March 12, 1968 R. A. SANFORD ET AL 3,372,573

CHROMATOGRAPHIC ANALYSIS METHOD AND APPARATUS THEREFOR Filed Feb. 24, 1954

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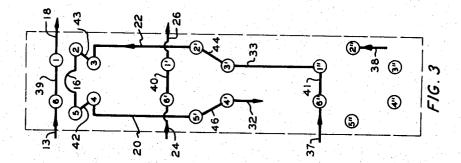
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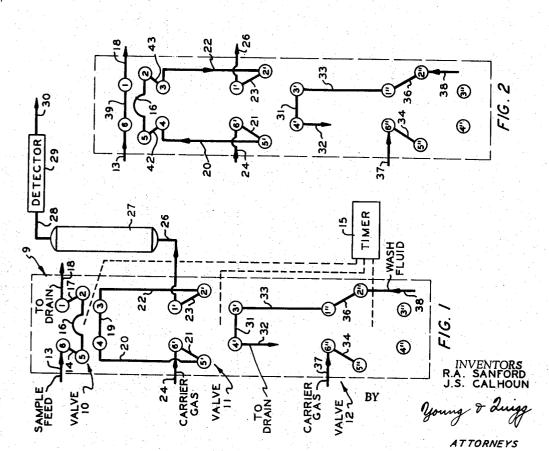
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United States Patent Office

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3,372,573 Patented Mar. 12, 1968

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3,372,573 CHROMATOGRAPHIC ANALYSIS METHOD AND APPARATUS THEREFOR

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6 Claims. (Cl. 73-23.1)

ABSTRACT OF THE DISCLOSURE

A valving system having three control units which, for example, operate sequentially to entrap a sample of a liquid containing non-volatile materials in a sample loop; flush vaporized components of the liquid sample from the sample loop; flush solvent through the sample loop to extract non-volatile components therefrom; and pass drying gas through the sample loop to thereby yield a dry sample loop containing no clogging deposits therein. 20

This invention relates to an improved chromatographic method of analysis and apparatus therefor. In another aspect, this invention relates to a chromatographic method of analysis and apparatus therefor wherein the sample²⁵ feed to the chromatographic analyzer contains a nonvolatile constituent.

A conventional method for the determination of the concentration of constituents in a fluid involves the use of 30 a chromatographic analyzer. In chromatography, a sample of the material to be analyzed is introduced into a column containing a selective sorbent or partitioning material. A carrier gas is directed into the column so as to force the sample material therethrough. The selective 35 sorbent, or partitioning material, attempts to hold the constituents of the material. This results in the several constituents of the fluid mixture flowing through the column at different rates of speed, depending upon their affinities for the packing material. The column effluent thus con-40sists initially of the carrier gas alone, the individual constituents of the fluid mixture appearing later at spaced time intervals. A conventional method of detecting the presence and concentration of these constituents is to employ a thermal conductivity detector which compares the 45 thermal conductivity of the column effluent gas with the thermal conductivity of the carrier gas directed to the column.

A conventional vaporous chromatographic analyzer cannot be employed for liquid samples containing soluble nonvolative constituents. These nonvolatile constituents upon vaporization of the liquid sample will become deposited in the sample valve and the lines of the chromatographic analyzer. This results in valve stoppage and plugged lines, substantially changing the operation of the chromatographic column. 55

Accordingly, an object of our invention is to provide an improved chromatographic method of analysis and apparatus therefor.

Another object of our invention is to provide a chromatographic method of analysis and apparatus therefor wherein a liquid to be analyzed contains a nonvolatile soluble constituent.

Another object of our invention is to provide an improved method and apparatus for obtaining a vaporous sample for introduction into a chromatographic column from a liquid containing a soluble nonvolatile constituent.

Other objects, advantages and features of our invention will be readily apparent to those skilled in the art from the following description, the drawing and appended claims.

By our invention, we have provided a chromatographic

method of analysis and apparatus therefor wherein a liquid containing a soluble nonvolatile constituent is passed to a sample zone; a carrier gas is passed to said sampling zone and from said sampling zone to a chromatographic column; a wash liquid is passed through said sampling zone; and a drying gas is passed through said sampling zone.

FIGURES 1, 2, 3 and 4 illustrate schematically one embodiment of the invention.

