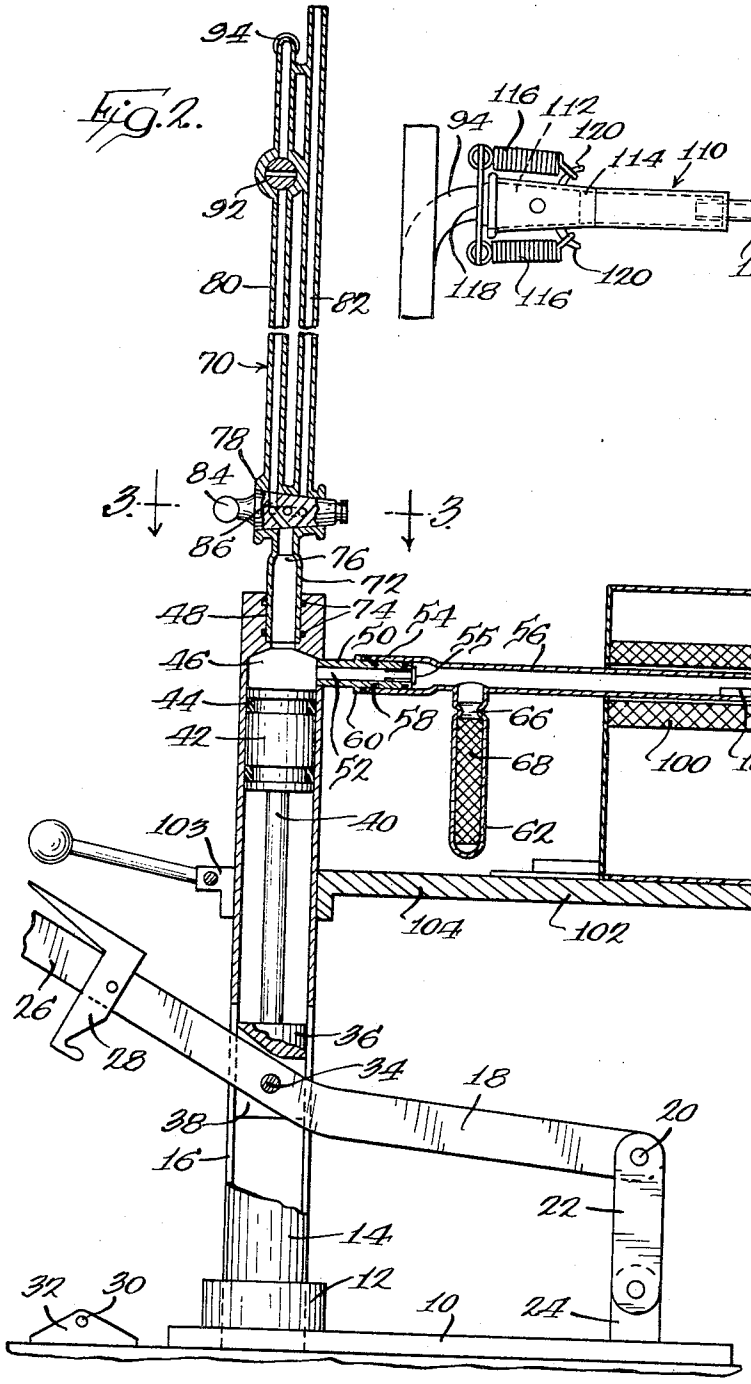


Fig. 4.

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HOT EXTRACTION HYDROGEN ANALYZER

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Int. Cl. G01n 7/16
U.S. Cl. 73—19 4 Claims

ABSTRACT OF THE DISCLOSURE

A method and apparatus for the determination of occluded or entrapped hydrogen in steel which comprises the steps of and means for physically flooding a sample chamber and contained sample and an upwardly extending burette tube with mercury, draining the mercury from the burette and sample chamber without the entry of air, heating the sample so as to release the gas therefrom and flooding the apparatus again to expel the evolved gas into the burette, the apparatus having an open ended tube laterally opposite the burette which likewise is flooded at the time of the gas transfer to provide an ambient pressure reference for the burette.

