

April 20, 1965

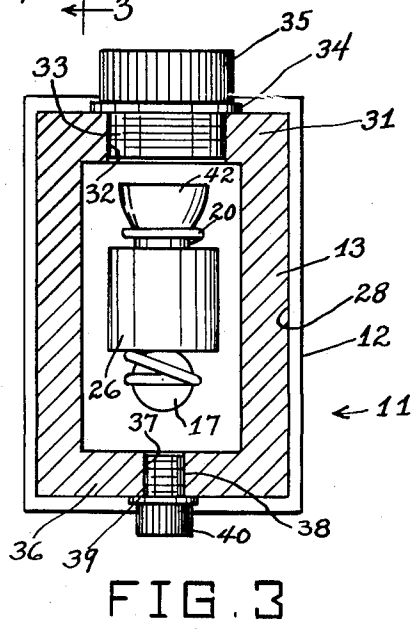
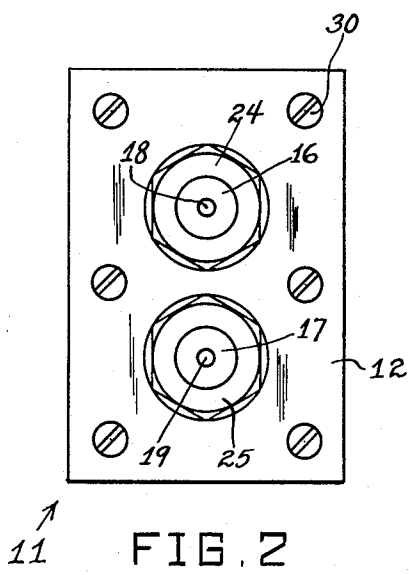
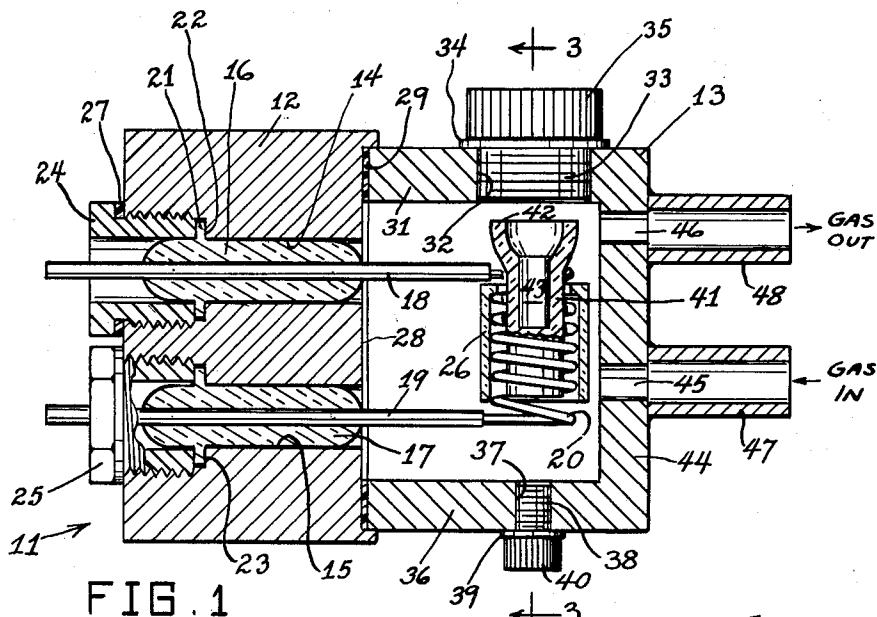
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3,179,499

PYROLYZER FOR GAS CHROMATOGRAPHY APPARATUS

Filed Dec. 12, 1961

3 Sheets-Sheet 1



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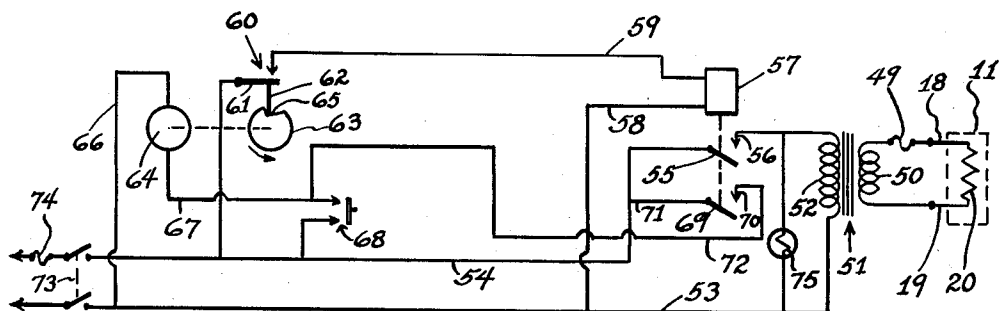


