

Feb. 21, 1967

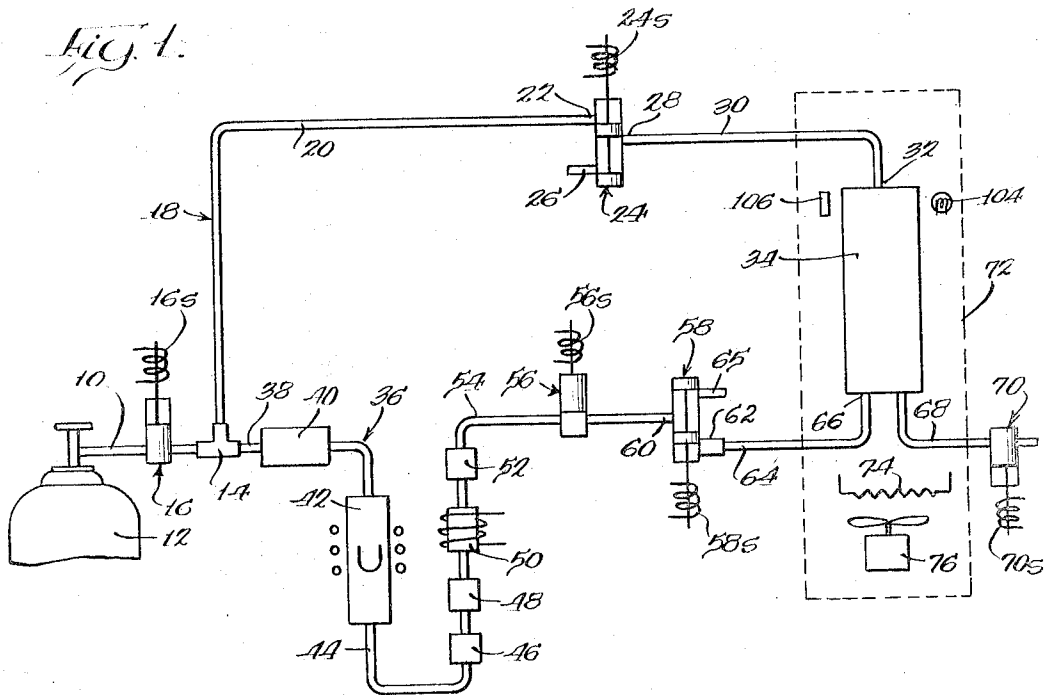
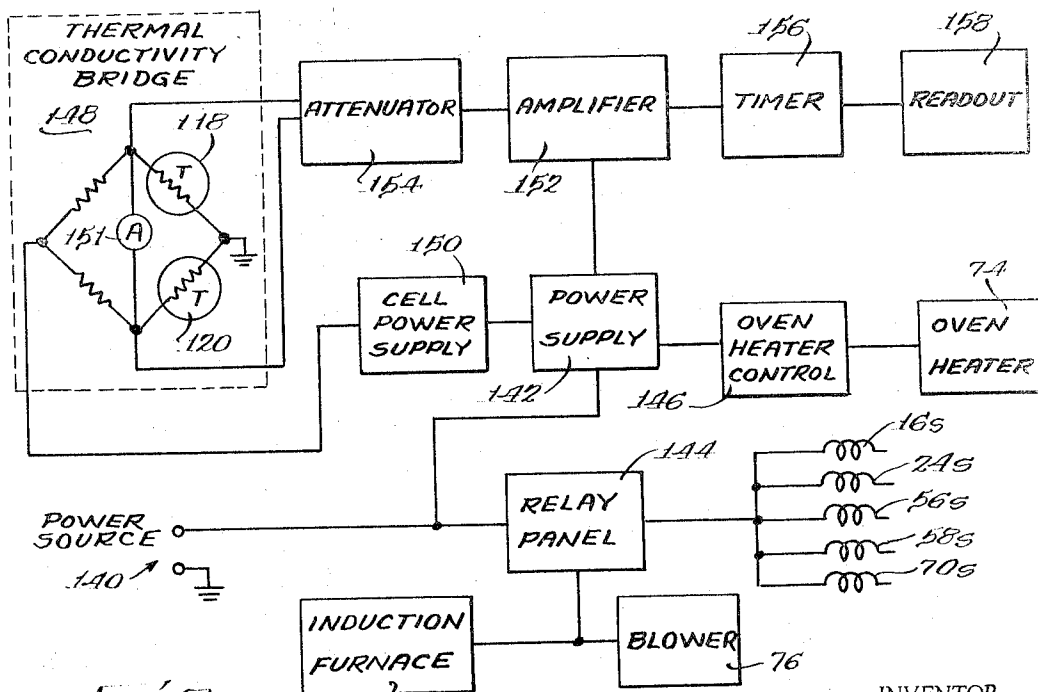
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3,305,318

