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SAMPLE INJECTION SYSTEM

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FIG. 1.

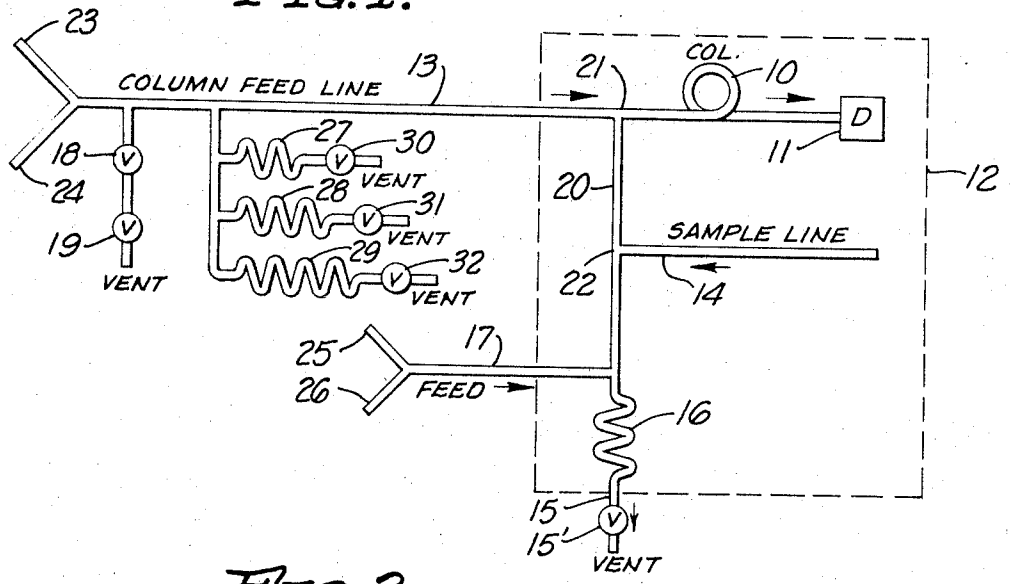
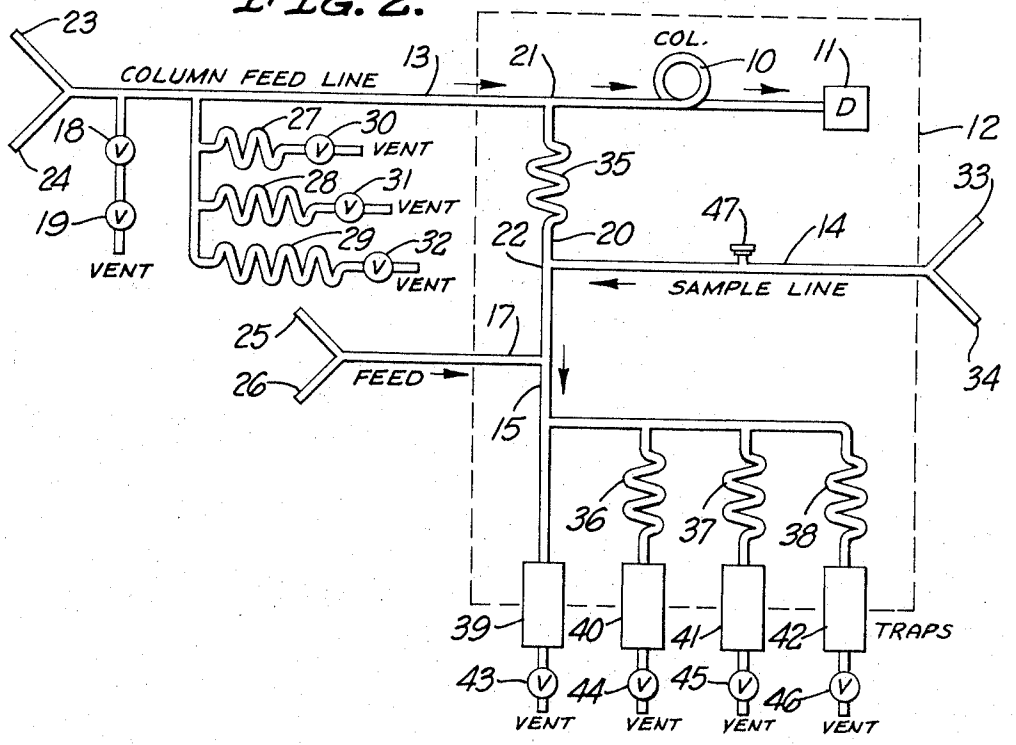