Referring to the drawing, therein is illustrated a chromatographic column 27, a detector 29, conduits 26, 28 and 30, and a sample zone 9 containing valves 10, 11 and 12, said valves positioned during the four stages of the inventive analysis procedure as illustrated in FIGURES 1, 2, 3 and 4, respectively.

Referring to FIGURE 1, values 10, 11 and 12 can be conventional multi-port values containing multiple interconnecting passages such as described in U.S. Patent 3,-095,746. As illustrated, value 10 contains a sample loop 16 and ports 1, 2, 3, 4, 5 and 6. Value 11 contains ports 1', 2', 3', 4', 5' and 6' and value 12 contains ports 1'', 2'', 3'', 4'', 5'' and 6''. It can readily be seen by referring to FIGURES 1, 2, 3 and 4 that it is within the scope of this invention to employ in place of value 12 a value having less than 6 ports with interconnecting passages.

Valves 10, 11 and 12 can be operated by a timer 15. This timer can be any type of apparatus known in the art for providing control signals in a desired sequence and positioning valves 10, 11 and 12 in the positions illustrated by FIGURES 1, 2, 3 and 4. The common type of timer utilizes a series of cam operated switches wherein the associated cams are rotated by a timing motor.

In the first stage as illustrated by FIGURE 1, a sample liquid feed containing a soluble nonvolatile constituent is passed via conduit means 13 to valve 10 and through conduit 14 within valve 10 to sample loop 16. With a continuous sample feed to valve 10, the sample passes from sample loop 16 through valve 10 via conduit 17 and from valve 10 via conduit means 18.

An inert carrier gas such as helium is passed via conduit means 24 to valve 11, through valve 11 via conduit 21, and from valve 11 to valve 10 via conduit means 20. The carrier gas is passed through valve 10 via conduit 19 and from valve 10 to valve 11 via conduit means 22. As illustrated, the carrier gas is passed through valve 11 via conduit 23 and from valve 11 to column 27 via conduit means 26. The carrier gas is withdrawn from column 27 via conduit means 28, passed through detector 29, and withdrawn from detector 29 via conduit means 30.

Column 27 is filled with a packing material which selectively retards the passage therethrough of constituents of a fluid sample mixture to be analyzed. Detector 29 can be a thermal conductivity detector which includes a temperature-sensitive resistant element placed in the path of fluid flow. A reference element, not shown, can be placed in the carrier gas flow. This detector provides signals representative of the difference in thermal conductivity between the column effluent and the carrier gas. The temperature differences between the resistance elements can be measured by electrical bridge circuits, such as a Wheatstone bridge, for example. It is, of course, within the skill of the art to employ other means of detecting the concentration of constituents in a sample fluid than the thermal conductivity detector herein described.

A wash solvent is passed via conduit means 38 to valve 12 and through valve 12 via conduit 36. The wash solvent must be a liquid capable of removing the nonvolatile constituents contained in the sample liquid passed to valve 10. The wash solvent is passed from valve 12 to valve 11 via conduit means 33, through valve 11 via conduit 31 and withdrawn from valve 11 via conduit means 32.

After completion of the first stage and upon positioning valves 10, 11 and 12 for the second stage as illustrated in FIGURE 2, the sample liquid containing a soluble nonvolatile constituent is passed via conduit means 13 to valve 10, through valve 10 via conduit 39 and 5 withdrawn from valve 10 via conduit means 18. The carrier gas is passed as previously described via conduit means 24 to valve means 11, through valve means 11 via conduit 21, and from valve 11 to valve 10 via conduit means 20. During the second stage, the carrier gas is 10 directed through valve 10 via conduit means 42. The sample liquid within sample loop 16 is vaporized by the carrier gas and is passed from valve 10 to valve 11 in the carrier gas via conduit means 43 and 22. The nonvolatile constituent or constituents remain in sample loop 16. 15 The carrier sample containing the volatilized sample is passed through valve 11 via conduit means 23 and from valve 11 via conduit means 26. The carrier gas containing the volatilized sample is passed into column 27. An effluent is withdrawn from column 27 via conduit means 28, 20 passed to detector means 29 wherein the concentration of sample constituents is determined and withdrawn from detector 29 via conduit means 30.

In the second stage, a wash solvent is passed via conduit means 38 to valve 12, through valve 12 via conduit 25 means 36, and from valve 12 to valve 11 via conduit means 33. The wash solvent is passed through valve 11 via conduit 31 and withdrawn from valve 11 via conduit means 32.

