

[54] BARRIER ATTACHMENT FOR GAS CHROMATOGRAPH

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[58] Field of Search 55/16, 158, 67, 197, 386

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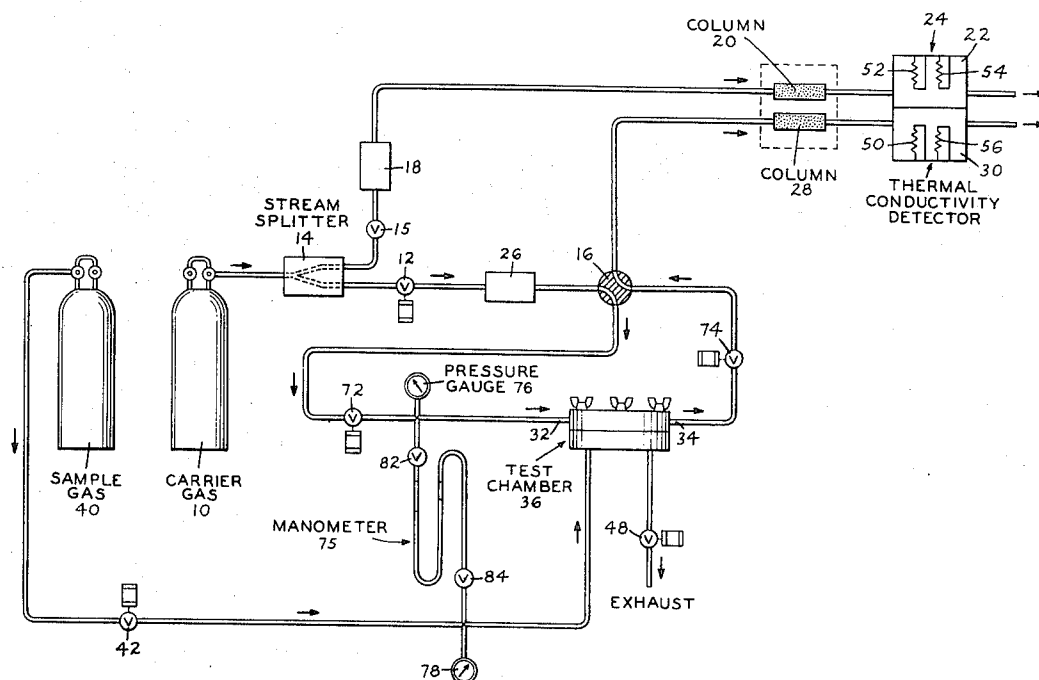
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[57] ABSTRACT

An apparatus integrated with a detection system of the type that establishes individual components in a sample gas mixture by the thermal conductivity thereof, which establishes the gas transmission rate of the sample gas through a given material. Sample gas is fed into a first cavity of a partitioned chamber and diffuses through the partition into a second cavity of the partitioned chamber. Diffused gas is swept from the second cavity with inlet carrier gas to a thermal conductivity detector in the detection system for analysis.