FIG. 2.



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SAMPLE INJECTION SYSTEM

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ABSTRACT OF THE DISCLOSURE

An apparatus and method for providing the introduction of a sample into a gas chromatograph utilizing a column feed stream and a sample feed stream connected by a tie line. Various vents and feed line arrangements are provided for adjusting the stream input pressures to divert a portion of the sample into the column feed line or to split the sample to introduce a controlled portion into the column feed line.

This invention relates to sample handling in gas chromatographs and the like and to new and improved methods and apparatus for introducing samples into gas chromatographic columns.

Gas chromatographs are often operated at elevated temperatures, sometimes as high as 700° C., and many problems have been encountered in the design and operation of valves at elevated temperatures, particularly in connection with leakage and operating life. Also, it is often desirable in the operation of a gas chromatograph to introduce samples for a very short period of time, typically in the order of 5 to 50 milliseconds. Conventional sampling valves, typically the widely used slider valve, can seldom be actuated to provide sample injection in less than about 100 milliseconds.

Accordingly, it is an object of the present invention to provide a new and improved sample injection system suitable for operation at the elevated temperatures encountered in present-day gas chromatographs. A further object is to provide such a system which functions to introduce samples in very short periods of time. A further object is to provide a system for introduction of a sample from an atmospheric pressure stream into the elevated pressure region at the head of a chromatographic column. An additional object is to provide such a system which does not utilize any moving parts in the sampling zone or steadily exposed to a hot area of the gas chromatograph.

It is an object of the invention to provide a new and improved apparatus for sample injection including a column feed line, a sample line, a tie line joining the column feed line at a first junction and the sample line at a second junction, a vent from the second junction with the pressures of the column feed line and sample line such that the pressure at the first junction is normally greater than the pressure at the second junction with resultant flow in the tie line from the first junction to the second junction, and means for changing the relative pressures at the first and second junctions to reverse the flow through the tie line for a period of time to introduce sample from the sample line into the column feed line.

It is a further object of the invention to provide a variety of configurations for producing the change in relative pressures and the reversal of flow in the tie line. An additional object is to provide such an apparatus which can be utilized both with sample lines having a continuous flow of sample and with sample lines in which a sample is introduced as a slug. Another object of the invention is to provide such apparatus which can be utilized for splitting or dividing a sample for introducing a controlled portion of the sample into the column feed line.

An additional object is to provide such apparatus which can be operated with the sample line at or near column pressure and with the sample line at atmospheric pressure.

It is an object of the invention to provide a method of introducing a sample into a gas chromatograph or the like utilizing a column feed stream and a sample feed stream connected by a tie line and including the steps of adjusting the stream input pressures such that the pressure column feed-tie line junction is greater than the pressure at the sample feed-tie line junction to introduce a portion of the column feed stream into the sample feed stream, and for a short period of time, changing the relative pressures at the junctions and reversing the flow in the tie line introducing a portion of the sample feed stream into the column feed stream.

It is a further object of the invention to provide a variety of methods for producing the change in relative pressures.

The invention also comprises novel combinations and arrangements of parts and steps, which will more fully appear in the course of the following description. The drawing merely shows and the description merely describes preferred embodiments of the present invention which are given by way of illustration or example.

