Sept. 24, 1963 H. J. NOEBELS ET AL 3,104,541

GAS CHROMATOGRAPH WITH IMPROVED ZERO SHIFT

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FIG. 1.

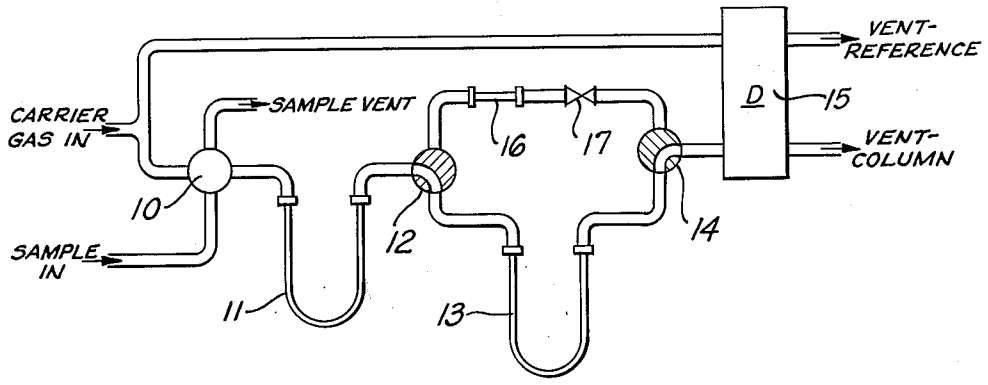


FIG. 2.

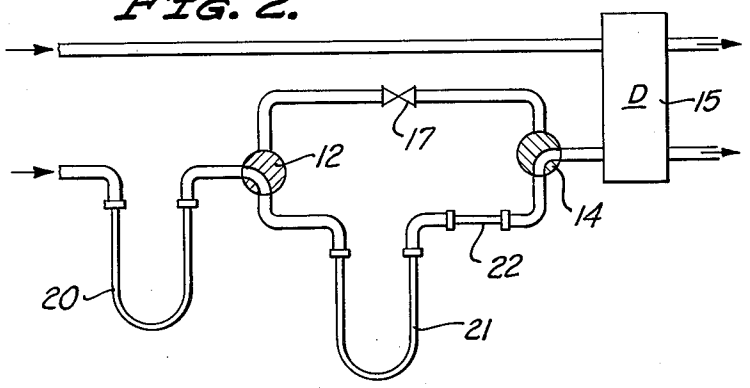
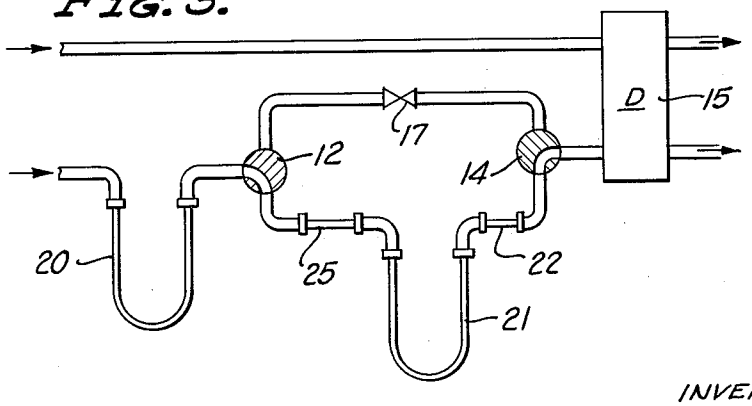


FIG. 3.



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GAS CHROMATOGRAPH WITH IMPROVED ZERO SHIFT

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This invention relates to multiple column gas chromatographs and, in particular, to improvements in such instruments which substantially eliminate zero shift at the detector. The invention is described herein in conjunction with a dual column chromatograph but is equally applicable to chromatographs with three, four or more columns.

