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RAPID GAS ANALYSIS

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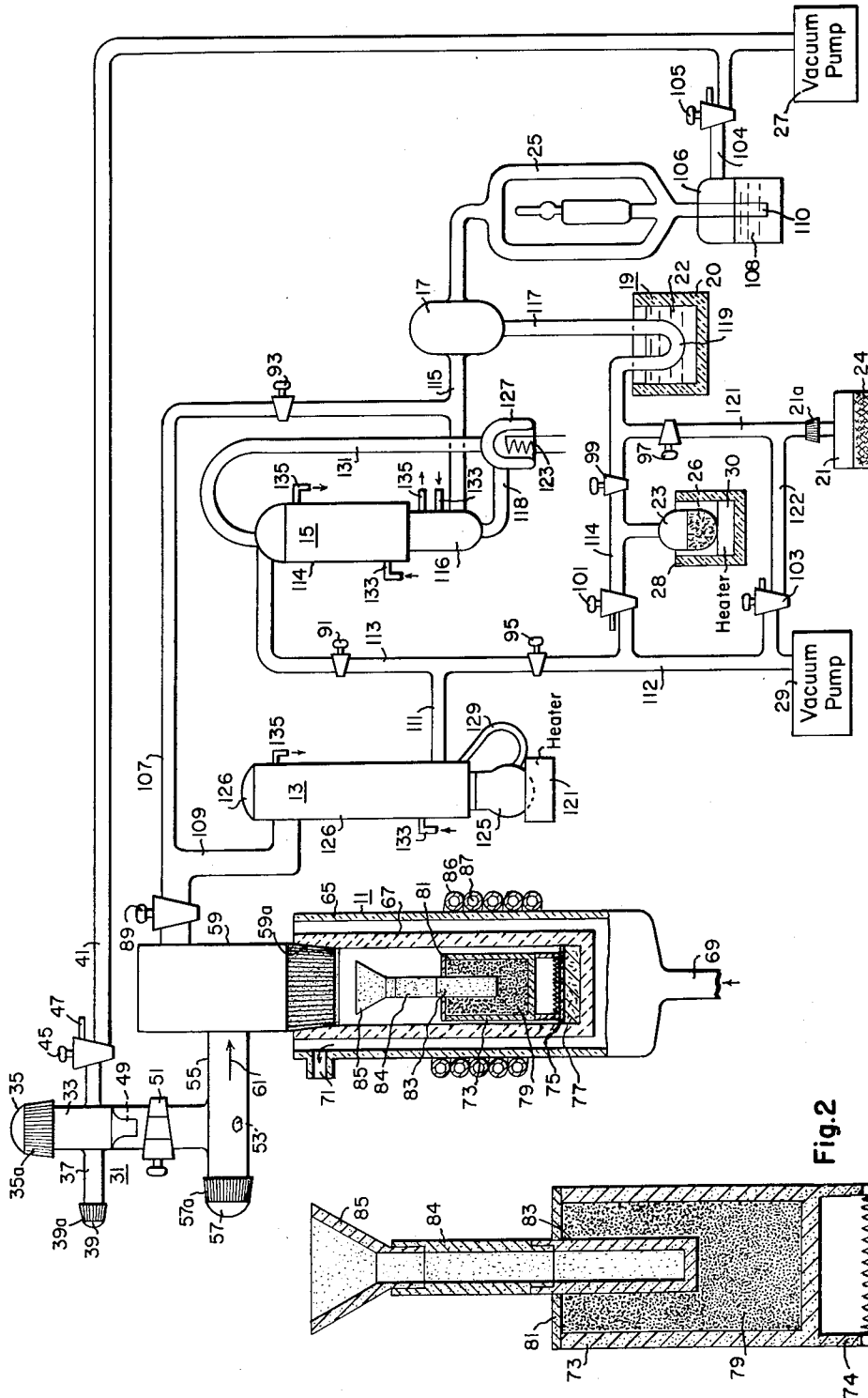


Fig. 1

Fig. 2

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RAPID GAS ANALYSIS

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This invention relates to an improved method and apparatus for the rapid analysis of gases in metal.

The control of the amount of oxygen, hydrogen and nitrogen in metals, such as iron, nickel, titanium, zirconium and base alloys of such metals, has become of great importance in recent years due to the increasing demand for maintaining stringent tolerances of the gaseous content. Such control can only be fully obtained by the proper addition of deoxidizers or purifiers or the application of vacuum, when and where necessary, during melting to obtain the desired metal quality through control of deoxidation, cleanliness and gas content. To achieve such control to the fullest requires the aid of an accurate method of gas analysis for the metal being melted of great enough speed that the analytical results would be available while the metal is still in the furnace awaiting treatment for deoxidation, etc. The time element then is of primary importance in obtaining useful analytical results that will be used to determine the mode and extent of this treatment.

