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A MASS SPECTROMETER WITH A GAS SWITCH THEREBETWEEN
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FIG. 1

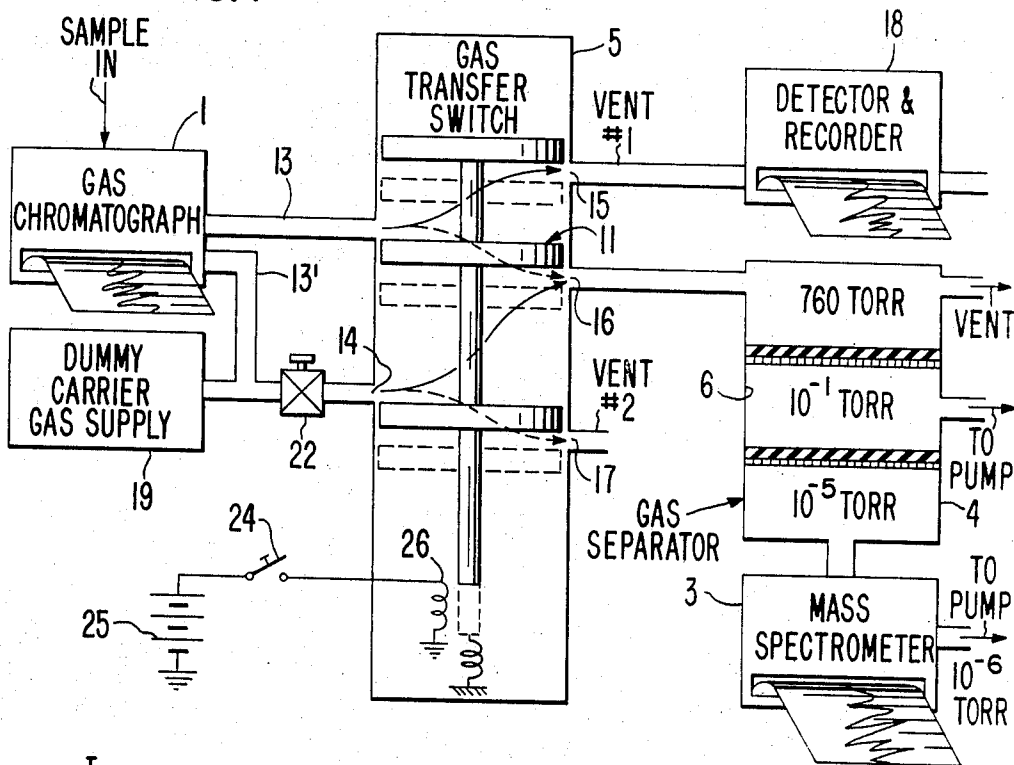


FIG. 2

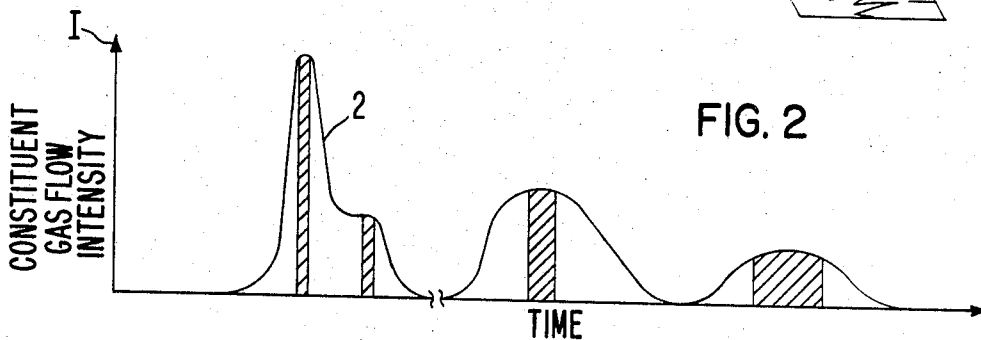
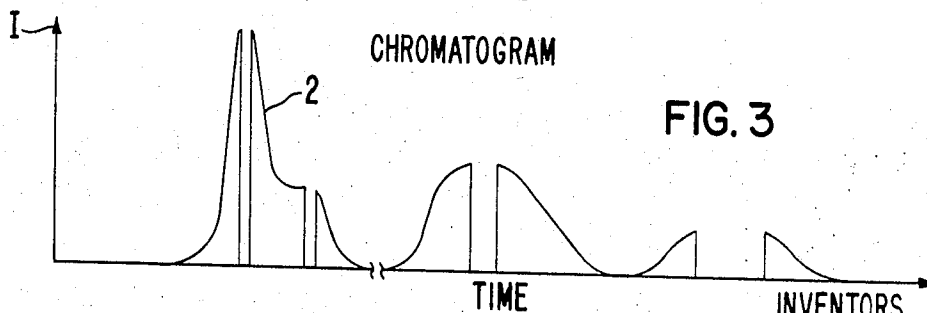