FIG. 4

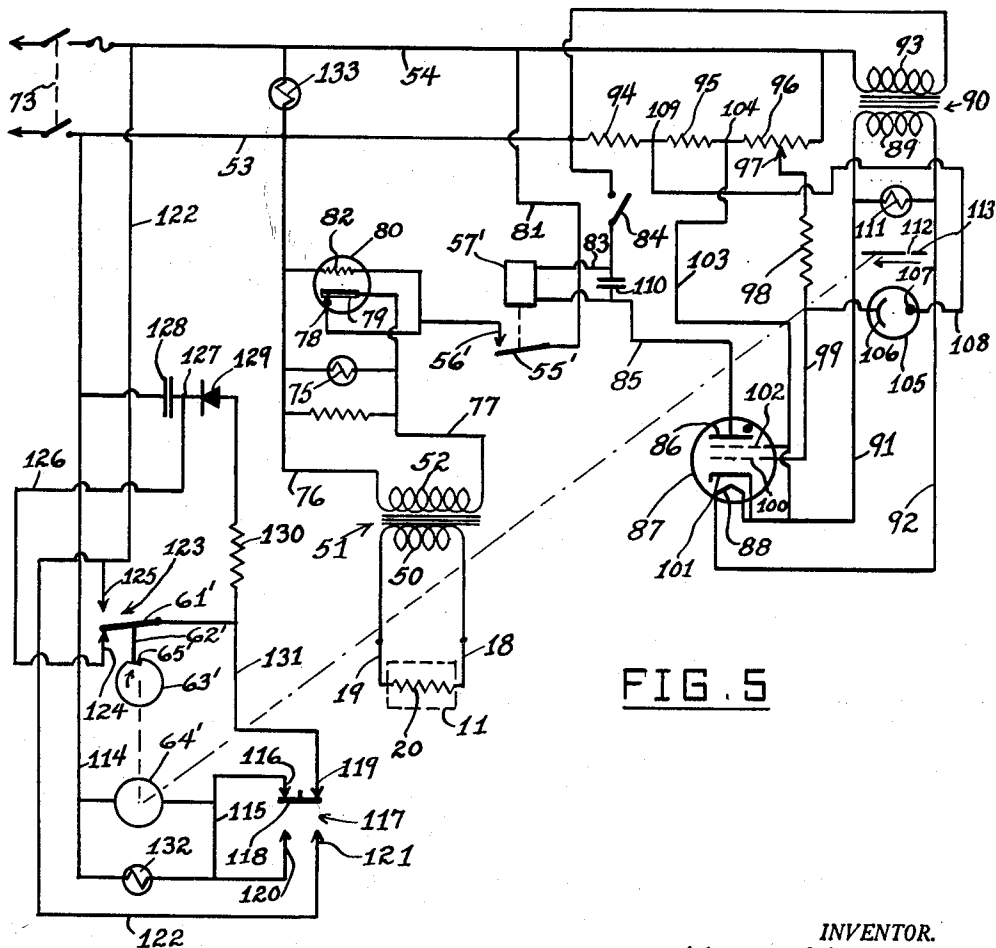


FIG. 5

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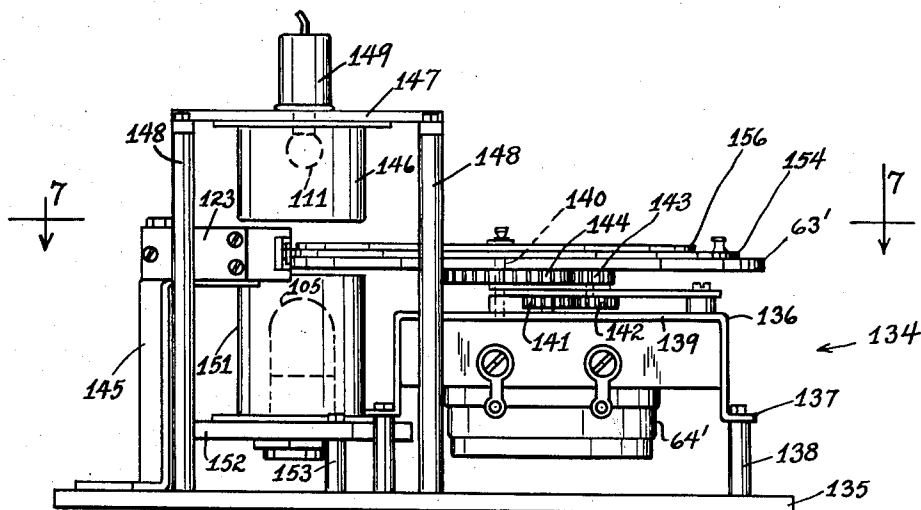


FIG. 6

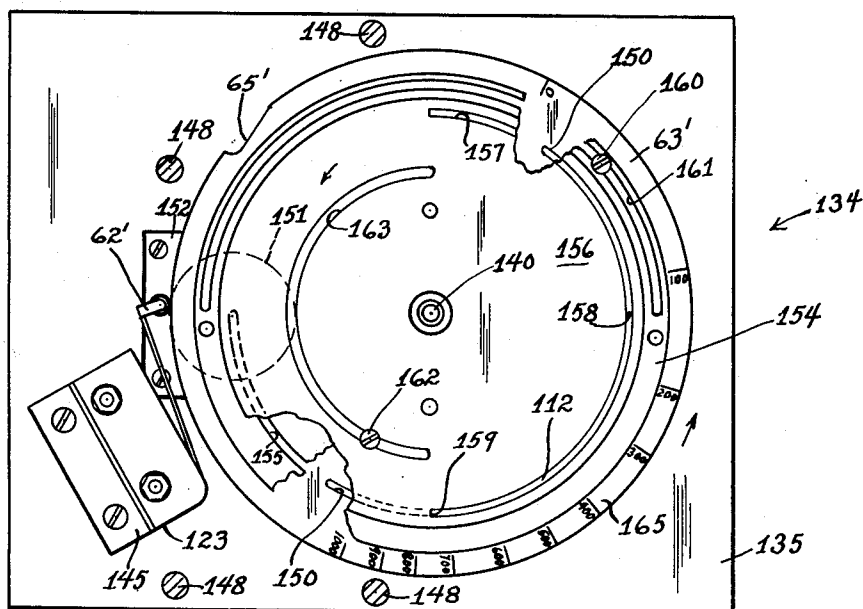


FIG. 7

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PYROLYZER FOR GAS CHROMATOGRAPHY APPARATUS

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4 Claims. (Cl. 23-253)

This invention relates to apparatus for analyzing materials, and more particularly to sample introduction devices for introducing samples of liquids or solids into the gas flow stream of a gas chromatography apparatus or a mass spectrometer.

A main object of the invention is to provide a novel and improved pyrolyzer for vaporizing a sample of material and for introducing the vaporized sample into the gas flow stream of a gas chromatography apparatus or a mass spectrometer, the pyrolyzer being relatively simple in construction, being easy to operate, and providing accurate control of the amount of vaporizing heat energy applied to the sample.

A further object of the invention is to provide an improved pyrolyzer to be employed with a gas chromatography apparatus or a mass spectrometer, the pyrolyzer being provided with a flash chamber assembly which can be made gas-tight, which is arranged so that known weights of samples can be easily loaded therein without requiring the assembly to be dismantled, which can be used in a vacuum, which employs a heater element which is adequately protected against grounding, which is provided with insulating means associated with the electrodes or connectors for its heating element which can withstand high temperatures without impairment of its insulating properties and which is suitably sealed, and which can be readily separated into convenient segments for cleaning or repair whenever required.