None of the conventional methods or equipment available will provide a nitrogen, oxygen and hydrogen result in the relatively short time available under these circumstances.

Conventional methods of metal gas analysis involve the extraction of gases at elevated temperatures from the molten metal sample in a vacuum furnace. Such gases are then pumped into a pressure chamber for pressure measurement and then through at least one oxidizer wherein carbon monoxide and hydrogen, which has evolved during heating of the sample in the furnace of the apparatus, is converted into carbon dioxide and water vapor, respectively, the nitrogen being unchanged. The gases are subsequently pumped through "freeze-out" chambers where first the water vapor and then the carbon dioxide is precipitated in the form of water ice and carbon dioxide ice causing in each case measurable decreases in gas pressure. The water vapor is precipitated first, in that it may be "frozen out" at a higher temperature than the carbon dioxide. The resultant drop in gas pressure is thus the basis for a measurement of the hydrogen content. The carbon dioxide is subsequently precipitated out at a lower temperature. The second decrease in pressure thus being a basis for the determination of oxygen content. The balance of the gaseous pressure is presumed to be nitrogen. Another variation of the prior art methods is to employ absorption chambers containing chemicals that preferentially combine with water vapor or carbon dioxide in place of "freeze-out" chambers. The prior art methods also embody the use of a carrier gas, such as argon, to sweep the extracted gases from the furnace and carry them through the analytical section of the apparatus.

One difficulty with the prior art methods is that the gases must be either pumped or swept through numerous chambers; first, from the furnace to the initial pressure vessel, then from that vessel to a chamber containing oxidizing agents, then to a "freeze-out" or absorption chamber for removing water vapor, then back to the pressure chamber to measure pressure decrease due to removal of water vapor, then to a second "freeze-out" or absorption chamber wherein carbon dioxide is removed, then finally back to a pressure chamber to measure pres-

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sure decrease due to the removal of carbon dioxide, and to obtain residue pressure due to nitrogen. There are several variations of this procedure in use which differ in that the measurement of the partial pressures of the gases removed might be made either in the first pressure chamber as a pressure decrease as already described or at the "freeze-out" trap by thawing the frozen gases (CO_2 and H_2O) separately and measuring their vapor pressure in the "freeze-out" trap. In the latter case the "freeze-out" trap is specially constructed so as to be of a known fixed volume suitably connected to a pressure measuring gauge. Also, in the latter procedure the nitrogen which does not freeze out must still be measured in the first pressure chamber. All such procedures entail the consumption of considerable time in that each step requiring pumping or the manipulation of absorbents or the manipulation of "freeze-out" equipment prolongs the process to a total of up to 60 minutes by conventional methods, exclusive of the time required to remove the gases from the metal sample.

Inaccuracies in gas measurements result in using such procedures because oxidation of the gases would not be complete unless the rate of oxidation were somehow increased, if attempts are made to shorten such analyses beyond the critical time periods established for a particular apparatus by decreasing circulation time. The present invention is so designed as to provide this needed increase in the rate of oxidation.

Materials commonly employed as agents to oxidize gases evolved from metals in vacuum or inert gas furnaces for gas measurement means are specially prepared and often mixed with other oxides when employed for such use. Some of these agents whose preparation are described in the literature are copper oxide (CuO) and manganese dioxide (MnO_2), the latter known commercially as Hopcalite. Another is iodine pentoxide (I_2O_5) specially prepared on a silica gel support. In employing the latter agent, one can obtain only the oxygen content of a gaseous mixture by conversion of carbon monoxide to carbon dioxide and cannot distinguish in the remaining gaseous pressure between hydrogen and nitrogen as there is no conversion of hydrogen to water vapor. When employing copper oxide, the carbon monoxide and the hydrogen are oxidized to carbon dioxide and water vapor, respectively, but these two gases cannot be distinguished without preferential absorption or preferential "freeze-out."

It has been found by the method and the apparatus of the present invention that a practical and useful gas analysis for all three gases (nitrogen, oxygen and hydrogen), commonly found in metals, may be obtained in the extremely short time of 7 minutes and even in less than 5 minutes.

It is the object of the present invention to provide a method and apparatus wherein the nitrogen, hydrogen and oxygen contents from the metal samples may be quickly and efficiently measured.

A further object of the present invention is to provide a method of rapid analysis wherein the oxygen, nitrogen and hydrogen contents of a metal may be determined from one sample.

Still further objects and advantageous features of the present invention will be obvious from the following description and drawings wherein:

FIGURE 1 is a general view, partially in cross section, of the apparatus embodying the features of this invention, and

FIG. 2 is an enlarged vertical cross sectional view of the furnace unit employed in the operation of FIG. 1.

