April 18, 1961 S. F. KAPFF 2,980,513

COMBUSTIBLES-IN-AIR INSTRUMENT

Filed Oct. 28, 1957 4 Sheets-Sheet 1

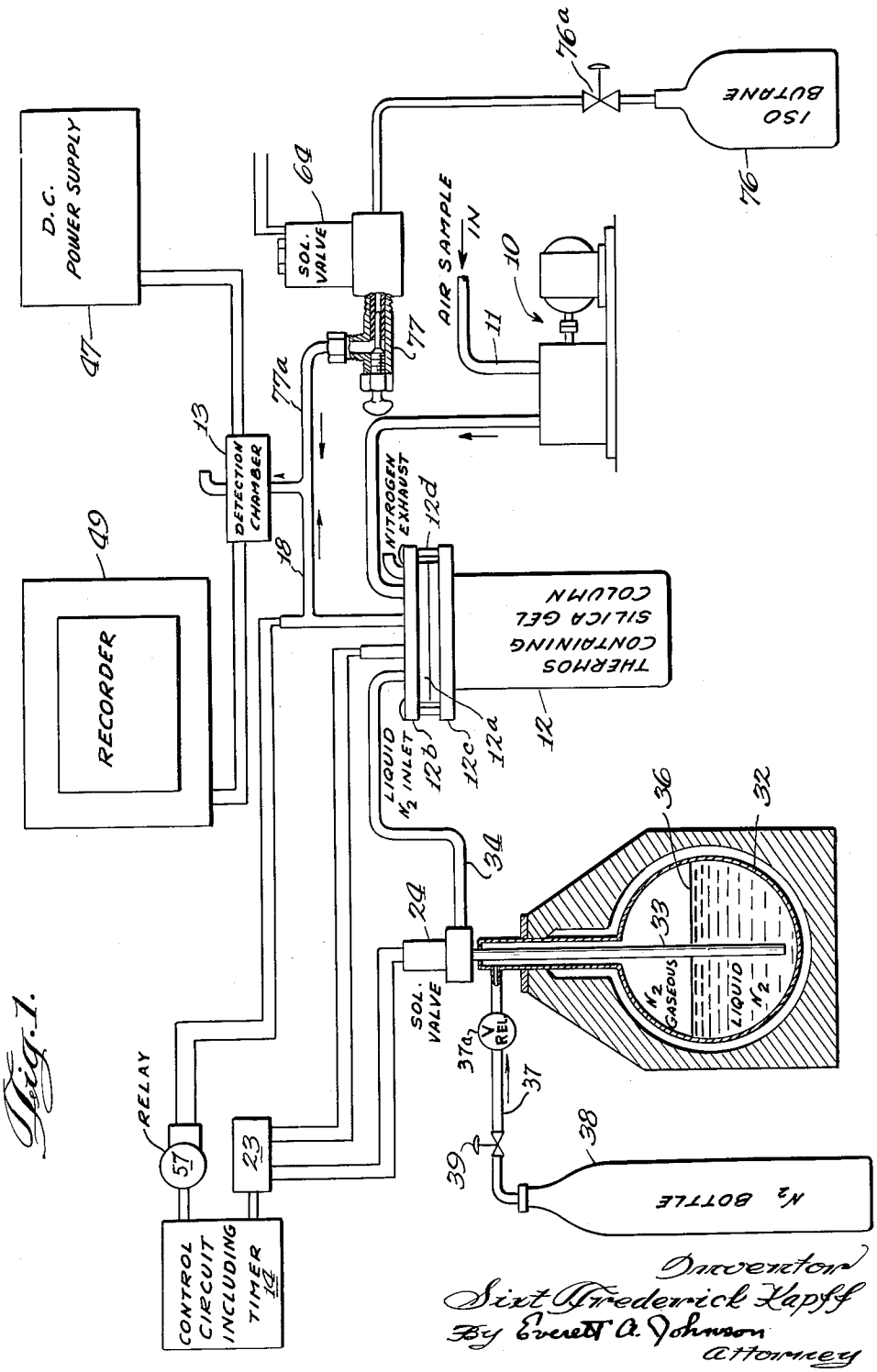


Fig. 1.