A still further object of the invention is to provide an improved electrical pyrolyzer for use with a gas chromatography apparatus or a mass spectrometer, the pyrolyzer being provided with a removable sample-carrying basket or container, and the pyrolyzer chamber being provided with means to facilitate the removal of the basket or container in the event that said basket or container becomes jammed or stuck within the heater coil of the pyrolyzer.

A still further object of the invention is to provide an improved sample pyrolyzer for use with a gas chromatography apparatus or a mass spectrometer which is arranged so that it permits sampling of stable liquids or solids into capillary columns without sample splitting.

A still further object of the invention is to provide an improved sample pyrolyzer for a gas chromatography or mass spectrometer apparatus wherein the chances of outside atmospheric contamination of a sample or loss of a sample are minimized.

A still further object of the invention is to provide an improved electrical pyrolyzer for use with a gas chromatography or mass spectrometer apparatus wherein the time of energization of the heating coil and the pyrolyzing temperature can be accurately controlled, wherein a relatively high pyrolyzing temperature can be obtained, and wherein the sample is located substantially in line with the exit port of the pyrolyzer chamber so that it is not affected by dead space in the chamber.

A still further object of the invention is to provide an improved pyrolyzer for use with gas chromatography or mass spectrometer apparatus, said pyrolyzer being provided with a range of temperature adjustment in its controlling system such that the pyrolyzer is suitable for replacing any other vaporizer system heretofore employed.

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A still further object of the invention is to provide an improved pyrolyzer providing relatively rapid and accurately controlled vaporization of a sample and which may be employed to provide high temperature vaporization of a sample in conjunction with low temperature columns, as used in gas chromatography techniques.

Further objects and advantages of the invention will become apparent from the following description and claims, and from the accompanying drawings, wherein:

FIGURE 1 is a longitudinal vertical cross-sectional view taken through a pyrolyzer chamber as employed in an improved sample-introducing apparatus according to the present invention.

FIGURE 2 is a front end elevational view of the pyrolyzer chamber of FIGURE 1.

FIGURE 3 is a transverse vertical cross-sectional view taken on line 3-3 of FIGURE 1.

FIGURE 4 is a wiring diagram showing one form of heater energizing circuit which may be employed in the present invention.

FIGURE 5 is a wiring diagram showing another form of heater energizing circuit which may be employed in the present invention.

FIGURE 6 is a side elevational view of a timing mechanism which may be employed with the heater energizing circuit of FIGURE 5.

FIGURE 7 is a horizontal cross-sectional view, with parts broken away, taken substantially on line 7-7 of FIGURE 6.

Referring to the drawings, FIGURES 1, 2 and 3 show the details of a heater or vaporizing oven assembly according to the present invention, suitable for attachment to a gas chromatography apparatus or to a mass spectrometer, at the sample injection location of the instrument. The heater is designated generally at 11 and comprises a housing made of stainless steel or other suitable material, consisting of two sections 12 and 13. Section 12 is a block formed with parallel bores 14 and 15 containing glass insulators 16 and 17 in which are axially molded the respective electrodes 18 and 19. A vertical heater coil 20 has its top and bottom ends rigidly secured respectively to the inner ends of the electrodes 18 and 19, whereby said coil is supported in a vertical position by the electrodes. The insulators 16 and 17 are provided with flanges 21 seated in annular recesses 22 and 23 formed in block 12 and clampingly engaged by annular fastening nuts 24 and 25 threadedly engaged in the recesses 22 and 23.

A quartz protective skirt 26 is mounted on and surrounds the major portion of the heater coil 20.

Annular Teflon sealing washers 27 are provided between the hexagonal outer flanges of the nuts 24, 25 and the adjacent end wall of block 12. The opposite end wall of block 12 is formed with a shallow rectangular recess 28 which receives the rim of housing section 13, which is in the form of a rectangular cup. A Teflon sealing gasket 29 is provided between the rim of section 13 and recess 29. A plurality of fastening bolts 30 extend horizontally through the side marginal portions of block 12 and threadedly engage in the rim portion of section 13, clampingly securing section 13 in recess 28.