1 Claim, 5 Drawing Figures



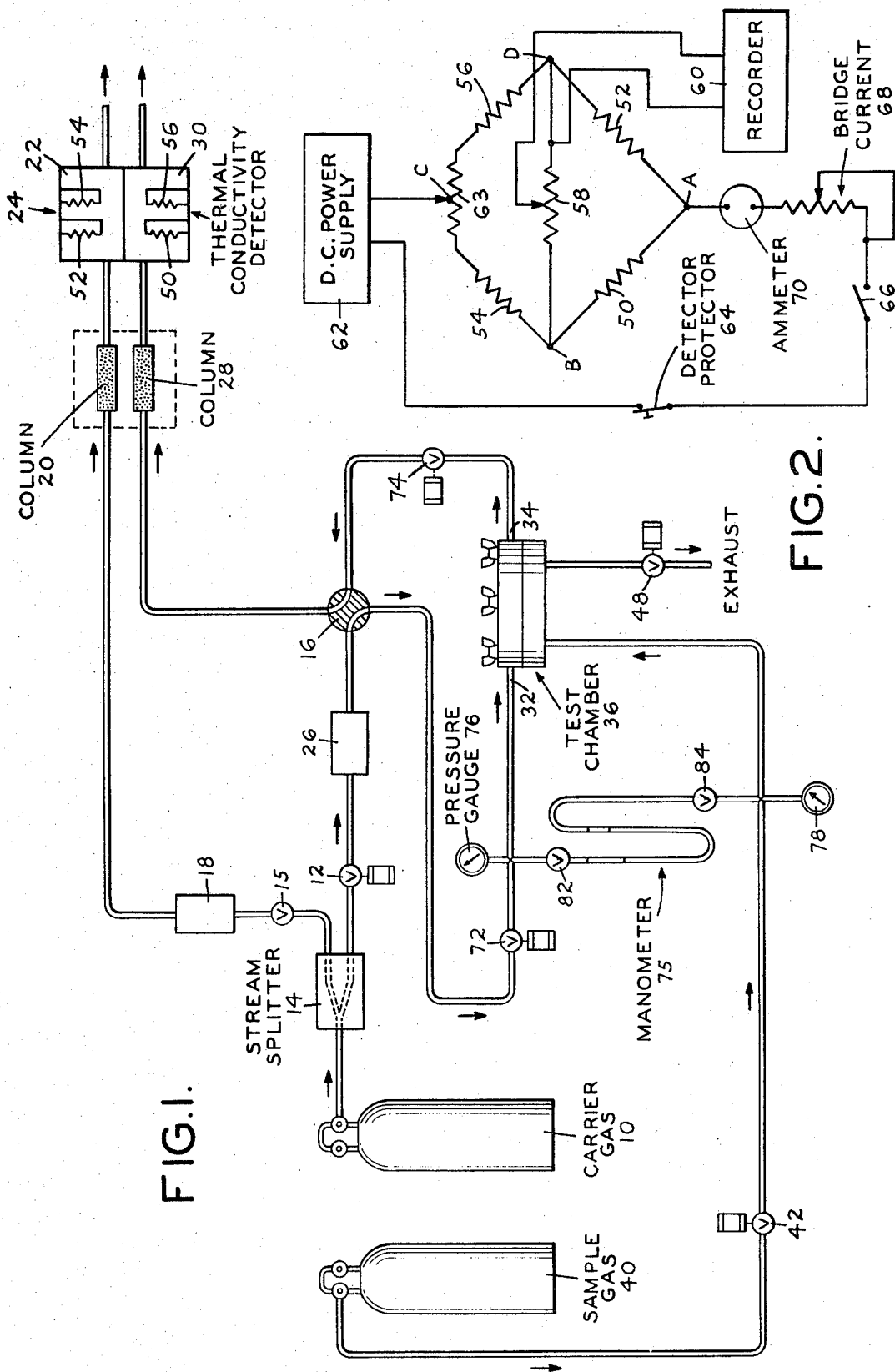


FIG. 1.

FIG. 2.