In the drawing:

FIG. 1 is a diagrammatic illustration of a preferred form of the sample injection system incorporated in a gas chromatograph; and

FIG. 2 is a diagrammatic illustration of an alternative form of a sample injection system particularly suited for use with samples at or near atmospheric pressure.

The system illustrated in FIG. 1 includes a column **10** and a detector **11** in a gas chromatograph **12**. A column feed line **13** is connected to the input of the column **10**. A sample line **14** is connected to a vent **15** through a restrictor **16**. A valve **15'** may be provided at the outlet of the vent **15**. A tie line **20** is connected to the column feed line **13** at a junction **21** and is connected to the sample line **14** at a junction **22**. A plurality of restrictors **27, 28, 29** may be connected in parallel to the column feed line **13**, with each restrictor terminating in a shutoff valve **30, 31, 32** leading to vent. A pair of valves **18, 19** separated by a fixed volume may be connected to the column feed line **13**, with the valve **19** leading to vent. The column feed line may be so connected as to be supplied alternately with a high flow rate through line **23** or a low flow rate through line **24**. An auxiliary carrier line **17** may be connected to the sample vent line between the junction **22** and the restrictor **16** and may be supplied with a high flow rate through **25** or at a low flow rate through **26**. In different modes of operation, certain components only are required and others can be omitted.

In a typical system, the column feed line **13** is connected to a source of carrier such as helium at a substantially constant pressure. The sample line **14** is connected to a substantially constant pressure source providing a stream which may be all sample or a mixture of sample and carrier. The flow conditions in the system are adjusted so that the pressure at the junction **21** is higher than the pressure at the junction **22**. Under these conditions, the sample feed stream in the line **14** will flow past the juction **22** and out the vent **15**. The column feed stream in the line **13** will divide at the junction **21**, with a portion flowing through the column **10** and detector **11** and a portion flowing through the tie line **20** out the vent **15**. It is preferable to have the pressure differential between the junctions **21** and **22** small and to have the volume of the tie line **20** small so that there is a minimum waste of carrier out the vent **15** and a minimum dead time in the sample introduction operation to

be described. This steady state condition may be achieved by suitably adjusting the pressures at the column feed source and sample feed source for the particular configuration being employed. It is realized that changes in column or tubing diameter, length and placement, location and size of restrictors, and other physical variations in the apparatus may require changes in the source pressures to obtain the desired steady state condition.. In a typical example, the steady state flow rates may be 30 cc./min. in the column **10**, 3 cc./min. from junction **21** to junction **22** in the tie line **20**, and 10 cc./min, in the sample line **14**.

In one form of the apparatus the components **15'**, **17**, **19**, and **23** through **32** may be omitted. A portion of the sample feed stream in the sample line **14** may be introduced into the column **10** in the following manner. The valve **18** is opened, venting a portion of the column feed stream to the atmosphere with a resultant lowering of the pressure at the junction **21**. The direction of the flow in the tie line **20** then reverses and a portion of the sample feed stream flows towards the junction **21**. Then valve **18** is closed, restoring the steady state conditions. The quantity of sample introduced into the column will be a function of the length of time valve **18** is open, thereby providing a direct control for the size of the sample. In this typical system, the valve **18** may be opened for 100 milliseconds.

In a modification of the apparatus of the preceding paragraph, the valve **19** and the fixed volume between valves **18** and **19** are added. Valve **19** is first opened to the atmosphere, and then closed. Sample introduction is effected by opening valve **18**. The venting of gas into the valves **18**, **19** to that of the column feed line, the pressure at junction **21** relative to that at junction **22**, leading to introduction of sample as previously described. This temporary diversion of a portion of the column feed stream produces a sample slug in the input to the column. When the valve **18** is opened, there is a decrease in pressure at the junction **21** with resultant flow of sample feed stream through the tie line **20** past the junction **21**. When the pressure builds up in the fixed volume between the valves **18**, **19** to that of the column feed line, the pressure at the junction **21** increases and the steady state flow conditions are reestablished, with some column feed stream flowing through the tie line **20**. The volume of sample injected into the column will be proportional to the volume of the line between the valves **18**, **19**. This system provides a means for rapid, repetitive introduction of very precise quantities of sample.