FIG. 3



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GAS ANALYZER SYSTEM EMPLOYING A GAS CHROMATOGRAPH AND A MASS SPECTROMETER WITH A GAS SWITCH THEREBETWEEN

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11 Claims

ABSTRACT OF THE DISCLOSURE

A gas analysis system is disclosed which employs a gas chromatograph and a mass spectrometer for identifying the peaks of the gas chromatograph. A gas transfer switch is disposed between the gas chromatograph and the mass spectrometer for switching only portions of the time sequenced gas peaks of the gas chromatograph into the mass spectrometer for identification by mass analysis. A dummy carrier gas stream is provided which is normally switched into the input of the mass spectrometer via a gas separator such that a normal carrier gas background is maintained in the mass spectrometer. The gas chromatograph peaks or portions of peaks which are switched into the mass spectrometer are carried in a carrier gas stream. The flow rate is controllable on the dummy carrier gas stream to a fraction of the flow rate from the gas chromatograph for time spreading the gas chromatograph peaks as fed to the mass spectrometer in order to obtain more accurate mass spectra. In a preferred embodiment, the gas separator is of a dual membrane type for substantially removing the carrier gas from the sample constituents before mass analysis. Also the preferred embodiment includes a detector and recorder in the vented gas chromatograph gas stream downstream of the gas switch for recording the gas peaks minus the sampled portions thereof.

DESCRIPTION OF THE PRIOR ART

Heretofore, gas analysis systems have employed a mass spectrometer for identifying the output peaks of a gas chromatograph. Such systems employed a gas flow constriction and a vacuum pump between the output of the gas chromatograph and the input of the mass spectrometer for reducing the gas pressure from atmospheric pressure at the output of the gas chromatograph, to 10^{-5} Torr, at the input to the mass spectrometer. A variable gas leak or vent into the input of the pump allowed control over the sample gas pressure applied to the input of the mass spectrometer. In this way a crude control over gas peaks passed to the spectrometer was obtained.

The problem with this prior art arrangement was that the crude control over the sample pressure to the mass spectrometer was reflected as pressure changes on the output of the gas chromatograph column. These pressure changes produced fluctuations in the resolution of the gas peaks obtained from the gas chromatograph.

In another prior art gas analysis system, the output gas peaks of a gas chromatograph were fed to an infrared spectrometer at atmospheric pressure and to a leak which leaked gas to a mass spectrometer. A first gas switch was connected in the output line between the gas chromatograph and the infrared spectrometer and mass spectrometer leak. Three additional gas switches were connected in the input system of gas lines to the gas chromatograph. In operation, the output peaks were sequentially and intermittently analyzed by closing the first gas switch and opening certain ones and closing other ones of the three input gas switches during analysis of the first peak.

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The gas switches stopped the flow through the gas chromatograph without adversely affecting resolution of the gas peaks. After analysis of the first peak, the gas switches were returned to their original position to re-start gas flow through the gas chromatograph to produce subsequent output gas peaks which were analyzed by intermittently stopping and starting the gas flow through the gas chromatograph in the manner as previously described for analysis of the first peak.

