Nov. 14, 1967 M. MODELL ETAL 3,352,089
METHOD AND APPARATUS FOR INTRODUCING SAMPLES
INTO A GAS CHROMATOGRAPHIC COLUMN
Filed July 7, 1965 2 Sheets-Sheet 1

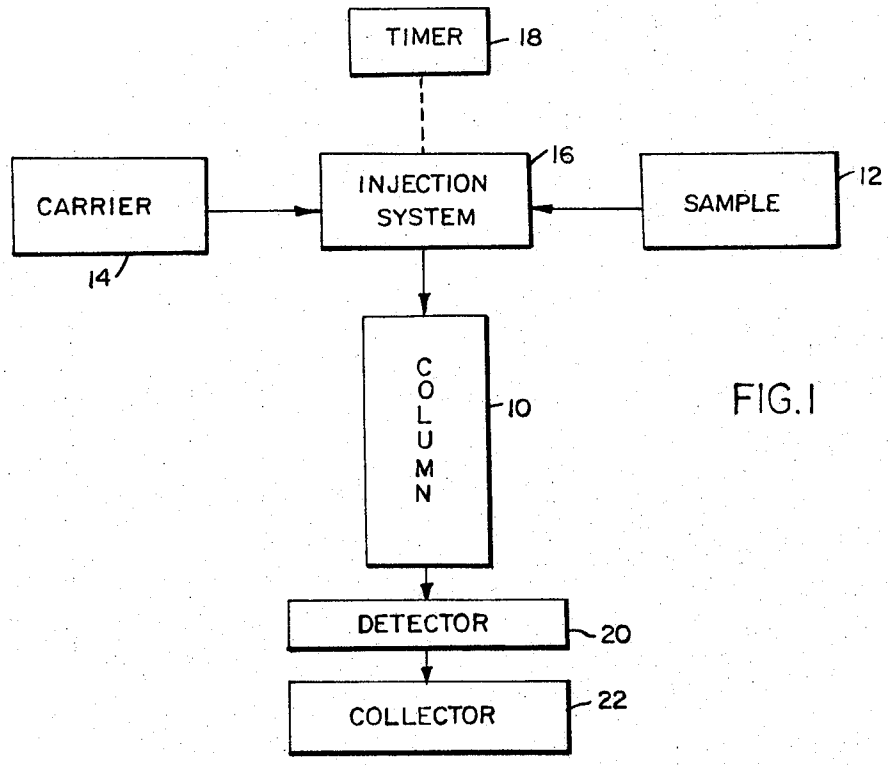

FIG. 1

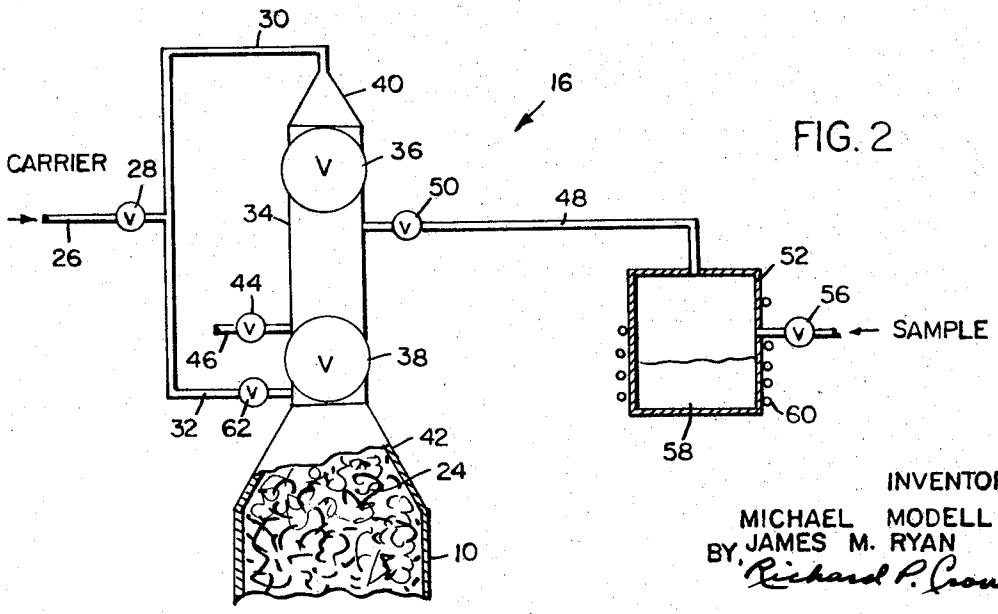

FIG. 2

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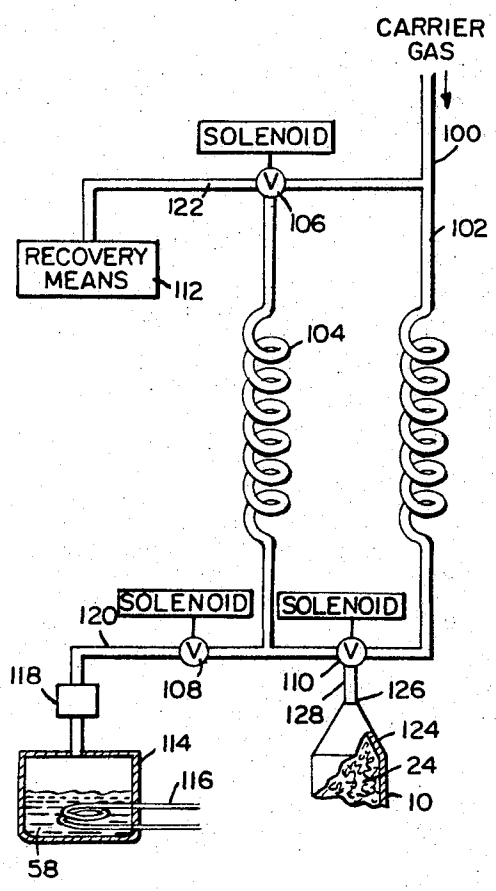

FIG. 3

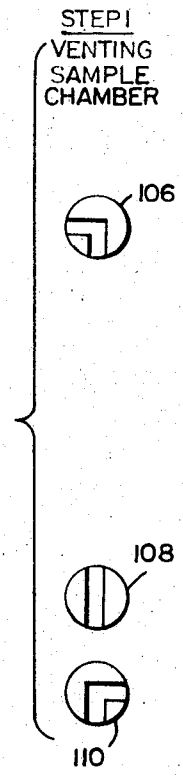

FIG. 3a

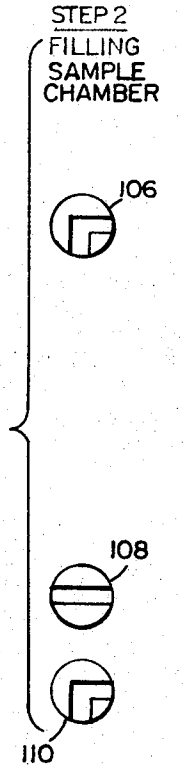

FIG. 3b

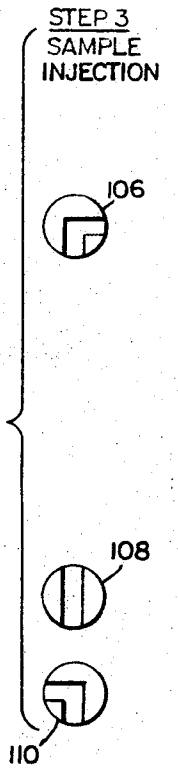

FIG. 3c

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METHOD AND APPARATUS FOR INTRODUCING SAMPLES INTO A GAS CHROMATOGRAPHIC COLUMN

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18 Claims. (Cl. 55—67)

ABSTRACT OF THE DISCLOSURE

A gas chromatographic system which includes, a sample gas injection system to vaporize externally a liquid sample and to introduce the gas sample so obtained from the vapor chamber into a gas chromatographic column in a non-diluted plug-like form to promote good sample separation. The sample ejection system includes an external autoclave for vaporizing a liquid sample and a vapor chamber to contain the vaporized gas sample. The vapor chamber is disposed directly adjacent the top of a chromatographic column so that valves at either end of the vapor chamber may be opened and the carrier gas permitted to sweep the gas sample directly into the column. Vent means are provided in the vapor chamber to remove the mixture of carrier gas and gas sample after each injection, while a tapered funnel connector packed with particulate material connects the discharge end of the vapor chamber and the top of the chromatographic column. Carrier gas may be introduced directly into the top of the column, bypassing the sample in the vapor chamber or be employed to flush the vapor chamber containing the gas sample. However, prior to each ejection the vapor chamber has any carrier gas removed to prevent dilution of the sample.

