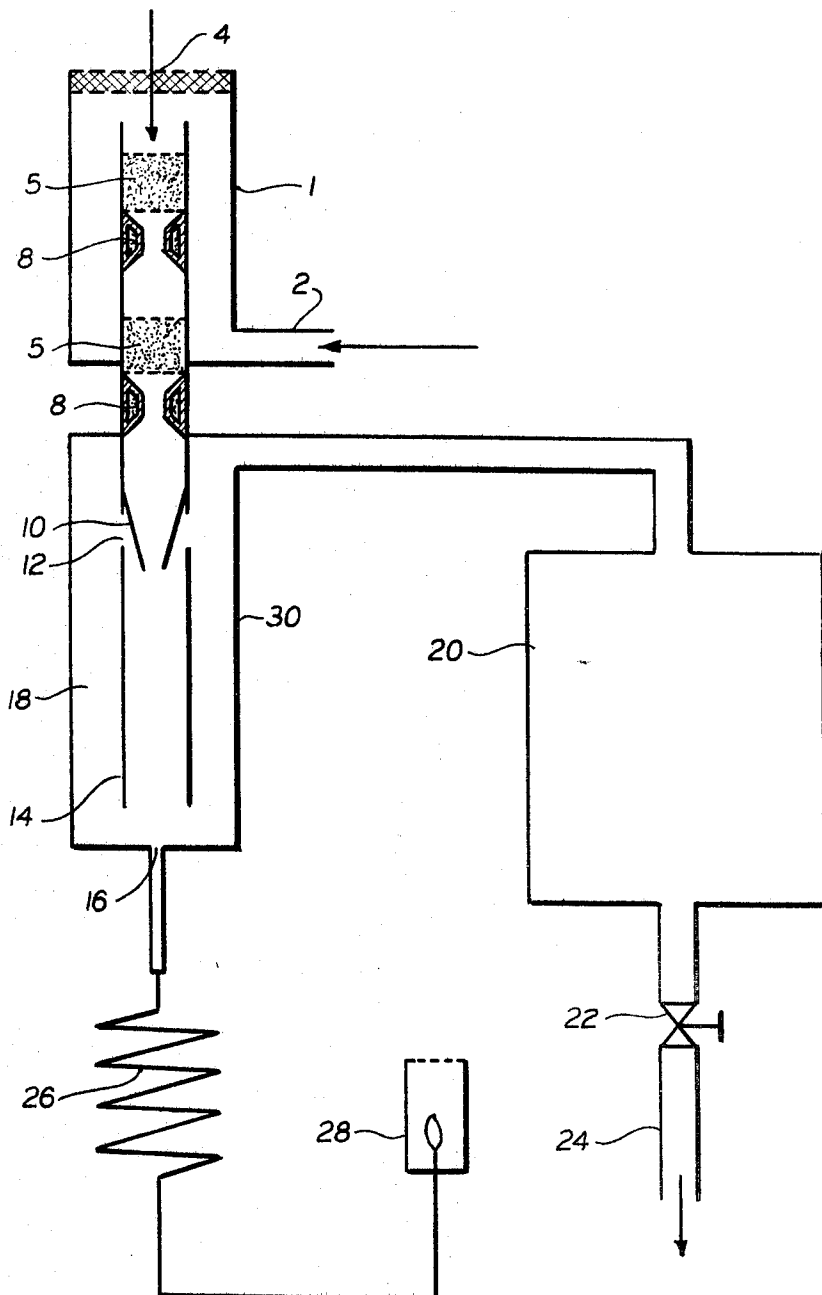


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GAS DIVIDER SYSTEM

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ABSTRACT OF THE DISCLOSURE

Divider system for gas streams, particularly for gas chromatograph feed, including a conventional gas stream divider or splitter and a second, compensating gas stream divider or splitter downstream from the first splitter.

In devices for analyzing gases, it is often necessary or desirable to utilize a very small stream for analysis purposes. Thus, it is often necessary or expedient to split a larger gas stream to be analyzed into smaller and larger volume components and to subject the smaller volume component to analysis while possibly venting or discarding the larger volume component.

For example, in the case of continuously operating analyzers, a high rate of flow must be used in the sampling lines in order to keep the analyzer dead time low, but this flow does not correspond to the amount of gas needed by the analyzer itself. Therefore, a by-pass (splitter) is placed upstream of the gas analyzer which taps from the main gas flow in the sampling line as much partial gas flow as is needed to provide the analyzer with the quantity which it requires.

There are many chromatographic separating columns having a relatively low loading capacity, and thus, very frequently, sample dividers or splitters are needed in gas chromatographs. The separating ability of these columns greatly diminishes as the quantity of the sample that is injected thereinto exceeds a certain very small amount. Examples of this type of separating column are the so-called capillary columns.