The top wall 31 of section 13, as seen in FIGURE 1, is formed with a relatively large internally threaded access hole 32 in vertical alignment with coil 20. A removable screw plug 33 is threadedly engaged in the access hole 32, a Teflon sealing gasket 34 being provided between the head 35 of screw plug 33 and the top wall 31. The bottom wall 36 of section 13 is formed with a smaller internally threaded hole 37 in vertical alignment with coil 20, in which is threadedly engaged a removable screw

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plug 33. A Teflon sealing gasket 39 is provided between the head 40 of screw plug 38 and bottom wall 36.

The bottom screw plug 38 may be removed to permit the insertion of a rod through the hole 37 to facilitate the release and upward removal of a sample basket or container 41 which may have become jammed or stuck in the heating coil 20.

The sample basket or container 41 comprises a rod-like body of refractory material, such as quartz, which has an upwardly flared top portion 42 adapted to supportingly engage on the top turn of the heating coil 20 when the body is inserted in the coil, as shown in FIGURE 1, whereby to support said body in the position illustrated. The container body is formed with an axial sample-receiving recess 43 of substantial depth so that it will receive heat efficiently from the coil 20 when said coil is energized.

The end wall 44 of section 13 is formed with the respective gas inlet and outlet ports 45 and 46 communicating with gas inlet and outlet conduits 47 and 48 for attachment in the sample injection portion of a gas chromatography apparatus or a mass spectrometer.

It will be noted that the outlet port 46 is located adjacent to and substantially in horizontal alignment with the open top end of the sample basket or container 41 so that vaporized material from the container will pass directly to the outlet port 46 with a minimum amount of diffusion inside the chamber 13. Thus, the dead space inside the chamber has very little adverse effect on the efficiency of vaporization and discharge of the sample material from the container 41.

The removal of the screw plug 33 provides access to the interior of chamber 13 for the insertion or removal of a sample basket or container 41. As previously mentioned, a rod may be inserted through the bottom opening 37 if necessary to assist in dislodging a container which may have become jammed or stuck in the turns of the heating coil 20.

The cylindrical quartz protective skirt 26 closely surrounding the major portion of coil 20 prevents it from becoming grounded and aids in maintaining its shape when heated to a high temperature.

In a typical design, the heating coil 20 was rated to receive 50 amperes at approximately 3 to 4 volts.

Removal or loading of the quartz basket 41 can be accomplished by means of tweezers or a similar implement, through the access hole 32.

The heater coil 20 may be of any suitable conductive material able to withstand high temperatures; platinum, or other suitable metals may be employed.

FIGURE 4 diagrammatically illustrates one form of heater energizing circuit which may be employed with the unit of FIGURES 1, 2 and 3. As shown, the heater coil terminal electrodes 18 and 19 are connected through a fuse 49 to the secondary 50 of a step-down transformer 51. The primary 52 of the transformer has one terminal thereof connected to a first line conductor 53 and the other terminal thereof connected to the second line conductor 54 through the normally open contacts 55 and 56 of a relay 57. One terminal wire 58 of the winding of relay 57 is connected to line conductor 53. The other terminal wire 59 of the relay winding is connected through a normally open switch 60 to the second line conductor 54.

The pole 61 of switch 60 is provided with a projection 62 which engages the periphery of a notched cam disc 63 driven by a timing motor 64. Switch 60 is open when projection 62 engages in the notch 65 of disc 63 and closes when projection 62 engages the circular normal periphery of the disc.

One terminal wire 66 of motor 64 is connected to line wire 53. The other terminal wire 67 thereof is connected to line wire 54 through a normally open push button switch 68.

Relay 57 is provided with a second pair of normally

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open contacts 69 and 70 connected in shunt with switch 68 by wires 71 and 72.

Line wires 53 and 54 are connected to a suitable alternating current supply source through a two-pole main control switch 73 and a fuse 74.

With switch 73 closed, motor 64 may be energized by closing push button switch 68, thus connecting motor 64 across line conductors 53 and 54 through wires 66, 67 and switch 68. Rotation of cam disc 63 closes switch 60 and connects relay 57 to the line conductors 53 and 54 through wires 58, 59 and switch 60. Contacts 69 and 70 close and maintain motor 64 energized as long as relay 57 remains energized, even with switch 68 open.

The closure of relay contacts 55 and 56 connects the transformer primary 52 to the line conductors 53 and 54, energizing the heater coil 20.