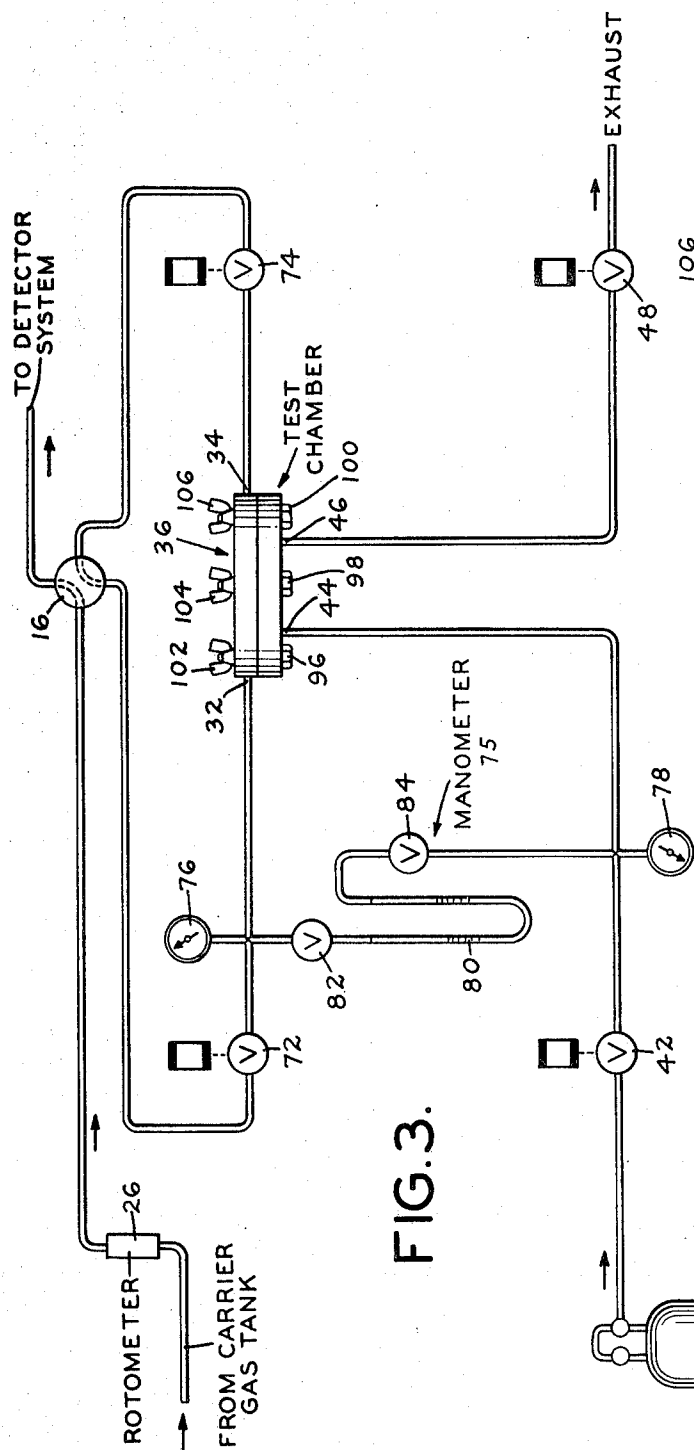
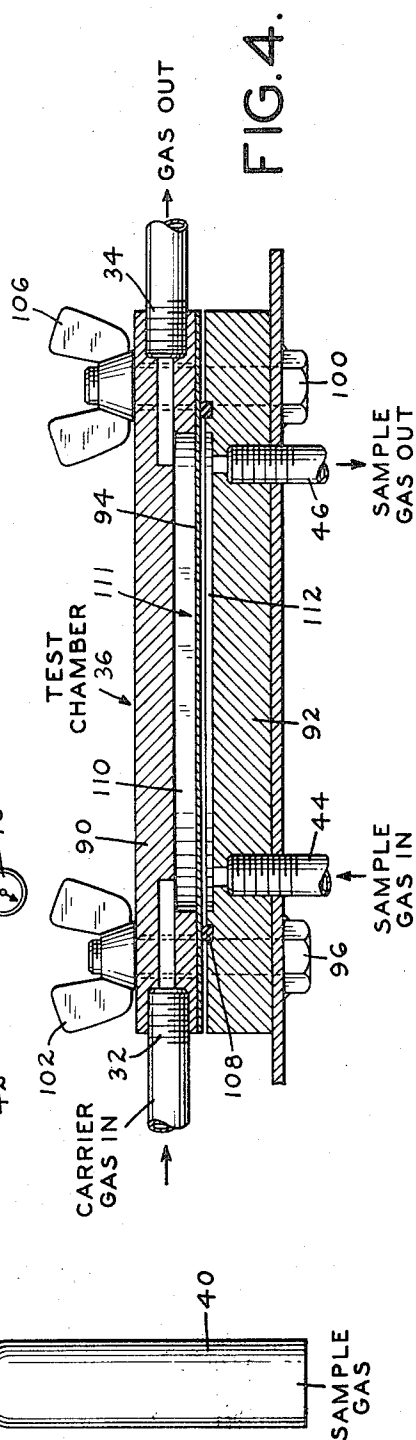