In general, the present invention relates to the process and the apparatus, which makes such process possible,

wherein a metal sample is heated to effect the evolution of the gaseous content of the metal, which consists of a mixture of hydrogen, nitrogen and oxygen, into a volume. Such gaseous mixture is initially exposed to carbon which at the temperature of evolution effects a transformation of the oxygen content to carbon monoxide. The gaseous mixture of hydrogen, nitrogen and carbon monoxide is transferred by means of the present apparatus to a reservoir area, the volume of which has been carefully calculated and which has been previously evacuated to a degree that the gaseous mixture is not materially contaminated. A reading of the pressure is taken at this point. The carbon monoxide is then converted to carbon dioxide by means of exposure to a selective catalyst (preferably I_2O_5). Due to the presence of a freeze-out zone, wherein the temperature of a section of the volume of the reservoir area is exposed to temperatures below that at which carbon dioxide precipitates as Dry Ice, such carbon dioxide precipitates out leaving only the hydrogen and nitrogen gas. A second reading of the pressures in the reservoir area enables easy calculation of the oxygen originally emitted from the sample. A subsequent exposure of the remaining gas in the reservoir area to a second catalyst (preferably copper oxide) results in a conversion of substantially all the hydrogen gas to H_2O or water which due to the free-out zone mentioned above precipitates out of the reservoir area into solid ice effecting a further measurable drop of the gaseous pressure inside the reservoir area, making possible the calculation of the hydrogen gas originally emitted from the sample piece. The remaining gaseous pressure is easily calculated to give the quantity of nitrogen gas originally emitted from the sample.

By maintaining the furnace temperature in the range of from about 1800°C . and above, it is possible by the use of the apparatus and method of the present invention to effect a complete analysis of the hydrogen, nitrogen and oxygen gases of a given metal sample within a period of time of less than 7 minutes.

Referring to the drawing, there is shown a gas analysis apparatus that constitutes one embodiment falling within the scope of the present invention. It is understood, however, that this embodiment is illustrative only and does not confine the application to the exact apparatus or method set forth. It will be appreciated that the various components, some of which are set forth in detail and others of which are merely illustrated generally, are optional types of conventional apparatus and may easily be substituted by other conventional and commercially available components that function to perform in a similar manner to that illustrated.

The apparatus of the drawing is composed generally of a conventional induction heated vacuum fusion gas analysis furnace indicated generally in FIG. 1 at 11, two mercury vapor pumps indicated at 13 and 15, a gas collection chamber 17, a freeze-out zone 19, two catalyst containers 21 and 23, a McLeod gauge 25 and two mechanical vacuum pumps 27 and 29.

Furnace 11 is provided with a vacuum lock shown generally at 31, the function of which is to provide a means of introducing the sample to be analyzed into the system without admitting air. Vacuum lock 31 is composed of an upwardly extending glass tube 33 which is sealed off at the top by a glass cap 35. The cap 35 and tube 33 are joined by a conventional ground glass joint, as shown at 35(a), and sealed with wax. Extending from tube 33 is a sample entry tube 37, also sealed at the open end by a glass cap 39 and a ground glass joint 39(a). The ground glass joints 39(a) and 35(a) permit the glass caps 39 and 35 to be readily removed and replaced. Tube 33 communicates with a tube 41 through a three-way stopcock valve 45. Tube 41 leads to the mechanical vacuum pump 27. Stopcock 45 is a three-way valve that may be adjusted so as to seal off tube 41 from tube 33

but bleed air into tube 33 through a port 47 located on this valve or it may be adjusted to provide communication between tube 41 and tube 33 or it may be adjusted so as to prevent access of tube 33 to either port 47 or tube 41. By this valve, tube 33 may be provided with air through port 47, a vacuum through tube 41 and pump 27 or the valve may be adjusted to seal off both. Located inside tube 33 is a funnel 49 that serves to funnel sample material inserted at sample entry tube 37 through a large stopcock valve 51 (when open) and avoids contact with the stopcock grease on valve 51. A sample is shown at 53 as having been projected through funnel 49 and stopcock 51, which is shown in the open position, into a furnace entry tube 55.

In operation, the entire vacuum lock 31 must be substantially evacuated of air and an accurate measurement of the gaseous content of a metal may not be ascertained if air is introduced into the furnace 11 along with the sample; however, a sample may be introduced into the present system through vacuum lock 31 while avoiding the introduction of air or atmosphere into the over-all system. Before introducing a sample into sample entry tube 37, stopcock valve 51 is adjusted so that tube 33 is sealed off from tube 55. Stopcock valve 45 is then adjusted so as to leak air through port 47 into tube 33.