In another form of the apparatus of FIG. 1, the components **15'**, **17**, **19** and **23** through **26** may be omitted. The valves **18**, **30**, **31** and **32** are normally closed. Sample introduction is accomplished as described above by opening and closing valve **18** or one of the other valves **30**, **31**, **32**. The selection of the particular valve and associated restrictor, if present, permits selection of the portion of the column feed stream being vented and thereby control of the quantity of sample injected. The provision of a plurality of vent control valves with different magnitudes of restriction permits varying the sample size without changing other parameters of the system.

The tie line **20** and the associated portions of the column feed and sample lines may be positioned within the chromatograph with the column and detector and may be operated at or above the temperture of the column. The valves **18**, **19**, **30**, **31** and **32** which are used for opening and closing the vents may be positioned at any location remote from the chromatograph and are operated at room temperature. The sample flow control taking place at the junctions **21**, **22** is accomplished without any moving parts in the sampling zone, thereby eliminating all of the problems normally encountered in operation of valves at elevated temperatures.

In another form of the apparatus the components **17**, **18**, **19** and **23** through **32** may be omitted. Sample introduction may be effected by a momentary closure of the vent line **15** by the valve **15'**, causing the pressure at the junction **22** to exceed that at the junction **21**, reversing the flow through the tie line **20** so that sample is introduced into the flow to the column **10**. Sample peaks as narrow as 5 milliseconds may be introduced in this manner. In a preferred form, the valve **15'** may be a silicone rubber bung which can be moved forcefully against the smoothly finished and clamped end of the hot vent tube **15**. In the brief contact time required for closure, the flexible bung will not be damaged even if the temperature of the chromatographic oven **12** (and the vent tube **15**) greatly exceeds the melting point of the flexible bung, permitting such a sealing member to be used for the introduction of many samples without deterioration.

In another alternative arrangement the components **15'**, **18**, **19**, **23**, **24** and **27** through **32** may be omitted, and sample introduction may be effected by switching an auxiliary carrier flow momentarily from low flow through **26** to high flow through **25**, elevating momentarily the pressure at junction **22** above that at junction **21**, so that sample introduction occurs as in the previous arrangement.

In still another alternative arrangement components **15'**, **17**, **18**, **19** and **25** through **32** may be omitted, and sample introduction may be effected through switching the flow to the column feed line **13** from a higher rate through **23** to a lower rate through **24**. This will decrease the pressure at junction **21** relative to junction **22**, forcing sample into the column. After a short interval of time sufficient for the desired sample injection, the flow is switched back from **24** to **23**, restoring normal operating conditions.

It is apparent that various combinations of the components and actions described in the preceding examples can also be used to effect the reduction of pressure at junction **21** relative to junction **22**, with the desired resultant introduction of sample from the sample line **14** into the column **10**.

The apparatus of FIG. 1 is particularly adapted to the introduction of samples from sample feed streams operating in the pressure range of the column feed stream. Where the sample feed stream is near atmospheric pressure, the apparatus of FIG. 2 is preferred, where components corresponding to those of FIG. 1 are identified by the same reference numerals. The principal difference between the two arrangements is the replacement of the restrictor **16** in the vent line **15** of FIG. 1 by a restrictor **35** in the tie line **20** of FIG. 2. With restrictor **35**, a sizeable pressure differential can exist between the column feed line **13** and the sample feed line **14**.