BACKGROUND OF THE INVENTION

Field of the invention

Analytical apparatus for the determination of gases in metals.

Description of the prior art

Interstitially held or occluded hydrogen in steel sample can be removed under the influence of heat or reduced pressure and thereafter easily measured. A combination of heat and reduced pressure accelerates the removal greatly. While apparatus has been developed which provides for this combination of effects, such apparatus has hitherto been expensive and fragile and unsuited for routine determinations in such on-site environments as foundries and the like.

SUMMARY OF THE INVENTION

The purpose and object of this invention is the provision of a method and appropriate apparatus for the determination of gases in metals or more narrowly of hydrogen in steel which is simple, quick, accurate, and which permits the use of inexpensive simple and sturdy apparatus entirely free from any possibility of nonobvious malfunctioning. To this end, a sample holder is connected to the bottom of a burette and appropriately disposed for heating. A quantity of mercury is held below the sample holder in an appropriate reservoir and is displaceable up into the sample holder and the burette by a plunger so as to flood both these parts and expel air therefrom. Thereafter the mercury is drained from the burette and sample holder, establishing a near perfect vacuum in the system, and the sample is heated to expel its occluded gases. The mercury is then again raised by the plunger to flood the sample holder and the burette to the extent permitted by the expelled gas and the gas quantity read on the calibrations of the burette tube.

DESCRIPTION OF THE DRAWINGS

FIG. 1 is an elevation of apparatus embodying the present invention;

FIG. 2 is an enlarged section taken along the line 2—2 of FIG. 1;

FIG. 3 is a section of the operating stopcock taken substantially along the line 3—3 of FIG. 1; and

FIG. 4 is a longitudinal section through an alternative form of gas exhaust outlet attachment.

DESCRIPTION OF A PREFERRED EMBODIMENT

The illustrated embodiment of the apparatus of the present invention is mounted to a flat base **10**. A collar **12** welded to the base supports vertically an elongated cylinder **14**. The sides of the cylinder are oppositely vertically slotted through about the lower third of its length as at **16**, and a lever **18** extends through the opposite slots. The lever **18** is pivotally connected at one end **20** to one end of a link **22**, and the other end of the link is pivotally connected to an upstanding ear **24** secured to the base plate **10**. The end **26** of the lever remote from the pivotally connected end **20** lies on the opposite side of the cylinder **14** and constitutes a handle **26** and is releasably engageable on a pin **30** supported between two ears **32** which are secured along their bottom edges to the base plate.

That portion of the lever **18** which lies within the cylinder is pivotally connected by pin **34** to a guide piston **36** which fits closely but slidably within the cylinder **14**. The piston has a split skirt so that the pin **34** may extend through an appropriate aperture in the lever and be received in appropriate holes in opposite skirt portions. A piston rod **40** is secured to the top surface of the guide piston **36** to extend upwardly within the cylinder and has secured to its upper end a main piston **42** which engages the walls of the cylinder in fluid-tight relationship. To permit easy reciprocation and, at the same time, maintain a fluid-tight seal, the piston incorporates polytetra-fluoroethylene sealing rings **44**. The spacing of the piston **42** above the lever **18** as achieved by the piston rod **40** results in the piston **42** reciprocating only within the upper, unslotted portion of the cylinder **14**.

The cylinder terminates at its upper end in a dome **46** and a vertical aperture **48** extending upwardly from the center of the dome.

A tubular side arm **50** is mounted in a bore in the side wall of the cylinder **14** to extend horizontally outward therefrom and define a passage **52** into the upper end of the cylinder cavity immediately under the dome **46**. The side arm **50** is adapted to have fitted thereover the open end **54** of a Y-shaped sample tube **56** in gas-tight relationship. To this end, sealing rings **58** are embedded in the outer surface of the side arm. Also, since the depth of insertion of the side arm into the open end **54** is somewhat critical, the side arm is provided with a collar **60** to determine exactly the depth of insertion. A spring clip **55** is contained in the outer end of the side arm to permit fluid passage thereby but block the passage of the sample to be tested and retain it in the sample tube **56**.