This arrangement of gas switches is relatively complex and to be avoided if possible. This system for gas analysis is described in a paper titled "Interrupted-elution Gas Chromatography Its Application, with Eluate Concentration, to the Automatic Production of Simultaneous Infrared and Mass Spectra," by R. P. Scott et al., paper 20, Sixth International Symposium on Gas Chromatography and Associated Techniques, Institute of Petroleum 1966, edited by A. B. Littlewood.

SUMMARY OF THE PRESENT INVENTION

The principal object of the present invention is the provision of an improved gas analysis system employing a gas chromatograph and a spectrometer.

One feature of the present invention is the provision, in a system for analysis of gases employing a gas chromatograph and a spectrometer, of a gas transfer switch connected between the output of the gas chromatograph and the input of the spectrometer for switching only selected portions of the output of the gas chromatograph to the spectrometer without producing excessive pressure fluctuations in the output pressure of the gas chromatograph.

Another feature of the present invention is the same as the preceding feature including a dummy carrier gas stream that is normally switched by the transfer switch into the input of the spectrometer and which provides a carrier gas stream for the selected portions of the output of the gas chromatograph which are switched into the spectrometer.

Another feature of the present invention is the same as the immediately preceding feature wherein the dummy carrier gas stream is derived from the output of the second column of a dual column gas chromatograph.

Another feature of the present invention is the same as any one or more of the preceding features including the provision of a gas separator connected between the gas transfer switch and the spectrometer for substantially eliminating the carrier gas and enriching the sample portion of the gas stream reaching the spectrometer.

Another feature of the present invention is the provision of a gas detector, such as a flame ionization detector, connected to the vented output of the gas chromatograph downstream of the gas switch for monitoring the gas peaks of the gas chromatograph minus the selected portions fed to the spectrometer.

Another feature of the present invention is the same as any one or more of the preceding features including the provision of a constriction or valve for controlling the flow rate of the dummy gas stream which carries the selected sample portion, such that by reducing the flow rate of the dummy stream to a fraction of the flow rate of the output of the gas chromatograph, the selected portions of the gas peaks can be spread out in time to facilitate analysis by the spectrometer.

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

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a schematic block diagram of a gas analysis system employing features of the present invention,

FIG. 2 is a chromatogram taken at the output of the gas chromatograph of FIG. 1, and

FIG. 3 is a chromatogram taken at a vent line downstream of the gas transfer switch in the system of FIG. 1.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

Referring now to FIG. 1, there is shown a gas analysis system employing features of the present invention. The gas analysis system includes a gas chromatograph 1 into which is introduced a sample to be analyzed. In the gas chromatograph 1 the sample is mixed with a carrier gas stream and passes through a gas chromatograph column. The column causes the various gaseous constituents of the sample to be separated in time within the carrier gas stream which emerges as the output of the gas chromatograph. Such constituents may be separated by as little as 5 seconds and as much as 5 minutes and the typical output contains numerous gas peaks of differing sizes in the carrier gas stream. These gas peaks are detected by a gas detector such as a flame ionization detector inside the gas chromatograph 1 and the detected output is recorded as a function of time to produce a chromatogram, as shown by line 2 in FIG. 2. The output gas stream of the gas chromatograph 1 is at atmospheric pressure. Typical carrier gases include the permanent gases such as He, H₂, N₂, Ar.

As seen from FIG. 2, the gas peaks of the chromatogram are separated in time and this is helpful in identifying the sample constituents. However, an extremely precise identification of the various constituent gases is obtained by feeding selected sample portions of the various gas peaks to a mass spectrometer.

Thus, a mass spectrometer 3 is connected to the output of the gas chromatograph 1 via a gas separator 4 and a gas transfer switch 5. The gas separator 4 is preferably of the dual stage membrane type as more fully described and claimed in copending U.S. patent application Ser. No. 555,613 filed June 6, 1966, now U.S. Patent 3,421,292 issued Jan. 14, 1969 as a continuation-in-part of U.S. patent application 511,576 filed Dec. 6, 1965, now U.S. Patent 3,455,092, issued July 15, 1969 and both assigned to the same assignee as the present invention.