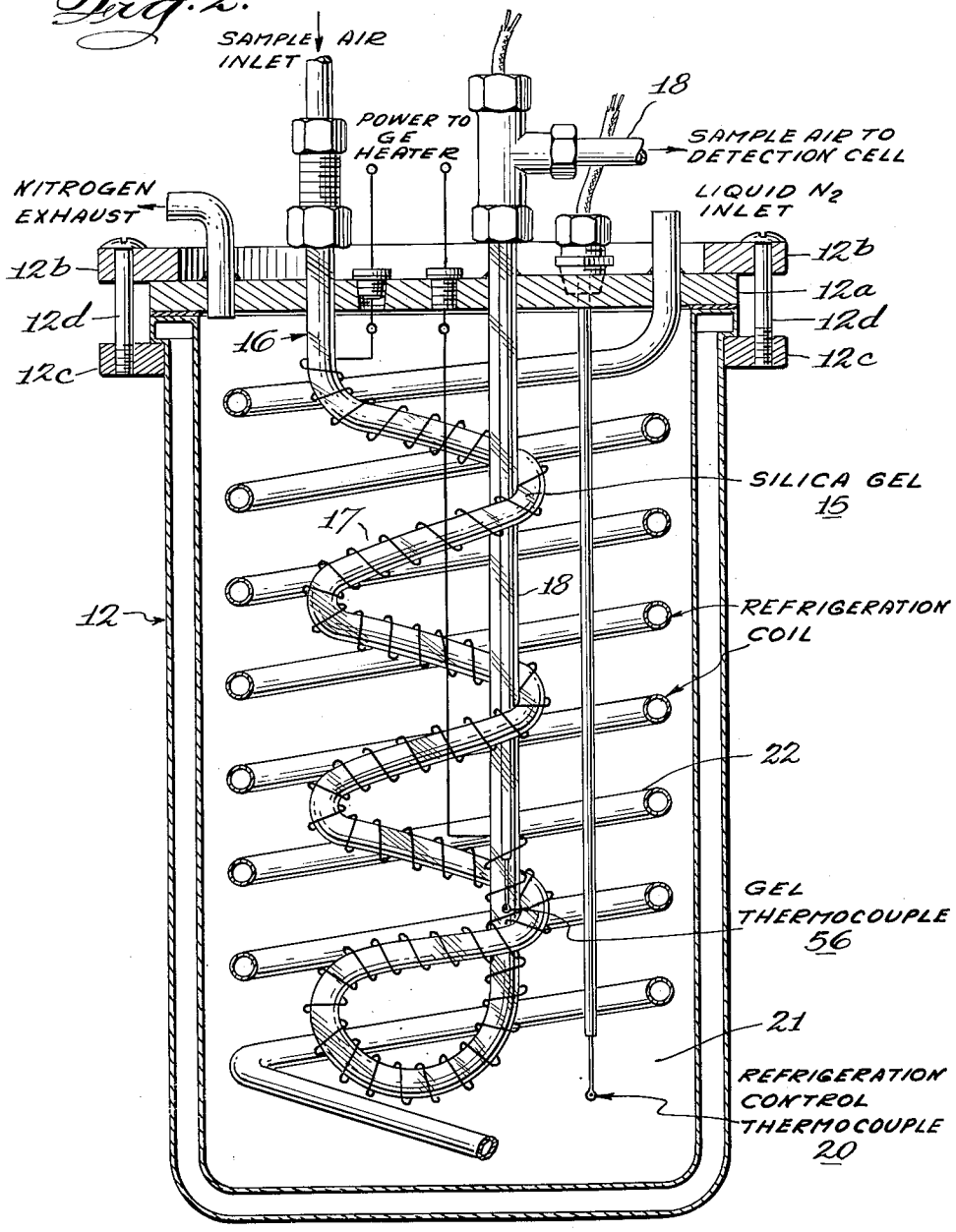
Inventor
Sixt Frederick Kapff
By Everett A. Johnson
Attorney

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Fig. 2.