A dual column chromatograph may be used with a sample having constituents with widely differing boiling points. The two columns of the instrument will have different characteristics, one being selected to provide resolution of the higher boiling point fractions and the other to provide resolution of the lower boiling point fractions of the sample. The instrument will have two possible gas flow paths and will be switched from one to the other at a particular time during the sample analysis. For example, the instrument is initially set to direct the carrier gas stream through the first column, then through the second column and then to the detector. At a particular time following injection of the sample, the flow path is changed to direct the carrier gas stream through the first column and then to the detector, bypassing the second column. The low boiling point fractions of the sample will pass through the first column very rapidly with little resolution while the higher boiling point fractions will be adequately separated. The low boiling point fractions will be adequately resolved in the second column but the higher boiling point fractions would take an exorbitantly long period of time to pass through the second column. Therefore, the instrument is operated with the two columns in series initially so that the low boiling point fractions will pass through the first column into the second column and be resolved. After the desired resolution has been obtained, the instrument is switched to the second flow path so that the higher boiling point fractions will bypass the second column and go directly to the detector.

This arrangement provides the desired sample analysis in a minimum operating time and is extensively used at the present time. However, the flow path switching technique introduces a problem of zero shift with non-specific types of detectors such as thermal conductivity devices, gas density devices, and interferometers, which are sensitive to and affected by variations in the partial pressure of constituents in the carrier gas. The output of the detector is different with each flow path for the zero or pure carrier gas condition, resulting in a zero shift when the flow paths are interchanged and introducing an error in the indicated output. Accordingly, it is an object of the present invention to provide an improved dual column chromatograph in which zero shift due to flow path switching is eliminated.

It is an object of the invention to provide a dual column chromatograph including means inserted in one of the flow paths between the first column and the detector for equalizing the partial pressure changes in the carrier gas which occur in each flow path. A further object is to provide such an instrument having means defining a first gas flow path from the source through the first column, the second column and the detector, and a second flow path from the source through the first column, a restrictor that is the equivalent of the second column in

impedance, and the detector, and including means inserted in the second flow path between the first column and the detector for changing the partial pressure of constituents in the carrier gas in the same manner as the partial pressure is changed by the second column as the gas passes therethrough. A further object is to provide such an instrument wherein the partitioning agent of the second column is picked up by the carrier gas passing therethrough and including a gas equilibrator unit inserted in the second flow path, with the unit containing a quantity of the partitioning agent of the second column for equilibrating the partial pressure of the partitioning agent in the carrier gas as it passes therethrough to the partial pressure of the partitioning agent in the eluent of the record column.

It is an object of the invention to provide a dual column gas chromatograph wherein each of the columns contains material that will change the partial pressure of the carrier gas passing therethrough and including means inserted in the flow path downstream from the second column that will change the partial pressure in the same manner as the first column. A further object is to provide such an instrument wherein the second column is of the type which will strip partitioning agent of the first column from the carrier gas as it passes through the second column, and including means inserted in the flow path downstream from the second column for introducing additional first column partitioning agent into the carrier gas stream. A further object of the invention is to provide such an instrument including a partitioning agent filter positioned upstream of the second column for blocking transmission of first column partitioning agent into the second column.

The invention also comprises novel details of construction and novel combinations and arrangements of parts, 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 representation of a dual column gas chromatograph incorporating the invention of the present application;

FIG. 2 is a view similar to FIG. 1 of an alternative form; and

FIG. 3 is a view similar to FIG. 1 of another alternative form.

In the dual column gas chromatograph of FIG. 1, the carrier gas flows from the gas source through a sample injection valve **10**, a first chromatographic column **11**, a valve **12**, a second chromatographic column **13**, another valve **14**, and the column side of a detector **15**. The valves **12**, **14** provide an alternate or second flow path through an equilibrator, such as a saturator unit **16**, and through a restrictor **17**. The carrier gas also flows directly from the source through the reference side of the detector **15**. The restrictor **17** is designed to have the same gas flow impedance as the second column **13** so that the pressures and rate of flow will be the same for both flow paths.

First, consider the operation of the instrument with the saturator unit **16** omitted. In a typical instrument, the first column will contain polyglycol as a partitioning agent for resolving water, acetonitrile and hydrocarbons, and the second column will contain bis (2(2-methoxyethoxy)ethyl) ether as a partitioning agent for resolving propane, propylene and butane. In the first portion of the analysis cycle, the carrier gas will be directed through the first and second columns. After the sample is injected at the injection valve **10**, the lower boiling point

fractions will pass through the first column relatively rapidly and will be resolved in the second column, while the higher boiling point fractions will be resolved in the first column. After the desired measurements have been made on the eluent of the second column, the valves **12**, **14** are switched to direct the carrier gas stream from the first column through the restrictor **17** to the detector so that the higher boiling point fractions will bypass the second column.