The usual sample injectors, however, require a certain minimum sample volume and ratio to carrier gas in order to provide for satisfaction and efficient sample injection and mixing. Therefore, only a small fraction of the sample quantity actually injected by the sample injecting means (e.g., injection syringe) may be permitted to get into the separating column and thus be analyzed.

In gas chromatography, the usual procedure is to inject a measured amount of the sample into a carrier gas current and mix it in the gaseous state, with the carrier gas. The sample may be liquid and transformed, if necessary, to the gaseous state. The dividing of the sample carrier mixture is then performed by dividing the composite gas current in a sample divider, which contains a flow dividing means. One part of the divided composite current is fed to the separating column, and the other (called the by-pass branch) is led away through an adjustable throttle and may be vented. This throttle makes it possible for the ratio of the two partial currents to be precisely adjusted.

If the ratio of the partial currents is adjusted before the injection of the sample, in such a manner, for example, that the partial current flowing through the separating column is in a ratio on the order of 1:99 to that which is tapped off ahead of the separating column and vented, then, when a sample of, for example, 5 milligrams, is in-

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jected by means of the sample injecting device into the carrier gas, theoretically 0.05 milligram enters the separating column, and 4.95 milligrams are by-passed around the separating column through a by-pass line.

In a sample divider of this kind, the relative quantity ratios of the individual components of the sample in the partial currents must not differ from those in the undivided sample since the portion of the sample being analyzed must reflect the content of the entire sample. This requirement, however, can be met easily only in the case of samples in which the masses of the molecules of the individual components do not differ greatly from one another.

In gas chromatography, this requires, for example, that the samples available for measurement have a relatively narrow boiling range.

The reason for this is that each molecule of a gas current has the same average linear velocity. This means that molecules of different mass have a different kinetic energy. Since each division of the gas current practically always necessitates a change in the direction of movement of individual molecules, molecules of different mass are differently affected by this change of direction, and therefore the gas current division based upon their different individual kinetic energies. If, for example, one of the partial gas currents is carried off in a branch at an angle to the original direction of flow, the heavier molecules will not follow this change in direction as easily as the light molecules, and will enter preferentially into the line that runs in the same direction as the original flow, so that the concentration of the components having heavier molecules will increase in this line, and the concentration of lighter molecules will increase in the angularly deflected line. This effect, which is actually exploited in practice for division according to molecular mass (E. W. Becker, "Separation of Isotopes," page 360, George Newnes Ltd., London, 1961), is undesirable in the dividing of samples for the purpose discussed herein, when substances of widely differing molecule size are involved, as in the case, for example, of a broad boiling range mixture being analyzed by gas chromatography.

It is therefore an object of this invention to provide a novel device for providing a gas sample for analysis.

It is another object of this invention to provide a novel gas stream splitter.

Other and additional objects of this invention will become apparent from a consideration of this entire specification, including the drawing and claims hereof.

In accord with and fulfilling these objects, one aspect of this invention resides in a gas stream splitting apparatus comprising a feed line; a first gas stream splitter, at least two lines extending from said first splitter, at least one of which extends in a different direction than said feed line; and a second gas stream splitter in said line of different direction, which second splitter has at least two lines extending therefrom, one of which extends in a different direction than the feed line to said second splitter and communicates with the feed line to said first splitter.

This invention eliminates the disparity of composition caused by a gas splitter, or at least compensates in such a manner that the initial feed to the splitter apparatus has the same composition as the partial gas stream being subjected to analysis.

In a sample dividing means for gas analyzers, especially gas chromatographs, having a flow divider (main splitter) for dividing the gas stream (main stream) fed into the sample dividing means into partial streams of different intensity, a second flow divider (compensation splitter) is provided between the main stream and one of the

partial streams which, by the variation of the composition of the partial currents which occurs in it, compensates for the corresponding variations occurring at the main splitter. In other words, between one of the partial streams and the main stream, a compensation splitter is introduced, which compensates the separation of the components of the samples which occurs at the main splitter due to differences in their molecular mass. This can be brought about, for example, by designing the compensation splitter in such a manner that it feeds back into the main stream preferentially those components which are present in its own partial stream in an excess above the original composition of the sample. The dimensions of the compensation splitter can be determined empirically.

It has proven to be desirable to insert the compensation splitter between the main stream and the larger partial stream of the main splitter. One advantageous system is to locate the compensation splitter at the point of discharge from a nozzle into the main stream. A suction effect then is caused by the nozzle, which positively draws a portion of the partial stream through the compensation splitter and feeds such back into the main stream.