When cam disc 63 completes one revolution, projection 62 enters notch 65 and opens switch 60, deenergizing relay 57 and causing its contacts 55, 56 and 69, 70 to open. This deenergizes primary 52 and heater winding 20, and also deenergizes motor 64, since switch 68 is no longer shunted. The apparatus is then ready for another cycle.

An indicator lamp 75 is provided, connected in parallel with primary 52 and energized simultaneously therewith to indicate the period of energization of heater coil 20.

The circuit arrangement of FIGURE 4 is primarily intended to provide relatively slow heating and relatively long cycles, such as, where vaporization of a sample is desired in about 30 to 40 seconds after the heater coil 20 becomes energized. Thus, in a typical arrangement, the coil 20 heats in 10 to 15 seconds to a final temperature between 600° C. and 1000° C., stays at this temperature between 20 and 30 seconds, and then is deenergized and cools. In said typical design, the heater coil 20 is made of platinum wire of 0.025 inch diameter, helically wound on a mandrel $\frac{3}{32}$ inch in diameter and has 10.5 turns. A heater current of 8.5 amperes at approximately 2.5 volts is employed.

FIGURE 5 shows a circuit arrangement providing a faster and more closely controlled pyrolyzing action than is obtainable with the arrangement of FIGURE 4. As shown, the heater coil terminal electrodes 18 and 19 are connected to the secondary 50 of a step-down transformer 51. The primary 52 has one terminal wire 76 thereof connected to the line wire 53. The other primary terminal wire 77 is connected through the normally closed contacts 78 and 79 of a thermal time-delay switch 80 to one contact 56' of a relay 57'. The cooperating contact 55' of the relay is connected by a wire 81 to the remaining supply line wire 54.

The heater winding 82 of delay switch 80 is connected between the wires 76 and 81 through the relay contacts 55', 56'. Should the relay contacts 55', 56' remain closed for more than a predetermined period of time, for example, two seconds, which represents the maximum safe permissible period of energization of heater coil 20, contacts 78 and 79 will open and deenergize said heater coil 20.

The winding of relay 57' has one terminal wire 83 thereof connected through a manually operated switch 84 to the line wire 53. The other terminal wire 85 of said relay winding is connected to the anode 86 of a thyratron tube 87.

The filament 88 of tube 87 is connected to the secondary 89 of a step-down transformer 90, as by the wires 91 and 92. The terminals of the primary 93 are connected to the respective line wires 53 and 54. Connected in series across the line wires 53 and 54 are the resistors 94, 95 and the winding of a potentiometer 96. The adjustable contact 97 of potentiometer 96 is connected through a resistor 98 and a wire 99 to the control grid 100 of tube 87.

The cathode 101 and suppressor 102 of tube 87 are connected to wire 91. A wire 103 connects the junction

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104 between resistor 95 and potentiometer 96 to the wire 91.

A photoelectric cell 105 has its anode 106 connected to wire 99 and its cathode 107 connected by a wire 108 to the junction 109 between resistors 94 and 95.

Contact 97 is adjusted so that with cathode 107 dark, the potential on grid 100 is insufficient to fire tube 87. However, with switch 84 closed, when cathode 107 is illuminated, the photocell 105 conducts, connecting grid 100 through wire 99, the photocell 105 and wire 108 to the bleeder junction point 109, which provides a sufficient potential on grid 100, in phase with the potential on plate 86, to fire the thyatron, causing relay 57' to become energized and close its contacts 55', 56', causing heater coil 20 to become energized.

A condenser 110 of substantial capacity is connected across the winding of relay 57' to maintain it energized during the reversal of the potentials on plate 86 and cathode 101 occurring in the alternating current cycle. Therefore, relay 57' will be maintained energized as long as the photocell cathode 107 is illuminated and for the relatively short time required for condenser 110 to discharge subsequent to termination of such illumination.

As will be presently described, a lamp 111 is mounted to illuminate photocell 105 through an aperture 112 in a rotary disc assembly 113 mounted between the lamp and the photocell. Lamp 111 is connected across wires 91 and 92, so as to be energized in parallel with filament 88 of tube 87.