After there is no longer a vacuum in tube 33, glass cap 39 is removed from sample entry tube 37 and the weighed metal sample, single or multiple, is introduced into the mouth of this tube. Glass cap 39 is then replaced, it being effectively sealed with grease. Three-way stopcock valve 45 is then adjusted so that air no longer leaks through port 47 into tube 33, but a common passage is provided between tube 41 and tube 33 and hence tube 37. Vacuum pump 27 will then substantially evacuate the air from tubes 33 and 37. The valve 45 is then adjusted so that both tube 41 and port 47 are sealed off from tube 33 and 37. Stopcock valve 51 is then rotated so that tubes 33 and 37 may communicate with the furnace entry tube 55 and the sample material may flow through the valve 51 when passed through funnel 49. Any remaining traces of air in the vacuum lock system 31 not removed by vacuum pump 27 may be swept through and out of the system by pumps 13 and 29 by opening valves 89 and 95 while keeping valves 91, 101 and 103 closed.

The sample material in tube 37 is projected into the funnel 49 by means of a magnet (not shown) traveled along the outside surface of the tube wall. If the sample is non-magnetic, a magnetic "pusher" (not shown) made of iron is disposed behind the sample so as to be moved by the magnet to push the sample along the tube 37 to project it into funnel 49. The magnetic "pusher" is then returned to rest in sample entry tube 37 by the magnet. Tube 55 is also shown to be sealed off with a glass cap 57 and a ground glass fitting 57(a) which is sealed as in conventional practice with the aid of wax. Before introducing the sample into the furnace 11 from tube 55, stopcock valves 89 and 91 are "opened" while valves 93, 95, 97 and 99 are closed. The sample is projected into the furnace by being propelled along the tube 55 in the direction shown by the arrow 61 by a magnet (not shown) as in the manner described for propelling the sample along tube 37. When the sample reaches furnace collection chamber 59, the magnet is withdrawn and the sample falls into the graphite crucible 83 of the furnace 11.

The furnace 11 of the present embodiment is very simply constructed, consisting of an outer Pyrex glass cooling jacket 65 and an inner quartz crucible retaining member 67. Coolant water flows into and out of the glass cooling jacket as shown at 69 and 71 and serves to cool the retaining member 67 and ground joint 59(a) and protect the equipment. The quartz retaining member 67 contains a graphite crucible retaining cup 73 which rests on a graphite disk 75 which in turn sits on a particulate re-

fractory 77 (usually periclase). Crucible retaining cup 73 is provided with an extension cylinder 74 (an integral part of cup 73, see FIG. 2). Extension cylinder 74 is, in turn, formed with a saw-toothed rim 76 which supports crucible retaining cup 73, hence crucible 83 and its surrounding supporting members, on disk 75. The saw-toothed construction 76 serves to minimize heat transfer from the crucible to the disk 75 and surrounding support components. The cup 73 is filled with powdered graphite 79. On top of cup 73 there rests an annular shaped member 81 made of compressed graphite which encloses the particular graphite 79. The member 81 is provided with a centrally disposed opening through which is inserted the cylindrical crucible 83 having an upwardly extending extension 84 in the form of a graphite tube, which is provided with a graphite funnel 85 adapted to receive the sample projected into the furnace 11. The crucible within cup-shaped member 73 is subjected to induction heating so that cup-shaped member 73, particulate material 79 and annular shaped member 81, all serve to both retain the intense heat of the crucible within and protect outside members from such heat. Heat is supplied by a conventional water cooled copper tube induction coil shown at 86. A high frequency alternating current flow through the coil 86 induces a countercurrent or flux in the walls of crucible 83, and thus the induction heating principle is applied.

It is to be noted by FIG. 2 that the crucible 83 is extended above container 73 and annular shaped member 81 by means of graphite condenser tube 84. Graphite tube 84 approximately doubles the length of the crucible but is not subjected to direct induction heating due to the fact induction coil 86 does not surround this member and that the tube 84 and crucible 83 are separate members. Such construction has been found to greatly enhance the speed at which gas is quantitatively emitted from samples in crucible 83 and to facilitate the conversion of oxygen to carbon monoxide without subsequent absorption by metallic vapors and contributes materially to the obtaining of a more accurate rapid gas analysis.

Quartz crucible retaining member 67 of furnace 11 is joined to gas collection chamber 59 through a ground glass sealed fitting 59(a). Collection chamber 59 in the present embodiment is fabricated from Pyrex glass as are all the components of the apparatus except the quartz, graphite and magnesia components of the furnace and the electric heating units and the mechanical vacuum pumps.

The furnace may be heated to any desired temperature up to about 2500° C. Common practice is to employ temperatures in the range of about 1550° C. to 1700° C.; however, to effect the desired rapid analysis when analyzing steel or high temperature alloys, we prefer to employ a temperature in the range of about 1800° C. to 2200° C. At these temperatures, the gaseous content of the metal sample consisting of oxygen, hydrogen and nitrogen is driven off within several minutes or less. The oxygen reacts almost immediately with the graphite of the crucible to form carbon monoxide gas so that the gases that rise into the furnace collection chamber 59 are essentially carbon monoxide, hydrogen and nitrogen.