Inventor
Sixt Frederick Kapff
By Everett A. Johnson
Attorney

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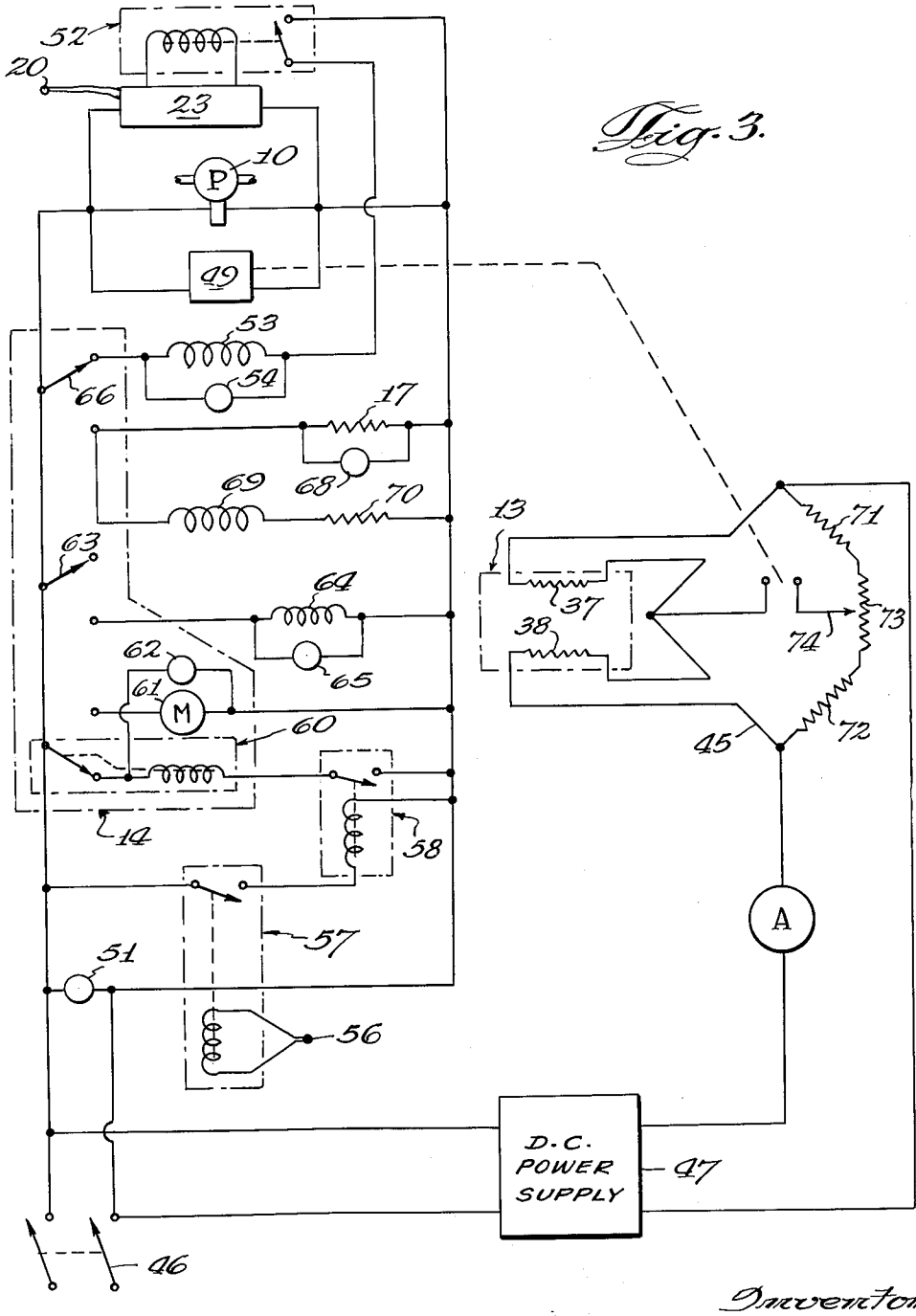


Fig. 3.

Inventor
Sixt Frederick Kapff
By Everett A Johnson
Attorney

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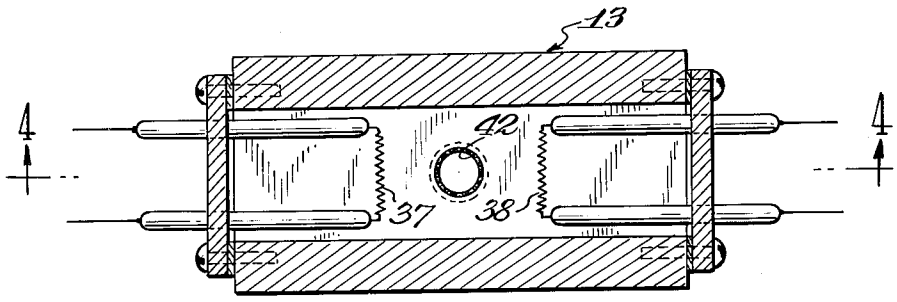


Fig. 5.