The sample tube **56** is desirably formed of heat and thermal shock resistant tubing such as Vycor (a trademark of the Corning Glass Co.), a synthetic fused quartz. As stated, the sample tube is Y-shaped and the open end **54** may be considered the stem of the Y. The other two arms **62** and **64** have closed ends and make about a right angle with respect to each other. The shorter **62** of the two arms is a desiccant holder and incorporates a constriction **66** adjacent its mouth to retain a screen-enclosed capsule **68** of an appropriate desiccant material or a molecular sieve. The open end **54** extends at about a 60° angle from the plane of the right angle defined by the arms **62** and **64**, and the projection of the open end on that plane lies about 135° from each of the closed arms.

A burette **70** has a lower end fitting **72** contained in the aperture **48** in the top end of the cylinder. Sealing rings **74** are provided in the inside surface of the aperture so as to make a gas-tight seal on the received end fitting **72**. The passage **76** of the fitting extends upwardly to a stopcock housing **78**. Upwardly from the stopcock

housing, a calibrated burette tube **80** and an open pressure balancing tube **82** extend in side-by-side relation. The stopcock plug **84** (FIG. 4) has two passage systems therethrough at right angles to each other. One of them **86** provides a simple connection of the passage **76** of the fitting to the calibrated burette tube. The other **88** is Y-shaped and opens both the burette tube and the pressure balancing tube **82** to the passage **76**.

The burette tube is calibrated as at **90** over only a portion of its length. Upwardly from the calibrated portion, a simple stopcock **92** is provided. The burette tube terminates upwardly of the stopcock **92** in an open, right-angle lateral bend **94**. A drying tube **96** containing an appropriate desiccant may be coupled to the open upper end of the burette tube **94** by a sleve **98** or other appropriate structure. The pressure balancing tube **82** extends straight upward from the stopcock **78** and terminates in an open upper end above the level of the upper end of the burette tube **80**.

The device is completed by a small, tubular, resistance furnace **100** having an interior cavity adapted to enclose the sample arm **64** of the sample tube **56**. The heater will be carried on a table **102** which may be mounted on the exterior of the cylinder **16** as by a clamp **103** and arm **104**. The table should provide room enough to permit sliding the furnace off or on the sample arm.

The operation of the above described device is as follows. The cylinder **16** above the piston **42** is filled with mercury to a level somewhat below the side arm **50** when the piston is lowered. It will be understood that the capacity of the cylinder and the scope of movement of the piston **42** will be sufficient to accomplish the purposes to be described.

The mercury forms a part of the permanent equipment of the apparatus.

To start an analysis, the furnace **100** will be withdrawn from the sample arm and the sample tube disconnected from the apparatus for the deposit of a sample **106** therein. The sample as illustrated is about a quarter of an inch in diameter and three-quarters of an inch long and weighs about 5 grams. The desiccant arm will be filled with mercury to keep the desiccant from unnecessary contamination, as will be described later. It will be understood of course that the sample tube is freely rotatable on the side arm without breaking the gas-tight seal.

The sample tube is then reconnected to the side arm **50** and rotated so that both the desiccant arm and the sample arm are tilted downwardly with the sample arm desirably having a greater downward inclination. The open end or mouth **54** of the sample tube **56** is straight and about one inch long, and the telescoping attachment of the open end to the side arm **50** occupies entirely this straight portion. In other words, with the sample tube oriented as described on the side arm, the spring clip **55** occupies a position over the steeply downwardly sloping floor of the sample arm.