RAPID CARBON DETERMINATION

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2 Sheets-Sheet 1



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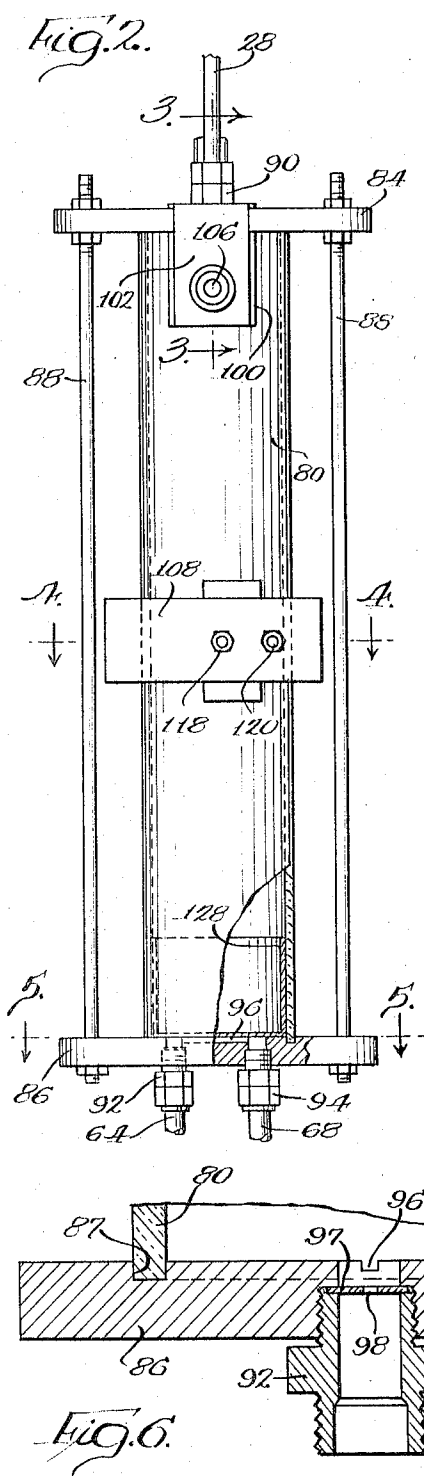
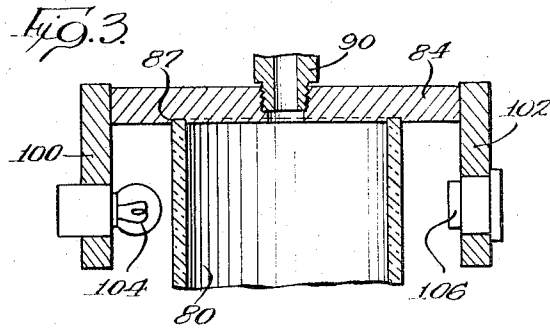
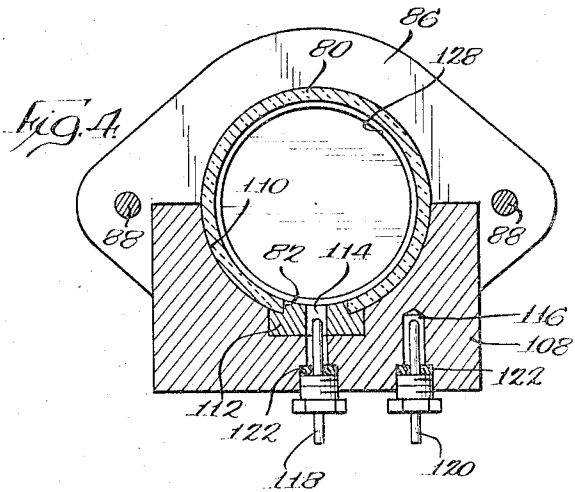
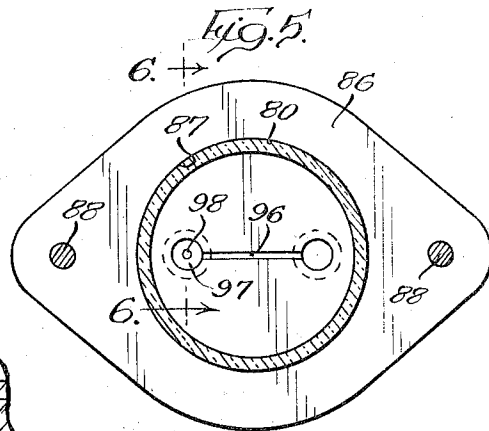
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RAPID CARBON DETERMINATION