In the third stage and after completion of the second 30 stage operation, illustrated in FIGURE 3, the sample liquid is passed via conduit means 13 to valve 10, through valve 10 via conduit 39 and withdrawn from valve 10 via conduit means 18. The carrier gas is passed through a conduit means 24 to valve 11, through valve 11 via conduit 40, and from valve 11 to column 27 via conduit means 26. The carrier gas is passed through column 27 and through detector 29 via conduit means 28 and 30.

In the third stage, the carrier gas is passed via conduit means 37 to port 6" of valve 12 and through valve 12 via conduit 41 to port 1". The wash solvent contained in conduit means 33 is passed by means of the carrier gas through valve 11 via conduit 44 and from valve 11 to valve 10 via conduit means 22. The wash solvent is passed through conduit 43 and sample loop 16 of value 4510, thereby removing any nonvolatile constituents contained within conduits 22, 43 and sample loop 16. The wash solvent employed must be capable of dissolving the nonvolatile constituents contained in the sample liquid feed. The wash solvent is withdrawn from valve 10 via conduit 42 and conduit means 20, and passed through valve 11 via conduit 46 and conduit means 32. After removal of the wash solvent from the chromatographic system is complete, the passage of carrier gas via conduit means 37, through valve 12 via conduit 41, and from 55 valve 12 to valve 11 and 10 in the previously described manner for the third stage, operates to dry the valve and interconnecting conduits so as to remove any traces of wash solvent therefrom. The carrier or drying gas is passed to valve 12 via conduit means 37 and can be the 60 same or different than the carrier gas passed via conduit means 24 to valve means 11.

In the fourth stage, the sample liquid is passed via conduit means 13 to valve 10 and to sample loop 16 contained within valve 10 via conduit 14. The sample 65 liquid is withdrawn from valve 10 via conduit 17 and conduit means 18. A drying gas is passed via conduit means 37 to valve 12, through valve 12 via conduit 41, and from valve 12 to valve 11 via conduit means 33. The drying gas is passed through valve 11 via conduit 44 and from valve 11 to valve 10 via conduit means 22. The drying gas is passed through valve 10 via conduit 19, from valve 11 to valve 11 via conduit means 32. The sampling zone or system is thus washed free of any non-75

volatile constituents contained therein and thoroughly dried prior to the passage of a second measured sample to chromatographic column 27. During the fourth stage, the carrier gas is passed as previously described via conduit means 24 to valve 11, through valve 11 via conduit

40 and from valve 11 to column 27 via conduit means 26. Although not to be limited thereto, the invention has been found to be particularly applicable to the analysis of ethyl alcohol in water wherein the water also contains nonvolatile sugars and other organic constituents. When applied to the analysis of ethyl alcohol and water, a preferred cycle time of four minutes has been found to be particularly effective to complete the sampling, analysis, washing and drying steps. Valves, 10, 11 and 12 were maintained in the first stage for about 2 percent of the cycle time, in the second stage for about 18 percent of the cycle time, and in the fourth stage for the remainder of the cycle time.

As will be evident to those skilled in the art, various modifications of this invention can be made, or followed, in the light of the foregoing disclosure, without departing from the spirit or scope thereof.

We claim:

1. A chromatographic valving apparatus comprising a first, second and third valve means, each of said first, second and third valve means containing multiple ports and interconnecting passages, said first valve means containing a sampling means, first conduit means communicating with said first valve means for passing sample fluid thereto, second conduit means communicating with said first valve means for withdrawing sample fluid therefrom, third conduit means communicating between said second valve means and said first valve means, fourth conduit means communicating between said first valve means and said second valve means, fifth conduit means communicating with said second valve means for passing a first carrier gas stream thereto, sixth conduit means communicating with said second valve means for passing sample fluid 40 and carrier gas therefrom, seventh conduit means communicating with said second valve means for withdrawing carrier gas and wash fluid therefrom, eighth conduit means communicating between said second valve means and said third valve means, ninth conduit means communicating with said third value means for passing a second carrier gas stream thereto, tenth conduit means communicating with said third valve means for passing a wash fluid thereto, each of said valve means having a first and second valve positions, with each of said first, second and 50