It is important to the perfect operation of the invention that the composition of the sample gas be uniform over the entire flow cross section at the point where stream splitting occurs. If this requirement is not already satisfied—and this may be the case in gas chromatography, for example, if the injection of the sample into the carrier gas is performed just upstream of the main splitter—one or more mixing means, such as cross-sectional restrictions (mixing nozzles), can be provided in the line leading to the main or first splitter.

Thus, understanding of this invention will be facilitated by reference to the accompanying drawing, the single figure of which is a schematic diagram of one embodiment of this invention.

In the drawing, the invention is explained in its special application in a gas chromatograph. A mixing chamber 1 is provided having a carrier gas inlet line 2 and a sample injector 4. Where the mixing chamber 1 is not sufficient to intimately mix the carrier gas and the sample to provide a uniform gas phase mixture of the two, additional mixing and vaporizing systems 5 and 8 are provided. The vaporizing systems 5 may consist of metal chips packed in a tube. The mixing means 8 may be cross-sectional restrictions of this tube. Thus a homogeneous mixture of carrier gas and sample is fed through a nozzle 10 which discharges into a mantle tube 14. As the gas mixture flows out of the mantle 14, a small portion of it maintains its line of flow through a tap 16. The greater part of the gas mixture is deflected from its original direction of flow and flows through the annular space 18 formed by the mantle tube 14 and an outer wall 30, exiting into a holding vessel 20. From the holding vessel 20, the gas flows through a needle valve 22 to an outlet 24 from which it may be vented. The smaller portion of the gas stream passes without deflection through the tap 16 into a capillary column 26 and passes on into a flame ionization detector 28 or other analyzing means.

A compensation splitter according to one embodiment of this invention is formed by apertures 12. By the action of the nozzle 10, a portion of the gas flowing through the annular gap 18 is continually aspirated through the apertures 12, brought back into and mixed into the nozzle effluent upstream of the tap 16. Thus, the sample stream nozzle effluent is enriched with material from the by-pass stream.

By the appropriate geometrical dimensioning and positioning of the nozzle 10, apertures 12, mantle tube 14 and annular gap 18, the sample stream is enriched with lighter molecules from the by-pass stream in such a manner as to compensate for the heavier molecules preferentially passing through the tap 16, by reason of their

momentum as set forth above, and into the separating column. The optimum dimensions of the above-mentioned structural components can be determined by experiment with respect to any given system under consideration.

In determining the appropriate operating parameters of the system described for any given system by way of experimentation, the following general rules, which apply to the system without regard to the components of the gas being analyzed, should be observed. In the portion of the sample mixture that gets into the separating column, the percentage of low-boiling substances, i.e., those of lower molecular mass, or lighter molecules, increases if, while the other conditions of operation remain the same:

(1) *The diameter of the nozzle orifice is reduced.*—In that case, the efflux velocity at the end of the nozzle increases and, hence, so does the rate of flow of the gas aspirated through the apertures 12. The favoring of the heavier molecules in entering the capillary column, which is caused by the now greater velocity of flow in the mantle tube, and which is not desired in this case, is wholly or partially compensated by the simultaneous increase in the velocity of flow in the annular gap, depending on the dimensions of the mantle tube and annular gap. The drawing of gas into the main stream from the departing gas stream takes place perpendicularly to the direction of flow. Thus, if the velocity of flow increases, the lighter molecules are preferentially drawn into the main stream.

(2) *The inside diameter of the mantle tube is increased.*—In this case, the velocity of flow of the gases in the mantle tube decreases. The difference in kinetic energy between heavy and light molecules thus becomes slighter. Consequently, the amount of heavy substances reaching the capillary column simultaneously diminishes.

(3) *The inside diameter of the outer jacket is reduced, or the outside diameter of the mantle tube is increased, or, in other words, the cross-sectional area of the annular gap diminishes.*—This increases the velocity of flow in the annular gap. The consequences have been described under (1).

(4) *The lateral apertures on the mantle tube are enlarged.*—This causes larger quantities of the escaping gas mixture to be aspirated into the interior of the mantle tube. The consequences have been described under (1).

A sample splitter of the kind described above has the special peculiarity that the splitting of a gas stream can be performed homogeneously, i.e., without difference in the concentration of the components in the partial, split streams.

The advantages achievable by the invention consist in that very small amounts of a sample having a wide boiling range corresponding to great mass differences in the sample molecules, e.g., n-heptane and n-hexadecane, can be divided, without any difference in the relative quantity ratio of the individual components of the sample after division as compared with the relative quantity ratios in the original sample before division. In the arrangement described, this is possible in the case of:

Different split-ratios;
Different velocities of flow in the gas-chromatographical separating column;
Different temperatures in the splitter system.