Our invention concerns a method of and an apparatus for introducing gas samples into gas chromatographic columns. In particular our invention concerns means to vaporize externally a liquid sample and to introduce the vapor from an external vapor chamber into a gas chromatograhpic column in non-diluted plug-like form.

In gas chromatography, a sample of the mixture to be separated is introduced into a chromatographic column which is filled with a stationary phase of separatory material such as a solid adsorbent in the case of gas-solid chromatography or an inert solid coated with a liquid absorbent in gas-liquid chromatography. An axial coefficient of velocity is imparted to the gas sample mixture in the column by the introduction of an inert carrier gas. The stationary phase is chosen in such a way that different components of the sample mixture have different affinities for the adsorbent or absorbent material. Thus, different components of the sample mixture are retained by a column for different lengths of time. As the band of sample mixture travels down the length of the column, the sample band gradually breaks into bands of the individual components. Complete separation of the components is obtained when the individual bands of each component no longer overlap in the axial direction.

One of the more important elements for promoting good sample separation is the apparatus used for sample introduction and the process of introducing the sample. The gas sample should be introduced and the apparatus should permit introduction into the column in the form of a plug (i.e. with a "top-hat" distribution or a square wave form with sharp back and frontal border). It is important that both the front and back borders of the plug are not diffused with the carrier gas. Furthermore, the length of the plug should be as short as possible for

a given weight of sample to be introduced. It is also desirable to minimize the volume of the sample plug by, for example, preventing dilution or mixing of the sample plug with the carrier gas.

There are two conventional methods which have been used in the past for introduction of liquid samples in gas chromatography. In both methods, a liquid sample is injected directly into the chromatographic system. The first method involves injection of the liquid into a heated chamber placed in the carrier gas line to the column. The chamber is either empty or packed with solid material such as metallic spheres to give a large heat transfer surface and heat capacity. The chamber is continually flushed with carrier gas to sweep the vaporized sample into the column. The second method involves the injection of the liquid sample directly on top of the stationary phase in the chromatographic column, with the column being continually flushed with carrier gas to impart an axial coefficient of velocity to the sample. In either of these systems, the sample must be vaporized internally, i.e., within the conventional gas chromatography system. Since the volume into which the liquid has been injected is continually flushed with carrier gas, the desired "plug" distribution can only be obtained if the sample is flash vaporized. Also, since in-line instantaneous vaporization is most difficult and almost a practical impossibility, the sample is necessarily diluted with carrier gas before and as it enters the column. Furthermore, with the first method of sample introduction, the heated sample chamber must have a geometry such that the surface area is large to insure rapid heat transfer, and the solid mass must be large to insure proper heat capacity for vaporization. For injection of relatively large liquid volumes the sample chamber is usually packed with metallic spheres. In this case the carrier gas must flush the vaporized sample out of the heated sample volume. Since this is a relatively inefficient process, the sample leaving the heated chamber will have an exponentially decaying concentration, and the heated sample chamber will act as a back-mixed hold up volume.

In the second conventional method for liquid introduction, the heat of vaporization of the sample must be supplied by the stationary phase onto which the sample is injected. Consequently, the stationary material will be cooled in the process, and a thermal imbalance in the sample will be created. Furthermore, since the solid material in the stationary phase is usually an insulator, such as diatomaceous earth or crushed fire brick, the rate of vaporization will be relatively slow.

Our present invention avoids the difficulties associated with both of the previously used methods for liquid sample introduction. Our discovery concerns vaporizing the liquid sample mixture externally and then introducing the vaporized sample into a vapor chamber, which is periodically flushed or displaced by carrier gas, so as to introduce a more nearly compact "top-hat" plug distribution of the sample into the chromatographic column.

