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SAMPLE SYSTEM FOR CHROMATOGRAPHIC ANALYZERS

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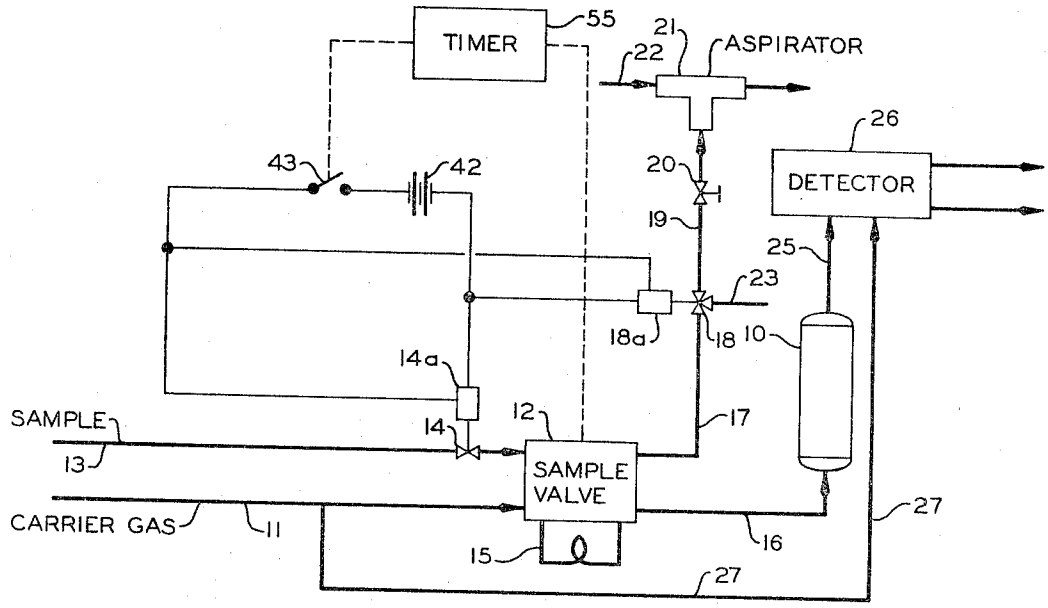


FIG. 1

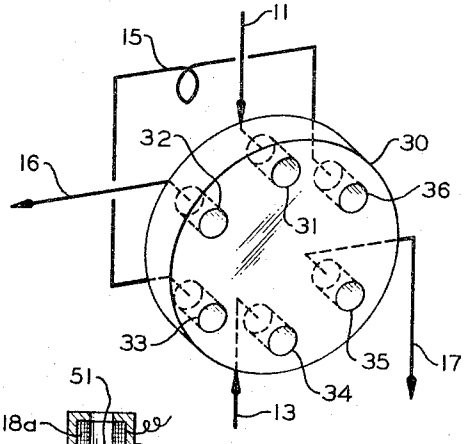


FIG. 2a

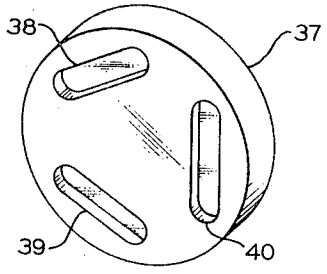


FIG. 2b

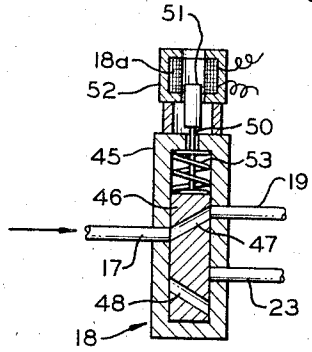


FIG. 3

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SAMPLE SYSTEM FOR CHROMATOGRAPHIC ANALYZERS

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ABSTRACT OF THE DISCLOSURE

Improved sample system to supply a constant volume, constant pressure sample from a vacuum source to chromatographic analyzers.

This invention relates to the distribution of fluids. In another aspect it relates to systems for introducing fluid samples and carrier gas into chromatographic columns.

In various analytical and industrial operations, there is a need for systems which are capable of controlling the flows of fluid streams in a preselected manner. One particular need for such a system occurs in chromatographic analyzers. It is common practice to analyze fluid mixtures by introducing a preselected volume of a sample of the mixture into the inlet of a column which contains material that selectively retards the passage of individual constituents of the mixture. A carrier gas is introduced into the column to displace the constituents of the sample toward the outlet. A detector is employed to measure changes in composition of the column effluent in order to provide information which is representative of the constituents of the fluid mixture. Various types of sample valves have been developed to control the introduction of preselected volumes of the sample into the column.