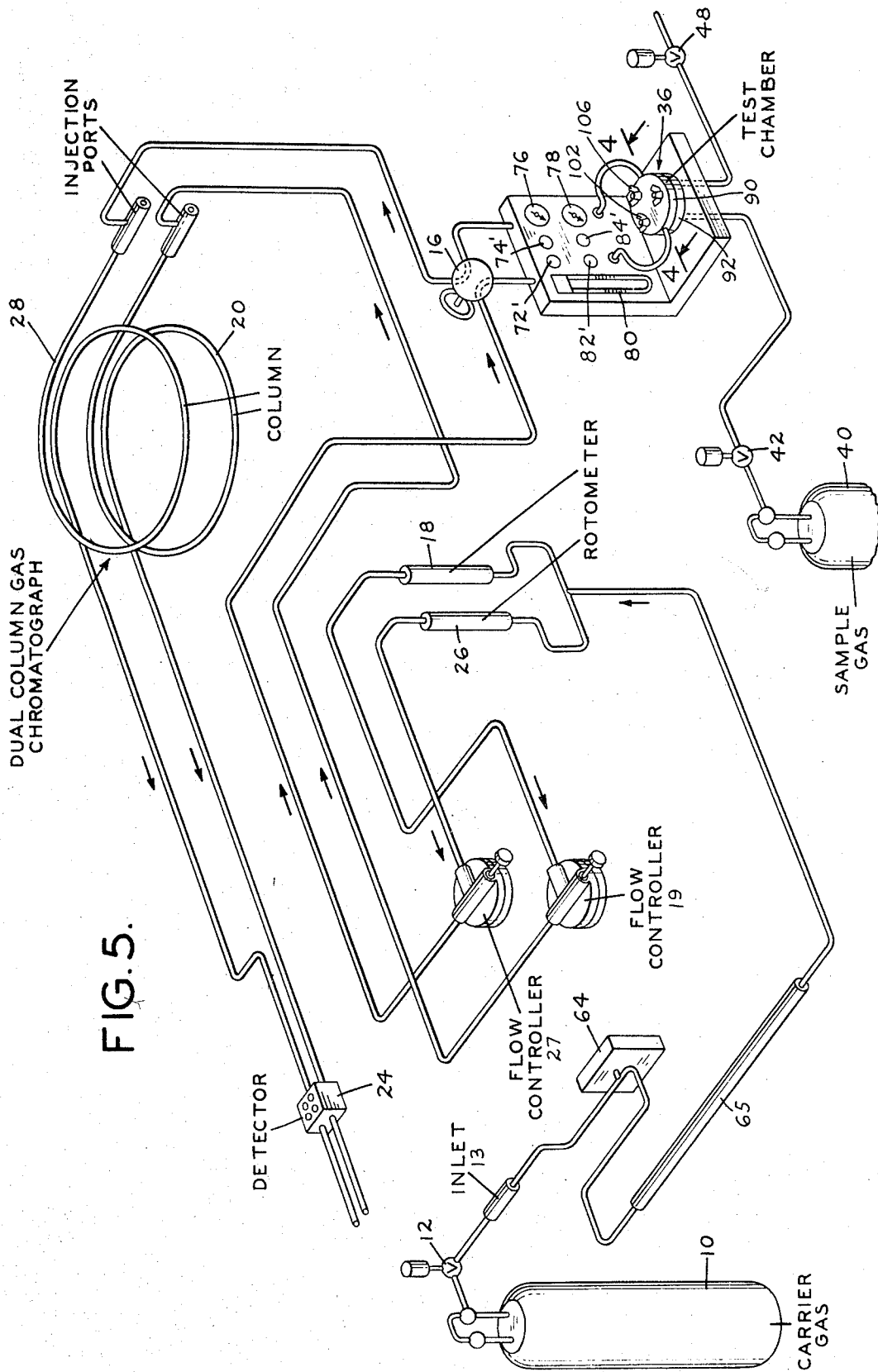