It is therefore an object of our invention to provide a method of and apparatus for avoiding the difficulties associated with prior means of introducing liquid samples into a gas chromatographic column and particularly into columns of one to six inches or more. It is also an object of our invention to provide means whereby a liquid sample may be vaporized and introduced into a chromatographic column in a concentrated non carrier gas-diluted, plug-like form with sharp back and frontal plug borders thereby promoting more efficient separation of a sample material within the chromatographic column. These and other objects of our invention will be more apparent to those persons skilled in the art from the following more

detailed description of our invention taken in conjunction with the accompanying drawings wherein:

FIG. 1 shows schematic representation of a typical gas chromatographic system employing our sample injection system;

FIGS. 2 and 3 show an enlarged partially schematic and sectional more detailed view of different embodiments of our sample injection apparatus.

FIGURE 1 illustrates a typical composite gas chromatographic system of our invention including: a source of an inert carrier gas **14**, such as helium, nitrogen, argon, or the like; a source of sample material **12** which may be a liquid or solid material which is to be vaporized or a gas to be introduced into a gas chromatographic column **10**, containing a packed bed of separatory material **24**. The separatory material may be a particular solid, a solid coated with a liquid, resin particles, or even a gas permeable gel. Our system is particularly directed toward liquid samples which are vaporized externally such as a liquid hydrocarbon, proteins, solvents, solutions of solids, flavor essences, fruit extracts and the like. Our injection system generally represented by **16** and shown in more detail in FIGURES 2 and 3 is placed in fluid flow communication with the carrier source **14** and sample source **12** and the top of the column **10**. A timer **18** may be employed in pneumatic, hydraulic, electrical, or other responsive communication with our injection system or the system elements to provide for the correct timed and sequential opening and closing of the valves and operation of other sample system components. Means to detect the components emerging from the opposite end of the chromatographic column are usually provided and identified as a detector **20** such as a thermal conductivity cell, flame ionizing devices or other detecting means. A collector **22** may be employed to collect the separate fractions of the sample material separated in and emerging from the chromatographic column **10**.

In general our process comprises vaporizing a sample material externally of the chromatographic column or in-line carrier gas conduit, filling a sample chamber with the vaporized sample while introducing carrier gas from a bypass conduit into the top of the chromatographic column, and periodically displacing the vaporized sample from the sample chamber by stopping the flow of carrier gas from the by-pass conduit into the chromatographic column and employing carrier gas upstream of the sample chamber to sweep the vaporized sample from the sample chamber into the top of the chromatographic column in plug-like and substantially non-diluted form. Between sample injecting steps carrier gas in the vapor chamber is removed to prevent dilution of the next sample. Removal may be accomplished by pumping, venting, flushing with vaporized sample material or other means. To insure a sharp back border to the vaporized sample plug ejected from the vapor chamber, the outlet or downstream valve of the vapor chamber is closed before the entire sample has been ejected from the chamber. In this manner any diffusion or backtail of the back of the sample plug with the carrier gas is cut off during the injection step. In one embodiment of our invention (illustrated more particularly in FIG. 2) the valve chamber is devoid of any internal obstructions or restrictions to the flow of the vaporized sample from the chamber and contains inlet and outlet valve means having a cross sectional bore substantially the same as the internal cross section of the vapor chamber. In this embodiment the valves may be open and the entire plug injected with straight line flow into the top of the column. Preferably this vapor chamber comprises a large cylinder with the valves at either end and the chamber aligned with and near the top of the column. However for relatively large size chromatographic columns the valves of the first embodiment may be inordinately expensive as the size of the vapor chamber (or sample to be injected) becomes large.

In another embodiment of our invention, illustrated more particularly in FIG. 3, the valves enclosing the vapor chamber need not be of the same cross sectional bore as the vapor chamber. This embodiment permits a large volume straight or coiled vapor chamber to be used with valves of smaller bore cross section. Also switching of or closing of the outlet valve during sample injection permits greater control, less back diffusion of the sample tail, and a sharper back border of the plug than possible with larger bore valves of FIG. 2.

In both embodiments the size of the vapor chamber will depend in part on the size of the vaporized sample to be injected. The vapor chamber may be a straight or coiled tube or in other container form. Injection of the sample is normally and best accomplished by opening the inlet and outlet valves simultaneously so that carrier gas will smoothly and continuously sweep or flush the sample plug from the inlet to the outlet of the chamber and into the column.