Most of these sample valves comprise a member having a plurality of ports, and means for connecting the ports selectively. A sample loop of predetermined volume is connected to the valve so as to be filled initially with the material to be analyzed. The carrier gas then displaces this volume of sample into the analyzer. A valve system of this type is capable of introducing a constant volume of sample into the analyzer at all times. However, it is essential that the sample be supplied to the loop at a constant pressure in order to insure that a constant amount of sample is introduced. This presents a problem, particularly when it is necessary to obtain samples at relatively high temperatures and from sources which vary in pressure. If the source pressure is not adequate to insure a positive flow, a vacuum device is usually employed to "pull" the sample.

In accordance with the present invention, a fluid distribution system is provided which is particularly useful in supplying samples to chromatographic analyzers. A vacuum source is connected downstream of the sample valve so as to pull fluid samples from the collection point through the sample loop of the valve. Immediately prior to the time that the valve is actuated to pass the carrier gas through the sample loop into the column, additional control valves are actuated in the sample conduit upstream and downstream from the valve. The upstream control valve is closed and the downstream control valve is opened to the atmosphere. This serves to equalize pressure within the control loop with atmospheric pressure so that a sample of constant volume and constant pressure is supplied to the column each time the valve is actuated.

Accordingly, it is an object of this invention to provide improved systems for controlling the distribution of fluids.

Another object is to provide novel valve systems for use with analytical instruments.

A further object is to provide chromatographic analyzers having improved sample systems incorporated therein.

Other objects, advantages and features of the invention should become apparent from the following detailed description which is taken in conjunction with the accompanying drawing in which:

FIGURE 1 is a schematic representation of a chromatographic analyzer having the sample introduction system of this invention incorporated therein.

FIGURES 2*a* and 2*b* illusrtate schematically a sample valve of a type which can be employed in the analyzer of FIGURE 1.

FIGURE 3 is a view, shown partially in section, of a solenoid actuated valve which can be employed in the system of FIGURE 1.

Referring now to the drawing in detail and to FIGURE 1 in particular, there is shown a column 10 which is filled with a material that selectively retards the passage of individual constituents of fluid mixtures to be analyzed. A carrier gas is passed through a conduit 11 to the first port of a sample valve 12. A conduit 13, which has a control valve 14 therein, communicates with a second port of valve 12. A conduit 15 communicates between two additional ports of the sample valve. Conduit 15 has an internal volume which is equal to the desired volume of sample to be introduced into column 10 for each analysis. A conduit 16 extends from sample valve 12 to the inlet of column 10. A conduit 17 extends from valve 12 to a valve 18. When valve 18 is in a first position, conduit 17 is connected to a conduit 19, which has an adjustable valve 20 therein. The downstream end of conduit 19 is connected to an aspirator 21 or other vacuum producing means. Air or other fluid is introduced into the aspirator through a conduit 22 to provide the pressure reduction. When valve 18 is in a second position, conduit 17 is connected to a vent conduit 23 which is in communication with the atmosphere.

The effluent from column 10 is passed by a conduit 25 to the first inlet of a detector 26. A second portion of the carrier gas is directed to a second inlet of detector 26 by means of a conduit 27. Detector 26 can advantageously comprise two temperature sensitive resistance elements which are positioned in the respective flows of the fluids carried by conduits 25 and 27. These elements are connected in a suitable network to compare the thermal conductivities of the two fluid streams. This provides an indication of changes in composition of the column effluent as the individual constituents of the fluid sample are eluted by the carrier gas. However, it should be evident that other types of detectors well known in the art can be employed for this purpose.

A suitable sample valve for use in the system of FIGURE 1 is illustrated schematically in FIGURES 2*a* and 2*b*. A first member 30 is provided with six ports 31, 32, 33, 34, 35 and 36. Inlet conduits 11 and 13 communicate with respective ports 31 and 34. Outlet conduits 16 and 17 communicate with respective ports 32 and 35. Sample loop 15 communicates between ports 33 and 36. A second element 37 is provided with three elongated slots 38, 39 and 40 in the face thereof. The face of element 37 which contains these slots is normally positioned against the face of element 30 so that the slots can connect selected pairs of ports of element 30.

