United States Patent [19]

Penton

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[54] **SAMPLE INTRODUCTION SYSTEM FOR A FLUID CHROMATOGRAPH**

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[73] Assignee: **Varian Associates,** Palo Alto, Calif.

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[52] **U.S. Cl.** .....**73/422 GC,** 23/253, 23/259

[51] **Int. Cl.** **G01n 1/22**

[58] **Field of Search** .....73/23, 23.1, 61.1 R, 73/61.1 C, 421 R, 421.5 R, 422 GC; 23/253, 253 PC, 259, 292

[56] **References Cited**

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3,063,286 11/1962 Nerheim .....73/422 GC X

3,421,857 1/1969 Reichle et al.....73/422 GC UX

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Assistant Examiner—Daniel M. Yasich
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[57] **ABSTRACT**

A gas chromatograph system wherein a sample filled capsule is inserted into the system through an airtight lock. The sample capsule is punctured by a puncture tube in fluid communication with the carrier stream. The carrier stream passes through the tube and flushes the sample material from the capsule into the chromatographic column for separation and analysis.

3 Claims, 4 Drawing Figures

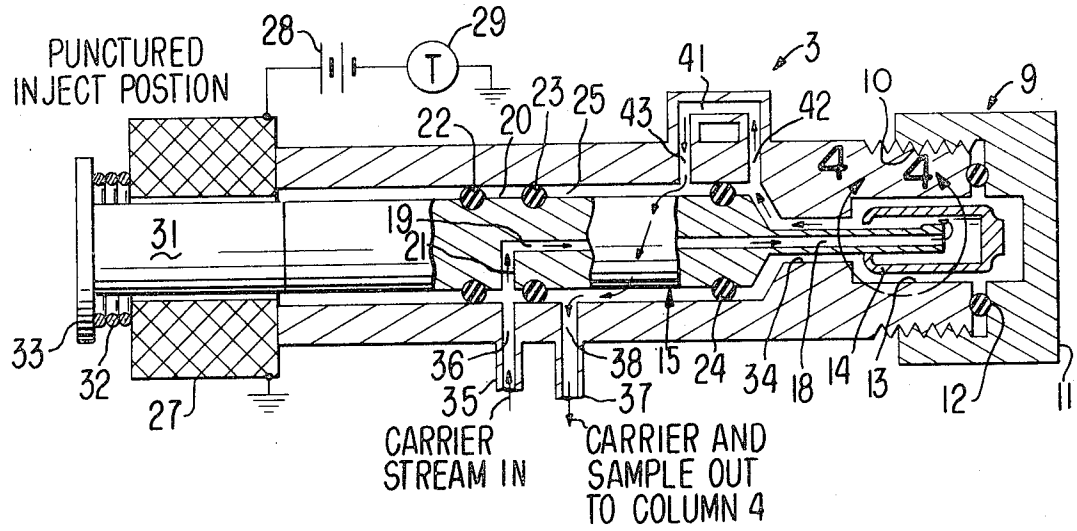
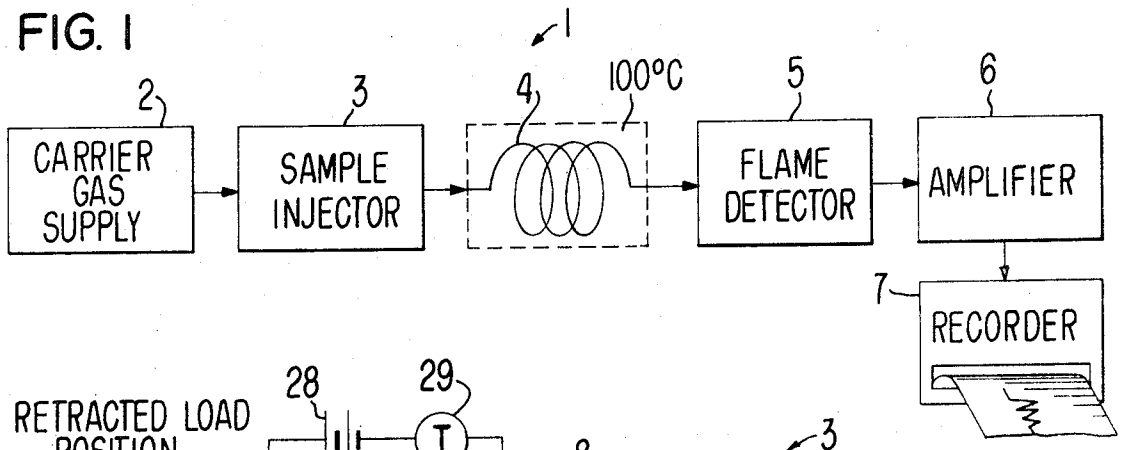