Between sample injection steps the vapor chamber should normally be vented essentially free of residual vaporized sample and carrier gas. The residual sample may be collected by the use of a condenser, cold trap or other means, while the carrier gas may be recycled back to the main carrier gas stream after cleanup. In general the vaporized sample plug should be essentially free of carrier gas on injection or non-diluted with carrier gas. Dilution of the sample with carrier gas can deliberately be accomplished when necessary because of temperature limitations of heat sensitive materials.

We have also discovered that for improved efficiency and good sample injection the vaporized sample should be injected into a gradually sloped, e.g. connecting element, outwardly flared or funnel-shaped element. The top of a chromatographic column and the connecting funnel should be packed with packing material up to the sample injection inlet point or inlet valve for good results. In the embodiment of FIG. 2 the large cross section of the valves permits good injection of the sample in plug form with an angular funnel connection. With a narrow vapor chamber or small point source as in FIG. 3, the slope of the funnel or tapered connecting element should be extended to obtain a relatively straight frontal border to the sample plug in accordance with the Huygen's principle of overlapping waves. For example with a 2" to 4" vapor chamber diameter the length of the slope should be greater than 4" to obtain a straight frontal border of the sample plug.

FIGURE 2 is a detailed view of our injection sytem **16** which includes an autoclave **52** or other liquid sample holding means containing a liquid sample **58** to be vaporized, and a tubular straight line sample vapor chamber **34**. The sample chamber **34** shown is an elongated cylinder having a smooth straight line interior and is in gas flow communication with the source of carrier gas **14** through a conduit **26**, including valve **28** and first and second carrier conduits, **30** and **32**, including valve **62**. The conduits **30** and **32** are in fluid flow communication with either end respectively of the sample vapor chamber **34**. Conduit **30** has an outwardly flared and funnel-shape connection **40** to the top of the sample chamber **34**. The sample chamber **34** includes inlet and outlet valves, e.g., ball or plug valves **36** and **38** respectively located at either end of the sample chamber, while intermediate these valves, and in gas flow communication with the interior of the sample chamber is a vent conduit **46** containing valve **44**. In a preferred embodiment shown the sample chamber **34** is placed in an axial straight line flow relationship with the top of the chromatographic column **10** through a funnel packed connecting element **42**.

The sample chamber **34**, as shown being smaller in diameter than the cylindrical column **10** into which the sample is to be introduced, the connecting element **42** is preferably so designed to provide a gradual diverging connection **42** from the sample chamber outlet valve **38** to the internal column **10** diameter. This funnel connec-

tion 42 should be packed with any packing material of similar size as the separatory material of the column, but preferably with the chromatographic separatory material 24 up to or as close as possible to the valve 38 outlet of the sample chamber 34. A connecting element so packed helps to preserve the sharpness of the frontal borders of the vaporized plug sample 58 introduced into the column 10.

The design of the sample injection apparatus 16 and in particular the design of the sample chamber 34 and its connection with the top of the chromatgraphic column 10 has a considerable influence on the efficiency of our sample introduction system. In particular the sample chamber 34, valves 36 and 38, and connecting element 42 should be designed to eliminate or considerably reduce any constriction or rapid expansion or contraction of the gas sample in the sample chamber 34 or in the sample flow connections leading from the sample chamber 34 to the separatory material 24 in the column 10. Any variation in interior flow design which is not gradual tends to reduce considerably the efficiency of our sample injection system.

Poorly designed vapor chambers 34 tend to create disturbances which result in hold up or mixing volumes in which the carrier gas and the vaporized sample becomes mixed prior to or during entry of the vaporized sample plug into the column. As a result the vaporized sample plug becomes diluted with carrier gas and the front and tail of the plug become diffuse prior to being introduced into the column 10. It is therefore necessary in this embodiment that the ball or plug valves 36 and particularly 38 be so selected and designed to have a bore cross sectional area similar to or identical with that of the sample chamber, so as to minimize any flow disturbance to the vaporized sample on injection. Likewise, any conduits between valve 38 and the separatory material 24 in the chromatographic column 10 should be a similar cross section, or present a gradual sloping or curved interior or converging flow path, as the case may be, to the vaporized plug sample.