FIG. 3.



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BARRIER ATTACHMENT FOR GAS CHROMATOGRAPH

BACKGROUND OF THE INVENTION

The present invention relates to apparatus integrated with a detection system of the type that establishes individual components in a sample gas mixture by the thermal conductivity thereof, which establishes the gas transmission rate of a sample gas through a given material. More particularly, this invention establishes the gas transmission rate of a sample gas through various packaging materials.

Food processors and new product developers continually require new packaging materials which effectively protect the enclosed product from contaminants while minimizing additional packaging costs. As new packaging materials are developed, however, it is necessary to determine the ease with which various gaseous contaminants may permeate the packaging material and thereby decrease the normal shelf-life of the packaged product.

It is, of course, understood that the nature of a gaseous contaminant varies with the type of product to be packaged. For instance, perishable foods may be air-sensitive and begin to deteriorate upon excessive exposure to air. Detergents, however, may be impervious to contact with air, but may deteriorate upon exposure to excessive amounts of water vapor.

When a gas chromatograph, of the type described, is adapted as disclosed herein, one can easily and efficiently determine the gas transmission rate of gaseous contaminants through the packaging material under consideration. In addition, the present invention provides a means for approximating the extent to which product shelf-life may be shortened by use of a packaging material that may be only marginally satisfactory with respect to gas permeation, but which may be desirable for other purposes.

Other advantages of the present invention will become apparent from the description below.

SUMMARY OF THE INVENTION

According to the present invention, a test chamber hereafter described in detail, is positioned upstream of the analytical portion of a gas chromatography system. The gas chromatography system is of the type that establishes individual components in a sample gas mixture by their thermal conductivity.

The test chamber comprises two female dies mated to form an airtight hollow chamber at the interface of their closure. A packaging material, through which the transmission rate of particular gases is to be determined, is inserted between the mating surfaces of the dies and partitions the hollow chamber into two cavities. A gas sample is introduced into a first cavity of the hollow chamber and is permitted to diffuse through the partition or barrier packaging material into the second cavity. A carrier gas, preferably an inert gas such as helium, is introduced into the second cavity and a substantially, zero pressure differential is maintained between the first and second cavities across the partition.

At the end of a predetermined dwell period the admixture of carrier gas and diffused sample gas is swept from the second cavity into the analytical portion of the gas chromatograph. The quantity of sample gas

reaching the analytical detector may be determined by comparison with known volumes of sample gas injected by syringe into the gas chromatograph under the same operating conditions. Since the amount of sample gas that diffuses through the packaging material barrier is readily determined for a specified dwell-time in a fixed volume container with substantially a zero pressure differential across the barrier packaging material, the gas transmission rate of the gas sample through the packaging material sample is easily approximated.

Any conventional gas chromatograph, of the type previously described, can be adapted to accommodate the test chamber of this invention. The basic operation of a gas chromatograph usually requires that a small quantity of sample gas be injected into a carrier gas stream through an injection port in the system. The injected sample is then swept as a "slug" onto a partition column. Individual components of the gas sample move through the partition column at different velocities. The most commonly used partition columns are of the gas-liquid type wherein the velocity of individual components in the gas sample is dependent upon its partition coefficient between the liquid phase and the carrier gas.

The individual components in the gas sample emerge from the column as individual narrow bands of pure compounds diluted with carrier gas. As the bands leave the column, they pass through a thermal conductivity detector that develops an electrical signal proportional to the concentration of a component in the carrier gas. The generated signal is then delivered to a potentiometric recorder and a chromatogram appears as a series of peaks approximating gaussian distribution curves.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a schematic block diagram illustrative of a test chamber integrated with a gas chromatography system according to one embodiment of the present invention.

FIG. 2 is illustrative of one embodiment, in schematic form, for the electric circuit in a dual channel gas chromatograph, as shown in FIG. 5.

FIG. 3 is a schematic view of the piping system shown in FIG. 1 wherein the carrier gas conduit is shown in a by-pass position to by-pass the test chamber.

FIG. 4 is an exploded cross-section view of the test chamber taken along line 4—4 of FIG. 5.

FIG. 5 is a view in perspective of a preferred embodiment of this invention, illustrative of the gas flow system in a dual channel gas chromatograph coupled with a test chamber to establish gas transmission rates wherein the carrier gas conduit is shown in a test chamber inlet position.

DETAILED DESCRIPTION OF THE INVENTION

Referring to FIGS. 1 and 4, pressurized carrier gas, preferably an inert gas such as helium, is released from tank 10 through stream spitter 14. A first carrier gas stream, regulated by manual valve 15, moves through rotometer 18, which measures the gas flow, into partition column 20 and is released into passage 22 of thermal conductivity detector 24 from which it exhausts. Resistors 52, 54 in passage 22 may be actuated to generate heat and variations in the thermal conductivity

ty of fractionated gas portions are detected and transmitted to a potentiometric recorder, not shown.