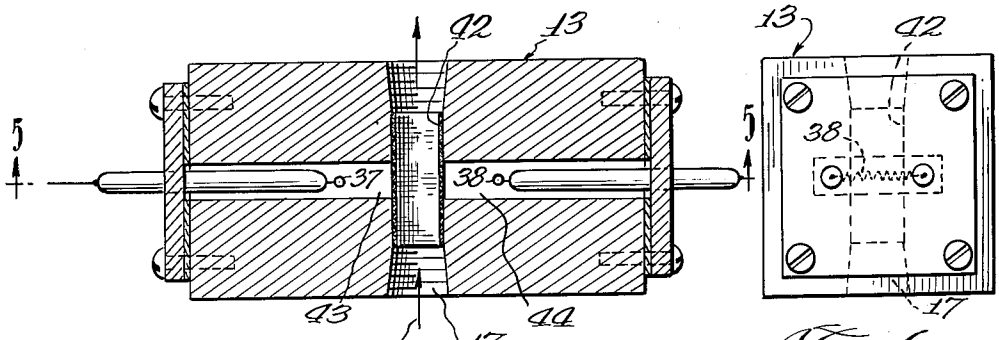


Fig. 4. Fig. 6.

Inventor
Sixt Frederick Kapff
By Everett A. Johnson
attorney

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COMBUSTIBLES-IN-AIR INSTRUMENT

Sixt Frederick Kapff, Homewood, Ill., assignor to Standard Oil Company, Chicago, Ill., a corporation of Indiana

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2 Claims. (Cl. 23—255)

This invention relates to the operation of an air separation process. More particularly, the invention relates to a method and means for detecting total C_2–C_4 hydrocarbons present in air charged to an oxygen plant.

The operation of plants for the production of pure oxygen or nitrogen from air basically involves a liquefaction of the air and subsequent fractionation of the components in a distillation tower. This distillation is performed at low temperatures and produces an overhead product of pure nitrogen and a bottoms product of liquid oxygen. In the liquid oxygen will be found any substances present in the entering air which are not trapped out in the early cooling stages and have boiling points higher than oxygen. Some of the materials of interest are the hydrocarbons in the C_2–C_4 range of molecular weights. The presence of sizable quantities of these in the liquid oxygen presents a serious explosive hazard.

The safe operation of such a plant therefore involves maintaining the hydrocarbon concentrations as low as possible in the liquid oxygen. The concentrations considered tolerable vary for the different hydrocarbons. Acetylene is by far the most dangerous since in concentrations of a few p.p.m. it reaches its solubility limit in liquid oxygen. The solid acetylene which then separates can detonate under certain conditions causing serious explosions. The concentrations of other hydrocarbons from ethylene to the butanes are not so critical since these are much more soluble in liquid oxygen. However, it is desirable to hold their concentrations as low as possible, since, if any explosion should occur, these would furnish an additional fuel supply.

Monitoring of the air stream at various points in the process is desirable for early detection of hydrocarbon contamination. An object of this invention is, therefore, to provide an instrument capable of analyzing for hydrocarbons in air or oxygen streams in the concentration range of 0–10 p.p.m.

Detection of hydrocarbons in air in this concentration range normally requires highly accurate instrumentation and extremely sensitive detectors. It is, however, a further object of this invention to provide means whereby the hydrocarbon can be concentrated from a large volume of air into a small volume for detection and measurement.

According to my invention, CO_2 and H_2O are removed from a monitoring sample stream. The sampling point is generally chosen so that this has been done by the plant. If not, then removal means must be provided in connection with the instrument. The sample stream is then passed through a cold silica gel column for concentration of the hydrocarbons on the cold silica gel. Periodically the gel is heated to remove the adsorbed hydrocarbons as a sudden burst which can readily be detected.

Such detection of the hydrocarbons in the air stream after desorption from the gel is by means of a catalytic platinum filament upon which the hydrocarbons can oxidize. This combustion changes the temperature (and therefore the resistance) of the catalytically active platinum wire. A Wheatstone bridge circuit containing the catalytically active platinum filament and an identical but non-catalytic filament permits accurate measurement of such changes. Both filaments are exposed to the air stream but only one increases in temperature.