The autoclave 52 contains a liquid sample 58, which is usually vaporized by heating means such as by steam or surrounding electric heating coils 60, an immersion heater, or the like, while fresh liquid sample is provided through the sample introduction conduit containing valve 56 which is in flow communication with the source of liquid sample 12. A vaporized sample from the autoclave 52, is introduced into the sample chamber 34 through conduit 48 containing a control valve 50.

In operation, carrier gas such as helium, is passed continually through conduit 26, valve 28, by-pass conduit 32, valve 62 and into the top of the chromatographic column 10, while valve 36, 38 and 44 remain closed. In this manner the previous gas plug introduced into the column 10 is given an axial coefficient of velocity, while sample chamber 34 is filled with a vaporized sample of material 58. Since valve 36 is closed, the carrier gas in conduit 30 is prevented from entering the sample chamber 34.

While the carrier gas is flowing continually into the column 10, the sample chamber 34 is filled with a 20–100 ml. vaporized sample of liquid material 58 such as a cis-trans pentene mixture at a temperature of 100–150° C. from autoclave 52 by opening valve 50 in conduit 48. The pressure of the vapor in the autoclave 52 is desirably maintained at a higher pressure than the carrier gas pressure, so that a driving force for filling the sample chamber 34 is present. The time spent in filling the sample chamber 34 with sample should be less than the time required for the time required for the separation process in the chromatographic column 10. Where this is the case, sufficient time is then available for vaporizing more liquid in the autoclave 52, so that the rate of vaporization in the autoclave need not be excessive. This has a distinct disadvantage in that the autoclave then does not have to be maintained at an exceptionally high temperature, so that the possibility of thermal degradation of the liquid sample 58 is greatly reduced. The introduction of the vaporized sample in the sample chamber 34 to the column 10 is accomplished by closing valves 62, 50 and 44, and opening valves 36 and 38 simultaneously. Valves 36 and 38 as well as the other valves in the sample injection system may be solenoid actuated valves in electrical or other responsive communication with a timer 18, so as to provide for the proper timed or sequential opening of these valves. When valves 36 and 38 are opened, carrier gas in conduit 30 pushes or sweeps the cylindrical plug of vaporized sample from the sample chamber 34 through valve 38, and connector 42 into the top of the chromatographic column in a compact plug form with the plug having a minimum dilution of carrier gas.

After the vaporized sample is injected, valves 36 and 38 are closed, and valve 62 is again opened to sweep the plug through the column 10. Valve 38 is closed prior to the complete ejection of the entire sample from the chamber 34, preferably when the tail of the sample is diffused with carrier gas, e.g. when 90% of the sample has been injected. Closing valve 38 in this manner provides a sharp back border to the sample plug, but entraps residual vaporized sample and carrier gas in the chamber 34. The carrier gas and sample trapped within the sample chamber 34 is then vented or pumped out through conduit 46 by opening valve 44. When the sample chamber 34 is essentially free of carrier gas valve 44 is closed, and the next sample is introduced by opening valve 50 and closing valve 50 when the desired vaporized sample pressure is obtained, and the sequence of steps repeated for each sample injection. The vaporized sample pressure should normally be close to the pressure of the carrier gas, so that any mixing by a change in pressure is avoided during the injection process.

FIG. 3 is a detailed view of another embodiment of our sample injection system 16 which includes: the schematic illustration of the operation of the valve during the filling of the sample chamber and the sample injection steps. Our sample injection system 16 includes a main carrier gas conduit 100, connected to the source of carrier gas 14, a coiled tube 104 as a sample chamber of predetermined volume, a coiled tube 102 as a carrier gas by-pass conduit, a 3-way valve 106 at the upper end of the vapor chamber 104, and 3-way control valve 110 at the lower end of the vapor chamber to control the flow of carrier gas from by-pass conduit 102 or the vaporized sample from the vapor chamber 104 into the column 10 containing separatory material 24. Valves 106 and 110 are usually of the same size, with valve 110 used to cut off the tail of the plug. Each valve is shown in communication with an individual solenoid or other means for automatic and manual timed operation as hereinafter described with the solenoids connected to one or more timers 18. Inlet valve 106 is also in communication with vent conduit 122 connected to a recovery means 112 such as a pump, a condenser, a vent or other means to remove residual sample vapor and carrier gas from the sample chamber 104. Sample control valve 108 may be a relatively small and inexpensive valve compared to 106 and 110, and communicates through conduit 120 with a liquid sample container or boiler 114 containing an immersion heater 116 used to vaporized the liquid sample material 58, and a deentrainment device 118 to remove liquid drops from the vaporized sample. The column 10 contains a funnel-shaped connector 124 diverging outwardly from a source 126 represented by the inlet of conduit 128 to the connector 124 from which the carrier gas or sample is introduced from control valve 110. The connecting element is packed with separatory material to the narrowest part of the funnel 126, and has a smaller interior angle than in FIG. 2 and a longer funnel side length to provide for the introduction of the sample plug from the source 126 with a straight frontal border on the