At the beginning of the analysis cycle, member 37 is positioned with respect to member 30 so that port 31 is in communication with port 32, port 33 is in communication with port 34, and port 35 is in communication with port 36. Carrier gas from conduit 11 thus flows through the sample valve and conduit 16 to column 10. This purges the column of any sample which may remain from a previous analysis. At the same time, the fluid sample flows from conduit 13 through sample loop 15 into conduit 17

and is vented through conduit 19 and the aspirator, valve 14 being open and valve 18 being in its first position at this time. At the beginning of the actual analysis cycle, sample valve 12 is switched by rotating member 37 relative to member 30 so that port 31 communicates with port 36, port 34 communicates with port 35, and port 32 communicates with port 33. It can be seen that the sample which previously occupied loop 15 is displaced into column 10 by the flow of carrier gas through the sample loop.

In accordance with this invention, valves 14 and 18 are actuated immediately prior to the time that the sample valve is switched to the second mentioned position. Valves 14 and 18 can advantageously be solenoid operated to permit this simultaneous switching. To this end, the respective solenoids 14*a* and 18*a* of the two valves are connected to a current source 42 by a switch 43. Closure of switch 43 thus energizes the solenoids. When solenoid 14*a* is energized, valve 14 is closed. This blocks communication between the sample source and valve 12. When solenoid 18*a* is energized, valve 18 is actuated so that conduits 17 and 23 are in communication. The sample trapped in loop 15 thus is adjusted in pressure to atmospheric because conduit 17 is in communication with the atmosphere. However, conduit 17 should be sufficiently long to prevent any flow of atmospheric air back into the sample loop in the event that the sample initially is supplied at a pressure lower than atmospheric. As previously mentioned, a vacuum source is needed whenever the sample source pressure is not adequate to insure a positive flow through the sample loop. Source pressures of less than about 5 p.s.i. generally require the vacuum source to which this invention is applicable.

A suitable valve for use as element 18 is illustrated schematically in FIGURE 3. This valve comprises a housing 45 which has a movable plug 46 therein. Plug 46 is provided with two passages 47 and 48. Conduits 17, 19 and 23 communicate with the valve as illustrated. A rod 50 connects plug 46 to a member 51 of magnetic material which is positioned in a housing 52 that supports solenoid 18*a*. A spring 53 within housing 45 normally retains plug 46 in the position illustrated wherein conduits 17 and 19 are in communication through passage 47. When solenoid 18*a* is energized, plug 46 is lifted so that passage 48 connects conduit 17 and 23. However, it should be evident that this particular valve is merely illustrative of a suitable three-way valve which can be employed for this purpose.

Sample valve 12 and switch 43 can be operated manually or they can be operated automatically by means of a timer 55. A suitable timer 55 which can be employed to actuate sample valve 12 is described in detail in U.S. Patent No. 3,069,849. The sample valve illustrated in FIGURES 2*a* and 2*b* is merely illustrative of one type of sample valve which can be employed for this purpose. In addition to this rotary type valve, other types of sample valves which can be employed are described in U.S. Patents 3,085,440, 3,095,746, 3,111,849, 3,139,755 and 3,140,615, for example. Valve 20 is provided in conduit 19 for the purpose of permitting the rate of flow of sample through the system to be adjusted. In the event that a diaphragm sample valve of the type disclosed in U.S. Patent 3,140,615 is employed, for example, an additional conduit can be connected between the aspirator and the sample valve to pull a vacuum on the diaphragm to tend to keep the valve in the first position.

While this invention has been described in conjunction with presently preferred embodiments, it should be evident that it is not limited thereto.

What is claimed is:

1. A fluid distribution system comprising a sample loop, an aspirator, a three-way valve selectively connectable to said aspirator or the atmosphere, a chromatographic column, a source of sample, a source of carrier gas, a sample valve having two positions, said sample valve upon movement to its first position connecting the sample source through said sample loop and three-way valve to said aspirator, means operable at a predetermined time after such movement to disconnect the sample source from the sample valve and connect the three-way valve to the atmosphere, said sample valve thereafter moving to its second position to pass carrier gas into said loop and displace the trapped sample into said chromatographic column.

2. The fluid distribution system of claim 1 further comprising means to simultaneously disconnect the said sample source from the said sample valve and connect the said three-way valve to the atmosphere.

3. The fluid distribution system of claim 1 further comprising means to simultaneously disconnect the said sample source from the said sample valve and connect the said three-way valve to the atmosphere and shortly thereafter to move said sample valve from its first position to its second position.

4. The fluid distribution system of claim 1 wherein said means to disconnect the sample source from the sample valve and the said three-way valve means are solenoid operated, said system further comprising a means to actuate the said solenoids simultaneously.

5. The fluid distribution system of claim 1 further comprising a valve between said three-way valve and aspirator to permit adjustment of the rate of flow of fluid to the said aspirator.

6. The fluid distribution system of claim 1 further comprising a conduit of sufficient volume between said sample valve and said three-way valve to prevent the flow of atmospheric air into the sample loop.

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