Briefly, the gas separator 4 serves to eliminate the carrier gas from the gaseous constituents of the sample and, thus, to enrich the sample gases as fed to the mass spectrometer 3. The separator 4 comprises a conduit 6 with two membranes 7 and 8 as of 1 mil thick silicone rubber film formed on a porous substrate support plate, sealed across the conduit 6 in spaced relation. The sample constituents, such as hydrocarbons, are dissolved in the silicone rubber and diffuse through the membrane to the other side under an applied pressure differential. The permanent carrier gases are not appreciably dissolved in the membrane and, thus, are largely excluded. Differential flow rates of 1:1000 through each membrane 7 and 8 are obtainable for certain hydrocarbons and carrier gases.

The mass spectrometer 3 typically operates at a pressure on the order of 10^{-6} torr. The spectrometer 3 is evacuated to this pressure by a high vacuum pump, not shown, such as, for example, a 15 liter per second cold-cathode getterion multiple Penning cell pump. The sample and carrier gas flow from the switch 5 passes into the first stage of the gas separator 4 at atmospheric pressure. The gas stream is directed across the surface of the first stage membrane 7 and out a vent to the atmosphere. A vacuum pump, not shown, which is operable at a pressure of on the order of 10^{-3} torr evacuates the region between the two membranes 7 and 8. A pressure of 10^{-5} torr exists on the spectrometer side of the second membrane 8. An enrichment of sample material on the order of 10^5 to 10^6 is obtainable through the gas separator 4. By varying the pressure in the region between the gas separating membranes 7 and 8, between 80% and 2% of the sample material is passed through to the mass spectrometer 3.

This pressured controlled throughput feature is described and claimed in copending U.S. application Ser. No. 626,194 filed Mar. 27, 1967, now U.S. Patent 3,398,505, issued Aug. 27, 1968 and assigned to the same assignee as the present invention.

The gas transfer switch 5 comprises a shuttle valve member 11 axially movable between two positions in a housing 12 having a pair of input ports 13 and 14 and three output ports 15, 16 and 17. In a first position of the gas switch, indicated by solid lines, the output flow of the gas chromatograph enters the switch 5 at port 13 and is directed by the shuttle 11 to the first output port 15, which is vented to the atmosphere via a second flame ionization detector and recorder 18.

Thus, when the gas transfer switch 5 is in the first position, the output of the gas chromatograph is being vented to the atmosphere and being recorded in two places. A first recording is obtained internally of the gas chromatograph 1. A second recording is obtained downstream of the switch 5 such that it will record the affects of the switch 5.

Also, when the switch 5 is in the first position, the dummy carrier gas stream is being fed to the mass spectrometer 3. The dummy carrier gas stream provides a continuously flowing carrier gas stream through the separator 4 to the atmosphere. A throttle valve 22 is provided between the dummy carrier gas supply 19 and the switch 5 for regulating or controlling the dummy carrier gas flow rate. The throttle valve 22 may be set to flow the dummy carrier gas stream at a selected fraction of the flow rate of the output gas stream of the gas chromatograph for reasons which will be fully described below. Alternatively the throttle valve 22 may be set to flow the dummy stream at a higher flow rate than that of the chromatogram.

In the second position of the gas transfer switch 5, as indicated by dotted lines, the output gas stream from the gas chromatograph 1 is directed via shuttle 11 to output port 16 which leads to the gas separator 4 and mass spectrometer 3. Also, in the second position of the switch 5, the dummy gas stream is directed via shuttle 11 to output port 17 which is vented to the atmosphere.

The gas transfer switch 5 is solenoid operated via switch 24 connected between a current source 25 and a solenoid 26 which operates the shuttle 11. Typical operating times between the first and second positions of the switch 5 are on the order of 10 milliseconds.