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RAPID CARBON DETERMINATION

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6 Claims. (Cl. 23—230)

This invention relates to analytical apparatus and methods, and more particularly to the quick determination of the carbon percentage in samples of steel and iron and similar materials.

One of the objects of my invention is to provide novel apparatus and methods for the accurate determination of carbon more easily and quickly than has heretofore been possible so far as I am aware.

Another object is to provide a novel method and apparatus to determine accurately the carbon content of steel and similar samples within fifty seconds or less.

Yet another object is to provide novel automatic apparatus for accomplishing the above at a rate of one determination every fifty seconds or less.

Other objects and advantages will become apparent from the following description of a preferred embodiment of the invention.

In the drawings in which similar characters of reference refer to similar parts throughout the several views:

FIG. 1 is a diagrammatic representation of the physical portion of the apparatus;

FIG. 2 is a side elevation of the analysis chamber of FIG. 1;

FIG. 3 is a section through the top end of the chamber of FIG. 2, taken substantially along the line 3—3 looking in the direction of the arrows;

FIG. 4 is a section taken substantially along the line 4—4 of FIG. 2 looking in the direction of the arrows;

FIG. 5 is a top plan view of the bottom closure plate of the chamber taken substantially from the line 5—5 of FIG. 2;

FIG. 6 is an enlarged section taken substantially along the line 6—6 of FIG. 5 looking in the direction of the arrows; and

FIG. 7 is a diagrammatic illustration of the electrical circuitry.

The general approach used in the method and apparatus of this invention is briefly as follows. A sample to be tested is, for convenience in direct interpretation of the results, standardized at one gram. The sample can be in the form of turnings, drillings, pins, or a solid chunk. In the interest of speed of sampling, pins are probably to be preferred. They are obtained by sucking the molten metal from the batch into a precision bore borosilicate glass tube, such as that sold by Corning Glass Company under its trademark "Pyrex." When this is done, the glass fractures or crazes, but still holds together. It can easily be broken away from the solidified pin, however, and the pin can be cut to length in an appropriate fixture. With such sampling technique, the standard length uniform diameter pin will weigh within a few milligrams of whatever is desired.

The one gram sample in pin or other form is then placed in a crucible, along with a combustion accelerator, such as tin for instance. A suitable crucible is illustrated and described in Patent No. 2,930,602, issued March 29, 1960, to William C. Rohn. The loaded crucible is then placed in combustion apparatus of the general type disclosed in Patent No. 2,809,100, issued October 8, 1957, to George J. Krasl, where the sample is burned in the presence of oxygen. In this type of apparatus, the sample is heated in an induction field and is burned in a jet of oxygen, combustion being completed in less than ten seconds.

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During combustion, the iron and tin form solid oxides. The carbon in the sample, however, is converted to carbon dioxide which passes from the combustion chamber mixed with an excess of oxygen. Although some carbon monoxide, water vapor, and sulfur oxides may also be formed and some nitrogen be present, any carbon monoxide is easily converted to carbon dioxide, while the water, nitrogen, and sulfur oxides can be removed from the system by chemical absorption.

Essentially, therefore, the combustion step results in the production of a quantity of oxygen mixed with carbon dioxide, and thus any method which determines the quantity of carbon dioxide determines also the quantity of original carbon.