At this point of the analysis, stopcock valves 89 and 91 are open while valves 93 and 95 are closed so that mercury vapor pumps 13 and 15 are operating to draw the gaseous content from crucible 83 and furnace collection chamber 59 through the valve 89, tube 109, pump 13, tube 111, tube 113, valve 91, mercury vapor pump 15, tube 115 and into gas collection chamber 17. It should be noted that stopcock 89 is of larger bore than ordinary and that the vacuum tubing from the furnace area through stopcock 89 then to pump 13 is of a larger diameter to provide rapid evacuation of the gases from the furnace 11. Valves 97, 99, 101 and 103 remain closed during this period so that the gas to be analyzed is actually confined to the area of reservoir 17, the part of tube 115 on reservoir side of pump 15, the part of tube 107 up to valve 93, the area of the McLeod gauge, tube 117 including freeze out zone

119, to closed valve 99 and a portion of tube 121 to closed valve 97. The over-all volume of this entire section has been previously measured so that the volume relationship of the gas versus pressure is a measure of the gaseous content of the sample in crucible 83. After degassing of the sample is completed, valve 91 is now closed since the gases have been transferred past mercury vapor pump 15 which is a conventional constant volume pump that will act as a one-way valve and will not permit the gases to flow back through the pump, but which will not affect the pressure of the gases in reservoir 17 and adjacent reservoir areas. Valve 95 may now be opened so that blank gases from the furnace, generated during the period that the previously collected gases are being analyzed, will be transferred through pump 13 and tube 112 to mechanical vacuum pump 29 and out of the system in preparation for the next sample to be introduced into the furnace 11.

A reading is taken at this point of the analysis on McLeod gauge 25. This reading represents the total pressure of the carbon monoxide, hydrogen and nitrogen in reservoir 17 and adjacent areas.

Freeze-out zone 19 is composed of a container 20, shown in cross section, containing a coolant 22 which in the present embodiment is liquid nitrogen so that the area of tube 117 or loop 119 which projects into coolant 22 is maintained at a sufficiently low temperature to "freeze out" or transform any carbon dioxide gas present into frozen carbon dioxide or Dry Ice.

Catalyst container 21 contains a quantity of iodine pentoxide (I_2O_5) 24. The iodine pentoxide 24 will cause a carbon monoxide gas, which comes into contact with it, to instantaneously oxidize or convert into carbon dioxide gas so that when stopcock valve 97 is opened, permitting access of catalyst container 21 to the reservoir 17 and adjacent reservoir areas, the carbon monoxide of the gas formed in the furnace 11 from the oxygen evolved from sample 53 is converted to carbon dioxide. This gas having access to loop 119 of tube 117 in freeze-out zone 19 and this area being at a temperature below the freezing temperature of carbon dioxide due to coolant 22 (about -320° F.), the total carbon dioxide of the sample, and thus the total oxygen content, crystallizes and precipitates out. A new reading on the McLeod gauge 25 will reflect the drop in pressure and will enable an easy calculation of the carbon dioxide present, thus the oxygen present and consequently the total original amount of oxygen emitted from the metal sample in furnace 11. Of course, appropriate allowance must be made for the added area or volume added to the reservoir area by catalyst container 21, tubes 121 and 122 by the opening of valve 97.

Catalyst container 23 contains a particulate copper oxide 26 which when exposed to hydrogen gas converts it to H_2O or water. Container 23 is surrounded with a heat retaining envelope 28 and a heater 30 which serves to increase and enhance the catalytic or oxidizing powers of the CuO in converting the hydrogen content to water vapor. When stopcock valve 99 is revolved and opened, access to the remaining gases in reservoir 17 and adjacent reservoir areas is given to container 23 and all the hydrogen present in this area is quickly converted to H_2O vapor and since freeze-out area 19 or loop 119 is at a temperature that will freeze or precipitate out carbon dioxide which freezes only at a temperature far below that of water, the water vapor or H_2O will immediately freeze out in this area, and thus the hydrogen content of the gas will be removed. A new reading on McLeod gauge 25 reflects the additional drop in gaseous pressure and enables the additional calculation of the hydrogen content. The remaining gas pressure indicated by this third reading is, of course, a measurement of the remaining gas which is the nitrogen content. As before in these calculations, allowance must be made for the added volume of the catalyst containers 21 and 23 added to the total reservoir area. Allowance must also be made of the effect of the extremely

low temperature of freeze-out zone 19 and the heated area of container 23 on pressure measurements involved.