While the apparatus of FIG. 1 can be used for batch samples (by placing an injection port **47** in the sample line **14**), the apparatus of FIG. 2 is preferred for batch sample introduction because of the greater ease of introduction of such samples at atmospheric rather than elevated pressure. In the apparatus of FIG. 2 several components not shown in FIG. 1 have been added. The new components which may be used include the injection port **47**, sources of high flow **33** and low flow **34** in the sample feed line, the restrictor **35** in the tie line **20** (replacing the restrictor **16** which was in the vent line **15** of FIG. 1), the additional parallel restrictors **36**, **37** and **38** from the vent line **15**, and the vent valves **43**, **44**, **45** and **46** located in a room temperature portion of the apparatus. The vent valves **43** through **46** may be isolated from the hot box **12** by absorbent-containing traps **39**, **40**, **41** and **42** to prevent sample from reaching the valves and condensing therein.

Sample introduction by means of the apparatus of FIG. 2 is generally similar to that employing the apparatus of FIG. 1 except that it is necessary in every case employing the apparatus of FIG. 2 to elevate the pressure at junction **22** to inject sample from line **14** into the column **10**. For atmospheric pressure sample injection

into the inlet 47, the valve 43 must be open to atmosphere during introduction of the sample into the inlet. The pressure elevation at junction 22 then requires closure or partial closure of the vent 15. Complete closure is obtanied with valves 43 through 46 all simultaneously closed, while varying degrees of partial closure are obtained by closing valve 43 while leaving one or more of the valves 44 through 46 open, providing various restrictions in the flow to vent. The various restrictions make possible varying degrees of sample splitting so that where desired, only a portion of the sample injected into 47 is introduced onto the column, while the rest of the sample is vented through one or a combination of the restrictors 36 through 38.

Sample introduction without splitting is accomplished by closing valve 43 (with valves 44 through 46 all closed), or by closing valve 43 and simultaneously or shortly thereafter employing one or a combination of the following operations:

(1) decreasing flow to the column feed line 13 by switching from high flow through 23 to low flow through 24;

(2) decreasing flow to the column feed line 13 by opening valve 18 or by opening one of the valves 30, 31 or 32;

(3) increasing the sample carrier flow through 14 by switching from a low flow through 34 to a high flow through 33;

(4) increasing the sample purge flow through 17 by switching from a low flow through 26 to a high flow through 25.

In a preferred embodiment of the apparatus of FIG. 2 the components 18, 19, 27 through 32, 36, 37, 38, 44, 45 and 46 may be omitted. The system is operated before sample introduction with a high flow through 23 into the column feed line 13. This flow splits at the junction 21, a portion passing through the column 10 and the remainder passing through the restrictor 35 towards the junction 22. A low flow rate of carrier is introduced into the sample line 14 through 34, and another low flow rate is introduced into line 17 through 26. The vent 15 is open to atmosphere through valve 43. A sample is then introduced through 47, by means of syringe injection or by fragmentation of a sample placed in a fragmentation inlet at that point. Sample vapors are allowed to evolve slowly through vaporization or fragmentation and are contained in the volume between 47 and 22; a sample loop may be included to enlarge this volume if desired. After ample time for sample volatilization and collection in the sample loop at low flow rate, the valve 43 is closed and simultaneously sample and column feed carrier flows are switched to provide a low flow 24 into the column feed line 13 and a high flow into the sample line 14 through 33. This results in a complete sweeping of the sample volatiles onto the chromatographic column 10.

The various embodiments of the invention described herein illustrate how the invention may be utilized for the injection of samples into gas chromatographs without requiring any moving parts in the sampling area of the apparatus. The valves utilized may be conventional open-and-shut type valves which are not required to operate in the high temperature environment of the chromatograph. Problems of leakage, short life and rapid action encountered in conventional sampling valves are eliminated. At the same time, sampling periods materially shorter than those previously obtainable are achieved.

Although exemplary embodiments of the invention have been disclosed and discussed, it will be understood that other applications of the invention are possible and that the embodiments disclosed may be subjected to various changes, modifications and substitutions without necessarily departing from the spirit of the invention.