- third valve means in said first valve position, (1) passage means communicating between said first conduit means and said sampling means,
 - (2) passage means communicating between said sam-
 - pling means and said second conduit means, (3) passage means communicating between said fifth
 - conduit means and said third conduit means, (4) passage means communicating between said third
 - and fourth conduit means, (5) passage means communicating between said fourth
 - and sixth conduit means,
 - (6) passage means communicating between said seventh and eighth conduit means,
 - (7) passage means communicating between said eighth and tenth conduit means,

with said first, second and third valve means in said second valve position,

- (1) passage means communicating between said first conduit means and said second conduit means,
- (2) passage means communicating between said third conduit means and said sampling means,
- (3) passage means communicating between said fourth conduit means and said sampling means,
- (4) passage means communicating between said fifth and sixth conduit means,

- (5) passage means communicating between said third and seventh conduit means,
- (6) passage means communicating between said fourth and eighth conduit means, and
- (7) passage means communicating between said ninth 5 and eighth conduit means.

2. The apparatus of claim 1 to include means for sequentially positioning said first, second and third valve means in said first and second valve positions.

3. Apparatus comprising a chromatographic column 10 having an inlet end and an outlet end and containing a packing material that selectively retards the passage therethrough of a sample fluid directed to said column, means for measuring a property of an effluent withdrawn from said outlet of said chromatographic column repre- 15 sentative of the composition thereof, a first, second and third valve means, each of said first, second and third valve means containing multiple ports and interconnecting passages, said first valve means containing a sampling means, first conduit means communicating with said 20 first valve means for passing sample fluid thereto, second conduit means communicating with said first valve means for withdrawing sample fluid therefrom, third conduit means communicating between said second valve means and said first valve means, fourth conduit means com- 25 municating between said first valve means and said second valve means, fifth conduit means communicating with said second valve means for passing a first carrier gas stream thereto, sixth conduit means communicating between said inlet of said chromatographic column and 30 said second valve means for passing sample fluid and carrier gas therethrough, seventh conduit means communicating with said second valve means for withdrawing carrier gas and wash fluid therefrom, eighth conduit means communicating between said second valve means and said 35 third valve means, ninth conduit means communicating with said third valve means for passing a second carrier gas stream thereto, tenth conduit means communicating with said third valve means for passing a wash fluid thereto, each of said valve means having a first and second valve position, with each of said first, second and third valve means in said first valve position.

- (1) passage means communicating between said first
- conduit means and said sampling means,
- (2) passage means communicating between said sam- 45 pling means and said second conduit means,
- (3) passage means communicating between said fifth conduit means and said third conduit means,
- (4) passage means communicating between said third and fourth conduit means, 50
- (5) passage means communicating between said fourth and sixth conduit means,
- (6) passage means communicating between said seventh and eighth conduit means,
- (7) passage means communicating between said eighth 55 RICHARD C. QUEISSER, Primary Examiner. and tenth conduit means,

with said first, second and third valve means in said second valve position.

- (1) passage means communicating between said first conduit means and said second conduit means,
- (2) passage means communicating between said third conduit means and said sampling means,
- (3) passage means communicating betwene said fourth conduit means and said sampling means,
- (4) passage means communicating between said fifth and sixth conduit means,
- (5) passage means communicating between said third and seventh conduit means,
- (6) passage means communicating between said fourth and eighth conduit means, and
- (7) passage means communicating between said ninth and eighth conduit means.

4. The apparatus of claim 3 further comprising means for sequentially positioning said first, second, and third valve means in said first and second valve positions.

- 5. A method of analyzing a liquid containing at least one soluble non-volatile constituent comprising:
 - (a) passing said liquid through a sample trapping zone:
 - (b) trapping a portion of said liquid within said sample trapping zone;
 - (c) passing a carrier gas through said sample trapping zone to thereby vaporize volatile constituents of said liquid trapped in said zone thereby leaving a residue of said non-volatile constituents therein;
 - (d) passing said vaporized constituents to a chromatographic analysis zone;
 - (e) isolating said residue in said sample trapping zone while continuing the passage of said vaporized constituents to said chromatographic analysis zone by said carrier gas; and
- (f) passing a wash solvent through said sample trapping zone to remove said residue therefrom.

6. The method of claim 5 further comprising passing a drying gas through said sample trapping zone after said 40 solvent is passed therethrough.

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