FIG. 1



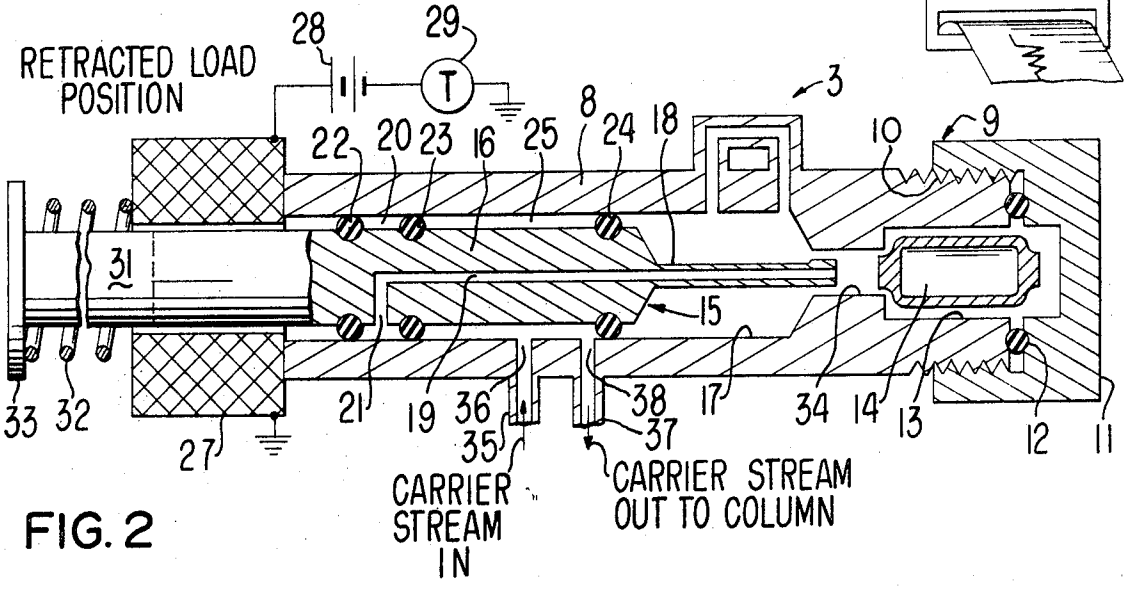


FIG. 2

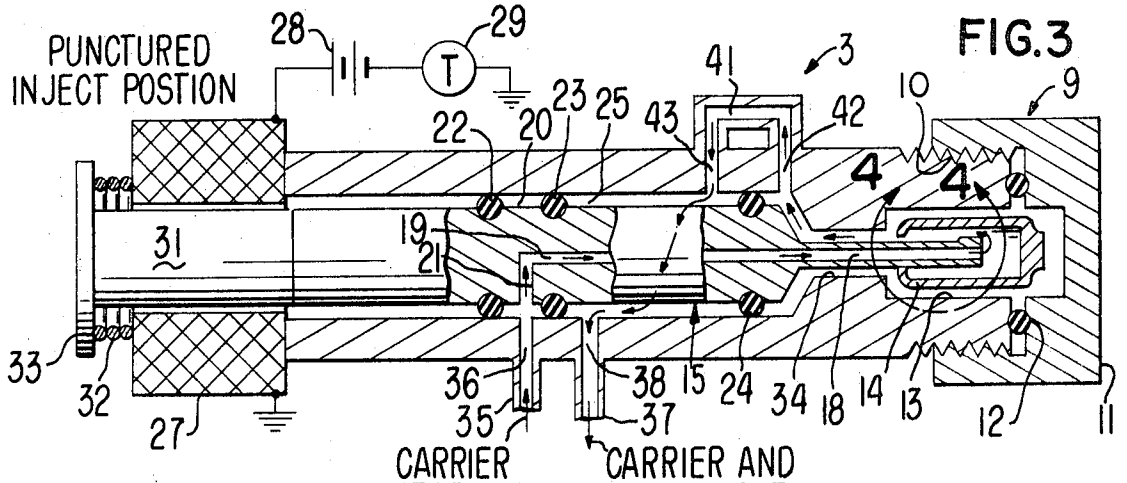


FIG. 3

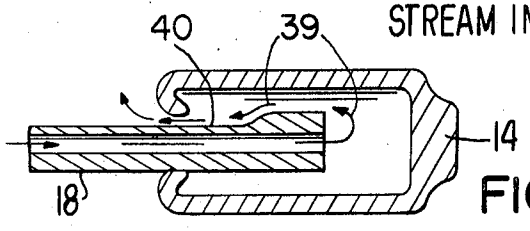


FIG. 4

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SAMPLE INTRODUCTION SYSTEM FOR A FLUID CHROMATOGRAPH

DESCRIPTION OF THE PRIOR ART

Heretofore, encapsulated samples to be introduced into a chromatographic column have been introduced via an air lock into a heated melt zone through which passes the chromatographic carrier stream. In the melt zone, the capsule containing the sample is melted thereby releasing the sample into the carrier stream to be carried through the chromatographic column for separation and analysis. Such a sample introduction system is disclosed in U.S. Pat. No. 3,119,252 issued Jan. 28, 1964. One of the problems with this prior art system is that the encapsulating material preferably has a low melting point as of 150° Centigrade, such as that obtained by indium metal, and as a result the encapsulating material contains impurities which are released along with the sample material by the melting process. In certain applications of chromatographs it is desirable to avoid introduction of foreign materials such as those trapped in the metal of the capsule since such trapped materials show up as peaks in the detected output chromatogram. For example, when analyzing breath samples for alcohol content it is desirable to avoid the presence of certain spurious output peaks in the chromatogram.

SUMMARY OF THE PRESENT INVENTION

The principal object of the present invention is provision of an improved sample introduction system for a fluid chromatograph.

One feature of the present invention is the provision of a sample introduction system wherein the sample capsule is inserted through an air lock and then the capsule is punctured to permit the sample material to be introduced from the capsule into the carrier stream for passage through the chromatographic column, whereby materials trapped in the encapsulating material are not released into the carrier stream.

Another feature of the present invention is the same as the preceding feature wherein the sample capsule is punctured by a puncture tube connected in fluid communication with the carrier stream such that the carrier stream is directed through the puncture tube and into the sample capsule for flushing the sample material into the carrier stream.