plug on reaching the interior diameter of the column **10**.

In operation carrier gas is introduced from conduit **100** through by-pass conduit **102**, and valve **110** into the top of column **10**, while the sample chamber **104** is filled with a vaporized sample by positioning valve **106** and valve **108**, as shown. Vaporized sample from the boiler **114** is introduced through device **118**, conduit **120**, and valve **108** into the chamber **104**, until the chamber is filled at a predetermined sample pressure. Valve **108** is then closed. The sample is then injected into the column **10** by simultaneously switching valves **106** and **110** to stop the flow of carrier gas through the by-pass conduit **102**, and to have carrier gas from conduit **100** through valve **105** push the vaporized sample from chamber **104** through valve **110**, conduit **128**, and connector **124** into the top of column **10**. Prior to the ejection of the entire sample from chamber **104**, valve **110** is closed to cut off that predetermined portion of the tail of the sample which has become diffused with the carrier gas introduced from conduit **100** and through valve **106**. With smaller valves than in FIG. 2 sharp back borders on the sample plug can be obtained. Valve **106** is then opened to the recovery means so that sample and carrier gas can be removed from chamber **104**. After the sample chamber **104** is essentially free of carrier gas, the filling of the sample chamber is repeated while carrier gas flows into the column **10** through by-pass conduit **102** and valve **110** and the sequence repeated for each sample injection, and after recovery of the carrier gas from the vapor chamber the carrier gas may be recycled back to the source of carrier gas for reuse in the system.

Our apparatus and sample injection method permits the introduction of externally vaporized samples into a relatively large diameter chromatographic gas column in a highly concentrated vaporized plug-like form and thereby avoids many of the difficulties and problems associated with prior processes in the art.

What we claim is:

1. A gas chromatographic system which comprises:
- a source of carrier gas;
- a gas chromatographic column containing separatory material;
- a source of sample gas to be introduced into and separated by said separatory material in the column;
- a sample gas injection system to introduce the sample gas into the chromatographic column which system comprises:
  - an empty vapor chamber having a first valve at the one end and a second valve at the other end of the chamber;
  - connecting means to place the other end of the vapor chamber in gas flow communication with the chromatographic column, said means designed to prevent disturbance to the sample ejected from the sample chamber;
  - means to introduce the gas sample from the source into the vapor chamber intermediate the first and second valves;
  - means to remove carrier gas from the vapor chamber;
  - means to introduce the carrier gas from the source directly into the chromatographic column and to bypass the vapor chamber;
  - means to introduce the carrier gas from the source into the one end of the vapor chamber; and
  - means to permit the carrier gas to be introduced into either the one end of the vapor chamber to eject the sample gas therein directly into the chromatographic column or directly into the chromatographic column bypassing the vapor chamber, whereby a sample gas produced from a liquid material and vaporized externally from the sample gas injection system may be introduced from the vapor chamber directly into the chromatographic column in plug-like form with sharp back and frontal borders and non-diluted with carrier gas.

2. The apparatus of claim **1** which includes a means external to the gas sample injection system to vaporize a liquid material to a gas sample to be introduced into the vapor chamber.

3. The apparatus of claim **1** which includes:
- means to provide for the simultaneous opening of the first and second valve of the vapor chamber and the diversion of the carrier gas flow from the source to the column and to the one end of the vapor chamber.

4. The apparatus of claim **1** wherein the means to place the vapor chamber in gas flow communication with the chromatographic column includes an outwardly diverging funnel-like connecting element between the second valve of the vapor chamber and the top of the chromatographic column, which connecting element is packed with particulate material.