Passage of the carrier gas through the second column will result in a change in the partial pressure in the gas so that the carrier gas following the first flow path will have a partial pressure different from that of the carrier gas following the second flow path, resulting in a different zero value at the detector. In order to compensate for this error, it has been necessary to determine the magnitude of this zero shift and correct the indicated output therefor. The present invention provides an instrument which substantially eliminates the zero shift and, hence, no compensation is required. The saturator unit **16** is placed in the second flow path for producing the same effect on the carrier gas as is produced by the second column **13**. In the particular embodiment shown herein, the carrier gas picks up partitioning agent as it passes through the second column and ordinarily becomes saturated therewith resulting in a change in partial pressure in the carrier gas, which directly affects the thermal conductivity of the gas and, hence, the indicated output of the detector. The saturator unit **16** contains a quantity of the partitioning agent of the second column and is designed to saturate the carrier gas therewith as it passes therethrough. Typically, the saturator could be a short length of chromatographic column but, of course, any suitable device for flowing a gas past a liquid may be utilized. The effect of the saturator unit on the resolution of the instrument will be negligible because it is small relative to the chromatographic columns. For example, the column **13** may be six feet in length while the saturator unit may be three inches in length. However, this length of saturator will be adequate to produce the same change in partial pressure as is produced by the column **13**. Hence, the partial pressure in the gas and, therefore, its thermal conductivity will be the same regardless of whether the carrier gas follows the first flow path or the second flow path. Under these circumstances, the detector does not undergo any change when the flow paths are changed and the zero shift is eliminated.

There may be instances in which the carrier gas picks up some partitioning agent but does not become saturated, e.g., where the column is relatively short. Then the unit **16** would be operated as an equilibrator to add substantially the same quantity of partitioning agent to the carrier gas so as to have the desired equal charge in partial pressure in both paths.

The particular location of the unit **16** in the second flow path is not critical. In FIG. 1, the unit **16** is shown between the valve **12** and the restrictor **17**, but could equally well be placed downstream of the restrictor **17**, or between the first column and the valve **12**.

An alternative form of the invention is shown in FIG. 2, this form being particularly adapted for use in instruments where the second column does not add any material to the carrier gas but does remove material from the carrier gas. For example, a first column **20** may use paraffin oil as a partitioning agent for separating ethane, propane and butane. A second column **21** may be in the form of a molecular sieve for separating oxygen, nitrogen and carbon monoxide. As the carrier gas passes through the first column, it will pick up partitioning agent producing a partial pressure in the carrier. However, the second column will remove this partitioning agent from the carrier gas as it flows therethrough so that the eluent from the second column will have a different partial pressure than the eluent from the first column. Therefore, the partial pressure of the carrier gas as it follows the first and second flow paths will be different, producing the undesired zero shift at the detector. In this embodiment of the invention, a gas saturator unit **22** is positioned in the first flow path between the second column and the detector. This saturator unit contains a quantity of the partitioning agent of the first column so that the eluent from the second column will have the partitioning agent replaced therein with the resultant increase in partial pressure to match that in the carrier gas following the second flow path. The unit **22** functions as a partial pressure equalizer to restore the carrier gas to the condition it was in as it entered the second column (i.e., to the condition it was in as it left the first column).

The partitioning agent that is picked up by the carrier gas in the first column and which is stripped out by the second column sometimes tends to saturate the second column and render it useless. FIG. 3 shows an alternative form of the apparatus of FIG. 2 including a filter unit **25** inserted in the flow path ahead of the second column **21**. The filter unit is selected to remove the partitioning agent of the first column from the carrier gas as it passes therethrough before arriving at the second column. Typically, the filter may be a short length of column filled with activated charcoal that will absorb the partitioning agent. The instrument of FIG. 3 will protect the second column from becoming saturated with partitioning agent from the first column and will also eliminate the zero shift problem in the same manner as the instrument of FIG. 2.