Many methods have been proposed for making this determination and several of these are or have been used commercially. One rather modern system of this type for determining the quantity of carbon automatically in about four minutes forms the subject matter of Patent No. 2,962,360, issued to Eugene L. Bennet and William C. Rohn on November 29, 1960. The present invention, therefore, may be considered as constituting an improvement over that system, both in that it is considerably simpler and less expensive, and also because the results are obtainable in less than one minute as compared with about four minutes for the earlier system. The principles upon which the two systems operate are, however, quite dissimilar.

In FIG. 1 is illustrated a somewhat diagrammatic representation of the apparatus by which the carbon determination is made. A duct 10 is connected to a source of oxygen 12 at one end and to a T 14 at the other to provide two streams of oxygen flow. Duct 10 has a normally closed, solenoid operated, two-way valve 16 therein. One branch 18 leading from the T 14 consists of a duct 20 connected at one end to the T and at the other end to a port 22 of a solenoid operated, three-way valve 24. A second port 26 is open to atmosphere. The third port 28 is connected to a duct 30 which leads to the top 32 of an analysis chamber 34. The valve 24 is operable to connect duct 20 to duct 30 or alternatively to connect the analysis chamber to atmosphere through outlet 26 and close off duct 20.

The other branch 36 of the apparatus leading from T 14 consists of a duct 38 incorporating a flow control valve and a purifying train indicated generally by 40 and leading to a combustion apparatus 42 of the type disclosed in the beforementioned patent to Krasl. A duct 44 conducts combustion gases from the apparatus 42 consecutively through a dust trap 46, a trap 48 containing manganese dioxide for the absorption of nitrogen and sulfur oxides, a heated catalyst tube 50 containing Hopcalite, a commercial mixture of manganese and copper oxides, which catalyzes the oxidation of carbon monoxide to carbon dioxide, and a moisture trap 52 containing Anhydron, magnesium perchlorate. From these traps a duct 54 conveys the gases to a two-way valve 56 and thence to a three-way valve 58. Three-way valve 58 has an inlet 60, an outlet 62 connected to a duct 64 and an outlet 65 open to atmosphere. Duct 64 is connected to the bottom end 66 of the analysis chamber 34.

An outlet duct 68 is also connected to the bottom end of the analysis chamber and leads through a two-way valve 70 to atmosphere.

The analysis chamber and the duct portions leading immediately thereto are contained within an oven 72 equipped with a heating element 74 and a blower 76 to maintain an exact temperature conveniently over ambient.

The analysis chamber is particularly illustrated in FIGS. 2 through 6. The chamber consists of a glass tube 80 having an internal capacity of, for instance, 500 milliliters and having accurately ground ends. The tube has

a circular window 82 cut in the side thereof at about its midpoint. Upper and lower closure plates 84 and 86, grooved at 87 for the reception of the ends of the tube, are clamped against the ends by tierods 88. The upper plate 84 is tapped to receive a fitting 90 through which duct 28 communicates with the interior of the chamber. The lower plate 86 has two tapped bores therethrough which are provided with, respectively, an inlet fitting 92 connected to duct 64 and an outlet fitting 94 connected to duct 68. The inside ends of the bores are connected by a channel 96. A plate 97 having a small central hole 98 therein, about $\frac{1}{16}$ to $\frac{1}{8}$ inch, is contained against the end of fitting 92 to provide a restricted aperture therefor.

The top plate 84 has a pair of dependent brackets 100 and 102 secured thereto which face each other across the top of the tube 80. A light source 104 is mounted to the inside of bracket 100 and a photocell 106 is mounted to the inside of bracket 102.

A thermistor block assembly 108 is cemented to the center of the glass tube in overlapping relation with the window 82. The thermistor block assembly consists of an aluminum block having a transverse semicircular concave recess 110 therein which conforms to the tube 80. At the bottom of the recess, a bore is provided which contains a plug 112 having an outwardly protruding end proportioned to fit snugly within the window 82 and curved to conform to the interior surface of the tube 80. A bore 114 is provided through the plug 112 and the block which is open on the inside of the plug 112. A second, blind bore 116 is provided in the block to one side of the bore 114 which is open only to the outside of the block. A matched pair of thermistors 118 and 120 are contained in the bores 114 and 116 and sealed within their respective bores by O-rings 122. Thermistor 120 contained in the blind bore 116 may be regarded as a reference thermistor. The thermistor 118 contained in the bore 114 and exposed to the atmosphere within the tube 80 may be regarded as the measuring thermistor.