5. The apparatus of claim **1** wherein the means to introduce the carrier gas from the source into the one end of the vapor chamber includes directly upstream of the first valve an outwardly diverging funnel-like connecting element.

6. The apparatus of claim **1** wherein the vapor chamber is a cylindrical tube of constant internal diameter, the first and second valves having a bore cross section substantially similar to the internal diameter of the vapor chamber, and the second valve is adjacent to and in direct gas communication to the connecting means.

7. The apparatus of claim **1** wherein the means to remove carrier gas from the vapor chamber includes means to recycle the carrier gas back to the source of carrier gas.

8. The apparatus of claim **1** wherein the vapor chamber includes a straight line smooth elongated cylindrical interior chamber.

9. The apparatus of claim **1** wherein the vapor chamber is a coiled tube of predetermined volume, and the first and second valves include multi-position valves, the first valve including a position to connect the vapor chamber with the source of carrier gas, and a position to connect the vapor chamber with a recovery means, and the second valve including a position to connect carrier gas with the connecting means and a position to connect the vapor chamber with the connecting means.

10. A method of injecting a sample in vaporized form into a chromatographic column which method comprises:
- introducing a carrier gas into a chromatographic column to impart an axial coefficient of velocity to sample material in the column;
- introducing a vaporized sample into an empty sample chamber external of the chromatographic column, the interior of the chamber characterized and designed to prevent flow disturbance to the flow of vaporized sample from the chamber;
- interrupting the flow of carrier gas directly into the column;
- introducing carrier gas upstream of the sample chamber and permitting the carrier gas to sweep the vaporized sample from the sample chamber and into the chromatographic column;
- closing the sample chamber after injection of the vaporized sample and reintroducing the carrier gas directly into the column;
- removing carrier gas from the sample chamber; and
- repeating this sequence of steps thereby providing for the injection of a vaporized sample into a chromatographic column in non-diluted, concentrated plug-like form.

11. The method of claim **10** wherein the sample chamber includes a first valve means at the one end and a second valve means at the other end and wherein both valves are opened simultaneously when the carrier gas flow directly to the column is interrupted.

12. The method of claim **10** wherein the injecting of the vaporized sample from the sample chamber directly

into the column is interrupted by closing the sample chamber at or before a time when the tail of the sample becomes diffused with carrier gas thereby providing for the injecting of a sample plug with a sharp back border.

13. The method of claim **10** which includes treating a source of liquid sample material to form a vaporized sample.

14. The method of claim **10** wherein the total pressure of the carrier gas and the vaporized sample in the sample chamber are approximately the same.

15. The method of claim **10** wherein the vaporized sample is injected into the top of the chromatographic column from an introductory opening in a gas flow diverging outwardly with a substantial straight line frontal border on the sample plug.

16. The method of claim **10** wherein the vaporized sample from the sample chamber is introduced into the top of the column through a funnel-shaped connecting element between the sample chamber and the top of the column, which element is packed with material of similar size as the separatory material in the column.

17. The method of claim **10** wherein the vaporized sample has a greater pressure than the pressure of carrier gas in the sample chamber.

18. A method of injecting a sample in vaporized form into a relatively large diameter chromatographic column containing separatory material which method comprises:

providing vaporized sample material;

introducing carrier gas into the chromatographic column to impart an axial coefficient of velocity to the previous sample introduced into the column;

introducing the vaporized sample into an empty sample chamber which includes a first valve means at the one end and a second valve means at the other end, the interior of the chamber characterized and designed to minimize disturbance to the flow of the sample from the chamber, the sample chamber being essentially free of carrier gas, to form a plug-like vaporized sample;

sweeping the vaporized sample from the sample chamber into the chromatographic column in plug-like form, by simultaneously opening the sample chamber valves and introducing carrier gas upstream of the vaporized sample and into the sample chamber while interrupting the flow of carrier gas downstream of the sample chamber;

closing the sample chamber valves at predetermined time after the discharge of a predetermined amount of the vaporized sample from the chamber to cut off the carrier diffuse tail of sample;

removing carrier gas from the chamber; and

thereafter repeating this cycle to provide for the injection of sample material in vaporized non-diluted plug-like form into the chromatographic column.

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