Various embodiments for equalizing the partial pressure in the carrier gas in different flow paths of gas chromatographs 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 dual column gas chromatograph, the combination of: a source of carrier gas; a first chromatographic column; a second chromatographic column containing a material that will change the partial pressure in a gas passing therethrough; a partial pressure sensitive detector; a flow restrictor having a gas flow impedance substantially equal to the gas flow impedance of said second column; means for selectively coupling said source, said first column, said second column and said detector to form a first gas flow path, or said source, said first column, said restrictor and said detector to form a second gas flow path; and means inserted in said second flow path between said first column and said detector, said means containing a quantity of said material whereby the partial pressure in the carrier gas passing therethrough is changed in the same manner as its partial pressure is changed by said second column.

2. In a dual column gas chromatograph, the combination of: a source of carrier gas; a first chromatographic column; a second chromatographic column containing a partitioning agent which is picked up by the carrier gas passing therethrough; a partial pressure sensitive detector; a flow restrictor having a gas flow impedance substantially equal to the gas flow impedance of said second column; means for selectively coupling said source, said first column, said second column and said detector to form a first gas flow path or said source, said first column, said restrictor and said detector to form a second gas flow path; and a gas equilibration unit inserted in said second flow path between said first column and said detector, said unit containing a quantity of the partitioning agent of said second column for picking up by the carrier gas passing therethrough to provide substantially equal partial pressures of partitioning agent in the carrier gas following said first and second flow paths respectively.

3. An apparatus as defined in claim 2 in which said equilibration unit is a gas saturator which saturates the

carrier gas passing therethrough with the partitioning agent.

4. In a dual column gas chromatograph, the combination of: a source of carrier gas; a first chromatographic column; a second chromatographic column containing a material that will change the partial pressure in a gas passing therethrough; a partial pressure sensitive detector; a flow restrictor having a gas flow impedance substantially equal to the gas flow impedance of said second column; means for selectively coupling said source, said first column, said second column and said detector to form a first gas flow path, or said source, said first column, said restrictor and said detector to form a second gas flow path; and means inserted in said first flow path between said second column and said detector, said means containing a quantity of said material whereby the partial pressure in the carrier gas passing therethrough is changed in the opposite manner as the partial pressure is changed by said second column.

5. In a dual column gas chromatograph, the combination of: a source of carrier gas; a first chromatographic column containing a partitioning agent which is picked up by the carrier gas passing therethrough; a second chromatographic column containing a material that will strip said partitioning agent from the carrier gas passing therethrough; a partial pressure sensitive detector; a flow restrictor having a gas flow impedance substantialiy equal to the gas flow impedance of said second column; means for selectively coupling said source, said first column, said second column and said detector to form a first gas flow path, or said source, said first column, said restrictor and said detector to form a second gas flow path; and a gas equilibration unit inserted in said first flow path between said second column and said detector, said unit containing a quantity of the partitioning agent of said first column for equilibrating the partial pressure of partitioning agent in the carrier gas passing therethrough to that of the eluent of said first column.

6. In a dual column gas chromatograph, the combination of: a source of carrier gas; a first chromatographic column containing a partitioning agent which is picked up by the carrier gas passing therethrough; a second chromatographic column containing a material that will strip said partitioning agent from the carrier gas passing therethrough; a partial pressure sensitive detector; a flow restrictor having a gas flow impedance substantially equal to the gas flow impedance of said second column; a partitioning agent filter for removing partitioning agent from gas passing therethrough; means for selectively coupling said source, said first column, said filter, said second column and said detector to form a first gas flow path, or said source, said first column, said restrictor and said detector to form a second gas flow path; and a gas equilibration unit inserted in said first flow path between said second column and said detector, said unit containing a quantity of the partitioning agent of said first column for equilibrating the partial pressure of partitioning agent in the carrier gas passing therethrough to that of the eluent of said first column.

7. In a dual column gas chromatograph, the combination of: a source of carrier gas; a first chromatographic column; a second chromatographic column containing a material that will be picked up by and saturate carrier gas passing through the column; a partial pressure sensitive detector; a flow restrictor having a gas flow impedance substantially equal to the gas flow impedance of said second column; means for selectively coupling said source, said first column, said second column and said detector to form a first gas flow path, or said source, said first column, said restrictor and said detector to form a second gas flow path; and means containing said material and inserted in said second flow path between said first column and said detector for saturating carrier gas in said second path with said material and at substantially the same line pressure that the carrier gas is saturated at in said first path, whereby the effluent of each path contains said material at substantially the same partial pressure.

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