Disc assembly 113 is driven by a motor 64'. One terminal wire 114 of motor 64' is connected to line wire 53. The other terminal wire 115 of the motor is connected to a fixed contact 116 of a push button double-throw switch 117. The pole 118 of the switch 117 normally connects contact 116 to another stationary contact 119 of the switch. Pole 118 may be manually operated to disengage from contacts 116, 119, opening same, and to bridgingly engage a pair of additional stationary contacts 120 and 121. Contact 120 is connected to wire 115 and contact 121 is connected to line wire 54 by a wire 122.

Motor 64' is drivingly coupled to a cam disc 63' having a triangular notch 65' in its periphery. A double throw switch 123 is provided, said switch having a pivoted pole 61' biased toward engagement with a first stationary contact 124. A projection 62' on pole 61' engages the periphery of disc 63' and allows pole 61' to engage contact 124 when the projection is received in the notch 65'. However, when the projection 62' engages the normal circular periphery of disc 63', the pole 61' is held in engagement with a second stationary contact 125. Contact 125 is connected to the wire 122. Contact 124 is connected by a wire 126 to the junction 127 between the series-connected condenser 128 and rectifier 129, shown in FIGURE 5. Condenser 128 is connected between wire 114 and junction 127. Rectifier 129 is connected between junction 127 and switch contact 119 through a resistor 130 and a wire 131. Switch pole 61' is connected to the wire 131.

A pilot lamp 132 is connected in parallel with motor 64' to indicate the energization of the motor. Another pilot lamp 133 is connected across line wires 53 and 54 to indicate that the apparatus is energized when main control switch 73 is closed.

With the parts in the positions shown in FIGURE 5, when switches 73 and 84 are closed, filament 88 is energized but tube 87 remains non-conducting because the potential on grid 100 is insufficient to trigger same. Push button switch 117 is then operated to cause pole 118 to bridge contacts 120 and 121. This energizes motor 64' through a circuit comprising line wire 54, wire 122, contact 121, pole 118, contact 120, motor 64', wire 114, and line wire 53. Cam disc 63' rotates to cause switch pole 61' to engage contact 125. When the push button of switch 117 is released, motor 64' remains energized

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through a circuit comprising line wire 54, wire 122, contact 125, pole 61', wire 131, contact 119, pole 118, contact 116, wire 115, motor 64', wire 114, and line wire 53. This also charges condenser 128 through a circuit comprising line wire 54, wire 122, contact 125, pole 61', wire 131, resistor 130, rectifier 129, condenser 128, wire 114, and line wire 53.

Apertured disc 113 rotates to expose photocell 105 to lamp 111, causing tube 87 to fire and energizing relay 57'. This closes the primary circuit of transformer 51 and energizes the heater coil 20. The duration of energization of said coil is determined by the angular size of the aperture 112.

As will be presently described, the disc assembly 113 is provided with means for adjusting the normal angular position of the leading edge of its aperture 112 as well as its angular size.

Heater coil 20 becomes deenergized when aperture 112 moves so that it is no longer in the optical path between lamp 111 and photocell 105. At the end of the cycle of revolution of cam disc 63', projection 62' enters the notch 65', causing pole 61' to disengage from contact 125 and to re-engage with contact 124. Motor 64' becomes deenergized and is connected across the charged condenser 128 through a circuit comprising wire 114, motor 64', wire 115, contact 116, pole 118, contact 119, wire 131, pole 61', contact 124, wire 126, and condenser 128. The condenser 128 discharges through the motor and acts as a brake thereon, insuring its stoppage at the end of the cycle. The apparatus is now ready for another pyrolyzing cycle.

Referring to FIGURES 6 and 7, 134 generally designates a flash timing mechanism which may be employed in the system diagrammatically illustrated in FIGURE 5. The timing mechanism 134 comprises a base plate 135 on which is mounted a bracket 136 of inverted U-shape, the bottom flanges 137 of the legs of said bracket being secured on upstanding posts 138 secured to the base plate. The motor 64' is secured to the underside of the horizontal bight portion 139 of the bracket and is thus supported above the base plate.

The cam disc 63' is journaled on a vertical shaft 140 secured on member 139 and is drivingly coupled to the motor shaft through suitable reduction gears shown at 141, 142, 143 and 144. Disc 63' is provided with the notch 65' in its periphery which cooperates with the follower arm 62' of a single pole, double throw microswitch 123 in the manner previously described. Microswitch 123 is mounted on a generally Z-shaped upstanding bracket 145 secured to base plate 135.