The analysis has now been concluded in that the three readings taken on the McLeod gauge 25 will enable anyone skilled in the art to calculate the quantity of oxygen, hydrogen and nitrogen gas that was present in the sample originally introduced. Stopcock valve 89 is now closed and stopcock valve 93 is opened and since valve 95 is already in the opened position, the remaining nitrogen in the system will be removed by being pumped through tubes 107, 109, pump 13, tube 111, tube 112 and out into the atmosphere by means of pump 29.

Stopcock valve 93 is now closed and stopcock valve 89 is opened. The next sample is now introduced into vacuum lock 31 and positioned in tube 55, or any time during the period that stopcock valves 91 and 93 were closed, another sample or samples could have been introduced into the vacuum lock 31 and positioned in tube 55. A few seconds later stopcock valve 95 is closed and stopcock valve 91 is opened. The system is now prepared for another analysis, the entire cycle for one sample taking less than 5 minutes to obtain the desired results.

Many of the valves and fittings of the illustrated apparatus are present to provide convenience and ease in the handling of samples and replacing and repairing the component parts, it being obvious that the apparatus could be effectively operated without them. For example, cap 35 and ground glass connection 35(a) permit easy access to the interior of the tube 33 of vacuum lock apparatus 31 when samples become stuck or are inadvertently projected on stopcock 51 when in a closed position. Likewise, fitting 57 and connection 57(a) permit easy access to tube 55. Three-way valves 101 and 103 could be eliminated entirely so long as the connection of tube 114 and tube 122 were sealed off from tube 112. These valves (101 and 103) are normally closed during operation of the system; however, three-way valve 101 may be adjusted to bleed atmosphere into chamber 23, when it is necessary to remove the container and replace the CuO catalyst, without disrupting the substantial vacuum in the rest of the system (valve 99 being closed). Admitted air can then be pumped out through tube 112 and pump 29 by adjustment of valve 101, thus eliminating the danger of contaminating pump 13 or 15. Likewise, three-way valve 103 may be used to bleed air into container 21 while valve 97 is closed to permit replacement of the catalyst 24. Container 21 is provided with a ground glass fitting 21(a) to permit easy removal and frequent replacement of the I_2O_5 catalyst.

Three-way stopcock valve 105 remains open and permits access of mercury container 106 of the McLeod gauge 25 to tube 41 and vacuum pump 27 through tube 104 and thus a substantial vacuum is maintained in container 106 causing the mercury 108 in McLeod gauge 25 to remain in container 106 and prevents it from projecting into tube 110. When it is desired to take a reading on the McLeod gauge, three-way valve 105 is rotated so as to permit air to pass into tube 104 (on the McLeod gauge side only) and mercury container 106 so that atmospheric pressure forces the mercury up into tube 110 and thus into the calibrated part of the gauge and a pressure reading on reservoir 17 and adjacent areas may be taken. At the conclusion of such a reading, the valve 105 may be adjusted so as to permit access of container 106 to tube 41 and pump 27 through tube 104, thus evacuating the atmosphere in container 106 permitting mercury 108 to return to the container 106 through tube 110. This may be repeated for each pressure measurement desired.

The detailed and intricate operation of all the illustrated components have not been demonstrated in that the functions of such components are well known to one skilled in the art. For example, mercury vapor pumps 13 and 15 are of conventional design consisting of a heater, such as shown at 121 and 123, and water cooling jackets 126, 114 and 116 containing coolant water inlets 133 and out-

lets 135. It is well known that in such pumps mercury is boiled and rushes upward through a vertical tube. Gas from the vessel to be evacuated enters the stream and is driven forward. The mercury is chilled by a water jacket, liquefied and returned to the heater while the gas is discharged above the level of the condensed mercury that is re-entering the heated zone.

In pump 13 of the present embodiment, designed for very rapid pumping, mercury is boiled in container 125 which is heated by a heater 121. The mercury vapors rise vertically in a tube (not shown) to which tube 109 communicates. The tube through which now both the mercury vapor and gases discharged from tube 109 flow projects downwardly through cooling jacket 126. The mercury is condensed by cooling jacket 126 and returns to container 125 through the tube shown partially at 129, the gaseous material discharges through tube 111. The gaseous material will not flow through tube 129 into container 125 because of the level of liquefied mercury in this tube and container 125. In pump 15, a constant volume pump, it may be seen the mercury is heated in container 127 by heating element 123, vapors rise in tube 131 where it picks up the gaseous material from tube 113, proceeds into cooling jackets 114 and 116 where the mercury condenses and returns to chamber 127 through tube 118 while the gaseous material is discharged through tube 115.

The mechanical pumps 27 and 29 are, of course, of such well known construction that they will not be discussed here.

The apparatus of the present invention as shown in FIGS. 1 and 2 may be supported by clamps and support stands (not shown) in the conventional manner and quartz container 67 of furnace 11 is easily held in place by ground glass joint 59(a) and the buoyancy of the cooling water in cooling jacket 65.