In operation, a sample is introduced into the gas chromatograph 1. The switch 5 is in the first position and the operator observes the chromatogram or internal detector output of the gas chromatograph. When a peak appears in the output, which the operator wishes to identify by means of the mass spectrometer 3, he closes switch 24 and causes the gas transfer switch 5 to switch a selected portion of the gas peak to the mass spectrometer 3, as indicated by the cross hatched portion of FIG. 2. The mass spectrometer 3 may have a gas handling capacity of 10^{-4} torr-liter/sec. and would be flooded by large peaks if they were fed in their entirety to the mass spectrometer 3. Thus, the gas transfer switch 5 is operated in the second position only long enough to obtain a sufficient amount of the peak for mass identification. For a large peak, this sampling period may only be a second or two, whereas, for a small peak, as indicated by the cross hatched portions under the curve of line 2 the sampling period may include the complete peak. The second chromatogram recorder 18 will record the output chromatogram minus the sampled portion, as shown in FIG. 3. The recording at 18 is, therefore, very useful in matching the mass spectrometer outputs to the chromatograph peaks.

The gas switch 5 is very useful for sampling portions of relatively complex gas peaks as indicated by the first peak in FIGS. 2 and 3. More specifically, certain gas peaks are not well resolved and actually comprise more than one gaseous constituent. In FIGS. 2 and 3 the first

peak is such an example. The composite peak is formed by two peaks as indicated by the dotted lines. The composite peak is changing composition in periods of 2 to 10 seconds. If the entire peak were fed to the mass spectrometer, the mass spectrometer would identify two separate gases but would not correlate each the separate constituents with any particular portion of the composite peak. However, these portions of the composite peak can be separately identified by sampling the composite peak at points indicated by the cross hatching.

It turns out that for certain cycloidal type mass spectrometers 3 that they have optimum accuracy and linearity if the mass spectrum is run in about 20 seconds. However, the typical small output peaks from the gas chromatograph 1 have a time span of less than 20 seconds. The selected portion of the gas chromatograph output peak can be spread out, for example, from 2 seconds to the desired 20 seconds by adjusting the dummy carrier gas flow rate to only $\frac{1}{10}$ that of the gas chromatograph flow rate. This is easily accomplished by proper adjustment of the throttle valve 22. Thus, the operator actuates the gas transfer switch 5 for two seconds or so to inject a two second portion of the sample peak into the stream leading to the mass spectrometer 3. This injected sample is then pushed and carried along to the mass spectrometer 3 in the slower moving dummy carrier gas stream. This provides sample to the mass spectrometer for the desired 20 seconds of the dummy stream has $\frac{1}{10}$ the flow rate of the stream from the gas chromatograph.

Alternatively, relatively long and low intensity gas peaks can be compressed in time and, thus, increased in intensity by adjusting the throttle valve 22 for a higher flow rate than that of the output stream of the gas chromatograph. This latter mode of operation facilitates identification of certain relatively long and low intensity gas peaks.

One feature of the gas switch 5 is that it switches the sample stream to either the vent or to the spectrometer 3 at atmospheric pressures such that the switching action does not produce pressure fluctuations in the output of the gas chromatograph 1. Such pressure fluctuation, if present, would cause unwanted line broadening and loss of resolution of the gas chromatograph 1.

Although the gas analysis system of FIG. 1 has been described as employing a gas chromatograph and a dummy carrier gas stream, the dummy carrier gas stream may be replaced by the carrier gas stream from a second gas chromatograph or the second column of a dual column gas chromatograph. This embodiment, which employs the second column of a dual column gas chromatograph as the dummy carrier gas supply, has a second output tubing 13' which is connected into the dummy gas passageway 14 between the dummy carrier gas supply 19 and the throttle valve 22. When using the output gas stream of the second column of a dual column gas chromatograph 1 as the dummy carrier gas stream, the dummy carrier gas supply 19 can be eliminated or valved off.