Further details and advantages of my invention will be described by reference to a preferred embodiment illustrated in the accompanying drawings wherein:

Figure 1 is a diagrammatic illustration of one system according to my invention;

Figure 2 is an elevation, partly in section, of the hydrocarbon concentration cell;

Figure 3 is a circuit diagram of the system including the hydrocarbon detector; and

Figures 4, 5 and 6 are views illustrating the hydrocarbon detector apparatus.

Referring to the drawings, the air sample, after drying and CO_2 removal, is pumped by pump **10** at a constant rate from line **11** through the refrigerated hydrocarbon accumulator **12** and then through the detector cell **13**. A timing mechanism **14**, which is started when the gel **15** in column **16** becomes cold enough to adsorb hydrocarbons such as ethylene, permits the passage of air through the gel **15** for a period of about an hour. The gel is then heated by heater **17** and the adsorbed material desorbed into the air stream **18** and measured by the detector cell **13**. Just prior to the desorption, a small amount of hydrocarbon is injected into the air stream **18** to check the detector **13** and to supply a standardization signal.

The temperature of the gel column **16** is controlled from a thermocouple **20** located in the air space **21** between the cooling helix **22** and the gel column **16**. The thermocouple output is fed to a controller **23** which operates valve **24** to introduce liquid nitrogen into coil **22**.

Details of the gel column **16**, the refrigeration coil **22**, and accumulator **12** are shown in Figure 2. The accumulator **12** is a double-walled vacuum vessel (Dewar flask) closed at its top by plate **12***a* which is secured by clamping rings **12***b* and **12***c* and bolts **12***d* to the flanged opening of vessel **12**.

The gel **15** is contained in the central glass helix **16** which has a length of about 4 ft. over-all and an inside diameter of 6 mm. About 2½ ft. of this length is filled with Davison #70 silica gel **15** of about 8 mesh. Around this glass tube **16** is tightly wound a coil **17** of bare Nichrome wire (0.032" diameter and 31 ohms total resistance) for heating the column **16** during the desorption step. At the outlet of gel column **16** is the thermocouple **56** to measure the temperature of the air leaving the gel **15**. This thermocouple **56**, through suitable relays **58** and **60**, starts the timer **14** when the air temperature reaches —170° F. The coil **22** of 3/16 inch copper tubing fitted closely to the inner wall of the insulated vessel **12** serves to conduct coolant (liquid nitrogen) into the system whenever the temperature at the thermocouple **20** is above —255° F.

The system used for pumping the liquid nitrogen into the low temperature bath comprises a reservoir **32** for liquid nitrogen which is delivered by lines **33** and **34** and solenoid valve **24** to the insulated low temperature bath **12**. A constant pressure controlled by valve **39** is maintained on the surface of the liquid nitrogen **36** by compressed gas introduced into reservoir **32** by line **37** from compressed gas cylinder **38**. A 15 p.s.i. pressure relief valve **37***a* is provided on valved line **37**.

Another system for pumping the liquid nitrogen may comprise a solenoid valve normally open to the atmosphere and in series with a heater (not shown) immersed in the liquid nitrogen **36**. Upon a signal from the controller **23**, this circuit is energized, closing the valve and turning on the heater. The evaporation of liquid nitro-

gen produces a pressure in the closed space forcing liquid nitrogen out of the reservoir 32 to the low temperature bath 12. When the accumulator 12 has cooled to a preselected temperature, the heater is turned off and the valve opens reducing the pressure to atmospheric.

The detector cell 13 shown in some detail in Figures 4, 5 and 6, includes two platinum wires 37 and 38 mounted in chambers 43 and 44 and exposed to the gas stream 18 by short diffusion paths. The use of two filaments 37 and 38, one catalytically active and one rendered inactive, in the same stream reduces the effects of flow rate and thermal conductivity changes in cell 13. The filaments 37 and 38 may comprise identical platinum wires, one of which has been deactivated by suitable treatment, such as by treating with silicone vapors according to a procedure described in the literature (J. Chem. Physics 16 (1948), p. 237).