A second carrier gas stream, regulated by solenoid valve 12, moves through rotometer 26 and is shunted by four-way valve 16, shown in a test chamber inlet position, through solenoid valve 72 to upper die 90 of test chamber 36. Carrier gas enters upper cavity 110 of partitioned chamber 111 through inlet port 32 and exits through outlet port 34. Exiting carrier gas may carry with it sample gas that diffuses through barrier packaging material 94. The flow of carrier gas through outlet port 34 is regulated by solenoid valve 74 and a controlled flow of carrier gas is shunted through four-way valve 16 into partition column 28. Fractionated portions of the gas filtering through partition column 28 are released into passage 30 of thermal conductivity detector 24. Resistors 50, 56 in passage 30 may be actuated to generate heat and variations in the thermal conductivity of fractionated gas portions are detected and transmitted to a potentiometric recorder, not shown.

A pressurized sample gas stream is released from tank 40, regulated through solenoid valve 42 and directed to lower die 92 of test chamber 36. Sample gas enters lower cavity 112 of partitioned chamber 111 through inlet port 44 and exits through outlet port 46. The flow of sample gas through outlet port 46 is regulated by solenoid valve 48.

Manometer 80 is serially positioned between the carrier gas test chamber inlet conduit and the sample gas test chamber inlet. One leg of manometer 80 extends through valve 82, terminates in pressure gauge 76 and joins the carrier gas test chamber inlet conduit intermediate solenoid valve 72 and inlet port 32. A second leg of manometer 80 extends through valve 84, terminates in pressure gauge 78 and joins the sample gas test chamber inlet conduit intermediate solenoid valve 42 and inlet port 44.

Referring to FIG. 2, which is illustrative of the bridge configuration of a thermal conductivity detector, four hot wire resistance type filaments 50, 52, 54, 56 are wired in a Wheatstone Bridge configuration. Two filaments 50, 56 project into the analytical flow stream traveling through passage 30 of thermal conductivity detector 24, as can be observed in FIG. 1. The remaining filaments 52, 54 project into the pure carrier or reference flow stream traveling through passage 22 of thermal conductivity detector 24, as shown in FIG. 1. When switch 66 is actuated and potentiometer 68 adjusted to a desired milliamp current, as reflected on ammeter 70, a DC current, supplied by source 62, passes through the Wheatstone Bridge. Careful adjustment of control 63 renders the total resistance of arm ABC equal to the total resistance of arm ADC. When this condition is achieved the bridge is "balanced," the current flowing through both arms equal and there is no voltage potential across points B and D.

When there is no voltage potential across points B and D, current does not flow through arm BD and a voltage drop is not detected across attenuator 58 which can be transmitted to recorder 60. DC current flowing in bridge arms ABC and ADC causes filaments 50, 52, 54, 56 to become hot. When pure carrier gas flows past filaments 50, 52, 54, 56, a specific amount of heat is conducted away from the filaments by the gas stream

and the filaments have a specific resistance value. The "balanced" condition of the bridge is dependent upon a specific filament temperature. Variations in the temperature of any one filament "unbalance" the bridge since arms ABC and ADC no longer have identical resistance values.

Referring to FIGS. 1 and 2, as admixed carrier gas and sample gas reach passage 30, the thermal conductivity of the admixture differs from the thermal conductivity of the carrier gas stream through passage 22. The temperature of filaments 50, 56 in passage 30 is higher than the temperature of filaments 52, 54 in passage 22. This temperature difference causes a difference in resistance and bridge arms ABC and ADC no longer offer equal resistance to incoming current at point A. As the resistance of filaments 50, 56 increases, current flows across path ADB generating a voltage drop across attenuator resistance 58. The voltage drop is transmitted to recorder 60 where it may be recorded as a chromatogram.

Fundamental operating aspects of the instant invention in establishing gas transmission rates of sample gases through a given packaging material are understood, in general, by referring to FIGS. 1, 3 and 4. Flexible packaging material 94 is inserted between upper die 90 and lower die 92 and fastened rigidly therebetween by tightening wing nuts 102, 104 and 106, respectively, over bolts 96, 98 and 100. The inner lip of the mating surface of lower die 92 is recessed to accommodate gasket 108, thereby forming an air-tight seal between dies 90, 92 and packaging material 94.