Another feature of the present invention is the same as any one or more of the preceding features including the provision of a slide valve for valving the carrier stream through the sample capsule to the chromatographic column when the capsule is punctured and for valving the carrier stream through a bypass which bypasses the capsule when the sample is not being introduced into the carrier stream.

Other features and advantages of the present invention will become apparent upon a perusal of the following specification taken in connection with the accompanying drawing wherein:

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a schematic block diagram of a chromatograph for analysis of injected samples,

FIG. 2 is a longitudinal sectional view, partially foreshortened, and partially schematic, depicting a sample introduction system of the present invention,

FIG. 3 is a view similar to that of FIG. 2 depicting the introduction system in the sample inject position, and

FIG. 4 is an enlarged detail view of a portion of the structure of FIG. 3 delineated by line 4—4.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

Referring now to FIG. 1 there is shown a gas chromatograph 1 incorporating features of the present invention. Briefly, the gas chromatograph includes a carrier gas supply 2 for supplying a suitable carrier gas such as a mixture of 40 percent hydrogen and 60 percent nitrogen at a pressure as of 5 p.s.i.g. to a sample injector 3. The sample injector will be described in greater detail with regard to FIGS. 2–4 but briefly includes means for rupturing an encapsulated sample to release the sample gas into the carrier stream to be carried to a gas chromatographic column 4 for separation of the constituents of the sample into time displaced peak concentrations in the eluted carrier gas stream emerging from the column. The eluted gas stream is passed to a flame ionization detector 5 which detects the sample peaks and converts the sample peaks into corresponding electrical signals. The electrical signals are fed to an amplifier 6 wherein they are amplified and thence fed to a recorder 7 for recording as a function of time to obtain an output chromatogram. The chromatogram yields qualitative and quantitative information concerning the sample constituents.