A cylindrical lamp housing 146 is secured to and depends from a horizontal supporting plate 147 secured on the top ends of upstanding posts 148 fastened rigidly to base plate 135 and located adjacent the periphery of disc 63', the lamp housing overlying the peripheral portion of the disc. The lamp 111 is mounted in the housing and is supported in a conventional lamp socket 149, the vertical axis of the lamp and socket being substantially at the same radial distance from the axis of disc 63' as an arcuate slot 150 formed in the disc.

A second cylindrical housing 151, containing the photocell 105, is mounted immediately below the disc, on the same vertical axis as lamp 111, being secured on a horizontal supporting plate 152 mounted on upstanding vertical posts 153 secured to base plate 135. The optical axis between lamp 111 and photocell 105 is therefore at the same radial distance from the axis of disc 63' as the slot 150.

A first masking disc 154 is coaxially and rotatably mounted on disc 63', said disc 154 being formed with an arcuate slot, concentric therewith, and shown at 155. Slot 155 has the same radius as and is registrable with slot 150. A second masking disc 156 is coaxially and rotatably mounted on disc 154, being formed with an arcuate slot 157 concentric therewith and also registrable with

slot 150. Discs 154 and 156 are angularly adjustable relative to disc 63' to define a resultant arcuate slot or aperture 112 comprising superimposed portions of slots 150, 155 and 157. With the disc assembly rotating counterclockwise, as viewed in FIGURE 7, the masking

discs 154 and 156 may be in positions such that the leading edge 153 of slot 112 reaches the optical axis defined between lamp 111 and photocell 105 at an accurately predetermined time after arm 62' is moved out of notch 65', and so that the trailing edge 159 of said slot reaches said optical axis at another accurately predetermined time in the cycle of rotation of disc 63'.

Disc 154 may be locked in adjusted position relative to disc 63' by tightening a headed clamping screw 160 extending through an arcuate slot 161 concentrically formed in the peripheral portion of disc 154, the screw being threadedly engaged in disc 63'. Disc 156 may be locked in adjusted position relative to disc 155 by tightening a headed clamping screw 162 extending through an arcuate slot 163 concentrically formed in disc 156, said screw 162 being threadedly engaged in disc 154.

A suitable flash timing scale 165 may be inscribed on the exposed peripheral portion of disc 63'.

While certain specific embodiments of an improved pyrolyzer have been disclosed in the foregoing description, it will be understood that various modifications within the spirit of the invention may occur to those skilled in the art. Therefore it is intended that no limitations be placed on the invention except as defined by the scope of the appended claims.

What is claimed is:

1. In a device for analyzing materials, a heating chamber, means to connect said heating chamber into a gas flow stream, a heating coil mounted in said chamber, a sample container in said chamber in heat-receiving relation to said coil, a source of heating current, means connecting said current source to said coil and including a normally open switch, a cam disc normally in a predetermined position, a relay, means closing said switch responsive to energization of said relay, photo-sensitive means, means energizing said relay responsive to irradiation of said photo-sensitive means, a light source adjacent

said photo-sensitive means, a masking member rotatably mounted between the light source and said photo-sensitive means, said masking member having an arcuate slot at the same radial distance from its axis of rotation as the optical path between the light source and the photo-sensitive means, means drivingly connecting said masking member to said cam disc, whereby the photo-sensitive means is irradiated when the leading end of said slot reaches said optical path and is no longer irradiated when the trailing end of said slot reaches said optical path, a driving motor connected to said cam disc, manually operated means to energize said motor when the disc is in said predetermined position, and means to maintain said motor energized until the disc completes one revolution and again reaches said predetermined position.

2. The structure of claim 1, and means to respectively adjust the angular positions of said leading and trailing ends of said slot.

3. The structure of claim 1, and means to deenergize said heating coil responsive to the energization of said relay for a period substantially greater than the time required for the arcuate slot to rotate past said optical path.

4. In combination with the structure of claim 1, a braking capacitor connected across the motor, and means to charge said capacitor while the cam disc is displaced from said predetermined position.

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