This offers all of the advantages—especially great saving of time and great accuracy—of operating with calibration factors that need to be determined only once (Analytical Chemistry, vol. 33, pp. 973–982, July 1961; vol. 36, pp. 461–473, March 1964; Gas Chromatography, 1962, Academic Press, Inc., New York, pp. 287–306), even in the case of samples having a broad boiling range, particularly in the case of temperature-programmed gas chromatography.

The hold tank 20 assures, in the case of the gas chromatograph shown in the embodiment of the drawing, that

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the gas composition at throttle 22 does not vary while the mixture of carrier gas and sample is passing through the tap at 16. Otherwise, it might happen that a mixture of carrier gas and sample might still be present at the tap while the mixture of carrier gas and sample is already flowing through throttle 22. That is, a change in the density and viscosity of the gas at point 22 induces a change in the velocity of flow at point 16. But a change in the velocity of flow at point 16 must not occur at the time when the mixture of carrier gas and sample is passing point 16, because otherwise serious trouble would have to be expected. Consequently, the hold tank volume is made sufficiently great so that the mixture of sample and carrier gas is not simultaneously passing through the tap 16 and the throttling means 22.

This invention is applicable to gas analyzers other than gas chromatographs since it is directed to providing a sample to be analyzed, rather than directed toward the analysis itself.

EXAMPLES

The dimensions of the described system are eligible if the general rules mentioned above are fulfilled. Critical dimensions of the system as they may be used for example are described below.

The length of the nozzle 10 is 4.0 mm., with an inner diameter of 15 mm. at the upper end and with an inner diameter of 0.7 mm. at the lower end. The mantle tube 14 has an inner diameter of 2.5 mm. and an outer diameter of 4.0 mm. The diameter of apertures 12 is 0.9 mm. Six apertures are situated in equal distance around the mantle tube 14 in equal height with the lower end of nozzle 10. The distance of the apertures from the lower end of the mantle tube 14 is 22 mm. The distance of the lower end of mantle tube 14 from the upper end of tap 16 is 1.5 mm.

The outer wall 30 has an inner diameter of 6 mm. The volume of the holding vessel 20 has to be larger than the volume of the injected and evaporated sample and the carrier gas in which it is evaporized under the temperature and pressure conditions in the said holding vessel 20. In the system described here the holding vessel 20 was a cylindrical tube, 200 mm. in length and with an inner diameter of 65 mm.

Each of the vaporizing systems 6 are 5 mm. in length, with an inner diameter of 2 mm. The inner diameters of the mixing means 8 are 0.5 mm.

All the other dimensions of the system described are uncritical and may be chosen at ease.

In order to test the performance of the divider system, synthetic mixtures of known quantities of straight-chain paraffins C_7 to C_{16} (9 compounds, except C_8) were prepared from the individual components. The quantities were weighed-in to the nearest 0.02 percent. The purity of the components was better than 99 percent. Mixtures having various concentrations were prepared. All these

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mixtures were quantitatively analyzed with the help of gas chromatography as described in Analytical Chemistry, vol. 33, pp. 973-982, July 1961; vol. 36, pp. 461-473, March 1964, etc., using the gas divider system described above instead of the old splitting system described in the above said papers. In these experiments, the bypass ratio was varied from 1:200 up to 1:5100; the inlet pressure of the nitrogen carrier gas varied from 1 to 5 atmospheres; the temperature of the gas divider system was varied between 200 and 300° C. Each single analysis was repeated at least eight times. The deviation of the averages of single runs was in any case smaller than $\pm 1\%$ relative, compared to the known figures of the weighed-in sample.

What is claimed is:

1. Apparatus for providing a small portion of a gas phase material having the same composition proportions as the entire gas phase from which it is derived, comprising
 - (A) a chamber means,
 - (B) a feed line communicating with said chamber means,
 - (C) a gas exhaust line extending from said chamber,
 - (D) an inner tube means within said chamber spaced from all walls thereof,
 - (E) a sample line extending from said chamber axially aligned with said inner tube,
 - (F) means communicating said feed line and said inner tube means,
 - (G) means adjacent said means defined in paragraph F communicating said inner tube means with the chamber surrounding such, and
 - (H) chromatographic column means communicating with said sample line.
2. Apparatus as claimed in claim 1, including a holding tank connected to said gas exhaust line.
3. Apparatus as claimed in claim 2, including a throttle valve downstream of said holding tank.
4. Apparatus as claimed in claim 1 wherein said means communicating said feed line to said inner tube means is a nozzle, and wherein said nozzle and said means defined in paragraph G together form a jet pump.
5. Apparatus as claimed in claim 4, including gas mixing means upstream of said nozzle.
6. Apparatus as claimed in claim 5, wherein said mixing means comprises line constrictions and further includes means for vaporizing a material into a gas.

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