In a typical example of gas chromatograph 1 as employed for the analysis of breath samples for the presence of alcohol, the carrier gas supply 2 delivers approximately 35 milliliters per minute of carrier gas to the sample injector 3. Breath samples of approximately one-fourth milliliters volume are captured in an indium sample capsule as of 1 inch long and 0.14 inches inside diameter and 0.200 inches outside diameter sealed at its ends via cold weld joints formed by crimping the capsule. Samples encapsulated in this manner are disclosed in U.S. Pat. No. 3,103,277 issued Sept. 10, 1963. The breath sample is injected into the carrier gas stream, as more fully disclosed below, and fed through a 12 inch long gas chromatographic column 4 packed with 100/120 mesh size porous polymer material marketed under the name Porapak Q available from Waters Associates Inc. of Framingham, Massachusetts, and maintained at 100° C. This packing material has the advantage that it is particularly suitable for separating ethanol (breath alcohol) from other constituents in the breath without encountering "bleed" that usually contaminates detectors and changes analysis time with age. The temperature of the column 4 is preferably accurately controlled to within ± 0.5° C. and the pressure of the gas applied to the column is preferably maintained constant to within ± 0.2 p.s.i.g. to yield retention time changes less than 1 second and response changes on the order of 2 percent.

Referring now to FIGS. 2 and 3, the sample injector 3 is shown in greater detail. The sample injector 3 includes a hollow cylindrical injector housing structure 8 as of stainless steel having an air lock 9 formed at one end. The air lock 9 includes a cylindrical internally threaded cap 11 for threadably mating with the external threads 10 on one end of the housing 8. An O-ring 12 seals the cap 11 to the end of the housing 8 to provide an airtight seal therebetween. A sample chamber

13 is formed in the end of the housing 8 for containing a sample capsule 14. Sample capsule 14 comprises a short length of malleable metallic tubing, as of indium, which contains the sample material, as of alveolar breath, such capsule being crimped at its ends to form cold weld seals at both ends of the capsule 14. Capsule 14 is inserted by removing the cap, inserting the capsule into chamber 13 and then replacing the cap 11.

The central portion of the injector housing 8 houses a slide valve structure 15. The slide valve structure 15 includes a cylindrical slide 16, as of stainless steel, axially slideable within a cylindrical bore 17 in the housing 8. A puncture tube 18, as of stainless steel, is affixed to one end of the slide 16. The slide includes an axially directed bore 19 disposed in fluid communication with the puncture tube 18. A port 21 in the slide 16 interconnects the annular space defined between a pair of sealing rings 22 and 23 and the bore 19. The sealing rings 22 and 23 are carried upon the slide 16 and provide a slideable gas tight seal with the interior surface of the bore 17. A third sealing ring 24 is carried on the slide 16 between sealing ring 23 and the puncture tube 18 to define an annular gas passageway 25 in the space between the slide 16 and the interior surface of the bore 17 between the sealings 23 and 24.

An electrical solenoid 27 is disposed at the other end of the injector housing 8. The solenoid 27 is energized with current from a source 28 which is controlled by a timing switch 29. A magnetic portion 31 of the slide 16 is acted upon by the magnetic field produced by the solenoid 27 to produce axial translation of slide 16. A compression spring 32 is coupled between the solenoid 27 and an outer retaining ring 33 affixed to the slide 16 for spring biasing the slide 16 to the retracted load position as shown in FIG. 2. A constricted passageway 34 interconnects the valve bore 17 with the sample chamber 13 to permit the passage of the puncture tube 18 therethrough.

A carrier stream input conduit 35 communicates with the valve bore 17 via input port 36 and a carrier stream output conduit 37 communicates with valve bore 17 via output port 38. In the retracted load position for the slide 16, the carrier stream bypasses the sample chamber 13 via annular passageway 25, as indicated by arrows 39.