It should be noted that the total volume of the present system, wherein the reactions resulting in the formation of carbon dioxide and water vapor and their precipitation take place, should be as small as is practical as this will result in the system being operated at higher pressures for a given mass of gas. This is advantageous in that it promotes reaction speed (oxidation of carbon monoxide, etc.) in contrast to the speed obtained in the conventional circulating procedure. Thus, deliberate advantage is taken of a chemical principle (law of mass action) which states that the rate at which a substance reacts at a constant temperature is proportional to its active mass; the active mass in the case of a gas is proportional to its partial pressure. Such rapid reactions do not occur in using prior art methods.

Note should be taken of another advantage of the method and procedure of the present invention, namely, that the removal ("freeze out") of the water vapor at liquid nitrogen temperature (-195°C.) is more complete (therefore more accurate) than with either prior art absorbents or Dry Ice "freeze out" (-70° to -100°C.), because the residual water vapor pressure at liquid nitrogen temperature is lower than it would be at any higher temperature (such as Dry Ice) or with any absorbent. Also, the low temperature of freeze-out zone 19 serves to materially reduce apparatus blank by constantly precipitating out any foreign gaseous matter present, such as that given off by the catalyst employed (presently I_2O_5 and CuO). In prior known apparatus, such equipment blank must be constantly accounted for and sometimes exceeds the quantity of the gases emitted by the metal sample. High equipment blanks contribute to the inaccuracies experienced in employing the prior known apparatus and method.

In the preferred embodiment of the present invention, it is highly desirable to retain iodine pentoxide and copper oxide as the catalyst employed in the apparatus of the present invention, because the iodine pentoxide is instantaneous in its effect and will only convert the carbon monoxide to carbon dioxide and will not effect the oxi-

dation of hydrogen to water so that in two operations both the oxygen and hydrogen content may be determined. Secondly, the copper oxide is rapid and highly efficient in converting the hydrogen content to H_2O , particularly while in the presence of the low temperature of the freeze-out zone which is far in excess of that required to freeze water but which materially speeds up the analysis of hydrogen due to the lowness of this temperature. Oxidizing agents other than iodine pentoxide and copper oxide may be employed; however, the suitability of such agents requires that the rate of oxidation obtained with them be rapid enough for practical application, and the completeness of the oxidation be great enough for such application. Also, there must be no serious decomposition of the agents over long periods of time in a vacuum of the degree used in such apparatus. In addition, the agent substituted for iodine pentoxide must not chemically or physically have any effect on the nitrogen or hydrogen. Any agent substituted for copper oxide must oxidize either hydrogen alone or both hydrogen and carbon monoxide but without chemical or physical effects on nitrogen.

The preferred catalysts or oxidizing agents employed in the preferred embodiment of the present invention are particulate oxides specially prepared for the purpose for which they are being employed. The CuO is prepared in a manner disclosed in Industrial and Engineering Chemistry, Analytical Edition, volume 22 (1950), by Dean I. Walter, on pages 297-300. The I_2O_5 preparation is taught in Berichte der Deutschen Chemischen Gesellschaft, volume 77B (1944), by Max Schutze, pages 484-487.

Note should be taken of another advantage of the method and procedure of the present invention; namely, that no "blank" correction is necessary for the oxidizers, as is the case for conventional processes and equipment, because the apparatus is so designed that the liquid nitrogen "freeze-out" area 19 effectively absorbs such "blank" gas and prevents it from contributing to the pressures being measured by gauge 25. This is of importance for increased accuracy and precision. When inserting steel samples into the furnace 11, it is highly desirable to simultaneously use platinum as an alloying agent flux, or catalyst to enhance the evolution of gas. Samples are usually prepared by cutting to size and removing surface contamination by filing or other suitable methods followed by rinsing in a pure reagent solvent, such as benzene, followed by pure acetone and drying in a warm clean current of air. The samples are thereafter weighed. If a flux, such as platinum, or tin, or both together, is to be employed, such material in foil form is wrapped around the sample, such foil having been previously weighed and degreased.

The use of platinum or tin flux or both together is often beneficial to accuracy in that it is possible to more completely remove from the furnace the gases extracted from the sample by its use, because conditions are less conducive to "gettering" (picking up surrounding gases and chemically combining therewith) of the gases by vaporized elements from the alloys being analyzed. The ratio of flux weight to sample weight varies between 1:1 and 20:1 depending on the composition of the sample.