The tube 80 contains a relatively deep skirted, very light weight, free aluminum piston or plunger 128. The piston 128 is oriented in the tube with the skirt up. The piston should have minimal weight and should fit exceedingly closely within the tube 80 but without any danger of binding therewithin.

FIG. 7 is a block diagram of the electrical circuit whereby the apparatus is powered and controlled. A source of power 140 is connected to a power supply assembly 142 and a relay panel 144. The relay panel in turn is connected to the valve control solenoids 16s, 24s, 56s, 58s and 70s, the induction furnace 42 and to the oven blower 76. The power supply delivers current to the oven heater 74 through a thermostatic control 146.

Power is likewise delivered from the power supply to the thermistor bridge circuit 148 incorporating the measuring thermistor 118 and the reference thermistor 120, through an appropriate bridge power supply 150 which rectifies and reduces the voltage to an appropriate bridge power level. The bridge circuit incorporates a microammeter 151 for balancing the bridge. The power supply also delivers power to an amplifier 152.

Bridge imbalance current is delivered to an attenuator 154. The attenuator 154 delivers a control voltage to the amplifier 152 in a number of steps, six, for instance, each of which doubles or halves the sensitivity over the next adjacent degree of attenuation.

The amplified output of the attenuator 154 is fed through a timer 156 to an appropriate readout device 158 such as a digital device, strip chart recorder, etc.

The method of employment of my apparatus is this. The device will be calibrated by standard samples in the fashion to be described and a curve drawn upon which unknown samples will be interpolated. The range of measurement of my device is from .01 to 9% carbon on the basis of one gram samples. The accuracy is superior

to that of the "wet" methods of analysis. The wide variation of carbon proportion to the determination of which my apparatus is suited makes necessary the presence of the attenuator to establish ranges of carbon proportion. A curve based on standard samples should be established for each of the attenuator ranges of the analyzer.

Given the curves for the attenuator ranges, a zero of the bridge circuit is established by running a blank sample.

At the start of a cycle, the apparatus is in read-out condition from the preceding determination. All valves are in their illustrated normal condition, and the piston 128 is at the top of the analysis chamber 34 resting on a cushion of oxygen and carbon dioxide from the previous determination. A sample such as the above described pin is introduced into the induction furnace 42 in a fashion described in the above mentioned patent to Krasl No. 2,809,100. The analysis cycle may be started by closing a START switch. Since the circuitry and the timer and relay mechanisms necessary for arranging the sequence of operations are matters of common knowledge and conventional design, it is believed that their description is unnecessary.

Upon initiation, the valve 16 is opened to deliver oxygen to the T 14. Valve 22 is energized so as to close off the exhaust port 26 and open communication of oxygen pressure to the top 32 of the analysis chamber to drive the piston 128 to the bottom of the analysis chamber. At the same time, in branch 36 of the oxygen system, valves 58 and 70 are energized. Normally open valve 56 and valve 58 permit a flow of oxygen through the combustion chamber, purifying train 46-52, valves 56 and 58, chamber inlet 92, channel 96, outlet 94 and to atmosphere through valve 70 to purge this train and the sample of any residual impurities remaining from the previous determination or introduced by the entry of the sample. At the same time, the gases expelled by the descending piston 128 also escape through valve 70. A timer determines this portion of the cycle. The time interval devoted to these operations of returning the piston to the bottom of the analysis chamber and purging the furnace and purification train may be about twenty seconds in a characteristic analysis.