Also more than one gas chromatograph may be employed in conjunction with the dummy carrier gas stream. Such systems employing the gas transfer switch for switching the outputs of plural gas chromatographs to one mass spectrometer has the advantage of permitting one relatively expensive mass spectrometer to be used for identifying the outputs of plural gas chromatographs. Also, the mass spectrometer may be replaced by other types of spectrometers such as an infrared spectrometer.

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 gas analysis apparatus, means forming a gas chromatograph for analyzing a sample and producing a plurality of sequential gas output peaks in a first stream of carrier gas, means forming a spectrometer for identifying at least certain of the gas output peaks of said chromatograph, the improvement comprising, means for producing a second carrier gas stream, means forming a gas transfer structure having a pair of separate input ports connected to receive said first and second gas streams, respectively, said gas transfer structure having a pair of output ports, means in said transfer structure for simultaneously opening a gas passageway interconnecting said first input port with said first output port and for simultaneously opening a second gas passageway interconnecting said second input port with said second output port, means for switching said interconnecting means in said gas transfer structure for opening a third gas passageway interconnecting said first input port and said second output port for diverting said first gas stream to said second output port such that the flow of gas in said first gas stream through said chromatograph is essentially uninterrupted by switching said interconnecting means in said gas transfer structure, and means forming a gas passageway connecting said spectrometer to said second output port for sampling the gas flow therefrom, whereby said first gas stream and said second gas stream are sequentially switchable to said spectrometer without producing substantial pressure fluctuation in the first carrier gas stream flowing through said gas chromatograph.

2. The apparatus of claim 1 wherein said spectrometer means is a mass spectrometer.

3. The apparatus of claim 1 wherein said gas chromatograph is a dual column gas chromatograph, and said second carrier gas stream is derived from the second column of said dual column gas chromatograph.

4. The apparatus of claim 1 including means for throttling the flow rate of the second carrier gas stream to less than the flow rate of the first carrier gas stream such that a selected portion of the gas peak output of said gas chromatograph which is switchable into the second carrier gas stream by said gas transfer means has its flow rate decreased as fed to said spectrometer means to facilitate spectral analysis thereof.

5. The apparatus of claim 1 including means for adjusting the flow rate of the second carrier gas stream to more than the flow rate of the first carrier gas stream such that a selected portion of the gas peak output of said gas chromatograph which is switchable into the second gas stream by said gas transfer means has its flow rate increased as fed to said spectrometer to facilitate spectral analysis thereof.

6. The apparatus of claim 1 including means forming a gas separator connected between said spectrometer means and said gas transfer means for substantially eliminating the carrier gas from and enriching the sample gas peak portion of the output gas stream of said gas transfer means which is directed into said spectrometer means.

7. The apparatus of claim 6 wherein said gas separator means is a membrane separator.

8. The apparatus of claim 1 including means forming a gas detector connected to said first output port of said gas transfer structure for monitoring the non-diverted portions of the output gas stream of said gas chromatograph.

9. The apparatus of claim 8 including, means for recording the output of said gas detector means.

10. The apparatus of claim 1 wherein said gas transfer means has its output ports, which are connected at various times through said gas transfer means to said gas chromatograph, operating at approximately atmospheric pressure.

11. In a method for gas analysis, passing a first gas stream containing a sample to be analyzed through a gas

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chromatograph to produce an effluent first gas stream containing sample constituents separated in time, producing a second gas stream of a carrier gas, passing the effluent first gas stream to a detector and recorder to detect the sample constituents and to record a gas chromatogram of the sample under analysis, passing the second gas stream to a gas separator and thence to a mass spectrometer to maintain a certain background carrier gas signal level in the output of the spectrometer, periodically diverting, without substantially interrupting the flow of the effluent first gas stream from the detector and recorded to the gas separator and mass spectrometer for mass analyzing the detected constituents of the

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effluent first gas stream, whereby the diverted portions of the effluent first stream are recorded in the gas chromatogram to be readily correlated with the detected peaks of the mass spectrometer.

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