Referring now to FIG. 3, the slide 16 is shown in the punctured sample inject position. To inject the sample, the timing switch 29 is actuated to energize the solenoid 27 for driving slide 16 to the right such that the puncture tube 18 passes through passageway 34 and is driven through the end wall of the capsule 14 into the interior thereof. In this position, the slide port 21 is brought into registration with the carrier stream input port 36 such that the carrier stream flows into slide port 21 and through axial passageway 19 into the capsule 14. The puncture tube 18 includes a peripherally relieved portion 40 near the end thereof (see FIG. 4) such that the carrier stream flowing into the capsule 14 can exit from the capsule 14 via the space between the relieved portion of the tube 40 and the marginal lip of the puncture hole. The carrier stream thus picks up the sample in the capsule 14 and passes the sample via the passageway 34 to the bore 17. A bypass conduit 41 is connected to the bore 17 via output port 42 and input port 43 for bypassing the sealing ring 24 and causes the carrier stream to flow into the annular passage 25 which communicates with output port 38 and output conduit 37 for flowing the carrier and sample to the column 4. When the sample material has been purged from the sample capsule 14, the timing switch 29 deactivates the solenoid 27 such that the compression spring 32 can return the slide 16 to the retracted position as shown in FIG. 2 to permit removal of the sample capsule 14 and reloading of the injector 3.

The advantage of the puncture type sample injector of the present invention, as compared to the prior art capsule melting injector is that it permits the sample introduction system to be operated at substantially reduced temperature as compared to the temperature of the prior art melting process, and in addition the puncture method avoids introducing impurities occluded within the low melting point capsule material, typically indium.

Since many changes could be made in the above construction and many apparently widely different embodiments of this invention could be made without departing from the scope thereof, it is intended that all matter contained in the above description or shown in the accompanying drawings shall be interpreted as illustrative and not in a limiting sense.

What is claimed is:

1. In a sample introduction system for a fluid chromatograph, means forming a carrier fluid conduit for transmitting a carrier fluid stream to a fluid chromatographic column, means forming an airtight lock for housing a capsule filled with a sample material to be introduced into the carrier stream and to be carried therein through the chromatographic column, THE IMPROVEMENT COMPRISING, slidable puncture tube means for rupturing the sample filled capsule within said lock means to permit the sample material to be introduced from the capsule into the carrier stream for passage through the chromatographic column, said slidable puncture tube includes a peripherally relieved portion spaced from the end which penetrates the capsule to provide a blow-by passageway between the puncture tube and the inside lip of the puncture opening in the capsule through which the carrier stream may flow between the punctured capsule and said slidable puncture tube for passage to said chromatographic column.

2. The apparatus of claim 3 wherein said slide valve structure includes a housing having a bore therein to slidably receive said slide member, said bore communicating with said lock means containing said sample capsule via a passageway through which said puncture tube is driven into said capsule, said housing having a plurality of ports communicating through the side wall thereof with said bore, said slide member having an axially directed passageway therein communicating with the fluid passageway in said puncture tube, means forming a port in said slide member communicating through the wall thereof with the axially directed passageway therein, and means forming a plurality of sealing rings carried upon said slide in axially spaced relation therealong, said sealing rings being positioned relative to the position of said ports such that in the retracted position of said puncture tube the carrier stream is directed through a first housing port and out a second housing port along a path which bypasses said

capsule, and such that in the punctured capsule position the carrier stream is directed along a path which includes said first housing port, said slide port, said puncture tube, said capsule, third and fourth housing ports to said second housing port and thence to the chromatographic column for flushing the sample from said capsule through the chromatographic column.

3. In a sample introduction system for a fluid chromatograph, means forming a carrier fluid conduit for transmitting a carrier fluid stream to a fluid chromatographic column, means forming an airtight lock for housing a capsule filled with a sample material to be introduced into the carrier stream and to be carried therein through the chromatographic column, THE IMPROVEMENT COMPRISING, means for rupturing the sample filled capsule within said lock means to permit the sample material to be introduced from the capsule into the carrier stream for passage through the chromatographic column, said means for rupturing the sample filled capsule includes a puncture tube defining a fluid passageway communicating with the carrier stream, means for driving said puncture tube through the wall of the capsule to place the interior of the capsule in fluid communication with the carrier stream, and means forming a slide valve structure having a slide member affixed to said puncture tube for valving the carrier gas stream through the sample capsule to the column when said puncture tube is driven into the capsule and for valving the carrier stream through a bypass which bypasses the capsule when the puncture tube is in a retracted position.

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