With termination of the twenty second interval, the induction furnace is energized to burn the sample. At the initiation of this stage of the cycle, valve 56 is energized to closure. Valve 24 is deenergized to block off admission of oxygen into the top end of the analysis chamber 34 and to open that end of the analysis chamber to atmosphere through valve 24-outlet 26. Likewise, valve 70 is deenergized to return to its closed position, thus blocking the exit of gases from the lower end of the analysis chamber to atmosphere. An appropriate time for this stage of the cycle, which I have termed the pre-burn or pre-combustion period, is about ten seconds. The furnace during this period of time heats the sample and the powdered tin combustion accelerator to combustion temperatures, and combustion begins. Since the oxides of tin and iron are solids, inflowing oxygen to the combustion chamber is absorbed or consumed at substantially the rate of its entry into the furnace, and there is thus no back pressure within the furnace to retard the admission of the oxygen. Since valve 56 is closed the combustion occurs within a relatively limited, closed volume, and thus the gaseous oxides accumulate in the combustion furnace and in the purification train 46-52 so as to achieve a maximum concentration. During the pre-burn period, the sample being analyzed is substantially if not completely oxidized.

At the end of the pre-burn period (about ten seconds), a burn or transfer period is initiated which continues the circumstances of the pre-burn period with additionally the deenergization of valve 56 and the energization of the valve 58 so as to open the passage from the furnace 42 into the lower end of the analysis chamber 34. During the transfer period, the oxidation of the sample within

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the furnace 42 proceeds to completion, and therefore positive oxygen pressure exists throughout the system to the lower end of the analysis chamber to convey the gaseous products of combustion to the chamber.

The measuring thermistor 118 will be exposed to the oxygen and carbon dioxide contained within the analysis chamber 34. The reference thermistor is in an established and permanent environment within its bore 116. Thus continuing oxygen flow through duct 38 after total combustion of the sample sweeps the gaseous products of combustion before it out of the combustion chamber 42, through the purification train 46-52 wherein dust, nitrogen, sulfur dioxide, and water are removed and carbon monoxide is oxidized to carbon dioxide, through the valves 56 and 58, and into the bottom end of the analysis chamber through the restricted orifice 98. The outlet valve 70 being closed, the piston is gradually raised by the incoming mixed oxygen and CO₂ until it intercepts the beam of the light source 104 actuating photocell 106. The interruption of the light beam marks the end of the transfer period.

Deenergization of the photocell signals a deenergization of valve 16 thereby shutting off the flow of oxygen from the oxygen source to the apparatus. It likewise shuts off the combustion furnace and deenergizes all solenoids to restore their associated valves to the illustrated positions. Particularly notable, valve 58 is deenergized to isolate the transferred products of combustion within the analysis chamber 34 and to relieve the pressure in the furnace and associated portion of the branch 36.

The deenergization of the photocell also energizes the timer 156. The timer is set for a delay of about seven seconds after which the readout device is coupled to the amplifier 152. The delay is introduced in order to allow for temperature equalization and a uniform diffusion of the gases within the analysis chamber 34. The readout device thus records the degree of unbalance of the bridge circuit 148 as attenuated by the attenuator 154 and amplified.

As is well known, of course, thermistors are sensitive to the composition of their environment. If the measuring thermistor is balanced against the reference thermistor in an environment of pure oxygen, it will be unbalanced against an atmosphere containing carbon dioxide. Since thermistors are also responsive to pressure, light, flow and temperature, however, it is vital that these circumstances be reduced to standard conditions. The oven, of course, produces the constant light and temperature circumstances, the latter being achieved by the delay time of the readout. Flow is at a standstill and thus standard. The floating piston is believed to be a particularly successful answer to the problem of constant pressure. The piston, of course, must float. It must have minimum inertia and must not bind. However, with such a piston, it will be evident that the gases within the analysis chamber as between separate determinations will be at a constant pressure subject only to atmospheric variation.

The restriction 98 in the inlet fitting 92 of the analysis chamber creates a high degree of turbulence in the gas entering the analysis chamber to mix the carbon dioxide quickly and uniformly with the oxygen. Without this restriction, there is an appreciable period during which the readout drifts severely.

It will be appreciated from the foregoing description that the method and apparatus of my invention are capable of rapid and accurate carbon determination in steel as stated initially. The complete cycle to readout can be completed in fifty seconds or less. The stated timer-determined times are twenty seconds for flushing, ten seconds for pre-burn, and seven seconds delay in readout, leaving thirteen seconds available for combustion completion and transfer which is more than sufficient.

The method and apparatus operate dependably and with a high degree of accuracy. The transfer of the gases from the combustion furnace 42 to the analysis chamber

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34 is chromatographic in nature, and the small aperture in the inlet to the analysis chamber mixes the CO₂-oxygen mixture quickly with the following oxygen which sweeps the mixture into the chamber.