Solenoid valve 12 is actuated to an open position, by means not shown, and four-way valve 16 is shunted to a test chamber by-pass position, as shown in FIG. 2, to sweep air from the analytical portion of the system. Solenoid valves 72, 74 are thereafter actuated to an open position, by means not shown, and four-way valve 16 is shunted to a test chamber inlet position, as shown in FIG. 1, to sweep cavity 110 with carrier gas and displace air therein. Four-way valve 16 is then shunted back to a test chamber by-pass position and pure carrier gas continues to sweep the analytical portion of the system. Carrier gas pressure in cavity 110 is reflected on pressure gauge 76.

Sample gas is introduced into cavity 112 by actuating solenoid valves 42, 48, by means not shown, and the gas is permitted to sweep through the cavity until it displaces air therein. Sample gas pressure through cavity 112 is reflected on pressure gauge 78 and it is important that inlet sample gas be regulated to substantially maintain a zero pressure differential between cavities 110 and 112. Any substantial pressure difference between cavities 110 and 112 is reflected in the difference between gauge readings on pressure gauges 76 and 78. The pressure in cavities 110 and 112 are substantially equalized by minimizing the difference between the gauge readings through regulation of inlet carrier and sample gases. The required zero pressure differential is attained by thereafter opening valves 82, 84 and adjusting inlet gas pressures according to the calibrations on manometer 75. Solenoid valves 42, 48, 72, 74 are then actuated to a close position, by means not shown, and the system is permitted to equilibrate for the desired test period.

At the end of the equilibration period valves 82 and 84 are placed in a close position, solenoid valves 72 and 74 are actuated to an open position, and four-way valve 16 is shunted to a test chamber inlet position. Newly inlet carrier gas sweeps the admixture of carrier gas and diffused sample gas from cavity 110 to the detector system for analysis. A chromatogram is provided which compares the admixture of gases with pure carrier gas.

The carrier gas used may be selected from a wide variety of gases which do not react with other elements in the system. The carrier gas may be more selectively chosen for its contrasting thermal conductivity with respect to the sample gas utilized. It is believed that optimum results are achieved when the selected gas is an inert gas and helium is found to be a preferred inert gas for a variety of reasons.

Dies 90 and 92, mated to form test chamber 36, may be constructed from a variety of materials, however, the material from which they are constructed should not react, under the process conditions described, with the sample gas used in the system.

FIG. 5 is included to show in perspective a preferred embodiment of the present invention. This embodiment includes the elements previously described and additional elements that increase the efficiency of the system. Inlet fitting 13 firmly secures the carrier gas tank outlet conduit to the chromatograph inlet conduit. Moisture trap 65 absorbs and entraps any moisture that may be present in the carrier gas entering the system. Actuators 72', 74', 82' and 84' respond to pressure and may be depressed to open or close solenoid valves 72, 74, 82 and 84, respectively. The addition of flow controllers 19, 27 facilitate regulation of carrier gas entering the system.

Although the preferred embodiment shown in FIG. 5, is a dual column gas chromatograph, it should be understood that satisfactory results are achieved when the apparatus of the present invention is integrated with a single column gas chromatograph. Use of dual column gas chromatograph simplifies the task of recording and interpreting a chromatogram.

The present invention may be adapted for use in conjunction with detectors other than gas chromatographs, such as flame ionization detectors and electron capture detectors. The method of adaption should be apparent to those skilled in the art.

The terms and expressions which have been employed are used as terms of description and not of limitation, and there is no intention in the use of such terms and expressions of excluding any equivalents of the features shown and described or portions thereof, but it is recognized that various modifications are possible.

What is claimed is:

1. A process for determining the permeability of a packaging material with respect to a plurality of gases which comprises:

- a. disposing said packaging material across a chamber so as to divide said chamber into a first and second cavity;
- b. filling said first cavity with a sample gas comprised of a number of component gases;
- c. sealing said first cavity after said first cavity is filled with said sample gas;
- d. filling said second cavity with a reference gas;
- e. sealing said second cavity when said second cavity filled with said reference gas;
- f. substantially equalizing the pressure in said first cavity with respect to said second cavity;
- g. maintaining said first cavity and said second cavity at equal pressures while in a sealed condition;
- h. displacing to a chromatography column the gas contained in said second cavity by passing reference gas through said second cavity;
- i. passing the gas from said second cavity through said chromatography column thereby partitioning the components of the gas from said second cavity; and
- j. thermal conductively analyzing the gas components discharged from said chromatography column.

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