In practice, the analyses are readily calculated for the various gases by use of the following equations:

$$\text{Percent oxygen} = \frac{[(k_1 P_1 - k_2 P_2) - (\text{blank})]}{\text{Sample weight}} \quad (F_1)$$

$$\text{Percent hydrogen} = \frac{[(k_3 P - k P_3) - (\text{blank})]}{\text{Sample weight}} \quad (F_2)$$

$$\text{Percent nitrogen} = \frac{[(k P_3) - (\text{blank})]}{\text{Sample weight}} \quad (F_3)$$

In the above equations, P_1 , P_2 and P_3 are the first, second and third pressure readings, respectively. The constants k_1 , k_2 , k_3 and k_4 must be determined experimental-

ly for the particular apparatus, the values of which depend on the geometrical and thermal relationships of the various parts of the analytical system. In my apparatus, they have the following numerical values:

$$k_1 = 1.024, k_2 = 1.185, k_3 = 1.087 \text{ and } k_4 = 1.153$$

The blank value that is used is a figure based on the pressure reading for the furnace components only if no flux is used, or if flux is used will consist of a figure based on the pressure reading obtained for the combined furnace components and a given flux. The flux blank is determined once for a given lot of flux material by analyzing it for all three gases just as for a regular sample. The constants F_1 , F_2 and F_3 for the gases, oxygen, hydrogen and nitrogen, respectively, are determined as part of the calibration of the analytical system and take into account the relative masses of the molecules of the respective gases, the gas constant, room temperature and the apparatus volumes in which the respective measurements are made.

The following data are examples of actual analysis of steel samples while obtaining hydrogen, nitrogen and oxygen contents:

Elapsed Time (Min.)		Type Sample		
		Iron 3% Silicon	O.H. Ingot Iron	AM-350
0	Sample admitted			
	Sample Wt. (grams)	.247	.251	.263
	Furnace temp., ° C	2,100	2,100	2,100
2	Extraction period (min.)	2	2	2
2½	1st pressure (mm. Hg)	0.098	0.851	0.620
4½	2nd pressure (mm. Hg)	0.040	0.038	0.440
	Pressure difference of above	0.058	0.813	0.180
	Oxygen equivalent of above diff. (wt. percent)	1 0.0059	1 0.101	1 0.0148
7	3rd pressure	0.017	0.012	0.352
	Press. diff. (2nd and 3rd)	0.023	0.026	0.088
	Hydrogen equivalent of above diff. (wt. percent)	1 0.00087	1 0.00044	1 0.00119
	Nitrogen equiv. of 3rd press (wt. percent)	1 0.0037	1 0.0020	1 0.089

1 Correction for furnace "blank" applied.

I claim:

1. The method of determining the oxygen, hydrogen and nitrogen content of a metal comprising, heating a known quantity of said metal in a substantial vacuum at a sufficiently high temperature to drive off the gases oxygen, hydrogen and nitrogen from said metal while simultaneously exposing said oxygen to carbon so as to convert said oxygen to carbon monoxide, transferring said gases to a known volume area that is substantially void of contaminating atmosphere, measuring the total pressure of the gases present in said known volume area, exposing said gases to a selective catalyst to convert said carbon monoxide to carbon dioxide without affecting said hydrogen or nitrogen while maintaining at least a portion of said known volume area at a temperature at which carbon dioxide will freeze so that substantially all the carbon dioxide present will crystallize out, measuring the total pressure of the remaining gases in said known volume area, the loss in pressure being a measure of the oxygen content of said metal, exposing said remaining gases to a catalyst that will convert said hydrogen to water while maintaining at least a portion of said known volume area at a temperature at which water will freeze so that substantially all the water will crystallize out, and measuring the pressure of the remaining gas in said known volume area, the loss in pressure being a measure of the hydrogen content of said metal and said pressure of the remaining gas in said known volume area being a measure of the nitrogen content of said metal.

2. The method of determining the oxygen, hydrogen and nitrogen content of a metal selected from the group consisting of iron, nickel, titanium, zirconium and base

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alloys of such metals comprising, heating a known quantity of said metal in a substantial vacuum at a temperature of from about 1800° C. to 2200° C. to drive off the gases oxygen, hydrogen and nitrogen from said metal while simultaneously exposing said gases to carbon so as to convert said oxygen to carbon monoxide, transferring said gases to a known volume area that is substantially devoid of contaminating atmosphere while maintaining at least a portion of said known volume area at a temperature of about -320° F., measuring the total pressure of the gases present in said known volume area, exposing said gases to iodine pentoxide to convert said carbon monoxide to carbon dioxide which will freeze and precipitate out in the portion of said known volume area having a temperature of about -320° F., measuring the total pressure of the remaining gases in said known volume area, the loss in pressure being a measure of the oxygen content of said metal, exposing said remaining gases to copper oxide to convert said hydrogen to water which will freeze and precipitate out in the por-

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tion of said known volume area having a temperature of about -320° F., and measuring the pressure of the remaining gas in said known volume area, the loss in pressure being a measure of the hydrogen content of said metal and said pressure of the remaining gas in said known volume area being a measure of the nitrogen content of said metal.

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