For rapid response the diffusion path from the stream 18 to the filaments 37 and 38 should be short and of large area. However, at air flow rates of 0.05 to 0.1 c.f.m., considerable turbulence near the wires 37 and 38 makes such an arrangement unsatisfactory unless special precautions are taken. The most satisfactory arrangement for giving fast response without the undesirable turbulence at the filaments 37 and 38 has been found to involve the insertion of a single layer of fine mesh Monel screen 42, as shown, around the gas stream as it passes through the cell 13.

Figure 3 illustrates the control circuit for the system including the filaments 37 and 38 in the hydrocarbon detector circuit. The detector circuit includes the catalytically active filament 37 and the inactive filament 38 in adjacent arms of the Wheatstone bridge circuit 45 including the 500 ohm bridge resistor 71, the 500 ohm bridge resistor 72, the 100 ohm potentiometer 73 provided with adjustable slide wire contact 74, and the recorder 49. The differences in resistance in the filaments 37 and 38 resulting from the occurrence of catalytic oxidation of trace amounts of hydrocarbons on catalytically active filament 37 unbalance the bridge circuit 45 which unbalance is recorded on recorder 49. Potentiometer 73 serves as a zero adjustment.

Closing the switch 46 energizes the D.C. power supply 47, the detector circuit 45, the sample feed pump 10, the recorder 49, the refrigeration-temperature control 23, and the pilot light 51. Refrigeration control 23 operates relay 52 providing power to valve 53 and pilot light 54 as long as thermocouple 20 indicates that the adsorption assembly 12 is too warm. When the proper temperature is reached, controller 23 operates relay switch 52 intermittently to maintain substantially constant temperature in adsorption assembly 12.

When the air stream 18 leaving gel column 16 of Figure 2 has reached a predetermined temperature, this is sensed by thermocouple 56 which actuates sensitive relay 57 which provides power to a heavy duty relay 58 starting timer 14 by closing relay 60. Relay 60 provides power to timer motor 61 and pilot light 62. Near the conclusion of the timing cycle, switch 63 is actuated by a timer cam (not shown) providing power to open standardizing gas valve 64 and illuminate pilot light 65. Switch 63 is next returned to its original position by timer cam de-energizing valve 64. Switch 66 next operates from a timer cam removing power from the refrigeration valve 53 and supplying power to the gel heater 17, pilot light 68, and the reset 69 and accompanying resistor 70 for sensitive relay 57.

The introduction of a standardization gas to check the activity of the platinum filaments 37 and 38 before starting desorption of the gel 15 may present difficulties because of the small volume of gas to be introduced into the air stream. The use of cylinders of pure gases is most desirable since then no calibration need be made when a new cylinder is required.

A system for introducing standardizing gas, such as isobutane or any other combustible gas of high purity, is provided which is shown in Figure 1. The cylinder gas system 76 is maintained at 1.5 p.s.i.g. by valve 76*a* up to the solenoid valve 64. Between this valve 64 and the detector cell 13 is a high resistance leak which may comprise a needle valve 77, a calibrated glass capillary of proper flow, and the like. When the valve 64 is opened by the timer 59, a small flow of gas (1.0 cc./min.) passes through valve 77 into the air stream 18 in line 77*a*.

A second system for introducing the standardizing gas is to provide two valves arranged to define a small volume of gas between them at a pressure slightly greater than atmospheric. The valve on the cylinder side is normally open and the valve toward the system is normally closed. When the valves operate, i.e. one opens and one closes, this volume of gas is introduced into the air stream as a single burst. The size of the signal from the detector will depend upon the volume between the valves and the gas pressure maintained on the cylinder system.

A third system for standardization involves the introduction of cylinder gas specially prepared to contain a small percentage of combustible in air. This has the advantage that special leaks need not be employed and higher flows which are more easily defined can be used.

A fourth system for standardization might involve the use of a 3-way valve and a liquid of low vapor pressure, such as dodecane. When standardizing, the entire air stream may be diverted to bubble through a layer of this liquid. Thermostating maintains the liquid at constant temperature (i.e. constant vapor pressure).

Calibration of the equipment has been accomplished by injection of small quantities of pure gases into the air stream followed by a desorption of same from the gel. It has been determined experimentally that such an addition is retained on the cooled gel for at least one hour so that the addition of hydrocarbon in a single burst is equivalent to small additions all during the adsorption period. Hence the injected sample can be considered to have been contained in the total volume of air passed through the gel during the adsorption period. As mentioned earlier, the calibration will vary somewhat for different hydrocarbon because of their different behavior during combustion on the detecting filaments.