We claim as our invention:

1. In a sample injection system for a gas chromatograph or the like, the combination of:
   - a column feed line;
   - a sample line;
   - a tie line joining said column feed line at a first junction and said sample line at a second junction;
   - a vent from said second junction, with the pressures of said column feed line and sample line such that the pressure at said first junction is normally greater than the pressure at said second junction with resultant flow in said tie line from said first junction to said second junction; and
   - means for changing the relative pressures at said first and second junctions by reducing the pressure in said column feed line at said first junction to reverse the flow through said tie line for a period of time.

2. A system as defined in claim 1 in which said means for changing relative pressures includes a second vent in said column feed line, and a valve for opening and closing said second vent.

3. A system as defined in claim 1 in which said means for changing relative pressures includes means for closing and opening said vent, a second vent in said column feed line upstream of said first junction, and a valve for opening and closing said second vent.

4. A system as defined in claim 1 in which said means for changing relative pressures includes a vent line from said column feed line, and first and second valves spaced along said vent line defining a volume between said first and second valves.

5. A system as defined in claim 1 including a sample input port in said sample line upstream of said second junction, and in which said means for changing relative pressures includes:
   - a vent line from said column feed line;
   - a flow restrictor in said vent line; and
   - a valve for opening and closing said vent line.

6. A system as defined in claim 1 including a sample input port in said sample line upstream of said second junction, and in which said means for changing relative pressures includes:
   - a vent line from said column feed line;
   - a plurality of flow restrictors in parallel in said vent line; and
   - a corresponding plurality of valves for selectively opening and closing said vent line through each of said restrictors.

7. A system as defined in claim 1 in which said means for changing relative pressures includes means for changing the flow in said column feed line from a higher rate to a lower rate.

8. A system as defined in claim 1 in which said means for changing relative pressures includes means for changing the flow in said sample line from a lower rate to a higher rate.

9. A method of introducing a sample into a gas chromatograph or the like utilizing a column feed stream and a sample feed stream connected by a tie line, including the steps of:
   - adjusting the stream input pressures such that the pressure at the column feed-tie line junction is greater than the pressure at the sample feed-tie line junction to introduce a portion of the column feed stream into the tie line; and
   - for a short period of time, changing the relative pressures at the junctions by reducing the pressure at the column feed-tie line junction and reversing the flow in the tie line introducing a portion of the sample feed stream into the column feed stream.

10. A method as defined in claim 9 in which the pressure changing step includes venting the column feed stream upstream of the column feed tie line junction and then closing such vent.

11. A method as defined in claim 9 in which the pressure changing step includes connecting the column feed stream at a point upstream of the column feed tie line junction into a closed line of predetermined volume,

and then closing such connection and venting the closed line.

12. A method as defined in claim **9** including the step of introducing a quantity of sample into the sample feed stream upstream of the sample feed-tie line junction, and in which the pressure changing step includes venting the column feed stream upstream of the column feed-tie line junction through a restriction thereby splitting the sample flow at the sample feed junction with the tie line, with the ratio of the splitting being a function of the magnitude of the restriction.

13. A method as defined in claim **9** including the step of introducing a quantity of sample into the sample feed stream upstream of the sample feed-tie line junction, and in which the pressure changing step includes venting the column feed stream upstream of the column feed-tie line junction through a first restriction and introducing a second restriction in the sample feed stream downstream of the sample feed-tie line junction for splitting the sample flow at the sample feed junction with the tie line, with the ratio of the splitting being a function of the magnitudes of the two restrictions.

14. A method of introducing a sample into a gas chromatograph or the like utilizing a column feed stream and a sample feed stream connected by a tie line, including the steps of:

adjusting the stream input pressures such that the pressure at the column feed-tie line junction is greater than the pressure at the sample feed-tie line junction to introduce a portion of the column feed stream into the sample feed stream;

introducing a quantity of sample into the sample feed stream upstream of the tie line junction; and

for a short period of time changing the pressure at the junctions by introducing a restriction in the sample feed stream downstream of the tie line junction for splitting the sample flow at the junction with the tie line, with the ratio of the splitting being a function of the magnitude of the restriction, and reversing the flow in the tie line introducing a portion of the sample feed stream into the column feed stream.

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