The stopcock **84** will be oriented to permit flow to both the pressure balancing tube **82** and the burette tube **80**. The stopcock **92** will be opened and the lever **18** will be in its lowermost position. Upon raising the lever, mercury will be displaced from its reservoir in the cylinder **14**, by the upward movement of the piston **42**, out through the side arm to flood the sample tube entirely and upwardly through the burette and tube to a point above the stopcock **92**. The lever will be held in that upper position while the stopcock **92** is closed and stopcock **84** turned to connect the burette **80** only. The lever is then lowered to permit the return of the mercury again to the reservoir in the cylinder **14**. The sample tube will be rotated on the side arm **50** so that the two tubes each have an upward inclination and the mercury contained in them will drain into the reservoir. The spring clip **55**, it will be appreciated, prevents the passage of the steel sample into the side arm either in the course of floating up on the received mercury or in the course of tilting the sample tube upwardly so as to drain it. In this fashion a high vacuum is established in the apparatus above the mercury level in the reservoir.

Although this evacuating principle is ideally near perfect, there are areas where minor entrapments of air may occur such that the vacuum is not as perfect as may be. Notably, the interstices between the particles in the desiccant tube may trap some bubbles, and the juncture between the sample tube and side arm provides a lodgement for an air bubble. Both of these constitute a very small proportion of the total volume, but might introduce an appreciable error, depending on the order of accuracy desired. It is therefore suggested that the evacuating procedure be repeated or twice repeated to improve the vacuum by the same multiple as the original evacuation procedure. The additional evacuation steps are the same as those described before except that the stopcock **84** remains connected to the burette only and stopcock **92** remains closed until the mercury is in the burette.

After the apparatus has been successfully evacuated as described, the lever **18** is forced down and latched and the sample tube is turned on the side arm so that the sample arm is in its lowermost position. Thereupon, the sample will drop to the bottom of the sample arm. Thereafter the sample tube is turned so that the sample arm is horizontal. Throughout the evacuation, the furnace **102** has, of course, been removed from interference with the movement of the sample tube.

After the sample tube has been turned to a horizontal position, the furnace is positioned over it as illustrated in FIG. 2 and energized to bring the sample to a temperature of 600 to 1000° C. The hydrogen will be evolved from the sample and disseminated throughout the apparatus. After a suitable period of heating time, such as 10 minutes for instance, the furnace is withdrawn and the sample arm permitted to cool. The sample tube will then be turned downward again to insure the flooding of both arms and the lever arm raised to flood the sample tube again and extend a column up into the burette tube. At this point, the stopcock plug **84** is turned so as to establish communication of the passage **76** with both the burette tube and the pressure balance tube **82**. Thereafter, the level is manipulated by careful degrees so as to bring the level of mercury in the two tubes into equality, and the level in the burette tube then read, the gas above it being at atmospheric pressure. From this measurement the gas content of the steel sample can be readily computed. Following the reading the lower stopcock **84** is changed to its burette-only connection the top stopcock **92** is opened, and the lever **18** depressed to return the mercury to the cylinder **14**. The sample tube is rotated so that the sample arm **64** inclines upwardly to drain but the desiccant arm remains downwardly inclined to retain its mercury. The tube is then removed and the sample withdrawn.

The apparatus illustrated in FIG. 4 is intended for use where highly accurate hydrogen determinations are wanted or where it is suspected that other gases may be present in the evolved hydrogen in sufficient quantities to impair seriously the accuracy of the reading. Such an occurrence such as the latter is unlikely; tests have shown that 90 to 95% of the gas collected by hot extraction is hydrogen and no further separation is necessary except when a very high order of accuracy is desired. To meet this need for high accuracy, however, there is shown a hydrogen elimination tube **110** which, in essence, will be substituted for the drying tube **96** of FIG. 1. As illustrated, the upper horizontal end of the burette tube **94** is modified to provide a standard taper joint and the hydrogen elimination tube **110** possesses the matching joint part **114**. The joint may be held together by springs **116** secured to a ring **118** on the upper end of the burette and hooked over horns **120** on the hydrogen elimination tube. The tube **110** is a simple, open-ended length of borosilicate glass tubing formed to constitute the above-mentioned taper joint half and horns at one end and is

connected at its other end to a closed length of palladium tubing **122** through the medium of a length of tubing **124** adapted for a glass-in-metal seal. A heating coil **126** or equivalent furnace will be associated with the palladium.