For obtaining increased sensitivity, the operation of the instrument may be changed to permit desorbing adsorbed hydrocarbons into an air stream moving through the apparatus at lower velocity than that obtained during the collection period. This has the double effect of producing a greater hydrocarbon concentration by desorbing into a smaller air volume and of passing the sample through the detection cell 13 more slowly, permitting more time for diffusion into the filament chambers 43 and 44. Each of these effects will result in increased signals.

In a typical record, large standardization peaks occur at timed intervals while the peaks following closely thereafter are those arising from the desorption step.

It has been found that if the gel 15 is heated gradually, the various hydrocarbons adsorbed thereon will desorb at characteristic temperatures. This gradual heating may be accomplished, for example, by inserting between switch 66 and gel heater 17, by means of a stepping relay, suitable resistances in predetermined sequence to vary the current flowing in heater 17. Hence calibration with known gases will permit qualitative and quantitative estimation of the gases adsorbed.

If an analysis of the gas being desorbed from a gel is desired, the output of the detector 13 is plotted on one axis of an X–Y recorder with the other axis representing the temperature of the silica gel column. The record so obtained indicates hydrocarbon concentration as a function of the temperature of desorption.

It is contemplated that adsorbents other than silica gel may be used including molecular sieve-type adsorbents, activated carbon and alumina, and the like. A double

column system may be used in series for the adsorption and in parallel for desorption. Thus molecular sieve-type adsorbents may be used to accumulate methane after the C_2–C_5 hydrocarbons have been retained by the silica gel column. The desorption of the two columns may be suitably programmed and two desorption signals shown on the recorder.

The invention has been described in terms of a system for concentrating dilute hydrocarbons from oxygen-rich streams. The invention has further been described in connection with a detector for the concentrated hydrocarbons comprising a device wherein they are oxidized. However, in some circumstances, it may be desirable to preserve the hydrocarbon components and the detector may comprise non-destructive detectors, such as thermal conductivity cells, gas gravity balances, chromatographic analyzers, and the like. In any event, the concentration of the hydrocarbons as taught herein makes possible the use of rugged and less sensitive detectors and makes unnecessary expensive apparatus utilizing techniques, such as involved in mass spectrometers, infrared analyzers, and the like.

Although the invention has been described with reference to embodiments thereof, it should be understood that these are by way of illustration only and that the invention is not necessarily limited to such embodiments. Alternative components and operating techniques will become apparent to those skilled in the art in view of the foregoing disclosure and, accordingly, modifications in the construction and operation of the apparatus are contemplated without departing from the spirit of my invention.

What I claim is:

1. An apparatus for detecting micro amounts of combustibles in air which comprises accumulator chamber means, hydrocarbon adsorption means in said accumulator chamber means, means for cooling said accumulator chamber means while flowing a sample air stream containing micro quantities of combustibles through said adsorption means, heater means for said adsorption means, timing means adapted to terminate the cooling of the accumulator chamber means and for energizing the heater for the adsorption means, whereby accumulated combustibles are desorbed from said adsorption means, combustibles detector means, conduit means for flowing the desorbed combustibles from the accumulator chamber means through the combustibles detector means, and means actuated by said timing means for injecting into said conduit en route to said detector means a small amount of a standardizing combustible gas as a reference peak for indicating the accumulated amount of desorbed hydrocarbon combustibles.

2. An apparatus for detecting the concentration of combustibles in a flowing air stream which comprises a silica gel column for accumulaing hydrocarbons from said flowing air stream, means for controllably refrigerating said silica gel column during an adsorption cycle, means for injecting a standardizing combustible gas into said flowing air stream downstream of said silica gel column, said means for injecting including a supply of combustible gas maintained under pressure and valve means controlled by a timer hereinafter described and a calibrated leak means for injecting the combustible gas into the flowing air stream at a uniform rate for a selected period of time, combustibles detector means through which said air stream flows, said detector means being adapted to indicate the amount of combustibles flowing therethrough, controllable heating means for said silica gel column adapted to heat the column during a desorption cycle, whereby combustibles are accumulated to detectable concentration during the adsoprtion and refrigeration cycle and are released in relatively high concentration in a burst of short duration during the desorption cycle, and program timer means adapted to control the relative length of said adsorption and desorption cycles.

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