It will be understood that although I have described my invention primarily in reference to carbon in steels, it is as well suited to carbon in any combustible material; other metals, coal, oil, and carbides, for instance.

It will also be appreciated that certain variations within the practice of the method of my invention and alternatives in the apparatus thereof will suggest themselves to those skilled in the art, and I therefore desire that my invention be regarded as being limited only as set forth in the following claims.

I claim:

1. A method for determining carbon in an oxidizable material which comprises burning a sample of the material in oxygen, transporting the gaseous products of combustion and excess oxygen through a purifying train to remove components other than the carbon oxides from the oxygen and to oxidize carbon monoxide to carbon dioxide and into the lower end of an analysis chamber having a piston therein adapted to float on the introduced oxygen-carbon dioxide mixture, halting the filling of said chamber with the mixture at a desired level of filling, and measuring the thermal conductivity of said mixture in said chamber.

2. A method for determining carbon in an oxidizable material which comprises burning a sample of the material in oxygen, transporting the gaseous products of combustion and excess oxygen through a purifying train to remove components other than the carbon oxides from the oxygen and to oxidize carbon monoxide to carbon dioxide and into the lower end of an analysis chamber having a piston therein adapted to float on the introduced oxygen-carbon dioxide mixture, sensing the filling of said chamber with the mixture to a predetermined level, halting further transportation, and comparing the thermal conductivity of the mixture with the thermal conductivity of mixtures similarly derived from standard samples.

3. A method for determining the carbon content of an oxidizable material which comprises burning a sample of said material in oxygen, transporting the gaseous products of combustion and excess oxygen through a train to remove products other than carbon oxides from said mixture and to oxidize carbon monoxide to carbon dioxide into the bottom end of a vertical tubular analysis chamber having a close fitting, freely movable piston therein resting on the floor of said chamber to float said piston upwardly, sensing the arrival of the piston at a particular elevation in said chamber, halting further transportation, and comparing the thermal conductivity of said mixture with the thermal conductivity of mixtures similarly derived from standard samples.

4. Apparatus for the rapid determination of carbon in an oxidizable material which comprises a source of oxygen, a vertical tubular analysis chamber, a close fitting, freely movable piston in said analysis chamber adapted to float on a column of gas in said chamber, said chamber having an inlet and an outlet in the bottom thereof, means, connecting said inlet to said source of oxygen, said means including, in sequence, a combustion furnace for burning a steel sample and a purifying train for the removal of other than carbon oxides from the oxygen and for the oxidation of carbon monoxide to carbon dioxide, and means for sensing the carbon dioxide content of a carbon dioxide-oxygen mixture in said chamber.

5. The combination as set forth in claim 4, comprising additionally selectively operable means including means for applying pressure to the top of said piston and a valve in said outlet for moving said piston downward to expel gases from said chamber through said outlet.

6. Apparatus for the rapid determination of carbon in an oxidizable material which comprises a source of

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oxygen, a vertical tubular analysis chamber, a close fitting, freely movable piston in said analysis chamber, first means for conveying oxygen to the top end of said chamber including a first valve operable between a position of supplying oxygen to the top end of said cylinder and a position of blocking oxygen from said source and opening the top end of said cylinder to atmosphere, second means connecting said oxygen source to the bottom end of said chamber, said second means including a combustion furnace for burning a steel sample, a purifying train for the removal of other than carbon oxides from the oxygen and for the oxidation of carbon monoxide to carbon dioxide and a second valve to permit or block flow through said second means, an outlet from the lower end of said chamber having a third valve therein, and means for sensing the carbon dioxide content of a carbon dioxide-oxygen mixture in said chamber below the top thereof, and control means operable first to actuate said first valve to admit oxygen to the top end of said cylinder

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and to open said third valve to blow said piston down, second, to actuate said first valve to open said top end to atmosphere, to close said third valve, to burn a sample in said furnace in oxygen and to transport the gaseous products of combustion in an oxygen stream into the bottom end of said cylinder, and third, to stop transport into said cylinder upon attainment of a level of filling thereof and to energize said sensing means.

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