As is well known, hot palladium is permeable to hydrogen, but hydrogen only.

To use the hydrogen elimination tube **110**, the apparatus, as stated, will lack the drying tube **96**. Instead, the upper end of the burette tube will terminate in the open taper joint **112**. The before-described analysis will be conducted to the point where a reading is taken in the calibrated portion **90** of the burette tube. At this point, the hydrogen elimination tube will be connected to the outlet of the burette tube and the heater **126** energized. At the time of connection, the hydrogen elimination tube and the portion of the burette tube above the stopcock **92** will hold air at ambient conditions of temperature and pressure. After the connection of the hydrogen elimination tube and the heating of the palladium portion thereof, the stopcock **92** will be opened and the hydrogen contained above the mercury column will diffuse into the air contained above the stopcock **92** and out through the palladium tube. After an appropriate time interval sufficient to eliminate all the hydrogen through the palladium tube, the heating will be stopped and the palladium tube permitted to return to ambient temperature. Thereafter, the two mercury tubes will again be balanced, and the differences between the first and second readings will be the actual hydrogen present in the sample to a high degree of accuracy.

It will be appreciated that the method described above is an exemplification only and the apparatus is but a single embodiment of the invention herein.

We claim:

1. Apparatus for the determination of hydrogen in a metal sample which comprises a sample chamber, a burette connected to said sample chamber and extending upwardly therefrom, said burette having a valve at the top thereof, a reservoir having mercury therein below said sample chamber, means for displacing mercury from the reservoir to flood said sample chamber and said burette entirely, means for heating a sample in said sample chamber, a pressure balance tube aligned with said burette, and valve means interposed between the top of said sample chamber and the bottom of said burette and the bottom of said tube adapted optionally

to permit fluid flow from said sample chamber ino the bottom of said burette only and into the bottom of said burette and the bottom of said tube altogether.

2. Apparatus for the determination of hydrogen in a metal sample which comprises a sample chamber, a burette connected to said sample chamber and extending upwardly therefrom, said burette having a valve at the top thereof, a reservoir having mercury therein below said sample chamber, means for displacing mercury from the reservoir to flood said sample chamber and said burette entirely, means for heating a sample in said sample chamber, said sample chamber having a bend and being connected to said burette to be rotatable with respect thereto to be optionally upwardly or downwardly inclined.

3. Apparatus for the determination of hydrogen in a metal sample which comprises a sample chamber, a burette connected to said sample chamber and extending upwardly therefrom, said burette having a valve at the top thereof, a reservoir having mercury therein below said sample chamber, means for displacing mercury from the reservoir to flood said sample chamber and said burette entirely, means for heating a sample in said sample chamber, a palladium tube connected to the upper end of said burette above said valve, and a heater for said palladium tube.

4. Apparatus for the determination of hydrogen in a metal sample which comprises a sample chamber, a burette connected to said sample chamber and extending upwardly therefrom, said burette having a valve at the top thereof, a reservoir having mercury therein below said sample chamber, means for displacing mercury from the reservoir to flood said sample chamber and said burette entirely, means for heating a sample in said sample chamber, said sample chamber incorporating a bend and being rotatable so as to be optionally upwardly or downwardly tilted.

References Cited

UNITED STATES PATENTS

2,387,878	10/1945	Brown	73—19
2,361,844	10/1944	Horner	73—19
2,749,220	6/1956	Rochon	73—19
3,176,500	4/1965	Coe	73—19
3,177,700	4/1965	Sier	73—19

CHARLES A. RUEHL, Primary Examiner

PO-1050
(5/69)

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,490,266 Dated January 20, 1970

Inventor(s) Eugene L. Bennet and Robert N. Revesz

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Col. 4, line 42, "level" should be --lever--.

Col. 6, line 1, "ino" should be --into--;
line 3, "altogether"should be --together--.

SIGNED AND
SEALED
JUL 14 1970

(SEAL)
Attest:

Edward M. Fletcher, Jr.
Attesting Officer

WILLIAM E. SCHUYLER, JR.
Commissioner of Patents